Electronic Supplementary Information for Dalton Transactions

Cucurbit[7]uril-included neutral intramolecular charge-transfer ferrocene derivatives

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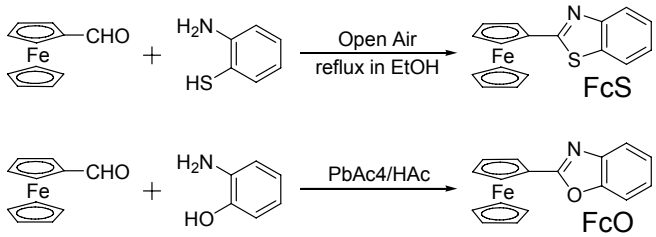
Electronic Supplementary Information

Materials. Ferrocenecarboxaldehyde was synthesized according to the literature method.[1] Other reagents and materials were used as received.

Scheme S1.



2-Ferrocenyl benzothiazole (FcS). The mixture of ferrocenecarboxaldehyde (214 mg, 1.00 mmol) and 2-aminothiophenol (120 μl, 1.12 mmol) was refluxed in 15 ml ethanol for 8 h. After the system cooled down, the product was furnished as reddish-brown crystalline solid (264 mg, 0.83 mmol, 83% yield), the filtrate could be concentrated and further neutral aluminum oxide chromatograph with petroleum ether and dichloromethane gave another 22 mg product, the total yield was 90%. MS: *m/z* = 319 (M^+). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.97 (d, J = 8 Hz, 1H), 7.82 (dd, J = 8 and 1 Hz, 1H), 7.45 (t, J = 8 Hz, 1H), 7.34 (t, J = 8 Hz, 1H), 5.01 (s, 2H), 4.50 (s, 2H), 4.15 (s, 5H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 169.7, 153.9, 134.7, 126.1, 124.4, 122.2, 121.3, 70.8, 70.4, 68.8. Anal. Cacld. for $C_{17}H_{13}FeNS$: C, 63.97; H, 4.10; N, 4.39. Found: C, 64.26; H, 4.21; N, 4.56.

2-Ferrocenyl benzoxazole (FcO). The mixture of ferrocenecarboxaldehyde (214 mg, 1.00 mmol) and 2-aminophenol (110 mg, 1.00 mmol) was stirred at r.t. in 5 ml acetic acid for 15 min, another 20 ml hot acetic acid solution of $PbAc_4$ (450 mg 1.01 mmol) was dropped into the system in 30 min, then the mixture was pored onto 30 g ice and extracted with dichloromethane, further neutral aluminum oxide chromatograph with petroleum ether and dichloromethane furnished the product as reddish-brown crystalline solid (101 mg, 0.34 mmol, 34% yield). MS: *m/z* = 303 (M^+). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.69 (m, 1H), 7.52 (m, 1H), 7.32 (m, 2H), 5.09 (s, 2H), 4.52 (s, 2H), 4.19 (s, 5H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 166.5, 150.7, 142.5, 124.4, 124.3, 119.3, 110.3, 71.2,

70.0, 69.8, 68.7. Anal. Cacld. for $C_{17}H_{13}FeNO$: C, 67.36; H, 4.32; N, 4.62. Found: C, 67.47; H, 4.24; N, 4.78. Crystallographic data for **FcO** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 643870.

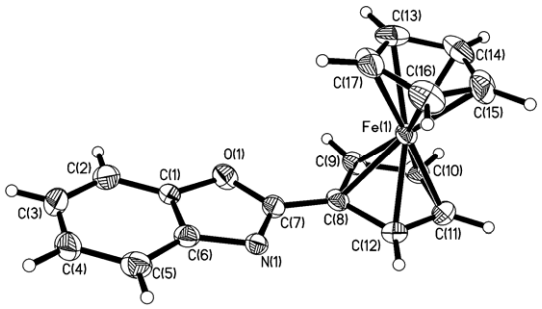


Figure. S1 X-ray crystal structure of **FcO**.

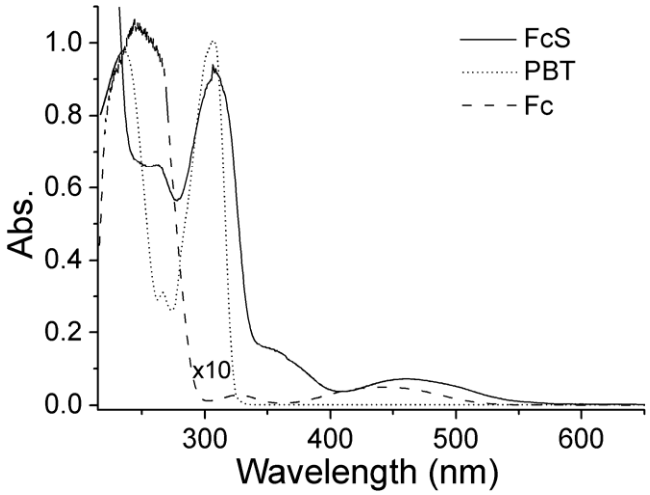


Figure S2. Absorption spectra of **FcS**, 2-phenyl benzothiazole (PBT) and Fc (~ 6×10^{-5} M) in methanol

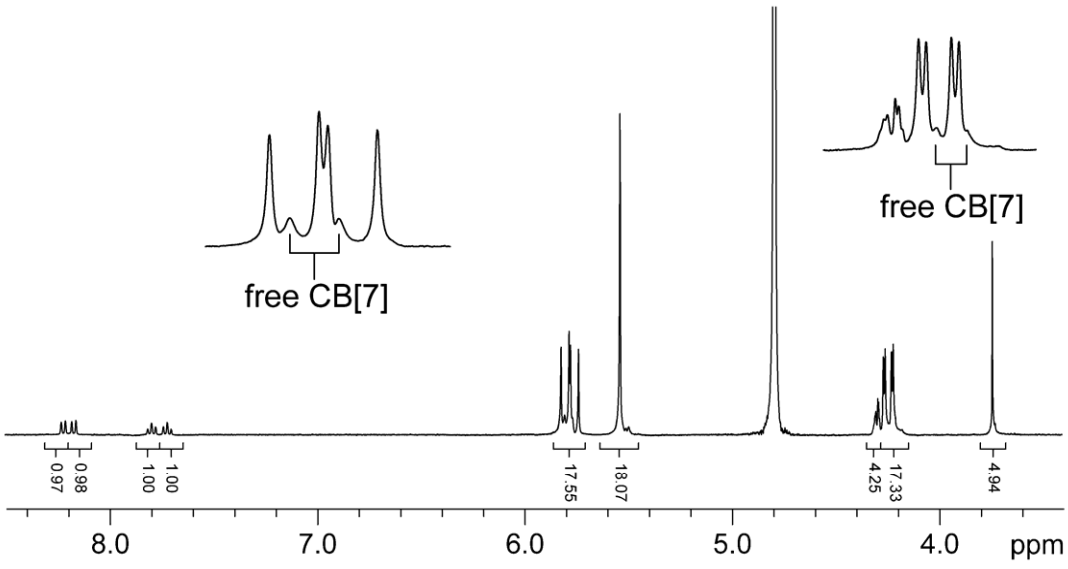


Figure S3. ^{1}H NMR integral on **FcS**@CB[7] in D_2O at 298 K.

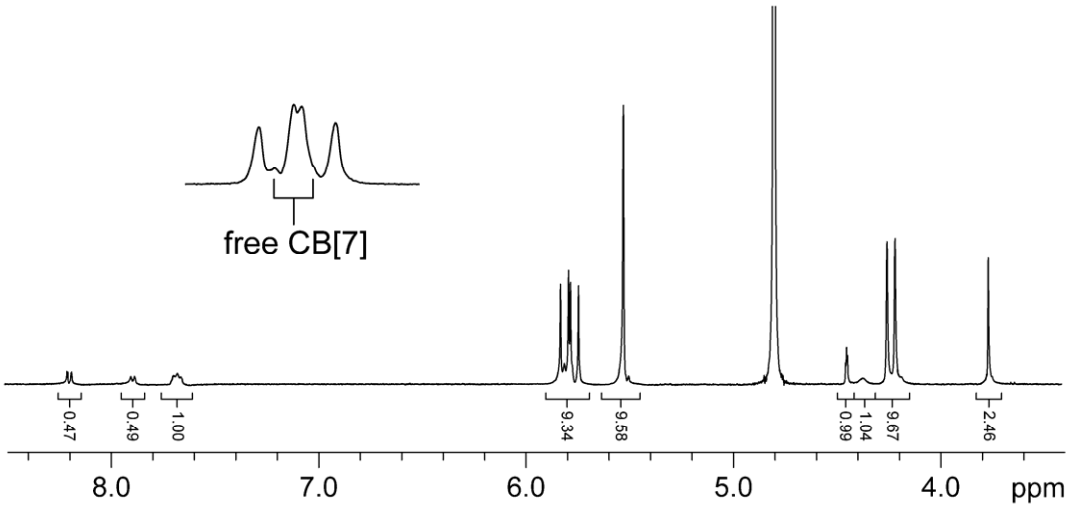


Figure S4. ^{1}H NMR integral on **FcO**@CB[7] in D_2O at 298 K.

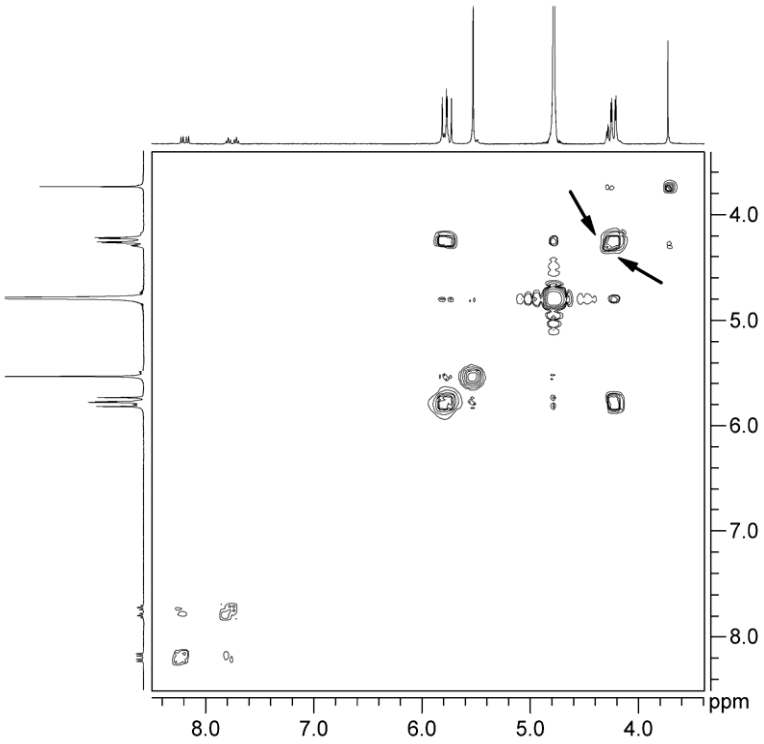


Figure S5. 2D COSY NMR spectrum of **FcS**@CB[7] in D_2O at 298 K.

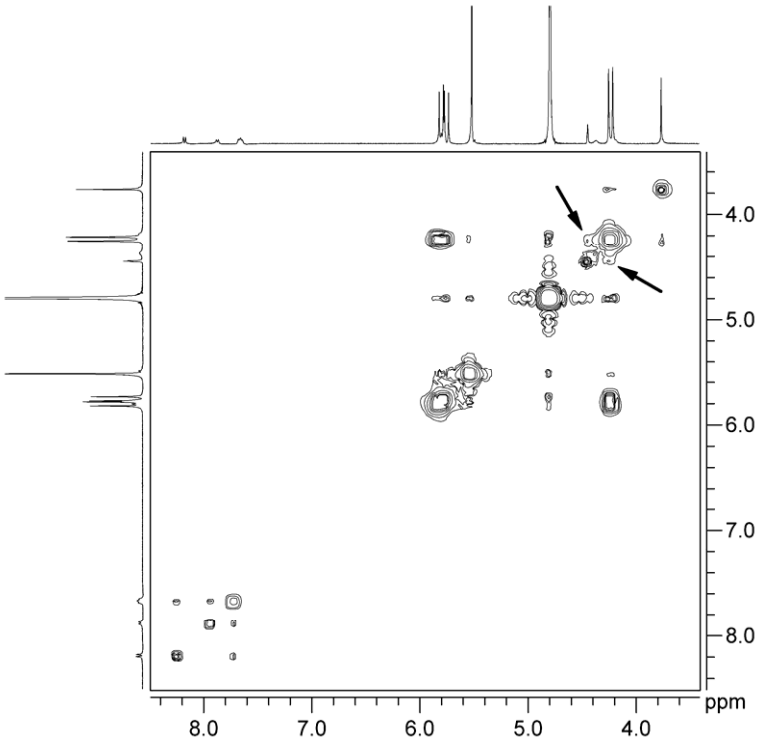


Figure S6. 2D COSY NMR spectrum of **FcO**@CB[7] in D_2O at 298 K.

References

(1) Graham, P. J.; Lindsey, R. V.; Parshall, G. W.; Peterson, M. L.; Whitman, G. M. *J. Am. Chem. Soc.* **1957**, *79*, 3416-3420.