Electronic Supplementary Information

Amidino ligands from coupling 1-methylcytosine and nitrile: a new method to incorporate biomolecules to luminescent Re(CO)3 complexes

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Synthesis and characterization of the complexes

General Remarks. All manipulations were performed under N_2 atmosphere following conventional Schlenk techniques. Solvents were purified according to standard laboratory methods.[1] *fac*-[$ReBr(CO)_3(NCMe)_2$],[2] *fac*-[$Re(CO)_3(NCMe)_3$]BF_4,[3] and 1-methylcytosine[4] were obtained as previously described. The microwave assisted reactions were carried out in an Anton Paar Monowave 300 apparatus. Infrared spectra were recorded in a Perkin-Elmer FT-IR spectrum BX apparatus using 0.2 mm CaF_2 cells for solutions or in a Perkin-Elmer Frontier spectrometer coupled to a Pike GladiATR-210 accessory for solid samples. NMR spectra were recorded in Varian MR500 instrument at room temperature (r.t.), and are referred to the internal residual solvent peak for ^1H and $^{13}C\{^1H\}$ NMR. Assignment of the $^{13}C\{^1H\}$ NMR data was supported by 2D HSQC and HMBC experiments and relative intensities of the resonance signals. UV-vis spectra were measured with a VARIAN-Cary 100 or Shimadzu UV-2550 spectrophotometers and emission spectra were recorded on a Jobin-Yvon FluoroLog 3.2.2 or in a Perkin–Elmer LS-55 luminescence spectrometer at room temperature. The luminescence quantum yields Ø of the complexes were determined using cresyl violet as a luminescence quantum yield standard.[5] All measurements were performed in deaerated solvents. Elemental analyses were performed on a Perkin-Elmer 2400B microanalyzer.

***fac*-[$ReBr(CO)_3${NH=C(Me)(MeCyH-κ^2N,N}], 1a**. A solution of *fac*-[$ReBr(CO)_3(NCMe)_2$] (0.216 g, 0.5 mmol) and 1-methylcytosine ($MeCyH_2$, 0.063 g, 0.5 mmol) in NCMe (20 mL) was stirred for 5 h at reflux. The volatiles were removed *in vacuo* and the yellow residue was crystallized in acetone/hexane at –20°C, giving a yellow microcrystalline solid, which was decanted, washed with hexane (3 x 3 mL approximately), and dried *in vacuo*, yielding 0.149 g (58 %). IR (THF, cm^{-1}): 2018 vs, 1912 vs, 1881 vs. IR (neat solid, cm^{-1}): 3462 m, 3225 m, 2027 vs, 1925 vs, 1902 vs, 1670 m, 1597 m, 1524 w, 1467 m, 1421 m, 1339 m, 1317 m, 1213 m, 1182 w, 1115 w, 1043 w, 806 w, 780 w, 650 w, 632 w, 552 w, 523 w. ^1H NMR (499.7 MHz, CD_3NO_2): 2.41 (s, NH=CCH_3, 3 H),

3.56 (s, CH_3 MeCy, 3 H), 6.21 (d, J = 7.0 Hz, C^5H MeCy, 1 H), 7.86 (d, J = 7.0 Hz, C^6H MeCy, 1 H), 8.73 (s, NH MeCy, 1 H), 9.89 (s, NH=CCH$_3$, 1 H). ^{13}C{^{1}H} NMR (125.7 MHz, CD_3NO_2): 24.3 (s, NH=CCH$_3$), 40.5 (s, NCH$_3$), 97.1 (s, C^5H MeCy), 150.9 (s, C^6H MeCy), 155.7 (s, CO MeCy), 161.6 (s, NH=CCH3), 162.1 (s, C^4 MeCy), 197.1 (s, ReCO), 198.0 (s, ReCO), 198.5 (s, ReCO). Anal. Calcd. for $C_{10}H_{10}BrN_4O_4Re$: C, 23.26; H, 1.95; N, 10.85. Found: C, 22.99; H, 2.01; N, 10.69.

***fac*-[ReBr(CO)$_3${NH=C(Ph)(MeCyH-κ^2N,N}], 1b**. The same procedure as for **1a**, using NCPh (7 mL) as solvent, gave 0.158 g (55%) of **1b** as a yellow microcrystalline solid. IR (THF, cm^{-1}): 2018 vs, 1913 vs, 1884 vs. IR (neat solid, cm^{-1}): 3194 w, 2918 m, 2849 m, 2015 vs, 1918 s, 1894 vs, 1867 vs, 1680 m, 1575 m, 1509 m, 1455 m, 1442 m, 1415 m, 1332 m, 1303 w, 1254 m, 1174 w, 1127 w, 1041 m, 1024 w, 874 w, 797 w, 776 w, 697 m, 650 w, 624 w, 607 w, 556 w, 523 m, 481 w, 399 w, 360 w, 303 w. ^{1}H NMR (499.7 MHz, CD_3NO_2): 3.61 (s, CH_3 MeCy, 3 H), 6.34 (d, J = 7.0 Hz, C^5H MeCy, 1 H), 7.6 (t, J = 7.5 Hz, *meta*-C_6H_5, 2 H), 7.69 (tt, J = 7.5 and 1.5 Hz, *para*-C_6H_5, 1 H), 7.77 (d, J = 7.5 Hz, *ortho*-C_6H_5, 2 H), 7.95 (d, J = 7.0 Hz, C^6H MeCy, 1H), 8.89 (s, NH MeCy, 1 H), 9.12 (s, NH=CCH$_3$, 1 H). ^{13}C{^{1}H} NMR (125.7 MHz, CD_3NO_2): 40.5 (s, NCH$_3$), 97.5 (s, C^5H MeCy), 128.2 (s, *ortho*-C_6H_5), 130.7 (s, *meta*-C_6H_5), 134.1(s, *para*-C_6H_5), 134.3 (s, *ipso*-C_6H_5), 151.1 (s, C^6H MeCy), 155.8 (s, CO MeCy), 161.8 (s, N=CPh$_3$), 162.8 (s, C^4 MeCy), 197.2 (s, ReCO), 197.7 (s, ReCO), 198.4 (s, ReCO). Anal. Calcd. for $C_{15}H_{12}BrN_4O_4Re$: C, 31.14; H, 2.09; N, 9.69. Found: 30.93; H, 2.28; N, 9.89.

***fac*-[Re(CO)$_3$(NCMe){NH=C(Me)(MeCyH-κ^2N,N}]BF$_4$, 2a.** *Method A.* A mixture of **1a** (0.103 g, 0.2 mmol) and $AgBF_4$ (0.045 g, 0.23 mmol) in NCMe (20 mL) was stirred at 30°C for 30 min with exclusion of light. Then the reaction mixture was filtered, the volatiles were dried *in vacuo*, and the yellow residue was crystallized in THF/Et_2O giving a pale yellow microcrystalline solid, which was decanted, washed with diethyl ether (3 x 3 mL approximately), and dried *in vacuo*, yielding 0.103 g (92 %). *Method B.* *fac*-[Re(CO)$_3$(NCMe)$_3$]BF$_4$ (0.048 g, 0.10 mmol), 1-methylcytosine (0.012 g,

0.10 mmol), and NCMe (2 mL) were placed in a dry 10 mL glass vessel equipped with a magnetic stirbar. The vessel was sealed with a septum and placed in the microwave apparatus, and heated at 180°C during 10 min. The reaction mixture was then cooled to 50 °C, and the contents were transferred into a schlenk flask, and the volatiles were removed *in vacuo*. Crystallization from THF/Et_2O yielded 0.044 g (76 %) of **2a**. IR (THF, cm^{-1}): 2031 vs, 1932 vs, 1912 vs. IR (neat solid, cm^{-1}): 3274 m, 2961 w, 2028 vs, 1949 w, 1899 vs, 1697 m, 1673 m, 1582 m, 1525 w, 1464 w,1418 w, 1346 w, 1313 m, 1260 w, 1188 w, 1078 vs, 1053 vs, 1004 vs, 878 w, 781 m, 709 w, 649 w, 626 m, 553 w, 536 w, 477 w, 399 w, 375 w. ^{1}H NMR (499.7 MHz, CD_3NO_2): 2.35 (s, NCC*H*$_3$, 3 H), 2.46 (s, NH=CC*H*$_3$, 3 H), 3.59 (s, C*H*$_3$ MeCy, 3 H), 6.28 (d, *J* = 7.0 Hz, C^5*H* MeCy, 1 H), 7.95 (d, *J* = 7.0 Hz, C^6*H* MeCy, 1 H), 8.73 (s, N*H* MeCy, 1 H), 9.02 (s, N*H*=CCH$_3$, 1 H). ^{19}F NMR (470.2 MHz, CD_3NO_2): −152.87 (s, $^{10}BF_4$, 4 F), −152.92 (s, $^{11}BF_4$, 4 F). ^{13}C{^{1}H} NMR (125.7 MHz, CD_3NO_2): 3.0 (s, NC*C*H$_3$), 24.1 (s, NH=C*C*H$_3$), 40.5 (s, N*C*H$_3$), 97.1 (s, *C*^{5}H MeCy), 122.8 (s, N*C*CH$_3$) 151.6 (s, *C*^{6}H MeCy), 155.9 (s, CO MeCy), 162.1 (s, NH=*C*CH3), 163.6 (s, *C*^{4} MeCy), 194.4 (s, Re*C*O), 195.5 (s, Re*C*O), 197.0 (s, Re*C*O). Anal. Calcd. for $C_{12}H_{13}BF_4N_5O_4Re$: C, 25.54; H, 2.32; N, 12.41. Found: C, 25.63; H, 2.44; N, 12.15.

***fac*-[Re(CO)$_3$(NCPh){NH=C(Ph)(MeCyH-κ^2*N*,*N*}]BF$_4$, 2b.** *Method A.* A mixture of **1b** (0.056 g, 0.1 mmol) and $AgBF_4$ (0.023 g, 0.12 mmol) in THF (10 mL) was stirred at 30°C for 30 min with exclusion of light. Then the reaction mixture was filtered, the volatiles were dried *in vacuo*, and the yellow residue was redissolved in NCPh (3 mL) and stirred for 30 min. The volatiles were again dried *in vacuo*, and the yellow residue was crystallized in THF/Et_2O giving a pale yellow microcrystalline solid, which was decanted, washed with diethyl ether (3 x 3 mL approximately), and dried *in vacuo*, yielding 0.057 g (83 %). *Method B.* The same microwave procedure as for **1b**, using NCPh (2 mL) as solvent gave 0.041 g (60 %) of **2b**. IR (THF, cm^{-1}): 2027 vs, 1920 vs, 1900 vs. IR (neat solid, cm^{-1}): 3293 m, 3262 m, 3196 w, 3112 w, 2027 vs, 1926 m, 1897 vs, 1654 m, 1567 m, 1506 w, 1492 w, 1454 m, 1447 m, 1406 m, 1338 w, 1302 w, 1243 w, 1131 w, 1054 s, 1025

s, 998 m, 809 w, 796 w, 779 w, 761 m, 699 m, 686 m, 633 m, 562 w, 529 m, 401 w, 363 w. ^{1}H NMR (499.7 MHz, CD_3NO_2): 3.66 (s, C*H*$_3$ MeCy, 3 H), 6.52 (d, *J* = 7.5 Hz, C^{5}*H* MeCy, 1 H), 7.58 (t, *J* = 7.5, *meta*-C_6H_5, 2 H), 7.62 (t, *J* = 7.5 Hz, *meta*-C_6H_5, 2 H), 7.73 (m, *para*-C_6H_5, 2 H), 7.81 (d, *J* = 7.5 Hz, *ortho*-C_6H_5, 2 H), 7.86 (d, *J* = 7.5 Hz, *ortho*-C_6H_5, 2 H), 8.06 (d, *J* = 7.5 Hz, C^{6}*H* MeCy, 1 H), 9.20 (s, N*H*, 1 H), 9.21 (s, N*H*, 1H). ^{19}F NMR (470.2 MHz, CD_3NO_2): −152.87 (s, $^{10}BF_4$, 4 F), −152.92 (s, $^{11}BF_4$, 4 F). ^{13}C{^{1}H} NMR (125.7 MHz, CD_3NO_2): 40.6 (s, N*C*H$_3$), 97.3 (s, *C*^{5}H), 128.6 (s, *ortho*-C_6H_5),130.6 (s, *ortho*-C_6H_5), 130.8 (s, *meta*-C_6H_5), 133.5 (s, *meta*-C_6H_5), 134.7 (s, *para*-C_6H_5), 136.4 (s, *para*-C_6H_5), 152.3 (s, *C*^{6}H MeCy), 156.0 (s, *C*O MeCy), 163.0 (s, N=*C*Ph$_3$), 163.1 (s, *C*^{4} MeCy), 194.1 (s, Re*C*O), 195.1 (s, Re*C*O), 196.9 (s, Re*C*O). *ipso*-C_6H_5 and N*C*Ph not detected. Anal. Calcd. for $C_{22}H_{17}BF_4N_5O_4Re$: C, 38.38; H, 2.49; N, 10.17. Found: C, 38.59; H, 2.29; N, 10.37.

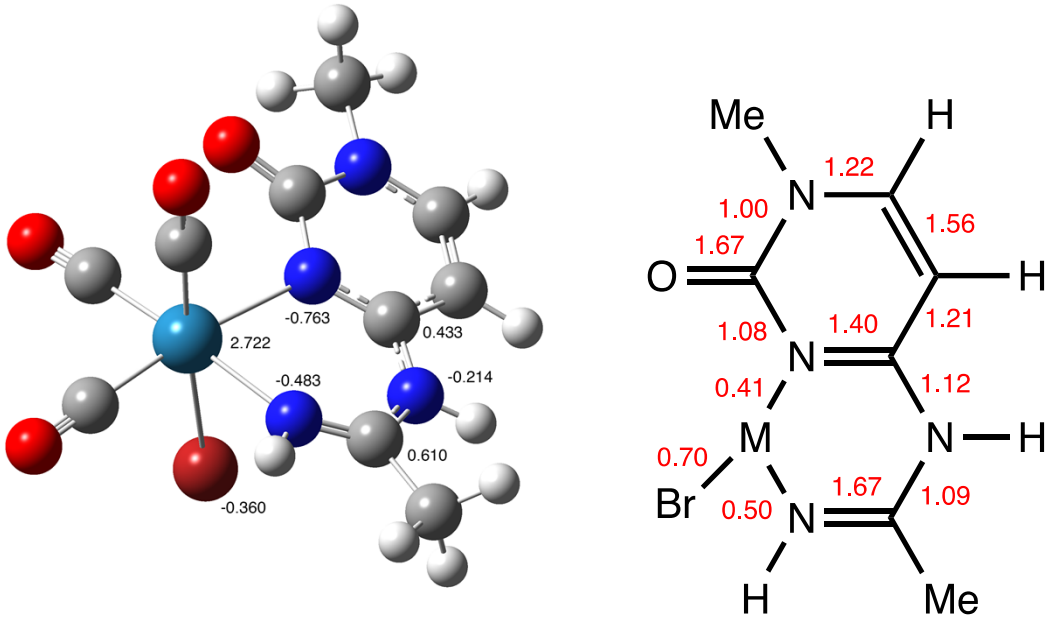
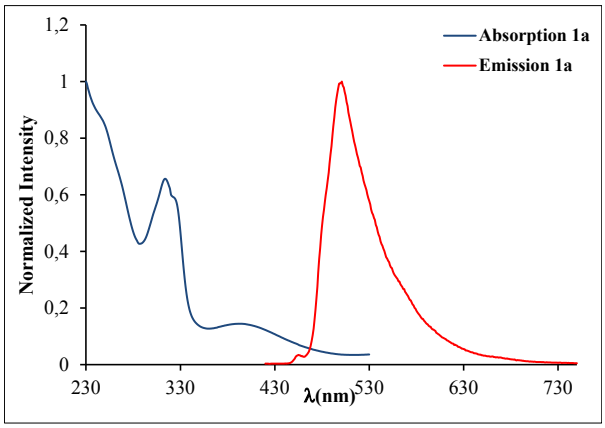


Figure S1. NBO charges and Wiberg indexes found for **1a**.



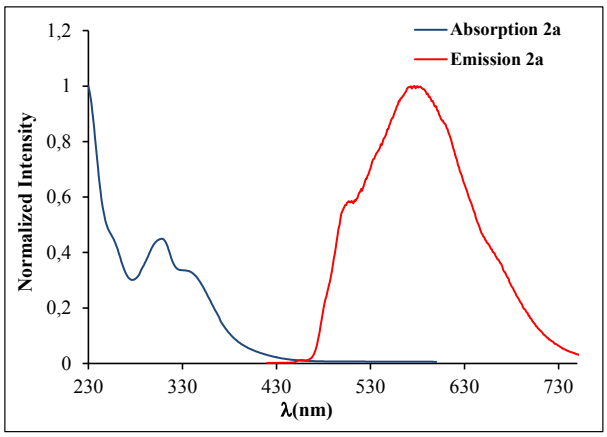


Figure S2. Normalized emission (red) and absorption (blue) spectra recorded in CH2Cl2 of complexes **1a** and **2a** at 298 K.

Table S1. Photophysical data:[(a)]

	Absorption	**Emission**	
	CH_2Cl_2[(b)] at 298 K λ_{abs} nm ε ($M^{-1}cm^{-1}$)	CH_2Cl_2[(b)] at 298 K λ_{em} (nm) [λ_{excit} =390 nm]	$\mathbf{Ø_L}$ x10^{-3} (%)
1a	316 (16100), 326 sh (14200), 399 (3580)	455 sh, 501	9
2a	259 sh (16800), 308 (17200), 337 sh (12700)	505 sh, 576	13

(a) Measurement Conditions: Concentration = 10^{-5} M; Excitation: 390 nm; Range: 420-800 nm.

(b) NMR and IR spectra demonstrate that some donor solvents such as MeCN produce partial substitution of the "sixth" ligand (Br in **1a**, MeCN in **1b**) and therefore the photophysical measurements in these solvents are not reliable. CH_2Cl_2 has been chosen because both complexes are stable, even though their solubility is low.

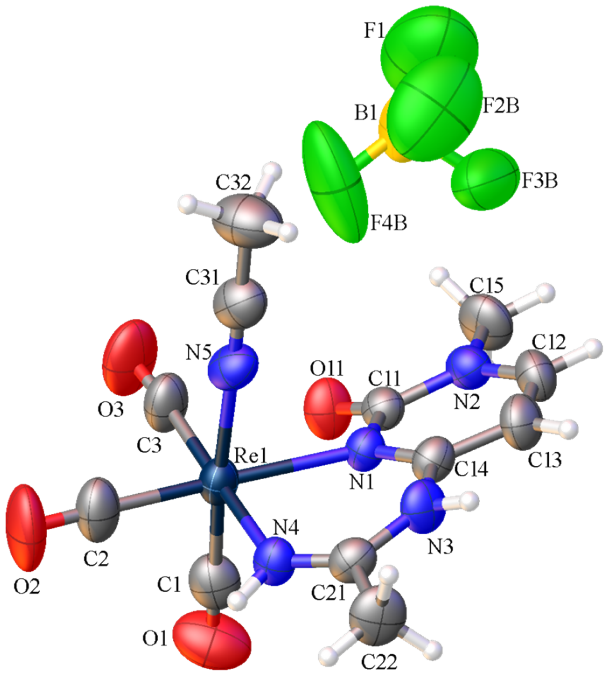


Figure S3. Perspective view of *fac*-[Re(CO)$_3$(NCMe){NH=C(Me)(MeCyH-κ^2*N,N*}]BF$_4$, **2a**, showing the atom numbering. Ellipsoids are drawn at 50 % probability. Selected bond lengths (Å) and angles (deg): Re1–N1 2.219(4), N1–C14 1.329 (6) N3–C14 1.379(6), N3–C21 1.379(6), N4–C21 1.255(6), Re1–N4 2.133(4); N1–C11 1.408(6), N2–C11 1.391(6), N2–C12 1.336(6), C12–C13 1.335(7), C14–C13 1.413(7); C14–N1–Re1 124.7(3), N1–C14–N3 122.8(5), C14–N3–C21 131.5(4), N4–C21–N3 122.0(4), C21–N4–Re1 131.1(4), N4–Re1–N1 83.65(14).

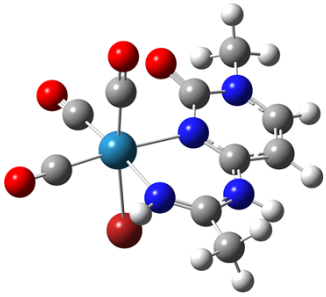
Computational Details.

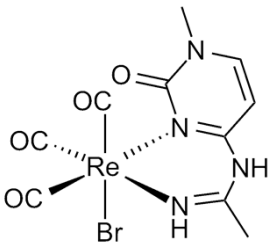
All calculations have been performed using the Gaussian 09 program package,[6] in which the PBE1PBE method was applied. This hybrid Hartree-Fock/ density functional model is based on the Perdew-Burke-Erzenhof (PBE) functional,[7] where the HF/DFT exchange ratio is fixed a priori to 1/4, and was used to optimize the ground and excited state geometries. Geometry optimizations were performed under no symmetry restrictions, using initial coordinates derived from X-ray data of the same complexes, and frequency analyses were performed to ensure that a minimum structure with no imaginary frequencies was achieved in each case. On the basis of the optimized ground and excited state geometries, the absorption and emission properties in dichloromethane solution were calculated by TD-DFT[8] at the PBE1PBE level associated with the PCM method to introduce the solvent effects.[9] Spin-orbital coupling is not included in the current TD-DFT method, and it influences the excitation energies in which the Re electrons are involved,[10] whereas it has a negligible effect on the transition character of this complexes. Hence, although TD-DFT cannot exactly estimate the excitation energies, it can still provide a reasonable spectral feature for our investigated complexes. This kind of theoretical approach has been proven to be reliable for transition-metal complex systems.[11] In the calculations, effective core potentials (ECP) and their associated double-ζ LANL2DZ basis set were used for the rhenium and bromide atoms,[12] while the light elements (O, N, C, and H) were described with the 6-31+G(d,p) basis.[13] This level of theory was proved to be adequate in our previous theoretical study of the similar pirazolylamidino complexes.[14] The contribution of every fragment in the molecules studied to the different orbitals involved in the optical transitions was calculated with the AOMix program,[15] and the graphical representation of the orbitals was made with the help of GaussView.[16] Wiberg bond indexes[17] were calculated with the NBO 5.9 program.[18]

Crystal Structure Determination for Compounds 1a and 2a. Crystals were grown by slow diffusion of hexane into concentrated solutions of the complexes in acetone (for **1a**) or THF (for **2a**)

at −20 °C. Relevant crystallographic details can be found in the CIF. A crystal was attached to a glass fiber and transferred to an Agilent SuperNova diffractometer fitted with an Atlas CCD detector. The crystals were kept at 293(2) K during data collection. Using Olex2,[19] the structure was solved for complex **1a** with the ShelXS structure solution program using direct methods,[20] and with olex2.solve structure solution program using Charge Flipping for complex **2a**,[20] and then, the structures were refined with the ShelXL refinement package using least squares minimisation.[21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All graphics were made with Olex2, and distances and angles of hydrogen bonds were calculated with PARST[22] (normalized values).[23]

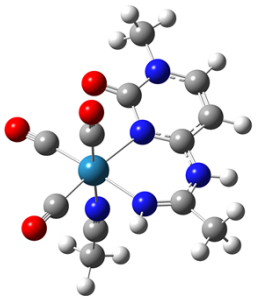
Table S2. Frontier Molecular Orbital Compositions (%) in the Ground State for Complex **1a** at the PBE1PBE Level

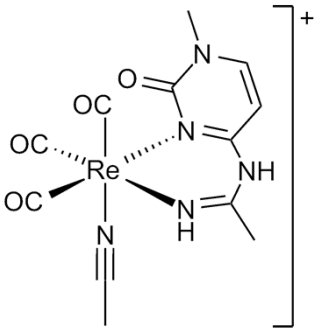




		Contribution (%)				
Orbital	Energy (eV):	Re:	Br:	CO:	nucleob:	main bond type
HOMO-3	-7.27	8.10	32.61	2.57	56.73	p(Br) + π(nucleob)
HOMO-2	-6.80	64.02	7.42	24.69	3.87	d(Re) + π(CO)
HOMO-1	-6.42	44.64	32.45	19.79	3.12	d(Re) + p(Br) + π(CO)
HOMO	-6.32	48.88	24.50	19.53	7.08	d(Re) + p(Br) + π(CO)
LUMO	-2.15	0.97	0.07	2.82	96.14	π*(nucleob)
LUMO+1	-0.92	27.18	4.64	21.20	46.98	p(Re) + π*(CO) + π*(nucleob)
LUMO+2	-0.54	12.37	1.49	30.90	55.24	p(Re) + π*(CO) + π*(nucleob)

Table S3. Frontier Molecular Orbital Compositions (%) in the Ground State for Complex **2a** at the PBE1PBE Level





		Contribution (%)				
Orbital	Energy (eV):	Re:	NCMe:	CO:	nucleob:	main bond type
HOMO-3	-7.89	7.56	1.11	2.42	88.91	π(nucleob)
HOMO-2	-7.37	68.88	0.98	25.95	4.19	d(Re) + π(CO)
HOMO-1	-7.22	58.19	3.90	24.43	13.48	d(Re) + π(CO)
HOMO	-7.03	58.13	3.33	23.15	15.40	d(Re) + π(CO)
LUMO	-2.57	0.85	0.00	2.79	96.52	π*(nucleob)
LUMO+1	-1.32	23.38	1.85	25.37	49.40	p(Re) + π*(CO) + π*(nucleob)
LUMO+2	-1.18	33.48	22.26	43.01	1.24	p(Re) + π*(NCMe) + π*(CO)

Table S4. Calculated Excited Energies, Dominant Orbital Excitations, and Oscillator Strength (*f*) from TD-DFT Calculations for Complex **1a**

state	excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	*f*	λ_{exp} (nm)	Character
S_1	HOMO ✂ LUMO HOMO-1 ✂ LUMO	0.66 0.25	3.23	384	0.0192	399	MLCT/LLCT/XLCT
S_2	HOMO ✂ LUMO HOMO-1 ✂ LUMO	-0.25 0.66	3.35	370	0.0426		MLCT/LLCT/XLCT
S_5	HOMO-3 ✂ LUMO	0.68	4.23	293	0.1858	316	XLCT/ILCT

Table S5. Calculated Excited Energies, Dominant Orbital Excitations, and Oscillator Strength (*f*) from TD-DFT Calculations for Complex **2a**

state	excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	*f*	λ_{exp} (nm)	Character
S_1	HOMO ✂ LUMO	0.69	3.50	354	0.0203	337	MLCT/LLCT
S_2	HOMO-1 ✂ LUMO	0.68	3.78	328	0.1331	308	MLCT/LLCT
S_4	HOMO-3 ✂ LUMO HOMO ✂ LUMO+1 HOMO ✂ LUMO+2	-0.35 -0.35 0.45	4.39	282	0.0441		MLCT/LLCT/ILCT
S_5	HOMO-3 ✂ LUMO HOMO ✂ LUMO+2	0.48 0.44	4.44	279	0.1103	259	ILCT

Table S6. Molecular orbital Compositions in the Excited States.

			Contribution (%)			
Complex	Orbital	Energy (eV):	Re:	NCMe:	CO:	nucleob:
1a	HOMO	-6.79	30.02	15.64	11.02	43.32
	LUMO	-3.83	1.57	0.05	3.01	95.38
2a	HOMO	-7.48	43.04	2.10	13.80	41.06
	LUMO	-4.28	14.05	0.56	4.76	80.62

Table S7. Calculated Emission Energies and Dominant Orbital Emissions from TD-DFT Calculations.

Complex	state	Excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	λ_{exp} (nm)	Character
1a	T_1	HOMO ✂ LUMO	0.94	1.71	725	501	^{3}MLCT/^{3}ILCT/
2a	T_1	HOMO ✂ LUMO	0.86	1.63	762	576	^{3}MLCT/^{3}ILCT/

[1] D. D. Perrin and W. L. F. Armarego, *"Purification of Laboratory Chemicals"*; 3rd ed.; Pergamon Press: Oxford, 1988.
[2] M. F. Farona and K. F. Kraus, *Inorg. Chem.*, 1970, **9**, 1700-1704.
[3] V. I. Zdanovitch, N. E. Kolobova, N. I. Vasyukova, Yu. S. Nekrasov, G. A. Panosyan, P. V. Petrovskii, and A. Zh. Zhakaeva, *J. Organomet. Chem.*, 1978, **148**, 63-71.
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