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.
Figure S2 Self-assembly pathway proposed to explain concomitant crystallization of H$_3$TMA•bipy-eta polymorphs I and II.$^{13b}$
Synthesis and co-crystallization

Dibromo-ethane-bipy (dibr-bipy-eta) was prepared using a literature procedure.\textsuperscript{18} $^1$H-NMR (CDCl$_3$, $\delta$ in ppm, J in Hz): 8.70 (d, J = 6, 2 H), 7.40 (d, J = 6, 2 H), 5.27 (s, 1 H).

$\text{H}_3\text{CTA}$•bipy•(bipy-eta)$_{0.5}$ (1)

1,3cis,5cis-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 $\text{H}_3\text{CTA}$-bipy-bipy-eta (2:2:1) obtained in a week. M.p. 175-180 °C. $^1$H-NMR (DMSO-$d_6$, $\delta$ 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).

$\text{H}_3\text{CTA}$•bipy-ete•(bipy-eta)$_{0.5}$ (2)

$\text{H}_3\text{CTA}$, bipy-ete and bipy-eta in 2:2:1 ratio in n-propanol was heated and allowed to crystallize at room temperature. Crystals of $\text{H}_3\text{CTA}$-bipy-ete-bipy-eta (2:2:1) obtained in a week. M.p. 207-210 °C. $^1$H-NMR (DMSO-$d_6$, $\delta$ 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), 7.92 (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).

$\text{H}_3\text{CTA}$•br-bipy-ete•(dibr-bipy-eta)$_{0.5}$ (3)

A mixture of $\text{H}_3\text{CTA}$ and dibr-bipy-eta in 2:3 ratio in EtOH/MeOH was heated and allowed to crystallize at room temperature. Crystals of $\text{H}_3\text{CTA}$-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-$d_6$, $\delta$ in ppm, J in Hz): 12.24 (br s, 3 H), 8.70 (br s, 6 H), 8.45 (br s, 2 H), 7.85 (s, 0.2 H), 7.70 (br s, 2.8 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).

$\text{H}_3\text{CTA}$•(bipy-eta)$_{0.8}$•(br-bipy-ete)$_{0.2}$•(dibr-bipy-eta)$_{0.5}$ (4)

Co-crystallization of $\text{H}_3\text{CTA}$, 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-$d_6$, $\delta$ 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.
A mixture of H$_3$CTA, 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$_3$CTA, 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), 7.25 (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). 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), 7.64 (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). 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), 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). 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).