Supplementary Information

Unprecedented host-induced intramolecular charge-transfer complex formation

Jae Wook Lee, a Kyungpil Kim, a SooWhan Choi, a Young Ho Ko, a Shigeru Sakamoto, b Kentaro Yamaguchi, b and Kimoon Kim a

a National Creative Research Initiative Center for Smart Supramolecules and Department of Chemistry, Division of Molecular and Life Sciences, Pohang University of Science and Technology, San 31 Hyojadong, Pohang 790-784, Republic of Korea
Fax: 82-54-279-8129; E-mail: kkim@postech.ac.kr
b Chemical Analysis Center, Chiba University, 1-33 Yayoicho, Inageku, Chiba 263-8522, Japan

2-(3,5-Dimethoxybenzyloxy)-6-(bromopropyloxy)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 K₂CO₃ (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 K₂CO₃ (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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) δ = 161.4, 155.7, 155.6, 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 C₂₂H₂₃BrO₄ 430.0780, found 430.0783.

**Synthesis of 1:** The solution of 2-(3,5-dimethoxybenzyloxy)-6-(bromoproyloxy)naphthalene (0.14 g, 0.32 mmol) and N-methyl-4,4’-bipyridinium iodide (97 mg, 0.32 mmol) in DMF (1 mL) and CH₃CN (2 mL) was refluxed for 40 h and then cooled to room temperature. The resulting precipitate was filtered, washed with CH₃CN and dried to yield 1 (0.13 g, 56%). ¹H NMR (300 MHz, DMSO-d₆) 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); ¹³C NMR (125 MHz, DMSO-d₆) δ = 161.5, 155.6, 155.2, 149.6, 149.0, 147.5, 147.0, 140.3, 130.4, 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) [M²⁺], 522 [M⁺]. For elemental analysis, the halide anions were exchanged with PF₆⁻. Elemental analysis (%) calcd for C₃₃H₃₄F₁₂N₂O₄P₂·1.5H₂O: 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 µmol) in D₂O (7 mL) was added CB[8](2H₂SO₄)·30H₂O (23.3 mg, 13.7 µmol) 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, D₂O): 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.
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 $^1$H NMR spectra measured by the bipolar pulse longitudinal encode-decode (BPPLED) 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 $V_{\text{complex}}$ represents the volume of the complex while $V_{\text{complex}}$ 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 $2.57 \times 10^{-10}$ m$^2$/s which is almost same with that of CB[8] measured in the presence of methylviologen ($2.82 \times 10^{-10}$ m$^2$/s). The estimated size from diffusion coefficient of the complex is 1.3 times larger than CB[8] alone.

Fig. S4  $^1$H-NMR spectra of (a) 1:1 complex 2 and (b) ternary complex 3 in D$_2$O at 25°C.