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 (CDCl₃, 400 MHz) \( \delta \): 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 (CDCl₃, 400 MHz) \( \delta \): 169.7, 153.9, 134.7, 126.1, 124.4, 122.2, 121.3, 70.8, 70.4, 68.8. Anal. Cacl. for C₁₇H₁₃FeNS: 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 PbAc₄ (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 (CDCl₃, 400 MHz) \( \delta \): 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 (CDCl₃, 400 MHz) \( \delta \): 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 FeS, 2-phenyl benzothiazole (PBT) and Fc (\(\sim 6 \times 10^{-5}\ M\)) in methanol.

Figure S3. \(^1\)H NMR integral on FeS@CB[7] in D$_2$O at 298 K.
Figure S4. $^1$H NMR integral on FeO@CB[7] in D$_2$O at 298 K.

Figure S5. 2D COSY NMR spectrum of FeS@CB[7] in D$_2$O at 298 K.
Figure S6. 2D COSY NMR spectrum of FeO@CB[7] in D$_2$O at 298 K.

References