Electronic Supplementary Information (ESI)

Channel confinement and separation properties in an adaptive supramolecular framework using an adamantane tecton

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Supplementary Information:

S1) Experimental information

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S1. Experimental information

Materials:

1,3,5,7-tetrakis(4-bromophenyl)adamantane (**1**) was obtained from Combi-Blocks. Solvents benzene (**C₆H₆**) and toluene (**tol**) were obtained from Sigma-Aldrich. Solvent chloroform (**CHCl₃**) was obtained from JT Baker. Solvent dichloromethane (**dcm**) was obtained from Macron. Solvent *p*-xylene (***p*-xyl**) was obtained from TCI. All reagents and solvent were used as received.

Single crystals of (**1**)·(**C₆H₆**) were generated by dissolving **1** (19.8 mg, 0.026 mmol) in **C₆H₆** (2.5 mL) and gently heating until complete dissolution. Single crystals of (**1**)·(**CHCl₃**) were generated by dissolving **1** (17.9 mg, 0.024 mmol) in **CHCl₃** (2.5 mL), no heat was required for complete dissolution. Single crystals of (**1**)·(***p*-xyl**) were generated by dissolving **1** (15.2 mg, 0.020 mmol) in ***p*-xyl** (2.5 mL), no heat was required for complete dissolution. Single crystals of (**1**)·(**tol**) were generated by dissolving **1** (17.9 mg, 0.024 µmol) in **tol** (2.5 mL) and gently heated until complete dissolution. Single crystals were formed from each solution after a 2-4 day period. Single crystals of **apo-1** were generated by dissolving **1** (15.8 mg, 20.89 mmol) in **dcm** (2.5 mL) and following the procedure above for solvates, no heat should be required for complete dissolution in **dcm**.

Instruments and methods:

^{1}H NMR spectra were recorded on a Bruker AV400 spectrometer with chloroform-d (7.26 ppm) and DMSO-d₆ (2.50 ppm) as internal standards. IR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer with an iD5 ATR accessory. NMR data was processed with Mnova suite, and IR data was processed with OMNIC™ Software and RStudio software. Single crystal X-ray diffraction (SCXRD) data was collected on a Rigaku XtaLAB Mini II diffractometer with a CCD area detector (λMoK*α* = 0.71073 Å, monochromator: graphite). Experiments were conducted at 100 K with a range of 2θ = 3-62°. The collected data was refined with CrysAlisPro through standard data reduction and background corrections (analytical for **apo-1**, (**1**)·(**CHCl₃**), (**1**)·(**tol**), and multi-scan for (**1**)·(**CHCl₃**), (**1**)·(***p*-xyl**)). Crystals were mounted in Paratone oil on a Mitegen magnetic mount. Structure solution and refinement were performed using SHELXT[1] and SHELXL,[2] respectively within the Olex2[3] and WinGX[4] graphical user interfaces.

Separation of **C₆H₆** and **tol** was performed by dissolving **1** (15.4 mg, 0.020 mmol) in 2.5 mL of solution of a 1:1 (v/v) binary mixture of the solvents. The resulting crystals (3-4 days of slow evaporation) were rapidly filtered, dried, and analyzed by ^{1}H NMR spectroscopy. To carry out repeated solvent uptake, a solution was prepared with the ratio of **C₆H₆** and **tol** observed by ^{1}H NMR spectroscopy from the previous batch of crystals.

S2. Single-crystal X-ray data

Table S1. Crystallographic parameters for **apo-1**

Compound name	**apo-1**
Empirical formula	$C_{68}H_{56}Br_8$
Formula weight	1512.431
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	10.8095(7)
b/Å	15.4233(9)
c/Å	19.8301(10)
α/°	67.615(5)
β/°	80.075(5)
γ/°	74.356(5)
Volume/Å^3	2934.7(3)
Z	4
ρ_{calc}g/cm^3	1.712
μ/mm^{-1}	5.508
F(000)	1488.0
Crystal size/mm^3	0.374 × 0.174 × 0.044
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.924 to 50.246
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -23 ≤ l ≤ 23
Reflections collected	39921
Independent reflections	10436 [R_{int} = 0.0676, R_{sigma} = 0.0914]
Data/restraints/parameters	10436/0/685
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0524, wR_2 = 0.1061
Final R indexes [all data]	R_1 = 0.1042, wR_2 = 0.1219
CCDC deposition number	2289644

Table S2. Crystallographic parameters for (**1**)·(**C₆H₆**)

Compound name	(1)·(C₆H₆)
Empirical formula	$C_{14.5}H_{13}Br$
Formula weight	267.16
Temperature/K	100.00(10)
Crystal system	tetragonal
Space group	P-42₁c
a/Å	18.4930(7)
b/Å	18.4930(7)
c/Å	7.1799(5)
α/°	90
β/°	90
γ/°	90
Volume/Å³	2455.5(3)
Z	1
ρ_{calc}g/cm³	1.445
μ/mm⁻¹	3.315
F(000)	1080.0
Crystal size/mm³	0.181 × 0.12 × 0.094
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.406 to 56.726
Index ranges	-23 ≤ h ≤ 24, -19 ≤ k ≤ 24, -9 ≤ l ≤ 9
Reflections collected	12261
Independent reflections	2967 [R_{int} = 0.0616, R_{sigma} = 0.0824]
Data/restraints/parameters	2967/0/142
Goodness-of-fit on F²	1.000
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.0728
Final R indexes [all data]	R_1 = 0.0684, wR_2 = 0.0820
CDCC deposition number	2289640

Table S3. Crystallographic parameters for (**1**)·(**tol**)

Compound name	(**1**)·(**tol**)
Empirical formula	$C_{41}H_{36}Br_4$
Formula weight	848.34
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$C2$
a/Å	19.2611(14)
b/Å	7.1873(7)
c/Å	25.1626(19)
α/°	90
β/°	94.187(8)
γ/°	90
Volume/Å^3	3474.1(5)
Z	4
ρ_{calc}g/cm^3	1.622
μ/mm^{-1}	4.662
F(000)	1688.0
Crystal size/mm^3	0.275 × 0.156 × 0.06
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.87 to 50.24
Index ranges	-22 ≤ h ≤ 22, -8 ≤ k ≤ 8, -28 ≤ l ≤ 30
Reflections collected	11552
Independent reflections	11552 [R_{int} = ?, R_{sigma} = 0.0824]
Data/restraints/parameters	11552/370/410
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0493, wR_2 = 0.1010
Final R indexes [all data]	R_1 = 0.0660, wR_2 = 0.1064
CCDC deposition number	2289643

Table S4. Crystallographic parameters for (**1**)·(*p*-**xyl**)

Compound name	(**1**)·(*p*-**xyl**)
Empirical formula	$C_{42}H_{38}Br_4$
Formula weight	862.36
Temperature/K	101.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.1953(3)
b/Å	25.4666(9)
c/Å	10.1699(4)
α/°	90
β/°	107.729(4)
γ/°	90
Volume/Å^3	1775.03(13)
Z	2
ρ_{calc}g/cm^3	1.613
μ/mm^{-1}	4.564
F(000)	860.0
Crystal size/mm^3	0.327 × 0.183 × 0.042
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.204 to 50.246
Index ranges	-8 ≤ h ≤ 8, -29 ≤ k ≤ 30, -12 ≤ l ≤ 12
Reflections collected	14726
Independent reflections	6146 [R_{int} = 0.0453, R_{sigma} = 0.0671]
Data/restraints/parameters	6146/1/417
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0374, wR_2 = 0.0644
Final R indexes [all data]	R_1 = 0.0458, wR_2 = 0.0665
CCDC deposition number	2289642

Table S5. Crystallographic parameters for (**1**)·(**CHCl₃**)

Compound name	(**1**)·(**CHCl₃**)
Empirical formula	$C_{17.5}H_{14.5}Br_2Cl_{1.5}$
Formula weight	437.79
Temperature/K	100.15
Crystal system	monoclinic
Space group	C2/c
a/Å	18.7063(12)
b/Å	7.1729(5)
c/Å	25.574(2)
α/°	90
β/°	101.643(7)
γ/°	90
Volume/Å³	3360.9(4)
Z	4
ρ_{calc}g/cm³	1.730
μ/mm⁻¹	5.053
F(000)	1720.0
Crystal size/mm³	0.194 × 0.135 × 0.022
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.952 to 50.24
Index ranges	-21 ≤ h ≤ 22, -8 ≤ k ≤ 7, -30 ≤ l ≤ 30
Reflections collected	11599
Independent reflections	2975 [R_{int} = 0.0758, R_{sigma} = 0.1008]
Data/restraints/parameters	2975/18/203
Goodness-of-fit on F²	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0672, wR_2 = 0.1635
Final R indexes [all data]	R_1 = 0.1150, wR_2 = 0.1851
CCDC deposition number	2289641
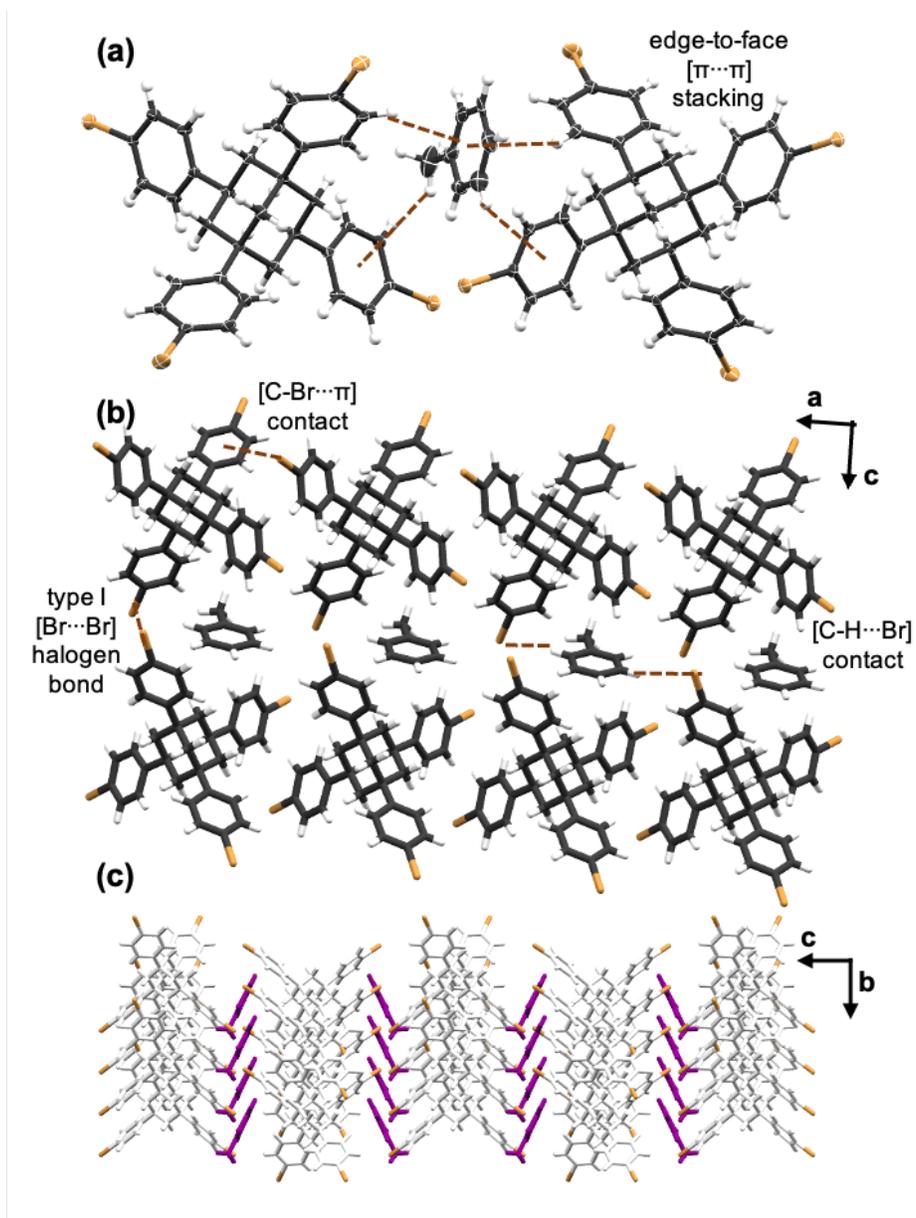
Figure S1. X-ray structure of **1**·(**tol**): (a) edge-to-face [π···π] stacking between **tol** and **1**, (b) [C-Br···π], [Br···Br], and [C-H···Br] contacts, (c) van der Waals contacts of **1** in *bc*-plane and channel formation along *b*-axis.
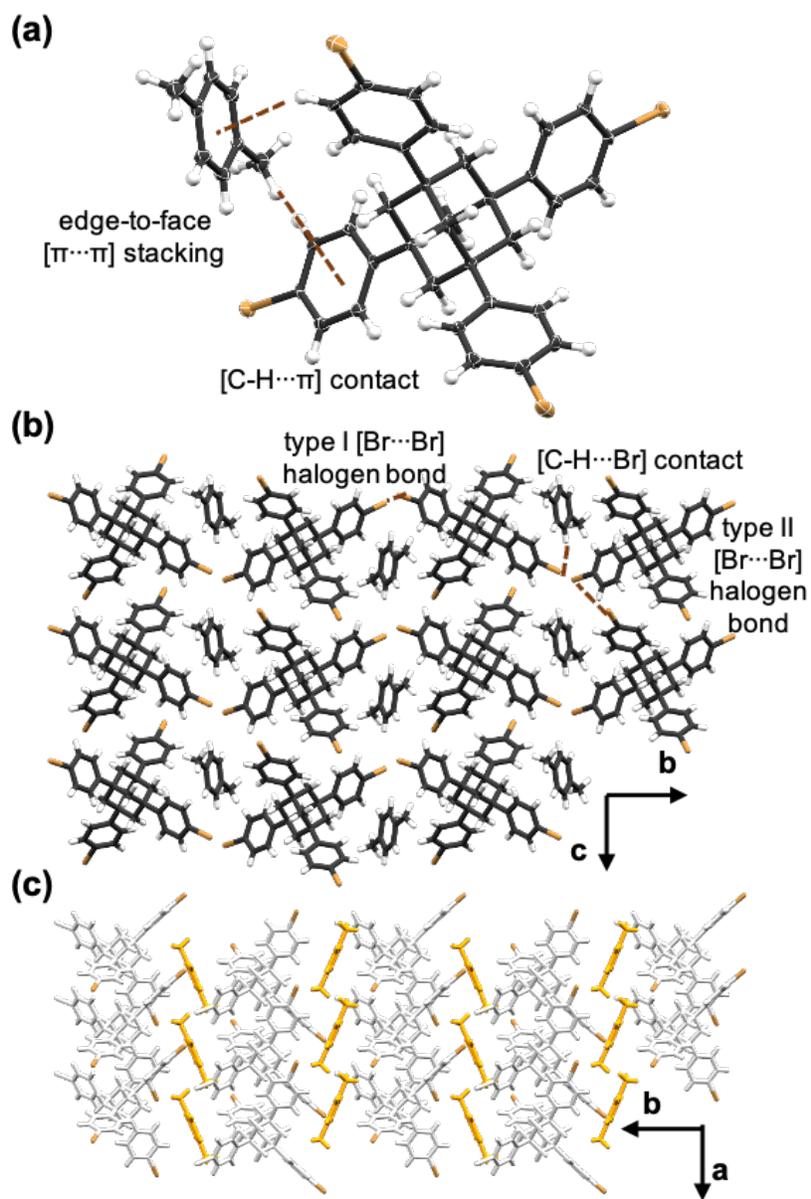
Figure S2. X-ray structure of **1**·(**p-xyl**): (a) edge-to-face [π···π] stacking and [C-H···π] contacts between **p-xyl** and **1**, (b) [Br···Br] (type I and II), and [C-H···Br] contacts, (c) van der Waals contacts of **1** in *ab*-plane and channel formation along *a*-axis.
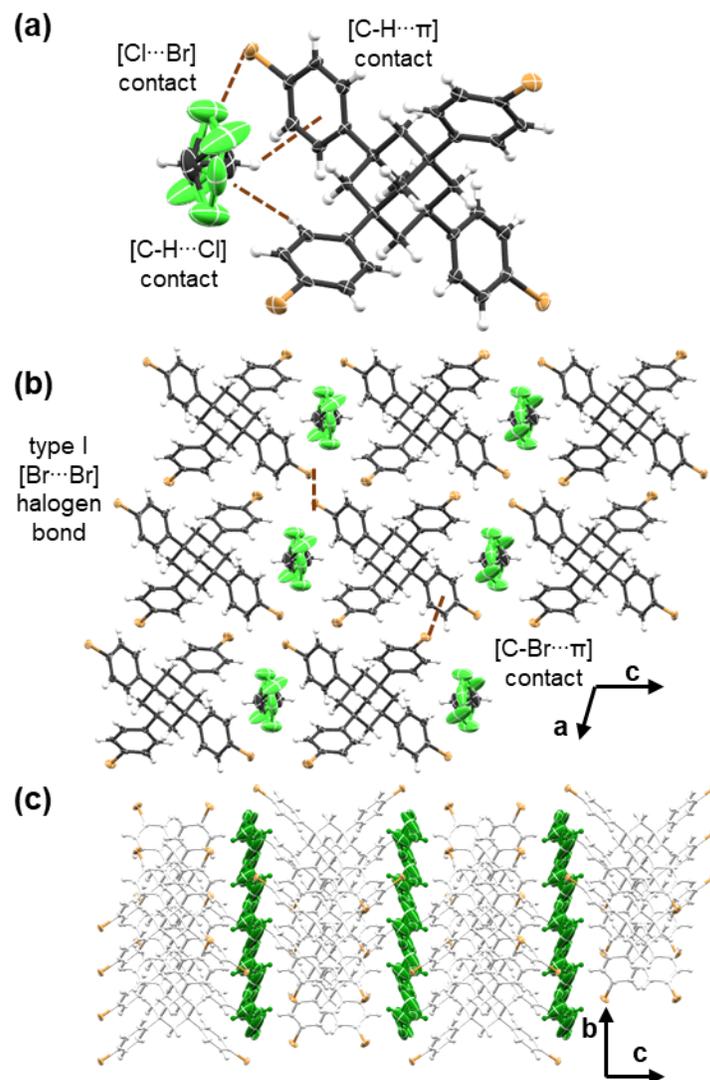
Figure S3. X-ray structure of **1**·(**CHCl₃**): (a) [Cl···Br], [C-H···π], and [C-H···Cl] contacts contacts between **CHCl₃** and **1**, (b) [Br···Br] (type I), and [C-Br···π] contacts, (c) van der Waals contacts of **1** in *bc*-plane and channel formation along *b*-axis.

Table S6. Selected intermolecular interactions in crystals

Crystal/parameter	d(C⋯X) (Å)	d(X⋯X) (Å)	d(C-H⋯π)	symmetry code
apo-1	3.708(6)[1]	-	-	(1+X, +Y, +Z)
	-	-	2.965(2)[2]	
1·(C₆H₆)	3.530 (5)[3]	-	-	(-1/2+X, 3/2-Y, -1/2-Z)
	-	-	2.987(2)[4]	
1·(*p*-tol)	3.594(12)[5]	-	-	(1/2-X, 3/2+Y, 1-Z)
	-	3.590(2)[7]	-	
	-	-	2.972(5)[8]	
1·(*p*-xyl)	3.442(8)[9]	-	-	(-1+X, +Y, 1+Z)
	-	3.6095(11)[10]	-	(3-X, -1/2+Y,1-Z)
	-	-	2.897(3)[11]	
1·(CHCl₃)	3.643(10)[12]	-	-	(1-X, 1-Y, 1-Z)
	-	3.637(2)[13]	-	(1/2-X, -1/2-Y, 1-Z)
	-	3.528(9)[14]	-	(+X, -1+Y, +Z)

[1]C40⋯ Br3, [2]C37-H37⋯ π (centroid: C13, C14, C15, C16, C17, C18), [3]C007⋯Br01, [4]C00A-H00E⋯ π (centroid: C00C, C00B, C00D, C00E, C00F, C00G), [5]Br1⋯C7, [7]Br2⋯⋯Br3, [8]C3-H3⋯π (centroid: C38, C39, C40, C41, C42, C43), [9]C1⋯Br3, [10] Br1⋯Br2, [11]C24-H24⋯π (centroid: C35, C36, C37, C38, C39, C40), [12]C11⋯Cl1, [13]Br1⋯Br1, [14]Br1⋯Cl3.

S4. NMR spectral data
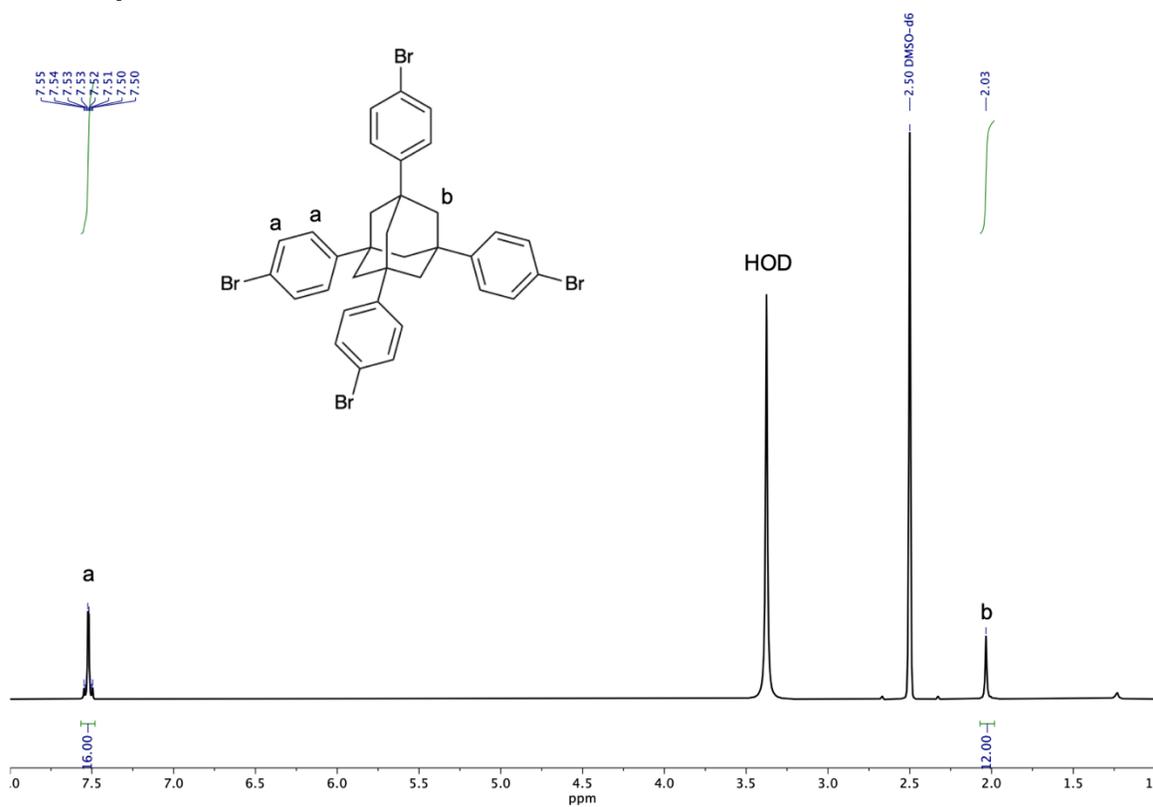
Fig. S4. ^{1}H NMR spectrum of **apo-1** (400 MHz, DMSO-d$_6$). We note the 1H NMR signals display solvent dependency as with similar adamantane systems.[5]
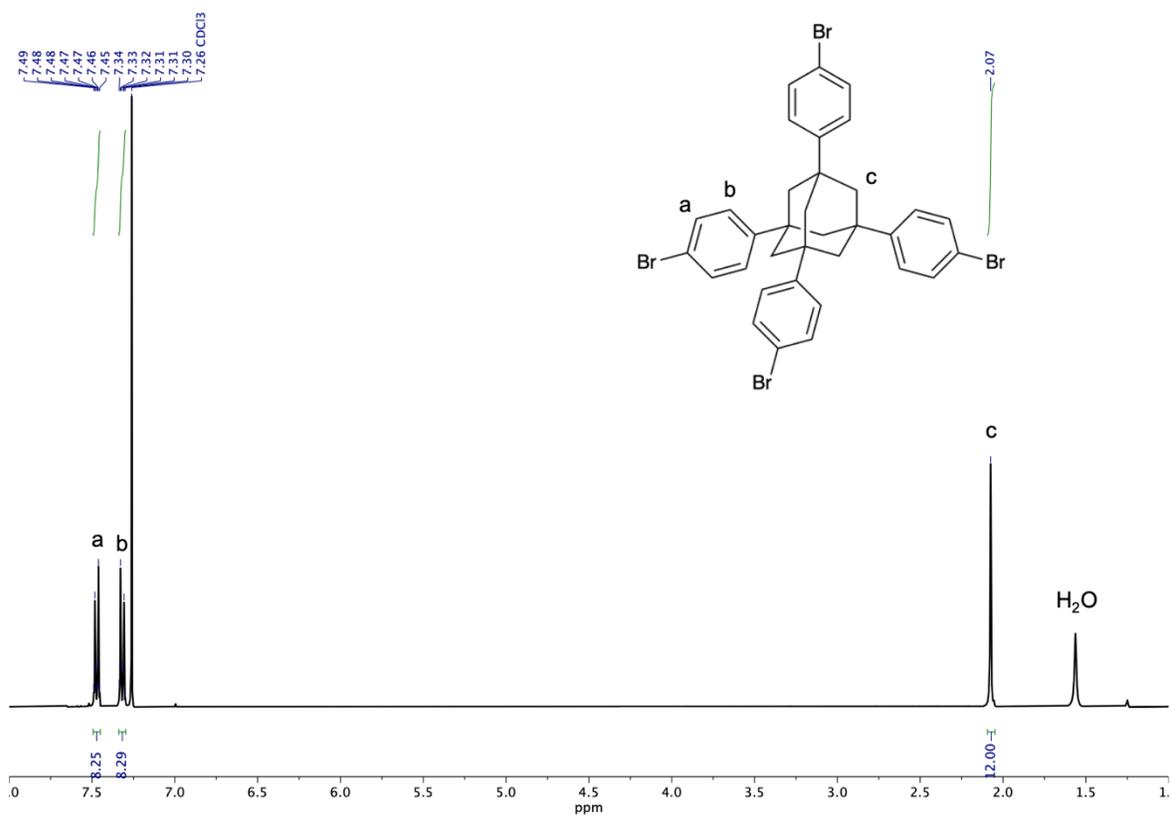
Fig. S5. ^{1}H NMR spectrum of **apo-1** (400 MHz, CDCl$_3$). We note the 1H NMR signals display solvent dependency as with similar adamantane systems.[5]
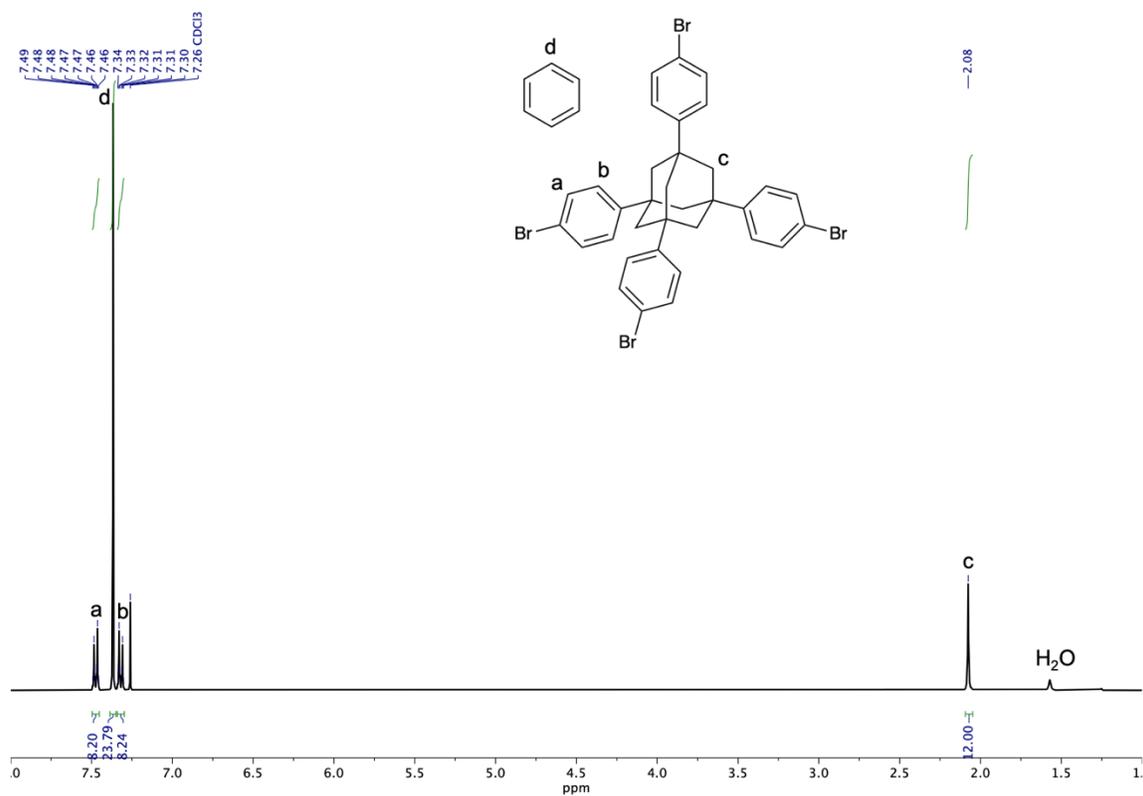
Fig. S6. ^{1}H NMR spectrum of (**1**)·(**C₆H₆**). Integrations show a 4:1 guest to host ratio (400 MHz, CDCl₃). We note the 1H NMR signals display solvent dependency as with similar adamantane systems.[5]
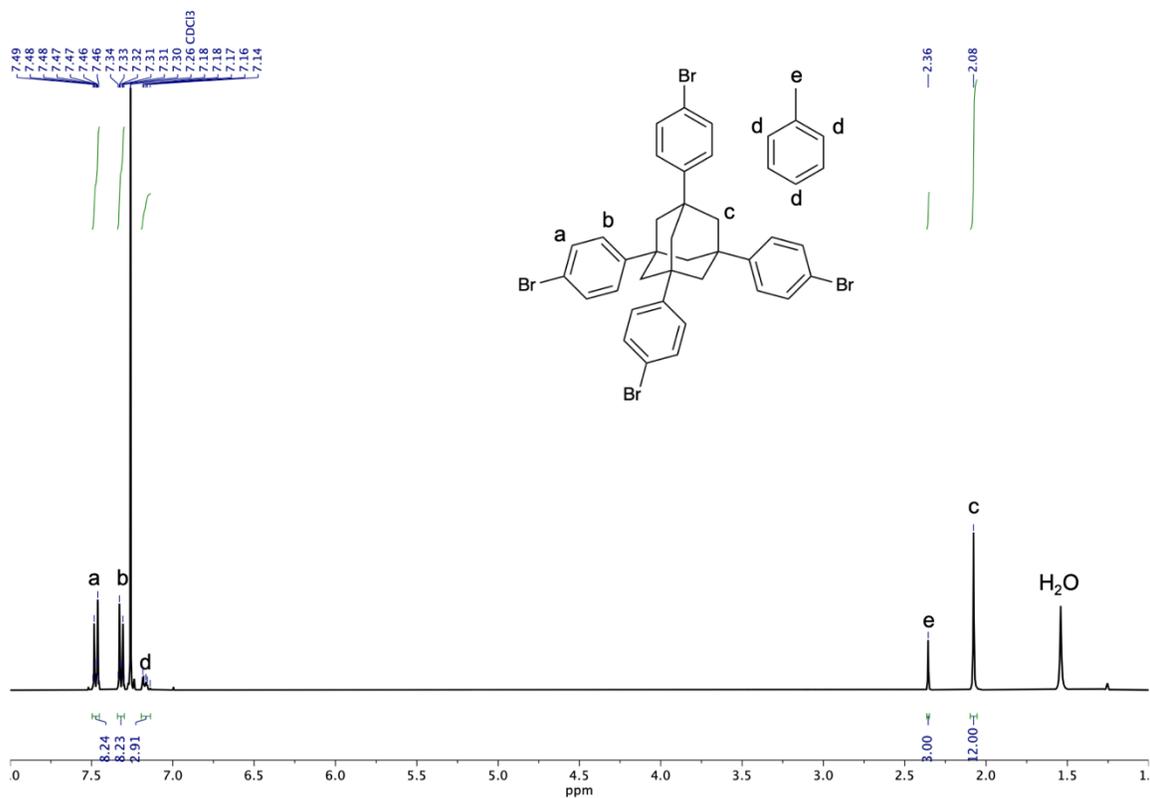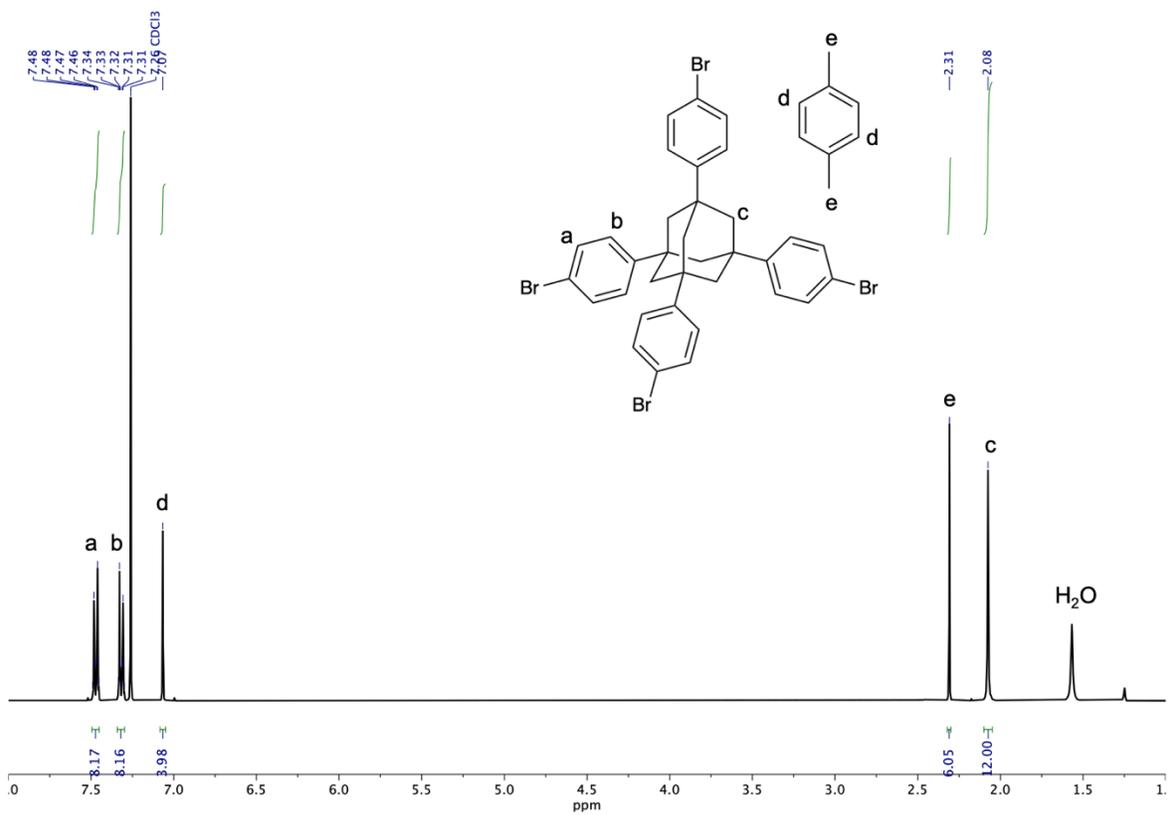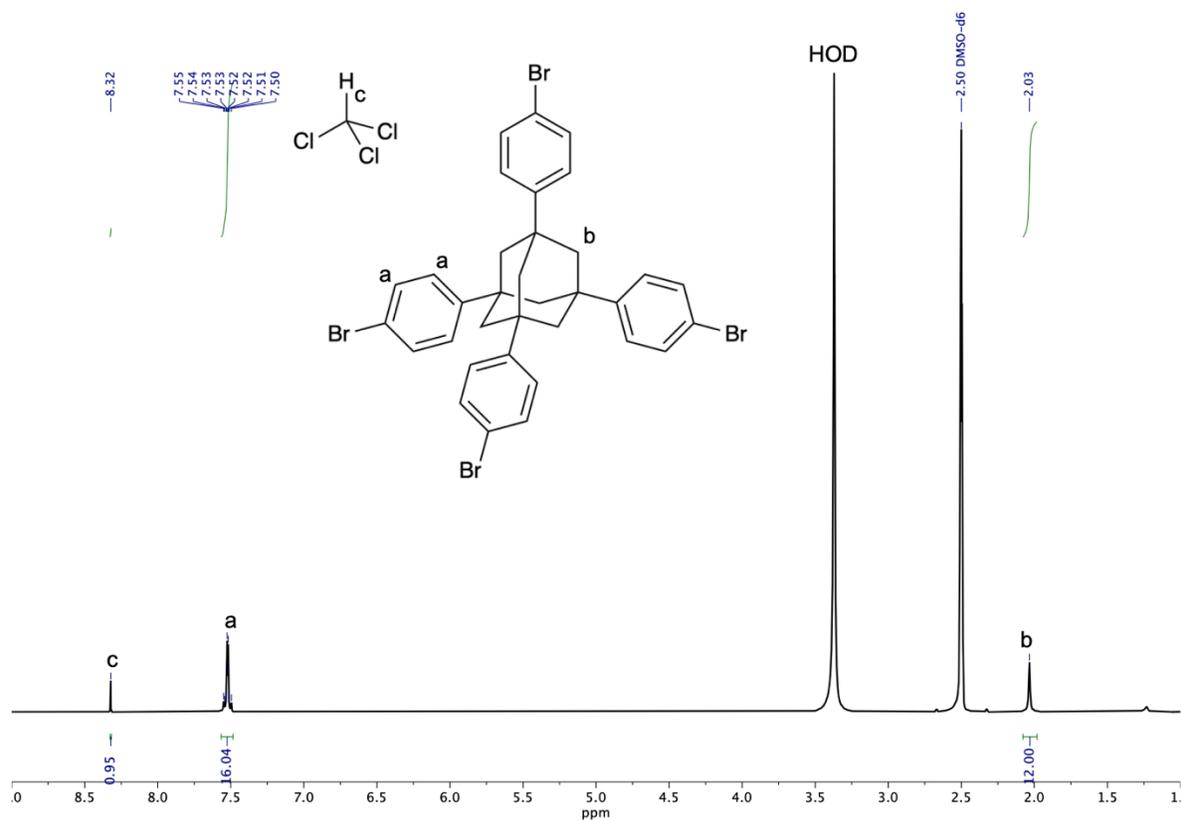
Fig. S7. ^{1}H NMR spectrum of (**1**)·(**tol**). Integrations show a 1:1 guest to host ratio (400 MHz, CDCl$_3$). We note the 1H NMR signals display solvent dependency as with similar adamantane systems.[5]
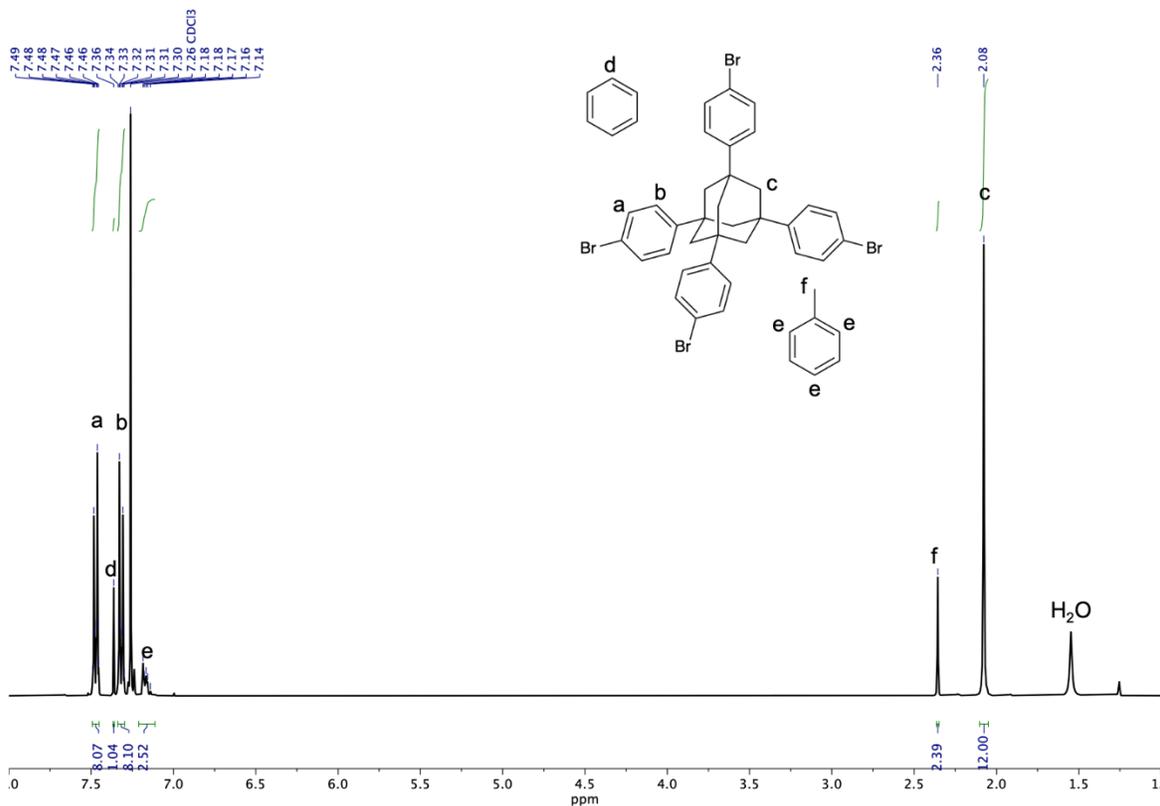
Fig. S8. ¹H NMR spectrum of (**1**)·(**p-xyl**). Integrations show a 1:1 guest to host ratio (400 MHz, CDCl₃). We note the 1H NMR signals display solvent dependency as with similar adamantane systems.[5]

Fig. S9. ^{1}H NMR spectrum of (**1**)·(**CHCl₃**). Integrations show a 1:1 guest to host ratio (400 MHz, DMSO-d₆). We note the 1H NMR signals display solvent dependency as with similar adamantane systems.[5]

Fig. S10. ^{1}H NMR spectrum of crystals of 1 grown in a 1:1 mixture of benzene-toluene, resulting in single crystals of **1** with solvent confinement of both. Normalized to adamantane protons. (400 MHz, CDCl$_3$). We note the 1H NMR signals display solvent dependency as with similar adamantane systems.[5]
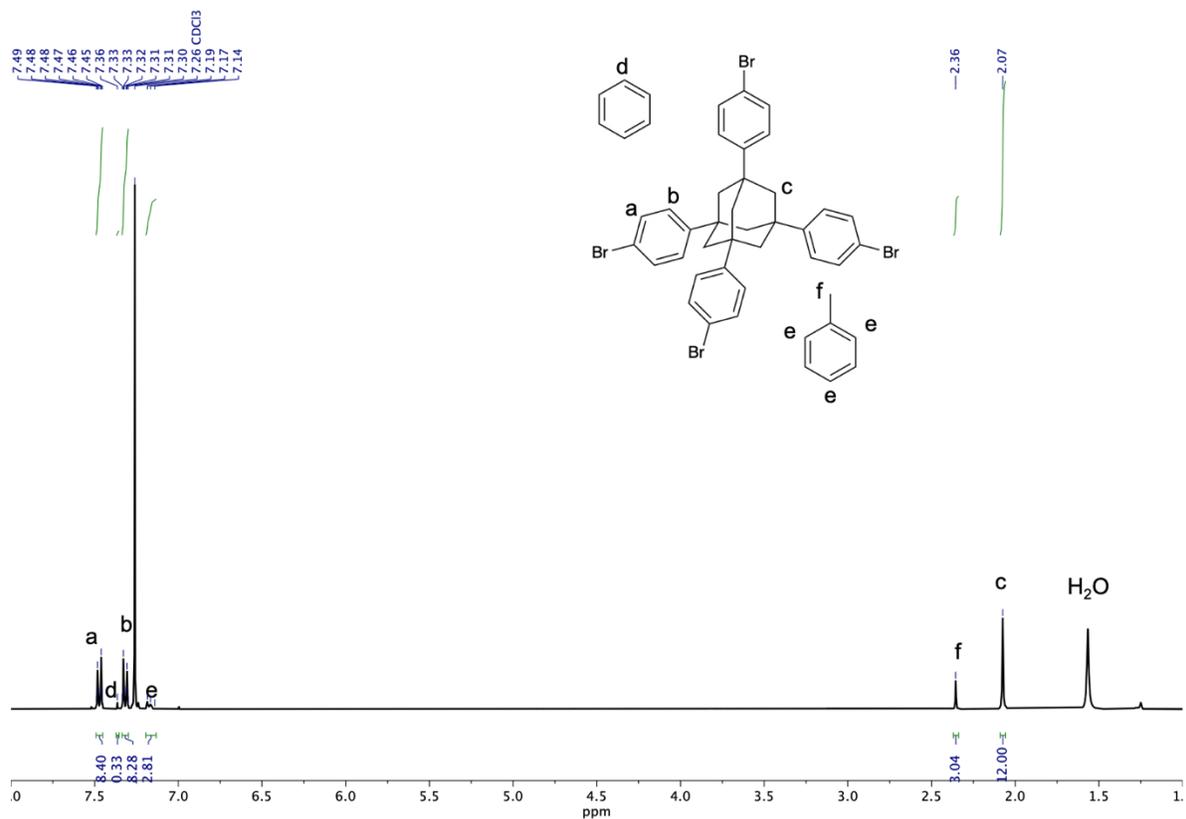
Fig. S11. ^{1}H NMR spectrum of crystals of 1 grown in a 4.1:0.9 ratio of benzene-toluene, resulting in single crystals of **1** with solvent confinement of both. Normalized to adamantane protons. (400 MHz, CDCl$_3$). We note the 1H NMR signals display solvent dependency as with similar adamantane systems.[5]

Table S7. Toluene uptake in comparison to benzene based on ^{1}H NMR data. Toluene content normalized.

Uptake Number	Relative M(Toluene)	Relative M(Benzene)	Toluene ratio (%)	Benzene ratio (%)
1st	6.00	1.31	82	18
2nd	6.00	0.33	95	5

The relative concentration analysis was carried out using the ^{1}H NMR signals of H(toluene) (3H of toluene) and H(benzene) (6H of benzene) taken from the single crystals after each uptake with **1**. The signals H(toluene) and H(benzene) were normalized for the number of protons and performed a ratio analysis following the formula:

$$\frac{M(toluene)}{M\;(benzene)} = \frac{I(toluene)}{I(benz)} \times \frac{N(benz)}{N(toluene)}$$

Where I is the integral, and N is the number of nuclei giving rise to the signal. Since H(toluene) consists of 3H (total H in molecule: 8H) and H(benzene) consists of 6H (total H in molecule: 6H), the equation can be expressed as:

$$\frac{M(toluene)}{M\;(benzene)} = \frac{I(toluene)}{I(benzene)} \times \frac{6}{3}$$
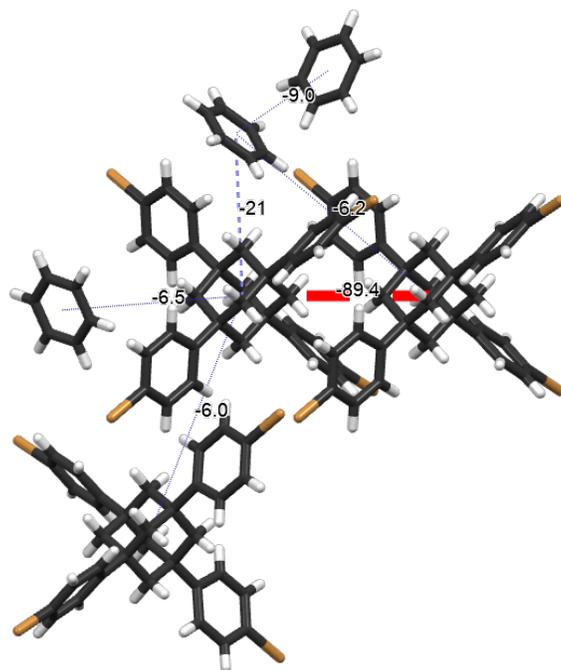
S5) UNI force field calculations

Fig. S12. Intermolecular contacts in **1**·(**C₆H₆**) using force field potential calculations (UNI) (energies in kJ mol⁻¹). Red indicates the strongest interaction.
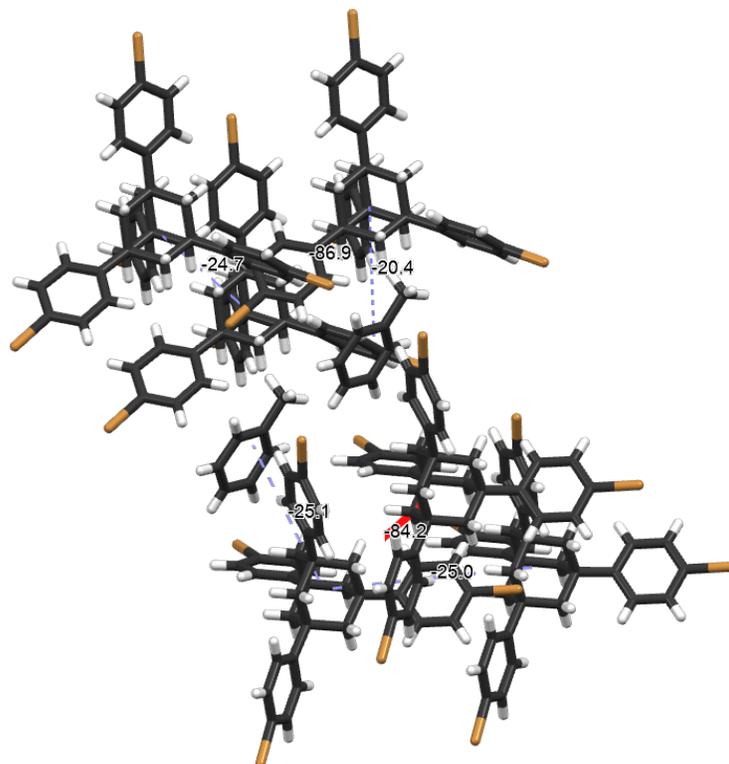
Fig. S13. Intermolecular contacts in **1·(tol)** using force field potential calculations (UNI) (energies in kJ mol^{-1}). Red indicates the strongest interaction.

References
(1)   Sheldrick, G. M. *Acta Cryst. A* **2015,** *71*, 3-8.
(2)   Sheldrick, G. M. *Acta Cryst. C* **2015,** *71*, 3-8.
(3)   Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A.; Puschmann, H. *J. Appl. Crystallogr.* **2009,** *42*, 339-341.
(4)   Farrugia, L. J. *J. Appl. Crystallogr.* **1999,** *32*, 837-838.
(5)   C. A. Gunawardana, A. S. Sinha, E. W. Reinheimer and C. B. Aakeröy, *Chemistry*, **2020**, *2*, 179-192.