

Supplementary Information

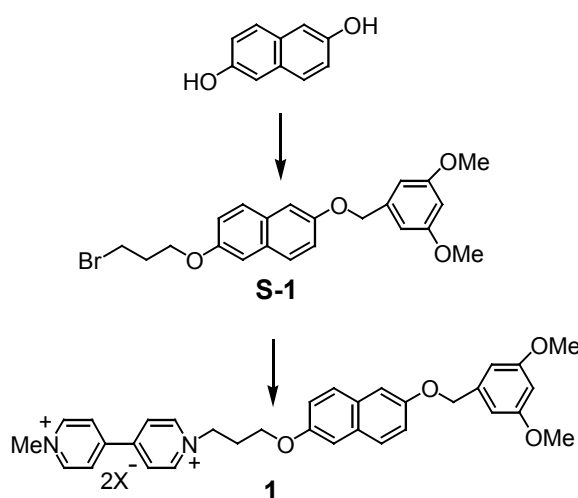
Unprecedented host-induced intramolecular charge-transfer complex formation

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Scheme S1

2-(3,5-Dimethoxybenzyloxy)-6-(bromopropoxy)naphthalene (S-1): The solution of 2,6-dihydroxynaphthalene (0.23 g, 1.0 mmol) and 3,5-dimethoxybenzyl bromide (0.50 g, 3.1 mmol) in acetone (15 mL) in the presence of K_2CO_3 (0.62 g, 4.5 mmol) was stirred for 40 h at room temperature, followed by usual aqueous workup and the purification using column chromatography to afford 2-(3,5-dimethoxybenzyloxy)-6-hydroxynaphthalene.

Subsequently, the solution of 2-(3,5-dimethoxybenzyloxy)-6-hydroxynaphthalene and excess dibromopropane in acetone (10 mL) in the presence of K_2CO_3 (0.10 g, 0.70 mmol) was refluxed for 10 h, followed by usual aqueous workup and the purification using column chromatography to provide the desired product (0.15 g, 35%). 1H NMR (300 MHz, $CDCl_3$) δ = 7.65 (d, J = 8.8 Hz, 1 H), 7.63 (d, J = 9.6 Hz, 1 H), 7.22 (dd, J = 2.4, 8.8 Hz, 1 H), 7.18 (s, 1 H), 7.13 (s, 1 H), 7.12 (dd, 1 H), 6.65 (s, 2 H), 6.43 (s, 1 H), 5.10 (s, 2 H), 4.20 (t, J = 5.8 Hz, 2 H), 3.81 (s, 6 H), 3.65 (t, J = 6.4 Hz, 2 H), 2.38 (quintet, J = 6.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.4, 155.7, 155.65, 139.8, 130.3, 130.2, 128.7, 128.6, 119.7, 119.5, 108.0, 107.6, 105.7, 100.3, 70.5, 65.8, 55.8, 32.8, 30.5; MS (EI): m/z 279, 430 [M^+]; HRMS (EI) calcd for $C_{22}H_{23}BrO_4$ 430.0780, found 430.0783.

Synthesis of 1: The solution of 2-(3,5-dimethoxybenzyloxy)-6-(bromopropoxy)naphthalene (0.14 g, 0.32 mmol) and N-methyl-4,4'-bipyridinium iodide (97 mg, 0.32 mmol) in DMF (1 mL) and CH_3CN (2 mL) was refluxed for 40 h and then cooled to room temperature. The resulting precipitate was filtered, washed with CH_3CN and dried to yield **1** (0.13 g, 56%). 1H NMR (300 MHz, $DMSO-d_6$) δ = 9.47 (d, J = 6.8 Hz, 2 H), 9.30 (d, J = 6.7 Hz, 2 H), 8.80 (d, J = 6.8 Hz, 2 H), 8.78 (d, J = 6.9 Hz, 2 H), 7.71 (d, J = 9.0 Hz, 1 H), 7.65 (d, J = 9.0 Hz, 1 H), 7.28 (d, J = 2.2 Hz, 1 H), 7.23 (d, J = 2.2 Hz, 1 H), 7.21 (dd, J = 2.5, 8.9 Hz, 1 H), 6.90 (dd, J = 2.3, 8.9 Hz, 1 H), 6.64 (s, 1 H), 6.63 (s, 1 H), 6.46 (dd, J = 2.2, 2.2 Hz, 1 H), 5.11 (s, 2 H), 4.94 (t, J = 6.4 Hz, 2 H), 4.50 (s, 3 H), 4.23 (t, J = 5.6 Hz, 2 H), 3.75 (s, 6 H), 2.56 (quintet, J = 6.1 Hz, 2 H); ^{13}C NMR (125 MHz, $DMSO-d_6$) δ = 161.5, 155.6, 155.2, 149.6, 149.0, 147.5, 147.0, 140.3, 130.4, 130.3, 129.0, 127.3, 127.0, 120.0, 119.4, 108.7, 108.1, 106.4, 100.3, 70.1, 65.8, 60.0, 56.1, 49.0, 30.8; MS (ESI): m/z (%): 261 (100) [M^{2+}], 522 [M^+]. For elemental analysis, the halide anions were exchanged with PF_6^- . Elemental analysis (%) calcd for $C_{33}H_{34}F_{12}N_2O_4P_2 \cdot 1.5H_2O$: C 47.21, H 4.44, N 3.34; found: C 47.27, H 3.97, N 3.46.

Formation of inclusion complex 2: To a solution of **1** (10 mg, 13.7 μ mol) in D_2O (7 mL) was added $CB[8] \cdot (2H_2SO_4) \cdot 30H_2O$ (23.3 mg, 13.7 μ mol) and the resulting mixture was sonicated with occasional heating until all solid materials were dissolved. The formation of inclusion complex **2** was confirmed by 1H NMR and UV-Visible spectroscopy. After the solvent was removed by evaporation, the violet solid was isolated and characterized by ESI-mass spectroscopy. 1H NMR (500 MHz, D_2O): δ = 8.74 (d, J = 6.2 Hz, 1 H), 8.63 (d, J = 6.2 Hz, 1 H), 8.62 (d, J = 6.3 Hz, 2 H), 7.13 (s, 2 H), 6.78 (d, J = 7.2 Hz, 2 H), 6.74 (d, J = 6.6 Hz, 2 H), 6.73 (d, J = 6.5 Hz, 1 H), 6.70 (s, 1 H), 6.67 (d, J = 6.5 Hz, 1 H), 6.58 (d, J = 7.2 Hz, 2 H),

6.57 (d, $J = 8.6$ Hz, 1 H), 6.47 (d, $J = 8.9$ Hz, 1 H), 6.03 (s, 1 H), 5.94 (s, 1 H), 5.72 (d, $J = 15.3$ Hz, 8 H), 5.70 (d, $J = 15.2$ Hz, 8 H), 5.54 (s, 16 H), 5.20 (d, $J = 11.3$ Hz, 1 H), 5.00 (t, $J = 5.5$ Hz, 2 H), 4.86 (d, $J = 11.5$ Hz, 1 H), 4.55 (d, $J = 5.9$ Hz, 2 H), 4.16 (s, 3 H), 4.15 (d, $J = 16.0$ Hz, 16 H), 3.95 (s, 6 H), 2.88 (m, 1 H), 2.80 (m, 1 H); MS (ESI): m/z (%): 926 (100) $[M^{2+}]$.

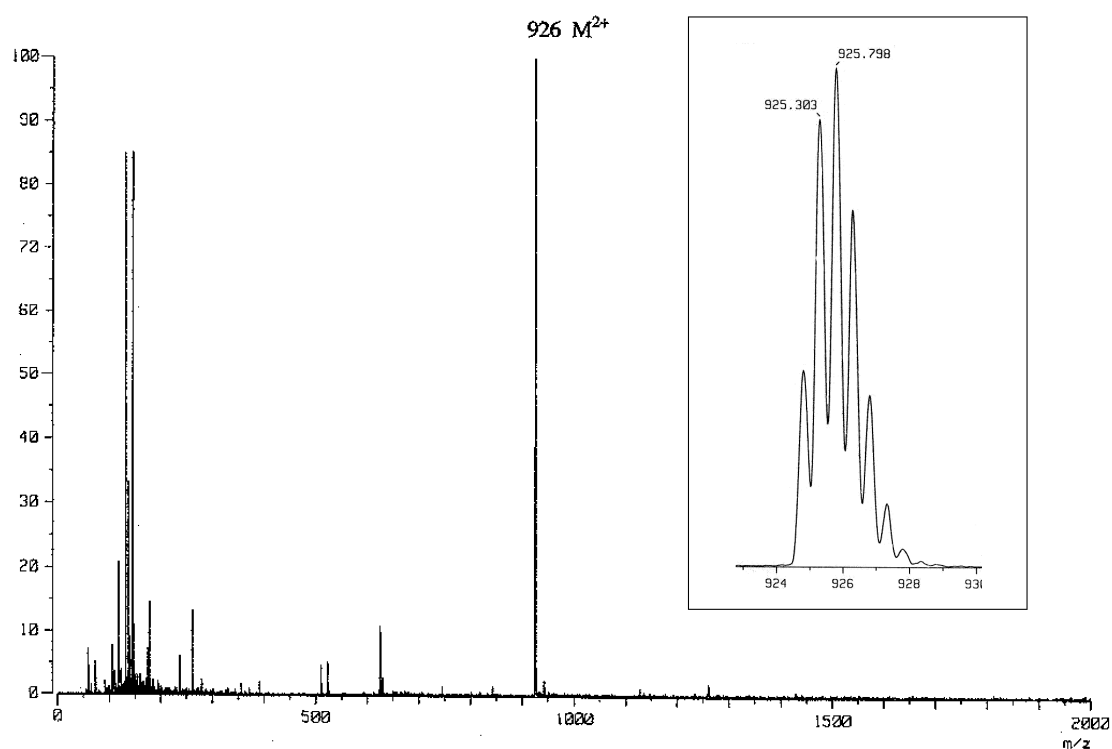


Fig. S1 ESI- mass spectrum of complex 2.

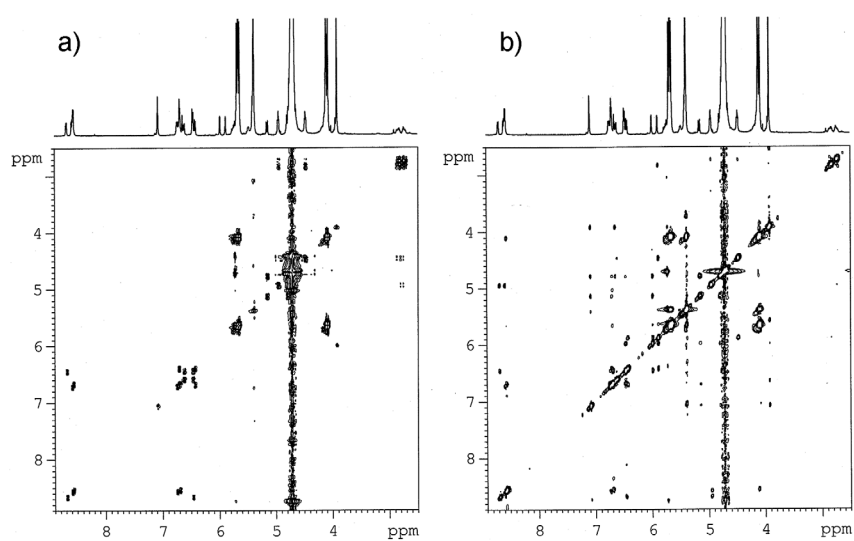


Fig. S2 (a) DQF-COSY and (b) ROESY spectra of complex 2.

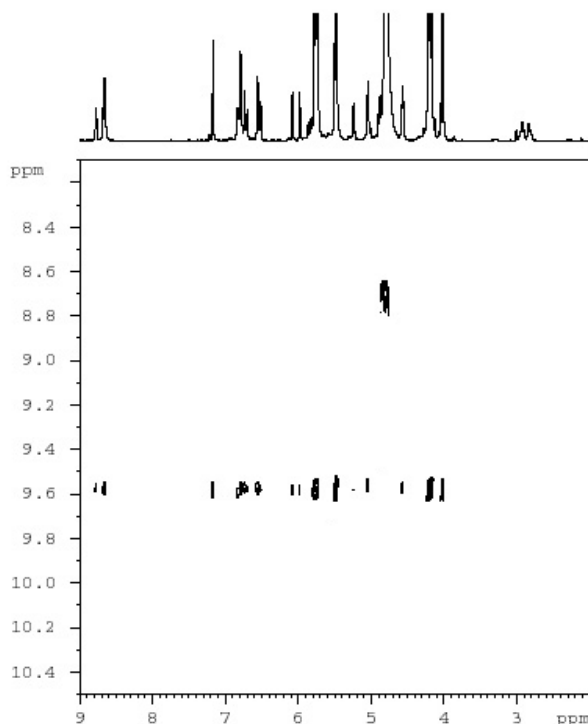


Fig. S3 2D diffusion-ordered NMR spectrum of complex **2**.

Measurement of diffusion coefficient of 1:1 complex 2: The diffusion coefficient measurements were carried out using a 5mm Bruker QNP probe with an actively shielded z gradient coil. Diffusion coefficients were extracted from a series of ^1H NMR spectra measured by the bipolar pulse longitudinal encode-decode (BPPLIED) pulse sequence^{S1} as a function of gradient amplitude. In each experiment, gradient duration time was 2.0 or 2.5 ms and the amplitudes of the gradient pulses ranged from 1 to 40 G/cm. The diffusion coefficients were calculated from the data using diffusion-ordered spectroscopy (DOSY). The complex size can be estimated by the ratio $V_{\text{complex}}/V_{\text{CB}[8]}$, where V_{complex} represents the volume of the complex while $V_{\text{CB}[8]}$ represents the volume of CB[8] alone. The volume ratio $V_{\text{complex}}/V_{\text{CB}[8]}$ was calculated from diffusion coefficient ratio as $(D_{\text{complex}}/D_{\text{CB}[8]})^3$. The diffusion coefficient was measured to be $2.57 \times 10^{-10} \text{ m}^2/\text{s}$ which is almost same with that of CB[8] measured in the presence of methylviologen ($2.82 \times 10^{-10} \text{ m}^2/\text{s}$). The estimated size from diffusion coefficient of the complex is 1.3 times larger than CB[8] alone.

Ref S1. D. Wu, A. Chen, C. S. Jr. Johnson, *J. Magn. Reson., Ser. A*, 1995, **115**, 260.

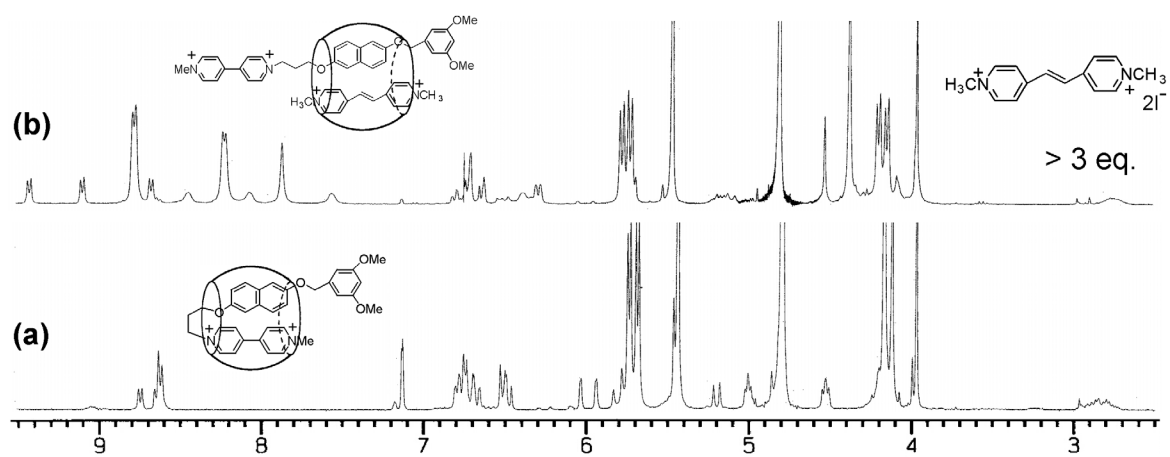


Fig. S4 ¹H-NMR spectra of (a) 1:1 complex **2** and (b) ternary complex **3** in D₂O at 25 °C.