Electronic Supplementary Information
(ESI)


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Experimental section

Materials. All solvents and reagents were used as supplied. *per*-Ethylated pillar[5]arene (C2) was synthesized according to the previous paper.1

Measurements. The 1H NMR spectra were recorded at 500 MHz and 13C NMR spectra were recorded at 125 MHz with a JEOL-ECA500 spectrometer. Thermogravimetric analysis was performed using a TG/DTA6200, SEIKO Instruments, Inc., with heating rate of 10 °C min⁻¹ under nitrogen atmosphere. Ionic conductivity was measured with a complex-impedance gain-phase analyzer (Solartron model 1260; Schlumberger) in the frequency range from 1 Hz to 1 MHz. The samples were thoroughly dried under vacuum at 60 °C for 24 h prior to the measurements. The samples were sandwiched in a cell constructed with a pair of stainless steel plates. UV-Vis absorption spectra were recorded with a JASCO V-670. For UV-Vis measurements, one centimeter quartz cuvets were used.

Determination of association constant. The association constant (K) of tetracyanoethylene (TCNE)-C2 complex was determined by probing the charge-transfer (CT) band of the complex by UV-Vis spectroscopy and employing titration method. Addition of C2 to a chloroform solution with the same concentration of TCNE resulted in an increase of the intensity of the CT band of the complex. By the non-linear curve-fitting methods, K for the complex in CHCl3 was estimated to be 63.5 ± 4.7 M⁻¹ for 1:1 stoichiometry. The non-linear curve-fitting was based on the equation:

\[ A = (A_\infty/[G]_0)(0.5[H]_0^2 + (0.5[H]_0/(1/K) + (1/K + [G]_0)^2))^{0.5} \] (Eq. S1)

Where A is the absorption intensity of the CT band at [H]₀, A_∞ is the absorption intensity of the CT band when the guest is completely complexed, [G]₀ is the fixed initial concentration of the guest, and [H]₀ is the initial concentration of the host.

4. To a solution of bis(1-bromopropoxy)benzene (3, 1.00 g, 2.84 mmol) and paraformaldehyde (0.269 g, 8.97 mmol) in 1,2-dichloroethane (20 mL), BF3•OEt2 (0.360 mL, 2.86 mmol) was added. The mixture was stirred at 30 °C for 30 min under nitrogen atmosphere. The resulting solution was poured into methanol and the precipitate was collected by filtration. Column chromatography (silica gel; hexane : dichloromethane = 3 : 2) afforded an white solid (4, 454 mg, 0.249 mmol, Yield: 44%).
1H NMR (CDCl₃, 500 MHz, ppm): δ 6.74 (s, 10H, phenyl), 3.99 (t, J = 6 Hz, 20H, methylene), 3.76 (s, 10H, methylene bridge), 3.52 (t, J = 6 Hz, 20H, methylene), 2.23 (m, 20H, methylene). 13C NMR (DMSO-d₆, 125 MHz, ppm): δ 149.8, 128.5, 115.3 (C of phenyl), 66.3, 32.7, 30.4 (C of methylene), 29.8 (C of methylene bridge). Anal. Calcd for C₆₅H₈₀Br₁₀O₁₀ ▪ 0.20C₆H₁₄ C, 43.27; H, 4.54; N, 0.00. Found: C, 43.30; H, 4.56; N, 0.00. FABMS: m/z Calcd for C₆₅H₈₅O₁₀Br₁₀ [M]+: 1820, found 1820.

1-Br. To a solution of 1-methylimidazole (5 mL), 4 (50.0 mg, 0.0275 mmol) was added. The mixture was heated at 80 °C for 24 h. The resulting solution was poured into diethyl ether and the precipitate was collected by filtration. The reprecipitation process was repeated three times. (1-Br, 60 mg, 0.0227 mmol, Yield: 83%). 1H NMR (DMSO-d₆, 500 MHz, ppm): δ 9.21 (br, 10H, imidazolium), 8.01 (br, 10H, imidazolium), 7.57 (br, 10H, imidazolium), 6.75 (s, 10H, phenyl), 4.51 (br, 20H, methylene), 3.85-4.20 (br, 20H, methylene), 3.76 (s, 30H, methyl), 3.60 (s, 10H, methylene bridge), 2.36 (m, 20H, methylene). 13C NMR (DMSO-d₆, 125 MHz, ppm): δ 149.4 (C of phenyl), 137.0 (C of imidazolium), 128.3 (C of phenyl), 124.0, 122.8 (C of imidazolium), 114.6 (C of phenyl), 65.6, 46.8 (C of methylene), 36.3 (C of methyl), 30.6 (C of methylene), 29.2 (C of methylene bridge). Anal. Calcd for C₁₀₅H₁₄₀Br₁₀N₂₀O₁₀ ▪ 11.7H₂O C, 44.22; H, 5.77; N, 9.82. Found: C, 44.16; H, 5.70; N, 9.75. ESIMS (CH₃OH): m/z Calcd for C₁₀₅H₁₄₀Br₁₀N₂₀O₁₀ [M-2Br]+: 1240, found 1240.

1-PF₆. To a solution of 1-Br (60 mg, 0.0227 mmol) in water (10 mL), NaPF₆ (70.0 mg, 0.417 mmol) was added. The reaction mixture was stirred at 25 °C for 10 min. The precipitate was collected by filtration. (1-PF₆, 54.0 mg, 0.0164 mmol, Yield: 72%). 1H NMR (CD₃CN, 500 MHz, ppm): δ 8.11 (s, 10H, imidazolium), 7.33 (br, 10H, imidazolium), 7.10 (br, 10H, imidazolium), 6.77 (s, 10H, phenyl), 4.35 (t, J = 7 Hz, 20H, methylene), 3.93 (br, 20H, methylene), 3.70 (s, 10H, methylene bridge), 3.66 (s, 30H, methylene), 2.33 (m, 20H, methylene). 13C NMR (CD₃CN, 125 MHz, ppm): δ 150.4 (C of phenyl), 137.0 (C of imidazolium), 129.7 (C of phenyl), 124.8, 123.2 (C of imidazolium), 115.3 (C of phenyl), 65.9, 47.9 (C of methylene), 36.8 (C of methyl), 30.9 (C of methylene), 29.7 (C of methylene bridge). Anal. Calcd for C₁₀₅H₁₄₀F₆₀N₂₀O₁₀P₁₀ ▪ H₂O C, 38.10; H, 4.32; N, 8.46. Found: C, 37.84; H, 4.36; N, 8.23. HRESIMS (CH₃CN): m/z Calcd for C₁₀₅H₁₄₀F₆₀N₂₀O₁₀P₁₀ [M-PF₆]+: 3000.81957, found 3000.81965.

1-TFSA. To a solution of 1-Br (50 mg, 0.0189 mmol) in DMF (10 mL) and methanol
(0.5 mL), LiTFSA (0.163 g, 0.570 mmol) was added. The reaction mixture was stirred at 25 °C for 168 h. The resulting solution was poured into water and the precipitate was collected by filtration. The reprecipitation process was repeated three times. (1-TFSA, 70.0 mg, 0.0151 mmol, Yield: 80%). $^1$H NMR (DMSO-$d_6$, 500 MHz, ppm): δ 9.10 (s, 10H, imidazolium), 7.73 (br, 10H, imidazolium), 7.71 (br, 10H, imidazolium), 6.74 (s, 10H, phenyl), 4.36 (t, J = 8 Hz, 20H, methylene), 3.7-4.1 (br, 20H, methylene), 3.85 (s, 30H, methyl), 3.63 (s, 10H, methylene bridge), 2.27 (m, 20H, methylene). $^{13}$C NMR (DMSO-$d_6$, 125 MHz, ppm): δ 149.3 (C of phenyl), 137.1 (C of imidazolium), 128.7 (C of phenyl), 124.4, 122.7 (C of imidazolium), 121.3 (C of TFSA), 118.7 (C of phenyl), 65.4, 46.9 (C of methylene), 36.4 (C of methyl), 30.2 (C of methylene bridge). Anal. Calcd for C$_{121}$H$_{140}$F$_{48}$N$_{28}$O$_{42}$S$_{16}$H$_{70}$N$_{7}$O$_{2}$ [M-TFSA]$^+$: 4080.44447, found 4080.44505.

2-TFSA. To a solution of 1-methylimidazole (6.72 mL), bis(1-bromopropoxy)benzene (3, 1.00 g, 2.84 mmol) was added. The mixture was heated at 80 °C for 24 h. The resulting solution was poured into diethyl ether and the precipitate was collected by filtration. The reprecipitation process was repeated three times (2-Br, 1.26 g, 2.44 mmol, Yield: 86%). To a solution of 2-Br (200 mg, 0.387 mmol) in DMF (10 mL) and methanol (0.5 mL), LiTFSA (1.11 g, 3.87 mmol) was added. The reaction mixture was stirred at 25 °C for 168 h. The resulting solution was poured into water and the precipitate was collected by filtration. The reprecipitation process was repeated twice. (2-TFSA, 242 mg, 0.264 mmol, Yield: 68%). $^1$H NMR (DMSO-$d_6$, 500 MHz, ppm): δ 9.12 (s, 2H, imidazolium), 7.78 (br, 2H, imidazolium), 7.70 (br, 2H, imidazolium), 6.83 (s, 4H, phenyl), 4.33 (t, J = 7 Hz, 4H, methylene), 3.94 (t, J = 6 Hz, 4H, methylene), 3.84 (s, 6H, methyl), 2.24 (m, 4H, methylene). $^{13}$C NMR (DMSO-$d_6$, 125 MHz, ppm): δ 153.0 (C of phenyl), 137.3 (C of imidazolium), 124.1, 123.0 (C of imidazolium), 121.3 (C of TFSA), 118.7 (C of phenyl), 65.4, 47.0 (C of methylene), 36.3 (C of methyl), 29.7 (C of methylene). Anal. Calcd for C$_{22}$H$_{28}$F$_6$N$_5$O$_6$S$_2$ [M-TFSA]$^+$: 636.13852, found 636.13848.
\textbf{1H and 13C NMR spectra of 4}

\textbf{Fig. S1} $^1$H and $^{13}$C NMR spectra of 4 in CDCl$_3$ at 25 $^\circ$C.
**Fig. S2** $^1$H and $^{13}$C NMR spectra of 1-Br in DMSO-$d_6$ at 25 °C.
**Fig. S3** $^1$H and $^{13}$C NMR spectra of 1-PF$_6$ in CD$_3$CN at 25 $^\circ$C.
HRESIMS spectra of 1-PF$_6$

Fig. S4 HRESIMS spectra (CH$_3$CN) of 1-PF$_6$. 
\textit{H and }^{13}\text{C NMR spectra of 1-TFSA}

\textbf{Fig. S5} $^1$H and $^{13}$C NMR spectra of 1-TFSA in DMSO-$d_6$ at 25 °C.
HRESIMS spectra of 1-TFSA

Fig. S6 HRESIMS spectra (CH$_3$OH) of 1-TFSA$\delta$. 
$^1$H and $^{13}$C NMR spectra of 2-TFSA

Fig. S7 $^1$H and $^{13}$C NMR spectra of 2-TFSA in DMSO-$d_6$ at 25 °C.
**DSC traces of 1-PF$_6$**

![DSC traces of 1-PF$_6$](image)

*Fig. S8* DSC traces of 1-PF$_6$ at the multicycle scanning (insert: photographs of optical microscope of 1-PF$_6$ below (a) and above (b) melting point).
DSC traces of 1-TFSA

**Fig. S9** DSC traces of 1-TFSA at the multicycle scanning (insert: photographs of optical microscope of 1-PF₆ below (a) and above (b) melting point).
DSC traces of 2-TFSA

Fig. S10 DSC traces of 1-TFSA at the multicycle scanning (insert: photographs of optical microscope of 2-TFSA below (a) and above (b) melting point).
Thermogravimetric analysis of 4 and 1-TFSA

![Graph showing weight loss vs. temperature for 1-TFSA and 4](image)

**Fig. S11** Thermogravimetric analysis of (a) 1-TFSA and (b) 4.
 Ionic conductivity of 1-TFSA

Fig. S12 Temperature dependences of ion conductivity of 1-TFSA (a) in the bulk and (b) upon addition of an equimolar amount of LiTFSA toward the imidazolium units.
UV-Vis spectra of TCNE and TCNQ with C2

Fig. S13 UV-Vis absorption spectra of (a) C2 (blue line), TCNE (black line) and an 1:1 mixture of C2 and TCNE (pink line) and (b) C2 (blue line), TCNQ (black line) and an 1:1 mixture of C2 and TCNQ (pink line) in 0.01 mM (insert: photographs of these samples). Observation of the charge-transfer (CT) band indicates complexation between C2 and TCNE.
Job Plot for a mixture of TCNE and C2

Fig. S14 Job plot between C2 (host) and TCNE (guest). The job plot was conducted by varying the mole fractions of the guest and host. Absorption bands at 754 nm were utilized. Concentration: \([C2] + [TCNE] = 2 \text{ mM}\). The plot indicates a 1:1 binding between the host and guest.
UV-Vis titration for TCNE-C2 complex

Fig. S15 The absorption spectral changes of TCNE upon addition of C2 (upper) and the absorbance changes upon addition of C2 (bottom); [TCNE] = 0.35 mM. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.
References