Supporting Information

Tiara[5]arenes: Synthesis, Solid-State Conformational Studies, Host–Guest Properties, and Application as Nonporous Adaptive Crystals

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1. General Methods

Starting materials, reagents, and solvents were purchased from commercial vendors and used as received, unless otherwise noted. All reactions were performed under an argon atmosphere and in dry solvents, unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets, precoated with silica gel GF254. Flash column chromatography was performed over silica gel (200–300 mesh or 300–400 mesh). $^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded on Bruker Advance 400 MHz and 600 MHz spectrometers at ambient temperature, unless otherwise noted. The chemical shifts are listed in ppm on the δ scale and coupling constants were recorded in Hz. Chemical shifts are calibrated relative to the signals of the non-deuterated solvents (CHCl$_3$: δ 7.26 ppm, CH$_3$OH: δ 3.31 ppm, (CD$_3$)$_2$CO, δ 2.05 ppm). High-resolution mass spectra (HRMS) were measured on a Q-Exactive™ HF/UltiMate™ 3000 RSLCnano using a Nano ProFlow meter with ProFlow technology in positive mode.

2. Synthetic Procedures

**Scheme S1.** Schematic representations of the preoriented synthesis of C$_5$-symmetric rim-differentiated pillar[5]arene (RD-P[5]). (a) Without retro-Friedel-Crafts reaction, the oligomerization in the presence of a Lewis acid proceeds in a “head-to-tail” fashion and leads to the exclusive formation of the regioregular linear pentamer, which eventually cyclizes into RD-P[5]. (b) The presence of water introduces retro-Friedel-Crafts reactions and results in a mixture of RD-P[5] and 3 other undesired constitutional isomers.
(OTf)$_5$-P[5]:$^{[1]}$ (2-(benzyloxy)-5-methoxyphenyl)methanol$^{[1]}$ (1.7 g, 7 mmol, 1.0 eq.) was dissolved in anhydrous 1,2-dichloroethane (DCE) (700 mL), and anhydrous FeCl$_3$ (114 mg, 0.7 mmol, 0.1 eq.) was added. Reaction mixture was stirred at 25 °C for 4 h, filtered and quenched with MeOH (100 mL) then solution concentrated to dryness. Column chromatography (silica, EtOAc/n-hexane, 1/4) followed by recrystallization from EA and Hexane afforded (OBn)$_5$-RD-P[5] as a white solid (378 mg, 0.33 mmol, 25%). Multiple reactions were set up in parallel for gram-scale synthesis. To a solution of (OBn)$_5$-RD-P[5] (1.0 g, 0.88 mmol, 1.0 eq.) in DCE (50 mL) was added Pd/C (10% wt, wetted with 55% H$_2$O, 1.0 g) and HCO$_2$NH$_4$ (1.1 g, 17.6 mmol, 20 eq.). Solution was heated to 60 °C and stirred for 4 h, filtered over a pad of celite and concentrated to dryness to afford (OH)$_5$-RD-P[5] as a white solid (600 mg, 0.88 mmol, quant.). Then a solution of (OH)$_5$-RD-P[5] (freshly obtained from 1.0 g (OBn)$_5$-RD-P[5], 0.88 mmol, 1.0 eq.) in dry pyridine (20 mL) was added Tf$_2$O (1.11 mL, 6.6 mmol, 7.5 eq.) at 0 °C (ice bath). The resulting solution was allowed to warm to 25 °C for 12 h. Water was added, and the precipitate was filtered and dried. Column chromatography (CH$_2$Cl$_2$/n-hexane, 1/4) afforded (OTf)$_5$-RD-P[5] as a white solid (1.027 g, 0.76 mmol, 87%).

**Figure S1.** (a) $^1$H NMR (600 MHz) and (b) $^{13}$C NMR (150 MHz) spectra of (OTf)$_5$-RD-P[5] (CDCl$_3$, 298 K).
**T[5]-(OMe)s:** To a solution of (OTf)_5-RD-P[5] (320 mg, 0.24 mmol, 1.0 eq.) in 1:1 MeOH:EtOAc (10 mL) was added diethylamine (0.15 mL, 1.43 mmol, 6 eq.) followed by Pd/C (10% wt, wetted with 55% H_2O, 250 mg). The resulting mixture was stirred under H_2 atmosphere at 25 °C for 24 h, filtered over a pad of celite and concentrated to dryness. Column chromatography (EtOAc/n-hexane, 1/9) afforded product (138 mg, 0.23 mmol, 96%) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 6.73 (d, J = 1.6 Hz, 5H), 6.69 (d, J = 7.7 Hz, 5H), 6.43 (dd, J = 7.7 Hz, 1.6 Hz 5H), 3.83 (s, 10 H), 3.75 (s, 15 H). ¹³C NMR (101 MHz, CDCl₃): δ 156.7, 141.0, 129.9, 127.3, 120.7, 111.3, 55.3, 35.3. HRMS (ESI) m/z [M + Na]^+ Calcd. for C₃₅H₃₀O₅Na 553.1991, found 553.2017.

**Figure S2.** (a) ¹H NMR (400 MHz) and (b) ¹³C NMR (101 MHz) spectra of T[5]-(OMe)s (CDCl₃, 298 K).
**T[5]**: To a solution of **T[5]**-(OMe)$_5$ (50 mg, 0.083 mmol, 1.0 eq.) in dry CHCl$_3$ (3 mL) was added BBr$_3$ (0.15 mL, 1.6 mmol, 19 eq.). The resulting mixture was stirred at 25 °C for 24 h. Water (10 mL) was added and the mixture was washed with copious amounts of water, brine, dried over Na$_2$SO$_4$, filtered and concentrated to dryness. Column chromatography (MeOH/CH$_2$Cl$_2$, 0/100 to 4/96) to afford product as a white solid (43 mg, 0.082 mmol, quant.).$^1$H NMR (400 MHz, (CD$_3$)$_2$CO): δ 7.97 (s, 5H), 6.85 (d, $J = 7.7$ Hz, 5H), 6.7 (d, $J = 1.7$ Hz, 5H), 6.58 (dd, $J = 7.7$ Hz, 1.7 Hz, 5H), 3.66 (s, 10H).$^{13}$C NMR (101 MHz, (CD$_3$)$_2$CO): δ 154.7, 142.3, 130.6, 127.1, 120.9, 116.7, 35.9. HRMS (ESI) $m/z$ [M + H]$^+$ Calcd. for C$_{40}$H$_{41}$O$_6$ 601.2954, found 601.2944.

**Figure S3.** (a) $^1$H NMR (400 MHz) and (b) $^{13}$C NMR (101 MHz) spectra of **T[5]** ((CD$_3$)$_2$CO, 298 K).
**p-Formyl-T[5]-(OMe)₅**: To a solution of T[5]-(OMe)₅ (50 mg, 0.083 mmol, 1.0 eq.) in trifluoroacetic acid (10 mL) was added hexamethylenetetramine (HMTA) (0.29 mg, 2.1 mmol, 25 eq.). The resulting mixture was vigorously refluxed for 6 h under inert atmosphere, then cooled to RT, diluted with ice-cold 1 M HCl (20 mL) and dichloromethane (20 mL), and vigorously stirred at RT for 3 h. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layer was washed with satd. NaHCO₃ (2 × 25 mL), brine (2 × 25 mL), dried over Na₂SO₄ and concentrated. Purification by column chromatography (EtOAc/n-hexane, 6/4) afforded **p-formyl-T[5]-(OMe)₅** (38 mg, 0.051 mmol, 61%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 10.37 (s, 5H, -CHO), 7.76 (s, 5H), 6.66 (s, 5H), 4.26 (s, 10H), 3.64 (s, 15H). ¹³C NMR (101 MHz, CDCl₃) δ 190.5, 160.9, 144.1, 131.9, 127.7, 127.1, 113, 55.1, 30.9. HRMS (ESI) m/z [M + Na]⁺ Calcd for C₄₅H₄₁O₇ 741.2694, found 741.2671.

Figure S4. (a) ¹H (400 MHz) and (b) ¹³C NMR (101 MHz) spectra of **p-formyl-T[5]-(OMe)₅** (CDCl₃, 298 K).
**T[5]-(OTf)s:** To a solution of T[5] (90 mg, 0.17 mmol, 1.0 eq.) in dry pyridine (2.5 mL) was added Tf₂O (222 μL, 1.36 mmol, 8.0 eq.) at 0 °C (ice bath). The resulting solution was allowed to warm to 25 °C for 24 h. Water (10 mL) was added and the mixture was extracted with CH₂Cl₂ (3 × 15 mL), dried over Na₂SO₄, filtered and concentrated to dryness. Column chromatography (MeOH/CH₂Cl₂, 1/19) afforded the product as a white solid (161.8 mg, 0.136 mmol, 80%). ¹H NMR (400 MHz, CDCl₃) δ 7.07 (s, 5H), 7.03 (d, J = 8.0 Hz, 5H), 6.97 (dd, J = 8.0, 1.2 Hz, 5H), 3.96 (s, 10H). ¹³C NMR (101 MHz, CDCl₃) δ 147.3, 140.4, 131.8, 131.3, 129.0, 122.0, 118.5 (q, J = 320.2 Hz), 35.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -73.79. HRMS (ESI) m/z [M + K]⁺ Calcd for C₄₀H₂₅F₁₅O₁₅S₅K 1228.9195, found 1228.9188.

**Figure S5.** (a) ¹H (400 MHz), (b) ¹³C (101 MHz), and (c) ¹⁹F (376 MHz) NMR spectra of T[5]-(OTf)s (CDCl₃, 298 K).
**o,p-Dibromo-T[5]**: To a solution of T[5] (10.3 mg, 0.02 mmol, 1.0 eq.) in dioxane (1.0 mL) was added bromine water dropwise (3.0 mL) at 0 °C (ice bath). The resulting solution was allowed to warm to 25 °C for 24 h and concentrated to dryness. Water (10 mL) was added and the mixture was extracted with CH₂Cl₂ (3 × 15 mL), dried over Na₂SO₄, filtered and concentrated to dryness. Column chromatography (MeOH/CH₂Cl₂, 1/99) afforded the product as a pale yellow solid (10.0 mg, 0.008 mmol, 41%). ¹H NMR (600 MHz, CDCl₃) δ 6.83 (s, 5H), 5.84 (s, 5H), 4.31 (s, 10H). ¹³C NMR (151 MHz, CDCl₃) δ 149.8, 137.2, 133.4, 126.0, 115.3, 114.1, 35.9. HRMS (ESI) m/z [M + Na]⁺ Calcd for C₃₅H₂₀Br₁₀O₅Na 1342.2934, found 1342.2992.

![Chemical structure](image)

**Figure S6.** (a) ¹H (600 MHz) and (b) ¹³C (151 MHz) NMR spectra of o,p-dibromo-T[5] (CDCl₃, 298 K).
**o,p-Dibromo-T[5]**: To a solution of T[5] (10.3 mg, 0.02 mmol, 1.0 eq.) in PEG-400 (1.0 mL) was added NBS (35.6 mg, 0.2 mmol, 10.0 eq.) in 5 min at 25 °C for 1 h. Water (10 mL) was added and the mixture was extracted with CH₂Cl₂ (3 × 15 mL), dried over Na₂SO₄, filtered and concentrated to dryness. Column chromatography (MeOH/CH₂Cl₂, 1/99) afforded the product as a pale yellow solid (2.1 mg, 1.6 μmol, 8%).

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**Figure S7.** (a) ESI mass spectrum of o,p-dibromo-T[5] and (b) simulated isotopic distribution for molecular formula C₃₅H₂₀Br₁₀O₅Na [M + Na].
**T[5]-2,3,4,5-(OMe)₄**: To a solution of **T[5]-(OMe)₅** (353.6 mg, 0.59 mmol, 1.0 eq.) in dry CHCl₃ (15 mL) was added BBr₃ (225.9 mg, 0.89 mmol, 1.5 eq.) at room temperature for 24 h. Water (30 mL) was added to quench the reaction and extracted with CH₂Cl₂ (3 × 45 mL). The combined organic extract was dried by anhydrous Na₂SO₄, concentrated in vacuum, and purified by column chromatography (EtOAc/n-hexane, 1/9) afforded the product as white solid. (110.6 mg, 0.19 mmol, 32%). ¹H NMR (600 MHz, CDCl₃) δ 6.82 (d, J = 7.7 Hz, 1H), 6.77 (d, J = 7.7 Hz, 1H), 6.75–6.69 (m, 5H), 6.67 (d, J = 7.7 Hz, 1H), 6.62–6.57 (m, 3H), 6.46 (td, J = 7.4, 1.6 Hz, 2H), 6.42 (dd, J = 7.7, 1.6 Hz, 1H), 6.36 (dd, J = 7.7, 1.6 Hz, 1H), 3.84 (s, 2H), 3.83 (s, 2H), 3.83 (s, 4H), 3.77 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 156.9, 156.8, 156.7, 156.6, 152.9, 141.7, 141.2, 141.0, 140.7, 140.0, 130.4, 130.0, 129.9, 129.8, 129.7, 127.9, 127.6, 127.5, 127.4, 125.1, 121.5, 121.0, 120.8, 120.6, 120.3, 116.3, 111.7, 111.6, 111.3, 111.1, 55.3, 55.3, 35.5, 35.3, 35.3, 35.2, 34.9. HRMS (ESI) m/z [M + H]+ Calcd for C₃₉H₃₈O₆H 585.2647, found 585.2660.

**Figure S8.** (a) ¹H NMR (600 MHz), (b) ¹³C NMR (151 MHz) NMR spectra of **T[5]-2,3,4,5-(OMe)₄** (CDCl₃, 298 K).
3. X-Ray Crystallography

Single crystals suitable for X-ray diffraction were selected and mounted in inert oil in cold gas stream and their X-ray diffraction intensity data was collected on a Rigaku XtaLAB FRX diffractometer equipped with a Hypix6000HE detector, using Cu Ka radiation (λ = 1.54184 Å). Crystals were kept at the temperature listed in Table S1-S7 during data collection. By the use of Olex2,[2] the structure was solved either (i) with the ShelXS[3] structure solution program using Direct Methods or (ii) with the ShelXT[4] structure solution program using Direct Methods or Intrinsic Phasing. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Some guest molecules were refined isotropically due to disorder that could not be modeled precisely. Distance restraints were also imposed on some disordered guest hexane molecules. Selected details of the data collection and structural refinement of each compound can be found within Table S1–S7 and full details are available in the corresponding CIF files. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre and may be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.
Figure S9. Top and side views of assorted T[5]-(OMe)₅ conformers found in crystal structures obtained under different crystallization conditions.
Table S1. Crystal data and structure refinement for T[5]-(OMe)s

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                            | C_{40}H_{40}O_{5}                          |
| Formula weight / g mol\(^{-1}\)               | 600.72                                     |
| Temperature / K                               | 160.00(10)                                 |
| Crystal system                                | triclinic                                  |
| Space group                                   | \(P\)-I                                    |
| \(a\) / Å                                     | 11.30470(10)                               |
| \(b\) / Å                                     | 12.60500(10)                               |
| \(c\) / Å                                     | 12.78350(10)                               |
| \(\alpha\) / °                                 | 76.1580(10)                                |
| \(\beta\) / °                                 | 88.8410(10)                                |
| \(\gamma\) / °                                | 66.9490(10)                                |
| Volume / Å\(^3\)                             | 1621.97(3)                                 |
| \(Z\)                                         | 2                                          |
| \(\rho_{\text{calc}}\) / g cm\(^{-3}\)     | 1.230                                      |
| \(\mu\) / mm\(^{-1}\)                       | 0.634                                      |
| \(F / 000\)                                   | 640.0                                      |
| \(2\theta\) range for data collection / °    | 7.164 to 149.378                           |
| Crystal size / mm\(^3\)                      | 0.2 \times 0.02 \times 0.02               |
| Index ranges                                  | \(-14 \leq h \leq 13, -15 \leq k \leq 15, -15 \leq l \leq 15\) |
| Reflections collected                         | 45791                                      |
| Independent reflections                       | 6363 [\(R_{\text{int}} = 0.0375, R_{\text{sigma}} = 0.0193\)] |
| Data/restraints/parameters                    | 6363/0/411                                 |
| Goodness-of-fit on \(F^2\)                    | 1.079                                      |
| Final R indices [I > 2\(\sigma(I)\)]         | \(R_I = 0.0513, wR_2 = 0.1435\)            |
| Final R indices [all data]                    | \(R_I = 0.0554, wR_2 = 0.1472\)            |
| Largest diff. peak / hole / e Å\(^3\)        | 0.53/-0.25                                 |
| CCDC No.                                      | 1957868                                    |
| Crystallization solvents                      | methanol/chloroform                        |
Table S2. Crystal data and structure refinement for CH$_3$CN⊂T[5]-(OMe)$_5$

| Property                                              | Value                                      |
|-------------------------------------------------------|--------------------------------------------|
| Empirical formula                                     | C$_{42}$H$_{43}$NO$_5$                     |
| Formula weight / g mol$^1$                            | 641.77                                     |
| Temperature / K                                       | 159.99(10)                                 |
| Crystal system                                        | triclinic                                  |
| Space group                                           | $P-1$                                      |
| $a$ / Å                                               | 12.0935(2)                                 |
| $b$ / Å                                               | 17.8479(3)                                 |
| $c$ / Å                                               | 17.9763(2)                                 |
| $\alpha$ / °                                         | 95.1170(10)                                |
| $\beta$ / °                                          | 106.5750(10)                               |
| $\gamma$ / °                                         | 105.9900(10)                               |
| Volume / Å$^3$                                        | 3515.19(9)                                 |
| $Z$                                                   | 4                                          |
| $\rho_{calc}$ / g cm$^3$                             | 1.213                                      |
| $\mu$ / mm$^{-1}$                                     | 0.626                                      |
| $F$ / 000                                             | 1368.0                                     |
| $2\theta$ range for data collection / °               | 5.216 to 149.272                           |
| Crystal size / mm$^3$                                | 0.2 × 0.2 × 0.2                            |
| Index ranges                                          | -14 ≤ h ≤ 15, -21 ≤ k ≤ 22, -18 ≤ l ≤ 22 |
| Reflections collected                                 | 34158                                      |
| Independent reflections                               | 12350 [R$_{int}$ = 0.0208, R$_{sigma}$ = 0.0283] |
| Data/restraints/parameters                            | 12350/1/1069                               |
| Goodness-of-fit on $F^2$                              | 1.140                                      |
| Final R indices [I > 2σ(I)]                           | $R_I = 0.0701$, $wR_2 = 0.1651$            |
| Final R indices [all data]                            | $R_I = 0.0727$, $wR_2 = 0.1681$            |
| Largest diff. peak / hole / e Å$^3$                   | 0.28/-0.28                                |
| CCDC No.                                              | 1896025                                    |
| Crystallization solvents                              | methanol/acetonitrile                      |
Table S3. Crystal data and structure refinement for PhMe@T[5]

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                             | C_{42}H_{40}O_6                            |
| Formula weight / g mol\(^{-1}\)              | 640.74                                    |
| Temperature / K                               | 301.60(10)                                |
| Crystal system                                | triclinic                                  |
| Space group                                   | P-1                                        |
| a / Å                                         | 10.1845(2)                                |
| b / Å                                         | 12.1980(2)                                |
| c / Å                                         | 15.5764(2)                                |
| α / °                                         | 98.7530(10)                               |
| β / °                                         | 102.834(2)                                |
| γ / °                                         | 107.544(2)                                |
| Volume/ Å\(^3\)                              | 1748.27(3)                                |
| Z                                             | 2                                          |
| ρ\(_{\text{calc}}\) / g cm\(^{-3}\)         | 1.217                                      |
| μ / mm\(^{-1}\)                              | 0.644                                      |
| F / 000                                       | 680.0                                     |
| 2θ range for data collection / °             | 5.988 to 149.204                          |
| Crystal size / mm\(^3\)                      | 0.2 × 0.2 × 0.2                           |
| Index ranges                                  | -12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -19 ≤ l ≤ 19 |
| Reflections collected                         | 33007                                     |
| Independent reflections                      | 6919 [R\(_{\text{int}}\) = 0.0218, R\(_{\text{sigma}}\) = 0.0147] |
| Data/restraints/parameters                    | 6919/577/604                              |
| Goodness-of-fit on F\(^2\)                   | 1.075                                     |
| Final R indices [I >2σ(I)]                   | R\(_{\text{f}}\) = 0.0531, wR\(_{2}\) = 0.1520 |
| Final R indices [all data]                   | R\(_{\text{f}}\) = 0.0604, wR\(_{2}\) = 0.1600 |
| Largest diff. peak / hole / e Å\(^3\)        | 0.41/-0.35                                |
| CCDC No.                                      | 1957871                                   |
| Crystallization solvent                       | toluene                                    |
Table S4. Crystal data and structure refinement for C₆H₆@[T[5]-(OMe)]$_{5}$

| Property                                      | Value                        |
|-----------------------------------------------|------------------------------|
| Empirical formula                             | C$_{52}$H$_{52}$O$_{5}$      |
| Formula weight / g mol$^{-1}$                 | 756.93                       |
| Temperature / K                                | 159.99 (10)                  |
| Crystal system                                | monoclinic                   |
| Space group                                   | $P2_1/c$                     |
| $a$ / Å                                       | 13.07000(10)                 |
| $b$ / Å                                       | 25.2860(2)                   |
| $c$ / Å                                       | 13.24560(10)                 |
| $\alpha$ / °                                  | 90                           |
| $\beta$ / °                                   | 106.9020(10)                 |
| $\gamma$ / °                                  | 90                           |
| Volume / Å$^3$                                 | 4188.42(6)                   |
| $Z$                                           | 4                            |
| $\rho_{\text{calc}}$ / g cm$^{-3}$            | 1.200                        |
| $\mu$ / mm$^{-1}$                             | 0.595                        |
| $F$ / 000                                      | 1611.0                       |
| $2\theta$ range for data collection / °       | 6.992 to 149.61              |
| Crystal size / mm$^3$                         | $0.15 \times 0.1 \times 0.1$|
| Index ranges                                  | $-16 \leq h \leq 16, -31 \leq k \leq 31, -15 \leq l \leq 16$ |
| Reflections collected                         | 78807                        |
| Independent reflections                       | 8439 [R$_{\text{int}} = 0.0320$, R$_{\text{sigma}} = 0.0158$] |
| Data/restraints/parameters                    | 8439/0/550                   |
| Goodness-of-fit on $F^2$                      | 1.020                        |
| Final R indices [I > 2σ(I)]                   | $R_l = 0.0409$, wR$_2 = 0.0984$|
| Final R indices [all data]                    | $R_l = 0.0441$, wR$_2 = 0.1006$|
| Largest diff. peak / hole / e Å$^3$           | 0.15/-0.21                   |
| CCDC No.                                       | 1957867                      |
| Crystallization solvent                       | benzene                      |
| Property                                      | Value                                    |
|----------------------------------------------|------------------------------------------|
| **Empirical formula**                        | C₈₂H₈₂Cl₂O₁₀                             |
| **Formula weight / g mol⁻¹**                 | 1298.37                                  |
| **Temperature / K**                          | 159.99(10)                               |
| **Crystal system**                           | triclinic                                |
| **Space group**                              | P-1                                      |
| **a / Å**                                    | 13.2135(10)                              |
| **b / Å**                                    | 16.4229(3)                               |
| **c / Å**                                    | 16.6046(3)                               |
| **α / °**                                    | 71.707(2)                                |
| **β / °**                                    | 82.4130(10)                              |
| **γ / °**                                    | 86.2830(10)                              |
| **Volume / Å³**                              | 6462.83(18)                              |
| **Z**                                        | 2                                        |
| **ρ_calc / g cm⁻³**                          | 1.272                                    |
| **μ / mm⁻¹**                                 | 1.354                                    |
| **F / 000**                                  | 1376.0                                   |
| **2θ range for data collection / °**         | 5.646 to 149.864                         |
| **Crystal size / mm³**                       | 0.2 x 0.2 x 0.2                          |
| **Index ranges**                             | -15 ≤ h ≤ 16, -20 ≤ k ≤ 20, -19 ≤ l ≤ 20|
| **Reflections collected**                    | 42039                                    |
| **Independent reflections**                  | 13437 [R_int = 0.0373, R_sigma = 0.0371]  |
| **Data/restraints/parameters**               | 13437/1/857                              |
| **Goodness-of-fit on F²**                    | 1.068                                    |
| **Final R indices [I > 2σ(I)]**              | R_I = 0.0499, wR₂ = 0.1379               |
| **Final R indices [all data]**               | R_I = 0.0586, wR₂ = 0.1461               |
| **Largest diff. peak / hole / e Å³**         | 0.59/-0.61                               |
| **CCDC No.**                                 | 1957869                                  |
| **Crystallization solvents**                 | methanol/trans-dichloroethene            |

**Table S5. Crystal data and structure refinement for trans-CICH=CHCl@T[5]-(OMe)₅**
Table S6. Crystal data and structure refinement for T[5]-(OMe)s

| Property                                      | Value                        |
|-----------------------------------------------|------------------------------|
| Empirical formula                            | C_{40}H_{40}O_{5}            |
| Formula weight / g mol\(^{1}\)               | 600.72                       |
| Temperature / K                               | 159.99(10)                  |
| Crystal system                                | monoclinic                   |
| Space group                                   | P2\(_{1}\)                   |
| \(a / \text{Å}\)                              | 12.1727(2)                   |
| \(b / \text{Å}\)                              | 42.9634(6)                   |
| \(c / \text{Å}\)                              | 12.7404(2)                   |
| \(\alpha / ^{\circ}\)                        | 90                           |
| \(\beta / ^{\circ}\)                         | 104.079(2)                   |
| \(\gamma / ^{\circ}\)                        | 90                           |
| Volume / \(\text{Å}^{3}\)                    | 6462.83(18)                  |
| \(Z\)                                        | 2                            |
| \(\rho_{\text{calc}} / \text{g cm}^{-3}\)   | 1.238                        |
| \(\mu / \text{mm}^{-1}\)                     | 0.637                        |
| \(F / 000\)                                  | 2574.0                       |
| \(2\theta\) range for data collection / \(^{\circ}\) | 4.114 to 104.49   |
| Crystal size / \(\text{mm}^{3}\)             | 0.1 \(\times\) 0.05 \(\times\) 0.05   |
| Index ranges                                  | -12 \(\leq\) h \(\leq\) 12, -43 \(\leq\) k \(\leq\) 43, -13 \(\leq\) l \(\leq\) 12 |
| Reflections collected                         | 68727                        |
| Independent reflections                       | 14411 [\(R_{\text{int}} = 0.0558, R_{\text{sigma}} = 0.0417\)] |
| Data/restraints/parameters                    | 14411/1/1641                 |
| Goodness-of-fit on \(F^{2}\)                  | 1.073                        |
| Final R indices [I > 2\(\sigma(I)\)]         | \(R_I = 0.0857, wR_2 = 0.2265\) |
| Final R indices [all data]                    | \(R_I = 0.0917, wR_2 = 0.2319\) |
| Largest diff. peak / hole / e \(\text{Å}^{3}\) | 0.58/-0.38                   |
| CCDC No.                                      | 1957870                      |
| Crystallization Solvents                      | methanol/ethyl acetate       |
Table S7. Crystal data and structure refinement for CH$_2$Cl$_2$@T[5]-(OMe)$_5$

| Property                                      | Value                                      |
|----------------------------------------------|--------------------------------------------|
| Empirical formula                            | C$_{81}$H$_{82}$Cl$_{12}$O$_{10}$          |
| Formula weight / g mol$^{-1}$                 | 1286.36                                    |
| Temperature / K                               | 159.99(10)                                 |
| Crystal system                                | monoclinic                                 |
| Space group                                   | C2/c                                       |
| a / Å                                        | 20.3292(5)                                 |
| b / Å                                        | 15.6783(4)                                 |
| c / Å                                        | 22.5018(6)                                 |
| α / °                                        | 90                                         |
| β / °                                        | 106.973(3)                                 |
| γ / °                                        | 90                                         |
| Volume/ Å$^3$                                 | 6859.5(3)                                  |
| Z                                            | 4                                          |
| $\rho_{\text{calc}}$ / g cm$^{-3}$            | 1.246                                      |
| μ / mm$^{-1}$                                 | 1.333                                      |
| F / 000                                       | 2728.0                                     |
| 2θ range for data collection / °              | 7.244–149.952                              |
| Crystal size / mm$^3$                         | 0.5 × 0.2 × 0.03                           |
| Index ranges                                 | -25 ≤ h ≤ 25, -19 ≤ k ≤ 19, -28 ≤ l ≤ 27  |
| Reflections collected                         | 61508                                      |
| Independent reflections                      | 6836 [R$_{int} = 0.0813$, R$_{sigma} = 0.0269$] |
| Data/restraints/parameters                    | 6836/0/435                                 |
| Goodness-of-fit on F$^2$                      | 1.067                                      |
| Final R indices [I > 2σ(I)]                   | $R_I = 0.1292$, wR$_2 = 0.3170$            |
| Final R indices [all data]                    | $R_I = 0.1343$, wR$_2 = 0.3201$            |
| Largest diff. peak / hole / e Å$^3$           | 0.94/-0.32                                 |
| CCDC No.                                      | 1896024                                    |
| Crystallization solvents                      | methanol/dichloromethane                   |
**Figure S10.** Unit cell of T[5]-(OMe)s (crystallized by vapor diffusion of MeOH into CHCl$_3$) viewing from [111] (top) and [1-10] (bottom) directions.
Figure S11. Unit cell of CH₃CN⊂T[5]-(OMe)₅ viewing from [100] (top) and [101] (bottom) directions.
Figure S12. Unit cell of PhMe@T[5] viewing from [100] (top) and [010] (bottom) directions. Color code: PhMe, sky blue.
Figure S1. Unit cell of PhMe@T[5] viewing from [100] (top) and [010] (bottom) directions. All solvent molecules are omitted for clarity.
Figure S14. Unit cell of C₆H₆@[5]-(OMe)₅ viewing from [101] (top) and [100] (bottom) directions. Color code: C₆H₆, orange.
Figure S15. Unit cell of trans-ClCH=CH@T[5]-(OMe)₃ viewing from [010] (top) and [100] (bottom) directions
Figure S16. Unit cell of T[5]-(OMe)s (crystallized by vapor diffusion of MeOH into EtOAc) viewing from [100] (top) and [001] (bottom) directions.
Figure S17. Unit cell of CH$_2$Cl$_2$@T[5]-(OMe)$_5$ viewing from [100] (top) and [010] (bottom) directions.
4. Host-Guest Binding Studies

$^1$H NMR titrations were performed in CD$_3$OD or (CD$_3$)$_2$CO procured commercially from Cambridge Isotope Laboratories at ambient temperature (298 K) by adding incremental amount of guest solution (1 M) into T[5] host solution (5 mM). For each titration experiment 20 equivalent of guest were added unless otherwise noted. Changes in chemical shift ($\Delta$$\delta$) of $^1$H NMR signals of T[5] aromatic protons (H$_p$, H$_o$, and H$_m$) were recorded. Titration curve-fitting and association constant values (listed in Table S8) were calculated by employing the BindFit program developed by Prof. Pall Thordarson of UNSW.$^{[5]}$ This program employs a nonlinear least-squares regression analysis and is available free of cost online through the following link: http://supramolecular.org/.

### Table S8. Association constants ($K_a$) between T[5] and various guests

| Guests | Solvents | $K_a$ / M$^{-1}$ | Binding Stoichiometry$^b$ |
|--------|----------|-----------------|---------------------------|
| MV·2Cl | (1.0 ± 0.2) × 10$^3$ |
| Py·Cl | (1.2 ± 0.2) × 10$^3$ |
| G$_3$ | Methanol-d$_4$ 57 ± 1.5 | 1:1 |
| G$_6$·Cl | N/A$^a$ |
| G$_7$·Cl | N/A$^a$ |
| G$_4$·2PF$_6$ | Acetone-d$_6$ 70 ± 3.1 | 1:1 |
| G$_5$·PF$_6$ | 55 ± 3.6 |
| G$_3$ | N/A$^a$ |
| G$_6$·PF$_6$ | N/A$^a$ |
| G$_7$·PF$_6$ | N/A$^a$ |

$^a$Changes of chemical shift observed were negligible for curve-fitting.

$^b$1:1 Binding stoichiometry was chosen in the BindFit program.$^{[6,7]}$

### Scheme S2. Various guest molecules employed in the host-guest binding studies.
Figure S18. Partial $^1$H NMR spectra (400 MHz, CD$_3$OD, 298 K) of T[5] at a concentration of 5.00 mM upon titration of MV·2Cl and (b) Py·Cl.

Figure S19. Partial $^1$H NMR spectra (400 MHz, CD$_3$OD, 298 K) of T[5] at a concentration of 5.00 mM upon titration of Py·Cl.
Figure S20. Partial $^1$H NMR spectra (400 MHz, CD$_3$OD, 298 K) of T[5] at a concentration of 5.00 mM upon titration of G$_3$.

Figure S21. Partial $^1$H NMR spectra (400 MHz, CD$_3$COCD$_3$, 298 K) of T[5] at a concentration of 5.00 mM upon titration of G$_3$. 
**Figure S22.** Partial $^1$H NMR spectra (400 MHz, $(CD_3)_2CO$, 298 K) of $T[5]$ at a concentration of 5.00 mM upon titration of $G_4^*2Cl$.

**Figure S23.** Partial $^1$H NMR spectra (400 MHz, $(CD_3)_2CO$, 298 K) of $T[5]$ at a concentration of 5.00 mM upon titration of $G_5^*Cl$. 
Figure S24. ESI mass spectra of (a) [MV⊂T[5]]^{2+} and (b) [Py⊂T[5]]^{-}. Samples were prepared by dissolving T[5] in MeOH (0.5 mg/mL) with 5 eq. of MV·2Cl and Py·Cl guests, respectively, before further dilution for analysis.
5. Vapor-Solid Sorption and Fractionation Experiments

For each solid-vapor sorption and fractionation experiment, an open 2 mL vial containing 2.0 mg of activated T[5]-(OMe)_5 adsorbent was placed in a sealed 20 mL vial containing 1 mL of solvent or solvent mixture (50:50 v/v). Relative uptake amount in the T[5]-(OMe)_5 crystals was determined by $^1$H NMR integrals of corresponding proton signals of completely dissolved material in CDCl$_3$. Gas chromatography characterizations were also performed in order to determine the relative uptake amounts of mixed solvents in T[5]-(OMe)_5 crystals more accurately. Desorption experiments after saturation were carried out by thermogravimetric analysis.

Thermogravimetric analysis (TGA) was conducted on a METTLER TOLEDO TGA 2 operated at 10 K min$^{-1}$. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/Max-2500 X-ray diffractometer. Data were collected over the range of 3−40° at a scan rate of 5°·min$^{-1}$. Gas chromatography (GC) measurements were carried out on a Shimadzu GCMS-QP2010 Plus with an FID detector. The following GC method was used: the oven was programmed from 30 °C, ramped at 5 °C·min$^{-1}$ increments to 300 °C within 15 min hold; injection temperature 300 °C; detection temperature 300 °C; helium (carrier gas) flow-rate 3.0 mL·min$^{-1}$; samples were analyzed using headspace injections and were performed by incubating the sample at 50 °C for 5 min followed by sampling 1 mL of the headspace.
Figure S25. $^1$H NMR spectra (400 MHz, 298 K, CDCl$_3$) of T[5]-(OMe)$_5$ after benzene/cyclohexane vapor adsorption/desorption.

Figure S26. Relative uptakes of benzene/cyclohexane (adsorption time 7 h) in activated T[5]-(OMe)$_5$ determined by gas chromatography.
Figure S27. Powder X-ray diffraction (PXRD) patterns of activated T[5]-(Me)₅ and T[5]-(Me)₅ after benzene/cyclohexane vapor adsorption/desorption experiments.

Figure S28. Thermogravimetric analysis of (a) activated T[5]-(OMe)₅. The 2.3% weight loss observed can be attributed to the loss of water in the sample; (b) T[5]-(OMe)₅ after adsorption of benzene. The 11.3% weight loss can be attributed to the loss of water and benzene combined. The net weight loss of benzene correspond to 0.8 benzene per T[5]-(OMe)₅ (mol/mol).
Figure S29. Relative uptake mole ratio of benzene and cyclohexane in T[5]-(OMe)$_5$ crystalline materials through six cycles of activation/adsorption determined by $^1$H NMR (400 MHz, CDCl$_3$, 298 K).
6. Computational Details

All quantum-chemical computations were performed using the Gaussian16 suite of programs (version B.1), with the wB97XD functional and basis sets referred to as implemented in there.\textsuperscript{18} Input files were made via Chem3D, and the results were visualized using Gaussview 6.

Figure S30. Optimized geometry of MeCN⊂T[5]-(OMe)$_5$ with the MeCN guest molecule in the experimentally observed orientation.

Figure S31. Optimized geometry of MeCN⊂T[5]-(OMe)$_5$ with the MeCN guest in the cavity antiparallel to the experimentally observed orientation.

The experimentally observed ‘ordered’ structure of CH$_3$CN⊂T[5]-(OMe)$_5$ is illustrated in Figure S30. The ‘rather chaotic’ structure of CH$_3$CN⊂T[5]-(OMe)$_5$ with the MeCN sitting in the cavity in the antiparallel orientation (Figure S31) is calculated to be 6.2 kcal/mol higher in energy and therefore not observed experimentally.
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8. Author Contributions

W.Y., K.S., X.W., T.U.T., Y.C., S.L. and K.D. synthesized all compounds in this study. W.Y., K.D. and J.X. collected and processed X-ray crystallographic data. W.Y. and K.S. conducted host-guest binding studies. W.Y. carried out adsorption and fractionation experiments. Y.G. performed mass spectrometry characterizations. H.Z. performed quantum-chemical calculations. H.Z. and A.C.-H.S. conceived the project and designed the experiments. W.Y., K.S., X.W., H.Z. and A.C.-H.S. analyzed the data and wrote the manuscript. All authors discussed the results and commented on the manuscript.