Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Tricarbonylrhenium complexes from 2-pyridyl-1,2,3-triazole ligands bearing a 4-substituted phenyl arm: a combined experimental and theoretical study

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Figure S2. Intermolecular "chlorophenyl-triazolyl" π-π stacking interactions for **3a**

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Figure S1. The molecular structure of **2a**. Displacement ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

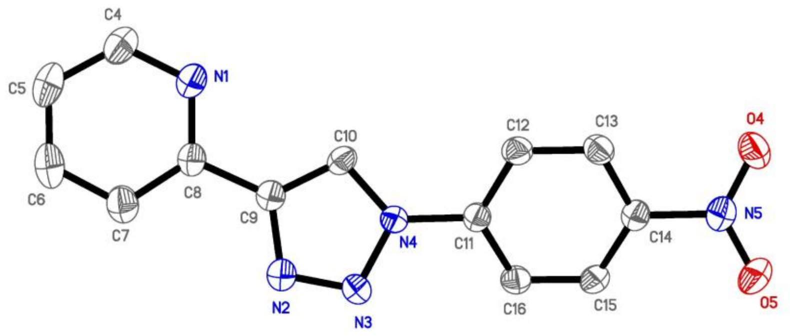


Figure S2. Intermolecular “chlorophenyl-triazolyl” π-π stacking interactions for **3a** (centroid-centroid distance of 3.792 Å). The solvent molecules were omitted for clarity.

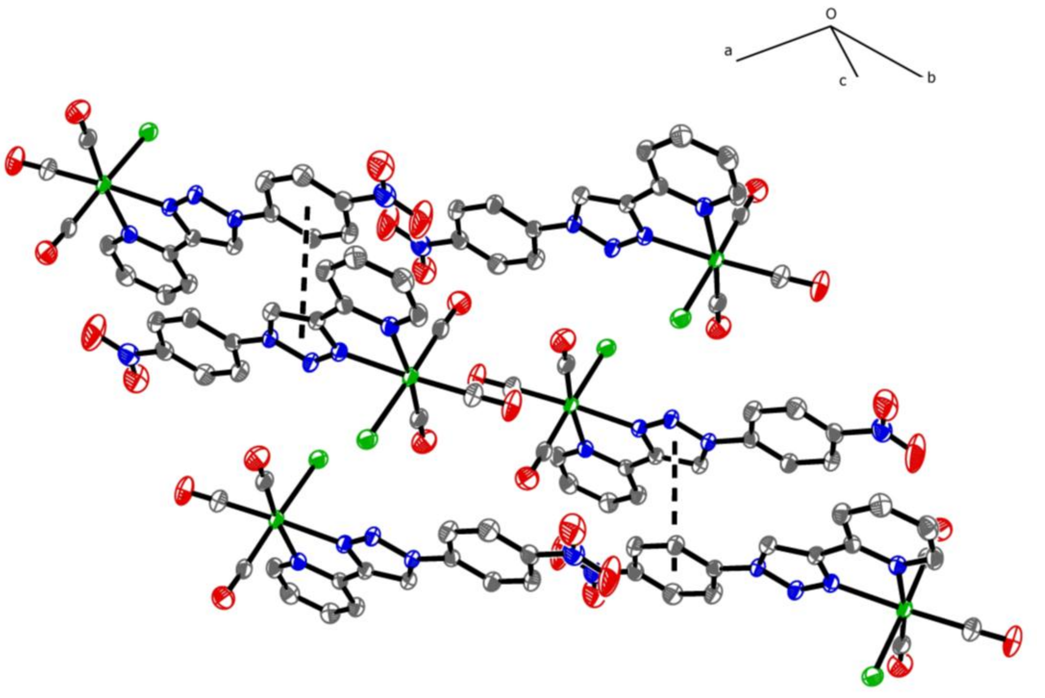
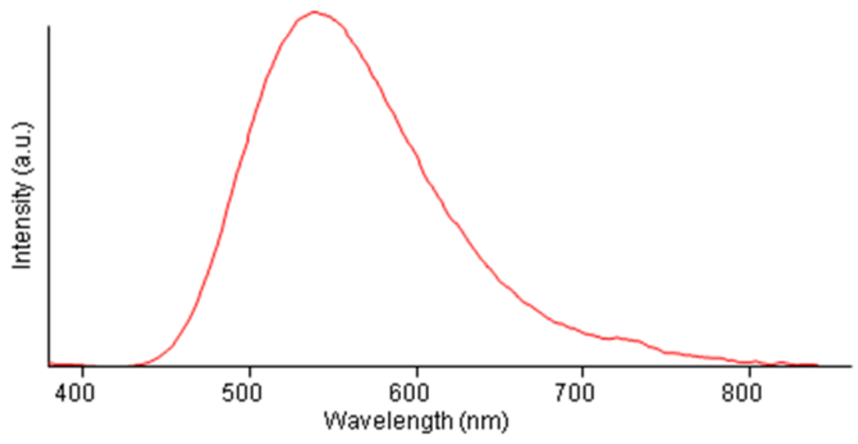


Figure S3. Room temperature emission spectra in methanol for **3b** (top) and **3c** (bottom)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400
500
600
700
800
Wavelength (nm)

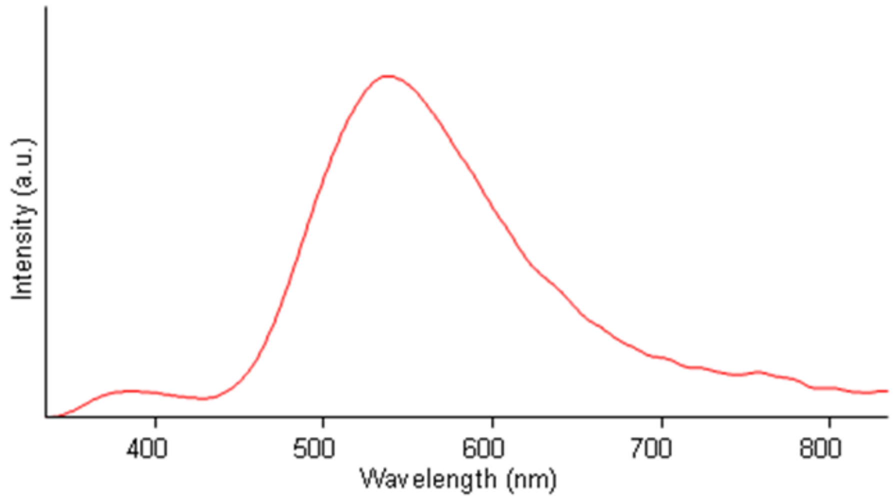
Intensity (a.u.)
400
500
600
700
800
Wavelength (nm)

Table S1. Selected experimental bond lengths [Å] and angles [°] for **2a**

Bond Lengths			
N(2)-N(3)	1.307(2)	C(9)-C(10)	1.359(3)
N(3)-N(4)	1.360(2)	C(10)-N(4)	1.355(2)
N(4)-C(11)	1.428(2)	C(9)-C(8)	1.474(2)
N(2)-C(9)	1.369(2)		
Bond Angles			
C(9)-N(2)-N(3)	108.98(15)	C(10)-C(9)-N(2)	108.50(16)
N(2)-N(3)-N(4)	107.23(14)	C(9)-C(8)-N(1)	115.09(16)
N(3)-N(4)-C(10)	110.15(15)	C(12)-C(11)-N(4)	119.46(16)
N(4)-C(10)-C(9)	105.14(16)		

Table S2. Hydrogen bonds for **3a** and **3b**.

D **A**	**D—H** [Å]	**H•••A** [Å]	**D•••A** [Å]	**D—H•••A** [°]
3a				
C(5)-H(5A)...O(5)#1	0.95	2.59	3.279(4)	129.8
C(10)-H(10)...O(6)#2	0.95	2.16	3.088(3)	167.0
C(12)H(12)...O(6)#2	0.95	2.39	3.329(4)	171.5
C(16)H(16)...N(3)	0.95	2.43	2.757(3)	99.7
C(16)H(16)...Cl(1)#3	0.95	2.83	3.693(3)	151.7
C(19)H(19B)...O(1)#4	0.98	2.48	3.343(4)	147.0
3b				
O(99)-H(99)...Cl(1)#1	0.82	2.35	3.164(4)	174.6
C(6)-H(6)...O(1)#2	0.93	2.43	3.253(6)	147.1

C(7)-H(7)...Cl(1)#3	0.93	2.73	3.507(5)	142.2
C(10)-H(10)...O(99)#4	0.93	2.39	3.301(5)	167.4
C(12)-H(12)...O(99)#4	0.93	2.44	3.358(6)	171.0
C(16)-H(16)...N(3)	0.93	2.46	2.776(5)	100.1

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z; #2 x,y-1,z+1; #3 -x+1,-y,-z+1; #4 -x+1,-y+1,-z+1

Table S3. The theoretical bond lengths [Å] and angles [°] for **3c** (in MeOH)

Bond lengths	Optimized			Bond angles	Optimized		
	S_0	S_1	T_1		S_0	S_1	T_1
Re(1)-C(1)	1.925	*1.932*	1.923	C(1)-Re(1)-C(2)	90.18	*90.31*	90.28
Re(1)-C(2)	1.928	*1.941*	1.933	C(1)-Re(1)-C(3)	90.92	*91.49*	90.90
Re(1)-C(3)	1.910	*1.907*	1.906	C(2)-Re(1)-C(3)	90.95	*90.31*	91.04
Re(1)-N(2)	2.180	*2.137*	2.153	C(1)-Re(1)-N(2)	97.51	*96.70*	97.42
Re(1)-N(1)	2.247	*2.195*	2.244	C(2)-Re(1)-N(2)	171.10	*171.46*	170.95
Re(1)-Cl(1)	2.556	*2.611*	2.582	C(3)-Re(1)-N(2)	93.34	*93.48*	93.57
O(1)-C(1)	1.163	*1.167*	1.165	C(1)-Re(1)-N(1)	170.85	*171.06*	170.84
O(2)-C(2)	1.164	*1.164*	1.166	C(2)-Re(1)-N(1)	98.08	*97.20*	97.80
O(3)-C(3)	1.167	*1.168*	1.169	C(3)-Re(1)-N(1)	92.87	*93.20*	93.25
				N(2)-Re(1)-N(1)	73.96	*75.43*	74.19
				C(1)-Re(1)-Cl(1)	91.65	*89.81*	91.49
				C(2)-Re(1)-Cl(1)	91.08	*89.35*	90.04
				C(3)-Re(1)-Cl(1)	176.72	*178.58*	177.38

				N(2)-Re(1)-Cl(1)	84.31	*85.81*	85.05
				N(1)-Re(1)-Cl(1)	84.30	*85.44*	84.23
				O(1)-C(1)-Re(1)	178.59	*178.77*	178.63
				O(2)-C(2)-Re(1)	179.16	*179.48*	179.17
				O(3)-C(3)-Re(1)	179.88	*179.80*	179.94

In the following Tables **S4** to **S6**, are presented selected DFT calculations for each complex including wavelengths (λ), calculated excitation energies (E), oscillator strengths (×c4), and dominant excitation character for low-lying singlet (S_n) and triplet (T_n) states.

Table S4. Selected data for complex **3a**.

State	Excitations	λ_{exp}, nm	E_{cal}, eV	λ_{cal}, nm	$\times c4_{cal}$	Character
			Singlet Excited States			
S_1	H→L		2.71	457.2	*0.0222*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_2	H-1→L		2.80	442.5	*0.0390*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_3	H-2→L		3.24	382.9	*0.0025*	d→π*(L) (MLCT)
S_4	H→L+1		3.27	378.7	*0.0028*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_5	H-1→L+1	330	3.43	361.7	*0.0734*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_6	H-3→L		3.65	340.1	*0.2394*	π(L)→π*(L) (IL)
S_7	H-9→L		3.71	333.9	*0.0084*	π(L)→π*(L) (IL)
S_8	H-2→L+1		3.75	331.0	*0.0005*	d→π*(L) (MLCT)
S_9	H→L+2		3.92	316.3	*0.0112*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_{10}	H-1→L+2		4.02	308.6	*0.0401*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_{11}	H-1→L+2		4.02	308.5	*0.1337*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_{12}	H-6→L		4.05	306.0	*0.0339*	π(L)→π*(L) (IL)
S_{20}	H-7→L	296	4.38	282.8	*0.4263*	π(L)/π(Cl)→π*(L) (LLCT)
S_{27}	H-4→L+1		4.73	262.2	*0.0408*	π(Cl)/π(L)→π*(L) (LLCT)
S_{31}	H-2→L+5		4.88	254.2	*0.0484*	d→π*(CO)/d (LF/LMCT)
S_{32}	H-3→L+2	267	4.97	249.6	*0.1802*	π(L)→π*(L) (IL)
S_{37}	H-7→L+1		5.28	234.8	*0.0799*	π(L)/π(Cl)→π*(L) (LLCT)
S_{48}	H-4→L+3	227	5.55	223.3	*0.0724*	π(Cl)/π(L)→π*(L) (LLCT)
S_{49}	H-3→L+4		5.56	223.0	*0.0417*	π(L)→π*(L) (IL)
S_{59}	H-3→L+6		5.77	215.0	*0.0316*	π(L)→π*(CO)/d (LMCT/LLCT)

S_{60}	H-12→L		5.78	214.6	*0.0781*	π(L)→π*(L) (IL)
S_{66}	H-4→L+4		5.94	208.6	*0.0328*	π(Cl)/π(L)→π*(L) (LLCT)
S_{87}	H-8→L+3		6.27	197.7	*0.0839*	π(Cl)→π*(L) (LLCT)
S_{89}	H-10→L+1		6.35	195.4	*0.0483*	π(L)/π(Cl)→π*(L) (LLCT)
	H-8→L+3					π(Cl)→π*(L) (LLCT)
S_{92}	H-6→L+4	205	6.41	193.3	*0.1791*	π(L)→π*(L) (IL)
S_{98}	H-3→L+7		6.52	190.2	*0.1731*	π(L)→π*(L) (IL)
S_{100}	H-7→L+5		6.52	190.0	*0.0802*	π(L)/π(Cl)→π*(CO)/d (LMCT/LLCT)
S_{101}	H-7→L+5		6.54	189.7	*0.0461*	π(L)/π(Cl)→π*(CO)/d (LMCT/LLCT)
S_{108}	H-7→L+6		6.60	187.7	*0.0353*	π(L)/π(Cl)→π*(CO)/d (LMCT/LLCT)
S_{110}	H-13→L+2		6.62	187.4	*0.1109*	π(L)→π*(L) (IL)
S_{111}	H-1→L+19		6.64	186.8	*0.0576*	d/π(Cl)→d/π*(CO) (LF/LLCT)
S_{119}	H-1→L+19		6.72	184.6	*0.0355*	d/π(Cl)→d/π*(CO) (LF/LLCT)
S_{122}	H-8→L+6		6.77	183.1	*0.0693*	π(Cl)→π*(CO)/d (LMCT/LLCT)
S_{123}	H-11→L+2		6.79	182.6	*0.1057*	π(L)→π*(L) (IL)
S_{125}	H→L+17		6.80	182.3	*0.0429*	d/π(Cl)→d/π*(L)/π*(CO) (LF/LLCT)
			Triplet excited states			
T_1	H→L		2.67	464.7	*0.0000*	d/π(Cl)→π*(L) (MLCT/LLCT)
T_2	H–1→L		2.76	449.1	*0.0000*	d/π(Cl)→π*(L) (MLCT/LLCT)
T_3	H–13→L		2.88	430.7	*0.0000*	π(L)→π*(L) (IL)
T_4	H–3→L		3.03	409.7	*0.0000*	π(L)→π*(L) (IL)
T_5	H→L+1		3.09	400.9	*0.0000*	d/π(Cl)→π*(L) (MLCT/LLCT)

.

Table S5. Selected data for complex **3b**.

State	Excitations	λ_{exp}, nm	E_{cal}, eV	λ_{cal}, nm	$\times c4_{cal}$	Character
			Singlet excited states			
S_1	H→L		3.29	377.1	*0.0036*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_2	H-1→L		3.44	360.2	*0.0723*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_3	H-2→L		3.76	330.1	*0.0009*	d→π*(L) (MLCT)
S_4	H→L+1		3.78	327.7	*0.0413*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_5	H-1→L+1	320	3.87	320.5	*0.0694*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_6	H→L+2		4.17	297.3	*0.0159*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_7	H-1→L+4		4.19	296.1	*0.0021*	d/π(Cl)→π*(CO)/d (LF/LLCT)
S_8	H→L+4		4.21	294.5	*0.0159*	d/π(Cl)→π*(CO)/d (LF/LLCT)
S_9	H-1→L+2		4.24	292.5	*0.0136*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_{10}	H-2→L+1		4.29	289.2	*0.0023*	d→π*(L) (MLCT)
S_{12}	H-3→L	295	4.35	285.3	*0.1431*	π(L)→π*(L) (IL)
S_{13}	H-3→L+1	264	4.60	269.2	*0.6147*	π(L)→π*(L) (IL)
S_{15}	H-4→L		4.65	266.4	*0.1363*	π(L)→π*(L) (IL)
S_{26}	H-5→L+1		5.13	241.8	*0.0539*	π(Cl)→π*(L) (LLCT)
S_{37}	H-8→L	226	5.49	226.0	*0.0550*	π(Cl)→π*(L) (LLCT)
S_{38}	H-1→L+13		5.53	224.3	*0.0446*	d/π(Cl)→d/π*(L) (LF/LLCT)
S_{39}	H-3→L+3		5.54	223.9	*0.0563*	π(L)→π*(L) (IL)
S_{43}	H-3→L+5		5.64	219.7	*0.0471*	π(L)→d/π*(CO) (LMCT/LLCT)
S_{74}	H-8→L+2		6.25	198.3	*0.0485*	π(Cl)→π*(L) (LLCT)
S_{85}	H-10→L+1		6.42	193.1	*0.0420*	π(L)→π*(L) (IL)
S_{88}	H-11→L+1	210	6.48	191.4	*0.1387*	π(L)→π*(L) (IL)
S_{89}	H→L+15		6.48	191.3	*0.0739*	d/π(Cl)→d/π*(L) (LF/LLCT)
S_{94}	H→L+19		6.56	189.0	*0.0793*	d/π(Cl)→d/π*(L) (LF/LLCT)
S_{95}	H→L+18		6.57	188.8	*0.0443*	d/π(Cl)→d/π*(CO) (LF/LLCT)

S_{97}	H-5→L+6	6.60	187.8	*0.0503*	π(Cl)/π(L)/d→π*(L) (LMCT/LLCT/IL)
S_{98}	H-5→L+6	6.60	187.7	*0.1323*	π(Cl)/π(L)/d→π*(L) (LMCT/LLCT/IL)
S_{99}	H-5→L+6	6.62	187.2	*0.0579*	π(Cl)/π(L)/d→π*(L) (LMCT/LLCT/IL)
S_{101}	H-7→L+6	6.65	186.3	*0.2868*	π(Cl)/d/π(L)→π*(L) (LMCT/LLCT/IL)
S_{102}	H-7→L+6	6.66	186.1	*0.1204*	π(Cl)/d/π(L)→π*(L) (LMCT/LLCT/IL)
S_{103}	H-11→L+1	6.67	185.8	*0.0940*	π(L)→π*(L) (IL)
	H-8→L+5				π(Cl)→d/π*(CO) (LMCT/LLCT)
S_{104}	H-6→L+6	6.69	185.2	*0.0753*	π(L)→π*(L) (IL)
S_{109}	H-13→L+2	6.74	183.9	*0.0405*	π(L)→π*(L) (IL)
S_{110}	H-12→L+1	6.75	183.8	*0.0743*	π(L)→π*(L) (IL)
	H-3→L+11				π(L)→d/π*(L) (LMCT/IL)
S_{111}	H-1→L+17	6.76	183.3	*0.0431*	d/π(Cl)→π*(L)/d (LF/LLCT)
S_{112}	H-8→L+5	6.77	183.1	*0.1326*	π(Cl)→d/π*(CO) (LMCT/LLCT)
S_{113}	H-12→L+1	6.77	182.9	*0.0955*	π(L)→π*(L) (IL)
S_{114}	H-4→L+7	6.78	182.6	*0.0539*	π(L)→π*(CO) (LLCT)
	H-1→L+24				d/π(Cl)→π*(L)/d (LF/LLCT)
			Triplet excited states		
T_1	H→L	3.10	400.0	*0.0000*	d/π(Cl)→π*(L) (MLCT/LLCT)
T_2	H–1→L	3.23	384.1	*0.0000*	d/π(Cl)→π*(L) (MLCT/LLCT)
T_3	H–3→L+1	3.39	366.0	*0.0000*	π(L)→π*(L) (IL)
T_4	H–4→L	3.41	363.5	*0.0000*	π(L)→π*(L) (IL)
	H–3→L				π(L)→π*(L) (IL)
T_5	H–2→L	3.68	336.5	*0.0000*	d→π*(L) (MLCT)

Table S6. Selected data for complex **3c**.

State	Excitations	λ_{exp}, nm	E_{cal}, eV	λ_{cal}, nm	$\times c4_{cal}$	Character
			Singlet excited states			
S_1	H→L		3.25	381.6	*0.0030*	π(L)→π*(L) (IL)

S_2	H-1→L		3.41	363.6	*0.0448*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_3	H-2→L		3.51	353.2	*0.0429*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_4	H-3→L		3.78	328.0	*0.0112*	d→π*(L) (MLCT)
S_5	H→L+1		3.83	323.9	*0.4871*	π(L)→π*(L) (IL)
S_6	H-1→L+1	300	4.04	307.1	*0.0231*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_7	H→L+2		4.11	301.6	*0.0423*	π(L)→π*(L) (IL)
S_8	H-2→L+1		4.14	299.5	*0.0183*	d/π(Cl)→π*(L) (MLCT/LLCT)
S_9	H-2→L+3		4.18	296.7	*0.0050*	d/π(Cl)→π*(CO)/d (MLCT/LLCT)
S_{10}	H-1→L+3		4.20	295.0	*0.0112*	d/π(Cl)→π*(CO)/d (MLCT/LLCT)
S_{25}	H-3→L+3		4.88	254.0	*0.0719*	d→π*(CO)/d (MLCT/LLCT)
S_{26}	H-4→L+1	258	5.14	241.2	*0.1514*	π(L)→π*(L) (IL)
S_{31}	H-4→L+2		5.28	235.0	*0.1037*	π(L)→π*(L) (IL)
S_{35}	H→L+7	227	5.42	228.8	*0.0912*	π(L)→π*(L)/π*(CO) (LLCT/IL)
S_{39}	H-8→L		5.51	225.0	*0.0414*	π(Cl)→π*(L) (LLCT)
S_{47}	H-7→L+2		5.67	218.6	*0.0381*	π(Cl)→π*(L) (LLCT)
S_{81}	H-8→L+2		6.28	197.3	*0.0442*	π(Cl)→π*(L) (LLCT)
S_{83}	H-11→L		6.32	196.2	*0.0373*	π(L)→π*(L) (IL)
S_{91}	H-9→L+1	209	6.45	192.3	*0.5366*	π(L)→π*(L) (IL)
S_{92}	H-3→L+11		6.47	191.6	*0.0744*	d→d/π*(CO) (LF/LLCT)
S_{99}	H-4→L+6		6.55	189.4	*0.0619*	π(L)→π*(CO)/π*(L) (LLCT/IL)
S_{100}	H-4→L+6		6.56	189.1	*0.1015*	π(L)→π*(CO)/π*(L) (LLCT/IL)
	H-5→L+5					π(L)→π*(L) (IL)
S_{106}	H-5→L+7		6.62	187.4	*0.0933*	π(L)→π*(L)/π*(CO) (LLCT/IL)
S_{107}	H-4→L+7		6.63	186.9	*0.0744*	π(L)→π*(L)/π*(CO) (LLCT/IL)
S_{110}	H-4→L+8		6.68	185.7	*0.0826*	π(L)→π*(L)/π*(CO) (LLCT/IL)
S_{117}	H-12→L+2		6.76	183.5	*0.0472*	π(L)→π*(L) (IL)
S_{121}	H-3→L+12		6.82	181.9	*0.0613*	d→d/π*(CO) (LF/LLCT)
S_{122}	H-10→L+1		6.82	181.7	*0.0564*	π(L)→π*(L) (IL)
S_{123}	H→L+22		6.83	181.5	*0.0501*	π(L)→π*(L)/π*(CO) (LLCT/IL)

Electronic Supplementary Material (ESI) for Dalton Transactions

		Triplet excited states			
T_1	H→L	3.04	407.4	*0.0000*	π(L)→π*(L) (IL)
T_2	H→L+1	3.13	396.5	*0.0000*	π(L)→π*(L) (IL)
T_3	H–2→L	3.22	385.2	*0.0000*	d/π(Cl)→π*(L) (MLCT/LLCT)
T_4	H–1→L	3.34	370.9	*0.0000*	d/π(Cl)→π*(L) (MLCT/LLCT)
	H–2→L				d/π(Cl)→π*(L) (MLCT/LLCT)
T_5	H–4→L	3.51	353.4	*0.0000*	π(L)→π*(L) (IL)

Table S7. Four low-lying singlet excited states of the three Re-complexes corresponding to the lowest singlet $^1S_1$ state optimized geometries with the TDDFT/B3LYP method.

State	Excitations	E_{cal}, eV	λ_{cal}, nm	×c4$_{cal}$	Character
			3a		
1	HOMO→LUMO	1.73	715.0	*0.0204*	d/π(Cl)→π*(L) (MLCT/LLCT)
2	H–1→LUMO	1.93	642.5	*0.0490*	d/π(Cl)→π*(L) (MLCT/LLCT)
3	H–2→LUMO	2.45	506.2	*0.0062*	d→π*(L) (MLCT)
4	HOMO→L+1	2.83	437.5	*0.0193*	d/π(Cl)→π*(L)
			3b		
1	HOMO→LUMO	2.60	477.8	*0.0033*	d/π(Cl)→π*(L) (MLCT/LLCT)
2	H–1→LUMO	2.90	428.3	*0.1272*	d/π(Cl)→π*(L) (MLCT/LLCT)
3	H–2→LUMO	3.23	383.9	*0.0017*	d→π*(L) (MLCT)
4	HOMO→L+1	3.29	376.9	*0.1040*	d/π(Cl)→π*(L) (MLCT/LLCT)
			3c		
1	HOMO→LUMO	2.60	477.0	*0.0336*	π(L)/d→π*(L) (LLCT/MLCT)
2	H–1→LUMO	3.09	401.7	*0.0441*	d/π(Cl)→π*(L) (MLCT/LLCT)
3	HOMO→L+1	3.18	390.4	*0.7395*	π(L)/d→π*(L) (LLCT/MLCT)
	H–2→LUMO				d/π(Cl)→π*(L) (MLCT/LLCT)
4	H–2→LUMO	3.25	382.0	*0.3410*	d/π(Cl)→π*(L) (MLCT/LLCT)
	HOMO→L+1				π(L)/d→π*(L) (LLCT/MLCT)

Table S8. The optimized Cartesian coordinates for all calculated states of **3a**.

S0			
75	-0.153371000	0.032855000	0.060718000
17	2.131703000	-0.143196000	-1.064233000
6	-0.975828000	0.625915000	-1.575835000
6	0.188939000	1.864806000	0.557846000
6	-1.840649000	0.071271000	0.958781000
8	-1.466272000	0.958737000	-2.576204000
8	0.411966000	2.965419000	0.860445000
8	-2.869962000	0.096693000	1.507901000
8	-2.321169000	-7.828018000	-5.797027000
8	-2.476745000	-9.231934000	-4.140913000
7	0.874553000	-0.962770000	1.794004000
7	-0.262100000	-2.110224000	-0.325319000
7	-0.776522000	-2.796829000	-1.305351000
7	-0.509103000	-4.090301000	-1.034375000
7	-2.223439000	-8.114909000	-4.600748000
6	1.420253000	-0.314285000	2.840067000
1	1.326266000	0.764832000	2.839878000
6	2.073383000	-0.975016000	3.877172000
1	2.494498000	-0.401087000	4.695257000
6	2.169836000	-2.366741000	3.835994000
1	2.672261000	-2.913040000	4.627865000
6	1.607864000	-3.049359000	2.759091000
1	1.661914000	-4.130781000	2.695591000
6	0.968534000	-2.320580000	1.754624000
6	0.341360000	-2.932180000	0.589279000
6	0.183321000	-4.222100000	0.130709000

1	0.518347000	-5.174384000	0.509261000
6	-0.945102000	-5.109575000	-1.932849000
6	-1.249715000	-6.381168000	-1.434798000
1	-1.187328000	-6.597754000	-0.374336000
6	-1.665718000	-7.375208000	-2.315600000
1	-1.909402000	-8.366057000	-1.953616000
6	-1.780446000	-7.068651000	-3.672339000
6	-1.487998000	-5.798878000	-4.174652000
1	-1.581720000	-5.592988000	-5.233501000
6	-1.060703000	-4.809499000	-3.295193000
1	-0.812286000	-3.820474000	-3.660575000
S1			
75	-0.107656000	0.011387000	0.066526000
17	1.967779000	-0.075064000	-1.144421000
6	-1.057195000	0.678731000	-1.531575000
6	0.188023000	1.888994000	0.530658000
6	-1.807550000	-0.038552000	1.084360000
8	-1.616092000	1.054759000	-2.460875000
8	0.368166000	2.995677000	0.793004000
8	-2.792626000	-0.067830000	1.672864000
8	-2.186904000	-7.871465000	-5.857459000
8	-2.583614000	-9.240887000	-4.116029000
7	0.900651000	-0.957783000	1.781496000
7	-0.242038000	-2.109648000	-0.319804000
7	-0.771590000	-2.790742000	-1.305451000
7	-0.514679000	-4.081536000	-1.039325000
7	-2.197392000	-8.103834000	-4.588371000
6	1.454817000	-0.300250000	2.820828000
1	1.373584000	0.779565000	2.810625000
6	2.103147000	-0.959126000	3.859477000

1	2.532878000	-0.383323000	4.671171000
6	2.185442000	-2.352352000	3.827467000
1	2.686169000	-2.896046000	4.622016000
6	1.614654000	-3.041933000	2.759651000
1	1.661658000	-4.123639000	2.704150000
6	0.975293000	-2.321910000	1.751081000
6	0.342435000	-2.934621000	0.592754000
6	0.171687000	-4.224659000	0.126367000
1	0.496144000	-5.183843000	0.496965000
6	-0.946875000	-5.102863000	-1.940699000
6	-1.383641000	-6.336878000	-1.434963000
1	-1.421432000	-6.512517000	-0.364189000
6	-1.794430000	-7.332538000	-2.309073000
1	-2.140575000	-8.286835000	-1.933838000
6	-1.780931000	-7.100933000	-3.703992000
6	-1.345816000	-5.849748000	-4.200091000
1	-1.331498000	-5.680146000	-5.268959000
6	-0.929409000	-4.859841000	-3.322989000
1	-0.581164000	-3.905230000	-3.702339000
		T	
75	0.086095000	-0.024477000	-0.038790000
17	2.372256000	-0.055859000	-0.825887000
6	-0.568719000	0.563361000	-1.780984000
6	0.306892000	1.907715000	0.410141000
6	-1.721575000	0.014732000	0.783367000
8	-0.941791000	0.889793000	-2.820836000
8	0.423346000	3.023700000	0.651182000
8	-2.761890000	0.039245000	1.267109000
8	-2.896729000	-7.723610000	-5.648339000
8	-2.076564000	-9.303764000	-4.286430000

7	0.901195000	-0.972206000	1.803977000
7	-0.115903000	-2.106023000	-0.355922000
7	-0.611191000	-2.786488000	-1.372132000
7	-0.490967000	-4.083033000	-1.040912000
7	-2.284599000	-8.066094000	-4.569735000
6	1.412262000	-0.313236000	2.861473000
1	1.398454000	0.768726000	2.811841000
6	1.936847000	-0.972153000	3.969464000
1	2.336715000	-0.393115000	4.794285000
6	1.935124000	-2.367677000	3.989391000
1	2.337144000	-2.910601000	4.838657000
6	1.409170000	-3.059873000	2.900452000
1	1.394461000	-4.143991000	2.883326000
6	0.898956000	-2.336987000	1.821540000
6	0.325297000	-2.944265000	0.629855000
6	0.087649000	-4.228758000	0.194483000
1	0.267684000	-5.185709000	0.653355000
6	-0.940609000	-5.091977000	-1.928361000
6	-0.707049000	-6.451647000	-1.636602000
1	-0.173980000	-6.752230000	-0.741562000
6	-1.150334000	-7.433410000	-2.504502000
1	-0.971035000	-8.478404000	-2.286440000
6	-1.838297000	-7.078502000	-3.692377000
6	-2.066838000	-5.707963000	-3.979381000
1	-2.594420000	-5.437554000	-4.885173000
6	-1.623469000	-4.729811000	-3.109345000
1	-1.804167000	-3.685313000	-3.333170000

Table S9. The optimized Cartesian coordinates for all calculated states of **3b**.

S0			
75	0.077645000	-0.059920000	-0.112402000
6	0.356507000	1.400280000	-1.335204000
6	-1.212876000	-0.832375000	-1.319160000
6	-1.299354000	0.915668000	0.784794000
8	0.550841000	2.286111000	-2.063192000
8	-1.983744000	-1.313767000	-2.045477000
8	-2.141497000	1.511473000	1.330825000
7	0.083929000	-1.697486000	1.427103000
7	1.597382000	0.494881000	1.351364000
7	2.394582000	1.524700000	1.442254000
7	3.145866000	1.317662000	2.539886000
17	1.966290000	-1.406896000	-1.183947000
17	7.193192000	5.350614000	4.202036000
6	-0.723745000	-2.774573000	1.407342000
1	-1.439068000	-2.824212000	0.595391000
6	-0.660155000	-3.780122000	2.368147000
1	-1.335863000	-4.625872000	2.302995000
6	0.278285000	-3.672374000	3.395817000
1	0.355361000	-4.438393000	4.160901000
6	1.119063000	-2.561910000	3.427319000
1	1.858731000	-2.446079000	4.212075000
6	0.998666000	-1.591976000	2.430243000
6	1.818905000	-0.388528000	2.371751000
6	2.826129000	0.145205000	3.149360000
1	3.299677000	-0.186204000	4.059874000
6	4.123496000	2.285488000	2.934586000

6	5.345017000	1.855412000	3.458306000
1	5.573845000	0.798004000	3.542475000
6	6.290176000	2.801522000	3.856172000
1	7.243111000	2.481390000	4.262957000
6	6.001019000	4.159204000	3.707651000
6	4.784761000	4.590434000	3.173183000
1	4.573396000	5.648922000	3.067693000
6	3.834847000	3.644896000	2.788338000
1	2.878543000	3.961579000	2.387325000
S1			
75	0.135493000	-0.095628000	-0.090262000
6	0.345202000	1.410952000	-1.333972000
6	-1.234542000	-0.757005000	-1.342677000
6	-1.238504000	0.830707000	0.972387000
8	0.470561000	2.301716000	-2.058050000
8	-2.037611000	-1.125772000	-2.084786000
8	-2.042073000	1.361719000	1.602770000
7	0.112538000	-1.713623000	1.370227000
7	1.624993000	0.463503000	1.329424000
7	2.431176000	1.517322000	1.414478000
7	3.145127000	1.323395000	2.527647000
17	1.851322000	-1.372409000	-1.269717000
17	7.193658000	5.360889000	4.185953000
6	-0.688128000	-2.815419000	1.353567000
1	-1.375606000	-2.886759000	0.517020000
6	-0.653006000	-3.800870000	2.313647000
1	-1.318106000	-4.653404000	2.230236000
6	0.267329000	-3.677256000	3.403645000
1	0.316902000	-4.438375000	4.175642000
6	1.088043000	-2.571443000	3.452072000

1	1.798527000	-2.442000000	4.263960000
6	1.019692000	-1.583736000	2.443684000
6	1.818335000	-0.411677000	2.390873000
6	2.822002000	0.167564000	3.167319000
1	3.277819000	-0.123998000	4.099455000
6	4.121153000	2.291511000	2.920968000
6	5.299874000	1.869185000	3.541393000
1	5.496057000	0.814251000	3.702254000
6	6.245480000	2.815702000	3.937382000
1	7.164811000	2.499201000	4.417809000
6	6.000757000	4.168098000	3.693172000
6	4.828373000	4.592819000	3.063934000
1	4.650469000	5.647578000	2.884341000
6	3.878830000	3.646881000	2.679215000
1	2.956013000	3.959138000	2.203770000
		T	
75	0.133603000	-0.141831000	-0.076664000
6	0.323979000	1.471012000	-1.250969000
6	-1.130148000	-0.934705000	-1.320644000
6	-1.326936000	0.765476000	0.869409000
8	0.445420000	2.413606000	-1.901357000
8	-1.872870000	-1.414971000	-2.068973000
8	-2.191985000	1.296923000	1.416418000
7	0.087572000	-1.676534000	1.362887000
7	1.634210000	0.461590000	1.348853000
7	2.437075000	1.502688000	1.428997000
7	3.163588000	1.313634000	2.540117000
17	2.027675000	-1.134727000	-1.335674000
17	7.205954000	5.369314000	4.167387000
6	-0.774502000	-2.755918000	1.384365000

1	-1.496503000	-2.792177000	0.576704000
6	-0.732533000	-3.737933000	2.332628000
1	-1.433838000	-4.563741000	2.275008000
6	0.244136000	-3.668191000	3.391990000
1	0.295735000	-4.443024000	4.149492000
6	1.100247000	-2.584285000	3.424212000
1	1.840138000	-2.486632000	4.214193000
6	1.024972000	-1.580910000	2.444500000
6	1.832879000	-0.412205000	2.400085000
6	2.839876000	0.156952000	3.178205000
1	3.294841000	-0.140167000	4.109159000
6	4.138961000	2.285852000	2.925527000
6	5.336291000	1.866593000	3.511225000
1	5.547678000	0.811260000	3.649406000
6	6.280202000	2.817653000	3.900783000
1	7.213862000	2.504054000	4.354857000
6	6.015106000	4.170770000	3.683521000
6	4.823915000	4.592202000	3.088404000
1	4.630500000	5.647588000	2.929808000
6	3.875579000	3.641820000	2.711553000
1	2.938280000	3.951726000	2.263366000

Table S9. The optimized Cartesian coordinates for all calculated states of **3c**.

S0			
75	-0.191870000	0.038035000	0.086016000
17	2.084751000	-0.081803000	-1.070185000
6	-1.045331000	0.633027000	-1.533308000
6	0.124521000	1.869601000	0.599609000
6	-1.866992000	0.036433000	1.004584000
8	-1.554610000	0.967533000	-2.524127000
8	0.331740000	2.971080000	0.912660000
8	-2.889952000	0.037386000	1.567133000
7	0.874537000	-0.957816000	1.795267000
7	-0.268453000	-2.102263000	-0.321230000
7	-0.790665000	-2.792826000	-1.301985000
7	-0.490146000	-4.080582000	-1.053372000
7	-2.114010000	-8.154070000	-4.574805000
6	1.421154000	-0.312512000	2.843171000
1	1.308172000	0.764825000	2.857032000
6	2.097351000	-0.973737000	3.864604000
1	2.517984000	-0.402712000	4.685001000
6	2.216840000	-2.363435000	3.804721000
1	2.737622000	-2.910579000	4.584180000
6	1.654251000	-3.042388000	2.726290000
1	1.725335000	-4.121942000	2.648649000
6	0.990572000	-2.313577000	1.736831000
6	0.360431000	-2.921800000	0.572335000
6	0.222907000	-4.210959000	0.095906000
1	0.583106000	-5.163951000	0.449740000
6	-0.919287000	-5.110613000	-1.949026000

6	-1.387721000	-6.325186000	-1.437699000
1	-1.452527000	-6.484559000	-0.365438000
6	-1.796297000	-7.329325000	-2.309279000
1	-2.161143000	-8.270636000	-1.907256000
6	-1.758113000	-7.133190000	-3.705846000
6	-1.292141000	-5.895352000	-4.198884000
1	-1.249103000	-5.725429000	-5.271394000
6	-0.871804000	-4.894314000	-3.330362000
1	-0.502693000	-3.951879000	-3.721256000
1	-2.716934000	-8.877101000	-4.199981000
1	-2.380967000	-7.878149000	-5.512478000
		S1	
75	-0.006657000	-0.013895000	-0.012758000
17	2.377287000	-0.249089000	-1.049568000
6	-0.696741000	0.554133000	-1.726254000
6	0.396636000	1.827638000	0.446259000
6	-1.733047000	0.122520000	0.784378000
8	-1.113716000	0.873505000	-2.768020000
8	0.648614000	2.929640000	0.725036000
8	-2.789626000	0.202518000	1.276122000
7	0.876549000	-0.941270000	1.768796000
7	-0.184454000	-2.115581000	-0.358331000
7	-0.680412000	-2.807921000	-1.357411000
7	-0.506697000	-4.103938000	-1.030532000
7	-2.243285000	-8.023863000	-4.549940000
6	1.395242000	-0.301017000	2.851093000
1	1.375040000	0.783285000	2.809418000
6	1.925317000	-0.944967000	3.949380000
1	2.325058000	-0.359018000	4.770171000
6	1.938597000	-2.375739000	3.980860000

1	2.346517000	-2.911253000	4.831872000
6	1.416154000	-3.056218000	2.899695000
1	1.402876000	-4.142872000	2.882064000
6	0.889131000	-2.350151000	1.797934000
6	0.322712000	-2.955857000	0.641218000
6	0.106701000	-4.246783000	0.188539000
1	0.332434000	-5.203392000	0.627509000
6	-0.940562000	-5.103465000	-1.918651000
6	-0.728261000	-6.468383000	-1.615022000
1	-0.226683000	-6.765827000	-0.703132000
6	-1.158124000	-7.440328000	-2.487705000
1	-0.996374000	-8.488539000	-2.260482000
6	-1.819344000	-7.077699000	-3.701339000
6	-2.022753000	-5.693330000	-3.996371000
1	-2.521565000	-5.409984000	-4.917172000
6	-1.590758000	-4.728355000	-3.120084000
1	-1.744294000	-3.680303000	-3.339706000
1	-2.107916000	-9.009232000	-4.355241000
1	-2.713078000	-7.789736000	-5.416809000
	T		
75	-0.013049000	0.038642000	-0.008242000
17	2.367832000	-0.220087000	-0.973998000
6	-0.689960000	0.639538000	-1.704597000
6	0.385774000	1.863023000	0.489664000
6	-1.749746000	0.170552000	0.765449000
8	-1.094979000	0.978240000	-2.742676000
8	0.640761000	2.958315000	0.797046000
8	-2.814524000	0.251712000	1.241076000
7	0.855924000	-0.967286000	1.800021000
7	-0.188798000	-2.076298000	-0.372108000

7	-0.708783000	-2.751267000	-1.408760000
7	-0.511820000	-4.122489000	-1.066083000
7	-2.239914000	-8.070797000	-4.532988000
6	1.361415000	-0.328723000	2.872898000
1	1.313390000	0.753508000	2.854695000
6	1.918056000	-1.001978000	3.956271000
1	2.310056000	-0.436305000	4.794489000
6	1.958114000	-2.398134000	3.933608000
1	2.386427000	-2.955116000	4.761062000
6	1.437289000	-3.068760000	2.830020000
1	1.451640000	-4.152149000	2.779292000
6	0.890740000	-2.329172000	1.776719000
6	0.309792000	-2.927593000	0.582758000
6	0.124100000	-4.221259000	0.179448000
1	0.371069000	-5.160982000	0.642641000
6	-0.926274000	-5.094479000	-1.905629000
6	-0.734965000	-6.487652000	-1.588390000
1	-0.247623000	-6.778022000	-0.665846000
6	-1.167255000	-7.453920000	-2.454076000
1	-1.019918000	-8.502236000	-2.210880000
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6	-1.574991000	-4.740086000	-3.147216000
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1	-2.123171000	-9.053739000	-4.319524000
1	-2.703128000	-7.843815000	-5.404383000