

ELECTRONIC SUPPLEMENTARY MATERIAL

Push-pull effect – how to effectively control photoinduced intramolecular charge transfer processes in rhenium(I) chromophores with ligands of D–A or D– π –A structure

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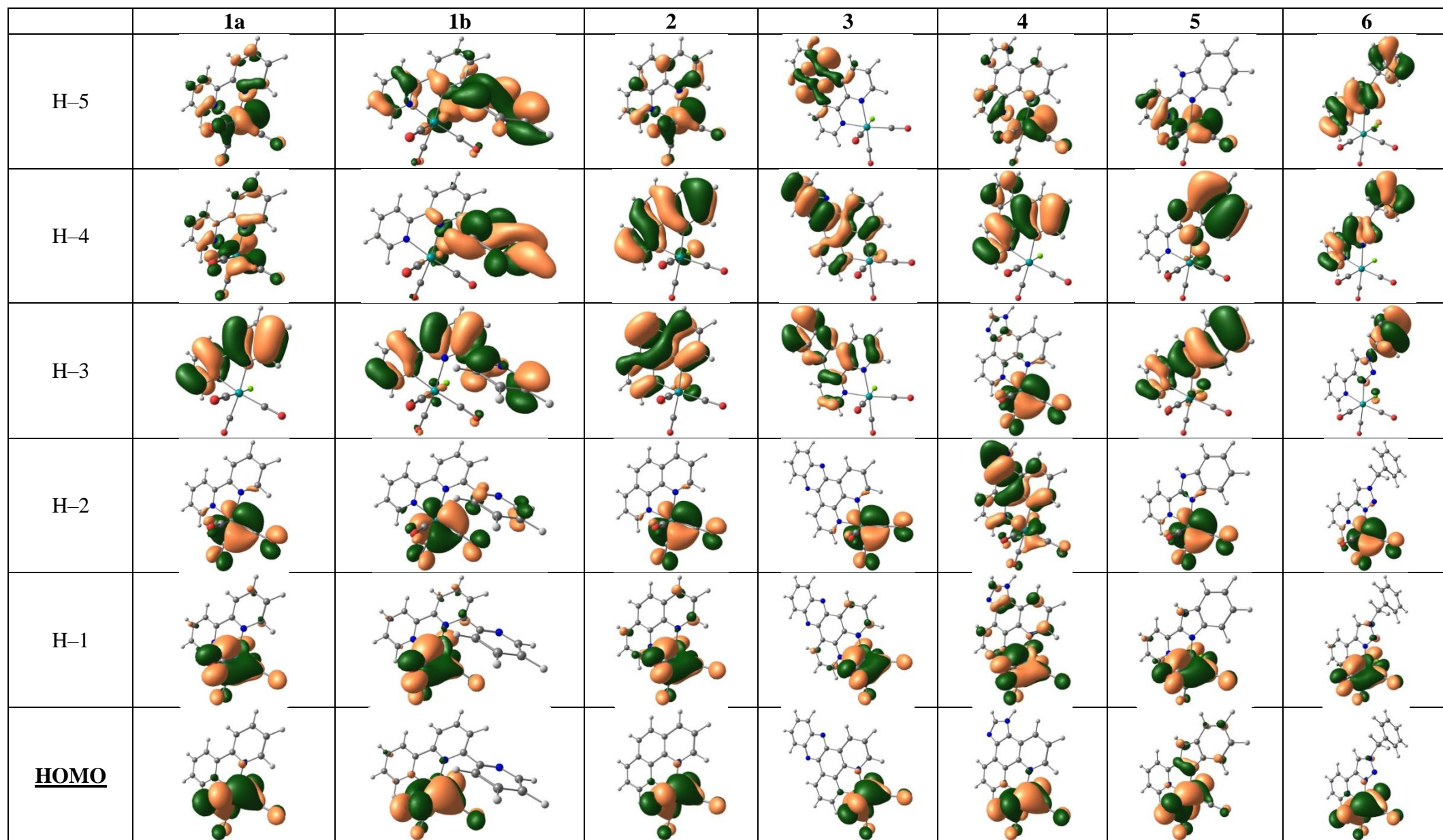
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Computational Details

Theoretical DFT and TD-DFT calculations of **1–6** have been performed using the GAUSSIAN-16 (C.01) program package¹ with the PBE1PBE hybrid exchange-correlation functional^{2,3}, and the def2-TZVPD basis set for rhenium and def2-TZVP basis set for other elements⁴⁻⁶. For all compounds, X-ray structural parameters were used as a starting point for the singlet ground-state optimization. After optimization of the singlet geometry, vibrational frequencies were calculated to verify the minimum on the potential energy surface. All the further calculations were obtained based on the optimized geometries. Absorption properties were calculated by the TD-DFT method. In all calculations, the polarizable continuum model (PCM) correction was used to simulate the acetonitrile solvent environment for all calculations⁷⁻⁹. The calculations have been carried out using resources provided by Wroclaw Centre for Networking and Supercomputing (<http://wcss.pl>).



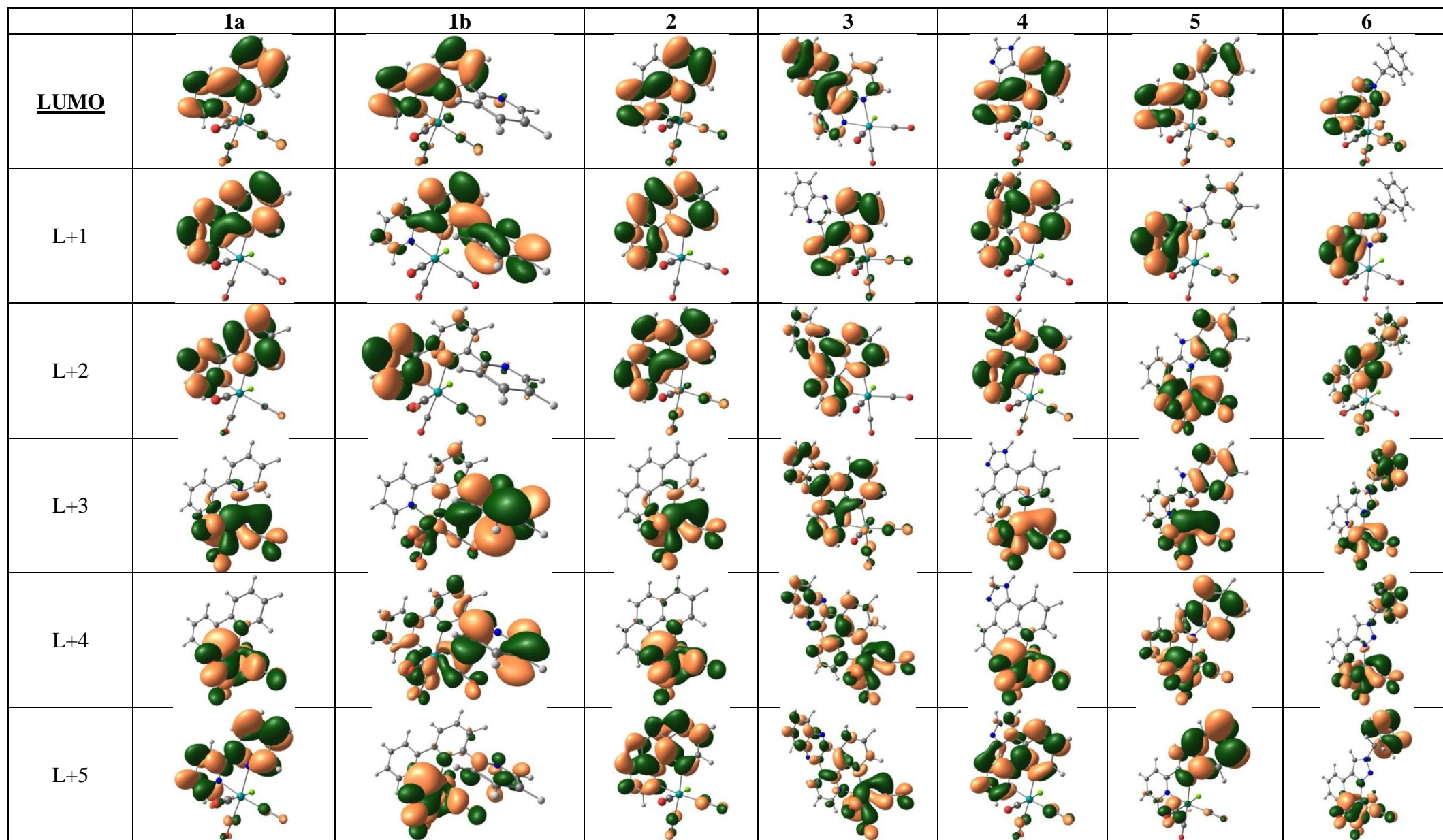
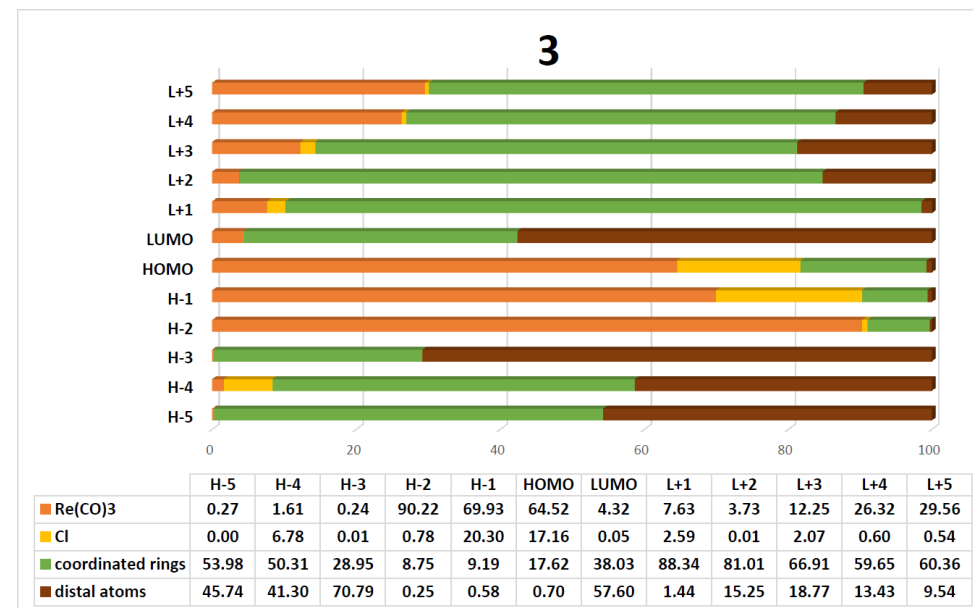
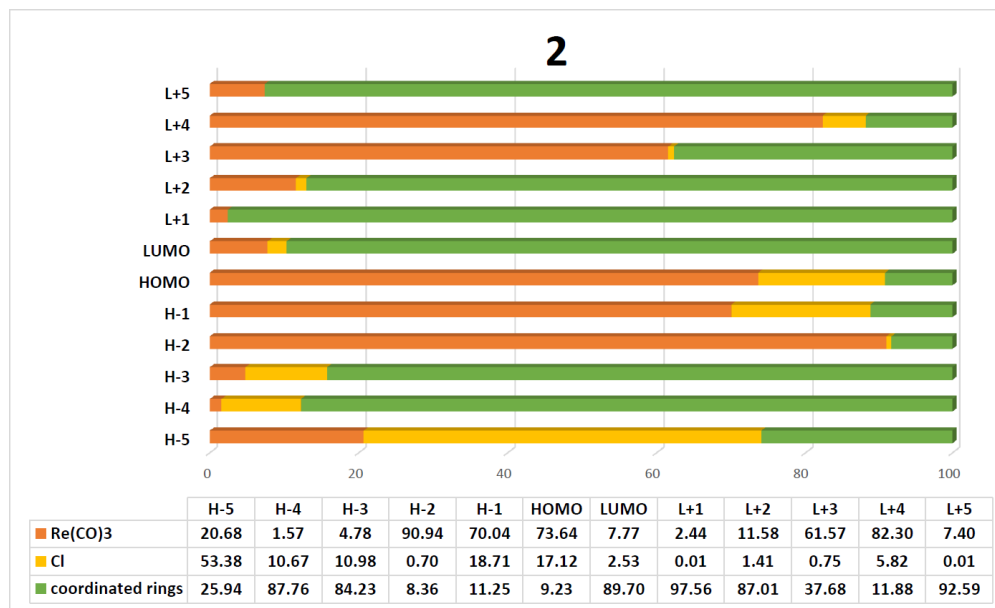
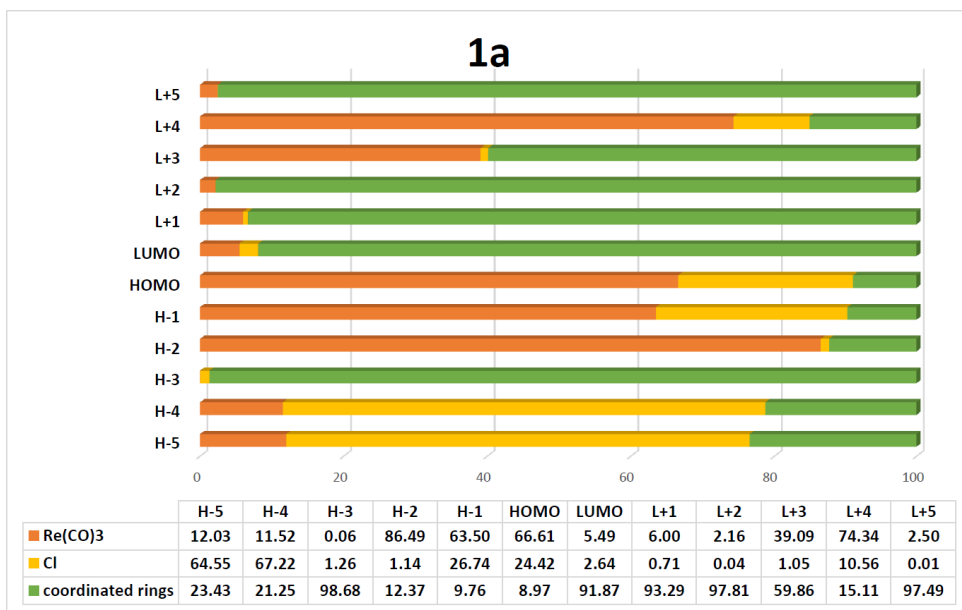


Figure S1. Electron density plots of the frontier molecular orbitals for complexes **1–6**. Calculated with the Gaussian-16 software (PBE1PBE/def2-TZVPD/def2-TZVP/PCM/acetonitrile).



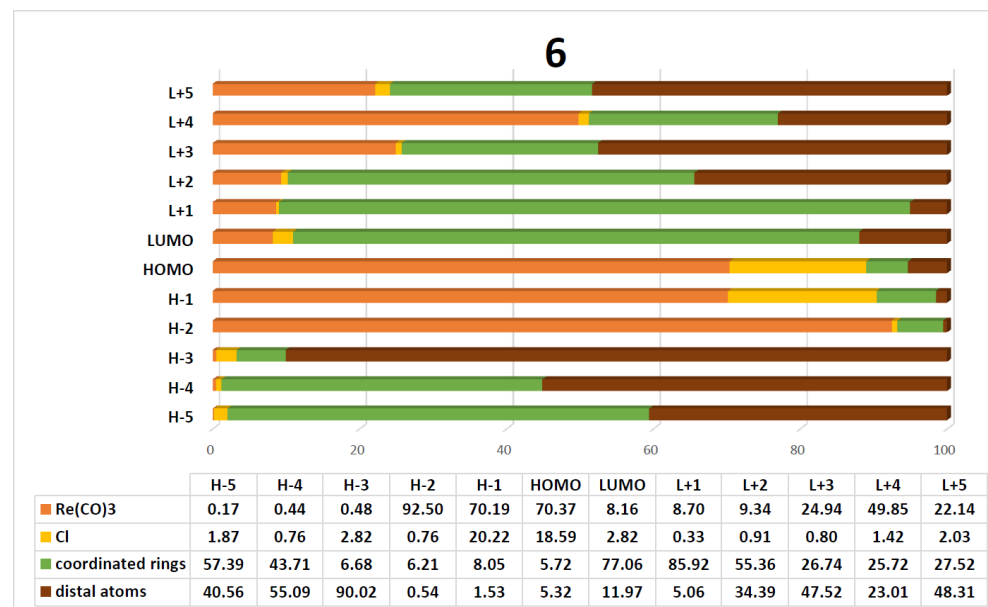
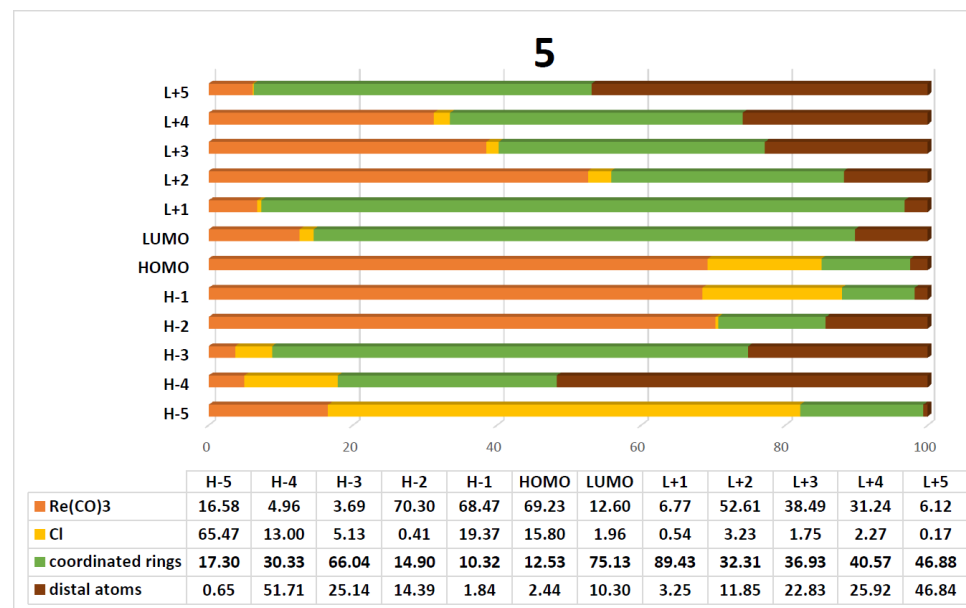


Figure S2. Percentage contribution of selected molecular fragments to the frontier molecular orbitals for complexes **1–6**. Calculated with the Gaussian-16 software (PBE1PBE/def2-TZVPD/def2-TZVP/PCM/acetonitrile).

Table S1. The relevant electrochemical data of 1–6.

[ReCl(CO)₃(bipy)] (1a)			
medium^a	E_{red}, peak [V] (ΔE [mV]) or E_{1/2red}	E_{ox}, peak [V] or E_{1/2ox}	Ref.
MeCN 0.1 M TBAP	E _{1/2} = -1.41	+1.35	10
MeCN 0.1 M TBATFB	E _{1/2} = -1.32	E _{1/2} = +1.36	11
MeCN 0.1 M TBAPF ₆	E _{1/2} = -1.35	E _{1/2} = +1.38	12
MeCN 0.1 M TBAP	E _{1/2} = -1.34	+1.33irr	13
MeCN 0.2 M TBATFB	-1.35irr	+1.32irr	14
THF 0.1 M TBAPF ₆	-1.91 (110), -2.38	-	15
DMF 0.1 M TBAPF ₆	-1.83 / E _{1/2} = -1.21	+1.55	16
DMF 0.1 M TBAP	E _{1/2} = -1.74 (70), -2.20	-	17
MeCN 0.05 M TEATFB -54 °C	E _{1/2} = -1.30, -1.95	E _{1/2} = +1.39	18
DMF 0.05 M TEATFB -54 °C	E _{1/2} = -1.38	E _{1/2} = +1.40	19
DMA 0.1 M TBAPF ₆	-1.77, -2.42irr	-	20
DMF 0.1 M TBAPF ₆	E _{1/2} = -1.13	-	21
MeCN 0.1 M TBAPF ₆	-	+1.41 / E _{1/2} = +1.82	22
MeCN 0.1M TEATBF	E _{1/2} = -1.67	-	23
MeCN 0.1 M TBAPF ₆	E _{1/2} = -1.34, -1.725irr	-	24
DMF 0.1 M TBAPF ₆	-1.78, -2.20	-	25
MeCN 0.1 M TBAPF ₆	-1.40, -1.78	-	26
MeCN 0.1 M TBAPF ₆	E _{1/2} = -1.73, -2.09irr	-	27
DMF 0.1 M TBAP	-1.26 (80) / E _{1/2} = -1.30	-	28
MeCN 0.1 M TBAP	-1.77 (70), -2.04	-	29
MeCN 0.1 M TBAPF ₆	E _{1/2} = -1.27, -1.57irr	+1.47irr, +1.89	30
DMF 0.1 M TBAPF ₆	-1.80, -2.25irr	-	31
DCM 0.1 M TBAPF ₆	-1.79, -2.10	+0.87, +1.15	32
MeCN 0.1 M TBAPF ₆	-1.79, -2.15	-	33
DMF 0.1 M TBAPF ₆	E _{1/2} = -1.75 (75), -2.22irr	-	34
MeCN 0.1 M TBAPF ₆	E _{1/2} = -1.77 (75), -2.18irr	-	35
DMF 0.1 M TBAPF ₆	-1.79, -2.24	+1.01	36
DMF 0.1 m TBAPF ₆	-1.69	-	37
DMF 0.1 M TBAPF ₆	E _{1/2} = -1.84, -2.34irr	-	
DMF 0.1 M TBAPF ₆	E _{1/2} = -1.275	-	
[ReCl(CO)₃(terpy-κ²N)] (1b)			
medium^a	E_{red}, peak [V] (ΔE [mV]) or E_{1/2red}	E_{ox}, peak [V]	Ref.
DMF TBAP	-1.40	-	38
MeCN KPF ₆	-	+1.19	17
DMF 0.1 M TBAP	E _{1/2} = -1.75 (60), -2.24irr	-	39
MeCN 0.1 M TBAPF ₆	-1.741	+0.786irr	31
DCM 0.1 M TBAPF ₆	-1.71, -2.15	+0.60, +0.85, +1.03	
[ReCl(CO)₃(phen)] (2)			
medium^a	E_{red}, peak [V] (ΔE [mV]) or E_{1/2red}	E_{ox}, peak [V] or E_{1/2ox}	Ref.
MeCN 0.1 M TBAP	E _{1/2} = -1.34	E _{1/2} = +1.33	40
MeCN 0.1 M TBAP	E _{1/2} = -1.35	+1.33irr	10
MeCN 0.1 M TBATFB	E _{1/2} = -1.27	E _{1/2} = +1.36	11
DMF 0.05 M TEATFB -54 °C	E _{1/2} = -1.42, -2.05	E _{1/2} = +1.41	18
MeCN 0.1 M TBAPF ₆	-	+1.41 / E _{1/2} = +1.84	21
DCM [C6mim][FAP]	E _{1/2} = -1.62	E _{1/2} = +0.96, +1.56	41
MeCN 0.1 M TBAPF ₆	E _{1/2} = -1.74, -2.11irr	+0.99	42
DMF 0.1 M TBAPF ₆	E _{1/2} = -1.75, -2.23irr	-	31
DCM 0.1M TBAPF ₆	-1.74, -2.05	+0.93	43
MeCN 0.1 M TBAPF ₆	E _{1/2} = -1.30 (108)	+1.45irr	44
MeCN 0.1 M TBAPF ₆	E _{1/2} = -1.10, -1.33, -1.82	E _{1/2} = +1.59, +2.06	
DMF 1 M TBAPF ₆	E _{1/2} = -1.06	-	
[ReCl(CO)₃(dppz)] (3)			
medium^a	E_{red}, peak [V] (ΔE [mV]) or E_{1/2red}	E_{ox}, peak [V]	Ref.
DCM 0.1 M TBAP or TBAPF ₆	E _{1/2} = -1.01 (60)	-	45,46
THF 0.1 M TBAPF ₆	-1.42, -2.00, -2.66irr	+0.92irr	47
[ReCl(CO)₃(imphen)] (4)			
[ReCl(CO)₃(pybimd)] (5)			
medium^a	E_{red}, peak [V]	E_{ox}, peak [V]	Ref.
MeCN 0.1 M TBAPF ₆	-1.74irr, -2.20	+0.96irr	48
[ReCl(CO)₃(pytri-Bn)] (6)			
medium^a	E_{red}, peak [V]	E_{ox}, peak [V]	Ref.
DCM 0.1 M TBAPF ₆	-1.72irr	+1.50irr	49
DMF 0.1 M TBAPF ₆	-1.69irr	+1.50irr	50

^a electrolytes used: TBAPF₆ – tetrabutylammonium hexafluorophosphate; TBAP – tetrabutylammonium perchlorate; TEATFB – tetraethylammonium tetrafluoroborate; TBATFB – tetrabutylammonium tetrafluoroborate; KPF₆ – potassium hexafluorophosphate; [C6mim][FAP] – 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate

Table S2. The absorption and emission properties of complexes **1–6**.

[ReCl(CO)₃(bipy)] (1a)						
medium	λ_{abs} (nm)	λ_{exc} (nm)	λ_{PL} (nm)	τ	ϕ_{PL} (%)	Ref.
MeCN	370	–	612	25 ns	–	11
DCM	384	–	612	50 ns	–	
DMF	373	–	610	26 ns	–	
EtOH	372	–	604	36 ns	–	
THF	388	–	614	65 ns	–	
dioxane	390	–	614	62 ns	–	
benzene	400	–	612	70 ns	–	
EtOH	–	–	612	–	–	
EtOH 175 K	–	–	529	–	–	
DCM	242, 256, 294, 320sh, 386	–	622	50 ns	–	
EtOH:MeOH (4:1) 77 K	–	–	550	2.78 μ s	–	
DMF 0.10 M TBAPF ₆	294, 318sh, 372	–	–	–	–	
2-MeTHF 80 K	375	–	532	2.7 μ s	2.8	
THF	389	–	612	45 ns	–	
DCM	239, 294, 387	–	–	–	–	
DMA	–	–	607	–	–	
H ₂ O:dioxane (1:4)	368	–	605	29 ns	0.4	
H ₂ O:dioxane (1:4) 77 K	–	–	536	2.9 μ s	–	
DCM	–	–	642	39 ns	0.31	
DMF	370	–	580	–	–	
DMF	–	–	637	25 ns	0.3	
MeCN	371	–	633	–	0.27	
77K 2-MeTHF	–	–	–	3.17 μ s	–	
DMSO	–	319	576	21 ns	26.1	
MeCN	291, 371	–	–	–	–	
DMF	~373, 400, 443, 466, 500	–	–	–	–	
DMF:MeOH	294, 317, 371	–	598	–	0.23	
DCM	385	385	600	51 ns	0.5	
DMF	369	–	611	–	–	
toluene	401	–	604	–	0.58	
EtOH:MeOH (4:1) 77 K	–	–	–	4.1 μ s	–	
EtOH:MeOH (4:1)	–	–	–	23.6 ns	–	
THF	372	–	613	25 ns	–	
DCM	293, 385	–	612	–	–	
THF	–	–	621	23.35 ns	0.5	
toluene	399	–	641	24.2 ns	–	
DCM	–	–	–	–	0.58	
MeCN	234, 290, 315, 370	–	611	29 ns	0.2	
PMMA (film)	–	–	562	332 ns	–	
DMF	293, 373	–	606	–	–	
CHCl ₃	–	393, 316sh, 295	622	51.0 ns	1.65	
MeCN	290, 332, 381	369, 299	639	26.4 ns	0.71	
solid	–	471	584	0.6 μ s	–	
DMF	370	370	574	46.6 ns	–	
DMF	317, 371	–	596	25 ns	0.56	
toluene:DCM (1:1)	–	404	625	–	–	
DCM	290, 390	–	620	45 ns	–	
EtOH	290, 365, 315	–	620	24 ns	–	
EtOH 77 K	–	–	530	2.8 μ s	–	
DMSO	368	455	631	22.69 ns	–	
[ReCl(CO)₃(terpy-κ^2N)] (1b)						
medium	λ_{abs} (nm)	λ_{exc} (nm)	λ_{PL} (nm)	τ	ϕ_{PL} (%)	Ref.
DMF:DCM (9:1) 77 K	–	–	530	3.4 μ s	–	38
MeCN	250–300, 320–400	360	506	–	–	39
DCM	220, 295, 378	442	509	2.02 μ s	0.3	68
solid	–	365	562	1.95 μ s	–	–
DMSO	~310, 380	–	–	–	–	69
CHCl ₃	–	393, 322sh, 301, 265	638	4.59 ns	0.42	31
MeCN	306, 323, 375	380, 323, 303	656	3.59 ns	<0.01	
solid	–	491	582	0.6 μ s	–	
DMSO:H ₂ O (1:9)	360	–	–	–	–	70
[ReCl(CO)₃(phen)] (2)						
medium	λ_{abs} (nm)	λ_{exc} (nm)	λ_{PL} (nm)	τ	ϕ_{PL} (%)	Ref.
MeCN	364	353	612	178 ns	–	11
DCM	374		604	288 ns	–	
DMF	366		614	155 ns	–	
EtOH	369		600	216 ns	–	

THF	382		622	335 ns	–	
Dioxane	384		620	340 ns	–	
Beznene	388		610	320 ns	–	
MeCN	373	–	–	–	–	71
EtOH:MeOH (4:1) 77 K	–	–	–	7.2 μ s	–	
MeOH	212, 265, 288, 365	–	–	–	–	72
DCM	~275, 380	–	–	–	–	73
2-MeTHF	386	400	606	227 ns	1.3	74
2-MeTHF 77 K	–	–	535	7.6 μ s	–	
MeCN	~215, 260, 360	337	573	1835 ns	1.77	75
MeCN	–	–	600	183 ns	1.7	76
DMSO	–	319	577	32 ns	60.3	56
THF	386	410	594	197 ns	1.3	77
2-MeTHF 77K	–	410	524	7.6 μ s	–	
DMF	~280, 370	–	–	–	–	78
DCM	380	380	577	–	–	60
		405	–	300 ns	–	
		355	–	–	3.6	
CHCl ₃	200, 265, 365	–	–	–	–	79
MeCN	–	355	600	183 ns	1.7	
DCM	200, 216, 265, 290, 365	–	–	–	–	80
MeCN	~220, 270, 375	–	600	0.18 μ s	1.7	
PMMA (film)	–	–	550	1.3 μ s	–	
MeCN	~260, 280, 360	370	605	–	–	81
MeCN	200, 216, 265, 290, 365	375	600	138 ns	1.66	64
PMMA (film)	–	375	550	1390 ns	–	
THF	–	–	~600	–	–	82
2-MeTHF 77 K	–	400	~520	–	–	
CHCl ₃	–	382, 292, 265	617	306.6 ns	2.39	
MeCN	–	369, 291, 246	629	130.3 ns	2.22	
solid	–	489	539	1.5 μ s	–	
MeCN	~220, 265, 365	375	602	147 ns	1.7	83
MeCN	266, 368	380	592	204 ns	3.2	43
EtOH	~220, 270	–	–	–	–	84
MeCN	200, 216, 265, 365	375	590	–	–	44
DMF	–	375	602	135 ns	1.6	
[ReCl(CO)₃(dppz)] (3)						
medium	λ_{abs} (nm)	λ_{exc} (nm)	λ_{PL} (nm)	τ	Φ_{PL} (%)	Ref.
DCM	280, 360	–	–	0.04 μ s*	–	45
DCM	360, 378	–	–	–	–	47
DCM	380	342	588	–	<0.01	85
DCM	380	–	–	–	–	86
DCM	280, 322, 376, 394	–	–	40 ns**	–	87
C ₃ H ₇ CN	–	–	–	3.5 ns**	–	
MeCN	–	–	–	2.5 ns**	–	
DCM	280, 360	–	–	–	–	46
[ReCl(CO)₃(imphen)] (4)						
medium	λ_{abs} (nm)	λ_{exc} (nm)	λ_{PL} (nm)	τ	Φ_{PL} (%)	Ref.
DMSO	260, 286, 301, 322, 340, 396	405	625	223.27 ns	3.11	88
EtOH:MeOH (4:1) 77 K	–	400	546	7.76 μ s	–	
[ReCl(CO)₃(pybimd)] (5)						
medium	λ_{abs} (nm)	λ_{exc} (nm)	λ_{PL} (nm)	τ	Φ_{PL} (%)	Ref.
DCM	~325	380	590	0.075 μ s	3.1	89
THF	~240, 320, 336		~605	–	–	
CHCl ₃	~240, 325		~590	–	–	
DMSO	~260, 320, 340		~585	–	–	
MeCN	~320, 330		~600	–	–	
MeOH	336		576	0.087 μ s	4.6	
solid	–		~555	–	–	
MeCN	~320, 340, 390		375	~600	3.3 μ s	
[ReCl(CO)₃(pytri-Bn)] (6)						
medium	λ_{abs} (nm)	λ_{exc} (nm)	λ_{PL} (nm)	τ	Φ_{PL} (%)	Ref.
MeCN	333	333	538	–	0.33	55
2-MeTHF 77 K	–	355	–	8.90 μ s	–	
MeCN	270, 290, 336	364	532	103 ns	1.2	49
DCM	346	351	547	0.80 μ s	4.9	50
MeCN	330		532	0.10 μ s	1.2	
DCM	348		383	538	–	–

* obtained from ns-TA measurements; ** obtained from TRIR measurements

Table S3. The spectroscopic and electrochemical properties of complexes 7–46.

complex	medium	λ_{abs} (nm)	λ_{exc} (nm)	λ_{PL} (nm)	τ	Φ_{PL} (%)	TA τ	TE τ	TRIR τ	$E_{\text{red, peak}}$ [V]	$E_{\text{ox, peak}}$ [V]	Ref.	
7	DCM	299, 348, 398	350	437, 640	4.4 ns, 13.8 ns	<1	–	–	–	–1.36	+1.14, +1.65	90	
	toluene	–		~400, 640	–	–	–	–	–	–	–		
	CHCl ₃	–		~440, 640	–	–	–	–	–	–	–		
	MeCN	–		~480	–	–	–	–	–	–	–		
8	DCM	362, 368, 448, 466	325	425, 500, ~650	–	–	190 ns	200 ns	20 ps, 124 ns	–	–	91	
	MeCN	350, 359, 437, 446		478, ~650sh	–	–	140 ns	< 6 ns	57 ps, ~2 ns, 100 ns	–	–		
9	DCM	345, 356, 405, 431	325	420, 445, ~650	–	–	100 ns	100 ns	20 ps, 88 ns	–	–	92	
	MeCN	349, 360, 429, 449		460, ~650	–	–	80 ns	< 6 ns	34 ps, 400 ps, 66 ns	–	–		
10	DCM	303, 376, 460	350	520	<10 ns	–	600 ns	–	–	–	–	92	
	MeCN	–		514	<10 ns	–	–	–	–	–	–		
11	DCM	389,479		510	<10 ns	–	1.7 μ s	–	–	–	–		–
	MeCN	–		510	<10 ns	–	1 μ s	–	–	–	–		–
12	DCM	343, 500	355	680	–	6.0	3.9 μ s	–	–	–1.16, –1.53irr	+0.92, +1.42irr, +1.74irr	93	
	2-MeTHF 77 K	–		589	–	–	–	–	–	–	–		
13	DCM	292, 336, 496		701	–	1.0	–	–	–	–	–1.14, –1.52irr		+0.98, +1.29irr, +1.72irr
	2-MeTHF 77 K	–		590	–	–	–	–	–	–	–		–
14	DCM	368, 498		686	–	4.0	–	–	–	–	–1.13, –1.48irr		+0.96, +1.48irr, +1.72irr
	2-MeTHF 77 K	–		582	–	–	–	–	–	–	–		–
15	DCM	348, 513		703	–	6.0	–	–	–	–	–1.20, –1.59irr		+0.90, +1.48irr, +1.61irr
	2-MeTHF 77 K	–		594	–	–	–	–	–	–	–		–
16	DCM	344, 524		708	–	7.0	4.4 μ s	–	–	–	–1.19, –1.62irr		+0.86, +1.41irr, +1.62irr
	2-MeTHF 77 K	–		619	–	–	–	–	–	–	–		–
17	DCM	378, 450	–	672	18 ns	5.0	–	–	–	–	–	94	
18	MeCN	420	456	695	14.6 ns	0.4	–	–	–	–1.72	+0.66	95	
	CHCl ₃	438	447	628	122.6 ns	0.8	–	–	–	–	–		
	solid (film)	463	320	369, 529	–	–	–	–	–	–	–		
	EtOH:MeOH (4:1) 77 K	–	453	569, 601sh	241.4 μ s	–	–	–	–	–	–		
19	DCM	389	355	604	2.98 μ s	1.3	–	–	–	–	–	96	
20	DCM	386		605	6 μ s	1.6	–	–	–	–	–		–
				607	3.9 μ s	0.5	–	–	37 ps	–	–		–
21	DCM	410		678	44 ns	0.2	–	–	44 ns	–	–		–
22	DCM	401	689	27 ns	0.1	–	–	27 ns	–	–	–		
23	DCM	–	355	–	–	–	28 ns	–	–	–1.28	+0.84, +1.52	97	
24	DCM	~347, 480		~610	290 ns	0.55	280 ns	–	–	–1.25	+1.51		
25	DCM	–		–	–	–	–	12.0 μ s, 42.5 μ s	–	–	–		–
26	DCM	–	–	–	–	–	12.4 μ s, 43.6 μ s	–	–	–	–	98	
27	DCM	–	–	–	–	–	0.06 μ s	–	–	–	–		
28	toluene	392	–	~600	–	–	0.06 μ s	–	–	–	–	99	
	dioxane	488	–	588	–	–	1.4 μ s	–	1.2 μ s	–	–		
	CHCl ₃	478	–	626	–	–	–	–	–	–	–		
	ethyl acetate	496	–	702	–	–	–	–	–	–	–		–
		473	–	709	–	–	–	–	–	–	–		–
	THF	476	–	709	–	–	–	–	–	–	–		
DCM	488	–	740	–	–	3.8 μ s	–	–	–0.97	+1.05			
MeCN	–	–	–	–	–	–	–	1.6 μ s	–0.81	+1.07			
29	toluene	497	–	641	–	–	1.8 μ s	–	–	–	–	99	
	dioxane	485	–	674	–	–	–	–	–	–	–		
	CHCl ₃	510	–	727	–	–	–	–	–	–	–		
	ethyl acetate	482	–	727	–	–	–	–	–	–	–		
	THF	492	–	724	–	–	–	–	–	–	–		

complex	medium	λ_{abs} (nm)	λ_{exc} (nm)	λ_{PL} (nm)	τ	Φ_{PL} (%)	TA τ	TE τ	TRIR τ	E_{red} peak [V]	E_{ox} peak [V]	Ref.	
	DCM	520	–	783	–	–	1.6 μs	–	–	–0.85	+1.05		
30	toluene	490	–	641	–	–	1.8 μs	–	–	–	–		
	dioxane	479	–	665	–	–	–	–	–	–	–		
	CHCl_3	504	–	717	–	–	–	–	–	–	–		
	ethyl acetate	479	–	715	–	–	–	–	–	–	–		
	THF	491	–	724	–	–	–	–	–	–	–		
	DCM	515	–	721	–	–	10.1 μs	–	20 ps, 300 ps, 2.8 μs	–0.88	+1.05		
	toluene	–	–	~410, 580	–	–	–	–	–	–	–	–	
	dioxane	–	–	~400, 620	–	–	–	–	–	–	–	–	
	chlorobenzene	–	–	~655	–	–	–	–	–	–	–	–	
	CHCl_3	–	–	~700	–	–	–	–	–	–	–	–	
	ethyl acetate	–	–	~405, 705	–	–	–	–	–	–	–	–	
	THF	–	–	~405, 705	–	–	–	–	–	–	–	–	
31	DCM	489	–	740	–	–	–	3.8 μs	–	–0.97	+1.05		
	toluene	–	–	~670	–	–	–	–	–	–	–		
	dioxane	–	–	~670	–	–	–	–	–	–	–		
	chlorobenzene	–	–	~700	–	–	–	–	–	–	–		
	CHCl_3	–	–	~710	–	–	–	–	–	–	–		
	ethyl acetate	–	–	~410	–	–	–	–	–	–	–		
	THF	–	–	~410, 690	–	–	–	–	–	–	–		
32	DCM	513	–	600	–	–	–	3.6 μs	–	–0.99	+0.78		
	DMF	–	–	~450	–	–	–	–	–	–	–		
	toluene	–	–	~410, 500	–	–	–	–	–	–	–		
	dioxane	–	–	~520	–	–	–	–	–	–	–		
	chlorobenzene	–	–	~670	–	–	–	–	–	–	–		
	CHCl_3	–	–	~680	–	–	–	–	–	–	–		
	ethyl acetate	–	–	~620	–	–	–	–	–	–	–		
33	THF	–	–	~620	–	–	–	–	–	–	–		
	DCM	433	–	620	–	–	–	3.0 μs	–	–0.95	+1.44		
	DMF	–	–	~700	–	–	–	–	–	–	–		
	toluene	456	–	581	–	–	–	–	–	–	–		
	dioxane	443	–	615	–	–	–	–	–	–	–		
	chlorobenzene	470	–	646	< 6 ns	–	–	–	–	–	–		
	CHCl_3	473	–	667	–	–	–	–	–	–	–		
34	ethyl acetate	440	–	679	–	–	–	–	–	–	–		
	THF	447	–	686	–	–	–	–	–	–	–		
	DCM	470	–	701	–	–	0.027 ns, 2.8 μs	–	43 ps, 2 ns, 2.9 μs	–	–		
	toluene	494	–	554	–	–	–	–	–	–	–		
	dioxane	485	–	601	–	–	–	–	–	–	–		
	chlorobenzene	495	–	660	< 6 ns	–	–	–	–	–	–		
	CHCl_3	504	–	675	–	–	–	–	–	–	–		
35	ethyl acetate	476	–	641	–	–	–	–	–	–	–		
	THF	479	–	646	–	–	–	–	–	–	–		
	DCM	491	–	685	–	–	0.03 ns, 3.9 μs	–	28 ps, 1.5 ns, 2.2 μs	–	–		
	DMF	477	–	714	–	–	–	–	–	–	–		
	DCM	443	–	–	–	–	2.1 μs	–	1.28 μs	–0.97	+1.00		
	chlorobenzene	–	–	~610	< 6 ns	–	–	–	–	–	–		
	36	DCM	413	–	–	–	–	1.2 μs	–	950 ns	–0.97	+0.97	
chlorobenzene		–	–	~620	< 6 ns	–	–	–	–	–	–		
37	DCM	505	–	–	–	–	3.2 μs	–	–	–0.91	+1.06		

complex	medium	λ_{abs} (nm)	λ_{exc} (nm)	λ_{PL} (nm)	τ	Φ_{PL} (%)	TA τ	TE τ	TRIR τ	E_{red} peak [V]	E_{ox} peak [V]	Ref.
38	chlorobenzene	–	–	~725	< 6 ns	–	–	–	–	–	–	
	DCM	505	–	–	–	–	800 ns	–	1.28 μ s	-0.95	+0.94	
39	chlorobenzene	–	–	~610	< 6 ns	–	–	–	–	–	–	
	DCM	420	–	–	–	–	600 ns	–	800 ns	-0.86	+1.00	
40	chlorobenzene	–	–	~450, 630	< 6 ns	–	–	–	–	–	–	103
	DCM	–	–	–	–	–	–	–	–	-1.907	+0.525, +0.970	
	CHCl ₃	294, 374, 398sh, 468	460	600	1.001 μ s	14.5	–	–	–	–	–	
	solid	–	450	685	260 ns	2.3	–	–	–	–	–	
	EtOH:MeOH (1:4) 77 K	–	445	556	741.2 μ s	–	–	–	–	–	–	
	MeCN	274, 361, 441	–	–	–	–	–	–	–	–	–	
41	DCM	227, 368, 424	–	592	204 ns	12.0	–	–	–	–	–	104
42	DCM	279, 303, 422	–	596	271 ns	18.0	–	–	–	–	–	
43	DCM	286, 366, 434	–	598	248 ns	9.0	–	–	–	–	–	
44	DCM	~260, 290, 340, 430	–	–	–	–	–	–	–	–	–	105
	solid (CBP film)	–	266	375	0.2 μ s	–	–	–	–	–	–	
45	CHCl ₃	295, 345, 437	–	~580	–	–	–	–	–	–	–	106
	solid	–	–	–	0.16 μ s	–	–	–	–	–	–	
46	DCM	295, 399	–	573	<10 ns	3.7	10 μ s	–	8 ps, 140 ps, 440 ns	–	–	107
	DMF	–	–	–	–	–	–	–	–	-1.58irr	+1.07, +1.56irr	

Table S4. The spectroscopic and electrochemical properties of complexes **47–58**.

complex	medium	λ_{abs} (nm)	λ_{exc} (nm)	λ_{PL} (nm)	τ	ϕ_{PL} (%)	TA τ	TRIR τ	$E_{\text{red, peak}}$ [V]	$E_{\text{ox, peak}}$ [V]	Ref.
47	CHCl ₃	280, 292sh, 326, 335, 390	395, 332, 274	588	336.8 ns	8.08	–	–	–	–	31
	MeCN	276, 292sh, 319, 381	393, 326, 267	607	178.6 ns	2.05	–	–	–	–	
	EtOH:MeOH (4:1) 77 K	–	393, 331, 268	527, 552sh	41.8 μ s	–	–	–	–	–	
	solid	–	439	565	3.1 μ s	16.93	–	–	–	–	
	solid (film)	324, 400	366, 272	416, 434, 524	–	–	–	–	–	–	
	DCM	–	–	–	–	–	–	–	–2.05, –2.31	+0.69, +0.85, +1.04	
48	MeCN	191, 248, 308, 414	257, 315, 365, 458	702	0.079 ns	0.36	774 ns	–	–1.84, –2.07, –2.23	+0.58, +0.81	108
	CHCl ₃	247, 307, 421	289, 329, 404	507	3.74 ns	0.14	84 ns	–	–	–	
			265, 303, 369, 432	617	40.15 ns						
	solid	–	302, 351, 522	625	2.28 μ s	1.29	–	–	–	–	
	EtOH:MeOH (4:1) 77 K	–	319, 429	588	240.93 μ s	–	–	–	–	–	
	solid (film)	312, 401	330	384, 575	–	1.65	–	–	–	–	
			370	415, 438	–						
49	MeCN	246, 305, 364, 404	445	698	23.00 ns	0.8	–	–	–1.74	+0.52	95
	CHCl ₃	249, 307, 418	358	510	4.1 ns	1.0	–	–	–	–	
			417	634	16.60 ns	0.8	–	–	–	–	
	solid	–	536	653	105.43 ns	0.4	–	–	–	–	
	EtOH:MeOH (4:1) 77 K	–	435	585	228.43 μ s	–	–	–	–	–	
	solid (film)	401	324	378, 531	–	–	–	–	–	–	
50	MeCN	248, 307, 398	420	661	37.72 ns	1.0	–	–	–1.75	+0.64	
	CHCl ₃	247, 307, 403	404	650	9.42 ns	0.6	–	–	–	–	
	solid	–	470	571	5.35 μ s	8.7	–	–	–	–	
	EtOH:MeOH (4:1) 77 K	–	419	570	190.23 μ s	–	–	–	–	–	
	solid (film)	418	323	374, 527	–	–	–	–	–	–	
51	CHCl ₃	405	405	645	8 ns	0.9	–	–	–	–	95,109
	THF	405	405	665	6 ns	1.0	–	–	–	–	
	MeCN	402	405	665	146 ns	0.1	–	–	–	–	
	DMF	409	409	650	248 ns	<0.1	–	–	–	–	
	EtOH:MeOH (4:1) 77 K	–	420	560	178 μ s	–	–	–	–	–	
	solid	–	475	613	553 ns	7.1	–	–	–	–	
52	CHCl ₃	247, 313, 380, 430	425	637	20.00 ns	1.3	170 fs, 10.75 ps, 145.59 ps, 3.67 ns	–	–	–	110
	THF	415	415	650	46.64 ns	4.5	–	–	–	–	
	MeCN	192, 246, 309, 354, 419	456	687	177.60 ns	2.0	340 fs, 3.06 ps, 64.45 ps	–	–1.76	+0.54	
	DMF	425	425	680	1.67 μ s	<0.1	–	–	–	–	
	EtOH:MeOH (4:1) 77 K	–	444	580	227.64 μ s	–	–	–	–	–	
	solid	–	494	636	1.37 μ s	0.7	–	–	–	–	
	DMF	425	–	532	380 ns	–	–	380 ns	–1.81	–	
	77K 2-MeTHF	–	–	560	–	–	–	–	–	–	
53	CHCl ₃	247, 313, 380sh, 430	421	636	20.16 ns	1.13	–	–	–	–	111
	MeCN	192, 246, 309, 354, 419	452	687	0.26 ns	1.91	–	–	–	–	
	solid	–	494	636	1.35 μ s	0.67	–	–	–	–	
	EtOH:MeOH (4:1) 77 K	–	312, 325, 368, 444	580	227.98 μ s	–	–	–	–	–	
53	CHCl ₃	270, 322, 339, 351, 425	268, 292sh, 323, 430	590	7.07 μ s	6.43	–	–	–	–	31

complex	medium	λ_{abs} (nm)	λ_{exc} (nm)	λ_{PL} (nm)	τ	Φ_{PL} (%)	TA τ	TRIR τ	$E_{\text{red, peak}}$ [V]	$E_{\text{ox, peak}}$ [V]	Ref.
	MeCN	271, 416	264, 292, 318, 419	643	489.8 ns	2.48	–	–	–	–	
	EtOH:MeOH (4:1) 77 K	–	293, 322, 439	567, 604sh	200.88 μ s	–	–	–	–	–	
	solid	–	331, 494	595	25.24 μ s	34.77	–	–	–	–	
	solid (film)	421	339	412, 585	–	–	–	–	–	–	
	DCM	–	–	–	–	–	–	–	–1.81, –2.13	+0.78	
54	EtOH:MeOH (4:1) 77 K	–	382	499, 535, 577	278.56 μ s	–	–	–	–	–	
	CHCl ₃	264, 313, 377	408	564	5.44 μ s	2.83	4.23 ps, 77.26 ps	–	–	–	
	MeCN	252, 276, 310, 378	390	557	1.32 μ s	0.51	–	–	–	–	
	solid	–	450	600	4.67 μ s	2.43	–	–	–	–	
55	EtOH:MeOH (4:1) 77 K	–	377	496, 532, 572	216.42 μ s	–	–	–	–	–	
	CHCl ₃	267, 312, 371	370	581	5.69 μ s	4.30	4.26 ps, 45.93 ps	–	–	–	
	MeCN	254, 273, 312, 371	370	575	2.86 μ s	0.64	–	–	–	–	
	solid	–	460	650	1.99 μ s	<0.05	–	–	–	–	
56	EtOH:MeOH (4:1) 77 K	–	380	498, 537, 578	210.11 μ s	–	–	–	–	–	
	CHCl ₃	267, 314, 371	375	582	6.67 μ s	1.95	5.29 ps, 103.32 ps	–	–	–	
	MeCN	258, 312, 370	395	578	4.73 μ s	0.58	–	–	–	–	
	solid	–	425	572	2.60 μ s	1.89	–	–	–	–	
57	DCM	499	–	–	–	–	6.1 μ s	2.3 μ s	–1.06	+1.19	102
	chlorobenzene	–	–	~470, 625	–	–	–	–	–	–	
58	CHCl ₃	296, 355, 391sh, 473	470	623	1.16 μ s	19.5	–	–	–	–	
	MeCN	287, 305, 342, 447	–	–	–	–	–	–	–	–	
	DMF	290, 310, 349, 457	–	–	–	–	–	–	–	–	
	THF	292, 308, 343, 444	–	–	–	–	900 fs, 6.32 ps, 141.31 ps	–	–	–	
	solid	–	450	650	0.117 μ s	4.8	–	–	–	–	
	EtOH:MeOH (4:1) 77 K	–	458	584	1.18 ms	–	–	–	–	–	
	DCM	–	–	–	–	–	–	–	–1.917	+0.438	

Table S5. The spectroscopic and electrochemical properties of complexes **59–71**.

complex	medium	λ_{abs} (nm)	λ_{exc} (nm)	λ_{PL} (nm)	τ	ϕ_{PL} (%)	TA τ	$E_{\text{red, peak}}$ [V]	$E_{\text{ox, peak}}$ [V]	Ref.	
59	CHCl ₃	260, 292, 333, 407	395	675	8.21 ns	0.22	–	–	–	113	
	MeCN	194, 258, 321, 381	380	664	5.57 ns	0.22	–	–1.35, –1.70	+0.72, +1.07		
	solid	–	458	604	430.59 ns	3.50	–	–	–		
	EtOH:MeOH (4:1) 77 K	–	307, 338, 369	525, 565	69.15 μ s	–	–	–	–		
	solid (film)	397	350	415, 438, 556	–	–	–	–	–		
			400	440, 465, 587	–	–	–	–	–		
solid (15% blend in PVK)	330, 345, 397	350	416, 440, 572	–	–	–	–	–			
		400	463, 558	–	–	–	–	–			
60	CHCl ₃	260, 327, 428	400	484	2.40 ns	0.15	–	–	–	114	
	MeCN	220, 257, 314, 406	371	516	3.14 ns	0.09	–	–1.37, –1.70	+0.71, +1.06		
	solid	–	500	689	24.41 μ s	1.19	–	–	–		–
				758	21.40 μ s						
EtOH:MeOH (4:1) 77 K	–	301, 374	410, 434, 467	1.01 ns	–	–	–	–			
61	DCM	330, 442	351	502	–	0.6	1.4 μ s	–0.94	+1.46	114	
	toluene	–		~420, 510	–	–	–	–	–		
	CHCl ₃	–		~450, 520	–	–	–	–	–		
	DMSO	–		~480, 590	–	–	–	–	–		
	acetone	–		~450, 575	–	–	–	–	–		
	MeCN	–		~480, 575	–	–	–	–	–		
62	DCM	350, 474	351	656	–	5.0	1200 ns	–0.92	+1.26	114	
	toluene	–		~590	–	–	–	–	–		
	CHCl ₃	–		~640	–	–	–	–	–		
	DMSO	–		~660	–	–	–	–	–		
	acetone	–		~685	–	–	–	–	–		
	MeCN	–		~675	–	–	–	–	–		
63	DCM	375, 492	351	697	–	7.0	2500 ns	–0.92	+1.04	114	
	toluene	–		~625	–	–	–	–	–		
	CHCl ₃	–		~697	–	–	–	–	–		
64	DMSO	261, 324, 350, 415	–	564	–	–	–	–	–	115	
	MeCN	–	–	–	–	–	–	–0.73	+1.23		
65	DCM	~380, 450	400	500	–	0.57	–	–0.95, –1.46	+0.2, +0.83	116	
	solid (ITO film)	~380, 488, 600	–	–	–	–	–	–	–		
66	PBS buffer	~260, 300, 422	425	685	–	0.04	–	–	–	117	
	DCM	~260, 300, 410		691	–	0.03	1.2 μ s	–	–		
	MeCN	~260, 300, 408		493	–	0.01	–	–	–		
67	DCM	291, 335, 417sh, 439	–	–	–	–	–	–0.75	–	46	
68	DCM	294, 321, 424sh, 447	–	–	–	–	–	–1.03	–	–	
69	DMF	~480, 560	–	–	–	–	–	–	–	118	
	DCM	~200, 250, 300, 325, 375, 580	560	–	–	–	<100 ps	–1.41	+0.28, +0.62		
70	DCM	~260, 330	–	–	214 ns	–	–	–	–	119	
71	CHCl ₃	253, 280, 302, 425	420	785	150 ns	0.81	0.17 ps, 2.78 ps, 84.9 ps, 684.13 ps	–	–	112	
	MeCN	252, 278, 296, 317, 406	–	–	–	–	–	–	–		
	solid	–	525	725	130 ns	2.31	–	–	–		
	EtOH:MeOH (4:1) 77 K	–	425	665	2.08 μ s	–	–	–	–		

Table S6. The spectroscopic and electrochemical properties of complexes **72–86**.

complex	medium	λ_{abs} (nm)	λ_{exc} (nm)	λ_{PL} (nm)	τ	ϕ_{PL} (%)	TA τ	$E_{\text{red, peak}}$ [V]	$E_{\text{ox, peak}}$ [V]	Ref.	
72	DCM	252, 296, 366	420	570	420 ns	–	–	–	–	120	
				688	6 μs						
				764	23 μs						
73	DCM	258, 296, 380	420	592	210 ns	–	–	–	–	121	
				700	15 μs						
				776	65 μs						
74	DCM	~260, 350, 370, 385	380	~540	15 ns	–	–	–	–	121	
75	DCM	~260, 350, 370, 385	–	~540	40 ns	–	42 μs	–	–	–	
76	DMF	~325, 350, 380, 395	375	~410, 425	0.141 ns	–	117.7 μs	–1.69, –1.97, –2.45	–	122	
77	MeCN	382, 402	402	674	–	–	11 μs	–1.32	+0.96, +1.4	123	
	DMSO	407	402	680	–	–	–	–	–		
	DCM	407	–	–	–	–	–	–	–		
	EtOH:MeOH (4:1) 77 K	–	402	~645, 710	~2 ms	–	–	–	–		
78	DMSO:H ₂ O (2:98)	~320, 420	380	~450	–	–	–	–	–	124	
	CHCl ₃	258, 308, 351, 368, 386, 416	445	511	4.91 ns	3.85	1.53 ps, 92.9 ps, 1.96 ns	–	–	125	
	MeCN	252, 311, 348, 365, 384, 407	430	627	2.26 ns	4.08	1.93 ps, 52.0 ps, 1.73 ns	–	–		
	DMSO	260, 316, 328, 349, 368, 388, 406	430	627	2.83 ns	0.02	2.18 ps, 269.6 ps, 1.62 ns	–	–		
	solid (film)	321sh, 370, 392, 456	–	711	14.28 μs						
	77 K BuCN	–	430	587	3.6 μs	–	–	–	–		
	DCM	–	–	688, 761	12 ms	–	–	–1.76	+0.67		
	79	CHCl ₃	259, 312, 423	450	580	7.30 ns	1.78	0.58 ps, 168.8 ps	–		–
MeCN		250, 292, 305, 412	430	609	3.97 ns	0.05	0.18 ps, 105.1 ps	–	–		
DMSO		262, 312, 360, 421	430	593	5.75 ns	1.40	0.29 ps, 465.3 ps	–	–		
solid (film)		326sh, 450	–	712	22.71 μs						
BuCN 77 K		–	470	707, 784	2.6 ms	–	–	–	–		
DCM		–	–	–	–	–	–	–1.69	+0.61		
DMSO:H ₂ O (2:98)		~320, 475, 490	380	~440	–	–	–	–	–		
80	MeCN	272, 324, 395	420	620	3.3 ns	6.1	–	–	–	126	
	CHCl ₃	274, 306, 321, 409	450	500	4.65 ns	<0.1	0.41 ps, 8.6 ps, 136 ps, 4.6 μs	–	–		
	solid (film)	304, 338, 429	–	650, 696sh	4.404 ns						
	BuCN 77 K	–	440	627, 680, 756	5.7 ms	–	–	–	–		
	DCM	–	–	–	–	–	–	–1.65, –1.97	+0.71, +0.97		
	DMSO:PBS buffer (1:99)	300, ~440	300	410	–	0.24	–	–	–		
82	DMSO:H ₂ O (1:9)	280, 377	280	403, 466	–	15.4	–	–	–	128	
	DMSO	285, 299, 374, 429	377	468	–	22.5	1.03 ps, 20.37 ps, 379.80 ps	–	–		
			375	460	1.77 ns						
			435	657, 720, 790	1.80 ms						
	EtOH:MeOH (4:1) 77 K	–	–	375	405, 430, 450, 494	9.49 ns	–	–	–	88	
DCM	–	–	370	631, 691, 762	169.67 ms	–	–	–			
83	DMSO	269, 280, 301, 331, 347, 375, 407	375	450	2.12 ns	1.06	1.64 ps, 66.94 ps, 597.35 ps	–	–		
	EtOH:MeOH (4:1) 77 K	–	420	636	1.51 ms						
84	DMF	~330, 350, 376	–	~410, 610, 660	12.1 ns	–	77.4 μs	–1.64	–	129	
	DMF 77 K	–	–	~600, 660	–	–	–	–	–		
85	DCM	258, 336, 346, 373, 393	370	395, 418, 440	–	~0.01	–	–1.94irr	+0.96irr, +1.33irr	130	
86	DCM	244, 267, 278, 317, 331, 347, 400sh		400	–	–	~0.01	–	–1.82	–	

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