Supporting Information for

Syntheses, Structures and Properties of Tricarbonyl (chloro) Rhenium(I) Complexes with Redox-Active Tetrathiafulvalene-Pyrazole Ligands

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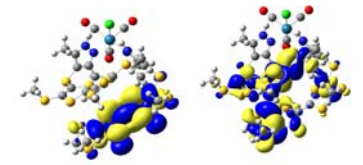
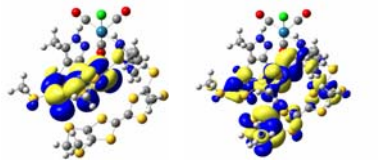
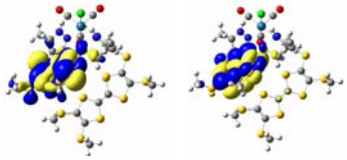
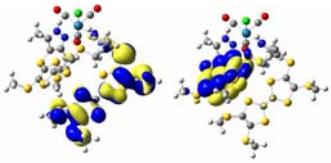
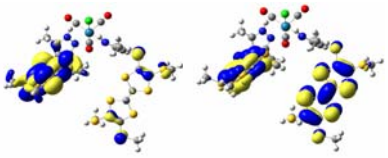
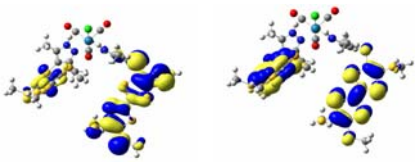
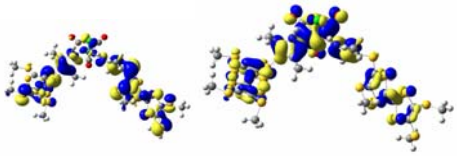
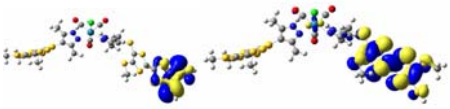
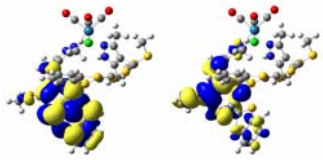
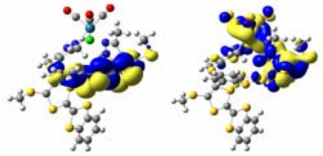
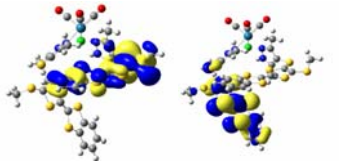
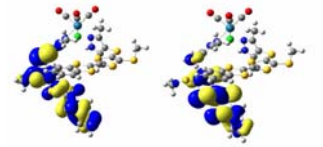
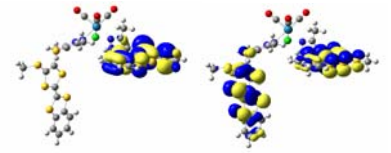
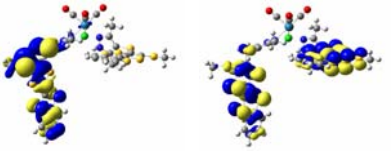
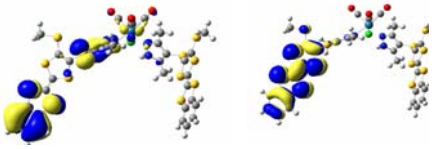
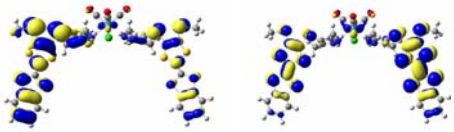
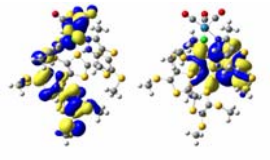
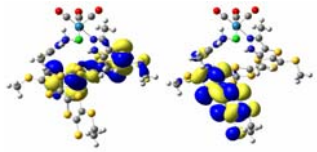
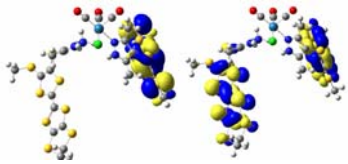
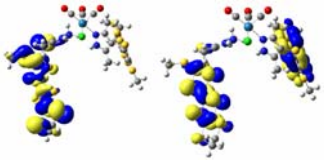
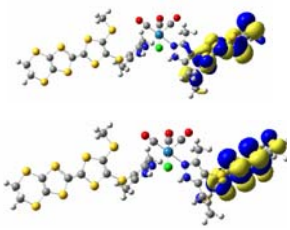
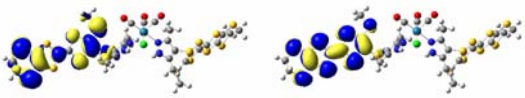
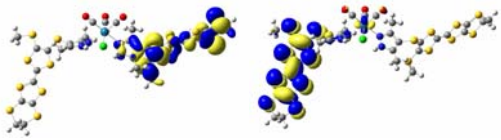
Table S1. Main experimental and calculated optical transitions for 5a–d and their corresponding oxidized states.

	Orbital Excitations [a]	Character	Calcd/nm	f [b]	Exptl/nm
5a	279→283	ICT	388	0.0336	333
					
	278→282	π→π*	375	0.0426	
					
5a$^{\bullet+}$	274β→279β	π→π*	923	0.0788	823
					
	273β→279β	ICT	829	0.0627	
					
5a^{2+}	274→279	ICT π→π*	926	0.1929	822
					
	273→279	π→π*	922	0.1160	
					
5a$^{\bullet3+}$	270α→279α	π→π*	1060	0.0292	822
					
5a^{4+}	273→278	π→π*	882	0.3561	821
					

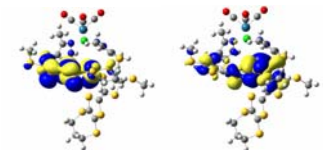
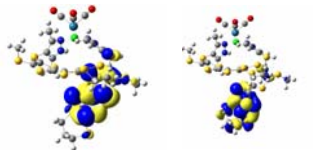
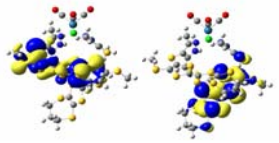
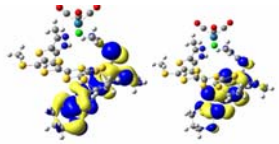
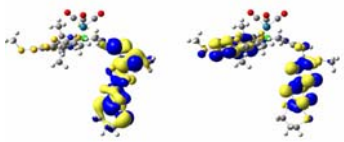
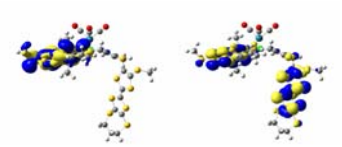
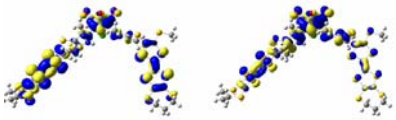
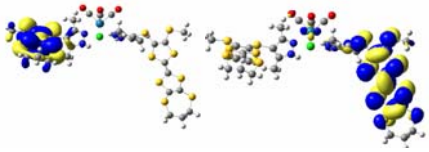
[a] The molecular orbital No. involved in each transition; [b] Oscillator strength.

	Orbital Excitations	Character	Calcd /nm	f^b	Exptl /nm
5b	256→261	π→π*	357	0.0337	358(sh)
					
	257→260	π→π*	367	0.0349	
					
5b$^{\bullet+}$	251*β*→257*β*	ICT	800	0.0986	776
					
	252*β*→257*β*	π→π*	804	0.0451	
					
5b^{2+}	252→257	ICT π→π*	835	0.2012	768
					
	251→257	ICT π→π*	877	0.1344	
					
5b$^{\bullet3+}$	252*α*→257*α*	π→π*	1015	0.0124	765
					
5b^{4+}	251→257	π→π*	821	0.0053	777
					

[a] The molecular orbital No. involved in each transition; [b] Oscillator strength.

	Orbital Excitations	Character	Calcd /nm	f^b	Exptl /nm
5c	276→281 	ICT	355	0.0295	343
5c$^{\bullet+}$	271*β*→277*β* 	ICT	968	0.0842	906
5c^{2+}	271→277 	ICT π→π*	985	0.1924	909
	272→277 	ICT π→π*	1011	0.1731	
5c$^{\bullet3+}$	274*β*→277*β* 	π→π*	937	0.0544	909
	275*β*→276*β* 	π→π*	954	0.3298	
5c^{4+}	271→277 	ICT	893	0.1683	903

[a] The molecular orbital No. involved in each transition; [b] Oscillator strength.

	Orbital Excitations	Character	Calcd /nm	f^b	Exptl /nm
5d	285→289 	π→π*	388	0.0367	337 392
	284→287 	π→π*	392	0.0242	
5d$^{\bullet+}$	279*β*→285*β* 	ICT	852	0.0875	815
	280*β*→285*β* 	π→π*	903	0.0587	
5d^{2+}	279→285 	ICT π→π*	929	0.1303	813
	280→285 	ICT π→π*	936	0.2113	
5d$^{\bullet3+}$	283*β*→285*β* 	π→π*	881	0.1647	812
5d^{4+}	279→285 	ICT	892	0.0015	814

[a] The molecular orbital No. involved in each transition; [b] Oscillator strength.

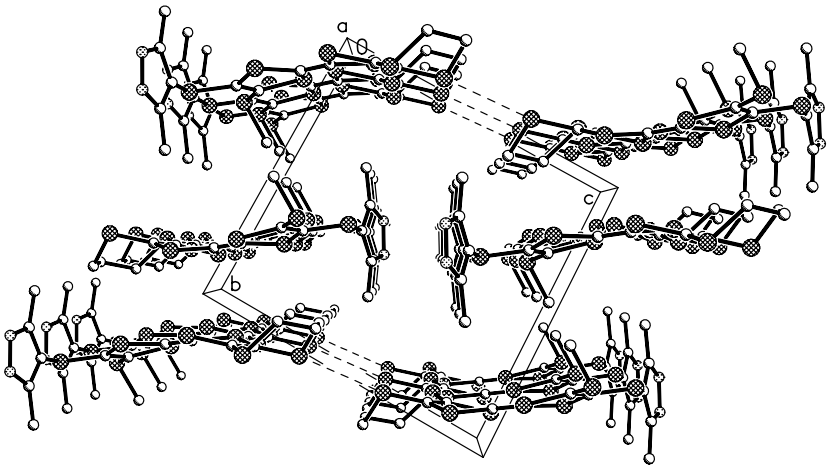


Figure S1. The packing diagram of compound **4d** view along the *a* axis(the dotted line representing the S···S non-bonded contacts less than 3.7 Å).

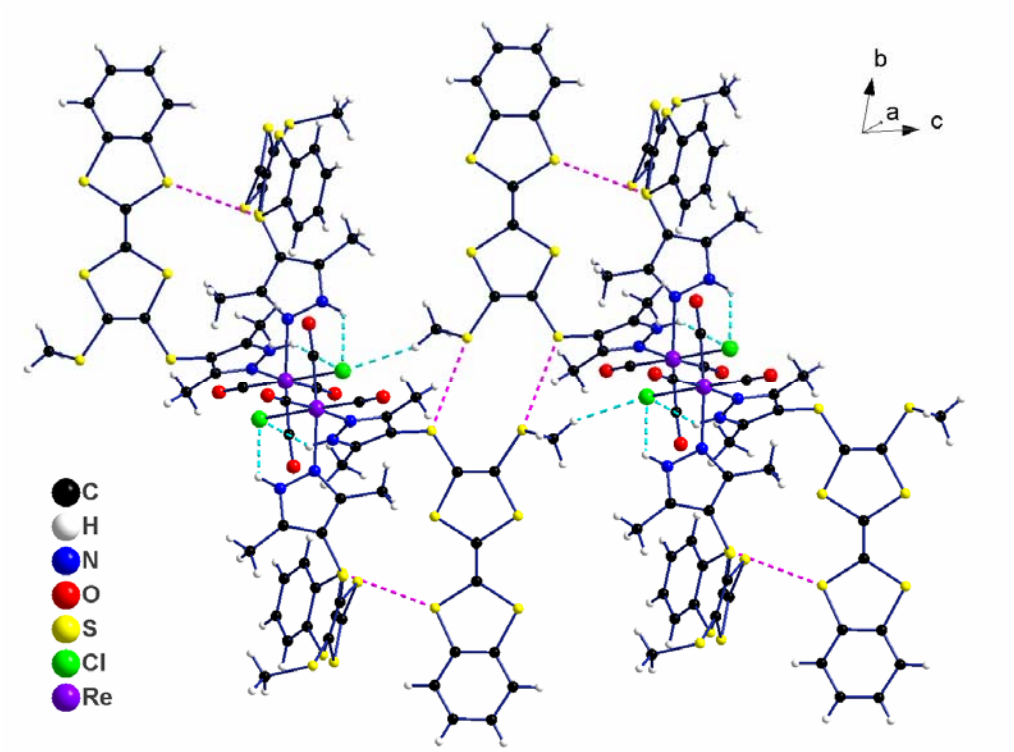


Figure S2. The packing diagram of compound **5b**. The dotted line representing the S···S non-bonded contacts (red) less than 3.7 Å and the H-bonding (blue).

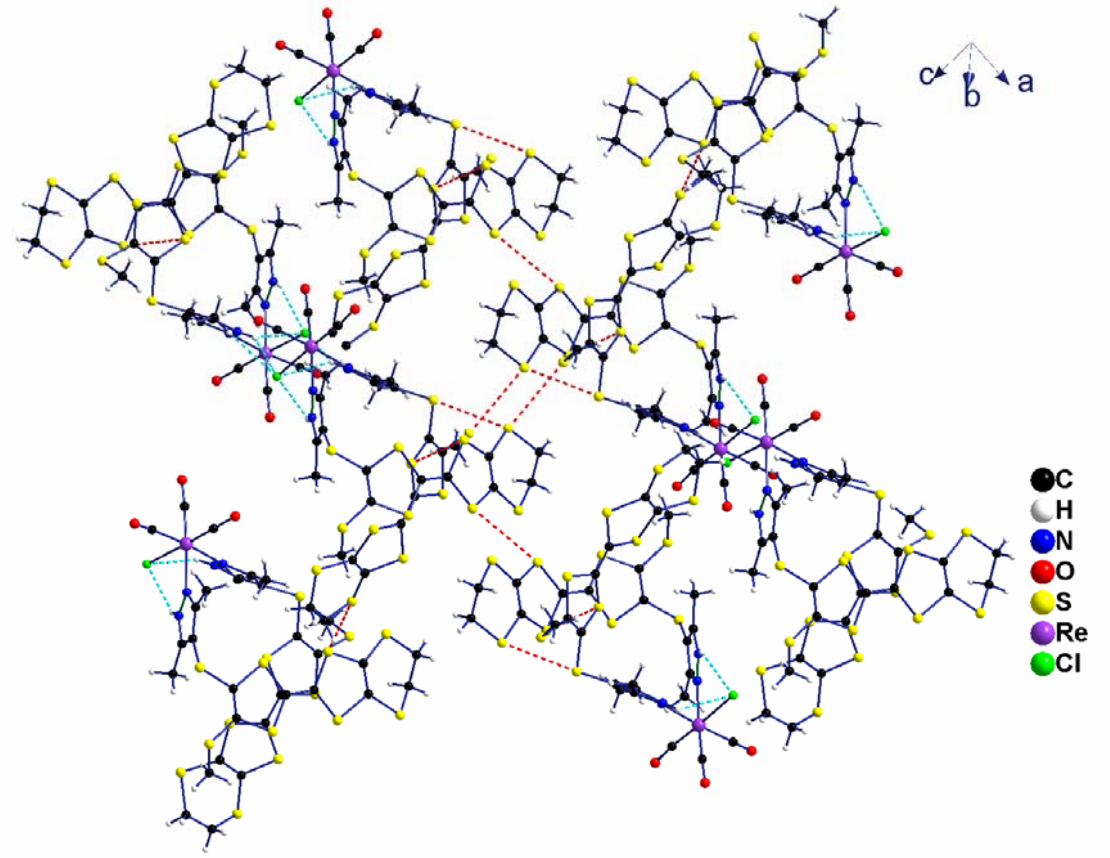


Figure S3. The packing diagram of compound **5c**. The dotted line representing the S···S non-bonded contacts (red) less than 3.7 Å and the H-bonding (blue).

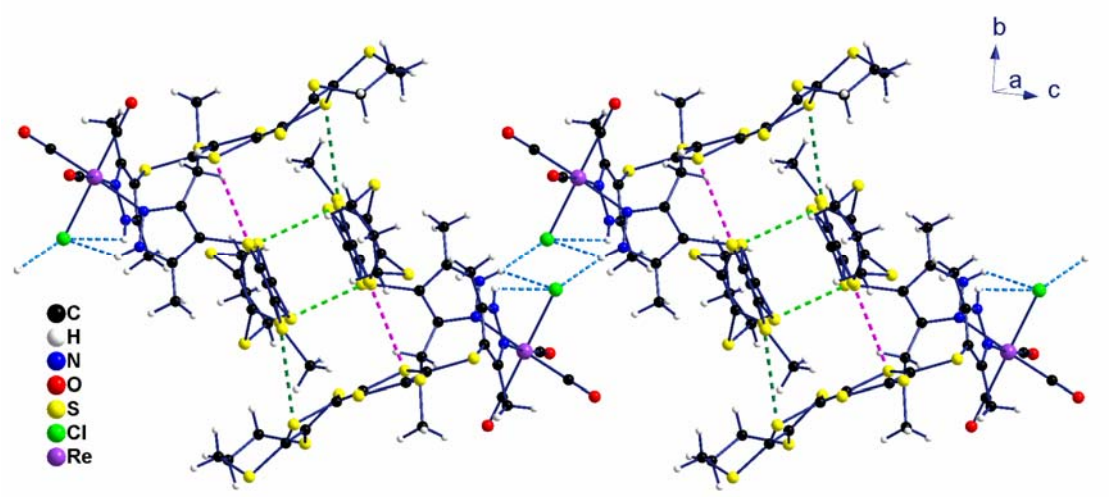


Figure S4. The packing diagram of compound **5d**. The dotted line representing the S···S non-bonded contacts (red and green) less than 3.7 Å and the H-bonding (blue).

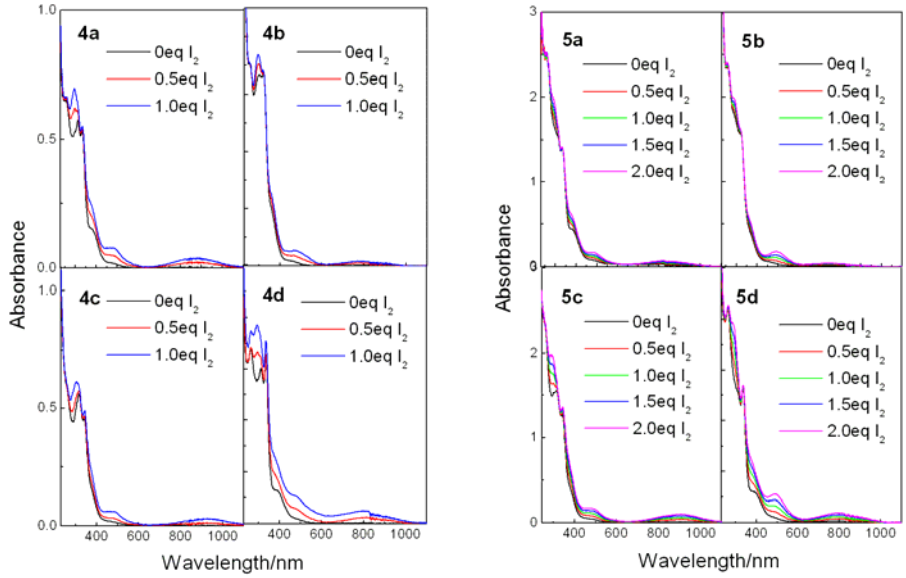


Figure S5. UV-vis absorption spectra for **4a–d** (4×10^{-5} M) and **5a–d** (4×10^{-5} M), in the presence of varying amounts of I_2, measured in CH_2Cl_2.

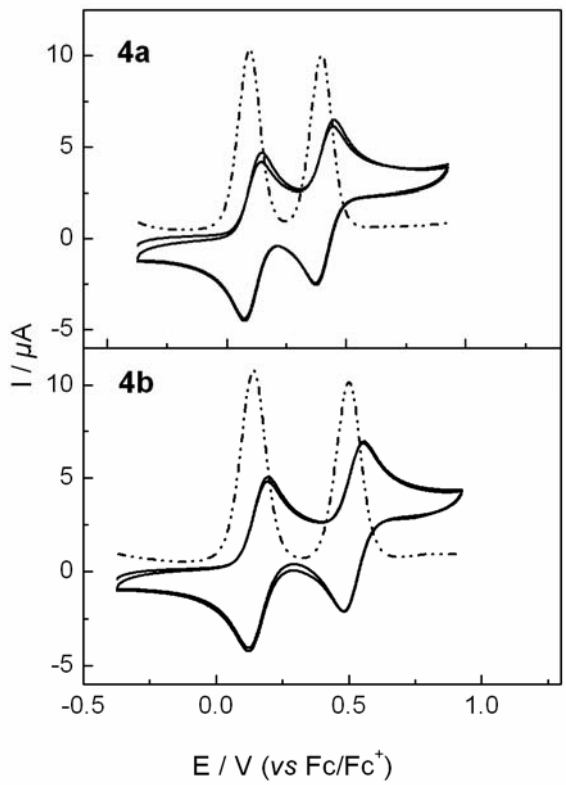
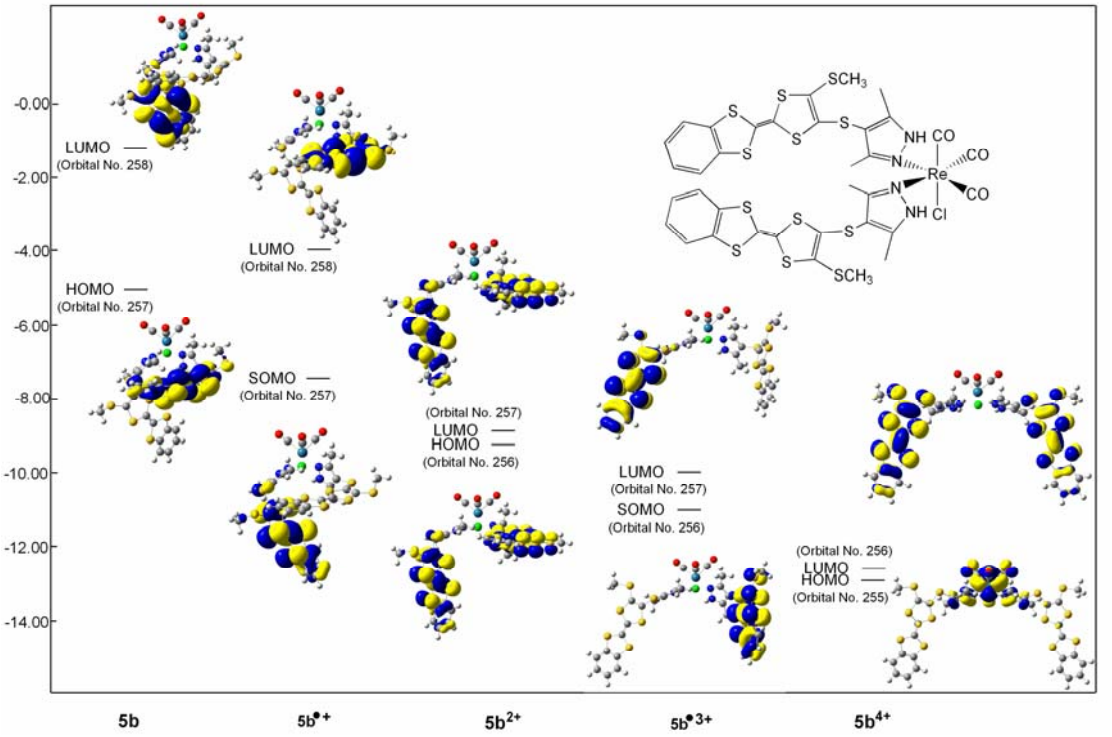
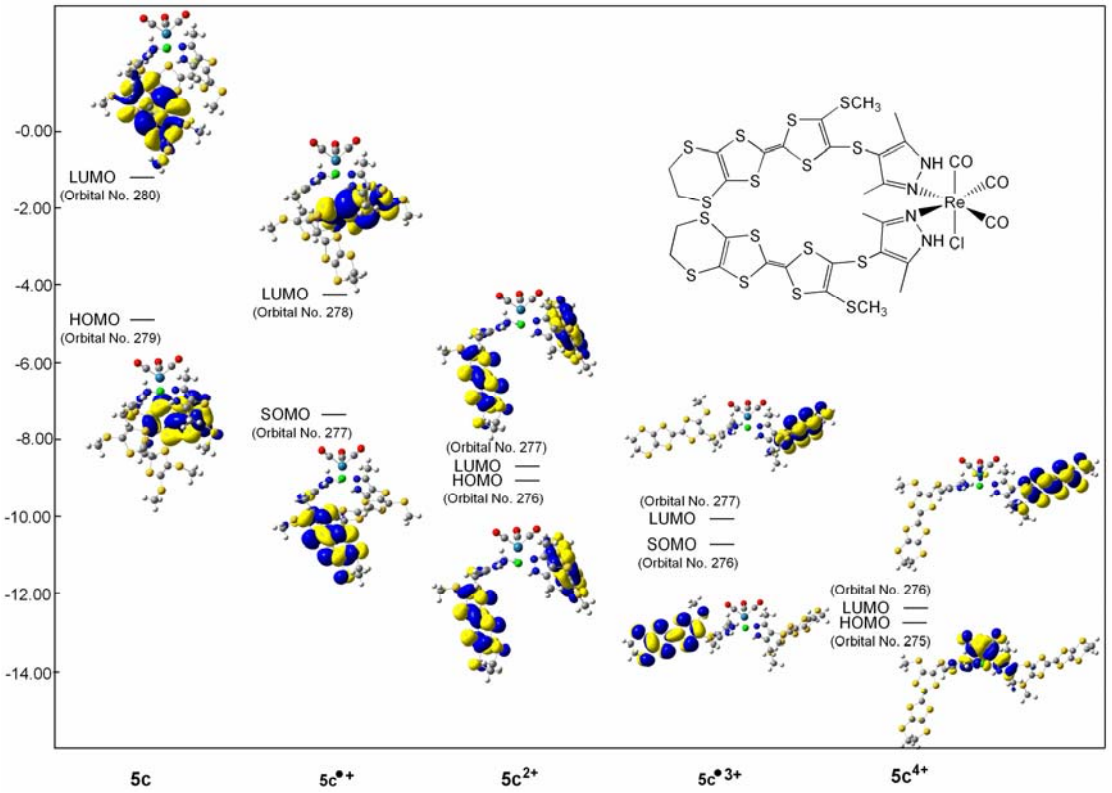


Figure S6. Cyclic voltammogram (solid line) and differential pulse voltammogram (dash-dotted line) for compounds **4a** and **4b** (10^{-3} M), measured in CH_2Cl_2 (vs Fc/Fc^+). The scan rate for CV measurements was 50 mV/s; the step increment and pulse width for DPV measurements were 4 mV and 0.05s, respectively.


-0.00
-2.00
-4.00
-6.00
-8.00
-10.00
-12.00
-14.00
LUMO
(Orbital No. 258)
HOMO
(Orbital No. 257)
LUMO
(Orbital No. 258)
SOMO
(Orbital No. 257)
(Orbital No. 257)
LUMO
HOMO
(Orbital No. 256)
LUMO
(Orbital No. 257)
SOMO
(Orbital No. 256)
(Orbital No. 256)
LUMO
HOMO
(Orbital No. 255)
SCH3
NH CO
CO
Re
CO
NH Cl
5b
5b•+
5b2+
5b•3+
5b4+


-0.00
-2.00
-4.00
-6.00
-8.00
-10.00
-12.00
-14.00
LUMO
(Orbital No. 280)
HOMO
(Orbital No. 279)
LUMO
(Orbital No. 278)
SOMO
(Orbital No. 277)
(Orbital No. 277)
LUMO
HOMO
(Orbital No. 276)
(Orbital No. 277)
LUMO
SOMO
(Orbital No. 276)
(Orbital No. 276)
LUMO
HOMO
(Orbital No. 275)
SCH3
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CO
Re
CO
NH Cl
5c
5c•+
5c2+
5c•3+
5c4+

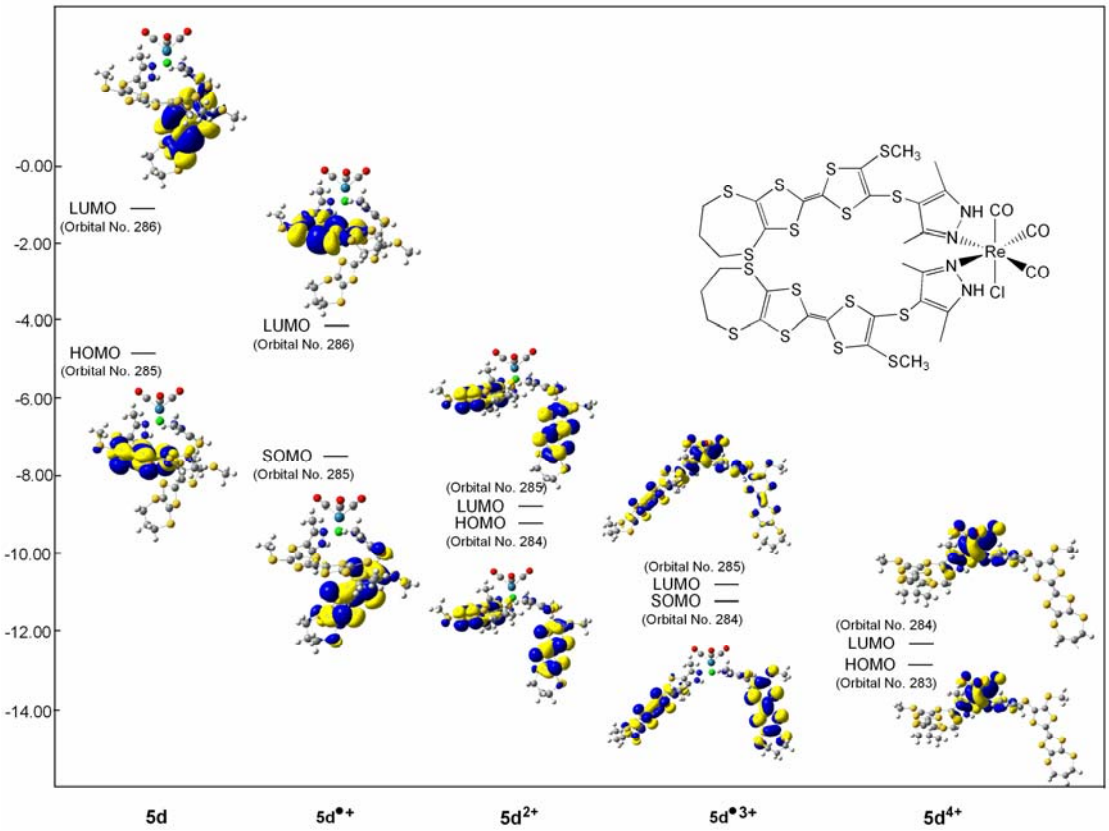

Figure S7. Frontier orbitals for complexes **5b–d** in the neutral, radical cation, dication, trication and tetracation states.