Supporting Information

Ferrocene-dithiolene hybrids: control of strong donor-acceptor electronic communication to reverse the charge transfer direction

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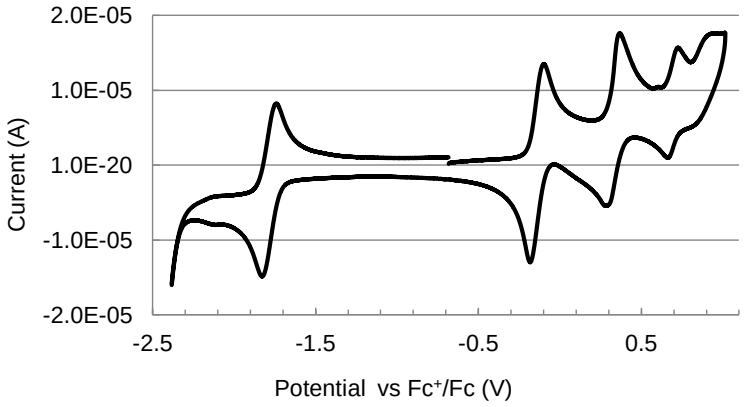

Figure S1. Cyclic voltammogram of $FcS_4dt[Pt(^tBu_2bpy)]$ with a sweep area from -2.4 V to 0.75 V. Condition: 0.1 M $Bu_4N{\cdot}ClO_4$ in CH_2Cl_2, room temperature, GC working electrode, Pt counter electrode, scan rate of 100 $mV{\cdot}s^{-1}$.

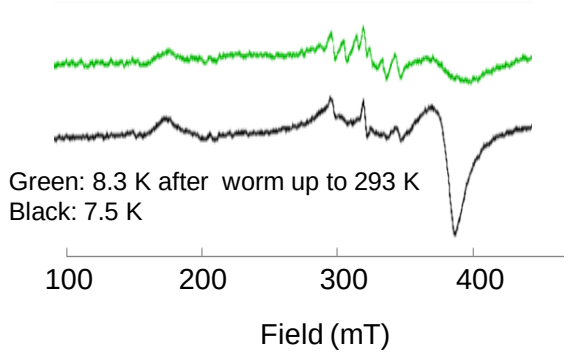

Figure S2. EPR spectra of $[FcS_4dt(Me)_2]^{\cdot+}$ in frozen CH_2Cl_2 measured at 7.5 K (black line). The sample was warmed up to 293 K and was again cooled down to 8.3 K, at which EPR spectrum was recorded (green line).

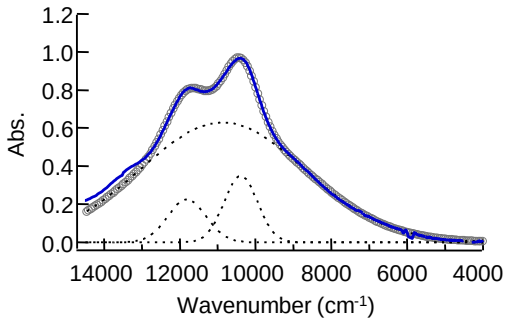

Figure S3. Deconvolution of the spectrum of $[FcS_4dt[Pt(^tBu_2bpy)]]^{\cdot+}$ (blue line) at NIR region. Dotted lines represent Gaussian curves, and gray circles show a sum of the Gaussian curves. It is noted that three Gaussian curves were used to reproduce the obtained spectrum in the range from 12500 to 4000 cm^{-1} and that the shoulder at 13260 cm^{-1} were not considered in this deconvolution to avoid over-parameterization.

Table S1. Crystal Data and Refinement Parameters for $FcS_4dt(Me)_2$, $FcS_4dt[Pt(^tBu_2bpy)]$, and $[FcS_4dt[Pt(^tBu_2bpy)]](F4TCNQ)\cdot C_6H_{14}\cdot CH_2Cl_2$

	$FcS_4dt(Me)_2$	**$FcS_4dt[Pt(^tBu_2bpy)]$**	**$[FcS_4dt[Pt(^tBu_2bpy)]](F4TCNQ)\cdot C_6H_{14}\cdot CH_2Cl_2$**
Empirical formula	$C_{16}H_{12}FeS_6$	$C_{32}H_{32}FeN_2PtS_6$	$C_{48}H_{41}Cl_2F_4FeN_6PtS_6$
Fw	452.57	887.90	1292.07
Crystal dimension (mm)	0.30 ×0.10 × 0.10	0.20 ×0.10 × 0.10	0.10 ×0.05 × 0.01
Crystal system	monoclinic	monoclinic	triclinic
Lattice parameters	*a* = 11.930(3) Å	*a* = 14.482(3) Å	*a* = 11.320(6) Å
	b = 15.096(3) Å	*b* = 11.329(2) Å	*b* = 12.296(6) Å
	c = 19.621(4) Å	*c* = 20.162(4) Å	*c* = 19.737(10) Å
			α = 95.252(9)°
	β = 96.861(3)°	β = 101.890(3)°	β = 97.482(10)°
			γ = 94.938(8)°
	V = 3508(1) Å^3	*V* = 3236(9) Å^3	*V* = 2699(2) Å^3
Space group	*P*2$_1$/*c*	*P*2$_1$/*a*	*P*-1
Z value	8	4	2
λ	0.7107 Å	0.7107 Å	0.7107 Å
T	113 K	113 K	93 K
μ(Mo Kα)	1.567 mm^{-1}	5.179 mm^{-1}	3.241 mm^{-1}
D(calc)	1.713 g/cm^3	1.822 g/cm^3	1.590 g/cm^3
R_1	0.0455	0.0647	0.083
WR_2	0.1363	0.1004	0.2088
Goodness of fit	1.076	1.123	1.034

Table S2. Absorption Wavelengths and Energies of $FcS_4dt(Me)_2$. and the Corresponding Transition Energies and Oscillator Strengths Calculated by the TD-DFT Method

λ_{max}[a]/ nm	E_{max}[a]/ eV	E_{calc}[b] / eV	Osillator strength f[c]	Configuration[d]	coefficient
322	3.85	3.76	0.184	111 ->117	-0.39
				113 ->119	0.35
		3.73	0.0837	111 ->117	0.51
		3.73	0.0203	114 ->120	-0.31
				115 ->120	0.30
374	3.31	3.49	0.0187	113 ->119	-0.34
				113 ->121	0.59
450	2.75	3.00	0.012	113 ->117	0.50
				115 ->119	-0.41
		2.891	0.0086	116 ->119	0.67

a: Absorption maxima.

b: Corresponding transition energy calculated by the TD-DFT method.

c: Oscillator strength calculated by the TD-DFT method.

d: Main contributions (> 0.3) are shown.

Table S3. Absorption Wavelengths and Energies of $FcS_4dt[Pt(^tBu_2bpy)]$ and the Corresponding Transition Energies and Oscillator Strengths Calculated by the TD-DFT Method

λ_{max}[a]/ nm	E_{max}[a]/ eV	E_{calc}[b] / eV	Osillator strength f[c]	Configuration[d]	coefficient
630	1.97	1.71	0.129	184 ->185	0.69
393	3.15	2.73	0.0197	183 ->185	0.68
		2.92	0.0107	184 ->188	0.70
		2.94	0.0471	181 ->185	0.67
360	3.44	3.30	0.0561	184 ->189	0.49
				184 ->191	-0.48

a: Absorption maxima.

b: Corresponding transition energy calculated by the TD-DFT method.

c: Oscillator strength calculated by the TD-DFT method.

d: Main contributions (> 0.3) are shown.

Table S4. Absorption Wavelengths and Energies of $[FcS_4dt[Pt(^tBu_2bpy)]]^{\bullet+}$, and the Corresponding Transition Energies and Oscillator Strengths Calculated by the TD-DFT Method

λ_{max}[a]/ nm	E_{max}[a]/ eV	E_{calc}[b] / eV	Osillator strength f[c]	Configuration[d]	coefficient
920	1.35	1.14	0.0965	183B ->184B	0.99
968 852 732	1.28 1.45 1.69	1.42	0.2705	181B ->184B	0.96
580	2.14	2.36 2.37	0.0262 0.01	184A ->185A 175B ->184B 177B ->184B	0.94 0.85 0.33
470	2.64	2.73	0.0164	173B ->184B	0.93

a: Absorption maxima.

b: Corresponding transition energy calculated by the TD-DFT method.

c: Oscillator strength calculated by the TD-DFT method.

d: Main contributions (> 0.3) are shown.