Electronic Supplementary Information†

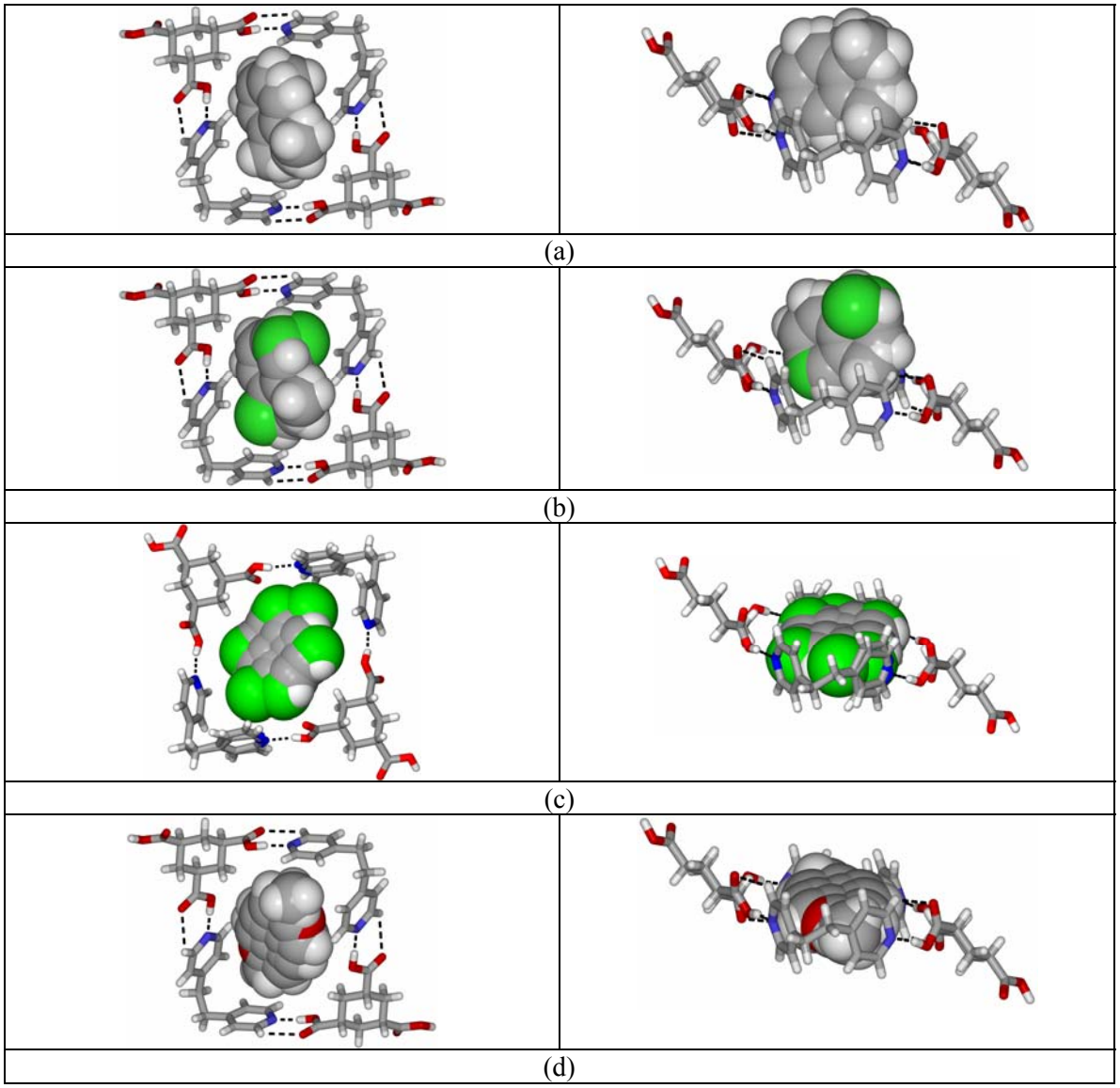
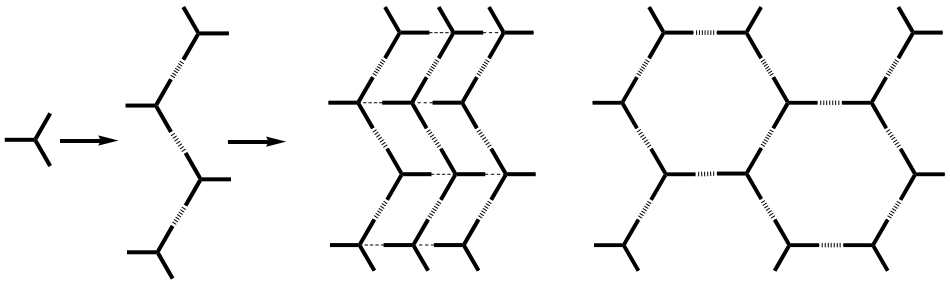
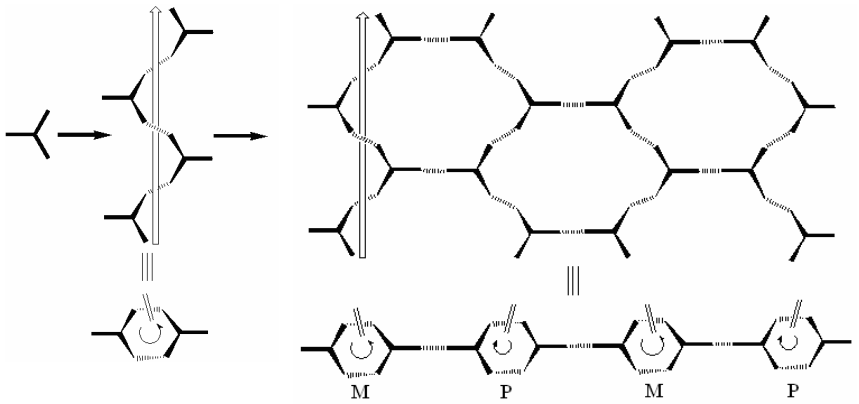


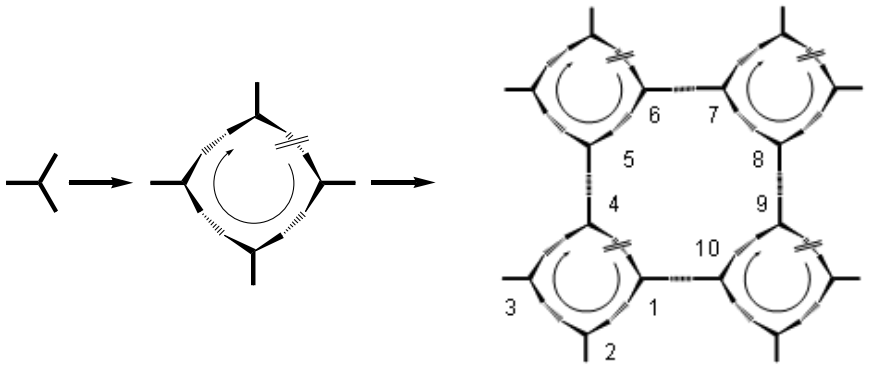
Figure S1 The orientation and location of guest molecules in the channel of ternary host **5**. (a) *o*-xylene in **5c**, (b) *o*-chlorotoluene in **5d**, (c) *o*-dichlorobenzene in **5e**, and (d) anisole in **5f**.



Trigonal node → 1D tape | 2D close packed | 2D (6,3) hexagonal network



Trigonal node → 2_1 helix | 2D (6,3) net built from 2_1 helices



Trigonal node → 4_1 helix | 3D (10,3)-*a* net from 4_1 helices

Figure S2 Self-assembly pathway proposed to explain concomitant crystallization of H_3TMA•bipy-eta polymorphs I and II.[13b]

Synthesis and co-crystallization

Dibromo-ethane-bipy (dibr-bipy-eta) was prepared using a literature procedure.[18] ^{1}H-NMR ($CDCl_3$, δ in ppm, J in Hz): 8.70 (d, J = 6, 2 H), 7.40 (d, J = 6, 2 H), 5.27 (s, 1 H).

H_3CTA•bipy•(bipy-eta)$_{0.5}$ (1)

1,3*cis*,5*cis*-Cyclohexanetricarboxylic acid, bipy and bipy-eta in 2:2:1 ratio in EtOH/benzene was heated and allowed to crystallize at room temperature. Crystals of H_3CTA·bipy·bipy-eta (2:2:1) obtained in a week. M.p. 175-180 °C. ^{1}H-NMR (DMSO-d_6, δ in ppm, J in Hz): 12.24 (br s, 3 H) 8.74 (d, J = 4, 4 H), 8.45 (br s, 2 H), 7.84 (d, J = 4, 4 H), 7.25 (d, J = 7, 2 H), 2.94 (s, 2 H), 2.34 (br t, J = 8, 3 H), 2.11 (br d, J = 10, 3 H), 1.28 (br q, J = 10, 3 H).

H_3CTA•bipy-ete•(bipy-eta)$_{0.5}$ (2)

H_3CTA, bipy-ete and bipy-eta in 2:2:1 ratio in n-propanol was heated and allowed to crystallize at room temperature. Crystals of H_3CTA·bipy-ete·bipy-eta (2:2:1) obtained in a week. M.p. 207-210 °C. ^{1}H-NMR (DMSO-d_6, δ in ppm, J in Hz): 12.20 (br s, 3 H), 8.62 (br s, 4 H), 8.45 (br s, 2 H), 7.60 (d, J = 8, 4 H), 7.50 (s, 2 H), 7.25 (d, J = 7, 2 H), 2.92 (s, 2 H), 2.32 (br t, J = 8, 3 H), 2.10 (br d, J = 10, 3 H), 1.27 (br q, J = 10, 3 H).

H_3CTA•br-bipy-ete•(dibr-bipy-eta)$_{0.5}$ (3)

A mixture of H_3CTA and dibr-bipy-eta in 2:3 ratio in EtOH/MeOH was heated and allowed to crystallize at room temperature. Crystals of H_3CTA·bipy-ete·bipy-eta (2:2:1) obtained in a week. M.p. 168-175 °C (crystals start to decompose at 145 °C and turned brown in color). ^{1}H-NMR (DMSO-d_6, δ in ppm, J in Hz): 12.24 (br s, 3 H), 8.70 (br s, 6 H), 7.88 (s, 1 H), 7.40 (br m, 6 H), 6.21 (s, 1 H), 2.35 (br t, J = 8, 3 H), 2.10 (br d, J = 10, 3 H), 1.27 (br q, J = 10, 3 H).

H_3CTA•(bipy-eta)$_{0.8}$•(br-bipy-ete)$_{0.2}$•(dibr-bipy-eta)$_{0.5}$ (4)

Co-crystallization of H_3CTA, bipy-eta and dibr-bipy-eta in 1:1:0.5 ratio in MeOH in refrigerator (4 °C) after one weak gave diffraction quality crystals of **4**. M.p. 170-175 °C (crystals starting decomposing at 150 °C and turned brown in color). ^{1}H-NMR (DMSO-d_6, δ in ppm, J in Hz): 12.24 (br s, 3 H), 8.70 (br s, 2.8 H), 8.45 (br s, 3.2 H), 7.85 (s, 0.2 H), 7.70 (br s, 2.8 H), 7.31 (br m, 3.2 H), 6.20 (s, 1 H), 2.94 (s, 3.2 H), 2.35 (br t, J = 8, 3 H), 2.10 (br d, J = 10, 3 H), 1.27 (br q, J = 10, 3 H). Fractional H atom integration due to partial occupancy of base components.

[5]•(guest)$_{0.5}$ [5 = H_3CTA·bipy-eta·(bipy-bu)$_{0.5}$] (5a-5h)

A mixture of H_3CTA, bipy-eta and bipy-bu in 2:2:1 ratio in n-propanol/and appropriate aromatic third component (= guest) gave crystals **5a**, **5c-5h** at room temperature in a week. H_3CTA, bipy-eta, bipy-bu and *p*-dichlorobenzene in 2:2:1:1.5 were co-crystallized in ethanol to get **5b**. Suitable crystals of **5h** for X-ray diffraction were obtained from *n*-propanol while trying to prepare **5b** by using exact amount (2:2:1:1) of *p*-dichlorobenzene in repeated crystallization of alcohols. The presence of all four components is conformed by ^{1}H-NMR. **5a**: M.p. 139 °C (T_{onset}, DSC). ^{1}H-NMR (DMSO-d_6, δ in ppm, J in Hz): 12.20 (br s, 3 H), 8.44 (br s, 6 H), 7.25 (br m, 6 H), 7.05 (s, 2 H), 2.94 (s, 4 H), 2.61 (br s, 2 H), 2.32 (br t, J = 8, 3 H), 2.24 (s, 3 H), 2.10 (br d, J = 10, 3 H), 1.61 (br s, 2 H), 1.27 (br q, J = 10, 3 H). **5b**: M.p. 159-162 °C. ^{1}H-NMR (DMSO-d_6, δ in ppm, J in Hz): 12.20 (br s, 3 H), 8.44 (br s, 6 H), 7.25 (br m, 6 H), 7.20 (s, 2 H), 2.94 (s, 4 H), 2.61 (br s, 2 H), 2.32 (br t, J = 8, 3 H), 2.10 (br d, J = 10, 3 H), 1.61 (br s, 2 H), 1.27 (br q, J = 10, 3 H). **5c**: M.p. 130-132 °C. ^{1}H-NMR (DMSO-d_6, δ in ppm, J in Hz): 12.20 (br s, 3 H), 8.44 (br s, 6 H), 7.25 (br m, 6 H), 7.12 (m, 1 H), 7.06 (m, 1 H), 2.94 (s, 4 H), 2.61 (br s, 2 H), 2.32 (br t, J = 8, 3 H), 2.21 (s, 3 H), 2.10 (br d, J = 10, 3 H), 1.61 (br s, 2 H), 1.27 (br q, J = 10, 3 H). **5d**: M.p. 133-135 °C. ^{1}H-NMR (DMSO-d_6, δ in ppm, J in Hz): 12.20 (br s, 3 H), 8.44 (br s, 6 H), 7.41 (m, 1 H), 7.35 (m, 1 H), 7.25 (br m, 6 H), 2.94 (s, 4 H), 2.61 (br s, 2 H), 2.33 (br t, J = 8, 3 H), 2.36 (s, 1.5 H), 2.10 (br d, J = 10, 3 H), 1.61 (br s, 2 H), 1.27 (br q, J = 10, 3 H) **5e**: M.p. 135-137 °C. ^{1}H-NMR (DMSO-d_6, δ in ppm, J in Hz): 12.20 (br s, 3 H), 8.44 (br s, 6 H), 7.64 (br m, 1 H), 7.38 (br m, 1 H), 7.25 (br m, 6 H), 2.94 (s, 4 H), 2.61 (br s, 2 H), 2.32 (br t, J = 8, 3 H), 2.10 (br d, J = 10, 3 H), 1.61 (br s, 2 H), 1.27 (br q, J = 10, 3 H). **5f**: M.p. 133-135 °C. ^{1}H-NMR (DMSO-d_6, δ in ppm, J in Hz): 12.20 (br s, 3 H), 8.44 (br s, 6 H), 7.25 (br m, 6 H), 7.15 (br s, 1 H), 6.93 (br s, 0.5 H), 6.32 (s, 1 H), 3.75 (s, 1.5 H), 2.94 (s, 4 H), 2.61 (br s, 2 H), 2.32 (br t, J = 8, 3 H), 2.10 (br d, J = 10, 3 H), 1.61 (br s, 2 H), 1.27 (br q, J = 10, 3 H). **5g**: M.p. 135-140 °C ^{1}H-NMR (DMSO-d_6, δ in ppm, J in Hz): 12.20 (br s, 3 H), 8.44 (br s, 6 H), 7.25 (br m, 6 H), 2.94 (s, 4 H), 2.61 (br s, 2 H), 2.32 (br t, J = 8, 3 H), 2.10 (br d, J = 10, 3 H), 1.61 (br s, 2 H), 1.27 (br q, J = 10, 3 H). **5h**: M.p. 137-140 °C. ^{1}H-NMR (DMSO-d_6, δ in ppm, J in Hz): 12.20 (br s, 3 H), 8.47 (br s, 7 H), 7.27 (br m, 7 H), 2.94 (s, 4 H), 2.61 (br s, 3 H), 2.32 (br t, J = 8, 3 H), 2.10 (br d, J = 10, 3 H), 1.61 (br s, 3 H), 1.27 (br q, J = 10, 3 H).