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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**



S15

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.

References

Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
(2) B. J. Ransil, J. Chem. Phys., 1961, **34**, 2109–2118.

(3) S. F. Boys and F. Bernardi, Mol. Phys., 1970, 19, 553–566.