Proton-controlled Non-exponential Photoluminescence in a Pyridyl-Amidine-substituted Re(I) complex

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Experimental Details

Synthetic Procedures

$[Re(bpy)(CO)_3(ACN)]PF_6$ and $[Re(bpy)(CO)_3(4\text{-}EtPy)]PF_6$ were prepared using literature procedures from Meyer *et. al.* [1]

$[Re(bpy)(CO)_3(o\text{-}DMSO)]PF_6$

An air-free, dark flask was charged with 20 mL of acetone and 265 µL of DMSO, 262.3 mg (0.57 mmol) of $Re(bpy)(CO)_3Cl$ and 300 mg (1.2 mmol) of AgOTf. The resultant solution was refluxed overnight. After the solution was cooled down to room temperature, the reaction mixture was filtered to remove precipitated AgCl and the solvent was evaporated to dryness, dissolved in approximately 15 mL dichloromethane, and washed with saturated, aqueous NH_4PF_6 (3 × 20 mL). The solution was concentrated to approximately 2 mL and diethyl ether was added dropwise to precipitate. 156.3 mg, 42% yield. This synthesis was developed from previously published preparations of the complex.[2,3] ^{1}H NMR (400 MHz, acetone-d_6): δ 9.27 (d, *J* = 4 Hz, 2H), 8.84 (d, *J* = 8 Hz, 2H), 8.52 (t, *J* = 4 Hz, 2H), 7.96 (d, *J* = 8 Hz, 2H), 2.77 (s, 6H)

$[Re(bpy)(CO)_3(4\text{-}Pam)]PF_6$ (Re(4-Pam))

An air-free flask was charged with 75 mL of acetone, 156.3 mg of $[Re(bpy)(CO)_3(o\text{-}DMSO)]PF_6$, and 294 mg of 4-pyridylamidine (4-Pam). The solution was refluxed overnight. The solution was cooled to room temperature and evaporated to dryness. The solid was dissolved in 30 mL of DCM and washed quickly with water (3 × 30 mL) and dried with $MgSO_4$. The solution was concentrated to approximately 2 mL and ether was added dropwise to precipitate solid. 30 mg, 18% yield. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.27 (d, *J* = 4 Hz, 2H), 8.81 (d, *J* = 8 Hz, 2H), 8.56 (d, *J* = 4 Hz, 2H),8.47 (t, *J* = 8 Hz, 2H), 7.92 (t, *J* = 8 Hz, 2H), 7.25 (d, *J* = 4 Hz, 2H)

$[Re(bpy)(CO)_3(4\text{-}Pam)]BArF$ (Re(4-Pam BArF))

An alternate synthesis was performed in which an air-free flask was charged with 10 mL of 1,2-difluorobenzene, 100.7 mg (0.22 mmol) of $Re(bpy)(CO)_3Cl$, 31.4 mg (0.26 mmol) of 4-pyridylamidine (4-Pam) and 200.4 mg (0.23 mmol) of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BArF). The solution was refluxed for 72 hours and then cooled to room temperature. The reaction mixture was washed with DI water (3 × 5 mL) and then dried with $MgSO_4$ and the solvent was removed via rotovap. The solid was then packed on silica gel, and diethyl ether was used to elute the pure product as a tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BArF) salt. 157.4 mg, 51% yield. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.27 (d, *J* = 8 Hz, 2H), 8.82 (d, *J* = 8 Hz, 2H), 8.55 (d, *J* = 4 Hz, 2H), 8.47 (t, *J* = 8 Hz, 2H), 7.92 (t, *J* = 4 Hz, 2H), 7.81 (br s, 8 H), 7.66 (br s, 4 H), 7.27 (d, *J* = 8 Hz, 2H); ^{13}C{^{1}H} NMR (400 MHz, acetone-d_6): δ 168.5 (s), 161.5 (q, $^1J_{B\text{-}C}$ = 50.0 Hz), 156.4 (s), 153.9 (s), 150.2 (s), 140.9 (s), 134.7 (s), 129.1 (q, $^2J_{C\text{-}F}$ = 31.5 Hz), 128.3 (s), 125.8 (s), 125.2 (s), 124.5 (s), 124.5 Hz (q, $^1J_{C\text{-}F}$ = 270 Hz), 123.1 (s), 121.2 (s), 120.4 (s), 117.5 (s).

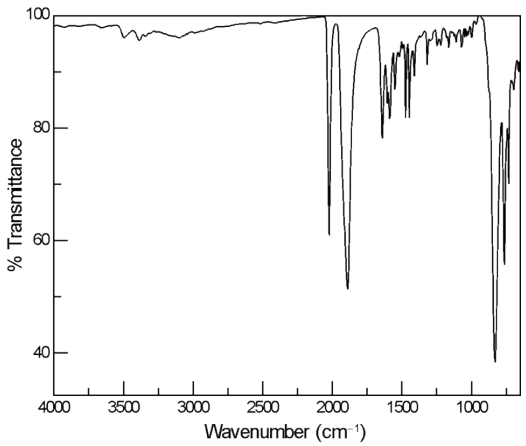
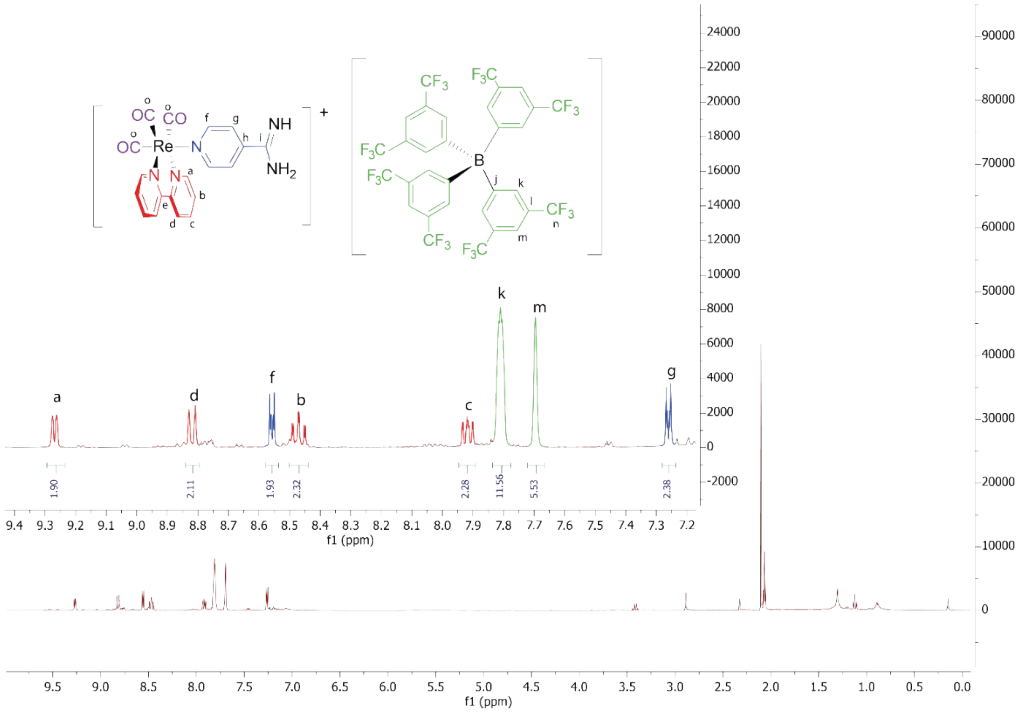


Figure S1. ATR-FT-IR of Re(4-Pam) *v*(CO) 2022, 1886 (br) cm^{-1}

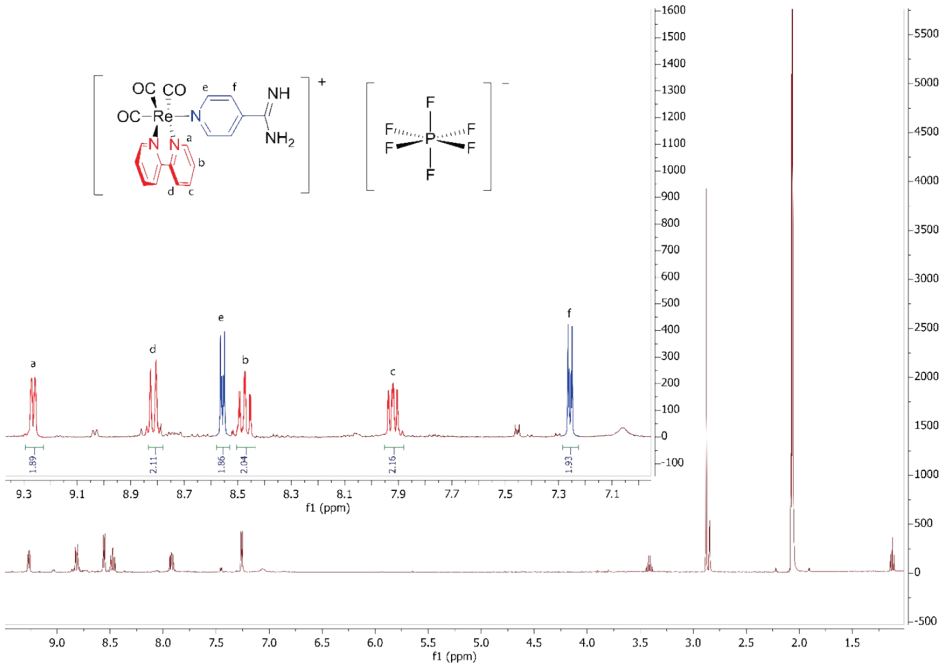
The ATR-FT-IR CO stretches are consistent with other *fac*-Re(I)(bpy)$(CO)_3$L complexes.[4–7]

^{1}H NMR

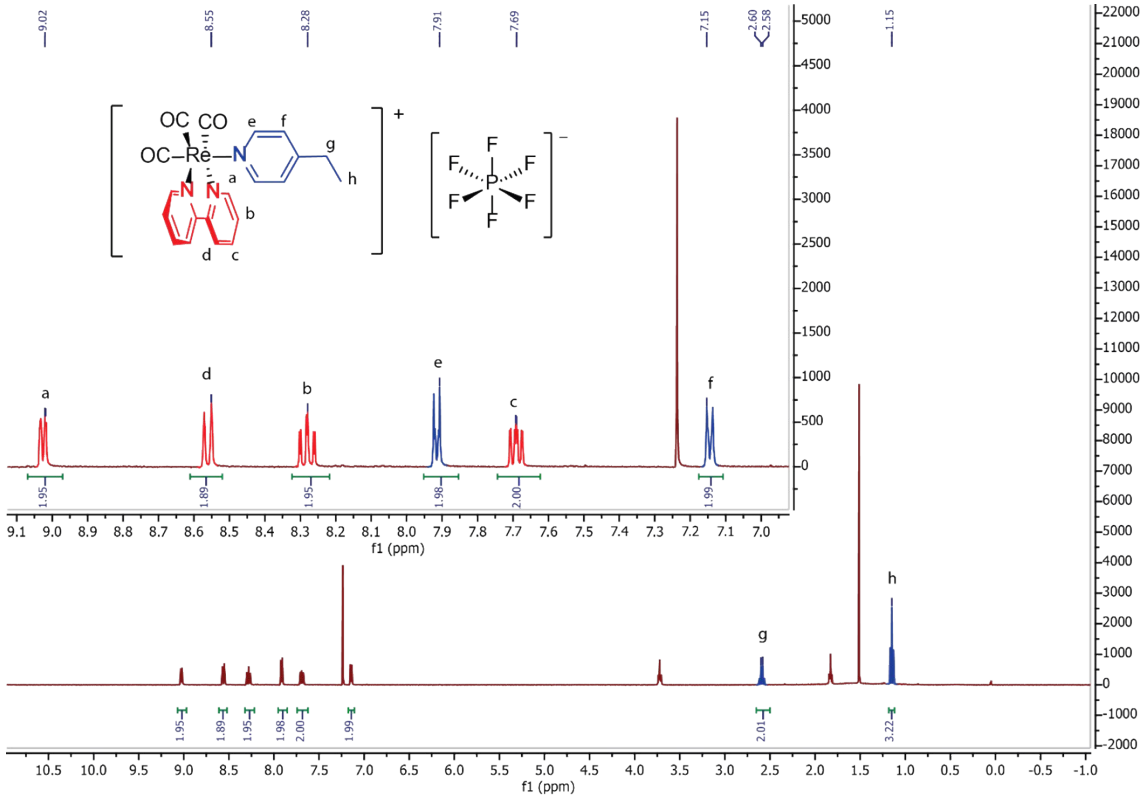
Re(4-Pam BArF) with peaks labeled



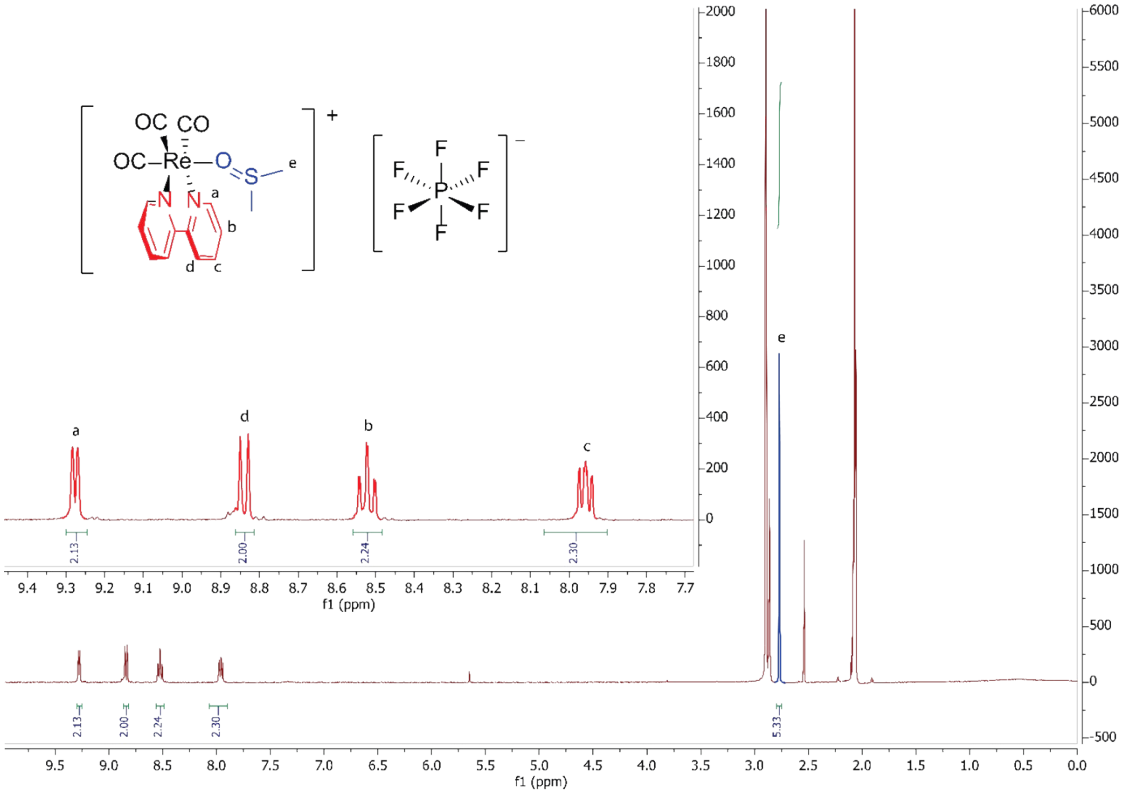
Re(4-Pam)



Re(4-EtPy)

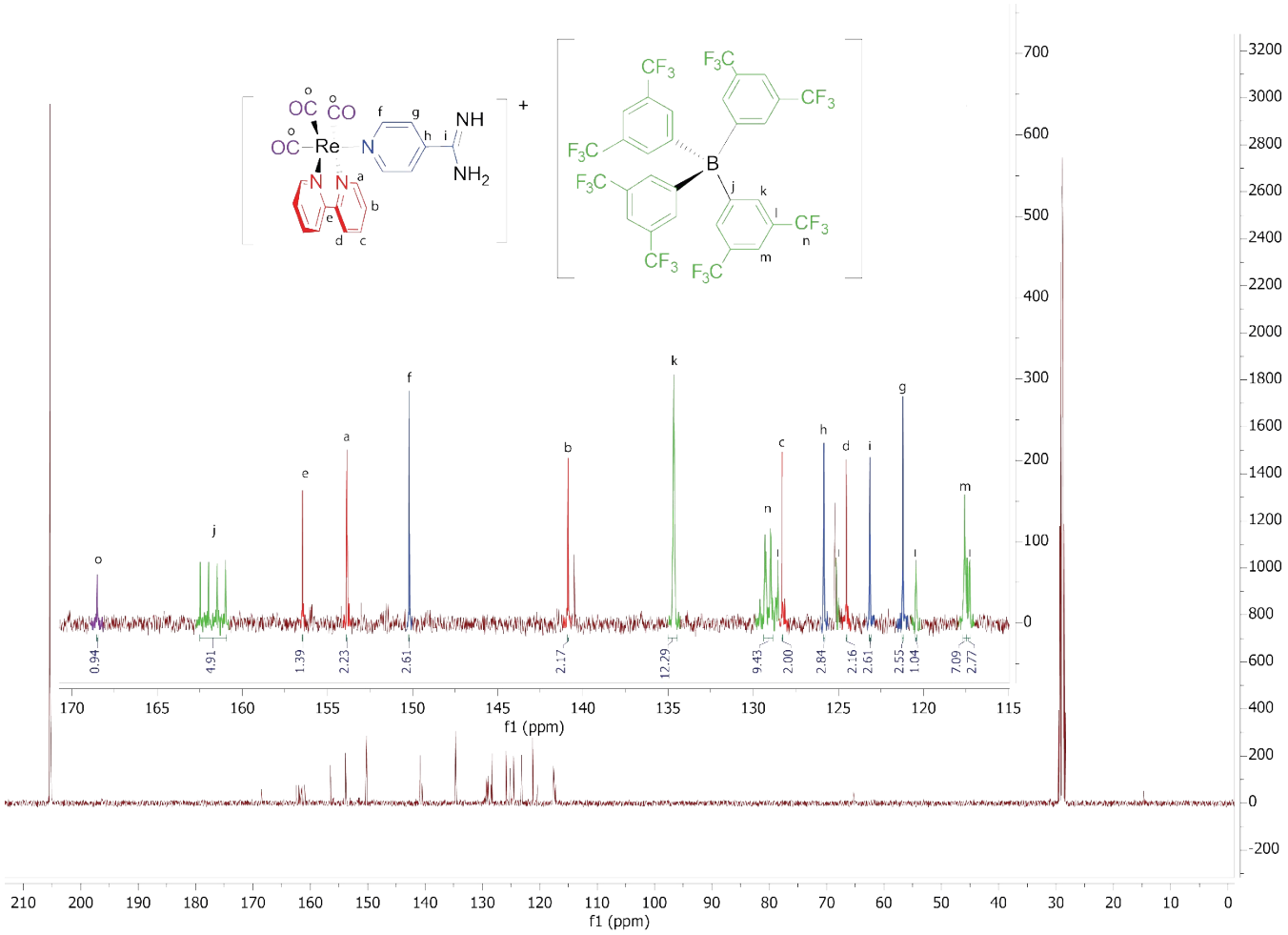


[Re(bpy)(CO)$_3$(o-DMSO)]PF$_6$



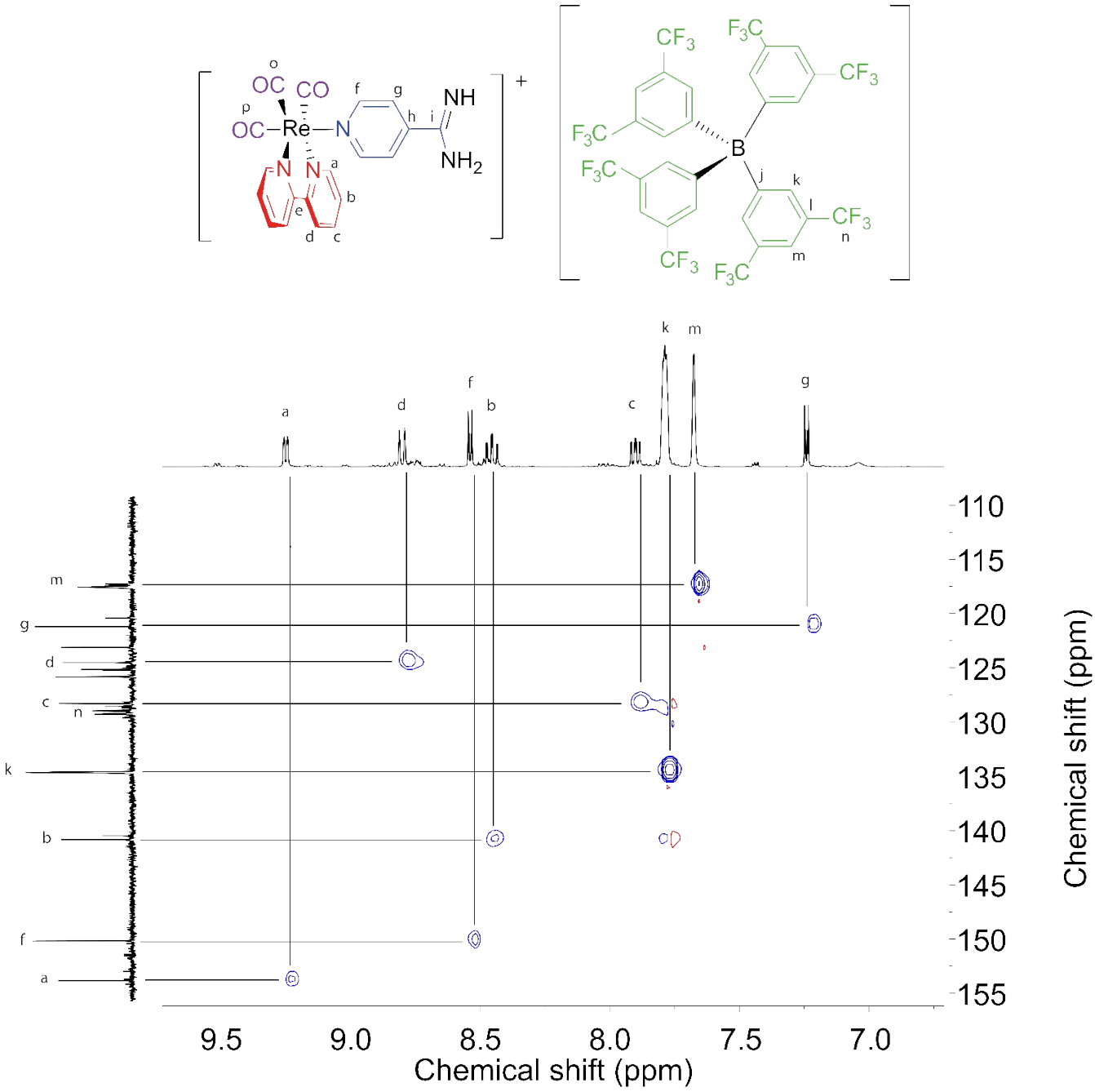
^{13}C NMR

Re(4-Pam BArF) with peaks labeled



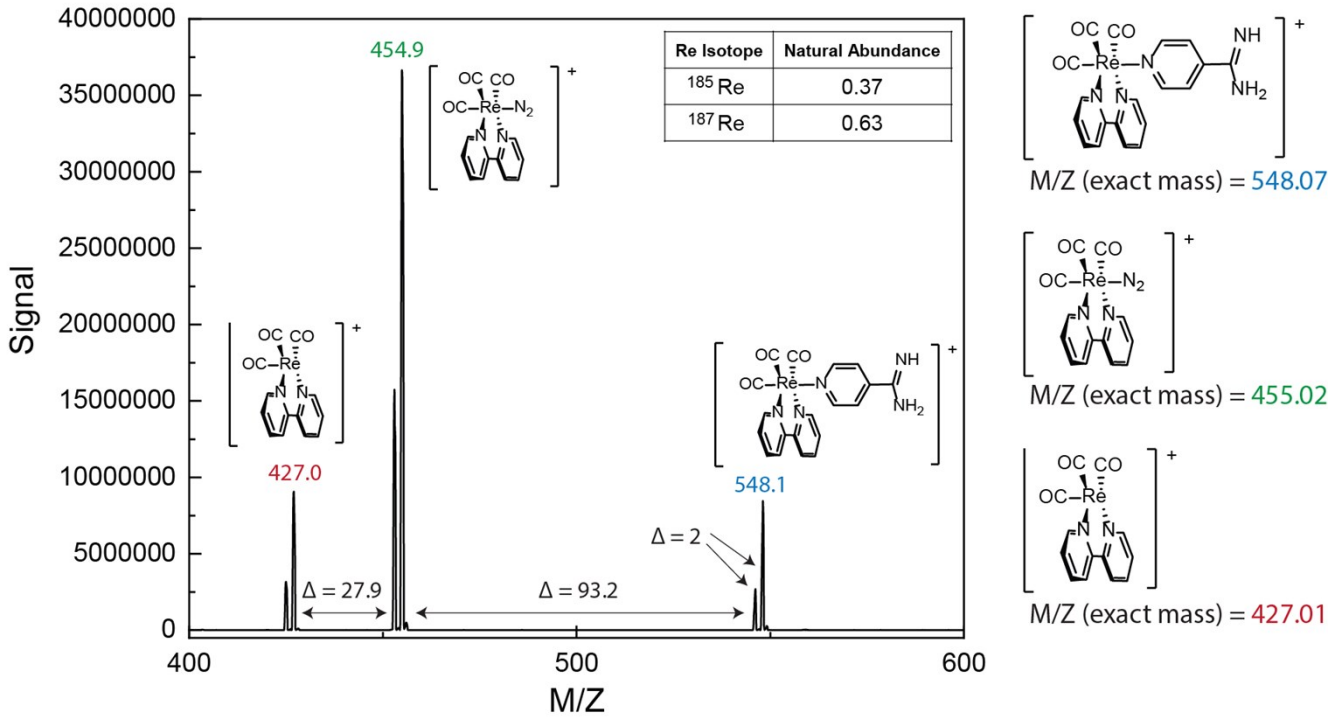
2D HSQC NMR

Re(4-Pam BArF) with peaks labeled



ESI-MS

Re(4-Pam BArF)



Electrospray ionization mass spectrometry (ESI-MS) of the Re(4-Pam BArF) complex show three peaks. The experiment was performed with 0.4 mL of sample at 1 mg/mL in acetonitrile was added via direct injection to the ionization source. The peak at 584.1 M/Z matches the exact mass of the complex (shown on the right side of the figure). The splitting of Δ= 2 M/Z in each of the three primary peaks occurs because of the two isotopes of Re. The isotopes of Re are listed with their relative abundance in the inset of the figure. The remaining two peaks are (1) at 427.0 and (2) at 454.9 M/Z. The peak at 427.0 M/Z represents the complex with the 4-Pam ligand displaced. The 4-Pam ligand is labile and would be expected to be the most likely to be removed during the measurement. The second remaining peak at 454.9 M/Z represents the nitrogen adduct of the complex with the 4-Pam removed. The carrier gas in the ESI-MS measurement is N_2, making this complex a likely product. Similar Re-N_2 adducts have previously been reported.[8–10]

Figure S2. Characterization: ^{1}H ^{13}C and 2D HSQC NMR spectra and peak assignments of Re(4-Pam), Re(4-Pam BArF) and Re(4-EtPy) in acetone-d_6 and ESI-MS of Re(4-Pam) acetonitrile.

NMR is reported in acetone-d_6. The shift of 8.56 ppm corresponds to the alpha-^{1}H of pyridyl of the 4-Pam, which indicates the N-pyridyl of 4-Pam is bound to the Re center. There is a similar shift of 8.58 that corresponds to the alpha-^{1}H of pyridyl of the 4-EtPy, which indicates that the pyridyl is bound to the Re center.

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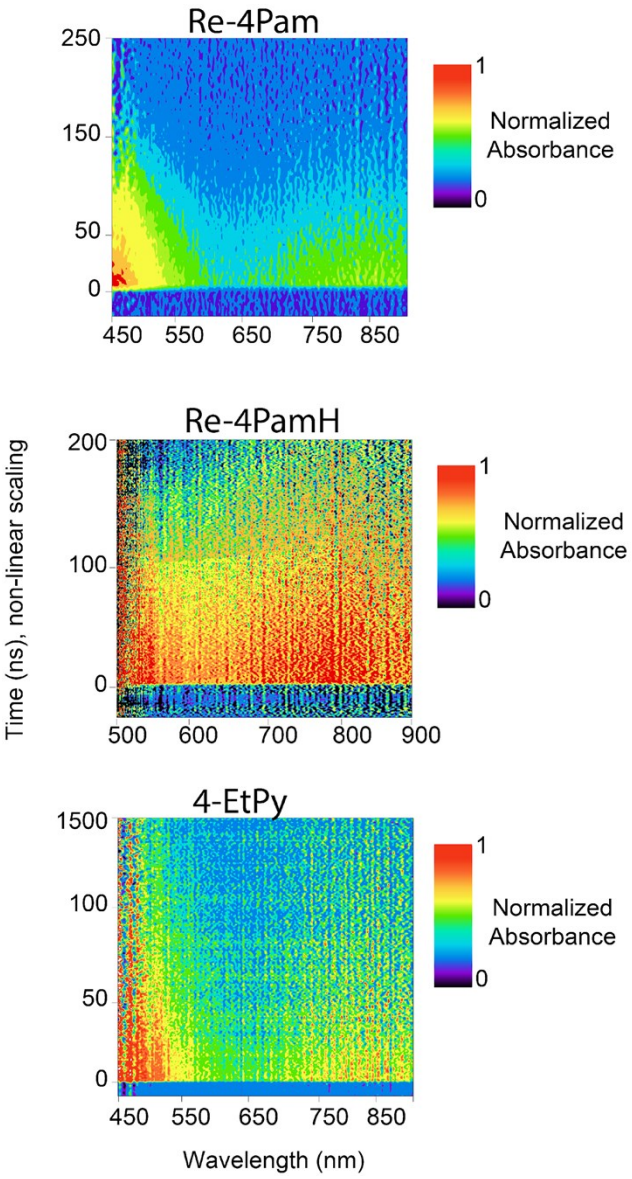


Figure S3. Heat map visualization of data for the ns-TA data collected with the EOS TA spectrometer.

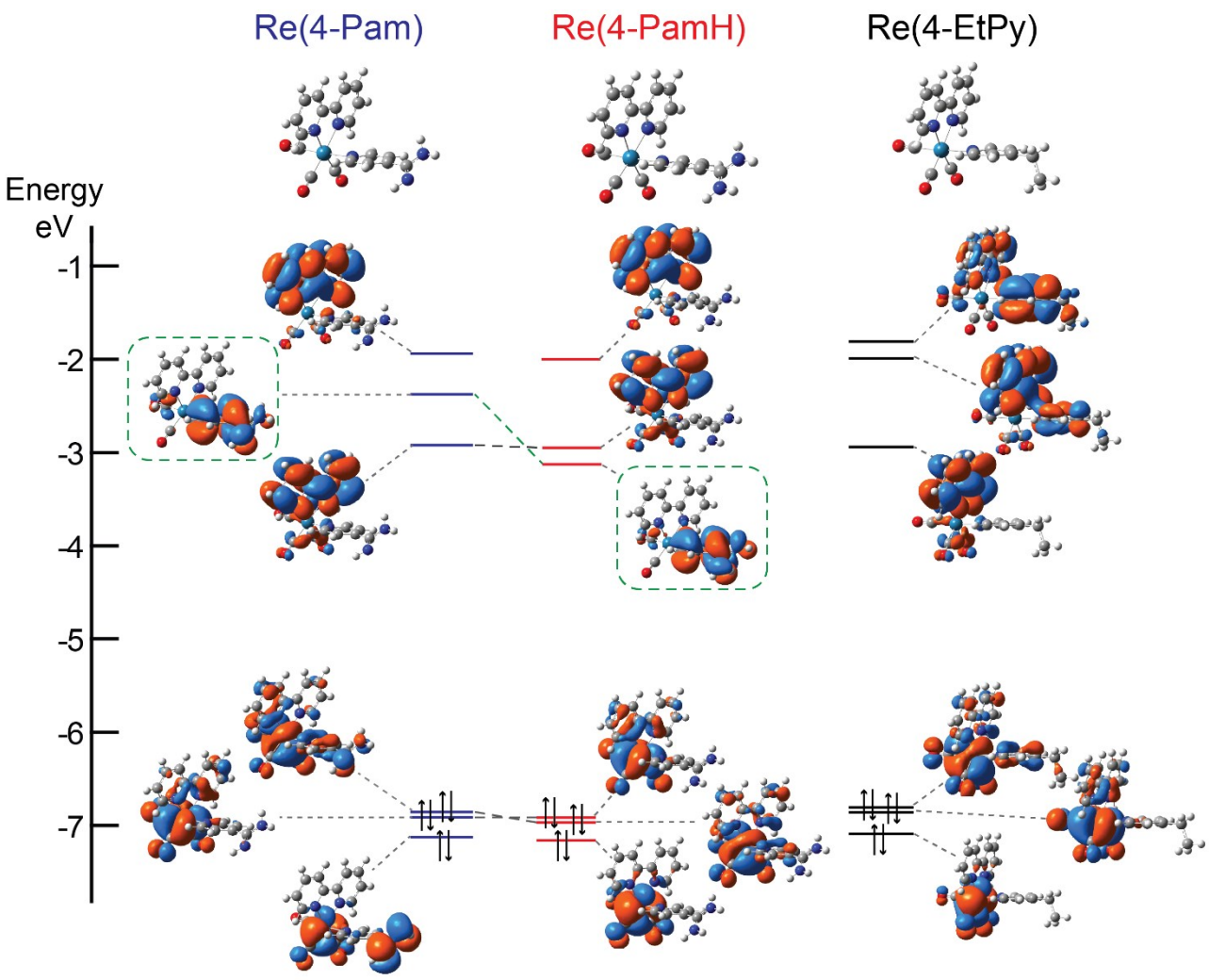


Figure S4. B3LYP/LANL2DZ [Re]+6-311G(d,p)[H,C,N,O]/PCM(ACN) frontier molecular orbital electronic structure of the Re(4-Pam), Re(4-PamH) and Re(4-EtPy) ground states.

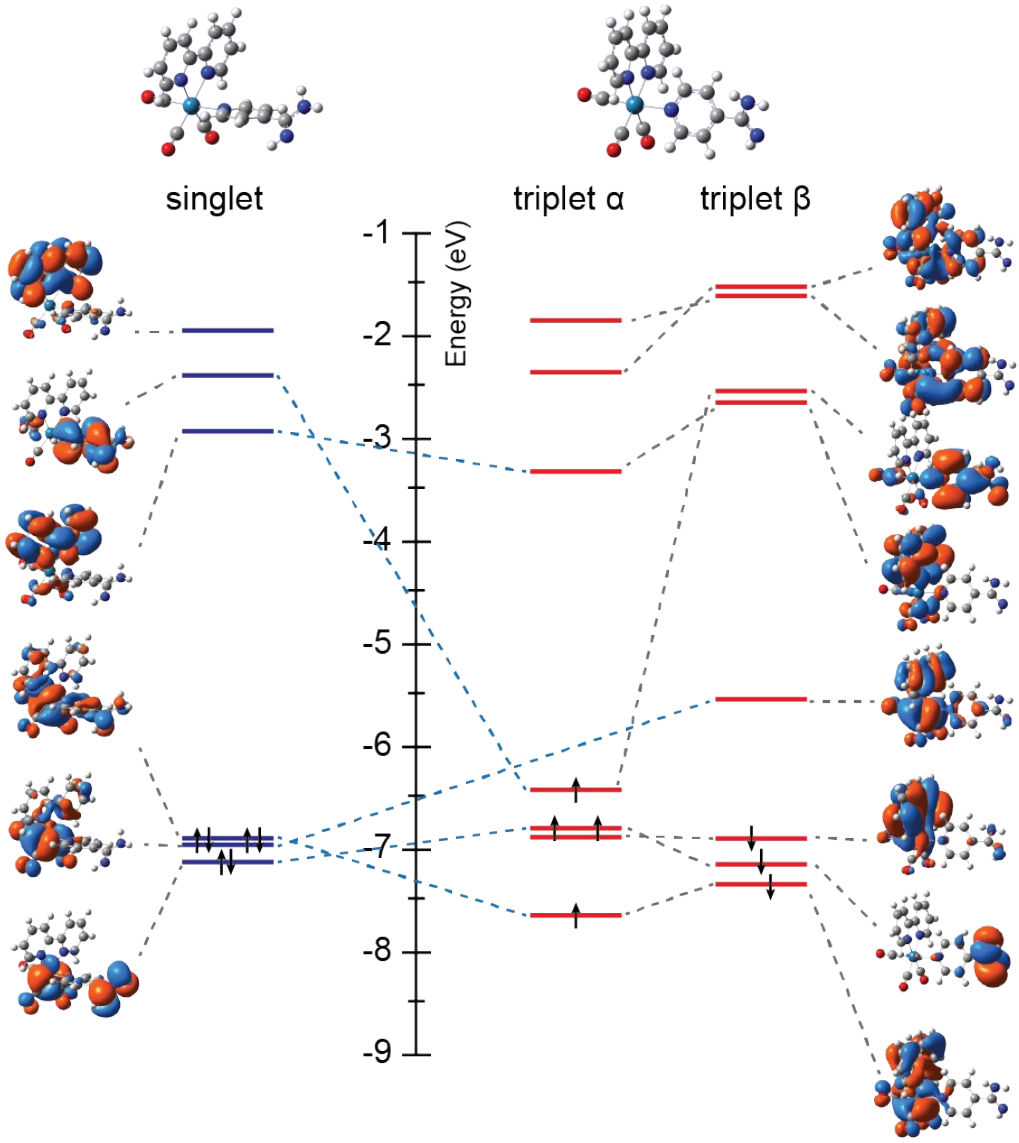


Figure S5. The singlet electronic structure of the fully optimized Re(4-Pam) singlet (GS) and triplet (T) geometries at the B3LYP/LANL2DZ [Re]+6-311G(d,p)[H,C,N,O]/PCM(ACN) level of theory.

The frontier MOs shown are the singlet configuration at each optimized singlet (S_0/GS) and triplet (S_0/T) geometries.

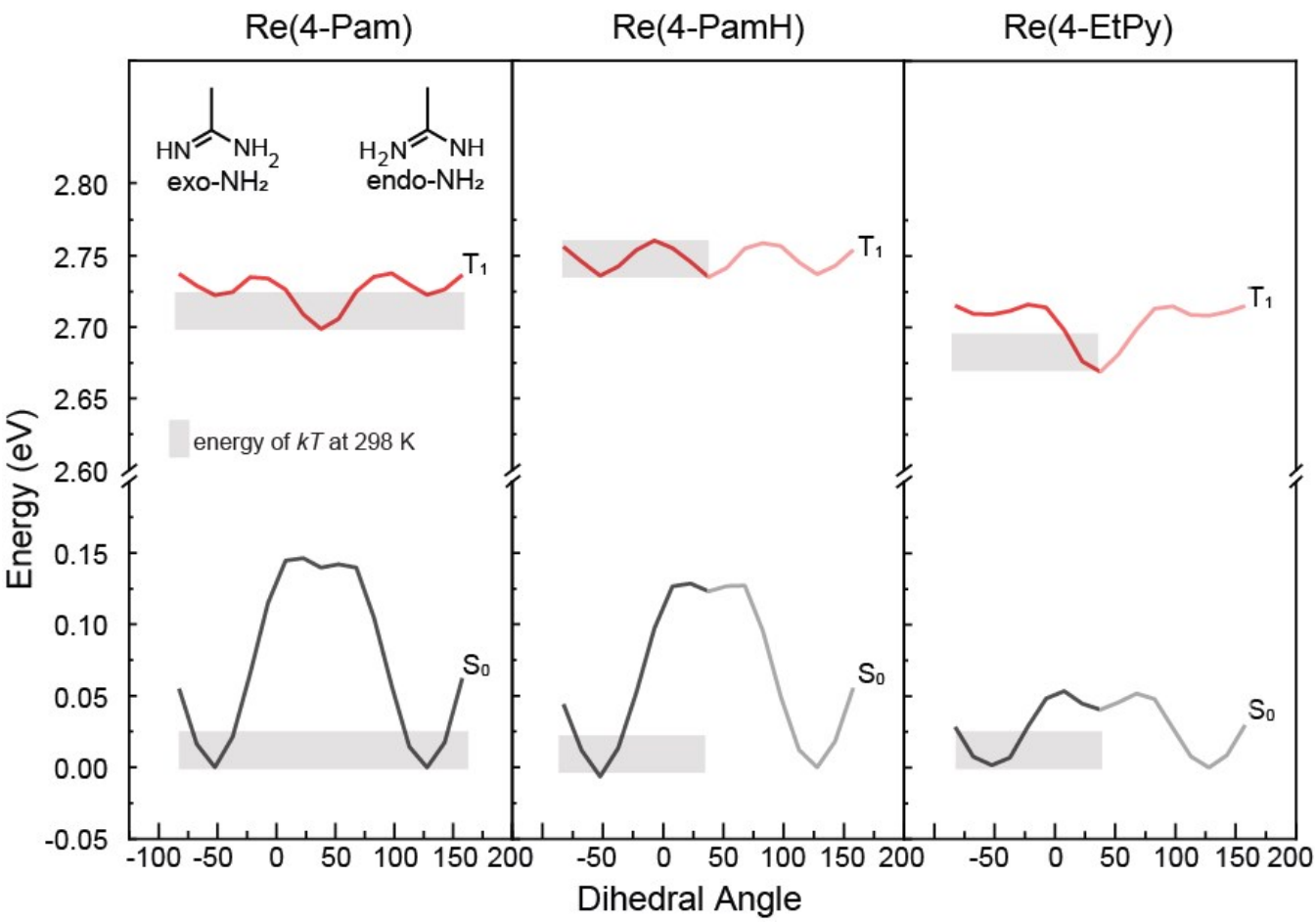


Figure S6. Comparison of the lowest energy singlet (S_0) and triplet (T_1) surfaces for Re(4-Pam), Re(4-PamH) and Re(4-EtPy).

Potential energy curves as a function of the dihedral angle between the pyridine and bpy ligands. The black line (lower energy curve) and red line (higher energy curve) are optimized lowest lying singlet and triplet of each complex, where only the dihedral angle was constrained and all other coordinates were freely optimized. The value of ~*kT* at room temperature is shown as a grey bar across the PEC for each surface. All calculations are B3LYP/LANL2DZ [Re]+6-311G(d,p)[H,C,N,O]/PCM(ACN).

Each potential energy curve is formed from relaxations of the geometry every 15° with only the bpy and pyridine dihedral angle constrained. Each point is a DFT optimization at the B3LYP/LANL2DZ [Re]+6-311G(d,p)[H,C,N,O]/PCM(ACN) level of theory.

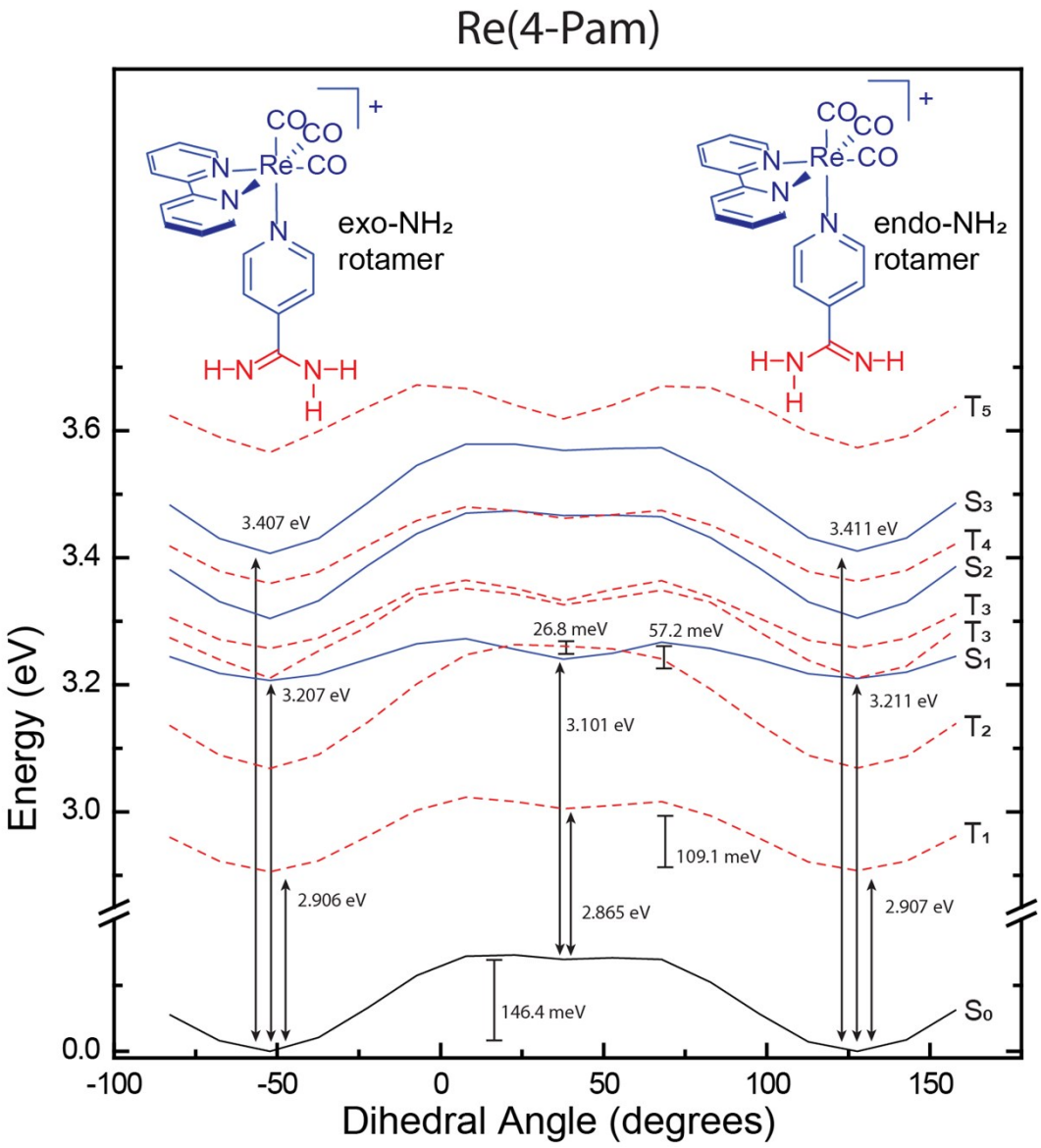


Figure S7. Re(4-Pam) ground state (S_0) and TDDFT excited state (S_{1-3} and T_{1-5}) potential energy curves between 0 and 3.8 eV as a function of dihedral angle.

The black line (lowest energy curve) is the constrained DFT optimized singlet ground state surface of each complex. The higher lying, singlet (blue solid lines) and triplet (red dotted lines) potential energy curves are TDDFT excitations from this GS curve. All calculations are B3LYP/LANL2DZ [Re]+6-311G(d,p)[H,C,N,O]/PCM(ACN). Several, relevant transition energies are labeled directly on the surface plots.

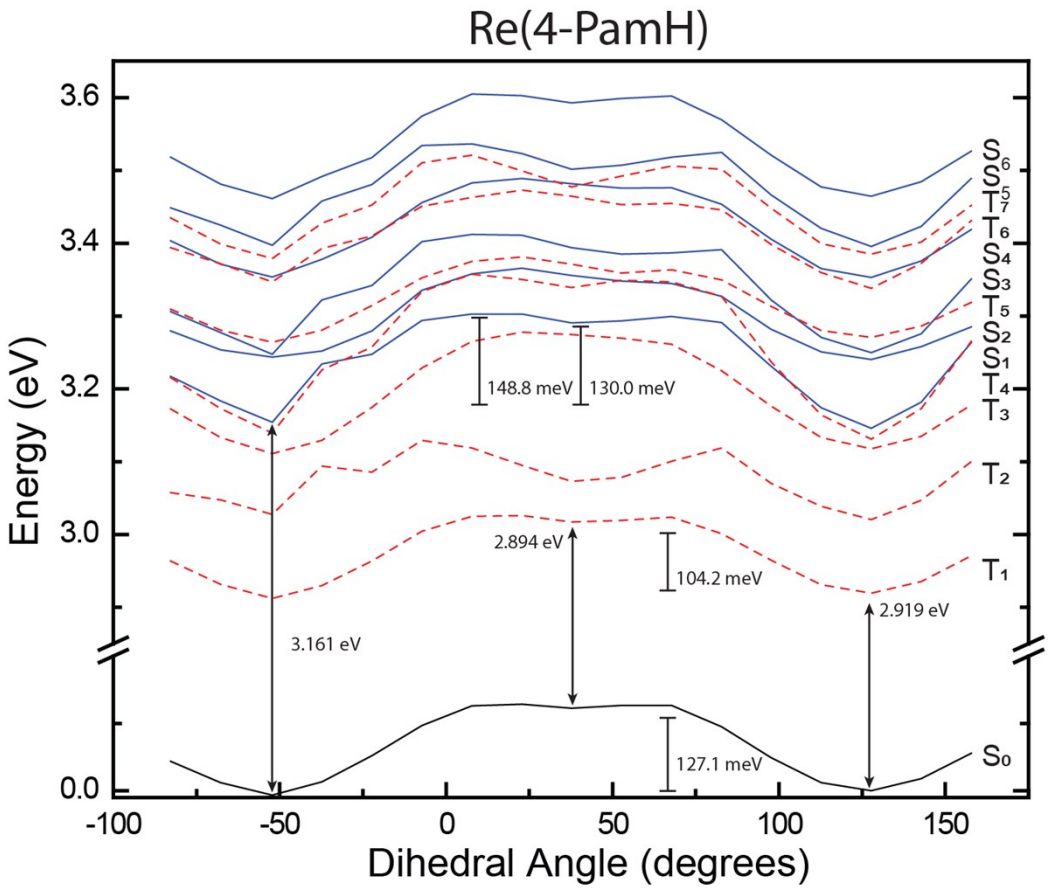


Figure S8. Re(4-PamH) ground state (S_0) and TDDFT excited state ($S_{1\text{-}6}$ and $T_{1\text{-}7}$) potential energy curves between 0 and 3.6 eV as a function of dihedral angle.

The black line (lowest energy curve) is the constrained DFT optimized singlet ground state surface of each complex. The higher lying, singlet (blue solid lines) and triplet (red dotted lines) potential energy curves are TDDFT excitations from this GS curve. All calculations are B3LYP/LANL2DZ [Re]+6-311G(d,p)[H,C,N,O]/PCM(ACN). Several, relevant transition energies are labeled directly on the surface plots.

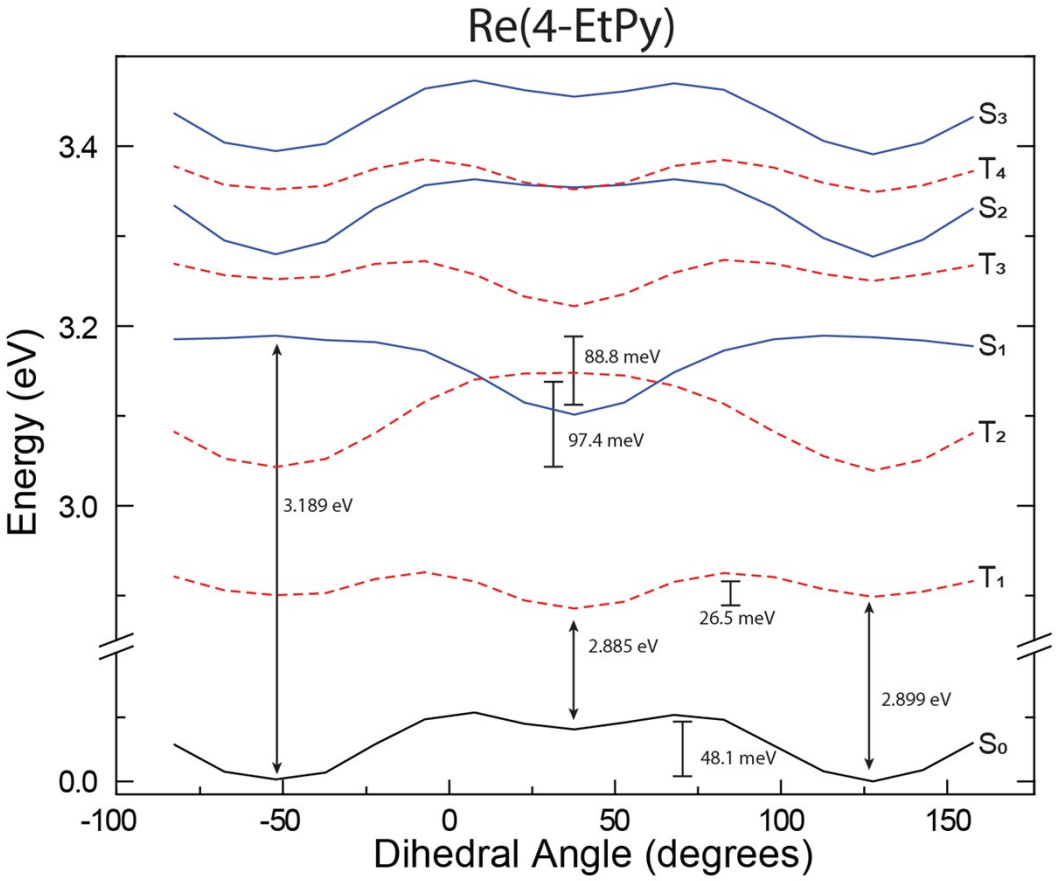


Figure S9. Re(4-EtPy) ground state (S_0) and TDDFT excited state (S_{1-3} and T_{1-4}) potential energy curves between 0 and 3.6 eV as a function of dihedral angle.

The black line (lowest energy curve) is the constrained DFT optimized singlet ground state surface of each complex. The higher lying, singlet (blue solid lines) and triplet (red dotted lines) potential energy curves are TDDFT excitations from this GS curve. All calculations are B3LYP/LANL2DZ [Re]+6-311G(d,p)[H,C,N,O]/PCM(ACN). Several, relevant transition energies are labeled directly on the surface plots.

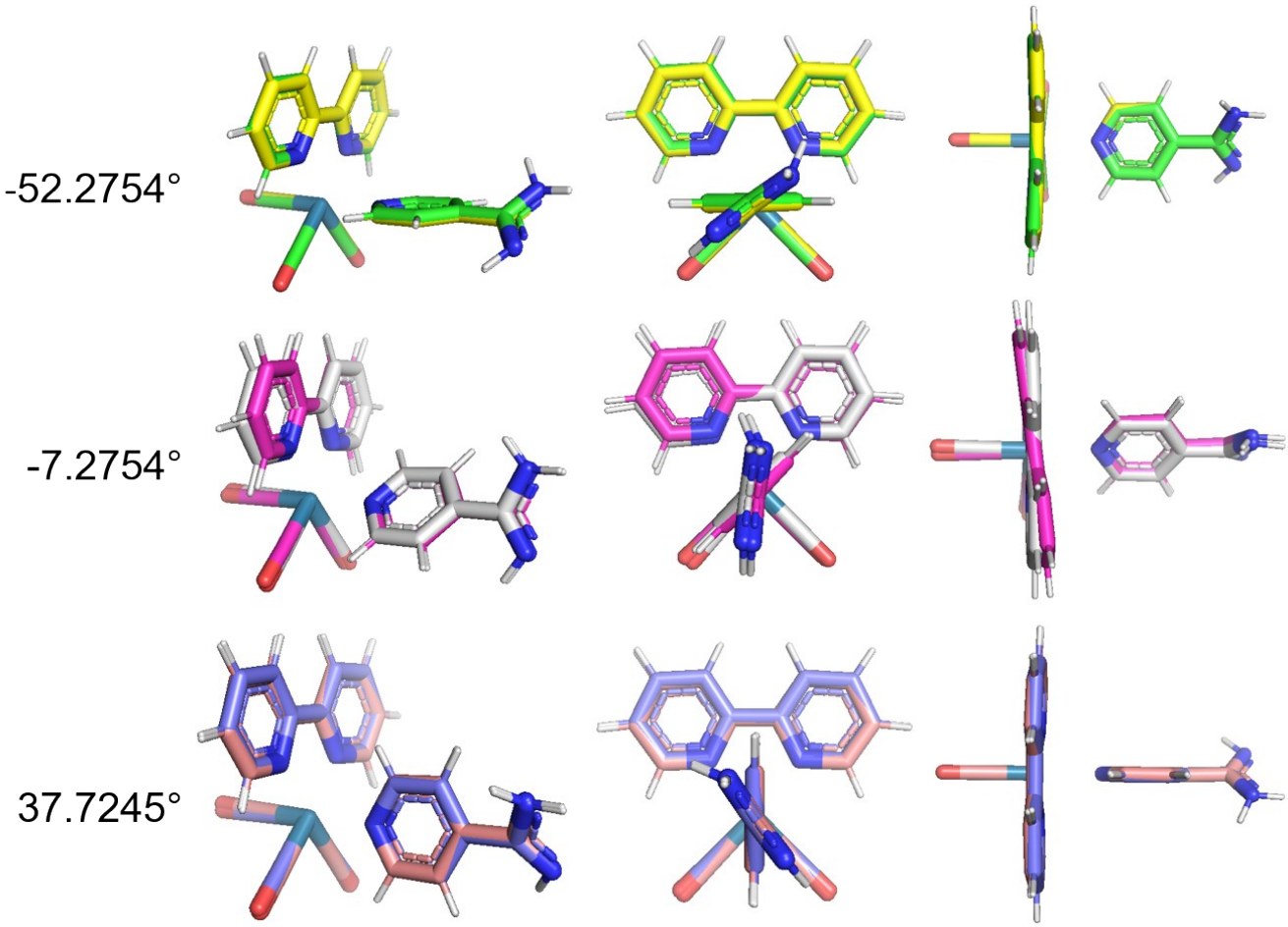


Figure S10. Comparison of optimized Re(4-Pam) S_0 and T_1 geometries along the dihedral scan.

The independently constrained geometry scans of the S_0 and T_1 surfaces results in very similar optimized geometries at each dihedral angle. Importantly only the dihedral is constrained and each scan started from the fully optimized global minimum on each surface. This indicates that there is no other obvious geometrical coordinate between the S_0 and T_1.

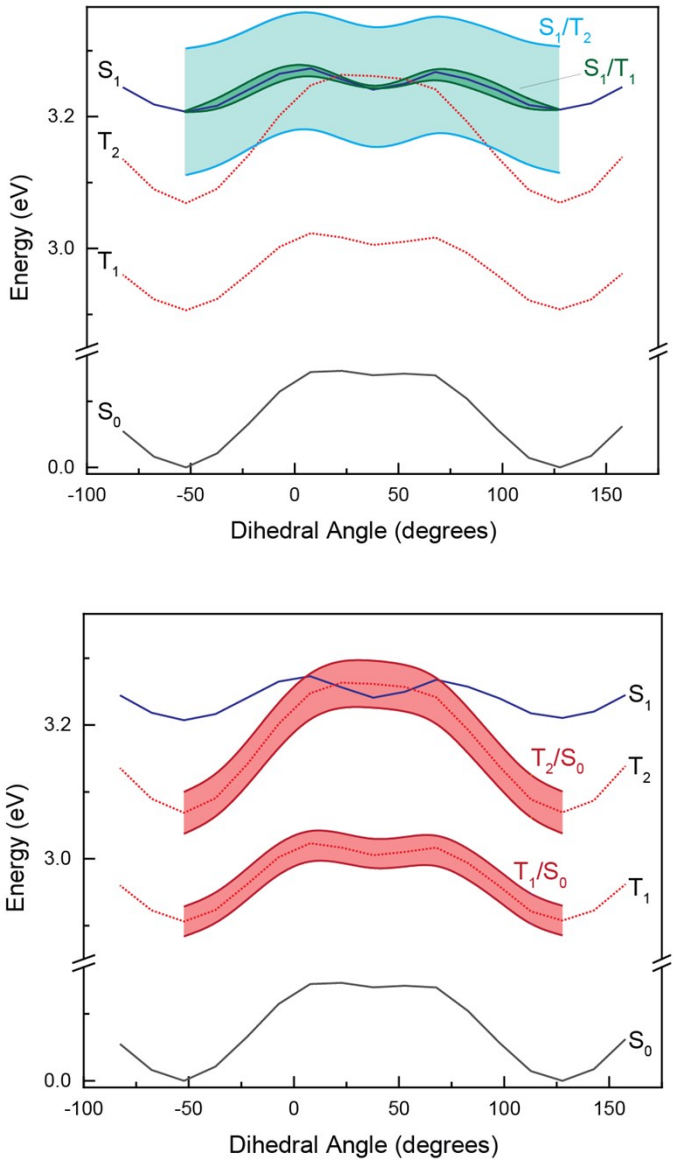


Figure S11. Representation of spin-orbit couplings between critical S_1-triplet (top) and triplet-S_0 (bottom) surfaces of Re(4-Pam).

The spin-orbit coupling (SOC) energies between the (top) S_1 and T_1 (darker green) or T_2 (blue green) and (bottom) between the T_2 or T_1 and S_0 surfaces. The SOCs are displayed as double the coupling (in eV) around the surface from which the transition originates. All of the calculated SOCs are in Table S1.

Table S1. Spin-orbit coupling in cm^{-1} for all surfaces less than 3.4 eV along the dihedral scan for Re(4-Pam).

Dihedral		T_1	T_2	T_3	T_4	T_5
	S_0	177.64159	250.59407	35.58175	219.33165	30.5761
	S_1	5.56094	767.43878	2.83968	22.5772	844.6377
-52°	S_2	530.27655	181.20206	6.30608	544.22766	620.39294
	S_3	503.31683	608.56354	7.83686	516.8385	178.45978
	S_4	13.71354	13.12953	230.98514	11.26961	15.52362
	S_5	59.99756	17.27553	8.87473	60.79902	80.32368
		T_1	T_2	T_3	T_4	T_5
	S_0	181.63161	252.95973	43.84499	221.7016	40.43677
	S_1	69.17043	750.2464	16.90375	138.95074	835.15472
-37°	S_2	542.92755	269.50671	20.70583	537.72546	609.1767
	S_3	502.57407	592.72961	21.31869	497.25488	235.43518
	S_4	33.48489	9.69055	181.39688	29.41672	32.80264
	S_5	48.49593	22.93669	140.31215	51.63493	72.60793
		T_1	T_2	T_3	T_4	T_5
	S_0	186.28822	261.42343	55.70821	225.50734	52.64732
	S_1	87.53074	720.52435	61.74385	209.7818	827.034
-22°	S_2	568.97516	362.6777	63.47153	527.77179	567.1825
	S_3	504.19949	552.27991	61.51597	459.23737	334.12943
	S_4	48.6102	28.94302	20.46177	48.95612	71.49475
	S_5	20.60301	8.36957	195.59653	60.34943	38.0123
		T_1	T_2	T_3	T_4	T_5
	S_0	185.95044	271.45636	195.69398	117.4066	47.75128
	S_1	89.15224	707.55048	226.79181	52.46413	827.78265
-7°	S_2	597.01196	415.8873	494.48145	180.37221	507.73032
	S_3	508.61771	505.83838	397.06152	151.0213	411.03
	S_4	35.11568	43.05714	41.98938	11.95979	71.15198
	S_5	30.86304	7.92124	35.56742	173.8979	52.35727
		T_1	T_2	T_3	T_4	T_5
	S_0	182.00052	272.50455	167.7205	139.11119	49.61835
	S_1	65.92094	707.86548	197.44698	78.36451	836.07831
7°	S_2	621.70227	441.01874	436.86972	273.03583	460.7504
	S_3	516.38641	464.01932	336.07867	221.02022	454.6691
	S_4	19.00545	56.06718	31.01549	10.63954	73.32145
	S_5	42.80155	7.91164	38.26494	120.6453	62.31588
		T_1	T_2	T_3	T_4	T_5
	S_0	176.65691	278.48877	159.42746	114.17696	32.14505
	S_1	33.62992	720.01068	133.87978	32.94396	847.45239
22°	S_2	639.8432	463.17993	462.44867	198.08673	427.81946
	S_3	524.06952	423.79971	364.1561	164.09209	481.91415
	S_4	3.86947	66.78119	16.61664	12.6912	78.84457
	S_5	52.67302	7.08298	17.92113	67.62845	65.89313
		T_1	T_2	T_3	T_4	T_5
	S_0	173.9552	282.18497	83.60638	157.40553	14.90661
	S_1	5.74118	729.77667	28.47561	14.06091	852.98004
37°	S_2	646.80481	475.73212	65.74252	494.36569	413.90952
	S_3	527.45886	402.8074	50.13207	401.02261	493.15179
	S_4	52.35461	22.98825	15.98355	39.26995	67.00422
	S_5	24.35611	66.59384	15.08879	18.9451	82.09577
		T_1	T_2	T_3	T_4	T_5
	S_0	176.23186	277.54501	156.42169	119.49876	37.38169
52°	S_1	34.9534	719.76843	133.10558	29.43862	846.40527
	S_2	640.23767	462.08154	452.46109	216.96385	428.16943
	S_3	524.81555	425.75064	354.64447	176.67053	481.86346

	S_4	17.67778	60.89967	15.33562	32.66612	71.91943
	S_5	54.10226	28.50469	16.99369	74.02678	76.35181
		T_1	T_2	T_3	T_4	T_5
	S_0	182.08632	273.74167	178.89601	132.11232	52.54879
	S_1	66.46023	705.26086	208.26402	56.86946	834.7959
67°	S_2	620.55908	440.25705	468.53726	220.30519	461.04913
	S_3	515.60565	465.03467	360.80435	178.28497	454.50757
	S_4	30.92968	59.06356	39.83979	13.08298	76.4571
	S_5	46.24491	7.89302	16.86177	128.19337	65.92307
		T_1	T_2	T_3	T_4	T_5
	S_0	186.27831	269.1485	172.17737	153.82394	50.48353
	S_1	87.09027	702.36523	214.81953	107.2569	828.00092
82	S_2	593.80939	414.3576	423.86111	301.13202	509.32141
	S_3	508.27365	505.0618	342.74734	247.15395	408.14951
	S_4	48.07241	52.3414	50.29057	19.36577	77.02209
	S_5	33.57084	7.77848	71.09341	165.22789	56.322
		T_1	T_2	T_3	T_4	T_5
	S_0	184.14589	261.54285	59.14603	228.40099	52.16275
	S_1	88.88322	716.51971	56.11987	216.48279	828.09265
97°	S_2	560.4032	361.65613	41.93003	530.6792	570.22748
	S_3	501.23578	551.59314	46.08707	470.7027	326.03448
	S_4	59.10924	46.93367	33.52602	56.16198	76.09397
	S_5	24.10422	14.90172	202.00659	59.39682	45.41108
		T_1	T_2	T_3	T_4	T_5
	S_0	179.20329	252.81905	44.63315	223.57417	39.50021
	S_1	69.22222	745.0918	15.53707	144.93747	837.75134
112°	S_2	533.1579	269.19238	11.23751	536.2384	609.9361
	S_3	501.45984	590.67249	12.97826	507.90106	227.81737
	S_4	18.8321	15.98543	223.00986	10.5592	9.64339
	S_5	64.57407	45.74818	63.4551	68.74268	84.24428
		T_1	T_2	T_3	T_4	T_5
	S_0	176.72197	249.66002	38.57011	220.37544	31.78813
	S_1	4.4889	766.60681	4.06764	10.6291	845.21423
127°	S_2	525.31787	178.83366	3.92752	544.8819	619.23352
	S_3	502.21466	607.51215	8.38654	520.86188	176.04478
	S_4	13.30146	13.4881	236.00748	11.05438	16.16772
	S_5	66.15148	44.7498	7.04851	67.91908	81.17381

Table S2. Spin-orbit coupling in cm^{-1} for all surfaces less than 3.4 eV along the dihedral scan for Re(4-PamH).

Dihedral		T_1	T_2	T_3	T_4	T_5
	S_0	170.39375	104.99918	313.03397	164.32098	269.78595
	S_1	10.21689	106.79472	726.06451	11.50535	44.10128
37°	S_2	156.48586	12.60709	35.71292	272.00266	773.65643
	S_3	40.18345	763.62158	98.43379	17.36686	42.76056
	S_4	577.44708	62.29958	522.81512	528.26874	237.20737
	S_5	45.83013	744.26917	37.8168	121.71793	653.72931
		T_1	T_2	T_3	T_4	T_5
	S_0	180.56129	109.69258	262.29254	110.35491	249.72375
	S_1	16.63759	726.3017	84.07458	47.6516	17.65905
52°	S_2	14.84642	81.20649	766.72675	30.24056	28.50745
	S_3	197.0815	219.89218	30.29694	805.22882	197.09955
	S_4	405.39725	332.13052	238.46497	531.57135	486.58386
	S_5	350.89676	433.6601	381.96411	568.77545	391.30466

		T_1	T_2	T_3	T_4	T_5
127°	S_0	180.31009	100.07715	265.16345	109.99453	249.85251
	S_1	16.13862	730.08728	71.5966	10.53469	17.9337
	S_2	175.35077	222.90131	54.75389	818.09906	179.56905
	S_3	14.17699	71.36964	767.15637	61.41105	21.23508
	S_4	376.43277	385.03174	195.84579	573.95538	448.3237
	S_5	374.05035	398.63025	382.53992	536.44641	426.14035

Table S3. Spin-orbit coupling in cm^{-1} for all surfaces less than 3.4 eV along the dihedral scan for Re(EtPy).

Dihedral		T_1	T_2	T_3
37°	S_0	175.32071	273.01819	141.23387
	S_1	6.01038	731.20074	15.02106
	S_2	678.4549	469.59869	459.70877
	S_3	554.87036	409.87885	374.07642
		T_1	T_2	T_3
52°	S_0	176.39174	241.43927	206.02515
	S_1	4.57224	765.11823	25.44425
	S_2	536.30432	139.22527	518.91235
	S_3	528.63068	619.04541	513.052
		T_1	T_2	T_3
67°	S_0	183.84534	267.77319	188.93393
	S_1	64.25043	702.51019	226.22246
	S_2	643.99219	422.02704	494.9913
	S_3	541.87042	477.23489	389.8132
		T_1	T_2	T_3
82°	S_0	187.83893	263.85355	203.16907
	S_1	87.1899	701.65588	245.58733
	S_2	612.8269	391.47192	499.15982
	S_3	532.10211	520.75214	423.96722
		T_1	T_2	T_3
127°	S_0	176.13571	237.69489	205.57658
	S_1	7.83694	765.11938	35.3829
	S_2	534.57983	134.06396	516.94244
	S_3	529.698	620.44165	514.30963

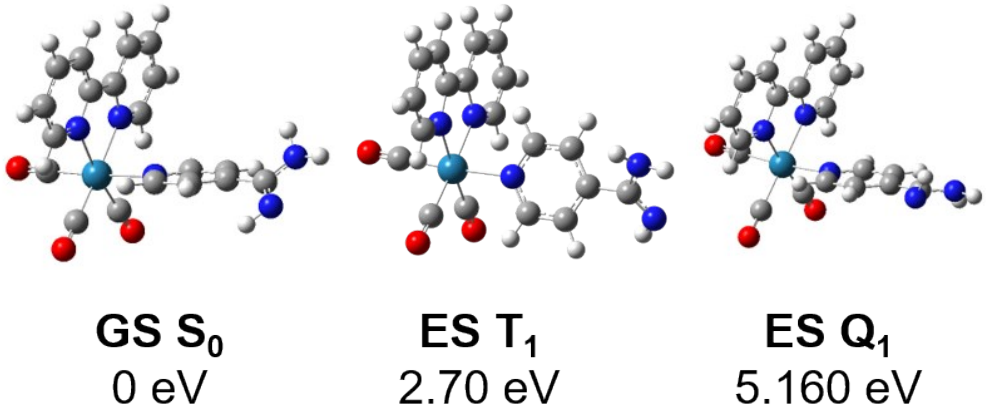


Figure S12. Fully optimized Re(4-Pam) GS on the S_0 surface and excited states (ESs) on the T_1 and Q_1 surfaces.

The energy of the lowest lying quintet clearly indicates that quintets are not at play within the energetic window of the experiments preformed (excitations ~ 370 nm, 3.35 eV).

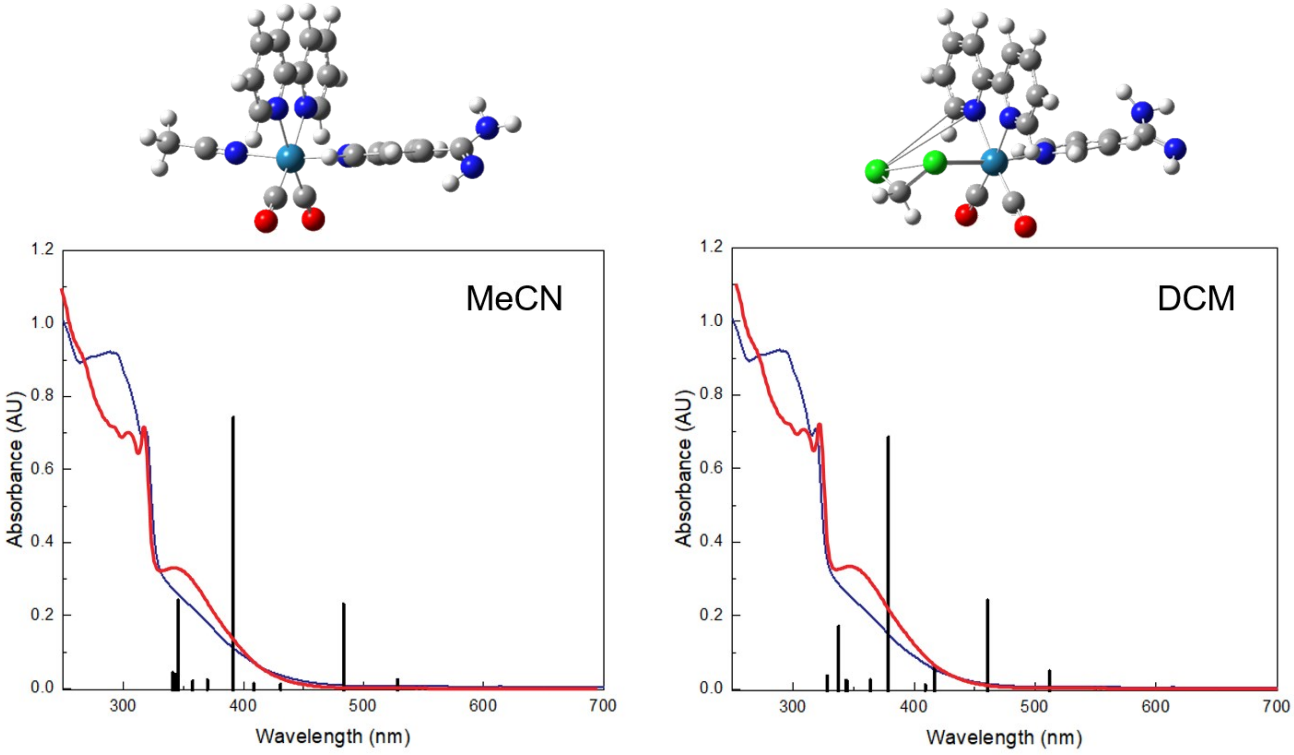


Figure S13. TDDFT calculated excitations for solvent-CO ligand exchanged Re(4-Pam) with MeCN and DCM.

The solvent coordination results in excitations a wavelengths > 450 nm which are not seen in the steady-state of transient absorption experiments.

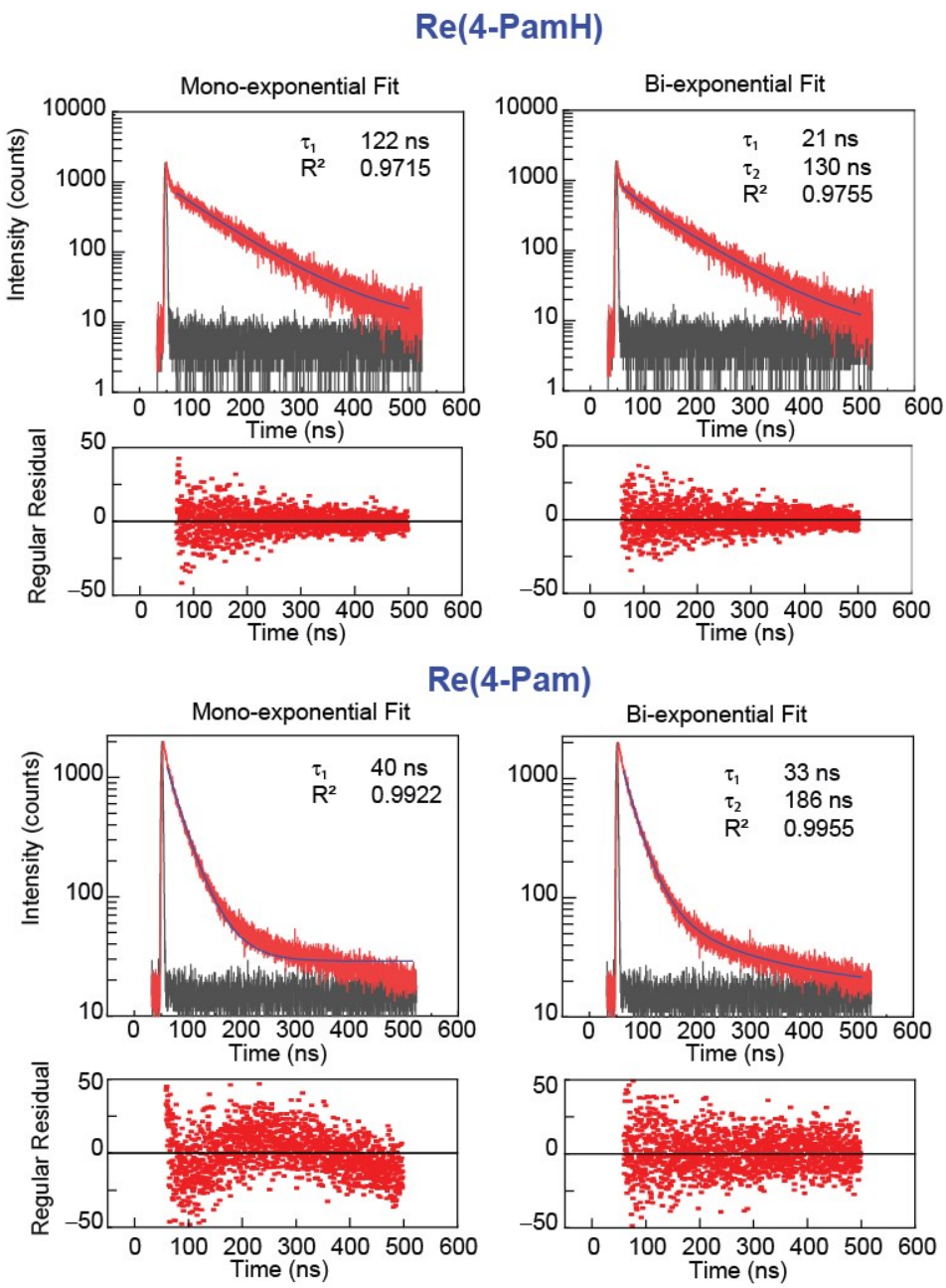


Figure S14. Time-resolved photoluminescence data fitting showing PL data (red), IRF (black) and residual after fitting to mono- or bi-exponential functions (below each data plot).

Fitting of the TSCSP time-resolve emission data fit to a mono- and bi-exponential function for (top) Re(4-PamH) and (bottom) Re(4-Pam). Fitting Re(4-PamH) shows a good residual and R^2 value that does not improve with addition of a second lifetime, indicating that a mono-exponential fit is most appropriate for the Re(4-PamH) moiety. On the other hand, fitting Re(4-Pam) data to a mono-exponential function shows a substantial, structured residual, indicating the presence of a second lifetime. Fitting of the data to a (right) bi-exponential function yield better residuals and better R^2 value.

All Variables Unfixed

	0 deg C	10 deg C	Room T	38 deg C
T1 (ns)	22.7	21.6	24.2	17.1
A1	0.51	0.42	0.6	0.45
T2 (ns)	75.7	75	77.1	56.3
A2	0.49	0.58	0.4	0.55
R^2	0.981	0.98	0.983	0.989

Lifetimes fixed 22 & 75 ns

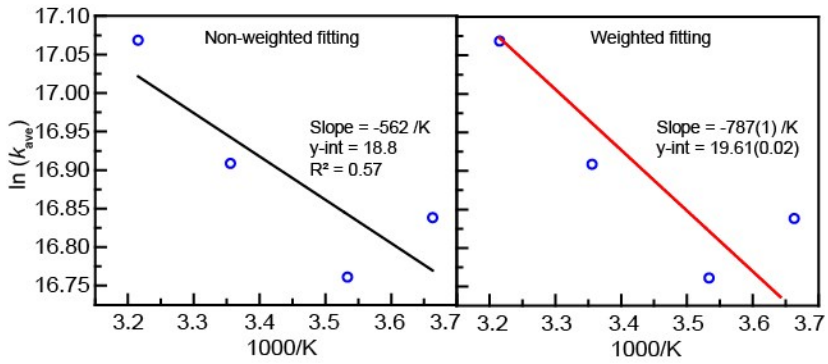
	0 deg C	10 deg C	Room T	38 deg C
T1 (ns)	22	22	22	22
A1	**0.47**	**0.42**	**0.56**	**0.64**
T2 (ns)	75	75	75	75
A2	**0.53**	**0.58**	**0.44**	**0.36**
R^2	0.982	0.98	0.983	0.982

Amplitudes fixed 50/50

	0 deg C	10 deg C	Room T	38 deg C
T1 (ns)	**23.3**	**25**	**21.3**	**19.1**
A1	0.5	0.5	0.5	0.5
T2 (ns)	**77.2**	**82.3**	**68.6**	**60.3**
A2	0.5	0.5	0.5	0.5
R^2	0.982	0.98	0.984	0.989

We performed fitting of the temperature-dependent photoluminescence data of Re4-Pam in three ways. First (top table), we allowed all of the variables to vary in the biexponential decay trace: the two lifetimes with the two corresponding amplitudes. Second (middle table), we took the average value of each lifetime from the top table and fixed those to be 22 ns and 75 ns, respectively, in order to isolate the variation of the amplitudes. Third (bottom table) we took the average of the amplitudes of the top table, approximately 50% for each lifetimes and fixed those values for the fit in order to isolate the variation of the lifetimes. The second and third fitting are less relevant to subsequent analysis, however, they do show that no matter how the data is fit, there is only a very slight temperature dependence of the fitted values.

The values obtained in the top table (for which all lifetimes and amplitudes varied), were used to calculate a weighted average to represent the temperature dependence of the lifetime $k_{ave} = \frac{1}{\tau_{ave}} = \frac{1}{A_1\tau_1 + A_2\tau_2}$. These values were plotted in an Arrhenius type plot (ln k_{ave} vs 1/T), shown below.

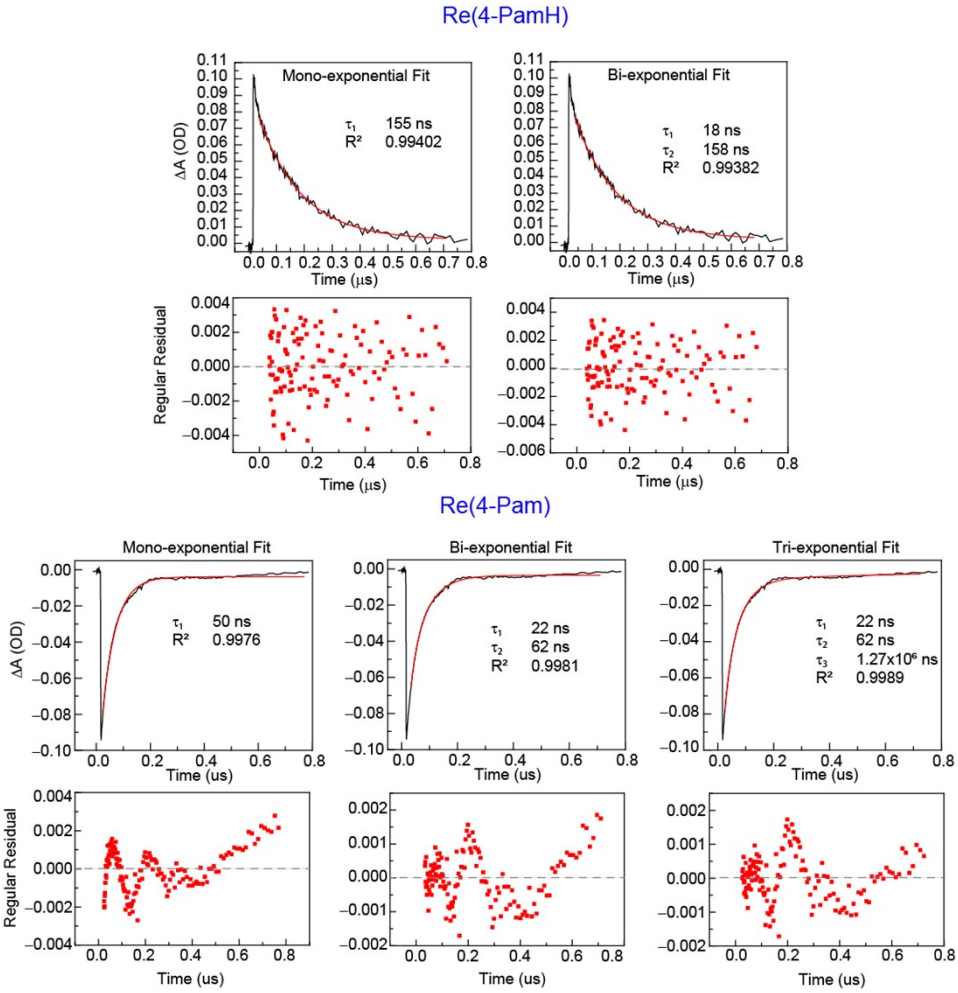


These data were fit with both a non-weighted (left) and weighted (right) linear regressions. The slope of the linear fit is related to the activation energy (E_a) of this process by E_a = slope × R. Given the two fits, activation energies of 48.4 meV (non-weighted fit) and 67.8 meV (weighted fit) are obtained. The very small values for the activation energy (room temperature ~ 25 meV for comparison) indicate that the process being measured possesses a very low activation barrier as we have calculated in our DFT computation.

Figure S15. Temperature-dependence photoluminescence and Arrhenius analysis for Re4-Pam.

Global analysis fitting of the nanosecond transient absorption (TA) data.

Each data set was fit to one principal component using the global analysis fitting of the Surface Xplorer program(Ultrafast Systes). The single principal component obtained from global analysis was fit to mono- or bi-exponential fits for Re(4-PamH) and mono-, bi-, or tri- exponential fits for Re(4-Pam) using Origin. The results of the fits and their residuals are shown below.



Global analysis fitting of the Re(4-PamH) nanosecond TA data (top) using a mono-exponential fit (left) reproduced the single lifetime obtained from the time-resolved PL data well. The data fit clearly to a mono-exponential fit with good residual. Addition of an additional lifetime (τ_2, on the right), does not improve the fit or the R^2 value.

Global analysis fitting of Re(4-Pam) is more complex, however does ***support*** the time-resolved PL data in assignment of two lifetimes for the deprotonated moiety. A single principal component was used (addition of the second component contributed less than 5%). The trace of the single principal component was fit to mono-, bi-, and tri- exponential fits with lifetimes, R^2 values, and residuals shown above. Addition of the second lifetime (middle column) improves the residual from the mono-exponential fit (left column) even though the residual is not ideal. However, addition of a third lifetime (right column) does not improve the residual (nor the R^2 value) appreciably. Further, the fitted τ_3 lifetime is essentially infinite on the timescale of the data collection.

Figure S16. Nano-second transient absorption fitting for Re4-PamH and Re4-Pam.

Time-resolved photoluminescence of Re(4-Pam) and Re(4-PamH) with the PF_6 and BArF counter ions reveal nominally different lifetimes for the two species. Importantly, when either counter ion is used, Re(4-Pam) shows biexpoential kinetics in both cases, and the Re(4-PamH) retains a clear monoexpoential fit.

Time-resolved Emission Lifetimes

	Counter ion	τ_1(Ampl[§]) (ns)	τ_2(Ampl[§]) (ns)
Re(4-Pam)	PF_6	23 ± 8 (59)	80 ± 30 (41)
	BArF	36 ± 5 (58)	234 ± 33 (42)
Re(4-PamH)	PF_6	131 ± 19	
	BArF	137 ± 12	

[§] Amplitude of the contribution of each lifetime to the overall signal.

Figure S17. Summary of emission lifetimes of the PF_6 and BArF counter ions of Re(4-Pam) and Re(4-PamH).

Re(4-Pam) TDDFT Tables

Table S4. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = -82.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1895	388.73	0.0072	100	→	102	-0.27046
			101	→	102	0.64641
3.3261	372.76	0.0584	98	→	102	-0.20201
			99	→	102	0.18793
			100	→	102	0.60292
			101	→	102	0.23043
3.4282	361.66	0.0334	98	→	102	0.60459
			99	→	102	-0.24403
			100	→	102	0.22742
			101	→	102	0.12738
3.8147	325.01	0.0027	98	→	102	0.29565
			99	→	102	0.63050
3.8396	322.91	0.021	100	→	103	-0.48879
			101	→	103	0.50004
3.9103	317.07	0.111	99	→	103	0.11861
			100	→	103	0.49538
			101	→	103	0.46904
4.067	304.86	0.0307	98	→	103	0.59223
			99	→	103	-0.34814
			101	→	103	0.11829
4.1227	300.74	0.0444	97	→	102	0.43307
			98	→	103	0.13659
			99	→	103	0.31226
			100	→	104	-0.21948
			101	→	104	0.34361
4.129	300.28	0.0557	96	→	103	-0.10489
			97	→	102	-0.22847
			98	→	103	0.33314
			99	→	103	0.49986
			100	→	104	0.11837
			101	→	104	-0.21754
4.2354	292.73	0.0642	97	→	102	-0.29519
			100	→	104	0.21116
			101	→	104	0.54840
			101	→	105	0.20247
			101	→	105	0.20247

Table S5. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = -67.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.2021	387.2	0.005	100	→	102	0.42069
			101	→	102	0.56296
3.315	374.01	0.0728	98	→	102	0.11502
			99	→	102	0.19791
			100	→	102	0.53772
			101	→	102	-0.38889
3.4144	363.12	0.0185	98	→	102	0.56651
			99	→	102	0.36136
			100	→	102	-0.15303
			101	→	102	0.13769
3.8116	325.28	0.0023	98	→	102	-0.39977
			99	→	102	0.56957
3.821	324.48	0.005	100	→	103	0.54194
			101	→	103	0.44363
3.9076	317.29	0.1168	99	→	103	-0.15073
			100	→	103	-0.43313
			101	→	103	0.51778
4.0588	305.47	0.0432	98	→	103	0.5003
			99	→	103	0.46181
			101	→	103	0.1415
4.1205	300.9	0.0059	96	→	103	0.11547
			97	→	102	-0.15017
			98	→	103	-0.45126
			99	→	103	0.48531
4.1339	299.92	0.1142	97	→	102	0.5063
			98	→	103	-0.14765
			99	→	103	0.12105
			100	→	104	0.29884
			101	→	104	0.28304
			101	→	105	-0.12809
4.2545	291.42	0.036	97	→	102	-0.21219
			100	→	104	-0.11334
			101	→	104	0.612
			101	→	105	0.20677

Table S6. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = -52.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.2073	386.57	0.0025	100	→	102	0.67828
			101	→	102	0.18724

3.3044	375.21	0.0788	99	→	102	0.19332
			100	→	102	-0.18008
			101	→	102	0.64628
3.4072	363.88	0.0137	98	→	102	0.53272
			99	→	102	0.42176
			101	→	102	-0.17393
3.8054	325.81	0.0002	100	→	103	0.67901
			101	→	103	0.18257
3.8112	325.32	0.0021	98	→	102	-0.45376
			99	→	102	0.53098
			101	→	102	-0.10265
3.8979	318.08	0.1216	99	→	103	0.16739
			100	→	103	-0.1759
			101	→	103	0.64847
4.0447	306.54	0.0453	98	→	103	0.46125
			99	→	103	0.49737
			101	→	103	-0.17483
4.1173	301.13	0.0138	96	→	103	0.11792
			98	→	103	0.51099
			99	→	103	-0.46018
4.1357	299.79	0.1146	97	→	102	0.53972
			100	→	104	0.39177
			101	→	105	-0.15753
4.2859	289.28	0.0177	99	→	104	0.10602
			101	→	104	0.66271
			101	→	105	0.13447

Table S7. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = -37.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1951	388.04	0.005	100	→	102	-0.39129
			101	→	102	0.58342
3.3111	374.46	0.0702	98	→	102	0.10956
			99	→	102	0.20849
			100	→	102	0.55571
			101	→	102	0.35835
3.4094	363.65	0.0201	98	→	102	0.52675
			99	→	102	0.41134
			100	→	102	-0.16751
			101	→	102	-0.13796
3.8091	325.5	0.0024	98	→	102	-0.45273
			99	→	102	0.53093
3.8229	324.32	0.0058	100	→	103	0.522

			101	→	103	-0.46814
3.9101	317.09	0.1149	99	→	103	0.15674
			100	→	103	0.45714
			101	→	103	0.49728
4.0603	305.36	0.0412	98	→	103	0.45922
			99	→	103	0.50231
			101	→	103	-0.13728
4.126	300.49	0.0499	96	→	103	0.10743
			97	→	102	0.21024
			98	→	103	0.45998
			99	→	103	-0.42928
			100	→	104	-0.12153
			101	→	104	0.13649
4.1304	300.18	0.0701	97	→	102	0.47358
			98	→	103	-0.23307
			99	→	103	0.16243
			100	→	104	-0.27592
			101	→	104	0.28824
			101	→	105	-0.11768
4.2475	291.9	0.0374	97	→	102	-0.22239
			100	→	104	0.15027
			101	→	104	0.60098
			101	→	105	0.20604

Table S8. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = -22.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1749	390.51	0.0072	100	→	102	-0.23541
			101	→	102	0.65977
3.3223	373.19	0.0542	98	→	102	0.20631
			99	→	102	-0.20855
			100	→	102	0.6073
			101	→	102	0.1943
3.421	362.42	0.0363	98	→	102	0.56695
			99	→	102	-0.30259
			100	→	102	-0.25451
			101	→	102	-0.12277
3.8032	326	0.0032	98	→	102	0.36063
			99	→	102	0.59806
3.8418	322.72	0.0298	100	→	103	-0.43459
			101	→	103	0.54775
3.9146	316.73	0.0999	99	→	103	-0.12015
			100	→	103	0.54376

			101	→	103	0.41478
4.0693	304.68	0.0291	98	→	103	0.5481
			99	→	103	-0.41224
			101	→	103	-0.1138
4.1167	301.17	0.0802	97	→	102	0.46585
			99	→	103	0.10192
			100	→	104	-0.21877
			101	→	104	0.44308
4.1332	299.97	0.0166	96	→	103	0.11855
			98	→	103	0.42522
			99	→	103	0.53762
4.2283	293.23	0.075	97	→	102	-0.32536
			100	→	104	0.23857
			101	→	104	0.51592
			101	→	105	0.2084

Table S9. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = -7.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1502	393.58	0.0062	100	→	102	-0.13701
			101	→	102	0.68539
3.3231	373.10	0.0387	98	→	102	0.28847
			99	→	102	-0.17946
			100	→	102	0.60698
3.4305	361.41	0.0552	98	→	102	0.57986
			99	→	102	-0.21063
			100	→	102	-0.31968
3.8004	326.24	0.0033	98	→	102	0.27181
			99	→	102	0.64350
3.8547	321.65	0.0759	100	→	103	-0.32796
			101	→	103	0.61132
3.9130	316.85	0.0695	100	→	103	0.61415
			101	→	103	0.31328
4.0657	304.95	0.0172	98	→	103	0.62060
			99	→	103	-0.29991
4.1083	301.79	0.0641	97	→	102	-0.44872
			100	→	104	-0.15119
			101	→	104	0.49335
4.1388	299.57	0.0214	96	→	103	0.11966
			98	→	103	0.30548
			99	→	103	0.61696
4.2378	292.57	0.1156	97	→	102	0.38425
			100	→	104	0.23015

			100	→	105	0.13191
			101	→	104	0.46324
			101	→	105	0.21654

Table S10. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 7.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1502	393.58	0.0062	100	→	102	-0.13701
			101	→	102	0.68539
3.3231	373.1	0.0387	98	→	102	0.28847
			99	→	102	-0.17946
			100	→	102	0.60698
3.4305	361.41	0.0552	98	→	102	0.57986
			99	→	102	-0.21063
			100	→	102	-0.31968
3.8004	326.24	0.0033	98	→	102	0.27181
			99	→	102	0.6435
3.8547	321.65	0.0759	100	→	103	-0.32796
			101	→	103	0.61132
3.913	316.85	0.0695	100	→	103	0.61415
			101	→	103	0.31328
4.0657	304.95	0.0172	98	→	103	0.6206
			99	→	103	-0.29991
4.1083	301.79	0.0641	97	→	102	-0.44872
			100	→	104	-0.15119
			101	→	104	0.49335
4.1388	299.57	0.0214	96	→	103	0.11966
			98	→	103	0.30548
			99	→	103	0.61696
4.2378	292.57	0.1156	97	→	102	0.38425
			100	→	104	0.23015
			100	→	105	0.13191
			101	→	104	0.46324
			101	→	105	0.21654

Table S11. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 22.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.11	398.67	0.0034	101	→	102	0.69817
3.3277	372.58	0.0239	98	→	102	0.37783
			99	→	102	0.16287
			100	→	102	0.56929

3.433	361.16	0.0747	98	→	102	0.51301
			99	→	102	0.24657
			100	→	102	-0.40582
3.8019	326.11	0.0012	98	→	102	-0.2942
			99	→	102	0.63636
3.8198	324.59	0.1763	101	→	103	0.68689
3.8731	320.12	0.0068	100	→	103	0.69026
			100	→	107	0.1083
4.0095	309.22	0.0029	98	→	103	0.62746
			99	→	103	0.29374
4.0905	303.1	0.053	97	→	102	-0.42004
			101	→	104	0.5376
4.1171	301.14	0.0206	96	→	103	0.11627
			98	→	103	-0.29222
			99	→	103	0.62519
4.2552	291.37	0.1968	97	→	102	0.47684
			100	→	104	0.10024
			100	→	105	0.22487
			101	→	104	0.40749
			101	→	105	0.14825

Table S12. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 37.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1011	399.81	0.0029	101	→	102	0.69907
3.3271	372.65	0.0218	98	→	102	-0.25829
			99	→	102	-0.34636
			100	→	102	0.55422
3.4293	361.54	0.0771	98	→	102	0.35227
			99	→	102	0.42746
			100	→	102	0.42667
3.8005	326.23	0.0108	98	→	102	0.52581
			99	→	102	-0.4236
			101	→	103	0.18638
3.8091	325.49	0.181	98	→	102	-0.15995
			99	→	102	0.10423
			101	→	103	0.66669
3.8622	321.02	0.0002	100	→	103	0.69398
			100	→	107	0.10922
3.9946	310.38	0.0008	98	→	103	0.41949
			99	→	103	0.55219
4.0848	303.52	0.0472	97	→	102	-0.41282
			101	→	104	0.54648

4.1112	301.58	0.0214	96	→	103	0.11502
			98	→	103	0.54917
			99	→	103	-0.42016
4.2577	291.2	0.2225	97	→	102	0.50203
			100	→	105	-0.24542
			101	→	104	0.40377

Table S13. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 52.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1077	398.96	0.0034	101	→	102	0.69799
3.3251	372.87	0.0240	98	→	102	-0.23293
			99	→	102	-0.34436
			100	→	102	0.56618
3.4301	361.46	0.0739	98	→	102	0.37607
			99	→	102	0.42497
			100	→	102	0.40784
3.8022	326.09	0.0103	98	→	102	0.52398
			99	→	102	-0.42745
			101	→	103	0.17572
3.8221	324.39	0.1657	98	→	102	-0.15162
			99	→	102	0.10069
			101	→	103	0.66287
3.8748	319.98	0.0086	100	→	103	0.68791
			100	→	107	0.10745
4.0103	309.16	0.0031	98	→	103	0.41258
			99	→	103	0.55586
4.0894	303.18	0.0486	97	→	102	0.41966
			101	→	104	0.53798
4.123	300.71	0.0213	96	→	103	0.11738
			98	→	103	0.55144
			99	→	103	-0.41311
4.2544	291.43	0.1950	97	→	102	0.47472
			100	→	104	-0.10576
			100	→	105	-0.2252
			101	→	104	-0.40433
			101	→	105	-0.15674

Table S14. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 67.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1280	396.37	0.0047	101	→	102	0.693490

3.3251	372.87	0.0294	98	→	102	-0.274150
			99	→	102	-0.267780
			100	→	102	0.586660
3.4337	361.08	0.0665	98	→	102	0.499820
			99	→	102	0.316630
			100	→	102	0.368770
3.8007	326.22	0.004	98	→	102	-0.403240
			99	→	102	0.558120
			101	→	103	-0.109880
3.8421	322.7	0.1309	100	→	103	-0.193560
			101	→	103	0.654910
3.8966	318.19	0.0314	100	→	103	0.667200
			100	→	107	0.100270
			101	→	103	0.181540
4.0405	306.85	0.0095	98	→	103	0.527880
			99	→	103	0.445800
4.1003	302.38	0.0565	97	→	102	0.438880
			100	→	104	-0.101430
			101	→	104	0.514250
4.1342	299.9	0.0203	96	→	103	-0.120260
			98	→	103	-0.443330
			99	→	103	0.524150
4.2476	291.89	0.1528	97	→	102	-0.427170
			100	→	104	0.174530
			100	→	105	0.176440
			101	→	104	0.431780
			101	→	105	0.214630

Table S15. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 82.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1525	393.29	0.0066	100	→	102	-0.15098
			101	→	102	0.68245
3.3275	372.61	0.0397	98	→	102	-0.24593
			99	→	102	0.24718
			100	→	102	0.60042
			101	→	102	0.10496
3.4316	361.3	0.054	98	→	102	0.53671
			99	→	102	-0.29942
			100	→	102	0.32204
			101	→	102	0.10109
3.8028	326.03	0.0024	98	→	102	0.37746
			99	→	102	0.57914

3.8554	321.59	0.0785	100	→	103	-0.32877
			101	→	103	0.60737
3.914	316.77	0.069	100	→	103	0.61322
			101	→	103	0.31248
4.0663	304.91	0.0172	98	→	103	0.52295
			99	→	103	-0.44655
4.1086	301.77	0.0641	97	→	102	0.44946
			100	→	104	-0.15894
			101	→	104	0.48989
4.1434	299.23	0.0163	96	→	103	0.11873
			98	→	103	0.45229
			99	→	103	0.51836
4.2364	292.67	0.1161	97	→	102	-0.3852
			100	→	104	0.2216
			100	→	105	0.12298
			101	→	104	0.46738
			101	→	105	0.21606

Table S16. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 97.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.183	389.53	0.0075	100	→	102	-0.25396
			101	→	102	0.65273
3.3274	372.61	0.0548	98	→	102	-0.17620
			99	→	102	-0.23515
			100	→	102	0.60177
			101	→	102	0.21012
3.4282	361.66	0.0355	98	→	102	0.54469
			99	→	102	0.34486
			100	→	102	0.24672
			101	→	102	0.12850
3.8106	325.37	0.002	98	→	102	-0.40455
			99	→	102	0.56043
3.8469	322.29	0.0303	100	→	103	-0.45107
			101	→	103	0.53014
3.9165	316.57	0.1035	99	→	103	-0.12425
			100	→	103	0.53041
			101	→	103	0.43039
4.0724	304.45	0.0262	98	→	103	0.46667
			99	→	103	0.50110
			101	→	103	0.11387
4.1209	300.87	0.0885	97	→	102	0.47489
			100	→	104	-0.23106

			101	→	104	0.42778
4.1409	299.41	0.0072	96	→	103	0.11664
			98	→	103	0.51482
			99	→	103	-0.45575
4.2313	293.02	0.0731	97	→	102	-0.31859
			100	→	104	0.21704
			101	→	104	0.52999
			101	→	105	0.20441

Table S17. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 112.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.2032	387.07	0.0052	100	→	102	0.42125
			101	→	102	0.56206
3.3161	373.89	0.0703	99	→	102	0.21483
			100	→	102	0.53670
			101	→	102	-0.38680
3.4175	362.79	0.0196	98	→	102	0.52292
			99	→	102	0.41958
			100	→	102	-0.15533
			101	→	102	0.14259
3.8154	324.95	0.0018	98	→	102	-0.44949
			99	→	102	0.50989
			101	→	103	-0.12667
3.8240	324.23	0.0065	99	→	102	0.11251
			100	→	103	0.53826
			101	→	103	0.42637
3.9073	317.32	0.1200	99	→	103	-0.15328
			100	→	103	-0.43198
			101	→	103	0.51939
4.0596	305.41	0.0382	98	→	103	0.40191
			99	→	103	0.54896
			101	→	103	0.13940
4.1307	300.15	0.0546	96	→	103	0.10125
			97	→	102	0.22917
			98	→	103	0.49683
			99	→	103	-0.37010
			100	→	104	0.13673
			101	→	104	0.13933
4.1338	299.93	0.0635	97	→	102	0.47483
			98	→	103	-0.26778
			99	→	103	0.15160
			100	→	104	0.28142

			101	→	104	0.25413
			101	→	105	-0.12344
4.2520	291.59	0.0355	97	→	102	-0.21399
			100	→	104	-0.10699
			101	→	104	0.61318
			101	→	105	0.20303

Table S18. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 127.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.2106	386.17	0.0024	100	→	102	0.70244
3.3056	375.08	0.0780	99	→	102	0.19914
			101	→	102	0.67011
3.4110	363.49	0.0134	98	→	102	0.49892
			99	→	102	0.46321
			101	→	102	-0.17500
3.8061	325.75	0.0000	100	→	103	0.70145
3.8184	324.70	0.0020	98	→	102	0.49239
			99	→	102	-0.49185
			101	→	102	0.11116
3.8951	318.30	0.1241	99	→	103	0.16895
			101	→	103	0.67002
4.0454	306.48	0.0441	98	→	103	0.38096
			99	→	103	0.56056
			101	→	103	-0.17823
4.1255	300.53	0.0045	96	→	103	-0.10954
			98	→	103	0.57499
			99	→	103	-0.37555
4.1369	299.70	0.1193	97	→	102	0.54135
			100	→	104	0.39597
			101	→	105	0.16254
4.2892	289.06	0.0132	99	→	104	0.11179
			100	→	105	-0.11888
			101	→	104	0.67713

Table S19. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 142.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.2028	387.11	0.005	100	→	102	-0.44672
			101	→	102	0.54247
3.3127	374.27	0.0729	99	→	102	0.20419
			100	→	102	0.52045

			101	→	102	0.41513
3.4142	363.15	0.0173	98	→	102	0.53478
			99	→	102	0.41144
			100	→	102	-0.13972
			101	→	102	-0.13905
3.8149	325	0.0035	98	→	102	-0.2384
			99	→	102	0.28334
			100	→	103	0.4616
			101	→	103	-0.37426
3.8183	324.71	0.0036	98	→	102	-0.37901
			99	→	102	0.45145
			100	→	103	-0.32211
			101	→	103	0.1963
3.8985	318.03	0.1188	99	→	103	0.15391
			100	→	103	0.41009
			101	→	103	0.53632
4.0531	305.9	0.0419	98	→	103	0.42749
			99	→	103	0.52951
			101	→	103	-0.14394
4.1264	300.47	0.0127	97	→	102	0.25321
			98	→	103	0.47502
			99	→	103	-0.38377
			100	→	104	-0.14835
			101	→	104	0.12202
4.1345	299.88	0.103	97	→	102	0.46569
			98	→	103	-0.26918
			99	→	103	0.18318
			100	→	104	-0.28827
			101	→	104	0.24287
			101	→	105	-0.12239
4.2536	291.48	0.0332	97	→	102	-0.20256
			101	→	104	0.61935
			101	→	105	0.20578

Table S20. 10 TDDFT singlet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 157.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1825	389.58	0.0077	100	→	102	-0.26495
			101	→	102	0.64872
3.3239	373.01	0.0575	98	→	102	0.17207
			99	→	102	-0.21844
			100	→	102	0.60401
			101	→	102	0.22478

3.4238	362.13	0.0321	98	→	102	0.56479
			99	→	102	-0.32538
			100	→	102	-0.22972
			101	→	102	-0.12502
3.8153	324.96	0.0017	98	→	102	0.37736
			99	→	102	0.57684
3.8415	322.75	0.0276	100	→	103	-0.46008
			101	→	103	0.51916
3.9124	316.9	0.1043	99	→	103	-0.12425
			100	→	103	0.52157
			101	→	103	0.44017
4.0692	304.69	0.0318	98	→	103	0.4954
			99	→	103	-0.47372
			101	→	103	-0.11859
4.1209	300.86	0.0782	97	→	102	0.48112
			99	→	103	0.10101
			100	→	104	-0.24411
			101	→	104	0.40926
4.1372	299.68	0.0146	96	→	103	-0.11271
			98	→	103	0.48675
			99	→	103	0.48142
4.2309	293.05	0.066	97	→	102	-0.30441
			100	→	104	0.21059
			101	→	104	0.54134
			101	→	105	0.20724

Table S21. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = -82.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9051	426.77	0	97	→	102	-0.37826
			97	→	104	-0.14785
			100	→	102	-0.3073
			101	→	102	0.44537
3.0806	402.47	0	99	→	102	0.10606
			100	→	102	0.51478
			101	→	102	0.4273
3.2194	385.12	0	94	→	103	0.15567
			95	→	106	0.1007
			98	→	103	0.16398
			99	→	103	0.47655
			99	→	114	0.12774
			100	→	103	-0.181
			101	→	103	-0.35164

3.2507	381.41	0	97	→	102	0.52073
			97	→	104	0.12687
			100	→	102	-0.31478
			101	→	102	0.29251
3.3634	368.63	0	98	→	102	0.62514
			99	→	102	-0.28846
3.5691	347.38	0	94	→	103	-0.17609
			95	→	106	-0.15475
			96	→	103	-0.13043
			98	→	103	0.21423
			99	→	103	0.36863
			100	→	103	0.11471
			101	→	103	0.43212
3.7974	326.5	0	96	→	103	-0.11657
			100	→	103	0.58269
			101	→	103	-0.26577
			101	→	107	-0.11695
3.8071	325.66	0	98	→	102	0.2666
			99	→	102	0.61909
			101	→	102	-0.12433
3.8865	319.01	0	92	→	102	-0.11351
			93	→	105	0.18739
			97	→	102	-0.22863
			97	→	104	0.49457
			100	→	104	-0.13214
			100	→	105	-0.18886
			101	→	105	-0.16199
3.9674	312.5	0	91	→	102	-0.12164
			92	→	105	-0.15741
			93	→	104	-0.18953
			97	→	105	-0.26788
			97	→	109	-0.12857
			98	→	103	-0.13155
			100	→	104	0.31095
			101	→	104	0.24795
			101	→	105	-0.24264

Table S22. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = -67.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9066	426.56	0	92	→	102	0.10189
			97	→	102	0.38383
			97	→	104	0.15011

			100	→	102	-0.37914
			101	→	102	-0.38112
3.0736	403.38	0	99	→	102	-0.10817
			100	→	102	-0.44952
			101	→	102	0.50008
3.2237	384.6	0	94	→	103	-0.15687
			95	→	106	-0.10041
			98	→	103	-0.22401
			99	→	103	0.44495
			99	→	114	0.12503
			100	→	103	-0.20511
			101	→	103	0.34174
3.2558	380.81	0	97	→	102	0.52535
			97	→	104	0.1284
			100	→	102	0.34525
			101	→	102	0.26271
3.363	368.68	0	98	→	102	0.57398
			99	→	102	0.39292
3.5741	346.9	0	94	→	103	-0.1797
			95	→	106	-0.15657
			96	→	103	-0.13526
			98	→	103	0.29174
			99	→	103	-0.32375
			100	→	103	-0.17169
			101	→	103	0.39849
3.7869	327.41	0	100	→	103	0.58156
			101	→	103	0.33792
3.8035	325.98	0	98	→	102	-0.37276
			99	→	102	0.56353
			101	→	102	0.12843
3.8859	319.06	0	92	→	102	0.11531
			93	→	105	0.18128
			97	→	102	-0.23025
			97	→	104	0.49276
			100	→	104	0.12787
			100	→	105	0.17607
			101	→	105	-0.19384
3.9589	313.18	0	91	→	102	0.12317
			92	→	105	-0.16045
			93	→	104	0.18004
			97	→	105	0.25641
			97	→	109	0.12496
			100	→	104	0.27071
			100	→	105	0.13655

			101	→	104	-0.26
			101	→	105	0.22235

Table S23. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = -52.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9062	426.62	0	92	→	102	0.10892
			97	→	102	-0.38518
			97	→	104	-0.15273
			100	→	102	0.51909
			101	→	102	0.13593
3.0678	404.14	0	99	→	102	0.10267
			100	→	102	-0.16398
			101	→	102	0.65452
3.211	386.12	0	94	→	103	-0.1568
			98	→	103	-0.26423
			99	→	103	0.42483
			99	→	114	0.1155
			101	→	103	-0.38803
3.2572	380.65	0	97	→	102	0.52794
			97	→	104	0.13151
			100	→	102	0.4228
3.3598	369.03	0	98	→	102	0.53612
			99	→	102	0.44626
3.5663	347.65	0	94	→	103	0.18178
			95	→	106	-0.15702
			96	→	103	-0.13283
			98	→	103	-0.32319
			99	→	103	0.29164
			101	→	103	0.42844
3.776	328.35	0	100	→	103	0.67711
			101	→	103	0.12646
3.8031	326.01	0	98	→	102	-0.42698
			99	→	102	0.52541
			101	→	102	-0.15749
3.888	318.89	0	92	→	102	-0.12351
			92	→	104	0.11042
			93	→	105	0.19146
			97	→	102	-0.23116
			97	→	103	-0.10013
			97	→	104	0.49283
			101	→	105	-0.26951
3.9535	313.61	0	91	→	102	-0.11411

			92	→	105	-0.14869
			93	→	104	-0.16763
			96	→	103	-0.18067
			97	→	105	-0.23264
			97	→	109	0.11471
			98	→	103	-0.14494
			99	→	103	-0.12284
			100	→	105	-0.22952
			100	→	106	-0.12874
			100	→	107	-0.13491
			101	→	103	-0.12423
			101	→	104	0.34053

Table S24. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = -37.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9021	427.22	0	92	→	102	-0.10206
			97	→	102	-0.37933
			97	→	104	-0.14817
			100	→	102	-0.36397
			101	→	102	0.40055
3.0692	403.96	0	100	→	102	0.47494
			101	→	102	0.47821
3.2325	383.55	0	94	→	103	-0.15846
			95	→	106	0.10259
			98	→	103	-0.26434
			99	→	103	0.42777
			99	→	114	0.1168
			100	→	103	-0.20233
			101	→	103	-0.3353
3.2527	381.18	0	97	→	102	0.52763
			97	→	104	0.12906
			100	→	102	-0.32719
			101	→	102	0.27675
3.3567	369.37	0	98	→	102	0.53339
			99	→	102	0.44453
3.5786	346.46	0	94	→	103	0.17875
			95	→	106	-0.15745
			96	→	103	-0.13265
			98	→	103	-0.31877
			99	→	103	0.29089
			100	→	103	0.16461
			101	→	103	0.40767

3.797	326.53	0	98	→	102	0.19736
			99	→	102	-0.23527
			100	→	103	0.53514
			101	→	103	-0.28453
3.8014	326.15	0	98	→	102	-0.37933
			99	→	102	0.47496
			100	→	103	0.2775
			101	→	102	-0.10112
			101	→	103	-0.14749
3.8852	319.12	0	92	→	102	0.11632
			93	→	105	0.1772
			97	→	102	-0.23053
			97	→	104	0.48992
			100	→	104	-0.13319
			100	→	105	-0.1859
			101	→	105	-0.18721
3.9518	313.74	0	91	→	102	-0.10438
			92	→	105	0.1372
			93	→	104	-0.15325
			95	→	103	0.11379
			96	→	103	-0.22102
			97	→	105	-0.21431
			97	→	109	-0.1071
			98	→	103	-0.17609
			99	→	103	-0.15704
			100	→	103	-0.10433
			100	→	104	0.24861
			100	→	105	0.11127
			101	→	103	-0.10063
			101	→	104	0.21537
			101	→	105	-0.19465
			101	→	107	-0.10405

Table S25. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = -22.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.896	428.12	0	97	→	102	-0.36861
			97	→	104	-0.14391
			100	→	102	-0.27542
			101	→	102	0.47478
3.0754	403.15	0	100	→	102	0.54126
			101	→	102	0.39313
3.2261	384.31	0	94	→	103	-0.15598

			95	→	106	-0.10517
			98	→	103	0.20762
			99	→	103	0.46656
			99	→	114	0.13457
			100	→	103	0.16696
			101	→	103	0.34018
3.245	382.08	0	97	→	102	0.52256
			97	→	104	0.12795
			100	→	102	-0.29728
			101	→	102	0.2976
3.3538	369.69	0	98	→	102	0.59211
			99	→	102	-0.35043
3.5719	347.11	0	94	→	103	-0.1763
			95	→	106	-0.16171
			96	→	103	-0.12546
			98	→	103	-0.24703
			99	→	103	-0.33213
			100	→	103	0.10543
			101	→	103	0.44675
3.7971	326.52	0	98	→	102	0.33419
			99	→	102	0.59272
			101	→	102	0.11334
3.8151	324.98	0	100	→	103	0.59766
			100	→	107	0.11479
			101	→	103	-0.24109
			101	→	107	-0.13015
3.8878	318.9	0	92	→	102	-0.1138
			93	→	105	0.18221
			97	→	102	-0.22579
			97	→	104	0.48724
			100	→	104	-0.11454
			100	→	105	-0.18851
			101	→	105	-0.17073
3.9489	313.97	0	95	→	103	-0.2358
			96	→	103	0.32141
			97	→	105	0.10411
			98	→	103	0.33774
			99	→	103	-0.21726
			100	→	103	0.13346
			100	→	104	-0.13279
			101	→	103	0.12972
			101	→	104	-0.10239
			101	→	105	0.1106
			101	→	107	0.12149

Table S26. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = -7.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8876	429.37	0	97	→	102	0.35837
			97	→	104	0.13998
			100	→	102	-0.20135
			101	→	102	0.51794
3.0868	401.65	0	97	→	102	-0.11426
			100	→	102	0.58625
			101	→	102	0.31512
3.2268	384.23	0	97	→	102	0.43357
			97	→	104	0.10788
			98	→	102	-0.10867
			99	→	103	-0.26309
			100	→	102	0.23095
			101	→	102	-0.25668
			101	→	103	-0.20702
3.2358	383.17	0	94	→	103	0.12839
			97	→	102	0.29392
			98	→	103	0.12916
			99	→	103	0.39523
			99	→	114	0.11243
			100	→	102	0.12764
			100	→	103	0.10189
			101	→	102	-0.19049
			101	→	103	0.3088
3.344	370.77	0	98	→	102	0.62712
			99	→	102	-0.26318
			100	→	102	0.11595
3.5575	348.51	0	94	→	103	0.15701
			95	→	106	-0.15446
			96	→	103	-0.11045
			98	→	103	-0.18301
			99	→	103	-0.37687
			101	→	103	0.45861
			101	→	107	0.10243
3.7974	326.5	0	98	→	102	0.24717
			99	→	102	0.63589
			101	→	102	0.11502
3.8167	324.84	0	97	→	104	0.10159
			100	→	103	0.59863
			100	→	107	0.16086
			101	→	103	-0.15154
			101	→	107	-0.14345

3.8913	318.62	0	92	→	102	-0.1146
			93	→	105	-0.19579
			97	→	102	-0.221
			97	→	104	0.47918
			100	→	103	-0.12332
			100	→	105	0.19943
			101	→	105	0.1395
3.9368	314.94	0	95	→	103	-0.23471
			96	→	103	0.31404
			98	→	103	0.41867
			98	→	107	0.16521
			99	→	103	-0.1752
			99	→	107	-0.10347
			101	→	103	0.13102
			101	→	107	0.16973

Table S27. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 7.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8785	430.72	0	97	→	102	0.3489
			97	→	104	0.13634
			100	→	102	-0.13025
			101	→	102	0.54655
3.103	399.57	0	97	→	102	-0.12348
			98	→	102	-0.10702
			100	→	102	0.61971
			101	→	102	0.2356
3.2073	386.57	0	94	→	103	-0.10921
			97	→	102	0.37991
			98	→	102	-0.10258
			99	→	103	-0.31917
			100	→	102	0.18591
			101	→	102	-0.23902
			101	→	103	-0.27412
3.2206	384.97	0	94	→	103	0.11261
			97	→	102	0.36585
			99	→	103	0.34717
			100	→	102	0.12507
			101	→	102	-0.24386
			101	→	103	0.29017
3.3358	371.68	0	98	→	102	0.64721
			99	→	102	-0.1989
			100	→	102	0.13615

3.5224	351.98	0	94	→	103	0.13866
			95	→	106	0.13341
			98	→	103	-0.13563
			99	→	103	-0.40967
			101	→	103	0.46046
			101	→	107	0.11947
3.7983	326.42	0	98	→	102	0.18264
			99	→	102	0.65105
			101	→	102	0.11433
3.8107	325.36	0	100	→	103	0.61816
			100	→	107	0.17565
			101	→	107	-0.1048
3.8897	318.75	0	92	→	102	-0.11246
			93	→	105	-0.20178
			97	→	102	-0.22017
			97	→	104	0.47639
			98	→	105	-0.10187
			100	→	105	0.22023
			101	→	104	-0.13625
3.9168	316.55	0	95	→	103	-0.18368
			96	→	103	0.22759
			98	→	103	0.50051
			98	→	107	0.2222
			99	→	103	-0.14278
			101	→	107	0.12239

Table S28. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 22.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8703	431.96	0	97	→	102	0.34108
			97	→	104	0.13414
			101	→	102	0.56381
3.1171	397.75	0	100	→	102	0.65405
			101	→	102	0.13287
3.1967	387.86	0	97	→	102	0.44598
			97	→	104	0.11883
			98	→	103	0.10727
			99	→	103	-0.23419
			100	→	102	0.13149
			101	→	102	-0.30172
			101	→	103	-0.24788
3.206	386.73	0	94	→	103	0.13264
			97	→	102	0.31091

			98	→	103	-0.1633
			99	→	103	0.34571
			101	→	102	-0.21269
			101	→	103	0.36258
3.3276	372.59	0	98	→	102	0.61811
			99	→	102	0.2839
			100	→	102	0.14117
3.4944	354.8	0	94	→	103	0.12033
			95	→	106	-0.11825
			98	→	103	0.18716
			99	→	103	-0.42526
			101	→	103	0.44003
			101	→	107	0.12569
3.798	326.45	0	98	→	102	-0.29228
			99	→	102	0.61616
			101	→	102	0.11296
3.8077	325.61	0	98	→	103	0.13325
			100	→	103	0.63627
			100	→	107	0.18831
3.8878	318.91	0	92	→	102	-0.10587
			93	→	105	-0.20205
			97	→	102	-0.21568
			97	→	104	0.46836
			99	→	102	0.11441
			100	→	105	0.2341
			101	→	104	-0.18473
3.8994	317.95	0	98	→	103	0.52654
			98	→	107	0.2587
			99	→	103	0.24449
			99	→	107	0.11133
			100	→	103	-0.15711

Table S29. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 37.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8655	432.68	0	97	→	102	0.33734
			97	→	104	0.13387
			101	→	102	0.56987
3.1217	397.17	0	100	→	102	0.67266
3.1868	389.06	0	94	→	103	-0.16146
			95	→	106	0.1145
			98	→	103	-0.3523
			99	→	103	0.29058

			101	→	103	0.44732
3.1929	388.31	0	97	→	102	0.55691
			97	→	104	0.15001
			101	→	102	-0.38377
3.3226	373.15	0	98	→	102	0.42238
			99	→	102	0.53686
			100	→	102	-0.13718
3.4794	356.34	0	94	→	103	-0.11708
			95	→	106	0.11458
			98	→	103	0.3622
			99	→	103	-0.30052
			101	→	103	0.43751
			101	→	107	0.12596
3.7965	326.58	0	98	→	102	0.53592
			99	→	102	-0.4265
			101	→	102	-0.11176
3.8059	325.77	0	99	→	103	-0.14634
			100	→	103	0.63968
			100	→	107	0.19032
3.8826	319.33	0	93	→	105	0.1306
			97	→	102	-0.13752
			97	→	104	0.30654
			98	→	103	0.28175
			98	→	107	0.13491
			99	→	103	0.33093
			99	→	107	0.1707
			100	→	103	0.15944
			100	→	105	-0.16378
			101	→	104	-0.1616
3.8924	318.53	0	93	→	105	0.1577
			97	→	102	-0.1738
			97	→	104	0.36846
			98	→	103	-0.25727
			98	→	107	-0.11464
			99	→	103	-0.30256
			99	→	107	-0.14446
			100	→	103	-0.13819
			100	→	105	-0.18037
			101	→	104	-0.10899

Table S30. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 52.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions

2.8681	432.29	0	97	→	102	-0.33885
			97	→	104	-0.13476
			101	→	102	0.56486
3.1148	398.04	0	98	→	102	0.11474
			100	→	102	0.65343
			101	→	102	0.13397
3.1949	388.07	0	97	→	102	0.45571
			97	→	104	0.12209
			98	→	103	0.18329
			99	→	103	-0.15808
			100	→	102	-0.13095
			101	→	102	0.30504
			101	→	103	-0.24167
3.2086	386.41	0	94	→	103	-0.13279
			97	→	102	0.30228
			98	→	103	-0.28829
			99	→	103	0.25391
			101	→	102	0.20377
			101	→	103	0.36966
3.3256	372.82	0	98	→	102	0.42147
			99	→	102	0.53373
			100	→	102	-0.13691
3.4988	354.37	0	94	→	103	-0.11845
			95	→	106	0.11831
			98	→	103	0.35566
			99	→	103	-0.30005
			101	→	103	0.43723
			101	→	107	0.12571
3.8007	326.22	0	98	→	102	0.52065
			99	→	102	-0.42984
			101	→	102	-0.11261
3.8112	325.32	0	99	→	103	-0.1497
			100	→	103	0.63046
			100	→	107	0.18807
3.8882	318.87	0	92	→	102	0.10402
			93	→	105	0.19824
			97	→	102	-0.21684
			97	→	104	0.47025
			100	→	105	-0.23505
			101	→	104	0.18505
3.8978	318.09	0	96	→	103	0.14082
			98	→	103	0.38161
			98	→	107	0.16433
			99	→	103	0.42232

			99	→	107	0.21488
			100	→	103	0.14734

Table S31. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 67.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.877	430.95	0	97	→	102	-0.34728
			97	→	104	-0.13739
			100	→	102	-0.13912
			101	→	102	0.54576
3.1018	399.72	0	97	→	102	0.12559
			98	→	102	0.12225
			100	→	102	0.61471
			101	→	102	0.24221
3.21	386.24	0	97	→	102	0.43982
			97	→	104	0.11341
			98	→	102	-0.10846
			98	→	103	0.1335
			99	→	103	-0.21402
			100	→	102	-0.20713
			101	→	102	0.27452
			101	→	103	-0.22622
3.2247	384.48	0	94	→	103	-0.12791
			97	→	102	0.29591
			98	→	103	-0.20921
			99	→	103	0.3375
			101	→	102	0.1951
			101	→	103	0.34299
3.3351	371.75	0	98	→	102	0.54513
			99	→	102	0.40252
			100	→	102	-0.13094
3.5309	351.14	0	94	→	103	-0.13481
			95	→	106	0.13342
			98	→	103	0.25596
			99	→	103	-0.35951
			101	→	103	0.44972
			101	→	107	0.11793
3.8005	326.23	0	98	→	102	-0.38327
			99	→	102	0.55312
			101	→	102	0.1169
3.8178	324.76	0	99	→	103	-0.12182
			100	→	103	0.61164
			100	→	107	0.17656

3.8901	318.71	0	92	→	102	0.10758
			93	→	105	0.19828
			97	→	102	-0.22139
			97	→	104	0.47793
			98	→	105	-0.1007
			100	→	105	-0.21733
			101	→	104	0.13309
			101	→	105	-0.10434
3.9183	316.42	0	95	→	103	0.18663
			96	→	103	0.24572
			98	→	103	0.42709
			98	→	107	0.17446
			99	→	103	0.28061
			99	→	107	0.15299
			101	→	107	-0.12927

Table S32. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 82.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8891	429.14	0	97	→	102	-0.35912
			97	→	104	-0.141
			100	→	102	-0.21117
			101	→	102	0.51364
3.0884	401.45	0	97	→	102	0.12313
			98	→	102	0.10988
			100	→	102	0.57368
			101	→	102	0.32862
3.2251	384.43	0	94	→	103	0.12865
			97	→	102	0.28891
			98	→	103	0.1833
			99	→	103	0.35574
			100	→	102	-0.17559
			100	→	103	-0.12547
			101	→	102	0.15773
			101	→	103	-0.3207
3.234	383.38	0	97	→	102	0.4356
			97	→	104	0.10856
			98	→	103	-0.12284
			99	→	103	-0.24267
			100	→	102	-0.21816
			101	→	102	0.26788
			101	→	103	0.21294
3.3473	370.4	0	98	→	102	0.57049

			99	→	102	-0.37309
			100	→	102	-0.10745
3.5631	347.97	0	94	→	103	-0.15474
			95	→	106	0.15499
			96	→	103	0.11608
			98	→	103	0.24211
			99	→	103	0.35575
			101	→	103	0.44903
3.8007	326.22	0	98	→	102	0.35463
			99	→	102	0.57815
			101	→	102	-0.12081
3.8211	324.48	0	97	→	104	0.10943
			100	→	103	0.59081
			100	→	107	0.1637
			101	→	103	-0.14474
			101	→	107	-0.14561
3.8912	318.62	0	92	→	102	0.1073
			93	→	105	0.192
			97	→	102	-0.22211
			97	→	104	0.4815
			100	→	103	-0.12984
			100	→	105	-0.19174
			101	→	105	-0.14855
3.9406	314.63	0	95	→	103	-0.23835
			96	→	103	0.29762
			98	→	103	0.38422
			98	→	107	0.15111
			99	→	103	-0.24583
			99	→	107	-0.13693
			101	→	103	-0.12308
			101	→	107	-0.17477

Table S33. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 97.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.902	427.24	0	97	→	102	-0.37343
			97	→	104	-0.1456
			100	→	102	-0.28929
			101	→	102	0.46177
3.0812	402.39	0	98	→	102	0.10185
			100	→	102	0.52348
			101	→	102	0.41071
3.2264	384.29	0	94	→	103	-0.15338

			95	→	106	-0.1054
			98	→	103	-0.23135
			99	→	103	0.42994
			99	→	114	0.12081
			100	→	103	0.18327
			101	→	103	0.36577
3.2485	381.66	0	97	→	102	0.52019
			97	→	104	0.1267
			100	→	102	-0.31317
			101	→	102	0.29056
3.3608	368.91	0	98	→	102	0.56107
			99	→	102	0.39983
3.5821	346.12	0	94	→	103	-0.17173
			95	→	106	-0.16147
			96	→	103	0.13256
			98	→	103	0.27382
			99	→	103	-0.33776
			101	→	103	0.42965
3.8052	325.83	0	98	→	102	-0.38217
			99	→	102	0.56139
			100	→	102	0.10501
			101	→	102	0.12494
3.8184	324.7	0	100	→	103	0.59794
			100	→	107	0.12348
			101	→	103	-0.23143
			101	→	107	-0.13381
3.8874	318.94	0	92	→	102	0.10904
			93	→	105	0.18281
			97	→	102	-0.2273
			97	→	104	0.49029
			100	→	104	-0.11593
			100	→	105	-0.18048
			101	→	105	-0.1715
3.9587	313.19	0	92	→	105	-0.10514
			93	→	104	0.1343
			95	→	103	0.20935
			96	→	103	0.25453
			97	→	105	0.17636
			98	→	103	0.24592
			99	→	103	0.19731
			100	→	103	-0.13292
			100	→	104	-0.20979
			101	→	104	-0.16879
			101	→	105	0.17093

			101	→	107	-0.11862

Table S34. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 112.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9076	426.42	0	92	→	102	-0.10143
			97	→	102	-0.38387
			97	→	104	-0.14966
			100	→	102	0.38279
			101	→	102	0.37689
3.0744	403.28	0	98	→	102	0.10149
			99	→	102	-0.1
			100	→	102	-0.4427
			101	→	102	0.50424
3.2243	384.53	0	94	→	103	-0.15539
			95	→	106	0.10139
			98	→	103	-0.26221
			99	→	103	0.4058
			99	→	114	0.11937
			100	→	103	-0.19889
			101	→	103	0.36647
3.2563	380.76	0	97	→	102	0.52439
			97	→	104	0.1276
			100	→	102	0.34962
			101	→	102	0.25746
3.3643	368.52	0	98	→	102	0.5259
			99	→	102	0.45448
3.5832	346.02	0	94	→	103	-0.17672
			95	→	106	0.15806
			96	→	103	0.13795
			98	→	103	0.32383
			99	→	103	-0.31105
			100	→	103	-0.13734
			101	→	103	0.3953
3.7989	326.37	0	100	→	103	0.60904
			101	→	103	0.29673
3.8084	325.55	0	98	→	102	-0.43258
			99	→	102	0.5175
			101	→	102	0.13284
3.8854	319.1	0	92	→	102	0.11561
			93	→	105	0.18101
			97	→	102	-0.2317
			97	→	104	0.4927

			100	→	104	0.13091
			100	→	105	0.17154
			101	→	105	-0.19457
3.9566	313.36	0	91	→	102	0.11633
			92	→	105	-0.1538
			93	→	104	0.17331
			96	→	103	0.15747
			97	→	105	0.24532
			97	→	109	0.11977
			100	→	104	0.26047
			100	→	105	0.13311
			101	→	104	-0.25083
			101	→	105	0.21339
			101	→	107	-0.11081

Table S35. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 127.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9077	426.4	0	92	→	102	0.10949
			97	→	102	-0.38741
			97	→	104	-0.15333
			100	→	102	0.53379
3.0694	403.94	0	98	→	102	-0.10254
			101	→	102	0.67281
3.2109	386.13	0	94	→	103	0.15528
			98	→	103	0.28889
			98	→	114	0.10384
			99	→	103	-0.38947
			99	→	114	-0.11248
			101	→	103	0.41419
3.2585	380.5	0	97	→	102	0.52653
			97	→	104	0.13058
			100	→	102	0.43553
3.3632	368.65	0	98	→	102	0.49804
			99	→	102	0.4885
3.5737	346.94	0	94	→	103	0.17943
			95	→	106	-0.15792
			96	→	103	0.13646
			98	→	103	-0.34503
			99	→	103	0.28546
			101	→	103	0.41962
3.7784	328.14	0	100	→	103	0.68999
3.8118	325.27	0	98	→	102	-0.46891

			99	→	102	0.4893
			101	→	102	-0.16524
3.8879	318.89	0	92	→	102	-0.12395
			92	→	104	0.11019
			93	→	105	-0.19322
			97	→	102	-0.23135
			97	→	103	-0.102
			97	→	104	0.49353
			101	→	105	0.27441
3.9552	313.47	0	91	→	102	-0.12197
			92	→	105	0.16036
			93	→	104	-0.18154
			96	→	103	0.12509
			97	→	105	0.24933
			97	→	109	0.12339
			100	→	105	0.25852
			100	→	106	-0.1499
			100	→	107	-0.16286
			101	→	104	0.36974

Table S36. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 142.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9053	426.75	0	92	→	102	0.10299
			97	→	102	0.38372
			97	→	104	0.15035
			100	→	102	0.40023
			101	→	102	-0.35904
3.0699	403.86	0	99	→	102	0.10159
			100	→	102	0.42319
			101	→	102	0.52222
3.212	386	0	94	→	103	-0.15479
			98	→	103	-0.25946
			99	→	103	0.41548
			99	→	114	0.12272
			100	→	103	-0.19737
			101	→	103	-0.36021
3.2564	380.74	0	97	→	102	0.52524
			97	→	104	0.12825
			100	→	102	-0.35475
			101	→	102	0.24773
3.3632	368.65	0	98	→	102	0.53577
			99	→	102	0.44257

3.5744	346.86	0	94	→	103	0.17876
			95	→	106	-0.15595
			96	→	103	0.1377
			98	→	103	-0.31076
			99	→	103	0.31146
			100	→	103	0.12866
			101	→	103	0.40891
3.7872	327.38	0	100	→	103	0.61363
			101	→	103	-0.29093
3.8107	325.36	0	98	→	102	-0.42359
			99	→	102	0.5294
			101	→	102	-0.13297
3.8859	319.06	0	92	→	102	0.11688
			93	→	105	0.18138
			97	→	102	-0.2299
			97	→	104	0.49184
			100	→	104	-0.12771
			100	→	105	-0.16887
			101	→	105	-0.20438
3.9576	313.28	0	91	→	102	-0.12393
			92	→	105	0.16541
			93	→	104	-0.18257
			97	→	105	-0.25958
			97	→	109	-0.12743
			100	→	104	0.26655
			100	→	105	0.15101
			101	→	104	0.27458
			101	→	105	-0.22176

Table S37. 10 TDDFT triplet excitations of Re(4-Pam) from S_0 $\theta_{dihedral}$ = 157.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8996	427.59	0	97	→	102	-0.37342
			97	→	104	-0.14600
			100	→	102	-0.30159
3.0764	403.02	0	100	→	102	0.51629
			101	→	102	0.42234
3.2251	384.44	0	94	→	103	-0.15511
			95	→	106	-0.10170
			98	→	103	0.21774
			99	→	103	0.43866
			99	→	114	0.13782
			100	→	103	0.19055

			101	→	103	0.36516
3.2492	381.58	0	97	→	102	0.52334
			97	→	104	0.12734
			100	→	102	-0.31672
			101	→	102	0.28564
3.3597	369.03	0	98	→	102	0.57828
			99	→	102	-0.37521
3.5751	346.8	0	94	→	103	-0.17109
			95	→	106	-0.15334
			96	→	103	0.13443
			98	→	103	-0.25666
			99	→	103	-0.35072
			101	→	103	0.43206
3.8083	325.56	0	98	→	102	0.28193
			99	→	102	0.44515
			100	→	103	0.37650
			101	→	103	-0.15228
3.8108	325.35	0	98	→	102	-0.22058
			99	→	102	-0.37198
			100	→	103	0.46970
			101	→	103	-0.18471
3.887	318.97	0	92	→	102	0.11164
			93	→	105	0.18029
			97	→	102	-0.22846
			97	→	104	0.49248
			100	→	104	-0.12579
			100	→	105	-0.18427
			101	→	105	-0.17351
3.9653	312.67	0	91	→	102	-0.12219
			92	→	105	0.15962
			93	→	104	-0.18831
			97	→	105	-0.26703
			97	→	109	-0.12989
			100	→	104	0.31125
			101	→	104	0.25553
			101	→	105	-0.25150

Re(4-PamH) TDDFT Tables

Table S38. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = -82.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1730	390.74	0.0141	100	→	102	-0.39854
			101	→	102	0.57566

3.2357	383.18	0.0133	100	→	102	0.14890
			100	→	103	-0.12716
			101	→	102	0.13085
			101	→	103	0.66128
3.2621	380.08	0.0814	99	→	102	-0.15477
			100	→	102	0.54592
			100	→	103	0.14922
			101	→	102	0.34835
			101	→	103	-0.17158
3.3594	369.06	0.0343	99	→	102	0.35313
			99	→	103	-0.28067
			100	→	103	0.52633
			101	→	103	0.11471
3.4044	364.18	0.0405	99	→	102	0.58476
			99	→	103	0.23344
			100	→	102	0.11278
			100	→	103	-0.25097
			101	→	102	0.14110
3.4739	356.9	0.0595	99	→	103	0.59921
			100	→	103	0.33219
			101	→	103	0.10728
3.9900	310.74	0.0017	98	→	102	0.70624
4.1289	300.28	0.1097	98	→	103	0.52595
			100	→	104	-0.17155
			101	→	104	0.39776
			101	→	105	0.10954
4.2457	292.03	0.0568	98	→	103	-0.27345
			100	→	104	0.28281
			101	→	104	0.54840
			101	→	105	-0.13700
4.3223	286.85	0.0899	98	→	103	0.25688
			100	→	104	0.58173
			100	→	106	-0.14900
			100	→	107	0.14079
			101	→	104	-0.13485

Table S39. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = -67.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1715	390.93	0.0046	100	→	102	0.32575
			101	→	102	0.62175
3.2416	382.48	0.0108	100	→	102	0.20144
			100	→	103	0.15921

			101	→	103	0.65040
3.2656	379.66	0.0815	99	→	102	0.15850
			100	→	102	0.56076
			100	→	103	-0.21776
			101	→	102	-0.28978
			101	→	103	-0.15841
3.3594	369.07	0.0414	99	→	102	0.32178
			99	→	103	0.27009
			100	→	103	0.53569
			101	→	103	-0.16352
3.4126	363.31	0.0421	99	→	102	0.57927
			99	→	103	-0.32070
			100	→	102	-0.14515
			100	→	103	-0.14686
			101	→	102	0.10910
3.4692	357.38	0.0641	99	→	102	0.17443
			99	→	103	0.56408
			100	→	102	-0.10814
			100	→	103	-0.33339
			101	→	103	0.12392
3.9965	310.23	0.0012	98	→	102	0.70543
4.1369	299.7	0.1292	98	→	103	0.55973
			100	→	104	-0.18020
			101	→	104	-0.32819
			101	→	105	0.13516
4.2674	290.54	0.0245	98	→	103	0.17650
			100	→	104	-0.30236
			101	→	104	0.56777
			101	→	105	0.15996
4.3198	287.01	0.0725	98	→	103	0.23982
			100	→	104	0.47731
			100	→	106	-0.22575
			100	→	107	0.25812
			101	→	104	0.20467
			101	→	106	0.10235
			101	→	107	-0.11475

Table S40. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = -52.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1606	392.28	0.0001	101	→	102	0.69935
3.2498	381.51	0.0030	101	→	103	0.69747
3.2540	381.02	0.0937	99	→	102	0.16231

			100	→	102	0.65438
			100	→	103	-0.19030
3.3599	369.01	0.0413	99	→	102	0.39229
			99	→	103	0.22608
			100	→	103	0.53313
3.4033	364.31	0.0432	99	→	102	0.52563
			99	→	103	-0.37620
			100	→	102	-0.18840
			100	→	103	-0.20224
3.4677	357.54	0.0658	99	→	102	0.20024
			99	→	103	0.54927
			100	→	102	-0.14523
			100	→	103	-0.35941
3.9922	310.56	0.0019	98	→	102	0.70496
4.1415	299.37	0.1396	98	→	103	0.57829
			100	→	105	-0.10194
			100	→	106	-0.11820
			101	→	104	0.34769
4.3056	287.96	0.0036	97	→	102	-0.10103
			100	→	104	0.13115
			100	→	105	0.53235
			100	→	106	-0.18792
			100	→	107	-0.34816
			101	→	105	0.10721
4.3295	286.37	0.0447	98	→	103	-0.20110
			100	→	104	0.23396
			100	→	106	0.20617
			100	→	107	0.14836
			101	→	104	0.47218
			101	→	105	0.30556

Table S41. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = -37.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.2209	384.93	0.0049	100	→	102	-0.30770
			101	→	102	0.61509
			101	→	103	-0.14815
3.2384	382.86	0.0035	100	→	102	-0.12091
			100	→	103	-0.20551
			101	→	103	0.65500
3.3084	374.75	0.0865	99	→	102	0.12889
			100	→	102	0.56682
			100	→	103	-0.29170

			101	→	102	0.26690
3.3642	368.54	0.0454	99	→	102	0.21114
			99	→	103	0.32336
			100	→	102	0.17982
			100	→	103	0.51464
			101	→	102	0.13736
			101	→	103	0.16815
3.4445	359.95	0.0239	99	→	102	-0.45997
			99	→	103	0.50812
			100	→	103	-0.13993
3.478	356.48	0.0766	99	→	102	0.47234
			99	→	103	0.36044
			100	→	102	-0.17388
			100	→	103	-0.28494
			101	→	102	-0.13165
			101	→	103	-0.11084
4.0541	305.82	0.0015	98	→	102	0.70496
4.1344	299.89	0.1240	98	→	103	0.55163
			100	→	104	-0.18717
			101	→	104	0.34121
			101	→	105	0.12972
4.2622	290.89	0.0287	98	→	103	-0.19022
			100	→	104	0.30510
			101	→	104	0.56696
			101	→	105	-0.15273
4.317	287.2	0.0749	98	→	103	0.24539
			100	→	104	0.49481
			100	→	106	-0.22862
			100	→	107	-0.23991
			101	→	104	-0.18612
			101	→	106	-0.10078
			101	→	107	-0.11445

Table S42. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = -22.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1952	388.03	0.0151	100	→	102	0.37029
			100	→	103	0.10870
			101	→	102	0.56407
			101	→	103	0.16611
3.2272	384.19	0.0099	100	→	103	0.11485
			101	→	102	0.17929
			101	→	103	0.66708

3.2897	376.89	0.0820	99	→	102	0.16877
			100	→	102	0.57904
			100	→	103	0.11226
			101	→	102	0.34221
3.3560	369.45	0.0349	99	→	102	0.24074
			99	→	103	0.32199
			100	→	103	0.56455
			101	→	103	0.10408
3.4284	361.64	0.0399	99	→	102	0.63867
			99	→	103	0.15928
			100	→	102	0.12113
			100	→	103	0.16472
			101	→	102	0.14018
3.4653	357.78	0.0582	99	→	103	0.60157
			100	→	103	0.33136
4.0239	308.12	0.0030	98	→	102	0.70594
4.1237	300.66	0.0993	98	→	103	0.51022
			100	→	104	0.16640
			101	→	104	0.42207
			101	→	105	0.10484
4.2384	292.53	0.0672	98	→	103	0.30063
			100	→	104	0.27899
			101	→	104	0.53415
			101	→	105	0.14624
4.3232	286.79	0.0899	98	→	103	0.25670
			100	→	104	0.59194
			100	→	106	0.12612
			100	→	107	0.11658
			101	→	104	0.11901

Table S43. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = -7.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1967	387.85	0.0127	100	→	102	-0.23582
			100	→	103	-0.11719
			101	→	102	0.38915
			101	→	103	0.52371
3.2384	382.86	0.0304	100	→	102	0.32492
			101	→	102	-0.41386
			101	→	103	0.46235
3.3048	375.17	0.0777	99	→	102	0.16149
			100	→	102	0.56140
			101	→	102	0.38002

3.3587	369.15	0.0238	99	→	102	0.22448
			99	→	103	0.33997
			100	→	103	0.56328
3.4371	360.73	0.0354	99	→	102	0.64308
			100	→	103	-0.21671
			101	→	102	-0.14708
3.4771	356.58	0.0608	99	→	103	0.60489
			100	→	103	-0.33337
4.0477	306.31	0.0078	98	→	102	0.70390
4.1194	300.98	0.0874	98	→	103	0.49544
			100	→	104	-0.11348
			101	→	104	0.46009
4.2503	291.71	0.1129	98	→	103	-0.36797
			100	→	104	0.23968
			100	→	105	-0.12854
			101	→	104	0.50063
			101	→	105	-0.10128
4.3311	286.27	0.0665	98	→	103	0.21317
			100	→	104	0.63472
			100	→	105	0.12826
			101	→	104	-0.10317

Table S44. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 7.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1762	390.36	0.0201	100	→	102	-0.19382
			101	→	102	0.39216
			101	→	103	0.54480
3.2312	383.71	0.0520	100	→	102	0.32692
			101	→	102	-0.43151
			101	→	103	0.43876
3.2854	377.38	0.0697	99	→	102	0.13269
			100	→	102	0.57909
			101	→	102	0.36274
3.3560	369.44	0.0111	99	→	102	0.34706
			99	→	103	0.35434
			100	→	102	-0.10557
			100	→	103	0.48703
3.4094	363.66	0.0258	99	→	102	0.59573
			99	→	103	-0.17502
			100	→	103	-0.29927
			101	→	102	-0.12911
3.4783	356.45	0.0715	99	→	103	0.57476

			100	→	103	-0.38788
4.0325	307.46	0.0086	98	→	102	0.70374
4.1156	301.25	0.0852	98	→	103	0.49284
			101	→	104	0.47228
4.2651	290.7	0.1605	98	→	103	-0.41665
			100	→	104	0.11880
			100	→	105	0.13678
			101	→	104	0.49409
			101	→	106	-0.10809
4.3403	285.66	0.0150	100	→	104	0.63575
			101	→	105	0.22848

Table S45. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 22.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1743	390.59	0.0051	101	→	102	0.14218
			101	→	103	0.68120
3.2370	383.02	0.1248	100	→	102	0.22430
			100	→	103	0.15825
			101	→	102	0.62520
			101	→	103	-0.16899
3.2822	377.75	0.0292	100	→	102	0.65753
			101	→	102	-0.23175
3.3604	368.95	0.0139	99	→	102	-0.22221
			99	→	103	-0.44026
			100	→	103	0.48824
			101	→	102	-0.11100
3.3944	365.26	0.0064	99	→	102	0.66509
			99	→	103	-0.14825
			100	→	103	0.15352
3.4738	356.91	0.0838	99	→	103	0.52545
			100	→	103	0.44928
			101	→	102	-0.11196
4.0434	306.64	0.0020	98	→	102	0.70581
4.1153	301.27	0.1015	98	→	103	0.51030
			101	→	104	-0.45446
4.2783	289.8	0.1588	98	→	103	0.39215
			100	→	105	-0.13977
			100	→	106	0.11737
			101	→	104	0.50440
			101	→	105	-0.15048
4.3203	286.98	0.0264	98	→	103	0.11899
			100	→	104	-0.19956

			101	→	105	0.63155

Table S46. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 37.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1675	391.43	0.0030	101	→	103	0.69723
3.2326	383.54	0.1607	100	→	103	0.17554
			101	→	102	0.67996
3.2707	379.08	0.0004	100	→	102	0.69820
3.3587	369.15	0.0161	99	→	103	-0.48125
			100	→	103	0.49044
			101	→	102	-0.12734
3.3784	367	0.0008	99	→	102	0.69794
3.4695	357.36	0.0864	99	→	103	0.50863
			100	→	103	0.46732
			101	→	102	-0.11741
4.0375	307.08	0.0010	98	→	102	0.70615
4.1148	301.31	0.1057	98	→	103	0.51633
			101	→	104	-0.45257
4.2865	289.24	0.0411	97	→	102	-0.10818
			98	→	103	0.15969
			100	→	104	0.11953
			101	→	104	0.20583
			101	→	105	0.61567
4.2900	289.00	0.1470	98	→	103	0.36839
			100	→	105	0.16670
			100	→	106	-0.12309
			101	→	104	0.46414
			101	→	105	-0.27067

Table S47. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 52.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1667	391.53	0.0195	100	→	102	0.14200
			101	→	102	-0.31781
			101	→	103	0.60865
3.2210	384.93	0.1011	100	→	102	-0.25690
			100	→	103	0.12725
			101	→	102	0.53734
			101	→	103	0.35109
3.2584	380.50	0.0391	100	→	102	0.63535
			101	→	102	0.28663

3.3488	370.24	0.0056	99	→	102	0.46432
			99	→	103	-0.34471
			100	→	103	0.39337
3.3801	366.81	0.0159	99	→	102	0.52334
			99	→	103	0.29049
			100	→	103	-0.35190
			101	→	102	0.10615
3.4721	357.09	0.081	99	→	103	0.53639
			100	→	103	0.43900
4.0210	308.34	0.0046	98	→	102	0.70518
4.1157	301.24	0.0971	98	→	103	0.50875
			101	→	104	0.45542
4.2786	289.78	0.1529	98	→	103	-0.38781
			100	→	105	-0.14092
			100	→	106	-0.11790
			101	→	104	0.50140
			101	→	105	0.16917
4.3149	287.34	0.0304	98	→	103	0.13295
			100	→	104	-0.18944
			101	→	105	0.62773

Table S48. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 67.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1725	390.81	0.0303	100	→	102	0.24850
			101	→	102	-0.43934
			101	→	103	0.48082
3.2174	385.36	0.0438	100	→	102	-0.29848
			101	→	102	0.37517
			101	→	103	0.50901
3.2598	380.35	0.0687	99	→	102	-0.11741
			100	→	102	0.57856
			101	→	102	0.37276
3.3488	370.23	0.0096	99	→	102	0.43686
			99	→	103	-0.32391
			100	→	103	0.43779
3.3907	365.66	0.0249	99	→	102	0.53825
			99	→	103	0.24404
			100	→	103	-0.35772
			101	→	102	0.12672
3.4749	356.80	0.0742	99	→	103	0.56984
			100	→	103	0.39716
4.0125	308.99	0.0059	98	→	102	0.70505

4.1160	301.23	0.0901	98	→	103	0.49855
			101	→	104	0.46538
4.2673	290.54	0.1546	98	→	103	-0.40756
			100	→	104	0.11649
			100	→	105	0.13847
			101	→	104	0.50111
			101	→	106	-0.10972

Table S49. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 82.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1955	388.00	0.0142	100	→	102	0.24729
			100	→	103	-0.12458
			101	→	102	-0.38578
			101	→	103	0.51909
3.2317	383.65	0.0329	100	→	102	-0.31206
			101	→	102	0.41824
			101	→	103	0.46781
3.2954	376.23	0.0758	99	→	102	-0.15268
			100	→	102	0.56654
			101	→	102	0.37872
3.3577	369.26	0.0231	99	→	102	0.24418
			99	→	103	-0.34634
			100	→	103	0.55163
3.4291	361.56	0.0330	99	→	102	0.64014
			100	→	103	-0.21938
			101	→	102	0.14366
3.4740	356.89	0.0639	99	→	103	0.59794
			100	→	103	0.34796
4.0411	306.81	0.0062	98	→	102	0.70478
4.1178	301.09	0.0865	98	→	103	0.49222
			100	→	104	-0.11611
			101	→	104	0.46332
4.2477	291.88	0.1116	98	→	103	-0.37009
			100	→	104	0.23832
			100	→	105	-0.12751
			101	→	104	0.49944
			101	→	105	-0.10642
4.3320	286.21	0.0673	98	→	103	0.21459
			100	→	104	0.63432
			100	→	105	0.12863

Table S50. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 97.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1822	389.62	0.0155	100	→	102	-0.39376
			101	→	102	0.56689
3.2328	383.51	0.0092	100	→	103	-0.12596
			101	→	102	0.13611
			101	→	103	0.67775
3.2729	378.82	0.0825	99	→	102	-0.16790
			100	→	102	0.56845
			100	→	103	0.10225
			101	→	102	0.35971
3.3564	369.39	0.0338	99	→	102	0.30176
			99	→	103	-0.30088
			100	→	103	0.54745
			101	→	103	0.10426
3.4172	362.82	0.0437	99	→	102	0.61305
			99	→	103	0.16994
			100	→	102	0.11320
			100	→	103	-0.23453
			101	→	102	0.14482
3.4716	357.14	0.0571	99	→	103	0.60958
			100	→	103	0.32213
4.0012	309.87	0.0026	98	→	102	0.70601
4.1263	300.47	0.103	98	→	103	0.51578
			100	→	104	-0.16619
			101	→	104	0.41464
			101	→	105	0.10513
4.2417	292.30	0.0644	98	→	103	-0.29407
			100	→	104	0.27926
			101	→	104	0.53885
			101	→	105	-0.14093
4.3238	286.75	0.0895	98	→	103	0.25580
			100	→	104	0.59693
			100	→	106	-0.12264
			100	→	107	0.10682
			101	→	104	-0.12412

Table S51. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 112.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.162	392.11	0.0045	100	→	102	0.33277
			101	→	102	0.61902

3.2389	382.8	0.0136	100	→	102	0.20811
			100	→	103	0.14624
			101	→	102	-0.10465
			101	→	103	0.64561
3.2587	380.47	0.0784	99	→	102	0.16582
			100	→	102	0.55598
			100	→	103	-0.20247
			101	→	102	-0.28557
			101	→	103	-0.19138
3.3531	369.75	0.0399	99	→	102	0.35106
			99	→	103	0.26158
			100	→	103	0.52821
			101	→	103	-0.15109
3.4079	363.81	0.048	99	→	102	0.57185
			99	→	103	-0.29344
			100	→	102	-0.15186
			100	→	103	-0.20331
			101	→	102	0.11715
3.4649	357.83	0.0605	99	→	102	0.12654
			99	→	103	0.58244
			100	→	103	-0.33052
			101	→	103	0.11863
3.9857	311.07	0.0009	98	→	102	0.70559
4.1356	299.79	0.1265	98	→	103	0.55554
			100	→	104	-0.18094
			101	→	104	-0.33555
			101	→	105	-0.13518
4.2636	290.80	0.0268	98	→	103	0.18685
			100	→	104	-0.30228
			101	→	104	0.56879
			101	→	105	-0.15135
4.3201	286.99	0.0766	98	→	103	0.24436
			100	→	104	0.50289
			100	→	106	-0.21440
			100	→	107	0.24007
			101	→	104	0.19313
			101	→	107	-0.10751

Table S52. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 127.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1461	394.09	0	101	→	102	0.70318
3.2406	382.59	0.0938	99	→	102	0.17058

			100	→	102	0.66159
			100	→	103	-0.16582
3.2497	381.52	0.0028	101	→	103	0.70098
3.3528	369.80	0.0392	99	→	102	0.45783
			99	→	103	0.19000
			100	→	103	0.49929
3.3955	365.14	0.0505	99	→	102	0.48270
			99	→	103	-0.36679
			100	→	102	-0.19747
			100	→	103	-0.29688
3.4646	357.86	0.0617	99	→	102	0.15811
			99	→	103	0.56897
			100	→	102	-0.13008
			100	→	103	-0.35769
3.9754	311.87	0.0015	98	→	102	0.70518
4.1415	299.37	0.1400	98	→	103	0.57850
			100	→	105	0.10629
			100	→	106	-0.11962
			101	→	104	0.35028
4.3058	287.95	0.0040	97	→	102	0.10424
			100	→	105	0.55128
			100	→	106	0.18769
			100	→	107	0.35431
4.3323	286.19	0.0425	98	→	103	-0.19504
			100	→	104	-0.28369
			100	→	106	0.19968
			100	→	107	0.12086
			101	→	104	0.43573
			101	→	105	0.32201

Table S53. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 142.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1635	391.92	0.004	100	→	102	-0.31947
			101	→	102	0.62454
3.2396	382.72	0.0172	100	→	102	-0.26745
			100	→	103	-0.14733
			101	→	103	0.62584
3.2573	380.63	0.0752	99	→	102	0.15488
			100	→	102	0.53622
			100	→	103	-0.23615
			101	→	102	0.28041
			101	→	103	0.22377

3.3572	369.31	0.0418	99	→	102	0.34079
			99	→	103	0.25617
			100	→	103	0.52952
			101	→	103	0.17018
3.4048	364.14	0.0428	99	→	102	0.56832
			99	→	103	-0.32779
			100	→	102	-0.14758
			100	→	103	-0.16405
			101	→	102	-0.10938
3.4663	357.69	0.0621	99	→	102	0.17449
			99	→	103	0.56654
			100	→	102	-0.10534
			100	→	103	-0.32853
			101	→	103	-0.12993
3.9916	310.62	0.0019	98	→	102	0.70560
4.1360	299.77	0.1284	98	→	103	0.55948
			100	→	104	-0.18765
			101	→	104	0.32453
			101	→	105	0.13597
4.2653	290.68	0.022	98	→	103	-0.16650
			100	→	104	0.30658
			101	→	104	0.56542
			101	→	105	-0.16549
4.3154	287.31	0.0714	98	→	103	0.24221
			100	→	104	0.45648
			100	→	106	-0.23810
			100	→	107	-0.26304
			101	→	104	-0.21461
			101	→	106	-0.11289
			101	→	107	-0.11696

Table S54. 10 TDDFT singlet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 157.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.2078	386.51	0.0161	100	→	102	-0.37254
			101	→	102	0.59161
3.2296	383.89	0.0067	100	→	103	-0.15698
			101	→	103	0.67949
3.2954	376.24	0.0844	99	→	102	0.14638
			100	→	102	0.57406
			100	→	103	-0.17907
			101	→	102	0.33240
3.3632	368.65	0.0381	99	→	102	0.20282

			99	→	103	0.33073
			100	→	103	0.56008
			101	→	103	0.13296
3.4331	361.14	0.0305	99	→	102	0.63469
			99	→	103	-0.25886
			100	→	102	-0.10392
			101	→	102	-0.11400
3.4710	357.20	0.0642	99	→	102	0.17227
			99	→	103	0.56264
			100	→	103	-0.33982
			101	→	102	-0.10277
			101	→	103	-0.11301
4.0344	307.32	0.0019	98	→	102	0.70625
4.1271	300.42	0.1075	98	→	103	0.52250
			100	→	104	-0.17591
			101	→	104	0.40110
			101	→	105	0.11070
4.2427	292.23	0.0586	98	→	103	-0.27777
			100	→	104	0.27661
			101	→	104	0.54864
			101	→	105	-0.14424
4.3229	286.81	0.0882	98	→	103	0.25474
			100	→	104	0.57442
			100	→	106	-0.15637
			100	→	107	-0.15418
			101	→	104	-0.12414
			101	→	107	-0.10444

Table S55. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = -82.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9195	424.68	0	98	→	103	-0.4039
			98	→	104	-0.13595
			100	→	103	-0.20548
			101	→	103	0.47435
3.0138	411.39	0	100	→	102	0.28614
			101	→	102	0.60814
3.1285	396.31	0	100	→	103	0.59705
			101	→	103	0.31638
3.1714	390.94	0	100	→	102	0.62618
			101	→	102	-0.30278
3.2654	379.69	0	98	→	103	0.50315
			99	→	103	-0.1074

			100	→	103	-0.23482
			101	→	103	0.3826
3.3498	370.13	0	99	→	102	0.65295
			99	→	103	-0.23139
3.3905	365.68	0	99	→	102	0.23832
			99	→	103	0.64234
3.8013	326.16	0	97	→	102	0.68572
3.8881	318.88	0	95	→	103	0.10505
			95	→	104	-0.11266
			95	→	106	-0.11416
			96	→	105	0.14068
			96	→	106	-0.11612
			98	→	103	-0.22671
			98	→	104	0.46083
			98	→	105	0.18873
			98	→	106	0.14813
			100	→	104	-0.11029
			100	→	105	0.13682
			100	→	106	-0.15494
3.9439	314.37	0	91	→	102	0.21927
			92	→	102	0.2524
			93	→	102	-0.13485
			96	→	102	-0.12741
			97	→	104	0.26205
			97	→	105	-0.25186
			97	→	106	-0.28787
			98	→	102	0.21415
			100	→	102	-0.10225
			101	→	102	-0.1279

Table S56. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = -67.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
1.9197	424.65	0	95	→	103	-0.10349
			98	→	103	0.40531
			98	→	104	0.13884
			100	→	103	0.19827
			101	→	103	0.47573
3.0358	408.41	0	100	→	102	-0.44852
			101	→	102	0.49745
3.1216	397.19	0	100	→	103	0.61382
			101	→	103	-0.29523
3.1612	392.21	0	100	→	102	0.50955

			101	→	102	0.47790
3.2687	379.31	0	98	→	103	0.50698
			98	→	104	0.10249
			100	→	103	-0.21479
			101	→	103	-0.39880
3.3599	369.01	0	99	→	102	0.66873
			99	→	103	0.17883
3.3870	366.06	0	99	→	102	-0.17933
			99	→	103	0.66822
3.8141	325.07	0	97	→	102	0.68596
3.8872	318.95	0	95	→	103	-0.11651
			95	→	104	0.10362
			96	→	105	-0.10773
			96	→	106	-0.17844
			98	→	103	-0.23793
			98	→	104	0.45296
			98	→	105	-0.23297
			100	→	104	-0.10252
			100	→	105	-0.10139
			100	→	106	-0.18756
3.9589	313.18	0	91	→	102	0.21762
			92	→	102	0.25444
			93	→	102	0.15603
			96	→	102	0.11555
			97	→	104	-0.25692
			97	→	105	-0.34566
			97	→	106	0.22925
			98	→	102	-0.13616
			100	→	102	0.13506
			101	→	102	-0.10171

Table S57. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = -52.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9190	424.75	0	95	→	103	0.10970
			98	→	103	-0.40391
			98	→	104	-0.16174
			101	→	103	0.50773
3.0341	408.64	0	92	→	102	0.12062
			100	→	102	0.66182
			101	→	102	0.10255
3.1177	397.68	0	100	→	103	0.68024
3.1460	394.10	0	100	→	102	-0.10488

			101	→	102	0.68993
3.2704	379.12	0	98	→	103	0.50435
			98	→	104	0.11985
			101	→	103	0.45326
3.3534	369.73	0	99	→	102	0.69237
			100	→	102	0.11118
3.3851	366.26	0	99	→	103	0.69471
3.8145	325.03	0	97	→	102	0.68585
3.8877	318.92	0	95	→	103	-0.12011
			95	→	104	0.10694
			96	→	106	0.19514
			98	→	102	-0.11563
			98	→	103	-0.24641
			98	→	104	0.50616
			100	→	105	-0.13427
			100	→	106	-0.21403
3.9620	312.93	0	92	→	102	0.32725
			93	→	102	-0.14671
			96	→	102	0.10747
			97	→	105	0.44268
			97	→	106	-0.20548
			100	→	102	-0.16851
			101	→	105	0.10808

Table S58. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = -37.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9166	425.09	0	95	→	103	0.10267
			98	→	103	-0.40154
			98	→	104	-0.13964
			100	→	103	-0.20524
			101	→	103	0.47727
3.0803	402.50	0	100	→	102	0.42478
			100	→	103	0.11379
			101	→	102	0.50171
3.1160	397.89	0	100	→	103	0.60261
			101	→	103	0.29590
3.2126	385.94	0	100	→	102	0.52062
			101	→	102	-0.46036
3.2670	379.50	0	98	→	103	0.50770
			98	→	104	0.10447
			100	→	103	-0.21202
			101	→	103	0.39026

3.3791	366.91	0	99	→	102	0.12682
			99	→	103	0.67865
3.4138	363.19	0	99	→	102	0.67991
			99	→	103	-0.12650
3.8463	322.35	0	97	→	102	0.68229
3.8874	318.94	0	95	→	103	-0.11694
			95	→	104	0.10756
			96	→	105	0.12078
			96	→	106	-0.16750
			98	→	103	-0.23361
			98	→	104	0.45994
			98	→	105	0.21541
			100	→	104	-0.11083
			100	→	105	0.11610
			100	→	106	-0.18436
3.9766	311.79	0	91	→	102	-0.18680
			92	→	102	-0.22657
			93	→	102	-0.13312
			96	→	102	-0.10217
			97	→	104	0.22699
			97	→	105	-0.31466
			97	→	106	-0.23298
			98	→	102	0.15449
			100	→	102	-0.12073
			100	→	104	-0.17838
			101	→	102	-0.10441
			101	→	105	-0.11238

Table S59. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = -22.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9114	425.85	0	98	→	103	-0.39345
			98	→	104	-0.13473
			100	→	103	-0.19954
			101	→	103	0.48132
3.0335	408.72	0	100	→	102	0.26225
			100	→	103	0.10279
			101	→	102	0.61049
3.1226	397.05	0	100	→	103	0.58563
			101	→	102	-0.11757
			101	→	103	0.32004
3.2050	386.84	0	98	→	103	-0.11464
			100	→	102	0.62856

			101	→	102	-0.26587
3.2623	380.06	0	98	→	103	0.49601
			99	→	103	0.10997
			100	→	102	0.11161
			100	→	103	-0.24922
			101	→	103	0.36437
3.3575	369.27	0	99	→	102	0.48156
			99	→	103	0.48849
3.3999	364.67	0	99	→	102	0.50019
			99	→	103	-0.47602
3.8185	324.69	0	97	→	102	0.68342
			97	→	109	-0.10347
3.8881	318.88	0	95	→	103	0.10623
			95	→	104	-0.11362
			95	→	106	-0.10465
			96	→	105	0.15799
			98	→	103	-0.22771
			98	→	104	0.46453
			98	→	105	0.16047
			98	→	106	0.16735
			100	→	104	-0.10931
			100	→	105	0.15919
			100	→	106	-0.13061
3.9545	313.53	0	91	→	102	-0.21323
			92	→	102	-0.25952
			93	→	102	-0.13601
			96	→	102	-0.12970
			97	→	104	0.26433
			97	→	105	-0.21328
			97	→	106	-0.33857
			98	→	102	0.15458
			100	→	102	-0.10166
			100	→	104	-0.10652
			101	→	102	-0.13672

Table S60. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = -7.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9073	426.47	0	98	→	103	-0.38155
			98	→	104	-0.13324
			100	→	103	-0.15848
			101	→	102	0.1678
			101	→	103	0.48348

3.0320	408.91	0	100	→	102	0.17803
			101	→	102	0.63088
3.1314	395.93	0	100	→	102	0.15545
			100	→	103	0.58656
			101	→	103	0.28268
3.2365	383.08	0	98	→	103	-0.33714
			100	→	102	0.5191
			101	→	102	-0.14015
			101	→	103	-0.26214
3.2554	380.85	0	98	→	103	0.36835
			99	→	103	0.11413
			100	→	102	0.40025
			100	→	103	-0.26386
			101	→	103	0.2878
3.3536	369.7	0	99	→	102	0.41715
			99	→	103	0.53226
			100	→	103	0.13284
3.4131	363.26	0	99	→	102	0.55418
			99	→	103	-0.41347
3.8306	323.67	0	97	→	102	0.67718
			97	→	109	-0.10588
3.8880	318.89	0	95	→	105	0.15033
			96	→	105	-0.14032
			98	→	103	-0.23717
			98	→	104	0.47217
			98	→	106	0.20412
			100	→	105	0.20089
3.9516	313.76	0	91	→	102	-0.22552
			92	→	102	-0.26153
			93	→	102	-0.10445
			96	→	102	0.13947
			97	→	104	0.25477
			97	→	105	0.15517
			97	→	106	-0.37623
			98	→	102	0.11422
			101	→	102	-0.14503
			101	→	107	-0.12256

Table S61. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 7.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8982	427.80	0	98	→	103	-0.36531
			98	→	104	-0.12914

			100	→	103	-0.10357
			101	→	102	0.23450
			101	→	103	0.48552
2.9923	414.35	0	98	→	103	0.12250
			100	→	102	0.10718
			101	→	102	0.62811
			101	→	103	-0.17181
3.1383	395.07	0	99	→	103	-0.11762
			100	→	102	0.23694
			100	→	103	0.59041
			101	→	103	0.21082
3.2309	383.75	0	98	→	102	0.10188
			98	→	103	0.47246
			98	→	104	0.10370
			100	→	102	-0.26792
			101	→	103	0.38620
3.2481	381.71	0	98	→	103	0.16471
			100	→	102	0.59045
			100	→	103	-0.27021
			101	→	103	0.12322
3.3362	371.63	0	99	→	102	0.49085
			99	→	103	0.46167
			100	→	103	0.15270
3.3939	365.31	0	99	→	102	0.48887
			99	→	103	-0.48674
3.8176	324.77	0	97	→	102	0.67577
			97	→	109	-0.10539
3.8890	318.81	0	95	→	105	-0.13311
			96	→	106	-0.12941
			98	→	103	-0.23798
			98	→	104	0.47170
			98	→	105	0.14584
			98	→	106	0.14082
			100	→	105	-0.16837
			100	→	106	0.13478
			101	→	104	0.11128
3.9422	314.51	0	91	→	102	0.23055
			92	→	102	0.26449
			96	→	102	-0.13532
			97	→	104	0.23067
			97	→	105	-0.28411
			97	→	106	-0.28749
			98	→	102	-0.13266
			101	→	102	0.14072

			101	→	104	0.12561
			101	→	107	0.16511

Table S62. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 22.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8976	427.88	0	98	→	103	0.38016
			98	→	104	0.13820
			101	→	102	0.11720
			101	→	103	0.52624
2.9665	417.95	0	101	→	102	0.66562
3.1491	393.72	0	99	→	103	0.13910
			100	→	102	0.10360
			100	→	103	0.64630
			101	→	103	-0.12537
3.2215	384.87	0	98	→	103	0.51877
			98	→	104	0.11923
			100	→	103	-0.12288
			101	→	103	-0.41588
3.2524	381.20	0	100	→	102	0.68745
3.3439	370.78	0	99	→	102	0.31902
			99	→	103	0.59897
			100	→	103	-0.15327
3.3707	367.83	0	99	→	102	0.61783
			99	→	103	-0.31432
3.8196	324.60	0	97	→	102	0.67993
			97	→	109	-0.10345
3.8903	318.70	0	95	→	105	0.10930
			95	→	106	-0.10497
			96	→	106	-0.14119
			98	→	103	-0.23136
			98	→	104	0.48078
			98	→	105	0.14958
			100	→	105	-0.15224
			100	→	106	0.16622
			101	→	104	-0.13124
3.9451	314.27	0	91	→	102	-0.23966
			92	→	102	-0.25767
			96	→	102	-0.11798
			97	→	104	0.17016
			97	→	105	-0.34546
			97	→	106	-0.24164
			98	→	102	-0.13952

		101	→	102	-0.13668
		101	→	104	-0.11649
		101	→	105	0.12217
		101	→	107	-0.18949

Table S63. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 37.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8944	428.35	0	95	→	103	0.10722
			98	→	103	0.38210
			98	→	104	0.14972
			101	→	103	0.54056
2.9498	420.31	0	101	→	102	0.67641
3.1513	393.44	0	99	→	103	0.14946
			100	→	103	0.66618
3.2158	385.54	0	98	→	103	0.52641
			98	→	104	0.13187
			100	→	102	0.10384
			101	→	103	-0.42350
3.2480	381.72	0	100	→	102	0.68902
3.3412	371.07	0	99	→	102	-0.15460
			99	→	103	0.66125
			100	→	103	-0.15733
3.3541	369.65	0	99	→	102	0.67812
			99	→	103	0.15248
3.8133	325.14	0	97	→	102	0.68172
			101	→	105	0.10515
3.8915	318.60	0	95	→	103	0.13126
			95	→	104	-0.11265
			96	→	105	-0.12020
			96	→	106	0.18002
			98	→	103	-0.22881
			98	→	104	0.50923
			100	→	105	0.15547
			100	→	106	-0.17444
			101	→	103	-0.10054
			101	→	104	-0.13250
3.9430	314.44	0	91	→	102	-0.24195
			92	→	102	-0.25767
			95	→	102	-0.15096
			97	→	105	0.38757
			97	→	106	0.23270
			98	→	102	-0.14449

		101	→	102	-0.13573
		101	→	105	-0.18121
		101	→	107	-0.19430

Table S64. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 52.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8928	428.59	0	98	→	103	-0.36162
			98	→	104	-0.13307
			101	→	102	-0.23600
			101	→	103	0.49957
2.9517	420.04	0	98	→	103	-0.12027
			101	→	102	0.63405
			101	→	103	0.18948
3.1431	394.46	0	99	→	103	0.13423
			100	→	102	-0.21687
			100	→	103	0.62317
			101	→	103	0.11414
3.2221	384.79	0	98	→	103	0.51473
			98	→	104	0.11944
			100	→	103	-0.10356
			101	→	103	0.41795
3.2325	383.55	0	100	→	102	0.66105
			100	→	103	0.19619
3.3262	372.75	0	99	→	102	0.54719
			99	→	103	-0.40489
			100	→	103	0.13633
3.3652	368.43	0	99	→	102	0.42719
			99	→	103	0.53878
			100	→	103	-0.10027
3.8041	325.92	0	97	→	102	0.67916
3.8904	318.69	0	95	→	105	-0.10912
			95	→	106	-0.10668
			96	→	106	-0.13990
			98	→	103	-0.23518
			98	→	104	0.47911
			98	→	105	-0.14928
			100	→	105	0.15231
			100	→	106	0.16719
			101	→	104	0.13101
3.9369	314.93	0	91	→	102	-0.23793
			92	→	102	0.26357
			96	→	102	0.12473

			97	→	104	-0.16934
			97	→	105	-0.34502
			97	→	106	0.24000
			98	→	102	0.16180
			101	→	102	-0.13794
			101	→	104	0.11103
			101	→	105	0.11964
			101	→	107	-0.17907

Table S65. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 67.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8967	428.02	0	98	→	103	-0.36333
			98	→	104	-0.12853
			100	→	103	-0.10536
			101	→	102	-0.23880
			101	→	103	0.48662
2.9733	416.99	0	98	→	103	-0.12795
			100	→	102	0.10329
			101	→	102	0.62779
			101	→	103	0.17570
3.1341	395.59	0	99	→	103	0.11553
			100	→	102	-0.23976
			100	→	103	0.59241
			101	→	103	0.20636
3.2198	385.07	0	98	→	103	0.20152
			100	→	102	0.61334
			100	→	103	0.15907
			101	→	103	0.17869
3.2362	383.12	0	98	→	103	0.46206
			99	→	103	-0.13293
			100	→	102	-0.20896
			100	→	103	-0.22426
			101	→	103	0.36287
3.3274	372.61	0	99	→	102	0.56293
			99	→	103	-0.37773
			100	→	103	0.13336
3.3789	366.93	0	99	→	102	0.40433
			99	→	103	0.55409
3.8014	326.15	0	97	→	102	0.67982
3.8883	318.86	0	95	→	105	-0.12932
			96	→	106	-0.13027
			98	→	103	-0.24223

			98	→	104	0.46883
			98	→	105	0.14740
			98	→	106	0.13263
			100	→	105	-0.16546
			100	→	106	0.13914
			101	→	104	0.10803
3.9349	315.09	0	91	→	102	0.23345
			92	→	102	0.27053
			96	→	102	0.13848
			97	→	104	-0.22504
			97	→	105	0.29195
			97	→	106	0.27876
			98	→	102	0.16210
			101	→	102	-0.14236
			101	→	104	0.11861
			101	→	107	-0.15137

Table S66. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 82.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9060	426.65	0	98	→	103	-0.38090
			98	→	104	-0.13270
			100	→	103	-0.15970
			101	→	102	-0.15992
			101	→	103	0.48801
3.0233	410.09	0	100	→	102	0.17171
			101	→	102	0.63500
3.1295	396.18	0	100	→	102	-0.14885
			100	→	103	0.58767
			101	→	103	0.28506
3.2313	383.69	0	98	→	103	0.27998
			100	→	102	0.57479
			101	→	102	-0.14712
			101	→	103	0.21677
3.2542	381.00	0	98	→	103	0.41735
			99	→	103	-0.12337
			100	→	102	-0.32175
			100	→	103	-0.26197
			101	→	103	0.31613
3.3501	370.09	0	99	→	102	-0.43981
			99	→	103	0.51474
			100	→	103	-0.12918
3.4058	364.03	0	99	→	102	0.53637

			99	→	103	0.43553
3.8243	324.20	0	97	→	102	0.67930
3.8873	318.94	0	95	→	104	-0.10026
			95	→	105	0.14854
			96	→	105	-0.14212
			98	→	103	-0.23640
			98	→	104	0.47184
			98	→	106	0.20485
			100	→	105	0.20023
3.9494	313.93	0	91	→	102	0.22592
			92	→	102	0.26402
			93	→	102	-0.10484
			96	→	102	0.13999
			97	→	104	0.25380
			97	→	105	0.15209
			97	→	106	-0.37679
			98	→	102	0.11995
			101	→	102	-0.14391
			101	→	107	-0.13255

Table S67. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 97.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9158	425.22	0	98	→	103	-0.39720
			98	→	104	-0.13428
			100	→	103	-0.19826
			101	→	102	-0.10258
			101	→	103	0.47639
3.0215	410.34	0	100	→	102	0.27051
			101	→	102	0.60695
3.1272	396.47	0	100	→	103	0.58303
			101	→	102	0.12706
			101	→	103	0.31501
3.1880	388.91	0	98	→	103	0.10363
			100	→	102	0.62329
			101	→	102	-0.26895
3.2645	379.80	0	98	→	103	0.49588
			99	→	103	-0.10812
			100	→	103	-0.24726
			101	→	103	0.37206
3.3495	370.15	0	99	→	102	0.57921
			99	→	103	-0.37102
3.3988	364.79	0	99	→	102	0.38195

			99	→	103	0.57248
3.8078	325.60	0	97	→	102	0.68445
3.8876	318.92	0	95	→	103	0.10607
			95	→	104	-0.11153
			95	→	106	-0.10618
			96	→	105	0.15749
			98	→	103	-0.22717
			98	→	104	0.46372
			98	→	105	0.16752
			98	→	106	0.16740
			100	→	104	-0.10517
			100	→	105	0.15609
			100	→	106	-0.13307
3.9481	314.04	0	91	→	102	0.22036
			92	→	102	0.25524
			93	→	102	-0.13670
			96	→	102	-0.13081
			97	→	104	0.26577
			97	→	105	-0.21459
			97	→	106	-0.32750
			98	→	102	0.19459
			100	→	102	-0.10144
			101	→	102	-0.13281

Table S68. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 112.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9188	424.77	0	95	→	103	-0.10309
			98	→	103	0.40461
			98	→	104	0.13761
			100	→	103	0.19671
			101	→	103	0.47890
3.0265	409.66	0	100	→	102	-0.44149
			101	→	102	0.50242
3.1210	397.26	0	100	→	103	0.61485
			101	→	103	-0.28898
3.1520	393.35	0	100	→	102	0.51821
			101	→	102	0.46842
3.2681	379.37	0	98	→	103	0.50847
			98	→	104	0.10210
			100	→	103	-0.21169
			101	→	103	-0.39832
3.3476	370.37	0	99	→	102	0.65631

			99	→	103	0.22022
3.3873	366.03	0	99	→	102	-0.22137
			99	→	103	0.65542
3.8056	325.79	0	97	→	102	0.68662
3.8862	319.03	0	95	→	103	-0.11546
			95	→	104	0.10318
			96	→	105	0.11057
			96	→	106	-0.17469
			98	→	102	-0.12036
			98	→	103	-0.23555
			98	→	104	0.44951
			98	→	105	0.23282
			100	→	104	-0.10541
			100	→	105	0.10473
			100	→	106	-0.18418
3.9549	313.50	0	91	→	102	0.21692
			92	→	102	0.25119
			93	→	102	0.15682
			96	→	102	0.11798
			97	→	104	-0.25618
			97	→	105	0.33225
			97	→	106	0.23262
			98	→	102	-0.18481
			100	→	102	0.13122
			101	→	102	-0.10256
			100	→	102	-0.10144
			101	→	102	-0.13281

Table S69. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 127.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9194	424.69	0	95	→	103	-0.10977
			98	→	103	-0.4049
			98	→	104	-0.16199
			101	→	103	0.51089
3.0204	410.49	0	92	→	102	0.11804
			100	→	102	0.67032
3.1176	397.69	0	100	→	103	0.68446
3.1308	396.01	0	101	→	102	0.69887
3.2705	379.1	0	98	→	103	0.5053
			98	→	104	0.11996
			101	→	103	0.45643
3.338	371.44	0	99	→	102	0.69157

			100	→	102	0.1111
3.3848	366.29	0	99	→	103	0.69358
3.8034	325.99	0	97	→	102	0.68691
3.8869	318.98	0	95	→	103	0.11864
			95	→	104	-0.10614
			96	→	106	0.19398
			98	→	102	-0.14262
			98	→	103	-0.24689
			98	→	104	0.50316
			100	→	105	0.13439
			100	→	106	-0.21334
3.9566	313.36	0	92	→	102	0.32897
			93	→	102	-0.15361
			96	→	102	0.10997
			97	→	105	-0.44581
			97	→	106	-0.20461
			100	→	102	-0.16961
			101	→	105	-0.10673

Table S70. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 142.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9172	425.01	0	95	→	103	0.10407
			98	→	103	-0.40329
			98	→	104	-0.13939
			100	→	103	-0.20721
			101	→	103	0.47300
3.0289	409.34	0	100	→	102	0.44443
			101	→	102	0.50314
3.1167	397.81	0	100	→	103	0.60691
			101	→	103	0.30827
3.1546	393.03	0	100	→	102	0.51332
			101	→	102	-0.47185
3.2681	379.38	0	98	→	103	0.50788
			98	→	104	0.10356
			100	→	103	-0.22145
			101	→	103	0.39378
3.3541	369.65	0	99	→	102	0.68729
3.3835	366.43	0	99	→	103	0.68601
3.8079	325.60	0	97	→	102	0.68585
			97	→	109	-0.10099
3.8879	318.90	0	95	→	103	-0.11790
			95	→	104	0.10385

			96	→	105	0.10653
			96	→	106	-0.18000
			98	→	103	-0.23657
			98	→	104	0.45438
			98	→	105	0.23189
			100	→	104	-0.10507
			100	→	105	0.10084
			100	→	106	-0.18963
3.9549	313.50	0	91	→	102	-0.20165
			92	→	102	-0.25613
			93	→	102	-0.14714
			96	→	102	-0.11077
			97	→	104	0.24403
			97	→	105	-0.34069
			97	→	106	-0.21732
			98	→	102	0.19314
			100	→	102	-0.12620
			101	→	102	-0.10326

Table S71. 10 TDDFT triplet excitations of Re(4-PamH) from S_0 $\theta_{dihedral}$ = 157.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.9153	425.29	0	98	→	103	-0.39991
			98	→	104	-0.13679
			100	→	103	-0.20891
			101	→	103	0.47914
3.0447	407.21	0	100	→	102	0.27217
			101	→	102	0.61370
3.1226	397.05	0	100	→	103	0.59345
			101	→	103	0.32612
3.2094	386.31	0	100	→	102	0.63258
			101	→	102	-0.29441
3.2634	379.92	0	98	→	103	0.50768
			98	→	104	0.10160
			99	→	103	0.10172
			100	→	103	-0.24456
			101	→	103	0.37118
3.3755	367.31	0	99	→	102	0.33183
			99	→	103	0.60082
3.3965	365.04	0	99	→	102	0.61028
			99	→	103	-0.32676
3.8258	324.08	0	97	→	102	0.68389
			97	→	109	-0.10181

3.8882	318.88	0	95	→	103	0.10531
			95	→	104	-0.11566
			95	→	106	-0.11011
			96	→	105	0.14502
			96	→	106	-0.10948
			98	→	103	-0.22609
			98	→	104	0.46367
			98	→	105	0.17795
			98	→	106	0.14769
			100	→	104	-0.11409
			100	→	105	0.14286
			100	→	106	-0.14732
3.9580	313.25	0	91	→	102	-0.21168
			92	→	102	-0.25617
			93	→	102	-0.13470
			96	→	102	-0.12519
			97	→	104	0.26052
			97	→	105	-0.24969
			97	→	106	-0.31274
			98	→	102	0.13612
			100	→	102	-0.10363
			100	→	104	-0.12460
			101	→	102	-0.13353

Re(4-EtPy) TDDFT Tables

Table S72. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = -82.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1567	392.76	0.0087	97	→	99	-0.23671
			98	→	99	0.66204
3.3051	375.13	0.0618	96	→	99	-0.22874
			97	→	99	0.62908
			98	→	99	0.21344
3.4078	363.82	0.0277	96	→	99	0.66419
			97	→	99	0.20443
			98	→	99	0.10554
4.1095	301.70	0.0582	95	→	99	-0.44002
			97	→	100	-0.22840
			98	→	100	0.47792
4.2031	294.98	0.0585	95	→	99	0.31250
			97	→	100	0.22835
			97	→	101	-0.12077
			98	→	100	0.45851

			98	→	101	-0.30179
			98	→	102	0.11966
4.2585	291.14	0.0176	97	→	100	0.16044
			97	→	101	0.54435
			97	→	103	0.10622
			98	→	101	-0.33792

Table S73. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = -67.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1786	390.06	0.0060	97	→	99	0.41825
			98	→	99	0.56572
3.2875	377.14	0.0757	96	→	99	0.16183
			97	→	99	0.55273
			98	→	99	-0.40255
3.3965	365.03	0.0138	96	→	99	0.68423
			97	→	99	-0.11790
			98	→	99	0.11226
4.1136	301.40	0.0657	95	→	99	0.45730
			97	→	100	0.34422
			98	→	100	0.37805
4.2192	293.86	0.0379	95	→	99	-0.21205
			97	→	100	-0.25875
			98	→	100	0.55904
			98	→	101	-0.21191
			98	→	102	0.13907
4.2337	292.85	0.0431	95	→	99	-0.26588
			97	→	100	0.43877
			97	→	101	0.43698
			97	→	103	0.11407
			98	→	102	0.14227

Table S74. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = -52.275, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1876	388.96	0.0024	97	→	99	0.70382
3.2780	378.23	0.0838	96	→	99	0.13019
			98	→	99	0.69060
3.3930	365.41	0.0087	96	→	99	0.69133
			98	→	99	-0.13004
4.1139	301.38	0.0665	95	→	99	-0.45726
			97	→	100	0.51104

			98	→	102	0.12813
4.2221	293.66	0.0253	97	→	102	-0.13446
			98	→	100	0.67545
4.2303	293.08	0.0778	95	→	99	0.35635
			97	→	100	0.41501
			97	→	101	-0.31040
			98	→	102	-0.27781

Table S75. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = -37.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1774	390.20	0.0056	97	→	99	0.41542
			98	→	99	0.56785
3.2867	377.23	0.0766	96	→	99	-0.15925
			97	→	99	0.55511
			98	→	99	-0.40035
3.3958	365.11	0.0134	96	→	99	0.68485
			97	→	99	0.11677
			98	→	99	-0.10957
4.1143	301.35	0.0676	95	→	99	0.46190
			97	→	100	0.34009
			98	→	100	0.37524
4.2225	293.62	0.0381	95	→	99	-0.21518
			97	→	100	-0.24587
			98	→	100	0.56071
			98	→	101	0.21124
			98	→	102	0.14708
4.2339	292.84	0.0367	95	→	99	0.24763
			97	→	100	-0.43107
			97	→	101	0.45410
			98	→	102	-0.13913

Table S76. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = -22.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1528	393.26	0.0087	97	→	99	-0.23082
			98	→	99	0.66413
3.3017	375.51	0.0612	96	→	99	0.22969
			97	→	99	0.63074
			98	→	99	0.20762
3.4050	364.13	0.0281	96	→	99	0.66384
			97	→	99	-0.20615

			98	→	99	-0.10420
4.1079	301.82	0.0564	95	→	99	0.43566
			97	→	100	-0.22800
			98	→	100	0.48224
4.1997	295.22	0.0603	95	→	99	-0.31514
			97	→	100	0.23874
			97	→	101	0.11075
			98	→	100	0.45668
			98	→	101	0.29687
			98	→	102	0.11906
4.2579	291.18	0.0221	97	→	101	0.51969
			97	→	102	-0.10243
			98	→	101	-0.39283
			98	→	103	-0.10350

Table S77. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = -7.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1237	396.91	0.0070	97	→	99	-0.12461
			98	→	99	0.69193
3.3080	374.81	0.0432	96	→	99	0.30495
			97	→	99	0.62581
3.4158	362.97	0.0488	96	→	99	0.63233
			97	→	99	-0.29336
4.0858	303.45	0.0397	95	→	99	-0.36839
			97	→	100	-0.13562
			98	→	100	0.56863
4.1905	295.87	0.0977	95	→	99	0.39045
			97	→	100	0.30788
			97	→	101	0.14088
			97	→	103	0.10955
			98	→	100	0.35289
			98	→	101	0.25704
			98	→	102	0.10007
4.2583	291.16	0.0403	97	→	100	-0.25909
			97	→	101	-0.35787
			97	→	102	0.14607
			97	→	105	0.10903
			98	→	101	0.44287
			98	→	102	-0.12032
			98	→	103	0.17745

Table S78. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 7.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.0929	400.86	0.0047	98	→	99	0.70092
3.3098	374.60	0.0306	96	→	99	0.36360
			97	→	99	0.60071
3.4197	362.56	0.0641	96	→	99	0.60077
			97	→	99	-0.35847
4.0632	305.14	0.0352	95	→	99	-0.33013
			98	→	100	0.60359
4.1943	295.60	0.1313	95	→	99	0.40043
			97	→	100	0.28695
			97	→	101	0.16892
			97	→	103	0.12286
			98	→	100	0.24932
			98	→	101	0.32848
			98	→	103	0.10700
4.2285	293.21	0.0438	97	→	100	-0.30834
			97	→	101	-0.33654
			97	→	103	-0.11542
			98	→	101	0.41078
			98	→	102	-0.19486
			98	→	103	0.17004

Table S79. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 22.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.0701	403.84	0.0034	98	→	99	0.70349
3.3121	374.34	0.0244	96	→	99	0.40761
			97	→	99	0.57321
3.4178	362.76	0.0716	96	→	99	0.57227
			97	→	99	-0.40458
4.0545	305.79	0.0296	95	→	99	0.32775
			98	→	100	0.60760
4.1726	297.14	0.1468	95	→	99	-0.17075
			97	→	105	0.10083
			98	→	100	0.10469
			98	→	101	0.60838
			98	→	102	-0.10246
			98	→	103	0.16320
			98	→	104	0.15481
4.2087	294.59	0.0230	95	→	99	-0.19877
			97	→	100	0.31132

		97	→	101	0.52555
		97	→	103	0.18798
		97	→	104	0.15149

Table S80. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 37.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.0607	405.08	0.0031	98	→	99	0.70405
3.3135	374.18	0.0226	96	→	99	0.42842
			97	→	99	0.55808
3.4146	363.11	0.0733	96	→	99	0.55708
			97	→	99	-0.42580
4.0529	305.91	0.0232	95	→	99	0.33447
			98	→	100	0.60584
4.1532	298.53	0.1497	97	→	105	0.10519
			98	→	101	0.64389
			98	→	102	-0.10827
			98	→	103	0.14432
			98	→	104	0.17084
4.2058	294.79	0.0091	95	→	99	-0.13021
			97	→	101	0.63709
			97	→	103	0.18625
			97	→	104	0.17974

Table S81. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 52.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.0692	403.97	0.0036	98	→	99	0.70325
3.3113	374.43	0.0245	96	→	99	-0.40866
			97	→	99	0.57237
3.4152	363.04	0.0706	96	→	99	0.57148
			97	→	99	0.40541
4.0529	305.91	0.0299	95	→	99	-0.32719
			98	→	100	0.60813
4.1756	296.92	0.1423	95	→	99	-0.17802
			97	→	105	-0.10101
			98	→	100	-0.10532
			98	→	101	0.60456
			98	→	102	0.10223
			98	→	103	0.16793
			98	→	104	0.15236
4.2118	294.37	0.0311	95	→	99	-0.22422

		97	→	100	-0.31134
		97	→	101	0.50419
		97	→	103	0.1829
		97	→	104	0.14238
		98	→	102	-0.12385

Table S82. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 67.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.0963	400.43	0.0054	98	→	99	0.69971
3.3111	374.45	0.0327	96	→	99	-0.35797
			97	→	99	0.60317
3.4180	362.73	0.0611	96	→	99	0.60419
			97	→	99	0.35195
4.0658	304.94	0.0365	95	→	99	-0.33241
			98	→	100	0.60165
4.1919	295.77	0.1182	95	→	99	0.40416
			97	→	100	0.29883
			97	→	101	-0.17407
			97	→	103	-0.12472
			98	→	100	0.26130
			98	→	101	-0.30606
4.2360	292.69	0.0500	97	→	100	0.29175
			97	→	101	-0.32096
			97	→	102	-0.10239
			97	→	103	-0.10411
			97	→	105	-0.10248
			98	→	101	0.42755
			98	→	102	0.19746
			98	→	103	0.18597

Table S83. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 82.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1248	396.78	0.0076	97	→	99	-0.13331
			98	→	99	0.69023
3.3089	374.7	0.0440	96	→	99	-0.30287
			97	→	99	0.62551
			98	→	99	0.10523
3.4149	363.07	0.0472	96	→	99	0.63336
			97	→	99	0.29018
4.0876	303.32	0.0408	95	→	99	-0.37435

			97	→	100	-0.14115
			98	→	100	0.56401
4.1913	295.81	0.0942	95	→	99	0.39132
			97	→	100	0.29643
			97	→	101	-0.13575
			97	→	103	-0.10234
			98	→	100	0.36428
			98	→	101	-0.25626
			98	→	102	0.10885
4.2628	290.85	0.0447	97	→	100	0.23681
			97	→	101	-0.35096
			97	→	102	-0.12746
			97	→	105	-0.11346
			98	→	101	0.46245
			98	→	102	0.12761
			98	→	103	0.19260

Table S84. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 97.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1572	392.70	0.0087	97	→	99	-0.23616
			98	→	99	0.66222
3.3042	375.23	0.0604	96	→	99	-0.22831
			97	→	99	0.62953
			98	→	99	0.21286
3.4078	363.83	0.0274	96	→	99	0.66429
			97	→	99	0.20391
			98	→	99	0.10572
4.1100	301.67	0.0587	95	→	99	0.44132
			97	→	100	-0.23097
			98	→	100	0.47526
4.2037	294.94	0.0581	95	→	99	-0.31280
			97	→	100	0.23254
			97	→	101	-0.11380
			98	→	100	0.46517
			98	→	101	-0.29058
			98	→	102	0.12315
4.2609	290.98	0.0199	97	→	100	0.11688
			97	→	101	0.53390
			98	→	101	-0.36690

Table S85. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 112.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1812	389.75	0.0059	97	→	99	0.42282
			98	→	99	0.56236
3.2896	376.90	0.0755	96	→	99	0.15768
			97	→	99	0.54995
			98	→	99	-0.40797
3.3977	364.91	0.0127	96	→	99	0.68525
			97	→	99	-0.11469
			98	→	99	0.10944
4.1156	301.26	0.0675	95	→	99	0.46127
			97	→	100	0.34367
			98	→	100	0.37299
4.2223	293.64	0.0407	95	→	99	-0.21804
			97	→	100	-0.24163
			98	→	100	0.56420
			98	→	101	-0.20296
			98	→	102	0.14792
4.2365	292.66	0.0407	95	→	99	-0.25818
			97	→	100	0.45005
			97	→	101	0.43233
			97	→	103	0.10755
			98	→	102	0.14149

Table S86. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 127.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1873	388.99	0.0025	97	→	99	0.69300
			98	→	99	-0.12301
3.2770	378.35	0.0828	96	→	99	-0.12373
			97	→	99	0.12173
			98	→	99	0.68097
3.3910	365.62	0.0076	96	→	99	0.69252
			98	→	99	0.12261
4.1125	301.48	0.0634	95	→	99	-0.45089
			97	→	100	0.51135
			98	→	102	0.12793
4.2163	294.06	0.0294	97	→	102	-0.13547
			98	→	100	0.67359
4.2282	293.23	0.0796	95	→	99	0.36207
			97	→	100	0.42027
			97	→	101	0.29665

			98	→	102	-0.28972

Table S87. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 142.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1752	390.48	0.0066	97	→	99	-0.39881
			98	→	99	0.57958
3.2872	377.17	0.0737	96	→	99	0.16217
			97	→	99	0.56604
			98	→	99	0.38338
3.3951	365.19	0.0134	96	→	99	0.68414
			97	→	99	-0.12174
			98	→	99	-0.10868
4.1125	301.48	0.0637	95	→	99	0.4547
			97	→	100	-0.33287
			98	→	100	0.39143
4.2162	294.07	0.0409	95	→	99	-0.22983
			97	→	100	0.24906
			98	→	100	0.54852
			98	→	101	0.22674
			98	→	102	0.14338
4.2355	292.73	0.0390	95	→	99	0.25295
			97	→	100	0.45070
			97	→	101	-0.43597
			97	→	103	-0.11947
			98	→	102	-0.13251

Table S88. 6 TDDFT singlet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 157.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
3.1478	393.88	0.0085	97	→	99	-0.22021
			98	→	99	0.66772
3.3009	375.61	0.0584	96	→	99	0.23860
			97	→	99	0.63112
			98	→	99	0.19607
3.4028	364.36	0.0290	96	→	99	0.66067
			97	→	99	-0.21617
			98	→	99	-0.10378
4.1043	302.09	0.0527	95	→	99	0.42812
			97	→	100	-0.21572
			98	→	100	0.49601
4.2003	295.18	0.0609	95	→	99	-0.32560

			97	→	100	0.24403
			97	→	101	0.12224
			98	→	100	0.44348
			98	→	101	0.29834
			98	→	102	0.12254
4.2597	291.06	0.0216	95	→	99	-0.10529
			97	→	100	-0.14634
			97	→	101	0.53397
			97	→	103	0.10549
			98	→	101	-0.35820

Table S89. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = -82.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8926	428.63	0	95	→	99	0.35800
			95	→	100	0.14241
			97	→	99	-0.28803
			98	→	99	0.47960
3.0536	406.03	0	97	→	99	0.53850
			98	→	99	0.41533
3.2406	382.60	0	95	→	99	0.53014
			95	→	100	0.13613
			96	→	99	0.10553
			97	→	99	0.30720
			98	→	99	-0.27716
3.3491	370.20	0	96	→	99	0.68849
3.7337	332.07	0	93	→	101	-0.26449
			93	→	102	-0.18760
			94	→	104	-0.28980
			97	→	101	0.14685
			98	→	101	0.44055
			98	→	102	0.19930
3.8827	319.33	0	91	→	99	0.11272
			91	→	100	-0.12090
			92	→	101	-0.11037
			92	→	102	0.15472
			95	→	99	-0.23017
			95	→	100	0.48312
			97	→	100	0.14376
			97	→	101	-0.15436
			97	→	102	0.16186
			98	→	102	0.15967

Table S90. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = -67.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8979	427.85	0	91	→	99	0.10488
			95	→	99	-0.36873
			95	→	100	-0.14063
			97	→	99	0.39538
			98	→	99	0.38314
3.0448	407.20	0	97	→	99	-0.44741
			98	→	99	0.52150
3.2485	381.67	0	95	→	99	0.53373
			95	→	100	0.13177
			97	→	99	0.34172
			98	→	99	0.24329
3.3493	370.18	0	96	→	99	0.69535
3.7330	332.13	0	93	→	100	-0.11427
			93	→	101	-0.25012
			93	→	102	-0.19351
			94	→	103	0.14756
			94	→	104	-0.26930
			97	→	100	-0.10846
			97	→	101	-0.14536
			97	→	102	-0.10559
			98	→	100	0.22708
			98	→	101	0.35982
			98	→	102	0.18533
3.8827	319.32	0	91	→	99	-0.11894
			91	→	100	0.10212
			92	→	101	-0.13658
			92	→	102	0.15726
			95	→	99	-0.23085
			95	→	100	0.45943
			95	→	101	-0.14469
			97	→	100	0.13180
			97	→	101	-0.14595
			97	→	102	0.14443
			98	→	101	0.10789
			98	→	102	-0.18343

Table S91. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = -52.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8984	427.77	0	91	→	99	-0.10904

			95	→	99	0.37314
			95	→	100	0.13755
			97	→	99	0.54701
3.0413	407.67	0	98	→	99	0.68943
3.2503	381.46	0	95	→	99	0.5351
			95	→	100	0.12719
			97	→	99	-0.42233
3.3501	370.09	0	96	→	99	0.69815
3.7283	332.55	0	93	→	100	-0.13685
			93	→	101	0.30203
			94	→	103	0.17756
			94	→	104	0.25204
			98	→	100	-0.29777
			98	→	101	0.40584
3.8829	319.31	0	91	→	99	-0.1258
			91	→	100	0.1061
			92	→	102	0.20487
			95	→	99	-0.23195
			95	→	100	0.45173
			95	→	101	0.17955
			97	→	100	-0.12678
			98	→	102	-0.29744

Table S92. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = -37.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8957	428.16	0	91	→	99	0.10391
			95	→	99	-0.36780
			95	→	100	-0.14016
			97	→	99	0.39477
			98	→	99	0.38495
3.0448	407.20	0	97	→	99	-0.45296
			98	→	99	0.51718
3.2482	381.70	0	95	→	99	0.53461
			95	→	100	0.13146
			97	→	99	0.33472
			98	→	99	0.24941
3.3492	370.19	0	96	→	99	0.69485
3.7323	332.19	0	93	→	100	-0.11072
			93	→	101	0.25493
			93	→	102	-0.18837
			94	→	103	-0.16315
			94	→	104	0.25992

			97	→	100	0.11122
			97	→	101	-0.15641
			97	→	102	0.10934
			98	→	100	-0.21496
			98	→	101	0.36413
			98	→	102	-0.17847
3.8843	319.20	0	91	→	99	-0.11828
			91	→	100	0.10431
			92	→	101	0.13079
			92	→	102	0.16163
			95	→	99	-0.22993
			95	→	100	0.46089
			95	→	101	0.14207
			97	→	100	0.13383
			97	→	101	0.14414
			97	→	102	0.15292
			98	→	101	-0.10292
			98	→	102	-0.18130

Table S93. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = -22.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8892	429.12	0	95	→	99	-0.35530
			95	→	100	-0.14130
			97	→	99	-0.28630
			98	→	99	0.48320
3.0515	406.31	0	97	→	99	0.54137
			98	→	99	0.41148
3.2401	382.66	0	95	→	99	0.53216
			95	→	100	0.13608
			96	→	99	0.10733
			97	→	99	-0.30314
			98	→	99	0.27671
3.3460	370.54	0	96	→	99	0.68821
3.7313	332.28	0	93	→	101	0.26579
			93	→	102	-0.18435
			94	→	104	-0.28232
			97	→	101	0.14941
			98	→	101	0.44491
			98	→	102	-0.19925
3.8837	319.24	0	91	→	99	-0.10941
			91	→	100	0.12378
			92	→	101	-0.10438

			92	→	102	-0.15148
			95	→	99	-0.22905
			95	→	100	0.48346
			97	→	100	-0.15112
			97	→	101	-0.14649
			97	→	102	-0.16470
			98	→	102	-0.16047

Table S94. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = -7.275°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8773	430.91	0	95	→	99	0.34141
			95	→	100	0.12985
			97	→	99	-0.19795
			98	→	99	0.53739
3.0671	404.24	0	95	→	99	-0.12465
			97	→	99	0.59230
			98	→	99	0.31819
3.2239	384.58	0	95	→	99	0.53132
			95	→	100	0.13052
			96	→	99	-0.13926
			97	→	99	0.26405
			98	→	99	-0.30012
3.3371	371.54	0	95	→	99	0.10319
			96	→	99	0.67951
			97	→	99	0.11321
3.7099	334.19	0	93	→	101	0.24446
			93	→	102	-0.14922
			94	→	104	-0.27232
			98	→	100	0.18061
			98	→	101	0.44437
			98	→	102	-0.22286
			98	→	103	0.12050
3.8823	319.36	0	91	→	99	0.11218
			91	→	100	-0.12041
			92	→	102	0.15372
			95	→	99	-0.22882
			95	→	100	0.46502
			95	→	101	-0.10974
			97	→	100	0.13661
			97	→	101	0.14490
			97	→	102	0.17289
			98	→	100	-0.11997

			98	→	102	0.12148

Table S95. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 7.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8619	433.22	0	95	→	99	0.32599
			95	→	100	0.12136
			97	→	99	-0.11730
			98	→	99	0.57250
3.0866	401.68	0	95	→	99	-0.13130
			97	→	99	0.62929
			98	→	99	0.22188
3.2039	386.98	0	95	→	99	0.54070
			95	→	100	0.13380
			96	→	99	-0.13193
			97	→	99	0.21309
			98	→	99	-0.32219
3.3241	372.99	0	96	→	99	0.67739
			97	→	99	0.13303
3.6655	338.25	0	93	→	101	0.23486
			94	→	103	-0.11198
			94	→	104	0.21554
			98	→	100	0.24626
			98	→	101	0.48418
			98	→	102	-0.15639
			98	→	103	0.11794
3.8822	319.36	0	91	→	99	0.12121
			91	→	100	-0.10812
			92	→	102	0.18049
			95	→	99	-0.22812
			95	→	100	0.44850
			95	→	101	-0.14018
			96	→	102	-0.10020
			97	→	101	0.10002
			97	→	102	0.21579
			98	→	100	-0.16989
			98	→	101	0.10581

Table S96. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 22.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8498	435.07	0	95	→	99	-0.31461

			95	→	100	-0.12050
			98	→	99	0.59035
3.1024	399.64	0	96	→	99	-0.11329
			97	→	99	0.65940
			98	→	99	0.11903
3.1879	388.93	0	95	→	99	0.56039
			95	→	100	0.14722
			97	→	99	-0.13202
			98	→	99	0.34482
3.3149	374.02	0	96	→	99	0.68245
			97	→	99	0.13487
3.6232	342.19	0	93	→	101	0.23321
			94	→	103	-0.16110
			94	→	104	0.15935
			98	→	100	0.19718
			98	→	101	0.54925
			98	→	104	0.10407
3.8806	319.5	0	91	→	99	0.12457
			91	→	100	-0.10676
			92	→	102	0.19492
			95	→	99	-0.22473
			95	→	100	0.44258
			95	→	101	-0.11597
			96	→	102	0.11028
			97	→	102	-0.24635
			98	→	100	0.22508

Table S97. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 37.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8448	435.83	0	95	→	99	-0.30964
			95	→	100	-0.12435
			98	→	99	0.59606
3.1074	399.00	0	96	→	99	-0.12167
			97	→	99	0.67514
3.1813	389.72	0	95	→	99	0.57279
			95	→	100	0.15955
			98	→	99	0.35576
3.3115	374.40	0	96	→	99	0.68567
			97	→	99	0.13040
3.6071	343.72	0	93	→	101	0.23751
			94	→	103	-0.17249
			94	→	104	0.13956

			98	→	101	0.59117
			98	→	104	0.10910
3.8785	319.67	0	91	→	99	-0.12437
			91	→	100	0.11079
			92	→	102	0.19416
			95	→	99	-0.22277
			95	→	100	0.45164
			96	→	102	0.10817
			97	→	102	-0.25293
			98	→	100	0.25824

Table S98. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 52.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8476	435.4	0	95	→	99	0.31367
			95	→	100	0.12062
			98	→	99	0.59047
3.0990	400.08	0	95	→	99	-0.10602
			96	→	99	0.10938
			97	→	99	0.65510
			98	→	99	0.13329
3.1895	388.73	0	95	→	99	0.55893
			95	→	100	0.14655
			97	→	99	0.15153
			98	→	99	-0.33927
3.3136	374.17	0	96	→	99	0.68314
			97	→	99	-0.13248
3.6259	341.94	0	93	→	101	-0.23663
			94	→	103	0.16110
			94	→	104	-0.16223
			98	→	100	-0.18966
			98	→	101	0.54955
			98	→	104	0.10095
3.8799	319.56	0	91	→	99	0.12293
			91	→	100	-0.10484
			92	→	102	0.19320
			95	→	99	-0.22399
			95	→	100	0.44329
			95	→	101	0.10986
			96	→	102	0.10883
			97	→	102	0.24440
			98	→	100	-0.22505

Table S99. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 67.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8634	432.99	0	95	→	99	0.32640
			95	→	100	0.12179
			97	→	99	-0.12675
			98	→	99	0.57010
3.0816	402.33	0	95	→	99	-0.14053
			97	→	99	0.62177
			98	→	99	0.23882
3.2073	386.57	0	95	→	99	0.53863
			95	→	100	0.13280
			96	→	99	0.12993
			97	→	99	0.23151
			98	→	99	-0.31410
3.3262	372.75	0	96	→	99	0.67882
			97	→	99	-0.12836
3.6708	337.76	0	93	→	101	-0.23648
			94	→	104	-0.22539
			98	→	100	-0.23870
			98	→	101	0.47816
			98	→	102	0.17398
			98	→	103	0.12058
3.8813	319.44	0	91	→	99	0.11715
			91	→	100	-0.10725
			92	→	102	0.17306
			95	→	99	-0.22850
			95	→	100	0.44943
			95	→	101	0.13614
			97	→	101	-0.11212
			97	→	102	0.20740
			98	→	100	-0.16337
			98	→	101	-0.10941
			98	→	102	0.10093

Table S100. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 82.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8772	430.91	0	95	→	99	0.34129
			95	→	100	0.13091
			97	→	99	-0.20039
			98	→	99	0.53663
3.0652	404.49	0	95	→	99	-0.13041

			97	→	99	0.58730
			98	→	99	0.32473
3.2257	384.37	0	95	→	99	0.53394
			95	→	100	0.13208
			96	→	99	0.11468
			97	→	99	0.27625
			98	→	99	-0.29479
3.3367	371.57	0	96	→	99	0.68422
			97	→	99	-0.10610
3.7131	333.91	0	93	→	101	-0.25121
			93	→	102	-0.15146
			94	→	104	-0.27566
			98	→	100	-0.15472
			98	→	101	0.45261
			98	→	102	0.21742
			98	→	103	0.11800
3.8813	319.44	0	91	→	99	0.10648
			91	→	100	-0.12077
			92	→	102	0.14770
			95	→	99	-0.23035
			95	→	100	0.47129
			97	→	100	0.13450
			97	→	101	-0.13755
			97	→	102	0.17297
			98	→	100	-0.11096
			98	→	102	0.13323

Table S101. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 97.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8925	428.63	0	95	→	99	-0.35838
			95	→	100	-0.14272
			97	→	99	-0.28866
			98	→	99	0.47889
3.0546	405.89	0	97	→	99	0.53738
			98	→	99	0.41657
3.2415	382.49	0	95	→	99	0.53102
			95	→	100	0.13613
			97	→	99	-0.30882
			98	→	99	0.27658
3.3486	370.26	0	96	→	99	0.68958
3.7329	332.14	0	93	→	101	-0.26889
			93	→	102	-0.18468

			94	→	104	-0.28669
			97	→	101	0.15137
			98	→	101	0.44165
			98	→	102	0.19697
3.8833	319.28	0	91	→	99	-0.10351
			91	→	100	0.12242
			92	→	102	-0.14436
			95	→	99	-0.23047
			95	→	100	0.48590
			97	→	100	-0.14508
			97	→	101	0.14426
			97	→	102	-0.16276
			98	→	102	-0.16103

Table S102. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 112.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8989	427.69	0	91	→	99	0.10262
			95	→	99	-0.37014
			95	→	100	-0.14050
			97	→	99	0.39602
			98	→	99	0.38088
3.0469	406.92	0	97	→	99	-0.44514
			98	→	99	0.52340
3.2498	381.51	0	95	→	99	0.53314
			95	→	100	0.13076
			97	→	99	0.34406
			98	→	99	0.24249
3.3511	369.98	0	96	→	99	0.69569
3.7337	332.07	0	93	→	100	-0.11742
			93	→	101	-0.25336
			93	→	102	-0.19045
			94	→	103	0.15309
			94	→	104	0.26699
			97	→	100	-0.11221
			97	→	101	-0.14735
			97	→	102	-0.10702
			98	→	100	0.22747
			98	→	101	0.35833
			98	→	102	0.18009
3.884	319.22	0	91	→	99	-0.11696
			91	→	100	0.10426
			92	→	101	-0.12852

			92	→	102	0.16193
			95	→	99	-0.23110
			95	→	100	0.45989
			95	→	101	-0.14631
			97	→	100	0.12769
			97	→	101	-0.14009
			97	→	102	0.14501
			98	→	101	0.10823
			98	→	102	-0.18760

Table S103. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 127.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8986	427.74	0	91	→	99	-0.10897
			95	→	99	0.37324
			95	→	100	0.13710
			97	→	99	0.54002
3.0389	407.99	0	97	→	99	0.10221
			98	→	99	0.68191
3.2502	381.47	0	95	→	99	0.53494
			95	→	100	0.12702
			97	→	99	-0.41904
3.3490	370.22	0	96	→	99	0.69835
3.7263	332.73	0	93	→	100	-0.14213
			93	→	101	-0.30649
			94	→	103	-0.16884
			94	→	104	0.25635
			98	→	100	0.30652
			98	→	101	0.40376
3.8822	319.36	0	91	→	99	-0.12562
			91	→	100	0.10509
			92	→	102	0.20904
			95	→	99	-0.23175
			95	→	100	0.44735
			95	→	101	-0.18715
			97	→	100	-0.12611
			98	→	102	-0.30462

Table S104. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 142.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8955	428.20	0	91	→	99	0.10226

			95	→	99	-0.36597
			95	→	100	-0.14028
			97	→	99	-0.38574
			98	→	99	0.39601
3.0421	407.56	0	97	→	99	0.45727
			98	→	99	0.51189
3.2484	381.68	0	95	→	99	0.53501
			95	→	100	0.13254
			97	→	99	-0.33919
			98	→	99	0.24334
3.3477	370.35	0	96	→	99	0.69530
3.7340	332.04	0	93	→	100	-0.11359
			93	→	101	0.24974
			93	→	102	-0.19677
			94	→	103	-0.13811
			94	→	104	-0.27420
			97	→	100	-0.10577
			97	→	101	0.14293
			97	→	102	-0.10359
			98	→	100	-0.22535
			98	→	101	0.36173
			98	→	102	-0.18711
3.8833	319.28	0	91	→	99	-0.11691
			91	→	100	0.10378
			92	→	101	0.13348
			92	→	102	0.15728
			95	→	99	-0.23035
			95	→	100	0.45869
			95	→	101	0.14144
			97	→	100	-0.13136
			97	→	101	-0.14952
			97	→	102	-0.14454
			98	→	101	-0.10725
			98	→	102	-0.18443

Table S105. 6 TDDFT triplet excitations of Re(4-EtPy) from S_0 $\theta_{dihedral}$ = 157.725°, B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.8861	429.59	0	95	→	99	-0.35215
			95	→	100	-0.14049
			97	→	99	-0.27409
			98	→	99	0.49310
3.0509	406.38	0	95	→	99	0.10083

			97	→	99	0.55013
			98	→	99	0.39813
3.2377	382.94	0	95	→	99	0.53377
			95	→	100	0.13741
			96	→	99	0.10330
			97	→	99	-0.29885
			98	→	99	0.27905
3.3424	370.94	0	96	→	99	0.68871
3.7343	332.01	0	93	→	101	0.26508
			93	→	102	-0.19024
			94	→	104	-0.29317
			97	→	101	0.14829
			98	→	101	0.43836
			98	→	102	-0.20454
3.8835	319.26	0	91	→	99	-0.10503
			91	→	100	0.12067
			92	→	101	-0.10138
			92	→	102	-0.14356
			95	→	99	-0.22996
			95	→	100	0.48277
			97	→	100	-0.14132
			97	→	101	-0.15516
			97	→	102	-0.16201
			98	→	102	-0.15937

Solvent Coordinated TDDFT Tables

Table S106. TDDFT singlet excitations of Re(bpy)(4-Pam)CO_2(MeCN), B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.3452	528.67	0.0048	105	→	106	0.70493
2.5646	483.44	0.0744	104	→	106	0.70081
2.8761	431.08	0.0006	105	→	107	0.70447
3.0360	408.38	0.0011	103	→	106	0.70161
3.1670	391.49	0.2460	104	→	107	0.69407
3.3515	369.94	0.0045	105	→	108	0.70039
3.4664	357.67	0.0035	104	→	108	0.61764
			105	→	109	0.34123
3.5838	345.96	0.078	103	→	107	0.19638
			104	→	108	-0.32436
			105	→	109	0.58395
3.6036	344.05	0.0100	103	→	107	0.67445
			105	→	109	-

						0.16692
3.6325	341.32	0.0113	101	→	106	-0.12877
			104	→	109	0.6905
3.8542	321.69	0.0213	105	→	105	0.68134
			105	→	105	0.17215
3.9276	315.68	0.0010	102	→	106	0.70434
3.9311	315.39	0.0001	104	→	110	0.66082
			104	→	111	0.22067
3.9917	310.61	0.0256	105	→	110	-0.17982
			105	→	111	0.65969
			105	→	114	0.10201
4.0647	305.03	0.0000	104	→	110	-0.21804
			104	→	111	0.6622

Table S107. TDDFT singlet excitations of Re(bpy)(4-Pam)CO_2(DCM), B3LYP/LAL2DZ[Re]+6-311G(d.p)[H,C,N,O]/PCM(ACN).

Energy (eV)	Wavelength (nm)	Oscillator Strength	Transitions			
2.4223	511.83	0.0132	114	→	116	-0.1885
			115	→	116	0.67804
2.6895	460.99	0.0779	114	→	116	0.67328
			115	→	116	0.1859
2.9722	417.14	0.0185	114	→	117	-0.29088
			115	→	117	0.63767
3.0295	409.25	0.0001	113	→	116	0.70037
3.2739	378.71	0.2268	114	→	117	0.63347
			115	→	117	0.28049
3.4061	364.01	0.0052	115	→	118	0.67953
3.5998	344.42	0.0045	113	→	117	0.55114
			114	→	118	0.40075
			115	→	119	0.11334
3.6103	343.42	0.0041	113	→	117	-0.41237
			114	→	118	0.44623
			115	→	119	0.32766
3.672	337.65	0.0543	113	→	117	0.1174
			114	→	118	-0.31251
			115	→	119	0.58468
			115	→	121	0.12536
3.7796	328.03	0.0091	114	→	119	-0.28224

			115	→	118	0.13234
			115	→	120	-0.22798
			115	→	121	0.48332
			115	→	122	0.10751
			115	→	123	-0.26085
3.8202	324.55	0.029	111	→	116	0.12294
			112	→	116	0.10444
			114	→	118	0.10039
			114	→	119	0.60838
			115	→	120	-0.13255
			115	→	121	0.19963
			115	→	123	-0.11558
3.8626	320.99	0.0035	112	→	116	0.69739
3.9418	314.54	0.0047	114	→	122	-0.11256
			115	→	120	0.62281
			115	→	121	0.19713
			115	→	122	0.1867
4.0053	309.55	0.0042	114	→	121	-0.1602
			114	→	122	-0.23959
			115	→	120	-0.14885
			115	→	121	-0.28725
			115	→	122	0.51496
4.0407	306.84	0.0305	113	→	118	-0.13272
			114	→	120	-0.22759
			114	→	121	0.53293
			114	→	122	0.10066
			114	→	123	-0.2391
			115	→	122	0.17758

DFT Optimized Geometries

Re(4-Pam) Fully Optimized Singlet

Re	-1.01510941	-0.87761753	-0.12731555
N	1.22112020	-0.51374978	-0.04470939
N	-1.08410021	1.04647788	-1.20985739
C	1.92446444	-0.23681056	-1.15959292
C	1.90252330	-0.58653842	1.11650477
N	-1.13159539	0.68117473	1.43252372

C	-2.93279099	-1.08654856	-0.18776113
C	-0.87969554	-2.42129724	1.02550544
C	-0.83789861	-2.05326887	-1.64979014
C	-1.12341580	1.16180785	-2.54986526
C	-1.07140723	2.17379887	-0.45260811
C	3.29377938	-0.02440315	-1.15605745
H	1.37068997	-0.18867430	-2.08642790
C	3.27114431	-0.39656346	1.20088225
H	1.32997064	-0.80492027	2.00654997
C	-1.21929276	0.42791287	2.75114274
C	-1.09697177	1.97162676	1.01090462
O	-4.07711440	-1.20613908	-0.22365507
O	-0.79938503	-3.32913043	1.73105306
O	-0.73444384	-2.73724525	-2.57166694
C	-1.13117413	2.38746787	-3.19729969
H	-1.15117176	0.23949069	-3.11291899
C	-1.07042240	3.43569663	-1.04633294
C	4.00015080	-0.10840029	0.04568663
H	3.79905861	0.18434217	-2.08931451
H	3.75316135	-0.46062781	2.16761785
C	-1.25411951	1.43162771	3.70659522
H	-1.26672965	-0.61259234	3.04036761
C	-1.12102752	3.02474434	1.92496365
C	-1.09655683	3.54601402	-2.43011804
H	-1.16277034	2.42104165	-4.27779594
H	-1.05445632	4.32770549	-0.43804623
C	5.48867019	0.06943998	0.10089967
C	-1.19572966	2.75468878	3.28492701
H	-1.32438247	1.17073127	4.75378276
H	-1.08722022	4.04876683	1.58375595
H	-1.09631476	4.52214923	-2.89808939
N	6.26865184	-0.60893190	0.86067358
N	5.99368690	0.98244086	-0.79177922
H	-1.21496351	3.56672916	4.00054601
H	5.74808976	-1.31275142	1.37946328
H	5.42367616	1.77789086	-1.03782846
H	6.97839368	1.18429856	-0.68832088

Re(4-Pam) Fully Optimized Triplet

Re	0.82440345	-0.91929800	-0.04974524
N	-1.33816115	-0.38729601	-0.01945471
N	1.17527630	0.63219197	1.36380676
C	-1.74462377	0.89207111	0.11458456
C	-2.29278258	-1.33818070	-0.13965836
N	1.17547795	0.77417285	-1.28598642
C	2.78136753	-1.27837265	-0.06947513
C	0.53340929	-2.26679945	-1.46760140
C	0.52391643	-2.40732371	1.22324822
C	1.11149064	0.51737780	2.71502877
C	1.58107215	1.86216557	0.80803279
C	-3.07956926	1.25679524	0.12791486
H	-0.97546281	1.64235127	0.21705263
C	-3.64460301	-1.05049061	-0.12485233
H	-1.95442485	-2.35778362	-0.25422639
C	1.11180481	0.80578063	-2.64218680
C	1.57511784	1.93976967	-0.60077886
O	3.90193178	-1.47112321	-0.08027485

O	0.38617648	-3.05512904	-2.28343284
O	0.36896383	-3.27123978	1.95606601
C	1.42830274	1.53831054	3.57415091
H	0.78912052	-0.44313672	3.09329724
C	1.93381282	2.93392216	1.67712052
C	-4.06611808	0.27380775	0.01244290
H	-3.34073362	2.29963806	0.24602527
H	-4.35555088	-1.85845506	-0.23632024
C	1.41799431	1.91635824	-3.38558947
H	0.79889674	-0.11096136	-3.12290468
C	1.91234399	3.10388713	-1.34884092
C	1.86016897	2.78196342	3.03228756
H	1.35150913	1.38461040	4.64153549
H	2.26083227	3.87329604	1.25432237
C	-5.52634708	0.61177068	0.07044185
C	1.83643080	3.09928194	-2.71218168
H	1.34157075	1.87822032	-4.46333483
H	2.22617925	3.99691028	-0.82703481
H	2.12811454	3.59935677	3.68988315
N	-6.40388261	-0.10665472	0.66998086
N	-5.86630928	1.81046122	-0.50384949
H	2.09134797	3.98690272	-3.27746059
H	-5.97015052	-0.90436972	1.12928200
H	-5.33578855	2.13120488	-1.30002590
H	-6.85823568	1.99680627	-0.55407148

Re(4-PamH) Fully Optimized Singlet

Re	-1.00507277	-0.89470708	-0.12594183
N	1.22464070	-0.45440288	-0.06516562
N	-1.17034505	1.02875680	-1.19804902
C	1.90243352	-0.15170547	-1.18827957
C	1.91751124	-0.52615908	1.08699529
N	-1.16733608	0.64975107	1.44225965
C	-2.91318080	-1.18011116	-0.16845339
C	-0.79932166	-2.43666545	1.02059192
C	-0.79719719	-2.05805750	-1.65582814
C	-1.24233653	1.14758966	-2.53669110
C	-1.19296465	2.15259925	-0.43535331
C	3.26929241	0.07979159	-1.20628457
H	1.33537528	-0.10182256	-2.10617263
C	3.28593318	-0.31630613	1.15887354
H	1.36141512	-0.76328803	1.98213465
C	-1.23414995	0.38648597	2.76034914
C	-1.19090537	1.94286815	1.02714137
O	-4.05124283	-1.34447820	-0.19392885
O	-0.67809816	-3.34188170	1.72281141
O	-0.67471695	-2.73426616	-2.58037359
C	-1.31358160	2.37464214	-3.17751727
H	-1.24710040	0.22720922	-3.10362968
C	-1.25519430	3.41568831	-1.02275826
C	3.97992794	-0.00847543	-0.01029532
H	3.75587675	0.29222424	-2.14843233
H	3.77926917	-0.37409750	2.11960173
C	-1.30205037	1.38320798	3.72128606
H	-1.23788854	-0.65645139	3.04440867
C	-1.24970521	2.98934717	1.94697596
C	-1.31109870	3.53038501	-2.40539913

H	-1.36927953	2.41132347	-4.25691292
H	-1.26703222	4.30493806	-0.41036503
C	5.45042766	0.20902555	0.01665333
C	-1.30110057	2.70955700	3.30618024
H	-1.35386381	1.11432615	4.76750284
H	-1.26183952	4.01555274	1.61090986
H	-1.36035879	4.50756467	-2.86852675
N	6.19790270	-0.61351919	0.72245032
N	5.95821329	1.21353257	-0.66648573
H	-1.34771013	3.51655625	4.02620065
H	7.19930513	-0.49471158	0.80509712
H	5.79873313	-1.44207993	1.13852113
H	5.35572150	1.89584886	-1.10276511
H	6.95433554	1.38387279	-0.71419487

Re(4-Pam) Fully Optimized Quintet

Re	-7.77925067	-4.75382884	0.00000000
N	-5.59375664	-4.39205726	-0.04046873
N	-7.91495832	-3.26966703	-1.49372978
C	-4.87898654	-4.45344146	-1.19955141
C	-4.89267324	-4.10478043	1.09424685
N	-7.87204088	-2.95026404	1.14812973
C	-9.76190559	-4.90746397	0.04831550
C	-7.58278907	-6.06110668	1.48345699
C	-7.62120746	-6.32824559	-1.16767414
C	-8.00730928	-3.47935224	-2.83493154
C	-7.89771514	-1.93755055	-1.01743510
C	-3.52658671	-4.24584253	-1.27181085
H	-5.43708887	-4.66788392	-2.10031458
C	-3.54069373	-3.88776568	1.11542459
H	-5.46029999	-4.05400376	2.01232834
C	-7.92570167	-2.84781634	2.49751834
C	-7.87791467	-1.77348170	0.38182497
O	-10.89853531	-4.97564597	0.07673901
O	-7.47439277	-6.82823261	2.32422044
O	-7.53125564	-7.25185800	-1.83964110
C	-8.04670394	-2.46710449	-3.75565979
H	-8.04670895	-4.51376848	-3.14931703
C	-7.92135148	-0.86659891	-1.95695842
C	-2.78193004	-3.95163897	-0.09007958
H	-3.05520059	-4.28324477	-2.24489592
H	-3.05617641	-3.68114381	2.06025981
C	-7.94885895	-1.64723470	3.16558621
H	-7.94804951	-3.78093475	3.04515754
C	-7.88821479	-0.51184142	1.04525238
C	-7.99204356	-1.11635849	-3.29628792
H	-8.11361971	-2.70133802	-4.80898394
H	-7.89029430	0.15253942	-1.59834394
C	-1.38951976	-3.73641669	-0.09557305
C	-7.92062215	-0.44466053	2.40929766
H	-7.98517682	-1.63503785	4.24604598
H	-7.87864220	0.39606300	0.45915365
H	-8.01258894	-0.29892475	-4.00597870
N	-0.72103501	-3.39643057	1.07881804
N	-0.60885833	-3.91507487	-1.20375089
H	-7.93124062	0.51550722	2.90977480
H	-0.34290823	-2.44103514	1.03151339

H	-0.86291230	-4.63998370	-1.86178896
H	0.38767636	-3.78048722	-1.10439447

Re(4-PamH) Fully Optimized Triplet

Re	0.95292677	-0.86124810	-0.05722862
N	-1.15635690	-0.55681674	-0.02925742
N	1.18930008	0.76209317	1.38552849
C	-1.87360507	-0.45737433	1.15175607
C	-1.89306264	-0.41639412	-1.19432754
N	1.18896797	0.92833791	-1.27644422
C	2.91180091	-1.31567786	-0.09072802
C	0.77895798	-2.10899266	-1.57805517
C	0.78782602	-2.29575712	1.29949687
C	1.27977350	0.60318700	2.72057933
C	1.20570660	2.01972862	0.86726136
C	-3.21043480	-0.21398171	1.20562780
H	-1.30953444	-0.56826080	2.06605292
C	-3.22929931	-0.16456022	-1.21770295
H	-1.34766174	-0.51975430	-2.12115606
C	1.26906680	0.93598044	-2.62182058
C	1.19577194	2.11224279	-0.60553572
O	4.01275041	-1.59662264	-0.11276327
O	0.70117046	-2.81190164	-2.47181976
O	0.71559630	-3.10576307	2.09654930
C	1.35513656	1.67368041	3.59615597
H	1.29073057	-0.41006835	3.09430686
C	1.27355004	3.13341143	1.69902383
C	-3.97283326	-0.04610228	0.00261320
H	-3.66914945	-0.11848026	2.18058453
H	-3.71584737	-0.10189199	-2.18174400
C	1.31905973	2.10695825	-3.35904157
H	1.29558432	-0.02431116	-3.11528026
C	1.23477384	3.32069620	-1.29466121
C	1.34247699	2.96201895	3.07630048
H	1.42267018	1.48850986	4.65917856
H	1.28150233	4.12889235	1.28186288
C	-5.37392408	0.20969653	0.01925830
C	1.29005772	3.32071739	-2.68343404
H	1.37890781	2.05579121	-4.43730993
H	1.22818366	4.25886852	-0.76034665
H	1.39593189	3.82423861	3.72832660
N	-6.01619863	0.63183458	-1.09062298
N	-6.09701209	0.03711006	1.14626061
H	1.32104980	4.25745016	-3.22479039
H	-7.01463788	0.77367264	-1.07823783
H	-5.51056088	1.11375917	-1.81636163
H	-5.77633888	-0.59702394	1.86020754
H	-7.08217455	0.25173529	1.15627363

Re(4-EtPy) Fully Optimized Singlet

Re	-0.70999855	-0.96854651	0.01638610
N	1.41659194	-0.18798603	-0.01104371
N	-1.14379118	0.72566240	-1.33347498
C	2.07366526	0.01686006	-1.17040054
C	2.09105192	0.05907022	1.13003478
N	-1.11475485	0.75764459	1.33398112

C	-2.55389869	-1.53876834	0.03616569
C	-0.28864387	-2.27159691	1.37745828
C	-0.30677829	-2.30330903	-1.31940976
C	-1.21199882	0.62890713	-2.67376060
C	-1.34906571	1.93481428	-0.75036006
C	3.38589783	0.45470054	-1.22691051
H	1.52583531	-0.18080150	-2.08120348
C	3.40348032	0.49882435	1.15077564
H	1.55735442	-0.10554748	2.05559955
C	-1.14226549	0.69559564	2.67779968
C	-1.31942851	1.95499097	0.72676963
O	-3.65532649	-1.87482162	0.04748561
O	-0.04016750	-3.03449230	2.20535723
O	-0.06882742	-3.08585163	-2.13191958
C	-1.46628669	1.71796189	-3.49286159
H	-1.06169927	-0.35522007	-3.09472186
C	-1.60714557	3.06787358	-1.52162882
C	4.09317652	0.70499242	-0.04755809
H	3.85017034	0.59795774	-2.19497054
H	3.88180469	0.67806232	2.10596305
C	-1.34795080	1.80989056	3.47636157
H	-0.99642084	-0.28043636	3.11874981
C	-1.51929798	3.11388758	1.47670176
C	-1.66216226	2.96197706	-2.90484363
H	-1.50874891	1.58222653	-4.56493223
H	-1.77158126	4.02613344	-1.05192606
C	-1.53020250	3.04385691	2.86327000
H	-1.35982126	1.70174225	4.55233563
H	-1.66733910	4.06545737	0.98818417
H	-1.86163259	3.83717138	-3.50992085
H	-1.68485259	3.93903080	3.45200434
C	6.49770913	-0.07322220	-0.02269473
H	7.53432931	0.27073137	-0.03769782
H	6.34728081	-0.66278224	0.88498822
H	6.34331277	-0.72887860	-0.88314440
C	5.53793426	1.13137067	-0.06570887
H	5.73317617	1.78123922	0.79134135
H	5.73023272	1.71691522	-0.96842879

Re(4-EtPy) Fully Optimized Triplet

Re	-0.61457940	-0.93063364	-0.10894085
N	1.47941209	-0.28782662	0.19869453
N	-0.91953704	0.79846971	-1.31275225
C	1.79663354	1.01317507	0.37829208
C	2.49648983	-1.18199924	0.21050916
N	-1.23027091	0.53241705	1.30924581
C	-2.53686433	-1.38821251	-0.38693872
C	-0.38717666	-2.46136158	1.12563321
C	-0.07265013	-2.19535207	-1.53201562
C	-0.69298995	0.89697302	-2.64870410
C	-1.47528520	1.90220604	-0.63865012
C	3.09503850	1.44767615	0.56698832
H	0.97991226	1.71887469	0.37147913
C	3.81563680	-0.81545713	0.39382776
H	2.23350982	-2.22080659	0.07070817
C	-1.32044399	0.35949358	2.65397478
C	-1.64180373	1.76037814	0.75698234

O	-3.63486902	-1.63599610	-0.54532902
O	-0.27436030	-3.35345567	1.83242063
O	0.22058201	-2.93597487	-2.35283986
C	-0.98235820	2.01876446	-3.38152669
H	-0.25892534	0.02598825	-3.12058020
C	-1.79979539	3.07487451	-1.37675636
C	4.15125722	0.52980844	0.57916561
H	3.27773409	2.50550135	0.70903379
H	4.57733530	-1.58515715	0.39592568
C	-1.79852832	1.32003809	3.50702842
H	-0.98594003	-0.59738329	3.03138065
C	-2.15825898	2.76989805	1.61704732
C	-1.56087026	3.13863209	-2.72047862
H	-0.77236253	2.03609384	-4.44194401
H	-2.23687659	3.91979478	-0.86353714
C	-2.23711382	2.56103082	2.96492331
H	-1.83889308	1.12262572	4.56923775
H	-2.48663061	3.70918014	1.19455483
H	-1.80836138	4.03322649	-3.27813761
H	-2.62901694	3.33247814	3.61589940
C	6.26116605	1.25437238	-0.60602358
H	7.29416576	1.56959749	-0.44433811
H	6.27167207	0.36178295	-1.23619264
H	5.74292848	2.04864842	-1.14861684
C	5.57978790	0.97070713	0.74725689
H	6.13573257	0.19318156	1.27748836
H	5.60819508	1.87201578	1.36465944

Re(bpy)(4-Pam)CO_2(MeCN) Fully Optimized Singlet

Re	-0.78679798	-0.86573273	-0.11743580
N	1.38728862	-0.57236608	-0.05458845
N	-0.89648814	1.06582083	-1.20118972
C	2.09261118	-0.29923336	-1.17249551
C	2.07649173	-0.62710574	1.10617251
N	-0.93511660	0.70449722	1.43994603
C	-0.70828311	-2.38627692	1.02450690
C	-0.67304160	-2.02875577	-1.62033349
C	-0.93234415	1.17871688	-2.54132015
C	-0.93260397	2.19508942	-0.44783795
C	3.45916797	-0.07237902	-1.17133094
H	1.53706248	-0.27151318	-2.09854912
C	3.44276288	-0.42219896	1.18607849
H	1.50657290	-0.84691156	1.99694251
C	-1.01108199	0.45286402	2.75952006
C	-0.95306281	1.99478735	1.01723637
O	-0.66265386	-3.29667830	1.74732729
O	-0.60512519	-2.71488907	-2.55723860
C	-0.98488267	2.40162539	-3.19268323
H	-0.91842497	0.25360462	-3.10104566
C	-0.97929358	3.45568544	-1.04388681
C	4.17022920	-0.13663461	0.02907838
H	3.95996720	0.13000613	-2.10860934
H	3.92482031	-0.47363173	2.15375859
C	-1.08478516	1.45593603	3.71395713
H	-1.01428469	-0.58866548	3.05031436
C	-1.01830589	3.04902235	1.92895313
C	-1.00189163	3.56275441	-2.42813964

H	-1.01066506	2.43203538	-4.27360404
H	-1.00279099	4.34896833	-0.43739011
C	5.65564662	0.05744241	0.08159712
C	-1.08046477	2.77989953	3.28987147
H	-1.14245555	1.19482443	4.76204310
H	-1.02534009	4.07292086	1.58526259
H	-1.03790340	4.53724751	-2.89837124
N	6.44429646	-0.59239748	0.85798687
N	6.15338571	0.95531855	-0.83172510
H	-1.13074025	3.59217044	4.00385845
H	5.93136972	-1.29146760	1.39066889
H	5.57589606	1.74070763	-1.09230146
H	7.13543068	1.17023073	-0.72904061
N	-2.86436486	-0.86479352	-0.14587758
C	-4.01517267	-0.80727327	-0.15562169
C	-5.46375346	-0.74663444	-0.17058296
H	-5.79356296	0.14805240	-0.70208815
H	-5.86668764	-1.62748809	-0.67431589
H	-5.84684381	-0.71514069	0.85114303

Re(bpy)(4-Pam)CO_2(DCM) Fully Optimized Singlet

Re	-0.58195694	-0.44001755	0.57746634
N	1.53951090	-0.56810892	0.27105971
N	-0.71792067	0.42761171	-1.45360472
C	2.06315187	-1.24022651	-0.77760736
C	2.41078525	0.04987161	1.10046727
N	-0.35753945	1.74873137	0.83160024
C	-0.43894876	-0.94639137	2.40629184
C	-0.82680080	-2.27522710	0.13201065
C	-0.94486611	-0.29053146	-2.56918475
C	-0.53264173	1.76895667	-1.56730610
C	3.42321007	-1.31132735	-1.02764916
H	1.36287011	-1.74522421	-1.42619320
C	3.78122390	0.01673659	0.91733305
H	1.98601746	0.58074439	1.93904013
C	-0.24069310	2.36379768	2.02447932
C	-0.34046479	2.50339815	-0.29859211
O	-0.34979425	-1.22464169	3.53091754
O	-0.97416085	-3.39017948	-0.16120142
C	-0.98337438	0.27484852	-3.83457891
H	-1.10365840	-1.35117476	-2.43326569
C	-0.55387950	2.39573009	-2.81330793
C	4.32199256	-0.67832076	-0.16628247
H	3.77204070	-1.88065229	-1.87880892
H	4.41569076	0.54327005	1.61857767
C	-0.08501269	3.73517613	2.15136275
H	-0.27704474	1.72709828	2.89798379
C	-0.18072999	3.88784724	-0.23552710
C	-0.77826421	1.64406784	-3.95914875
H	-1.17087655	-0.35240027	-4.69563098
H	-0.39989181	3.46167832	-2.89457790
C	5.80513067	-0.76653118	-0.36285011
C	-0.04816904	4.51113566	0.99807960
H	0.00388979	4.17514285	3.13543932
H	-0.16556580	4.48012108	-1.13856479
H	-0.79660528	2.12269061	-4.93001764
N	6.65717145	-0.85708468	0.59122416

N	6.21175439	-0.81988548	-1.67505932
H	0.07517129	5.58517746	1.05491564
H	6.18871845	-0.91799230	1.49252149
H	5.67250510	-0.31599303	-2.36314317
H	7.21221584	-0.78031375	-1.81210099
C	-4.17943316	-1.35315146	0.51192860
H	-3.71731909	-2.19995624	1.00367373
H	-5.14509081	-1.09204891	0.92876665
Cl	-3.11011478	0.08937086	0.83709354
Cl	-4.36275515	-1.69985815	-1.21958590