Supplementary materials

Synthesis, Photophysical Properties and Application in Organic Light Emitting Devices of Rhenium(I) Carbonyls incorporating Functionalized 2,2′:6′,2″-terpyridines

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Table S1. Comparison of experimental and theoretical bond lengths [Å] and angles [°] for **1**, **3**, **4** and **6**.

Bond lengths	Exp.	Opt.		Bond angles	Exp.	Opt.	
		S_0	T_1			S_0	T_1
				1			
Re(1)–C(1)	1.905(5)	1.939	1.938	C(2)–Re(1)–C(1)	87.02(17)	86.82	87.24
Re(1)–C(2)	1.899(5)	1.921	1.932	C(3)–Re(1)–C(1)	90.82(19)	91.11	90.83
Re(1)–C(3)	1.919(5)	1.912	1.912	C(3)–Re(1)–C(2)	90.18(18)	89.85	89.64
Re(1)–N(1)	2.160(3)	2.202	2.202	C(1)–Re(1)–N(1)	174.37(15)	174.51	174.68
Re(1)–N(2)	2.216(3)	2.267	2.212	C(2)–Re(1)–N(1)	95.86(15)	96.79	96.45
Re(1)–Cl(1)	2.4848(11)	2.549	2.565	C(3)–Re(1)–N(1)	94.00(15)	93.02	93.02
C(1)–O(1)	1.154(5)	1.164	1.165	C(1)–Re(1)–N(2)	101.97(14)	101.71	100.88
C(2)–O(2)	1.151(6)	1.167	1.166	C(2)–Re(1)–N(2)	168.64(14)	169.35	169.41
C(3)–O(3)	1.121(5)	1.170	1.170	C(3)–Re(1)–N(2)	96.55(14)	96.28	96.98
Re(2)–C(31)	1.918(5)			N(1)–Re(1)–N(2)	74.61(11)	74.25	75.02
Re(2)–C(32)	1.881(5)			C(1)–Re(1)–Cl(1)	89.59(14)	91.13	91.26
Re(2)–C(33)	1.902(5)			C(2)–Re(1)–Cl(1)	91.12(14)	91.27	89.56
Re(2)–N(4)	2.164(3)			C(3)–Re(1)–Cl(1)	178.65(12)	177.55	177.71
Re(2)–N(5)	2.216(3)			N(1)–Re(1)–Cl(1)	85.53(8)	84.68	84.94
Re(2)–Cl(2)	2.4979(10)			N(2)–Re(1)–Cl(1)	82.11(8)	82.29	83.51
C(31)–O(4)	1.150(5)			C(32)–Re(2)–C(31)	86.97(17)		
C(32)–O(5)	1.167(5)			C(33)–Re(2)–C(31)	87.85(18)		
C(33)–O(6)	1.144(5)			C(33)–Re(2)–C(32)	89.47(19)		
				C(31)–Re(2)–N(4)	175.63(15)		
				C(32)–Re(2)–N(4)	95.79(15)		
				C(33)–Re(2)–N(4)	95.54(15)		
				C(31)–Re(2)–N(5)	102.37(14)		
				C(32)–Re(2)–N(5)	168.94(14)		
				C(33)–Re(2)–N(5)	96.70(15)		
				N(4)–Re(2)–N(5)	74.54(11)		
				C(31)–Re(2)–Cl(2)	92.92(13)		
				C(32)–Re(2)–Cl(2)	92.51(15)		
				C(33)–Re(2)–Cl(2)	177.90(13)		
				N(4)–Re(2)–Cl(2)	83.60(8)		
				N(5)–Re(2)–Cl(2)	81.23(8)		
				3			
Re(1)–C(1)	1.929(8)	1.937	1.977	C(2)–Re(1)–C(1)	86.5(3)	86.78	82.66
Re(1)–C(2)	1.898(7)	1.919	1.982	C(3)–Re(1)–C(1)	93.7(3)	90.52	98.53
Re(1)–C(3)	1.969(8)	1.915	1.986	C(3)–Re(1)–C(2)	90.7(3)	90.18	86.98
Re(1)–N(1)	2.174(5)	2.202	2.161	C(1)–Re(1)–N(1)	175.3(2)	174.86	172.70
Re(1)–N(2)	2.231(5)	2.265	2.143	C(2)–Re(1)–N(1)	95.1(2)	96.40	99.78
Re(1)–Cl(1)	2.4650(18)	2.552	2.470	C(3)–Re(1)–N(1)	90.7(3)	93.50	88.49
C(1)–O(1)	1.156(8)	1.164	1.156	C(1)–Re(1)–N(2)	103.2(2)	102.23	101.06
C(2)–O(2)	1.156(8)	1.168	1.157	C(2)–Re(1)–N(2)	169.5(2)	169.34	175.24
C(3)–O(3)	1.065(8)	1.169	1.153	C(3)–Re(1)–N(2)	92.7(2)	95.39	95.34
				N(1)–Re(1)–N(2)	74.97(19)	74.24	76.16
				C(1)–Re(1)–Cl(1)	91.0(2)	91.23	89.04
				C(2)–Re(1)–Cl(1)	90.5(2)	91.82	88.56
				C(3)–Re(1)–Cl(1)	175.2(2)	177.41	170.65
				N(1)–Re(1)–Cl(1)	84.62(14)	84.64	84.17
				N(2)–Re(1)–Cl(1)	85.39(13)	82.38	88.54
				4			
Re(1)–C(1)	1.919(9)	1.937	1.977	C(2)–Re(1)–C(1)	86.5(3)	86.76	82.66
Re(1)–C(2)	1.894(8)	1.919	1.982	C(3)–Re(1)–C(1)	93.4(4)	90.52	98.56
Re(1)–C(3)	1.950(9)	1.915	1.986	C(3)–Re(1)–C(2)	91.0(3)	90.19	86.96
Re(1)–N(1)	2.164(6)	2.202	2.161	C(1)–Re(1)–N(1)	175.1(3)	174.86	172.66
Re(1)–N(2)	2.227(6)	2.265	2.143	C(2)–Re(1)–N(1)	95.3(3)	96.42	99.80
Re(1)–Cl(1)	2.459(2)	2.552	2.470	C(3)–Re(1)–N(1)	91.1(3)	93.49	88.51
C(1)–O(1)	1.163(9)	1.164	1.156	C(1)–Re(1)–N(2)	102.9(3)	102.22	101.06
C(2)–O(2)	1.162(9)	1.168	1.157	C(2)–Re(1)–N(2)	169.7(3)	169.35	175.20
C(3)–O(3)	1.063(10)	1.169	1.153	C(3)–Re(1)–N(2)	92.5(3)	95.38	95.42
				N(1)–Re(1)–N(2)	75.0(2)	74.24	76.14
				C(1)–Re(1)–Cl(1)	91.0(2)	91.26	89.02
				C(2)–Re(1)–Cl(1)	90.7(3)	91.82	88.53

				C(3)–Re(1)–Cl(1)	175.4(3)	177.38	170.61
				N(1)–Re(1)–Cl(1)	84.45(16)	84.62	84.15
				N(2)–Re(1)–Cl(1)	85.13(15)	82.37	88.51
6							
Re(1)–C(1)	1.925(8)	1.939	1.938	C(2)–Re(1)–C(1)	87.9(3)	86.83	86.96
Re(1)–C(2)	1.922(7)	1.921	1.929	C(3)–Re(1)–C(1)	88.5(3)	91.05	91.02
Re(1)–C(3)	1.884(8)	1.912	1.905	C(3)–Re(1)–C(2)	88.6(3)	89.86	89.62
Re(1)–N(1)	2.173(6)	2.203	2.191	C(1)–Re(1)–N(1)	175.2(3)	174.57	174.39
Re(1)–N(2)	2.200(5)	2.262	2.210	C(2)–Re(1)–N(1)	96.1(3)	96.76	96.11
Re(1)–Cl(1)	2.4995(17)	2.552	2.590	C(3)–Re(1)–N(1)	94.1(3)	93.02	93.70
C(1)–O(1)	1.159(9)	1.164	1.167	C(1)–Re(1)–N(2)	101.7(2)	101.73	101.14
C(2)–O(2)	1.130(8)	1.167	1.169	C(2)–Re(1)–N(2)	168.4(2)	169.36	169.56
C(3)–O(3)	1.167(9)	1.170	1.173	C(3)–Re(1)–N(2)	98.1(3)	96.22	96.75
				N(1)–Re(1)–N(2)	74.03(19)	74.27	75.30
				C(1)–Re(1)–Cl(1)	93.6(2)	91.16	90.62
				C(2)–Re(1)–Cl(1)	91.8(2)	91.14	89.75
				C(3)–Re(1)–Cl(1)	177.8(2)	177.63	178.21
				N(1)–Re(1)–Cl(1)	83.71(14)	84.72	84.70
				N(2)–Re(1)–Cl(1)	81.12(13)	82.47	83.63

Table S2. Short intra- and intermolecular contacts detected in the structures of the rhenium(I) complexes.

D—H•••A	**D—H**	**H•••A**	**D•••A [Å]**	**D—H•••A [°]**
1				
C(7)–H(7)•••Cl(2)#1	0.93	2.72	3.599(3)	158.00
C(37)–H(37)•••Cl(1)#2	0.93	2.71	3.593(3)	158.00
C(50)–H(50)•••Cl(1)#2	0.93	2.82	3.668(4)	153.00
C(57)–H(57)•••O(1)#3	0.93	2.50	3.344(6)	151.00
C(60)–H(60)•••Cl(2)#3	0.93	2.68	3.582(5)	163.00
3				
C(7)–H(7)•••Cl(1)#4	0.93	2.76	3.602(8)	151.00
C(17)–H(17)••• Cl(1)#1	0.93	2.76	3.534(8)	142.00
4				
C(7)–H(7)•••Cl(1)#5	0.93	2.77	3.609(8)	151.00
C(17)–H(17)••• Cl(1)#1	0.93	2.77	3.541(9)	141.00
C(20)–H(20)••• Cl(1)#5	0.93	2.82	3.728(10)	165.00

Symmetry codes: #1: -1+x,y,z; #2: 1+x,y,z; #3: 2-x,1-y,1-z; #4: x,1/2-y,-1/2+z; #5: x,3/2-y,-1/2+z

Table S3. Frontier molecular orbital composition (%) in the ground state for complex **1** calculated at the DFT/B3LYP/DEF2-TZVPD/6-31+G* level.

Orbital	Energy [eV]	Contribution (%)					Character
		Re	3CO	Cl	R	terpy	
LUMO+5	-0.99	30.36	28.97	2.66	15.89	22.13	d(Re) + π*(CO) + π*(terpy) + π*(R)
LUMO+4	-1.03	11.90	26.99	6.99	8.07	46.06	d(Re) + π*(CO) + π*(terpy)
LUMO+3	-1.27	14.41	12.70	0.49	10.23	62.17	π*(terpy) + d(Re) + π*(CO) + π*(R)
LUMO+2	-1.56	13.18	4.99	2.07	4.52	75.24	π*(terpy) + d(Re)
LUMO+1	-1.96	2.69	1.60	0.60	14.53	80.58	π*(terpy) + π*(R)
LUMO	-2.64	10.86	3.51	2.76	8.24	74.63	π*(terpy) + d(Re)
HOMO	-6.23	16.17	9.46	5.66	57.11	11.61	π(R) + d(Re)
HOMO-1	-6.33	41.31	23.91	21.28	6.68	6.82	d(Re) + π(CO) + p(Cl)
HOMO-2	-6.48	32.47	19.65	22.99	18.54	6.35	d(Re) + π(CO) + p(Cl) + π(R)
HOMO-3	-6.75	54.28	30.95	1.57	0.16	13.04	d(Re) + π(CO)
HOMO-4	-6.97	0.01	0.00	0.00	99.93	0.06	π(R)
HOMO-5	-7.12	3.25	2.72	0.12	4.17	89.74	π(terpy)

Table S4. Frontier molecular orbital composition (%) in the ground state for complex **2** calculated at the DFT/B3LYP/DEF2-TZVPD/6-31+G* level.

Orbital	Energy [eV]	Contribution (%)					Character
		Re	3CO	Cl	R	terpy	
LUMO+5	-1.01	31.23	31.60	0.87	7.34	28.95	d(Re) + π*(CO) + π*(terpy)
LUMO+4	-1.04	9.75	15.79	5.34	10.72	58.40	π*(terpy) + π*(CO) + π*(R)
LUMO+3	-1.26	8.37	3.72	0.30	37.28	50.33	π*(terpy) + π*(R)
LUMO+2	-1.52	7.89	4.27	1.65	4.68	81.51	π*(terpy)
LUMO+1	-1.89	1.12	1.19	0.45	15.00	82.24	π*(terpy) + π*(R)
LUMO	-2.59	13.75	3.43	3.11	5.76	73.95	π*(terpy) + d(Re)
HOMO	-5.80	1.86	1.23	0.40	84.97	11.54	π(R) + π(terpy)
HOMO-1	-6.25	44.24	26.70	21.87	0.64	6.54	d(Re) + π(CO) + p(Cl)
HOMO-2	-6.39	41.91	24.58	24.15	2.52	6.83	d(Re) + π(CO) + p(Cl)
HOMO-3	-6.71	56.57	32.17	1.59	0.04	9.63	d(Re) + π(CO)
HOMO-4	-6.95	0.56	0.03	0.01	97.51	1.89	π(R)
HOMO-5	-7.11	1.31	1.38	0.25	2.29	94.77	π(terpy)

Table S5. Frontier molecular orbital composition (%) in the ground state for complex **3** calculated at the DFT/B3LYP/DEF2-TZVPD/6-31+G* level.

Orbital	Energy [eV]	Contribution (%)					Character
		Re	3CO	Cl	R	terpy	
LUMO+5	-0.92	30.06	34.32	6.59	7.81	21.22	d(Re) + π*(CO) + π*(terpy)
LUMO+4	-1.04	23.95	23.84	2.49	0.99	48.74	π*(terpy) + d(Re) + π*(CO)
LUMO+3	-1.21	11.06	8.46	0.89	9.08	70.52	π*(terpy) + d(Re)
LUMO+2	-1.54	9.25	4.43	1.84	3.34	81.13	π*(terpy)
LUMO+1	-1.97	0.99	1.18	0.38	13.86	83.59	π*(terpy) + π*(R)
LUMO	-2.67	10.92	3.44	2.95	7.96	74.74	π*(terpy) + d(Re)
HOMO	-6.25	44.13	26.90	21.70	0.57	6.70	d(Re) + π(CO) + p(Cl)
HOMO-1	-6.38	42.20	24.37	21.69	3.74	7.99	d(Re) + π(CO) + p(Cl)
HOMO-2	-6.72	56.31	31.85	1.73	0.24	9.87	d(Re) + π(CO)
HOMO-3	-6.95	2.08	0.91	6.85	72.77	17.39	π(R) + π(terpy)
HOMO-4	-7.16	1.13	1.44	0.26	1.29	95.87	π(terpy)
HOMO-5	-7.50	1.04	0.05	0.03	94.89	3.98	π(R)

Table S6. Frontier molecular orbital composition (%) in the ground state for complex **4** calculated at the DFT/B3LYP/DEF2-TZVPD/6-31+G* level.

Orbital	Energy [eV]	Contribution (%)					Character
		Re	3CO	Cl	R	terpy	
LUMO+5	-0.92	29.91	34.31	6.39	8.22	21.16	d(Re) + π*(CO) + π*(terpy)
LUMO+4	-1.04	23.71	23.66	2.57	1.06	48.99	π*(terpy) + d(Re) + π*(CO)
LUMO+3	-1.21	10.93	8.10	0.83	9.51	70.63	π*(terpy) + d(Re)
LUMO+2	-1.55	9.20	4.43	1.85	3.46	81.06	π*(terpy)
LUMO+1	-1.98	0.99	1.18	0.37	14.08	83.38	π*(terpy) + π*(R)
LUMO	-2.68	10.94	3.43	2.95	8.03	74.66	π*(terpy) + d(Re)
HOMO	-6.26	44.11	26.89	21.71	0.61	6.69	d(Re) + π(CO) + p(Cl)
HOMO-1	-6.38	42.03	24.26	21.60	4.13	7.98	d(Re) + π(CO) + p(Cl)
HOMO-2	-6.72	56.22	31.80	1.75	0.36	9.87	d(Re) + π(CO)
HOMO-3	-6.90	2.26	1.05	6.01	75.72	14.95	π(R) + π(terpy)
HOMO-4	-7.16	1.13	1.45	0.26	1.25	95.91	π(terpy)
HOMO-5	-7.51	1.04	0.05	0.03	94.91	3.96	π(R)

Table S7. Frontier molecular orbital composition (%) in the ground state for complex **5** calculated at the DFT/B3LYP/DEF2-TZVPD/6-31+G* level.

Orbital	Energy [eV]	Contribution (%)					Character
		Re	3CO	Cl	R	terpy	
LUMO+5	-0.92	32.97	28.48	6.17	12.38	20.00	d(Re) + π*(CO) + π*(terpy) + π*(R)
LUMO+4	-1.04	24.86	25.10	2.19	0.49	47.36	π*(terpy) + d(Re) + π*(CO)
LUMO+3	-1.20	12.49	8.51	0.99	8.80	69.21	π*(terpy) + d(Re)
LUMO+2	-1.55	8.12	4.41	1.79	2.55	83.14	π*(terpy)
LUMO+1	-1.98	1.10	1.19	0.31	11.04	86.37	π*(terpy) + π*(R)
LUMO	-2.69	12.61	3.32	2.99	7.07	74.01	π*(terpy) + d(Re)
HOMO	-6.26	44.27	26.86	21.94	0.31	6.61	d(Re) + π(CO) + p(Cl)
HOMO-1	-6.39	42.73	24.82	22.93	2.10	7.42	d(Re) + π(CO) + p(Cl)
HOMO-2	-6.73	56.52	31.93	1.58	0.06	9.91	d(Re)+ π(CO)
HOMO-3	-7.14	1.03	0.40	7.72	69.38	21.47	π(R) + π(terpy)
HOMO-4	-7.18	1.18	1.41	0.59	3.57	93.25	π(terpy)
HOMO-5	-7.56	1.15	0.36	3.68	68.22	26.59	π(R) + π(terpy)

Table S8. Frontier molecular orbital composition (%) in the ground state for complex **6** calculated at the DFT/B3LYP/DEF2-TZVPD/6-31+G* level.

Orbital	Energy [eV]	Contribution (%)					Character
		Re	3CO	Cl	R	terpy	
LUMO+5	-0.77	16.55	25.25	2.86	0.31	55.03	π*(terpy) + d(Re) + π*(CO)
LUMO+4	-0.99	21.71	36.99	8.47	0.20	32.63	d(Re) + π*(CO) + π*(terpy)
LUMO+3	-1.18	22.53	19.23	0.84	2.43	54.98	π*(terpy) + d(Re) + π*(CO)
LUMO+2	-1.49	12.87	4.70	1.81	2.16	78.45	π*(terpy) + d(Re)
LUMO+1	-1.80	3.59	1.80	0.82	10.48	83.31	π*(terpy) + π*(R)
LUMO	-2.51	9.98	3.78	2.79	7.33	76.12	π*(terpy)
HOMO	-5.41	3.87	0.92	0.39	81.84	12.98	π(R) + π(terpy)
HOMO-1	-6.29	43.67	26.86	22.73	0.40	6.34	d(Re) + π(CO) + p(Cl)
HOMO-2	-6.42	41.60	24.49	24.50	2.31	7.09	d(Re) + π(CO) + p(Cl)
HOMO-3	-6.72	54.00	30.89	1.59	0.10	13.42	d(Re) + π(CO)
HOMO-4	-7.02	3.27	2.48	0.11	16.69	77.45	π(terpy) + π(R)
HOMO-5	-7.11	0.86	0.55	0.04	77.52	21.03	π(R) + π(terpy)

Table S9. Frontier molecular orbital composition (%) in the ground state for complexes **2**, **3**, and **6** calculated at the DFT/B3LYP level using different basis sets.

Compound	Basis Set	Orbital	Energy [eV]	Contribution (%)					Character
				Re	3CO	Cl	R	terpy	
2	def2-TZVPD/ 6-31+g*	LUMO	-2.59	13.75	3.43	3.11	5.76	73.95	π*(terpy) + d(Re)
		HOMO	-5.80	1.86	1.23	0.40	84.97	11.54	π(R) + π(terpy)
		HOMO-1	-6.25	44.24	26.70	21.87	0.64	6.54	d(Re) + π(CO) + p(Cl)
	TZVP	LUMO	-2.71	2.68	1.86	0.73	9.87	84.86	π*(terpy)
		HOMO	-6.01	4.34	2.68	0.61	54.16	38.21	π(R) + π(terpy)
		HOMO-1	-6.21	38.06	22.51	11.20	9.20	19.03	d(Re) + π(CO) + p(Cl) + π(terpy)
	def2TZVPD	LUMO	-2.70	7.72	9.57	0.92	6.47	75.32	π*(terpy)
		HOMO	-5.99	4.83	3.05	0.80	72.50	18.83	π(R) + π(terpy)
		HOMO-1	-6.21	49.19	25.13	16.62	2.05	7.02	d(Re) + π(CO) + p(Cl)
				Re	3CO	Cl	R	terpy	
3	def2-TZVPD/ 6-31+g*	LUMO	-2.67	10.92	3.44	2.95	7.96	74.74	π*(terpy) + d(Re)
		HOMO	-6.25	44.13	26.90	21.70	0.57	6.70	d(Re) + π(CO) + p(Cl)
		HOMO-1	-6.38	42.20	24.37	21.69	3.74	7.99	d(Re) + π(CO) + p(Cl)
	TZVP	LUMO	-2.79	2.69	1.84	0.67	8.75	86.05	π*(terpy)
		HOMO	-6.21	43.44	26.56	12.48	1.14	16.38	d(Re) + π(CO) + p(Cl) + π(terpy)
		HOMO-1	-6.34	44.32	19.56	14.93	2.99	18.19	d(Re) + π(CO) + p(Cl) + π(terpy)
	def2TZVPD	LUMO	-2.78	6.28	7.63	0.90	7.66	77.54	π*(terpy)
		HOMO	-6.21	50.39	26.08	16.51	0.37	6.65	d(Re) + π(CO) + p(Cl)
		HOMO-1	-6.34	45.85	23.78	18.64	2.33	9.40	d(Re) + π(CO) + p(Cl)
				Re	3CO	Cl	R	terpy	
6	def2-TZVPD/ 6-31+g*	LUMO	-2.51	9.98	3.78	2.79	7.33	76.12	π*(terpy)
		HOMO	-5.41	3.87	0.92	0.39	81.84	12.98	π(R) + π(terpy)
		HOMO-1	-6.29	43.67	26.86	22.73	0.40	6.34	d(Re) + π(CO) + p(Cl)
	TZVP	LUMO	-2.63	2.06	1.48	0.57	15.09	80.81	π*(terpy) + π*(R)
		HOMO	-5.57	1.72	1.11	0.17	49.49	47.51	π(R) + π(terpy)
		HOMO-1	-6.24	40.40	24.97	11.88	2.63	20.13	d(Re) + π(CO) + p(Cl) + π(terpy)
	def2TZVPD	LUMO	-2.63	8.50	10.66	0.91	12.44	67.50	π*(terpy) + π*(R) + π*(CO)
		HOMO	-5.57	2.05	1.43	0.34	81.33	14.85	π(R) + π(terpy)
		HOMO-1	-6.24	49.71	25.10	16.84	0.49	7.87	d(Re) + π(CO) + p(Cl)

Table S10. Main contributions to frontier molecular orbitals (%) in the ground state for complexes **2**, **3**, and **6** calculated at the DFT/B3LYP/TZ2P level using ADF software with ZORA relativistic approximation and COSMO solvent model.

Compound	MO orbital	Energy [eV]	Main contribution
2	LUMO	-2.82	π^*_{terpy} (91.84%)
	HOMO	-6.08	π_R (81.92%)
	HOMO-1	-6.37	d_{Re} (49.76%) + π_{CO} (20.60%) + p_{Cl} (18.56%)
3	LUMO	-2.88	π^*_{terpy} (80.51%)
	HOMO	-6.36	d_{Re} (50.61%) + π_{CO} (18.06%) + p_{Cl} (18.34%)
	HOMO-1	-6.49	d_{Re} (46.43%) + π_{CO} (18.22%) + p_{Cl} (19.47%)
6	LUMO	-2.74	π^*_{terpy} (86.41%)
	HOMO	-5.63	π_R (83.94%)
	HOMO-1	-6.42	d_{Re} (49.44%) + π_{CO} (20.76%) + p_{Cl} (16.77%)

Table S11. The energies and characters of the selected spin-allowed electronic transitions for **1** calculated with the TDDFT/B3LYP method, together with assignment to the experimental absorption bands.

Experimental absorption λ; nm (10^{-3} ε; $M^{-1}cm^{-1}$)	Calculated transitions				
	Major contribution (%)	Character	E [eV]	λ [nm]	Oscillator strength
383.9 (8.7)	H-1 → L (65%)	MLCT/LLCT	2.93	422.66	*0.0237*
	H → L (41%)	ILCT/IL	3.07	403.65	*0.2998*
	H-2 → L (64%)	MLCT/LLCT/ILCT	3.31	375.02	*0.2051*
	H-3 → L (91%)	MLCT	3.36	369.38	*0.0157*
315.0 (37.9)	H → L+1 (52%)	ILCT	3.70	335.58	*0.0933*
	H-5 → L (64%)	ILCT	3.90	317.63	*0.2001*
	H-2 → L+1 (72%)	MLCT/LLCT	3.95	313.75	*0.2063*
	H-1 → L+2 (30%) H → L+2 (23%)	MLCT/LLCT ILCT	4.02	308.36	*0.0624*
278.6 (28.4)	H-9 → L (25%) H-10 → L (23%) H-3 → L+2 (12%)	IL/LLCT LLCT/IL MLCT	4.39	282.34	*0.1031*
	H-2 → L+2 (26%) H-3 → L+2 (24%) H → L+2 (19%)	MLCT/LLCT/ILCT MLCT ILCT	4.42	280.64	*0.0606*
	H → L+3 (36%) H-5 → L+1 (13%)	ILCT IL/ILCT	4.62	268.67	*0.3036*
	H-11 → L (29%) H-5 → L+1 (21%)	LLCT/ILCT/IL IL/ILCT	4.65	266.58	*0.0775*
	H-11 → L (33%) H-5 → L+1 (12%)	LLCT/ILCT/IL IL/ILCT	4.72	262.64	*0.1188*
191.49 (126.9)	H-15 → L+1 (14%) H-14 → L+1 (14%)	IL IL/ILCT	6.22	199.42	*0.0531*
	H → L+14 (15%) H-2 → L+15 (11%)	LMCT/ILCT d-d/LLCT/ILCT	6.31	196.57	*0.0557*
	H-6 → L+7 (26%) H-6 → L+10 (19%)	IL/ILCT IL	6.34	195.68	*0.0405*
	H-10 → L+6 (17%)	LLCT/IL	6.36	195.01	*0.0411*
	H-5 →L+9 (11%)	LLCT/IL	6.39	194.14	*0.0489*
	H-7 → L+7 (45%)	LLCT/ILCT/IL	6.46	191.86	*0.0446*

ε – molar absorption coefficient; H – highest occupied molecular orbital; L – lowest unoccupied molecular orbital

Table S12. The energies and characters of the selected spin-allowed electronic transitions for **2** calculated with the TDDFT/B3LYP method, together with assignment to the experimental absorption bands.

Experimental absorption λ; nm (10^{-3} ε; $M^{-1}cm^{-1}$)	Calculated transitions				
	Major contribution (%)	Character	E [eV]	λ [nm]	Oscillator strength
374.0 (42.3)	H → L (97%)	ILCT/IL	2.74	453.34	*0.1923*
	H-2 → L (97%)	MLCT/LLCT	3.14	395.29	*0.0391*
	H → L+1 (98%)	ILCT	3.38	366.88	*0.1729*
306.0 (90.7)	H-5 → L (57%)	IL	3.95	314.02	*0.1443*
	H-1 → L+2 (57%)	MLCT/LLCT	4.04	307.31	*0.1263*
	H → L+3 (57%)	ILCT	4.10	302.80	*0.0805*
230.7 (184)	H-5 → L+1 (36%) H-7 → L+1 (17%)	IL/ILCT IL/ILCT	4.75	261.19	*0.1144*
	H-8 → L+1 (34%) H-7 → L+1 (12%)	IL/LLCT/ILCT IL/ILCT	5.09	243.74	*0.0765*
	H-12 → L (47%)	LLCT/ILCT/IL	5.19	239.05	*0.0688*
	H-13 → L (34%) H-4 → L+3 (27%)	LLCT/ILCT/IL ILCT/IL	5.38	230.64	*0.1315*
	H-5 → L+5 (18%) H-7 → L+2 (17%)	LMCT/IL IL	5.50	225.56	*0.0991*
206.35 (235.1)	H-10 → L+3 (15%) H-4 → L+7 (12%)	LLCT/IL/ILCT IL/ILCT	6.13	202.22	*0.0692*
	H-11 → L+2 (18%) H-7 → L+8 (12%)	IL IL/ILCT	6.22	199.27	*0.0960*
	H → L+14 (14%) H-14 → L+1 (13%) H-6 → L+7 (13%)	LMCT/ILCT IL/ILCT IL/ILCT	6.26	198.05	*0.0788*
	H-12 → L+2 (44%) H-11 → L+2 (25%)	LLCT/ILCT IL	6.27	197.80	*0.0817*

ε – molar absorption coefficient; H – highest occupied molecular orbital; L – lowest unoccupied molecular orbital

Table S13. The energies and characters of the selected spin-allowed electronic transitions for **3** calculated with the TDDFT/B3LYP method, together with assignment to the experimental absorption bands.

Experimental absorption λ; nm (10^{-3} ε; $M^{-1}cm^{-1}$)	Calculated transitions				
	Major contribution (%)	Character	E [eV]	λ [nm]	Oscillator strength
385.4 (3.3)	H-1 → L (98%)	MLCT/LLCT	3.05	406.77	*0.1248*
	H-3 → L (80%)	ILCT	3.79	327.31	*0.3658*
284.9 (19.6)	H → L+2 (57%)	MLCT/LLCT	4.01	309.38	*0.1121*
	H-2 → L+2 (54%)	MLCT	4.40	281.81	*0.0643*
	H-3 → L+1 (63%)	ILCT	4.42	280.68	*0.2227*
	H-9 → L (68%)	LLCT/IL	4.49	275.98	*0.0661*
264.0 (18.2)	H-4 → L+1 (58%)	IL/ILCT	4.72	262.49	*0.1216*
	H-2 → L+4 (28%) H-2 → L+3 (18%)	MLCT MLCT	4.76	260.39	*0.0763*
196.6 (178.2)	H-3 → L+6 (56%)	ILCT	5.75	215.48	*0.0517*
	H-17 → L (23%) H-15 → L (16%) H-11 → L+1 (13%)	IL/ILCT IL/ILCT/LLCT LLCT/ILCT	5.92	209.60	*0.0535*
	H-12 → L+1 (24%) H-3 → L+8 (23%)	IL/ILCT ILCT	6.24	198.80	*0.0444*
	H-11 → L+2 (59%)	LLCT	6.29	197.21	*0.0564*
	H-5 → L+6 (32%) H-6 → L+7 (23%)	ILCT ILCT/IL	6.43	192.99	*0.0441*
	H-18 → L (15%) H-16 → L+1 (13%) H-9 → L+6 (11%)	ILCT/IL IL LLCT/IL/ILCT	6.46	191.90	*0.0453*

ε – molar absorption coefficient; H – highest occupied molecular orbital; L – lowest unoccupied molecular orbital

Table S14. The energies and characters of the selected spin-allowed electronic transitions for **4** calculated with the TDDFT/B3LYP method, together with assignment to the experimental absorption bands.

Experimental absorption λ; nm (10^{-3} ε; $M^{-1}cm^{-1}$)	Calculated transitions				
	Major contribution (%)	Character	E [eV]	λ [nm]	Oscillator strength
385.4 (5.4)	H-1 → L (98%)	MLCT/LLCT	3.04	407.28	*0.1295*
	H-3 → L (70%)	ILCT	3.74	331.34	*0.2269*
	H-1 → L+1 (75%)	MLCT/LLCT	3.76	329.85	*0.1538*
294.5 (32.5)	H-4 → L (59%)	IL	3.91	317.10	*0.1073*
	H → L+2 (59%)	MLCT/LLCT	4.01	309.56	*0.1078*
	H-3 → L+1 (60%)	ILCT	4.38	283.40	*0.2062*
264.7 (30.8)	H-9 → L (69%)	LLCT/IL	4.48	276.70	*0.0597*
	H-4 → L+1 (68%)	IL/ILCT	4.72	262.74	*0.1510*
	H-2 → L+4 (28%) H-2 → L+3 (18%)	MLCT MLCT	4.76	260.46	*0.0742*
194.5 (71.8)	H-15 → L (19%) H-12 → L+1 (13%)	IL/ILCT LLCT	5.91	209.97	*0.0578*
	H-13 → L+1 (53%)	ILCT/LLCT/IL	6.07	204.12	*0.0528*
	H-5 → L+5 (70%)	LMCT/ILCT	6.28	197.59	*0.0403*
	H-6 → L+7 (23%) H-1 → L+16 (10%)	ILCT d-d/LLCT/MLCT	6.44	192.59	*0.0747*
	H-9 → L+6 (22%) H-4 → L+10 (15%) H-10 → L+3 (11%)	LLCT/IL LMCT/IL IL	6.47	191.80	*0.0430*

ε – molar absorption coefficient; H – highest occupied molecular orbital; L – lowest unoccupied molecular orbital

Table S15. The energies and characters of the selected spin-allowed electronic transitions for **5** calculated with the TDDFT/B3LYP method, together with assignment to the experimental absorption bands.

Experimental absorption λ; nm (10^{-3} ε; $M^{-1}cm^{-1}$	Calculated transitions				
	Major contribution (%)	Character	E [eV]	λ [nm]	Oscillator strength
383.2 (9.5)	H-1 → L (98%)	MLCT/LLCT	3.04	408.34	*0.1044*
300.5 (46.5)	H-4 → L (63%)	ILCT	3.88	319.63	*0.2750*
	H-3 → L (68%)	ILCT/IL	3.94	314.37	*0.0948*
	H → L+2 (51%)	MLCT/LLCT	4.01	309.23	*0.1209*
	H-8 → L (53%)	LLCT	4.38	283.09	*0.0535*
260.1 (60.9)	H-3 → L+1 (56%)	ILCT	4.55	272.55	*0.1689*
	H-3 → L+1 (23%) H → L+3 (14%) H-9 → L (12%)	ILCT MLCT/LLCT LLCT	4.56	271.68	*0.1958*
	H-2 → L+4 (31%) H-2 → L+3 (17%)	MLCT MLCT	4.77	260.23	*0.0851*
197.4 (125.8)	H-4 → L+7 (36%) H-5 → L+3 (15%)	IL/ILCT ILCT/IL	5.94	208.89	*0.0514*
	H-13 → L+1 (36%) H-11 → L+2 (14%)	IL/ILCT LLCT	6.28	197.37	*0.0659*
	H-5 → L+6 (26%) H-3 → L+8 (21%) H-5 → L+5 (16%)	IL ILCT/LMCT LMCT	6.36	194.94	*0.0647*
	H-3 → L+9 (23%)	ILCT/LMCT	6.49	191.15	*0.0803*

ε – molar absorption coefficient; H – highest occupied molecular orbital; L – lowest unoccupied molecular orbital

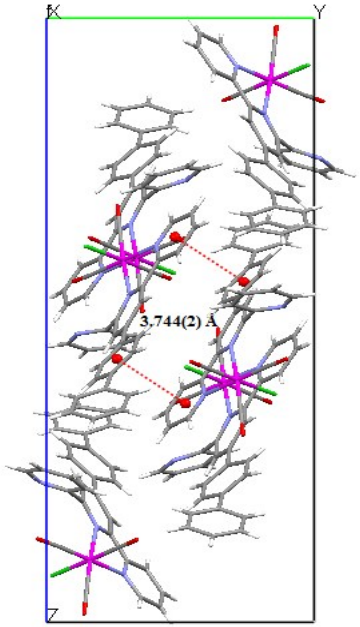
Table S16. The energies and characters of the selected spin-allowed electronic transitions for **6** calculated with the TDDFT/B3LYP method, together with assignment to the experimental absorption bands

Experimental absorption λ; nm (10^{-3} ε; $M^{-1}cm^{-1}$	Calculated transitions				
	Major contribution (%)	Character	E [eV]	λ [nm]	Oscillator strength
419.2 (16.5)	H → L (98%)	ILCT	2.54	487.62	*0.3663*
	H-1 → L (98%)	MLCT/LLCT	3.04	407.41	*0.0123*
	H → L+1 (96%)	ILCT	3.15	393.40	*0.3388*
354.1 (9.3)	H → L+2 (98%)	ILCT	3.53	351.70	*0.0739*
308.7 (14.2)	H → L+3 (89%)	ILCT/LMCT	3.83	323.46	*0.0907*
	H-4 → L (59%)	IL/ILCT	3.93	315.86	*0.1122*
	H-2 → L+1 (69%)	MLCT/LLCT	3.98	311.94	*0.0754*
	H-5 → L (42%) H-1 → L+2 (27%)	ILCT/IL MLCT/LLCT	4.07	304.86	*0.1067*
246.2 (17.7)	H-4 → L+1 (56%)	IL	4.73	262.08	*0.1767*
	H-11 → L (31%) H-3 → L+5 (13%) H-6 → L+1 (11%)	IL MLCT IL/LLCT/ILCT	5.13	241.81	*0.0792*
	H-10 → L+1 (13%) H-4 → L+5 (12%) H-1 → L+11 (10%)	LLCT/ILCT IL/ILCT d-d/LMCT	5.54	223.89	*0.0788*
192.2 (178.2)	H-4 → L+9 (23%) H-13 → L+1 (17%)	LMCT/IL/ILCT IL/ILCT	6.33	195.77	*0.0707*
	H-9 → L+6 (38%) H-11 → L+3 (16%)	LLCT/IL IL/LMCT	6.45	192.28	*0.0639*
	H-4 → L+9 (31%) H-13 → L+1 (14%) H-9 → L+6 (13%)	LMCT/IL/ILCT IL/ILCT LLCT/IL	6.47	191.69	*0.1285*

ε – molar absorption coefficient; H – highest occupied molecular orbital; L – lowest unoccupied molecular orbital

Table S17. The energies and characters of the of two lowest vertical electronic transitions for **6** complex obtained in TDDFT calculations with using different functionals.[a]

Solvent	State	E [eV]	λ [nm]	*f*	Character	
B3LYP						
ACN	S_1	2.54	487.62	0.3663	H → L	IL/ILCT
	S_2	3.04	407.42	0.0123	H-1 → L	MLCT
$CHCl_3$	S_1	2.58	481.02	0.3558	H → L	IL/ILCT
	S_2	2.86	433.58	0.0203	H-1 → L	MLCT
BP86						
ACN	S_1	1.80	688.30	0.1849	H → L	IL/ILCT
	S_2	2.36	524.72	0.1474	H → L+1	IL/ILCT
$CHCl_3$	S_1	1.84	673.14	0.1816	H → L	IL/ILCT
	S_2	2.19	566.45	0.0066	H-1 → L	MLCT
ωB97						
ACN	S_1	4.08	303.61	0.9425	H → L	IL/ILCT
	S_2	4.16	297.73	0.1424	H-1 → L H-1 → L+4	MLCT
$CHCl_3$	S_1	4.09	303.46	0.5399	H → L H-1 → L	IL/ILCT/MLCT
	S_2	4.13	299.94	0.4316	H-1 → L H → L	MLCT/IL/ILCT
ωB97x						
ACN	S_1	3.96	313.42	0.9364	H → L	IL/ILCT
	S_2	4.08	304.15	0.1124	H-1 → L	MLCT
$CHCl_3$	S_1	3.95	313.86	0.5395	H → L H-1 → L	IL/ILCT/MLCT
	S_2	4.01	308.93	0.3754	H-1 → L H → L	MLCT/IL/ILCT
CAM-B3LYP						
ACN	S_1	3.50	354.43	0.7935	H → L	IL/ILCT
	S_2	3.74	331.72	0.0702	H-1 → L	MLCT
$CHCl_3$	S_1	3.50	354.11	0.5606	H → L	IL/ILCT
	S_2	3.61	343.79	0.2192	H-1 → L	MLCT
LC-BLYP						
ACN	S_1	4.14	299.50	0.9031	H → L	IL/ILCT
	S_2	4.24	292.69	0.2125	H-1 → L H-1 → L+4	MLCT
$CHCl_3$	S_1	4.14	299.67	0.5605	H → L H-1 → L	IL/ILCT/MLCT
	S_2	4.21	294.65	0.4475	H-1 → L H → L	MLCT/IL/ILCT



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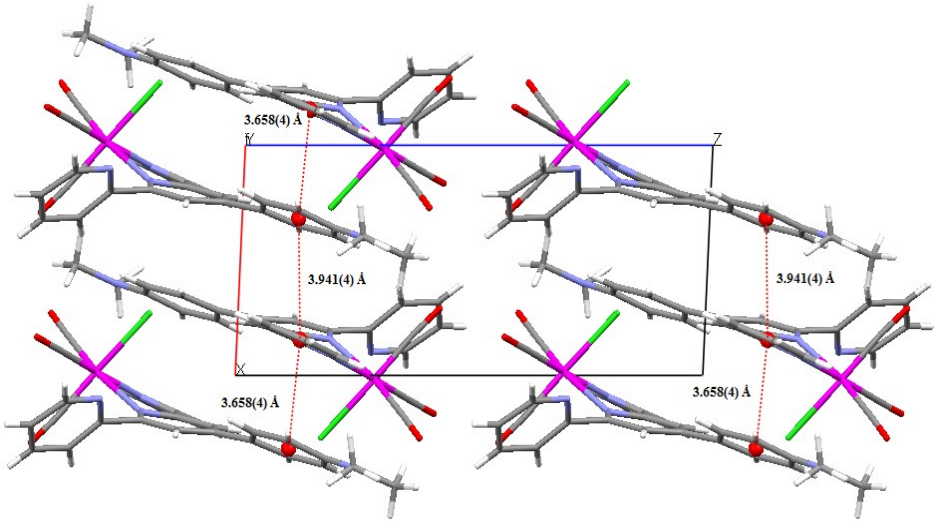


6

Figure S1. A view of the crystal packing showing intermolecular π–π stacking interactions for **1** and **6.**

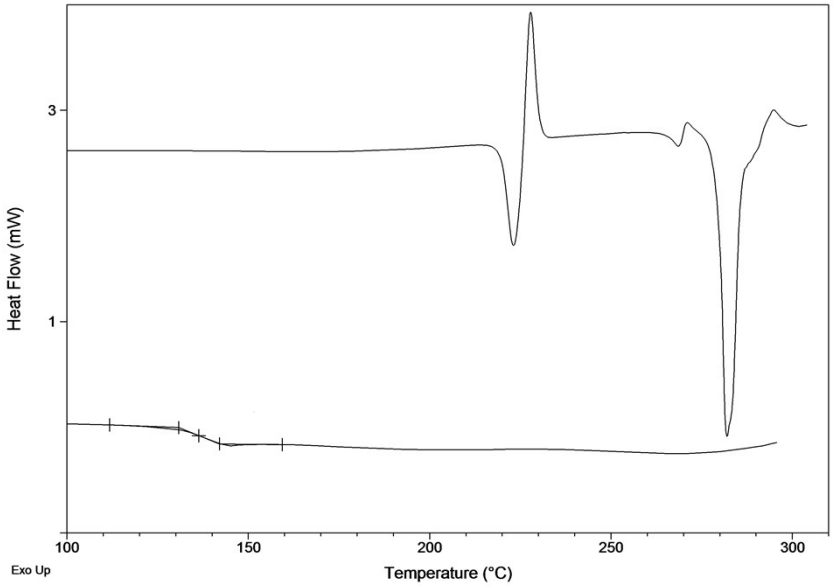


Figure S2. DSC thermograms of compound **2**. T_c: crystallization temperature; T_m melting point temperature; T_g glass transition temperature.

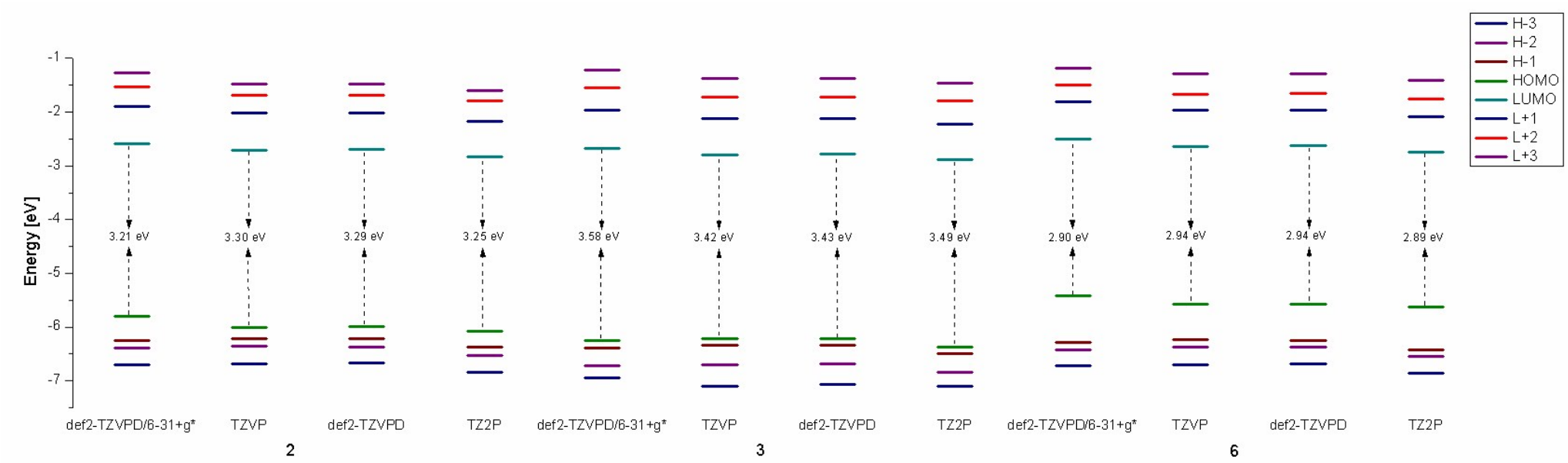
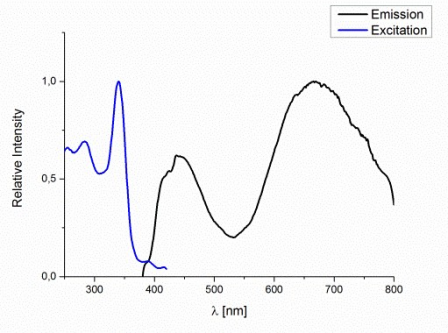
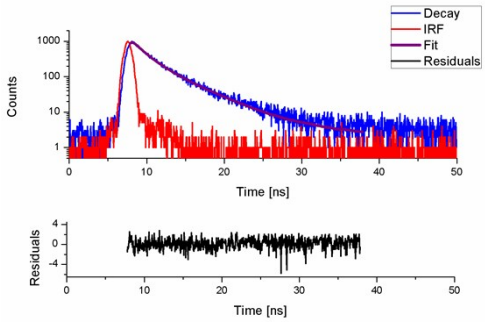
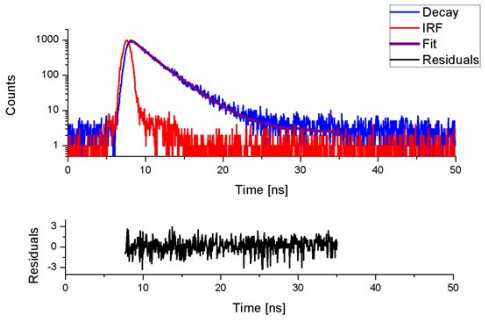
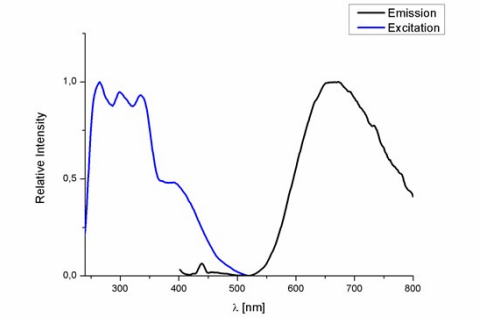
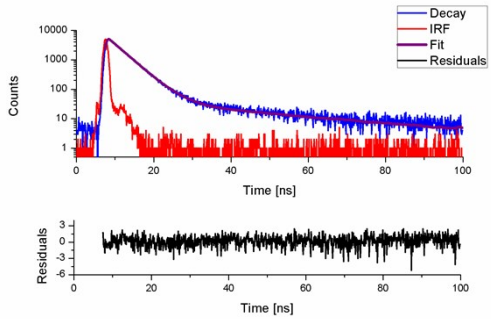
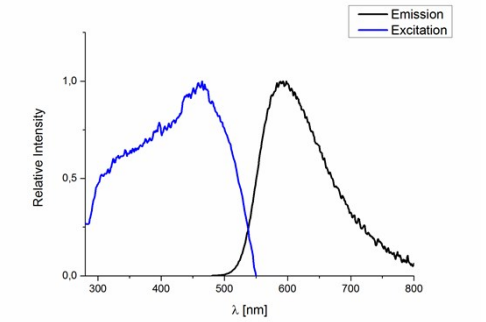
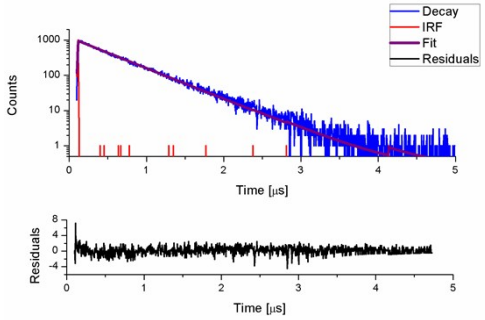
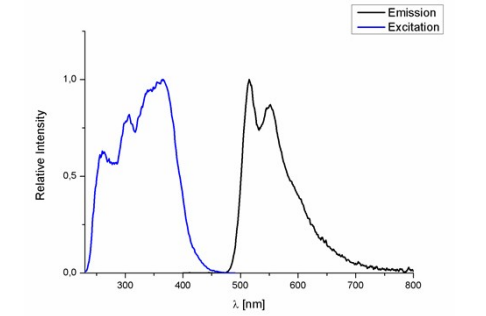
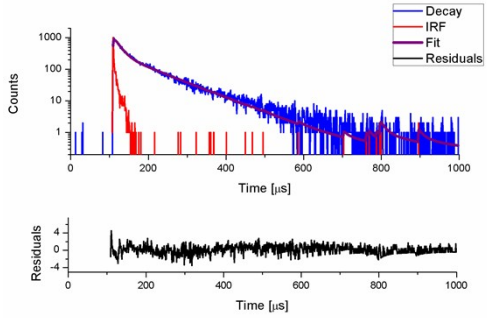


Figure S3. Molecular orbital energy level graph of complexes **2**, **3** and **6** at the DFT/B3LYP level using different basis sets.

Complex	Excitation and emission	Lifetime
	1	
MeCN		λ=442 nm  λ=671 nm 
$CHCl_3$		
solid		
77K		
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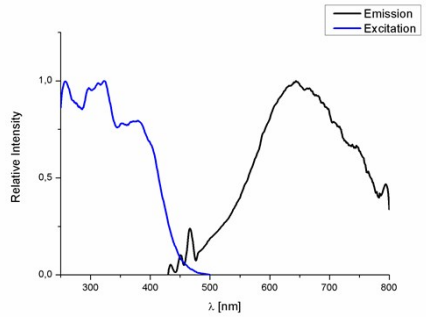
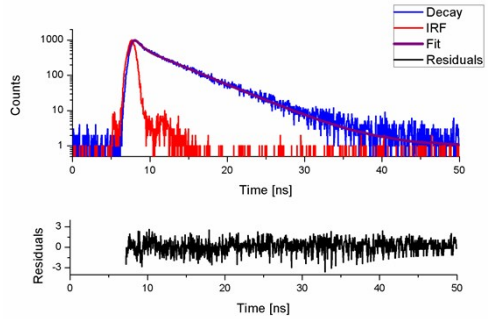
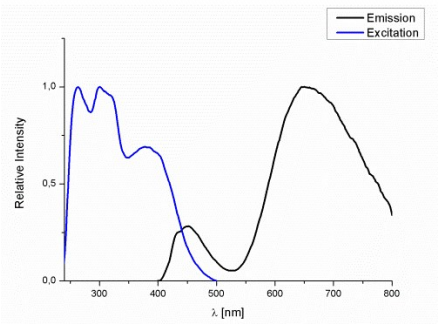
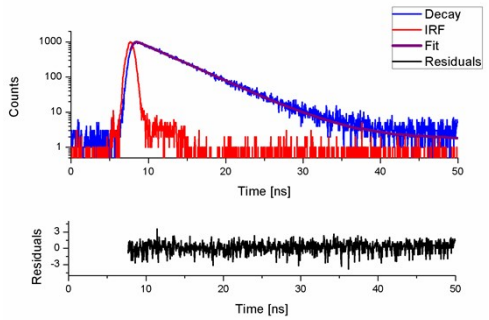
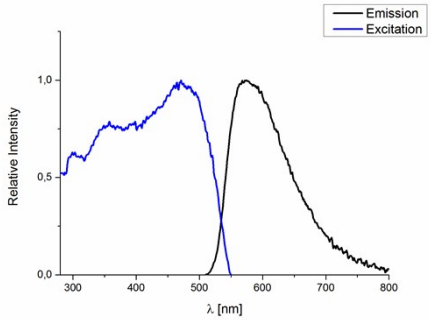
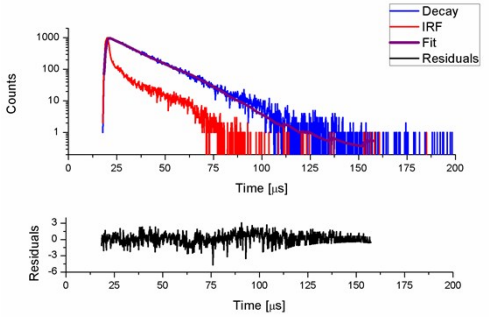
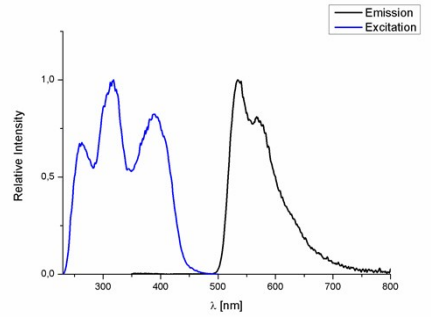
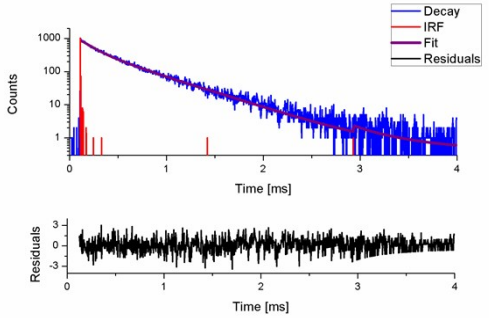
MeCN		
$CHCl_3$		
solid		
77K		
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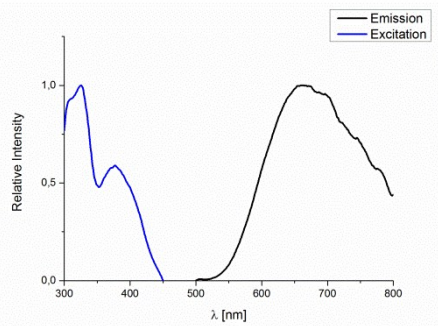
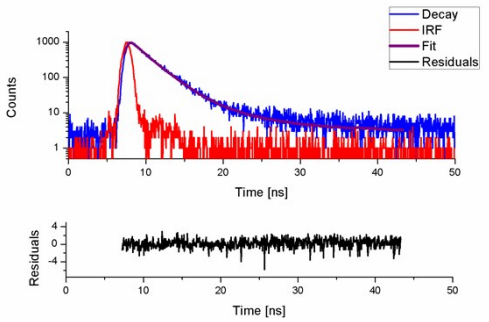
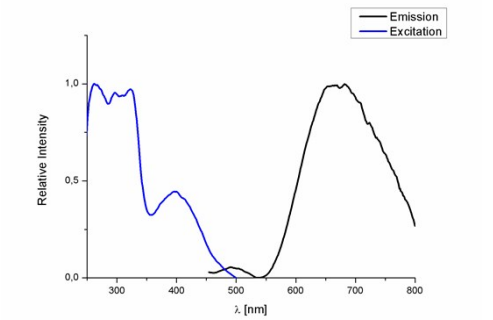
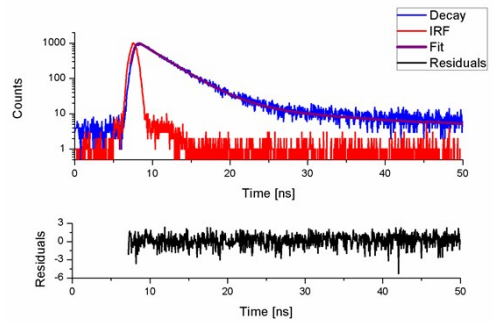
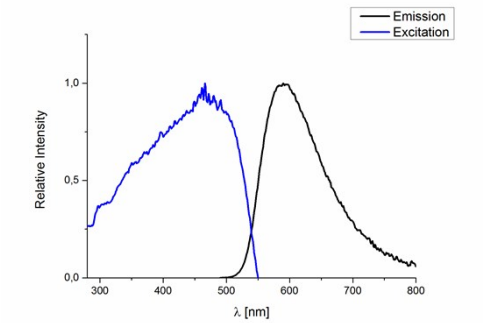
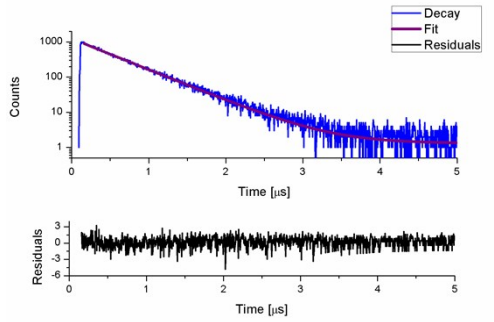
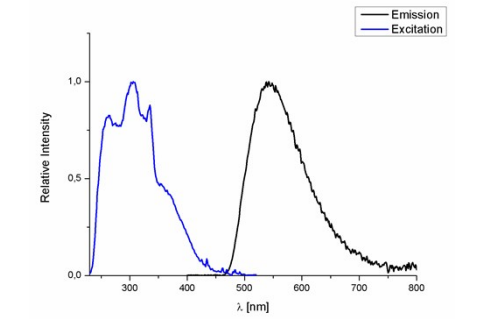
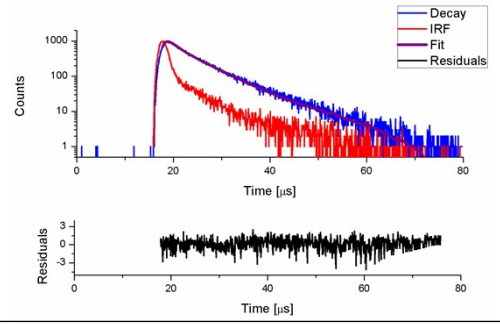
MeCN		

$CHCl_3$		
solid		
77K		
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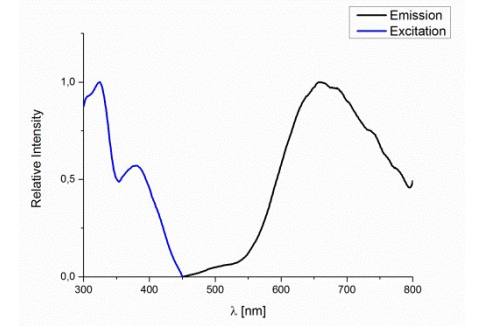
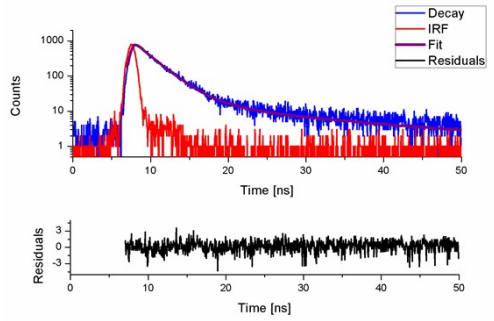
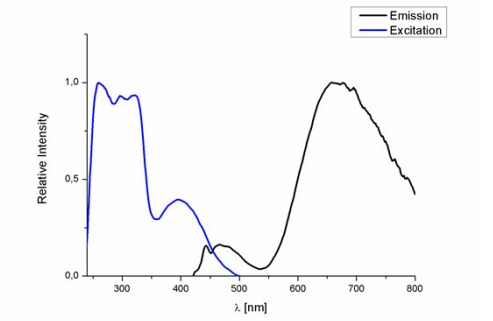
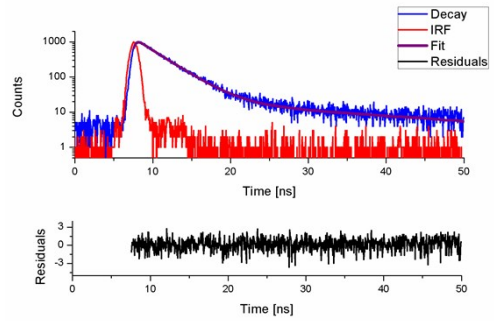
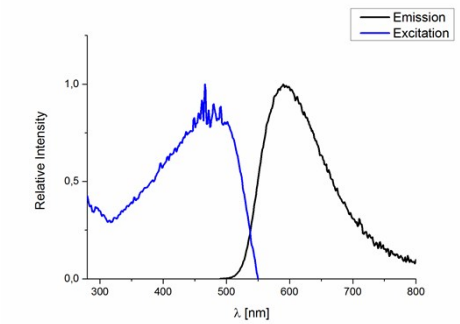
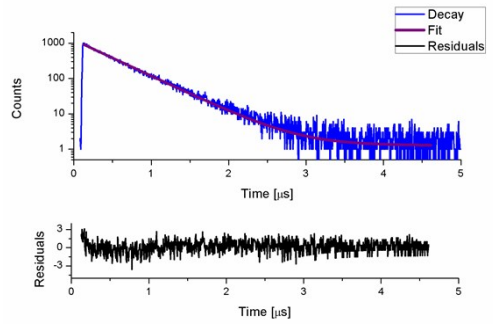
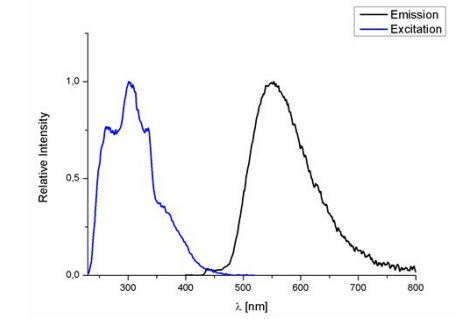
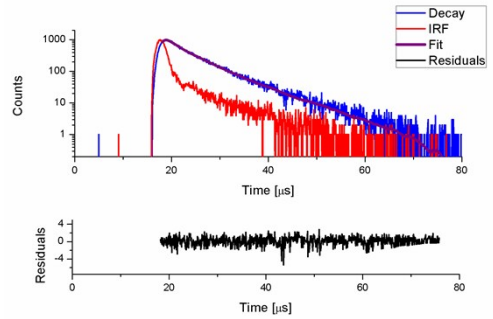
MeCN		
$CHCl_3$		

Solid		
77K		
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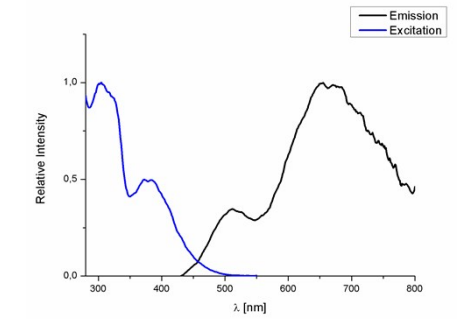
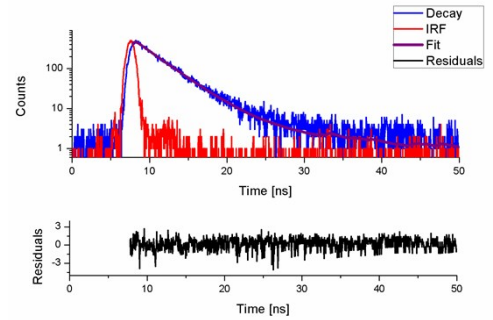
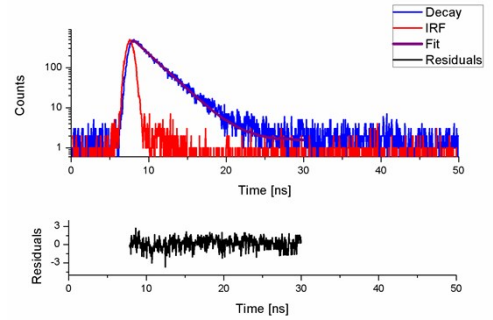
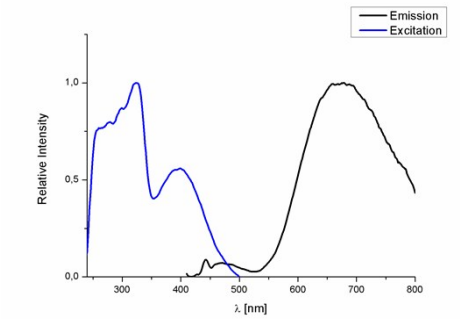
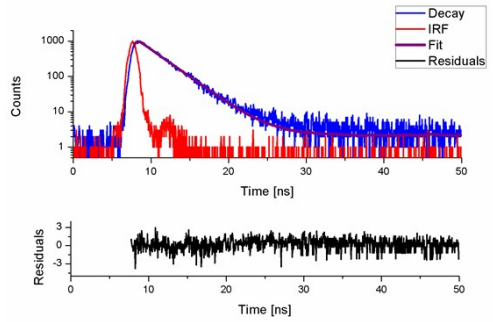
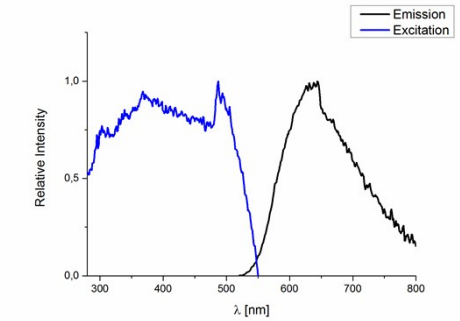
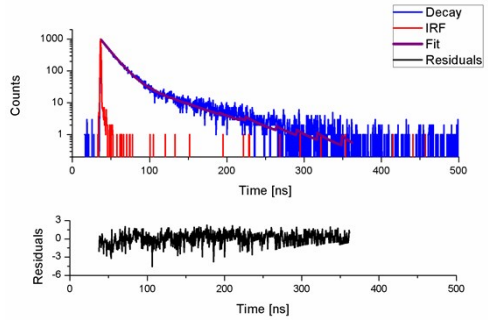
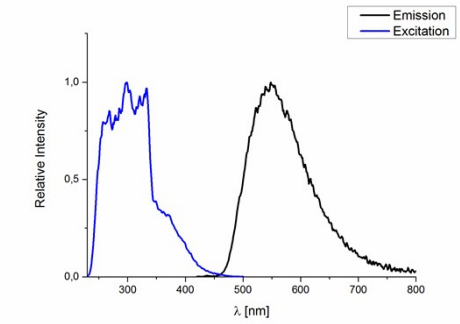
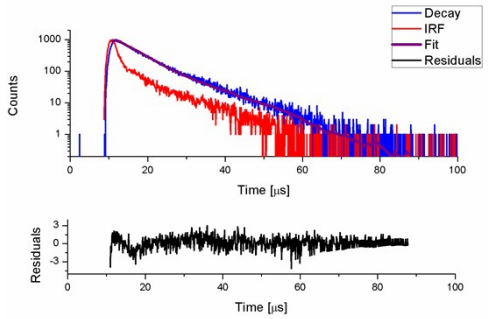
MeCN		λ=516 nm  λ=666 nm 
$CHCl_3$		

solid		
77K		
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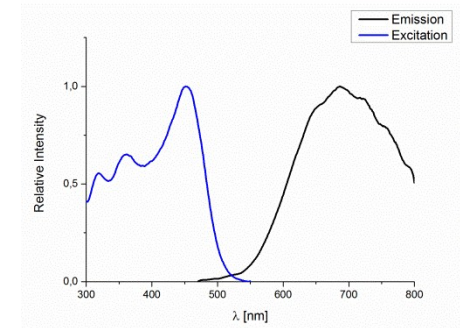
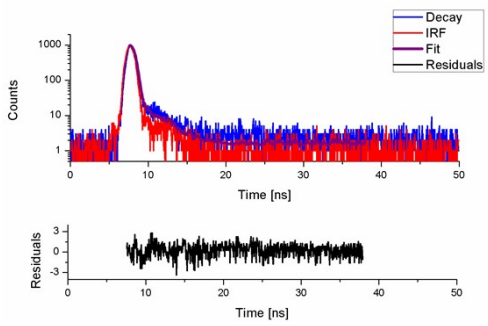
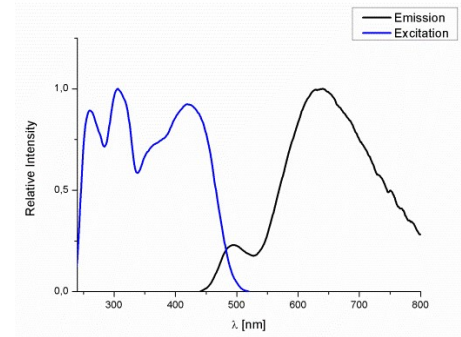
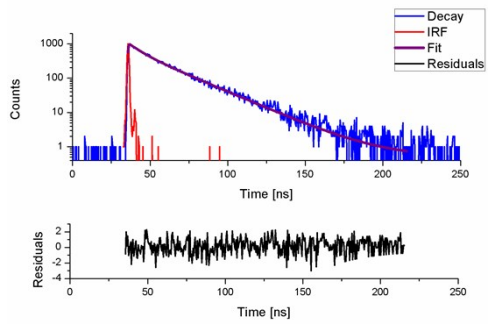
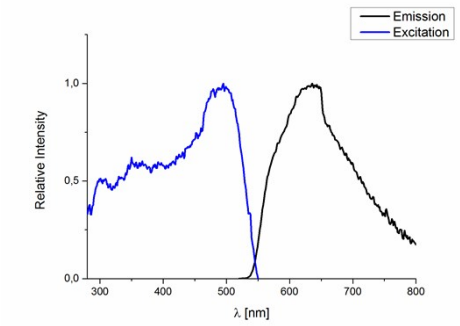
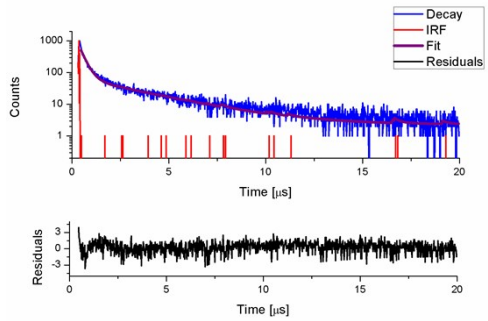
MeCN		
$CHCl_3$		
Solid		

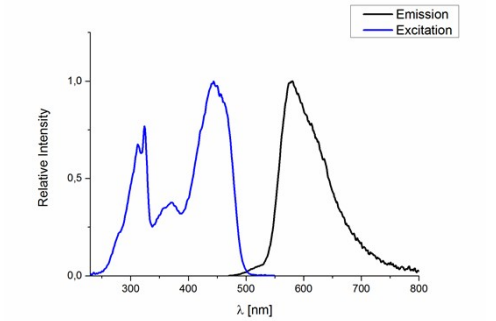
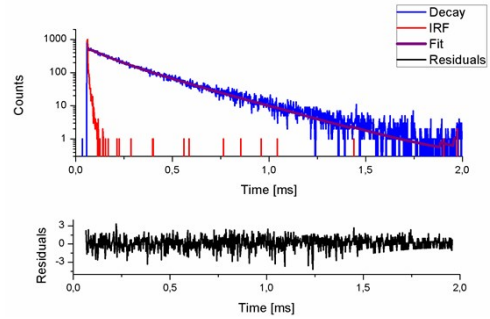
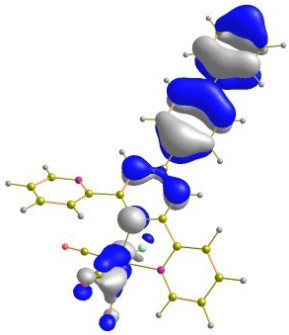
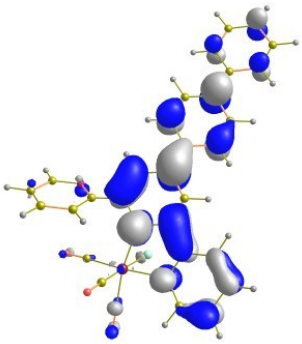
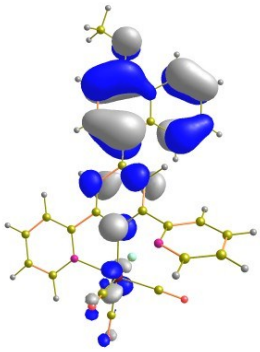
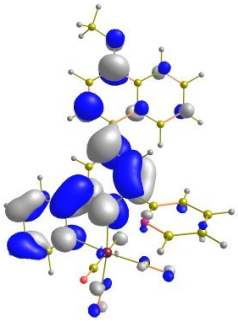
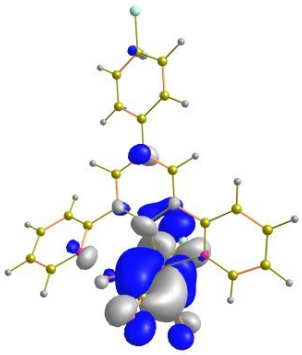
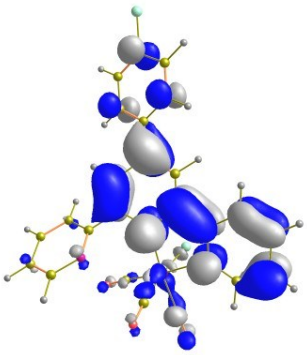
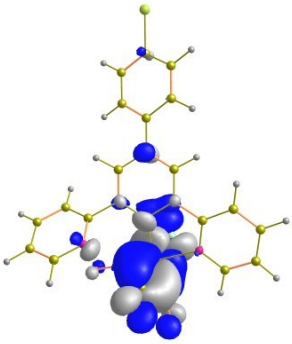
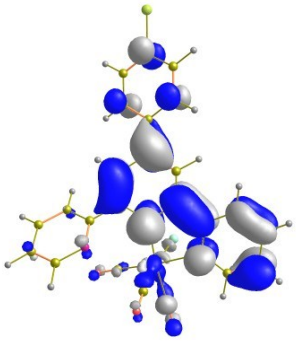
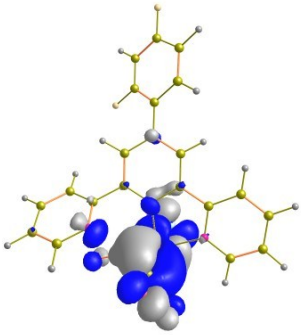
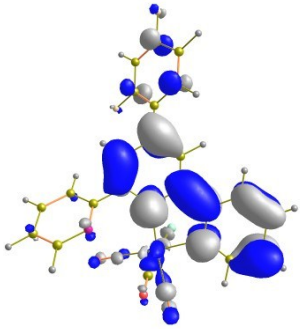
77K		

Figure S4 Excitation and emission spectra together with PL lifetime curves for **1-6** in $CHCl_3$, MeCN, low-temperature MeOH:EtOH glass matrix and in solid state.

Compound	**HSOMO**	**LSOMO**
1		
2		
3		
4		
5		

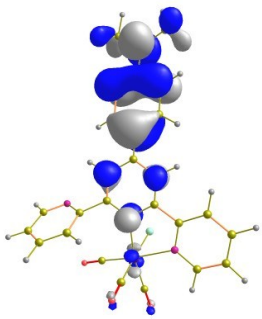
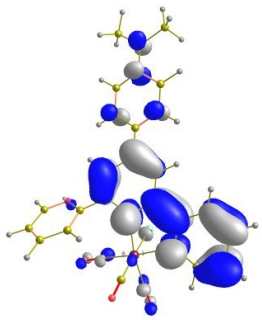
6		

Figure S5. Isodensity surface plots of the HSOMO and LSOMO for the complexes **1**–**6** at their T_1 state geometry calculated in MeCN medium at the TD-DFT/DFT/B3LYP level associated with the PCM model. Blue and grey colours show regions of positive and negative spin density values, respectively.

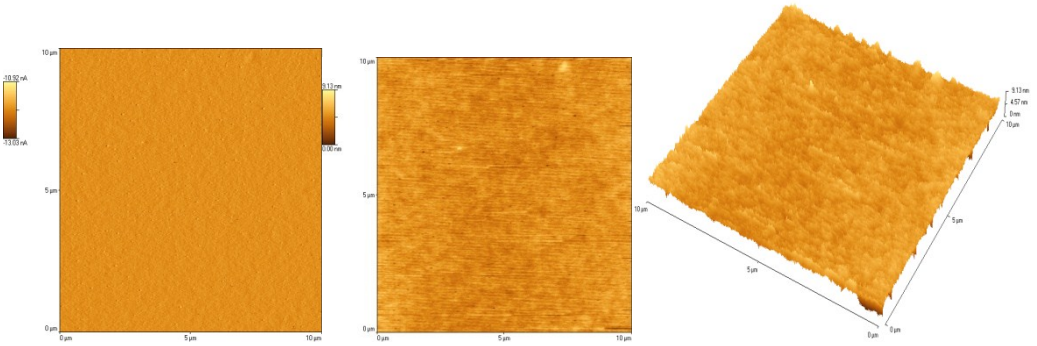


Figure S6. AFM images (10 µm x 10 µm) of the blend PVK with compound **3**