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Electronic Supporting Information

Reinforcement of guest selectivity through the self-assembly of host molecules: Selective recognition of lithium ions by dimerizable tricarboxylic acids

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General

Chemicals and solvents required were obtained from commercial suppliers. ¹H, ¹³C, and 2D NMR spectra were recorded on a JEOL JNM-ECA600 spectrometer. Mass spectra were measured on JMS-T100LC AccTOF (JEOL) or solariX FT-ICR-MS spectrometer (Bruker Daltonik GmbH) spectrometers.

Synthesis and physical properties



1,3,5-Tris(3-methoxycarbonylphenylmethyl)-2,4,6-triethylbenzene of (4). А mixture 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (100)0.23 mg, mmol), 3-methoxycarbonylphenylboronic acid (183 mg, 1.02 mmol), [Pd(C₃H₅)₂Cl]₂ (8.0 mg, 22 µmol), AsPh₃ (70 mg, 0.23 mmol) and Cs₂CO₃ (310 mg, 0.95 mmol) in 1,4-dioxane (30 mL) and H₂O (3.0 mL) was refluxed for 24 h under argon atmosphere. The reaction mixture was concentrated under reduced pressure, then H₂O and CH₂Cl₂ were added. Separated organic layer was washed with brine, and dried over Na₂SO₄. After removal of solvent, the crude mixture was purified by column chromatography (SiO₂ EtOAc/*n*-hexane = 1/15). Desired product **4** was obtained as white solid (55

mg, 41% yield).

M.p. 121-123 °C; ¹H NMR (CDCl₃) δ 1.07 (t, *J* =7.2 Hz, 9H), 2.40 (q, *J* =7.3 Hz, 6H), 3.89 (s, 9H), 4.19 (s, 6H), 7.12 (d, *J* =7.6 Hz, 3H), 7.31(dd, *J* = 7.6, 8.2 Hz, 3H), 7.79 (s, 3H), 7.82 (d, *J* =8.2 Hz, 3H); ¹³C NMR (CDCl₃) δ 15.1, 23.6, 34.2, 52.0, 127.0, 128.5, 129.1, 130.1, 132.0, 133.5, 141.46, 141.53; HRMS (ESI, M+Na⁺) calcd for C₃₉H₄₂NaO₆: 629.2879; found 629.2874.



1,3,5-Tris(3-carboxylphenylmethyl)-2,4,6-triethylbenzene (**1**). A mixture of **4** (185 mg, 0.31 mmol) and KOH (1.86 g, 33.1 mmol) in EtOH (5.0 mL) and H₂O (5.0 mL) was refluxed for 7.5 h under argon atmosphere. The reaction mixture was cooled in ice bath and added 1 M HCl. Obtained solid was collected by filtration and washed with *n*-hexane. Desired product **1** was obtained as white solid (170 mg, 99% yield).

M.p. >250 °C; ¹H NMR (DMSO- d_6) δ 0.94 (t, J =7.2 Hz, 9H), 2.37 (q, J =7.2 Mz, 6H), 4.17 (s, 6H), 7.15 (d, J =8.2 Hz, 3H), 7.36 (dd, J = 7.6, 7.6 Hz, 3H), 7.69 (s, 3H), 7.72 (d, J =7.6 Hz, 3H); ¹³C NMR (DMSO- d_6) δ 15.1, 23.2, 33.7, 126.8, 128.6, 130.8, 131.6, 133.4, 140.9, 141.6, 167.3; HRMS (ESI, M+Na⁺) calcd for C₃₆H₃₆NaO₆: 587.2410; found 587.2393.



1,3,5-Tris(3-cyanophenylmethyl)-2,4,6-triisopentylbenzene (5). A mixture of 1,3,5-tris(bromomethyl)-2,4,6-triisopentylbenzene (500 mg, 0.88 mmol), 3-cyanophenylboronic

acid (584 mg, 3.97 mmol), PdCl₂(PPh₃)₂ (125 mg, 0.18 mmol), AsPh₃ (270 mg, 0.88 mmol) and Cs₂CO₃ (3.87 g, 11.9 mmol) in 1,4-dioxane (120 mL) and H₂O (12 mL) was refluxed for 14 h under argon atmosphere. The reaction mixture was concentrated under reduced pressure, then H₂O and CH₂Cl₂ were added. Separated organic layer was washed with brine, and dried over Na₂SO₄. After removal of solvent, the crude mixture was purified by column chromatography (SiO₂ EtOAc/*n*-hexane = 1/15). Desired product **5** was obtained as white solid (207 mg, 37% yield). M.p. 130-132 °C; ¹H NMR (CDCl₃) δ 0.99 (d, *J* = 6.2 Hz, 18H), 1.20-1.25 (m, 6H), 1.45 (sep, 3H), 2.28-2.30 (m, 6H), 4.12 (s, 6H), 7.19 (d, *J* = 7.6 Hz, 3H), 7.26 (s, 3H), 7.41 (dd, *J* = 7.6, 8.2 Hz, 3H), 7.49 (d, *J* = 7.6 Hz, 3H); ¹³C NMR (CDCl₃) δ 22.2, 28.7, 28.9, 34.2, 40.0, 112.5, 118.9, 129.4, 129.8, 131.2, 131.9, 133.2, 140.5, 142.6; HRMS (ESI, M+Na⁺) calcd for C₄₅H₅₁N₃Na: 656.3981; found 656.3943.



1,3,5-Tris(3-carboxylphenylmethyl)-2,4,6-triisopentylbenzene (2). A mixture of **5** (100 mg, 0.16 mmol) and KOH (0.91 g, 16.3 mmol) in EtOH (0.5 mL) and H₂O (0.5 mL) was refluxed for 5.5 h under argon atmosphere. The reaction mixture was cooled in ice bath and added 1 M HCl. Obtained solid was collected by filtration and washed with *n*-hexane. Desired product **2** was obtained as white solid (58 mg, 53% yield).

M.p. 217-220 °C; ¹H NMR (DMSO- d_6) δ 0.73 (d, J = 6.6 Hz, 18H), 1.37-1.43 (m, 3H), 2.31-2.33 (m, 6H), 4.12 (s, 6H), 7.16 (d, J = 8.3 Hz, 3H), 7.38 (t, J = 7.4 Hz 3H), 7.69 (s, 3H), 7.74 (d, J = 7.4 Hz , 3H), 12.86 (brs, 3H); ¹³C NMR (CDCl₃) δ 22.02, 28.09, 33.93, 40.60, 126.82, 128.62, 128.63, 130.94, 131.67, 133.62, 139.63, 141.57, 167.36; HRMS (ESI, M+Na⁺) calcd for C₄₅H₅₄NaO₆: 713.3818; found 713.3819.



1,3,5-Tris(2-methoxy-5-cyanophenylmethyl)-2,4,6-triethylbenzene (6). of А mixture 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (1.00)2.26 g, mmol), 2-methoxy-5-cyanophenylboronic acid (1.80 mg, 10 mmol), $[Pd(C_3H_5)_2Cl]_2$ (165 mg, 0.45 mmol), AsPh₃ (345 mg, 1.13 mmol) and Cs₂CO₃ (3.30 g, 10 mmol) in 1,4-dioxane (200 mL) and H₂O (20 mL) was refluxed for 13 h under argon atmosphere. The reaction mixture was concentrated under reduced pressure, then H₂O and CH₂Cl₂ were added. Separated organic layer was washed with brine, and dried over Na₂SO₄. After removal of solvent, the crude mixture was purified by column chromatography (SiO₂ CH₂Cl₂). Desired product 6 was obtained as white solid (690 mg, 51% yield).

M.p. 197-200 °C; ¹H NMR (CDCl₃) δ 0.92 (t, *J* = 7.6 Hz, 9H), 2.34 (q, *J* = 7.6 Hz, 6H), 3.98 (s, 9H), 4.03 (s, 6H), 6.84 (d, *J* = 2.1 Hz, 3H), 6.91 (d, *J* = 8.2 Hz, 3H) 7.49 (dd, *J* = 2.1, 8.2 Hz, 3H); ¹³C NMR (CDCl₃) δ 15.3, 23.9, 28.8, 55.9, 104.0, 110.1, 119.6, 131.9, 132.0, 132.2, 133.1, 141.9, 160.6; HRMS (ESI, M+Na⁺) calcd for C₃₉H₃₉N₃NaO₃: 620.2889; found 620.2894.



1,3,5-Tris(2-hydroxy-5-cyanophenylmethyl)-2,4,6-triethylbenzene (7). A solution of BBr₃ (25 mmol) in CH₂Cl₂ (25 mL) was added dropwise to 6 (1.0 g, 1.67 mmol) at -78 °C. The reaction mixture was gradually warmed to room temperature and stirred for 48 h. Then sat. NaHCO₃ was

added to the mixture, and the aqueous layer extracted from EtOAc. Organic layer was washed with brine, and dried over Na_2SO_4 . After removal of solvent, the crude mixture was purified by column chromatography (SiO₂ CHCl₃/acetone = 20/1 to 10/1). Desired product **7** was obtained as white solid (875 mg, 94% yield).

M.p. >250 °C; ¹H NMR (acetone- d_6) δ 1.00 (t, J = 7.6 Hz, 9H), 2.51 (q, J = 7.6 Hz, 6H), 4.15 (s, 6H), 6.85 (d, J = 2.1 Hz, 3H), 7.07 (d, J = 8.2 Hz, 3H), 7.46 (dd, J = 2.1, 8.2 Hz, 3H), 9.66 (s, 3H); ¹³C NMR (acetone- d_6) δ 15.51, 24.42, 29.06, 103.84, 116.35, 119.75, 130.77, 132.61, 132.63, 134.34, 142.62, 159.74; HRMS (ESI, M+Na⁺) calcd for C₃₆H₃₃N₃NaO₃: 578.2420; found 578.2386.



1,3,5-Tris(2-isopentoxy-5-cyanophenylmethyl)-2,4,6-triethylbenzene (8). To a mixture of **7** (40 mg, 72 µmol) and K₂CO₃ (90 mg, 0.65 mmol) in DMF (0.7 mL) was added 1-bromo-3-methylbutane (39 µL, 0.32 mmol) under argon atmosphere at room temperature. The reaction mixture was stirred at 80 °C for 4 h. Insoluble K₂CO₃ was removed by filtration, then H₂O and CH₂Cl₂ were added. Organic layer was washed with brine, and dried over Na₂SO₄. After removal of solvent, the crude mixture was purified by column chromatography (SiO₂ EtOAc/*n*-hexane = 1/3). Desired product **8** was obtained as white solid (46 mg, 84% yield). M.p. 148-151 °C; ¹H NMR (CDCl₃) δ 0.92 (t, *J* = 7.6 Hz, 9H), 1.01 (d, *J* = 6.2 Hz, 18H), 1.78-1.81 (m, 6H), 1.91-2.04 (m, 3H), 2.34(q, *J* = 7.3, 6H), 4.05 (s, 6H), 4.14 (t, *J* = 6.2 Hz, 6H), 6.83 (d, *J* = 2.1 Hz, 3H), 6.89 (d, *J* = 8.9 Hz, 3H), 7.47 (dd, *J* = 2.1, 8.2 Hz, 3H); ¹³C NMR (CDCl₃) δ 14.9, 22.5, 23.7, 25.2, 28.4, 37.7, 66.8, 103.6, 110.6, 119.4, 131.76, 131.81, 131.84, 133.2, 141.6, 159.8;

HRMS (ESI, M+Na⁺) calcd for C₅₁H₆₃N₃NaO₃: 788.4767; found 788.4739.



1,3,5-Tris(2-isopentoxy-5-carboxylphenylmethyl)-2,4,6-triethylbenzene (3). A mixture of **8** (300 mg, 0.39 mmol) and KOH (360 mg, 6.4 mmol) in $(CH_2OH)_2$ (10 mL) and H_2O (1 mL) was stirred at 175 °C for 21 h under argon atmosphere. The reaction mixture was cooled in ice bath and added 1 M HCl (15 mL). The aqueous layer was with CH_2Cl_2 . The combined organic layer was washed with brine, and dried over Na₂SO₄. After removal of solvent, the crude solid was washed with acetone. Desired product **3** was obtained as white solid (283 mg, 88% yield).

M.p. 217-220 °C; ¹H NMR (DMSO- d_6) δ .84 (t, J = 7.2 Hz, 9H), 0.93 (d, J = 6.9 Hz, 18H), 1.66-1.69 (m, 6H), 1.83-1.91 (m, 3H), 2.39 (q, J = 7.6, 6H), 4.01 (s, 6H), 4.15 (t, J = 6.2 Hz, 6H), 7.08 (d, J = 8.2 Hz, 3H), 7.23 (s, 3H), 7.76 (dd, J = 2.1, 8.2 Hz, 3H), 12.21 (brs, 3H); ¹³C NMR (DMSO- d_6) δ 22.35, 23.35, 24.71, 37.28, 40.60, 66.39, 110.61, 122.43, 129.17, 129.23, 129.30, 133.42, 140.85, 159.66, 166.93; HRMS (ESI, M+Na⁺) calcd for C₅₁H₆₆NaO₉: 845.4605; found 845.4540.

¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of $\mathbf{4}$



 ^{13}C NMR spectrum (150 MHz, CDCl₃, 298 K) of **4**



¹H NMR spectrum (600 MHz, DMSO- d_6 , 298 K) of **1**



 13 C NMR spectrum (150 MHz, DMSO-*d*₆, 298 K) of **1**



 1 H NMR spectrum (600 MHz, CDCl₃, 298 K) of **5**



 ^{13}C NMR spectrum (150 MHz, CDCl₃, 298 K) of 5





 13 C NMR spectrum (150 MHz, DMSO-*d*₆, 298 K) of **2**



¹H NMR spectrum (600 MHz, DMSO- d_6 , 298 K) of **2**

¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of **6**



 ^{13}C NMR spectrum (150 MHz, CDCl₃, 298 K) of **6**



¹H NMR spectrum (600 MHz, acetone- d_6 , 298 K) of **7**



 $^{13}\mathrm{C}$ NMR spectrum (150 MHz, acetone- $d_6,$ 298 K) of 7







 ^{13}C NMR spectrum (150 MHz, CDCl₃, 298 K) of $\boldsymbol{8}$



¹H NMR spectrum (600 MHz, DMSO- d_6 , 298 K) of **3**



 13 C NMR spectrum (150 MHz, DMSO- d_6 , 298 K) of **3**



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Computational methods

The Gaussian 09 program¹ was used for the *ab initio* molecular orbital calculations. The basis set implemented in the program was used for the calculations. The geometries of monomer and dimer were optimized at the HF/6-311G^{**} level. The intermolecular interaction energy (E_{int}) was calculated by supermolecular method at the MP2/6-311G^{**} level. The basis set superposition error (BSSE)² was corrected by the counterpoise method³ in the interaction energy calculations. Electron correlation was accounted for by the second-order Møller-Plesset perturbation (MP2) method. The stabilization energy by the formation of the dimer from monomers (E_{form}) was calculated according to equation (1),

$$E_{\rm form} = E_{\rm int} + E_{\rm def}$$
 (1)

where the E_{def} denotes the sum of the increases of energies of the monomers by the deformation of molecular geometries associated with the dimer formation. The E_{def} was calculated at the MP2/6-311G** level.



Fig. S1 ¹H-NMR spectra (600 MHz, 298 K) of **1** (a) in DMSO- d_6 , (b) in CDCl₃.



Fig. S2 2D-NOESY spectrum (600 MHz, CDCl₃, 298 K) of 2 (0.5 mM).



Fig. S3 2D-NOESY spectrum (600 MHz, DMSO-*d*₆, 298 K) of 2 (1.0 mM).



Fig. S4 ¹H-NMR spectra (600 MHz) of (a) **2** (1.0 mM) in CDCl₃ at 223 K, (b) **3** (1.0 mM) in CDCl₃ at 223 K, (c) **2** (1.0 mM) and **3** (1.0 mM) in CDCl₃ at 223 K, (d) **2** (1.0 mM) in DMSO-*d*₆ at 298 K, (e) **3** (1.0 mM) in DMSO-*d*₆ at 298 K, (f) **2** (1.0 mM) and **3** (1.0 mM) in DMSO-*d*₆ at 298 K.



Fig. S5 ESI-FT-ICR MS spectrum of 2 and 3.



Fig. S6 ¹H-NMR spectra (600 MHz, CDCl₃, 298 K) of **2** (a) 1.6 mM, (b) 0.8 mM, (c) 0.4 mM, (d) 0.2 mM, (e) 0.1 mM, (f) 0.04 mM, (g) 0.01 mM.



Fig. S7 ¹H-NMR spectra (600 MHz, CDCl₃, 298 K) of **3** (a) 1.6 mM, (b) 0.8 mM, (c) 0.4 mM, (d) 0.2 mM, (e) 0.1 mM, (f) 0.04 mM, (g) 0.01 mM.



Fig. S8 van't Hoff plot for equilibrium of 2 and 2_2 in CDCl₃/CD₃CN (5/1).



Fig. S9 Energy minimized structure of **1** with intramolecular hydrogen bonds (left) and without intramolecular hydrogen bond (right).



Fig. S10 ¹H-NMR spectra (600 MHz, CDCl₃, 298 K) of (a) **2** (0.5 mM), (b) **2** (0.5 mM) and LiClO₄ (0.5 equiv), (c) **2** (0.5 mM) and LiClO₄ (0.75 equiv), (d) **2** (0.5 mM) and LiClO₄ (1.0 equiv), (e) **2** (0.5 mM) and LiClO₄ (25 equiv).



Fig. S11 ¹H-NMR spectra (600 MHz, $CDCl_3/CD_3CN = 110/1$, 298 K) of (a) **2** (0.5 mM), (b) **2** (2.0 mM) and LiClO₄ (1 equiv), (c) **2** (2.0 mM) and NaClO₄ (19 equiv).



Fig. S12 1 H-NMR spectra (600 MHz, CDCl₃, 298 K) of (a) 3 (1.0 mM), (b) 3 (1.0 mM) and LiClO₄

(1.0 equiv), (c) **3** (1.0 mM) and NaClO₄ (100 equiv), (d) **3** (1.0 mM) and KClO₄ (100 equiv).



Fig. S13 ¹H-NMR spectra (600 MHz, CDCl₃, 298 K) of (a) **2** (1.0 mM) and LiClO₄ (excess), (b) **3** (1.0 mM) and LiClO₄ (excess), (c) **2** (1.0 mM), **3** (1.0 mM) and LiClO₄ (excess).



Fig. S14 2D-NOESY spectrum (600 MHz, CDCl₃, 298 K) of 2 (1.0 mM) and LiClO₄ (1.0 equiv).



Fig. S15 ¹H-NMR spectra (600 MHz, CDCl₃, 298 K) of **2** and LiClO₄ (1.0 equiv) (a) 1.0 mM, (b) 0.75 mM, (c) 0.5 mM, (d) 0.25 mM, (e) 0.1 mM. The minimum association constant (K_{2-Li+}) for the **2**-Li⁺ complexation was calculated by following equation. $K_{2-Li+} = [2-Li^+]^2/[2\cdot 2][Li^+]^2$



Fig. S16 ¹H-NMR spectra (600 MHz, CDCl₃, 298 K) of **3** and LiClO₄ (1.0 equiv) (a) 1.0 mM, (b) 0.75 mM, (c) 0.5 mM, (d) 0.25 mM, (e) 0.1 mM. The minimum association constant (K_{3-Li+}) for the **3**-Li⁺ complexation was calculated by following equation. $K_{3-Li+} = [3-Li^+]^2/[3\cdot3][Li^+]^2$



Fig. S17 ¹H-NMR spectra (600 MHz, CDCl₃, 298 K) of **3** and LiClO₄ (0.5 equiv) (a) 1.0 mM, (b) 0.75 mM, (c) 0.5 mM, (d) 0.25 mM, (e) 0.1 mM.



Fig. S18 ¹H-NMR spectra (600 MHz, $CDCl_3/CD_3CN = 1/1$, 298 K) of **2** (0.5 mM) and $LiClO_4$ (a) 0 equiv, (b) 20 equiv, (c) 40 equiv, (d) 60 equiv, (e) 80 equiv, (f) 100 equiv, (g) 120 equiv. Association constant of Li^+ to **2** was determined by non-linear least squares analysis of the titration data.



Fig. S19 ¹H-NMR spectra (600 MHz, CDCl₃/CD₃CN = 1/1, 298 K) of **2** (0.5 mM) and NaClO₄ (a) 0 equiv, (b) 30 equiv, (c) 60 equiv, (d) 90 equiv, (e) 120 equiv, (f) 150 equiv, (g) 180 equiv. Association constant of Na⁺ to **2** was determined by non-linear least squares analysis of the experiments data.



Fig. S20 ¹H-NMR spectra (600 MHz, $CDCl_3/CD_3CN = 1/1$, 298 K) of **3** (2.0 mM) and $LiClO_4$ (a) 0 equiv, (b) 1.0 equiv, (c) 2.0 equiv, (d) 3.0 equiv, (e) 4.0 equiv, (f) 5.0 equiv, (g) 6.0 equiv, (h) 7.0 equiv, (i) 8.0 equiv, (j) 9.0 equiv, (k) 10.0 equiv. Association constant of Li^+ to **3** was determined by non-linear least squares analysis of the experiments data.



Fig. S21 ¹H-NMR spectra (600 MHz, $CDCl_3/CD_3CN = 1/1$, 298 K) of **3** (2.0 mM) and $NaClO_4$ (a) 0 equiv, (b) 11 equiv, (c) 26 equiv, (d) 29 equiv, (e) 48 equiv, (f) 56 equiv, (g) 66 equiv. Association constant of Na^+ to **3** was determined by non-linear least squares analysis of the experiments data.

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