Electronic Supplementary Information for Dalton Transactions

Supporting information:

Functionalized ferrocenes and ferroceniums: synthesis, crystal structures and electrochemical properties based on carbazole/ phenothiazine-ferrocene conjugated molecules

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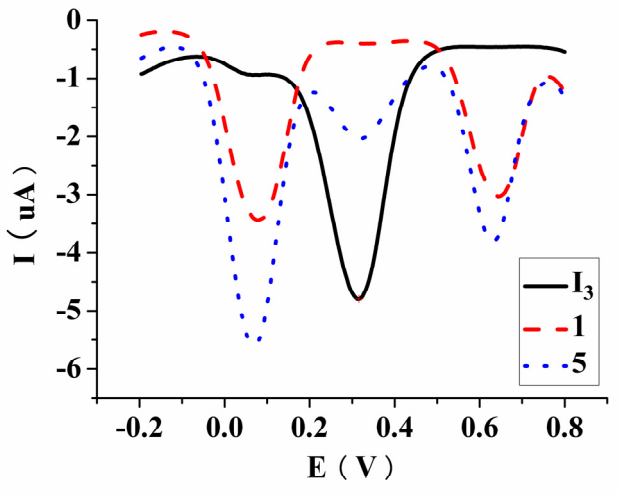

Fig. S1 Differential pulse voltammetry (DPV) response of 1 mM solution of **1** and **5** at the same scan rate of 50 mV/s in CH_2Cl_2 with 0.1 M TBAP at room temperature (Vs. Ag/AgCl; scan range: -0.2~0.8 V)

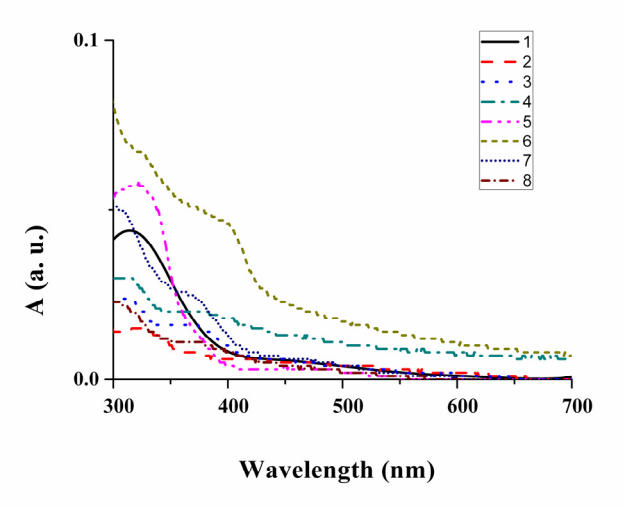

Fig. S2 The linear absorption spectra of **1-8** (1×10^{-5} mol L^{-1}) in benzene.

Table S1. Comparison of atomic distances (Å) and angles (°) for **1, 2, 3, 5**.

	1	**2**	**3**	**5**
C=C	1.240(6)	1.308(8)/ 1.333(8)	1.329(5)	1.173(1)
C-Cp	1.379	1.399 (Fe_1)/ 1.399 (Fe_2)	1.395	1.391
Fe(i)~C	2.026	2.025(Fe_1)/ 2.027 (Fe_2)	2.028	2.066
Fe(i)~Cp	1.650, 1.651	1.644,1.637; 1.644,1.639	1.638, 1.641	1.692, 1.696
Stag-Cp	17.00	3.39 (Fe_1)/ 16.61 (Fe_2)	3.31	2.37
Dihe-Cp	0.87	2.65 (Fe_1)/ 0.84 (Fe_2)	1.07	3.00
Dihe-Cp-ben	16.51	9.77 (Fe_1)/ 5.95 (Fe_2)	6.47	8.40
Dihe-ben	2.16	4.63	39.70	2.04

Table S2. Calculated energy (eV), composition (%) of selected frontier orbitals for **1-4** with BP/TZP method.

Orbitals	L+5	L+4	L+3	L+2	L+1	L	H	H-1	H-2	H-3	H-4	H-5
						1						
E / eV	-3.97	-4.47	-4.83	-4.99	-5.49	-5.77	-8.12	-8.24	-8.52	-8.68	-9.09	-9.43
Fe_1	0.5	2.1	38.3	55.3	7	10.6	62.7	83.2	31.8	83.1	1	2.3
Cp_1	3.7	4.8	37	44.2	5.6	9.4	12.1	16.4	17	8.4	4.4	22.5
Spacer	95.8	93.1	24.7	0.6	87.4	79.9	25.2	0.4	51.2	8.5	94.6	75.3
						2						
E / eV	-4.82	-4.98	-5.01	-5.53	-5.62	-5.79	-8.09	-8.20	-8.27	-8.28	-8.51	-8.66
Fe_1	18.1	55.0	0.0	7.0	3.6	8.7	23.4	38.2	0.0	82.7	18.3	26.1
Cp_1	17.9	44.5	0.0	5.7	3.0	7.5	5.3	7.3	0.0	17.0	8.7	6.0
Fe_2	23.2	0.0	54.9	7.8	3.3	8.0	29.0	33.9	82.9	0.0	21.8	46.7
Cp_2	23.2	0.0	44.6	6.3	2.8	7.0	6.4	6.4	16.8	0.0	10.1	5.4
Spacer	17.6	0.5	0.5	73.1	87.4	68.8	36.0	14.2	0.2	0.2	41.0	15.7
						3						
E / eV	-4.72	-4.94	-5.06	-5.09	-5.12	-5.86	-8.16	-8.33	-8.42	-8.74	-8.99	-9.47
Fe_1	7.9	32.9	53.3	3.3	1.4	14.0	43.1	83.0	37.3	87.2	10.9	1.1
Cp_1	10.7	29.3	43.3	2.6	1.1	12.2	9.1	16.7	10.2	7.5	21.9	11.0
Spacer	81.4	37.7	3.3	94.1	97.4	73.8	47.7	0.3	52.5	5.3	67.2	87.9
						4						
E / eV	-5.04	-5.05	-5.08	-5.12	-5.77	-5.95	-8.09	-8.24	-8.31	-8.33	-8.42	-8.70
Fe_1	0.5	53.4	5.5	1.2	7.7	6.7	17.1	36.0	0.6	83.0	25.2	3.5
Cp_1	0.4	43.4	4.4	0.9	6.6	5.9	4.2	6.8	0.1	16.8	7.2	0.7
Fe_2	53.5	0.7	5.7	1.4	7.6	6.8	19.3	39.2	82.1	0.0	22.0	85.1
Cp_2	43.4	0.5	4.6	1.2	6.5	6.1	4.6	7.4	16.8	0.0	6.8	7.3
Spacer	2.2	2.0	79.8	95.2	71.7	74.6	54.7	10.6	0.4	0.2	38.8	3.3