Supplementary Information (SI) for CrystEngComm.
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Supplementary Information

Solvent induced supramolecular self-assembly in the solid-state of A1/A2-difunctionlized pillar[5]arene host

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Single crystal X-ray diffraction analysis:

The asymmetric unit of **Pillar-D1** contain one molecule of Pillar co-crystalized with 2 molecules of chloroform and a half occupied tolualdehyde molecule at special position. One of the chloroform molecules exhibit positional disorder and this disorder has been handled with part commands during the crystal refinement (with 66% and 34% occupancies respectively). The tolualdehyde which is occupied at the special position too exhibited disorder with respect to CH_3 and CHO fragments and this disorder also handled by part command after assigning 50% occupancies to both fragments. The asymmetric unit of **Pillar-D2** contain two molecules of Pillar along with three and half molecules of DMF. The asymmetric unit of [**Pillar** ⊃ **ADN1**] contain one molecule of **Pillar** co-crystalized with a molecule of adiponitrile which is occupied at the cavity of the pillararene macrocycle. The n-bormodecoxy fraction of the pillararene is disordered in this crystal and this disorder is refined over two sites with 60% and 40% occupancies respectively. The encapsulated adiponitrile is also showed positional disorder which is refined with 80% and 20% occupancies respectively. The asymmetric unit of [**Pillar** ⊃ **ADN2**] contain one molecule of **Pillar** co-crystalized with a molecule of adiponitrile at the macrocyclic cavity along with another quarter occupancy of adiponitrile at spatial position. The propargyloxy group of the pillararene is disordered in this crystal and this disorder is refined over two sites with approximate 52% and 48% occupancies respectively. For the pictorial representation of the crystal's structures and their networks as well as for the quantitative calculation of intermolecular interactions those disordered fragments with higher occupancy have been only been considered.

Table S1. Summary on the nature and various crystallographic parameters of **[Pillar-D1**, **Pillar-D2**, [**Pillar** ⊃ **ADN1**] & [**Pillar** ⊃ **ADN2**] obtained after crystallization.

Crystal sample	**Pillar-D1**	**Pillar-D2**	**[Pillar ⊃ ADN2]**	**[Pillar ⊃ ADN1]**
Chemical formula	$C_{124}H_{146}Br_2Cl_{12}O_{21}$	$C_{245}H_{317}Br_4N_7O_{47}$	$C_{127}H_{154}Br_2N_5O_{20}$	$C_{62}H_{75}BrN_2O_{10}$
M_r	2557.62	4431.68	2230.36	1088.15
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, Cc	Monoclinic, $C2/c$	Triclinic, P-1
Temperature (K)	150	150	150	150
a, b, c (Å)	20.9763 (19), 12.9809 (10), 24.889 (2)	19.6591 (4), 16.4212 (4), 37.8641 (8)	19.665 (2), 16.584 (2), 38.621 (4)	11.2957 (12), 12.2233 (12), 24.689 (3)
α, β, γ (°)	106.730 (8)	90, 90.487 (1), 90	91.573 (6)	75.969 (5), 89.341 (6), 62.754 (4)
V (Å^3)	6490.2 (10)	12223.1 (5)	12591 (3)	2920.6 (5)
Z	2	2	4	2
Radiation type	Mo $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.94	1.39	1.34	0.76
Crystal size (mm)	0.20 × 0.19 × 0.03	0.21 × 0.19 × 0.11	0.22 × 0.21 × 0.02	0.09 × 0.07 × 0.05
Diffractometer	Rigaku R-AXIS RAPID	Bruker *APEX*-II CCD	Bruker *APEX*-II CCD	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan *ABSCOR* (Rigaku, 1995)	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction	Multi-scan *ABSCOR* (Rigaku, 1995)
T_{min}, T_{max}	0.223, 0.972	0.62, 0.87	0.52, 0.97	0.188, 0.963
No. of measured, independent & observed [$I > 2\sigma(I)$] reflections	49692, 11302, 4677	34180, 18068, 15880	64117, 11138, 8125	22026, 9923, 3156
R_{int}	0.100	0.027	0.068	0.103
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595	0.595	0.597	0.595
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.090, 0.315, 0.98	0.057, 0.187, 1.04	0.112, 0.347, 1.59	0.104, 0.343, 1.01
No. of reflections	11302	18068	11138	9923
No. of parameters	748	1388	731	741
No. of restraints	66	162	120	294
H-atom treatment	Constrained	Constrained	Constrained	Constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.55, −0.42	0.66, −0.44	1.65, −1.30	0.48, −0.36

Computer programs: *SHELXL2019*/2 (Sheldrick, 2019).

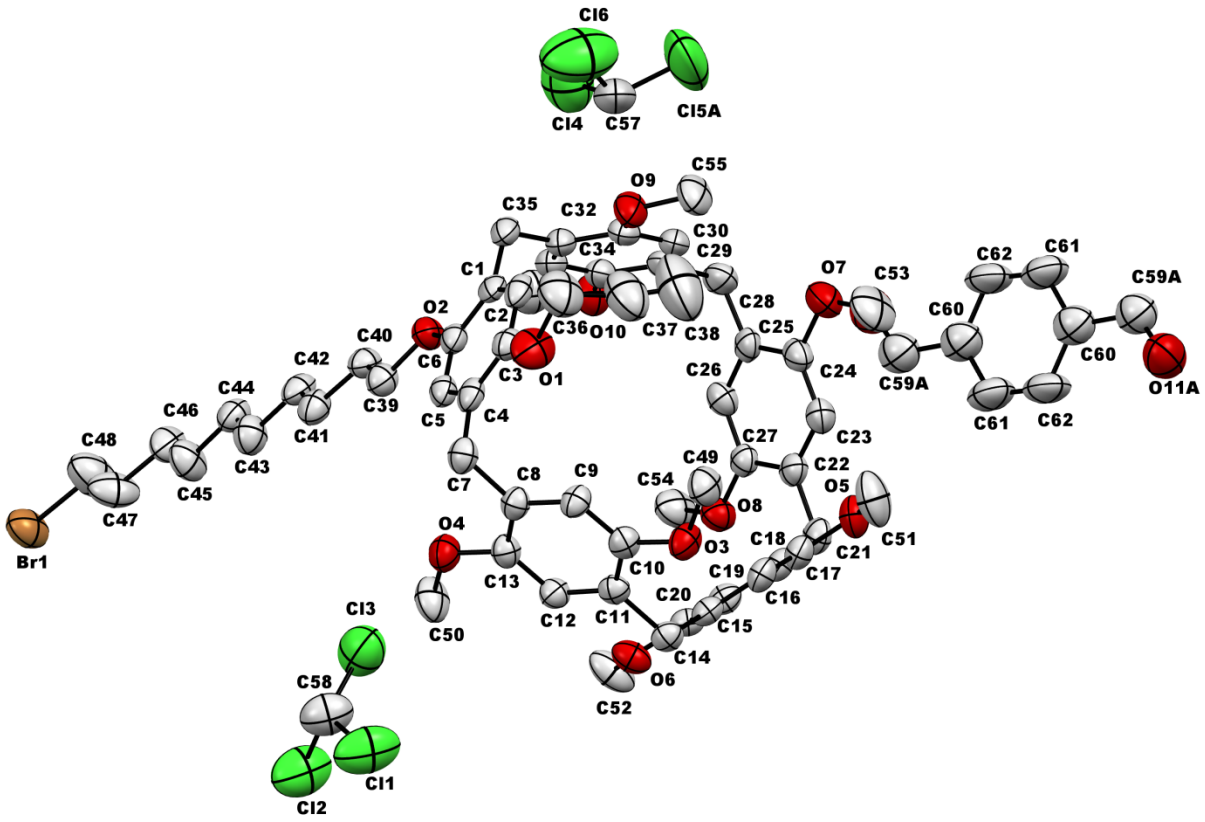

Figure S1. Thermal ellipsoid representation (30% probability) showing the asymmetric unit of **Pillar-D1** obtained after the crystallization from chloroform (Hydrogen atoms are hided for clarity).

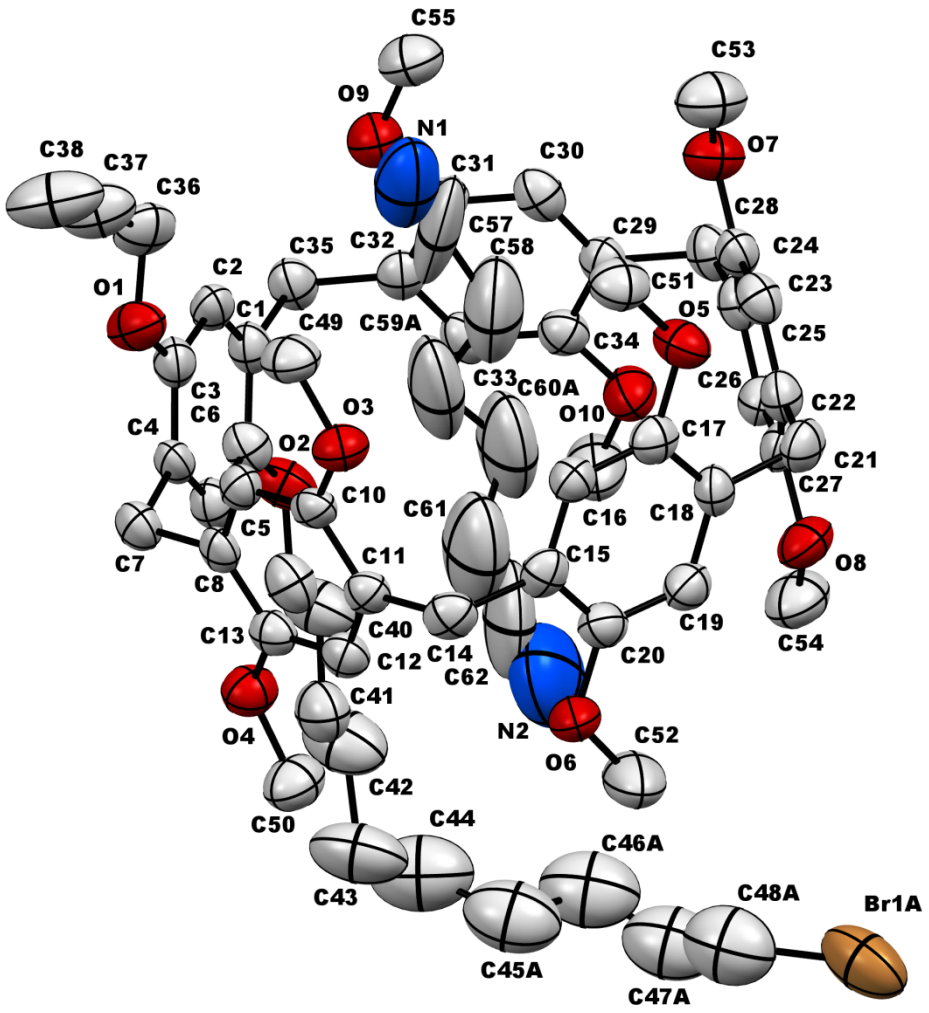

Figure S2. Crystal structure (thermal ellipsoid representation; 30% probability) of [**Pillar** ⊃ **ADN1**] obtained after the crystallization from chloroform and adiponitrile (Hydrogen atoms are hided for clarity).

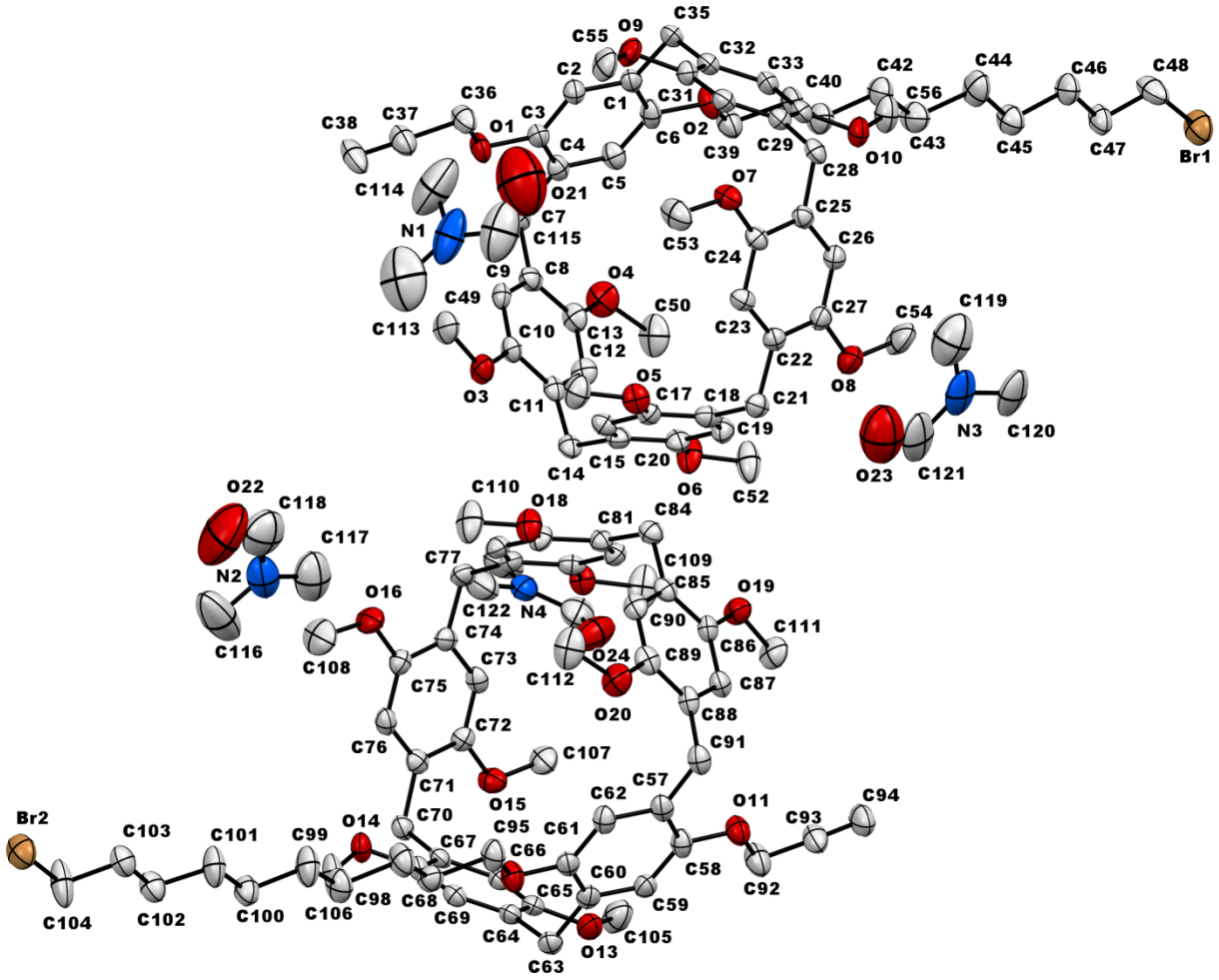

Figure S3. Thermal ellipsoid representation (30% probability) showing the asymmetric unit of **Pillar-D2** obtained after the crystallization from *N*, *N*-dimethyl formamide (Hydrogen atoms are hided for clarity).

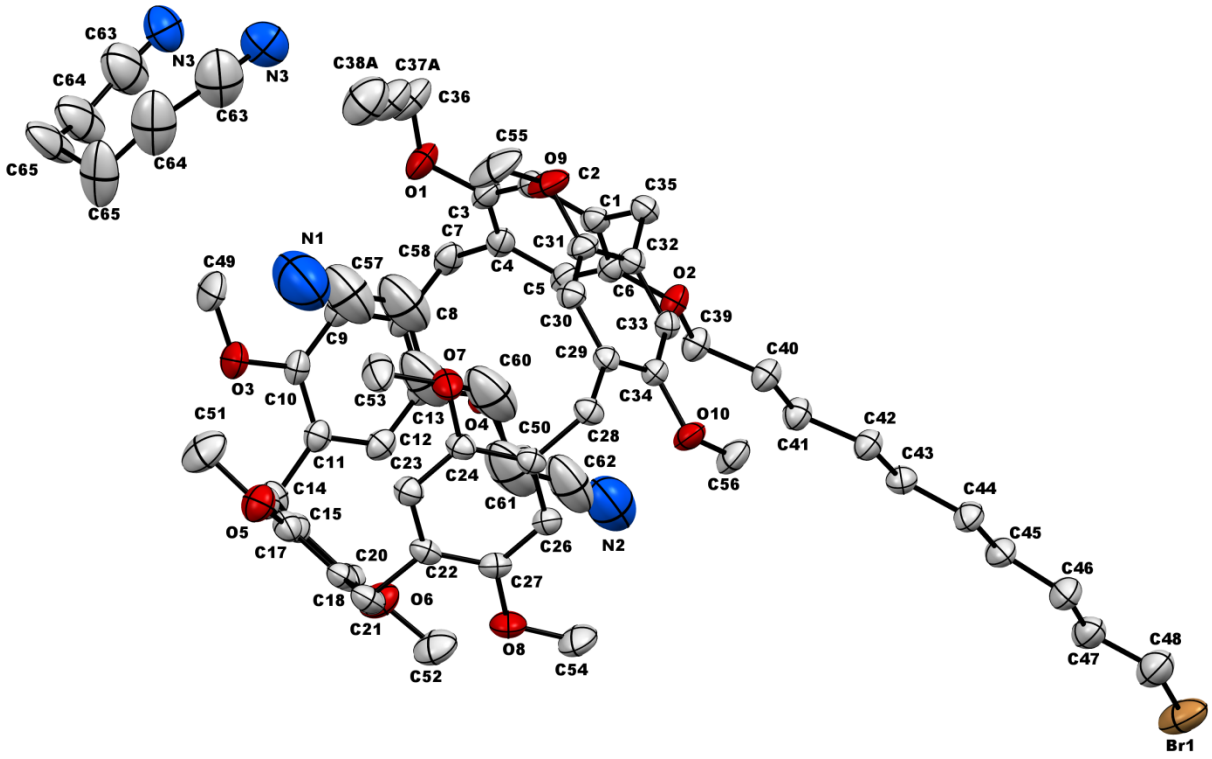

Figure S4. Crystal structure (thermal ellipsoid representation; 30% probability) of [**Pillar** ⊃ **ADN2**] obtained after the crystallization from *N*, *N*-dimethyl formamide and adiponitrile (Hydrogen atoms are hided for clarity).

Pillar_D2: Refined in space group Cc against in space group C2/c

The **Pillar-D2** crystal is better fit in space group C2/c with an inversion centre and one bromine-containing ligand in the asymmetric unit. However, in this article the crystal of **Pillar-D2** is reported in space group Cc with Z = 2 and two bromine-containing ligands in the asymmetric unit as explained below.

In **Pillar-D2** crystal, the DMF acts as a mediator that joins two cyclic [c2] daisy pillararenes. As stated above, the Pillar-D2 crystal is better fit in space group C2/c. However, in the C2/c space group the mediator DMF molecule is occupied in the special position and its interaction with pillarene macrocycles could not established exactly (**Figure A)**. At the same time this DMF molecule is no longer occupied in special position when the same crystal is refined in space group Cc and hence the supramolecular interactions of DMF with pillarene molecules are better explained (via two C-H···π (2.827 Å and 2.800 Å) and C-H···Br (2.822 Å) interactions) in the formation of the supramolecular polymer (**Figure B**).

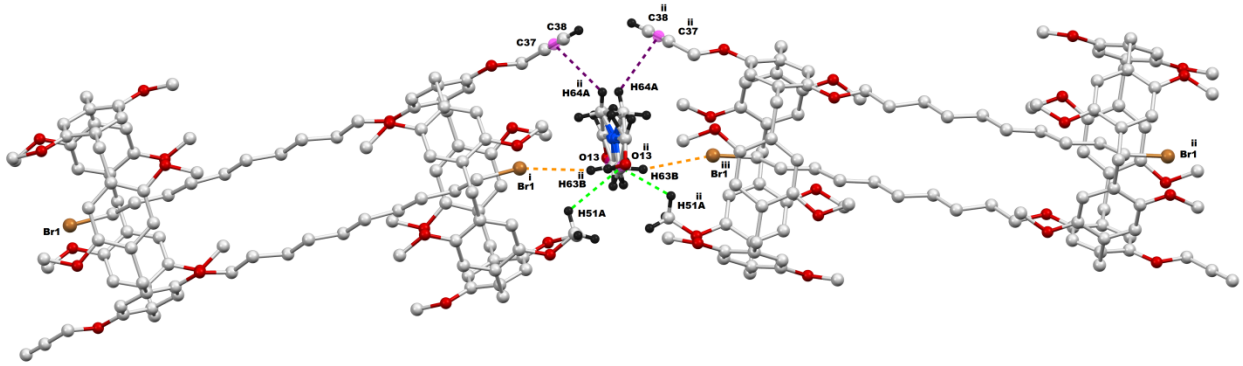

Figure A. Pillararene-DMF interaction in Pillar-D2 crystal when the crystal data is refined in space group C2/c. C-H…Br interactions are shown in brown, C-H…π (C≡C) are in purple and C-H…π (C=O) are in green color respectively. Symmetry code: (i) -x, -y, 1-z; (ii) 1-x, y, ½-z (iii) 1+x, -y, -½+z

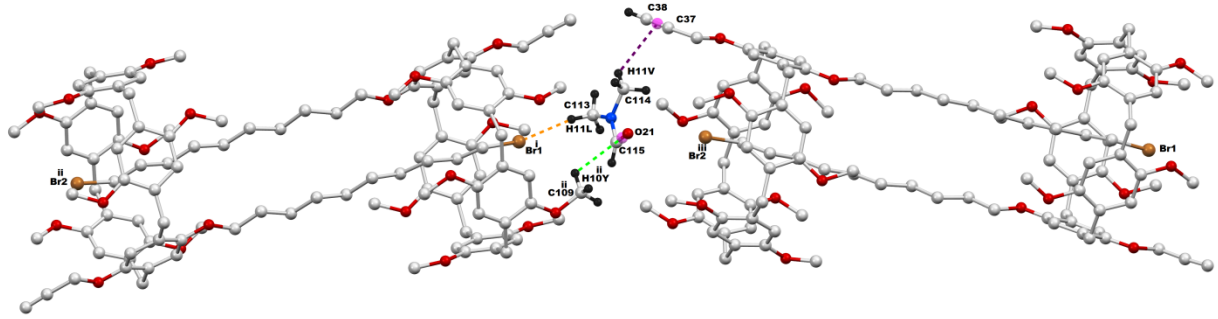

Figure B. Pillararene-DMF interaction in Pillar-D2 crystal when the crystal data is refined in space group Cc. C-H…Br interactions are shown in brown, C-H…π (C≡C) are in purple and C-H…π (C=O) are in green color respectively. Symmetry code: (i) 1+x, 1-y, -½+z; (ii) x, 1-y, -½+z (iii) -1+x, y, z

It is noteworthy that there is no interaction between the Br2 atom and the DMF molecule in Pillar-D2, which is refined in space group Cc. The minimum C-H…Br distance in this case is 3.319 Å (for C114-H11S…Br2iii) which is higher than the sum of the vdW radii (2.94 Å).. Also C-H…π (C≡C) interaction between DMF and C93≡C94 of pillararene as well as the expected C-H…π (C=O) between the DMF and any nearby CH_3 fraction of asymmetric pillararne is found to be absent as the minimum distance observed in these cases are higher than the sum of the vdW radii. So the crystal data of **Pillar-D2** refined in space group Cc provides better idea about the supramolecular polymer formation of pillararene-DMF system compared to that of data refined in space group C2/c.

Therefore, in the present article, we used the crystal data refined in space group Cc for Pillar-D2 crystal. (the crystal data of Pillar -D2 in space group C2/c has also been deposited in CCDC and its deposition number is 2375228).

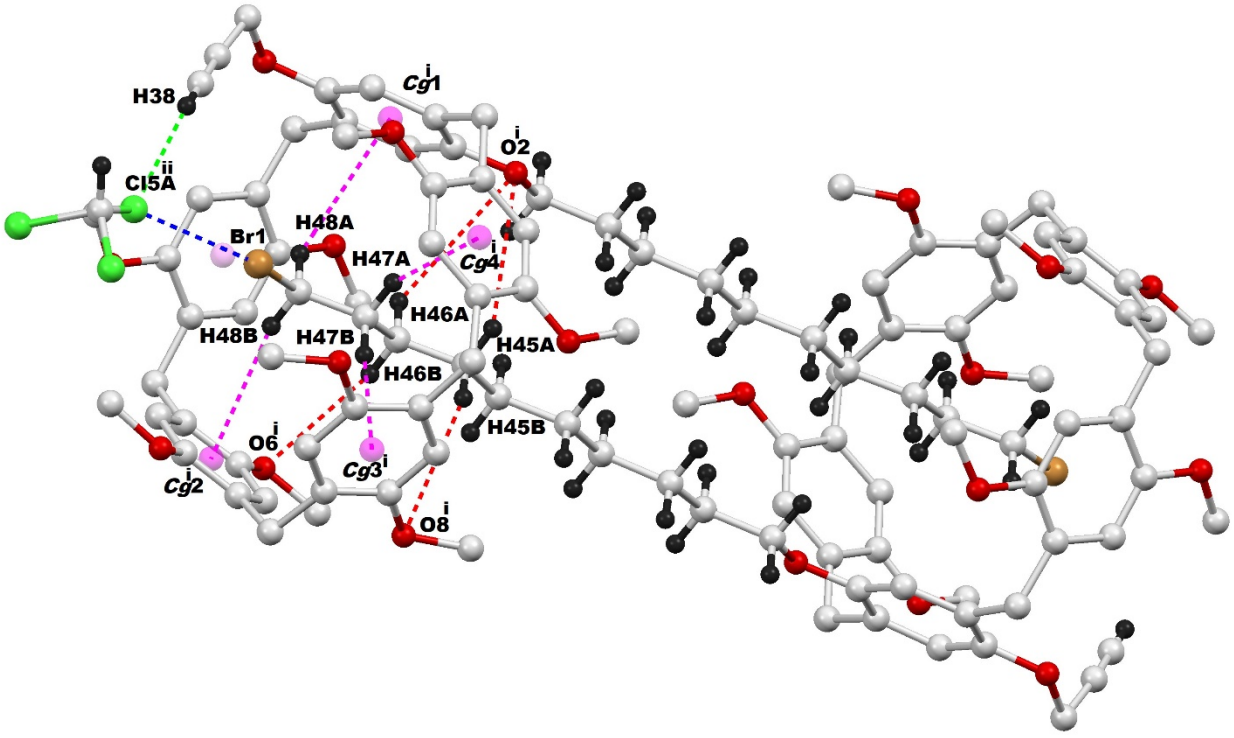

Figure S5. Possible noncovalent interactions in the crystal of **Pillar-D1**.

Table S2. Intermolecular non-bonding interactions (Å, °) in the **Pillar-D1** crystals which facilitated the formation of threaded dimer.

A-B···C		A-B	B···C	B···C	A-B···C
C48	H48A···*Cg*1 [i]	0.99	3.311	4.125	140.66
C48	H48B···*Cg*2 [i]	0.99	2.895	3.807	153.68
C47	H47B···*Cg*3 [i]	0.99	2.898	3.873	168.42
C47	H47A···*Cg*4 [i]	0.99	2.787	3.686	151.26
C46	H46A···O2 [i]	0.99	3.484	4.096(9)	122.1
C46	H46B···O6 [i]	0.99	3.183	4.165(9)	170.5
C45	H45A···O2 [i]	0.99	3.229	4.00(1)	136.4
C45	H45B···O8 [i]	0.99	3.211	4 .09(1)	149.3
C38	H38···Cl5A [ii]	0.95	2.60	3.46(2)	151
C48	Br1···Cl5A [ii]	1.86(1)	3.53(1)	5.32(2)	160.4(4)

*Cg*1 - *Cg*4 are the centroid of the pillararene phenyl rings constitute C1-C6, C15-C20, C22-27 and C29-C34 respectively; Symmetry code: (i)2-x,-y,1-z; (ii) 1+x, -1/2-y, 1/2+z

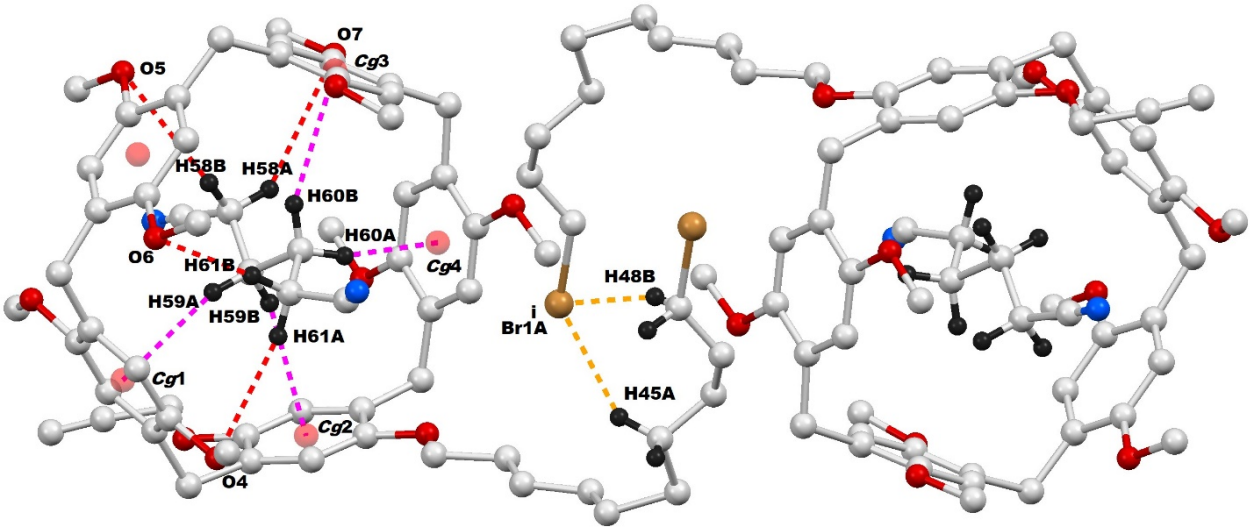

Figure S6. Possible noncovalent interactions in the crystal of [**Pillar** ⊃ **ADN1**].

Table S3. Intermolecular non-bonding interactions in the [**Pillar** ⊃ **ADN**1 crystals (Å, °) observed in the guest encapsulation site and tail-to tail bonds.

A-B···C		**A-B**	**B···C**	**B···C**	**A-B···C**
C45A	H45A···Br1A^{i}	0.99	2.948	3.81(3)	146
C48A	H48B···Br1A^{i}	0.98	2.965	3.91(2)	162
C58	H58A···O7	0.99	3.115	3.97(2)	146
C58	H58B···O5	0.99	2.961	3.88(2)	155
C59A	H59A···*Cg*1	0.99	2.803	3.642	143.14
C59A	H59B···*Cg*2	0.99	2.915	3.877	165.37
C60A	H60B···*Cg*3	0.99	2.839	3.722	148.78
C60A	H60A···*Cg*4	0.99	2.882	3.767	149.25
C61	H61A···O4	0.99	2.998	3.78(3)	136
C61	H61B···O6	0.99	3.186	4.13(2)	160

*Cg*1 - *Cg*4 are the centroid of the pillararene phenyl rings constitute C1-C6, C8-C13, C22-27 and C29-C34 respectively; Symmetry code: (i)-1-x, 1-y, 1-z.

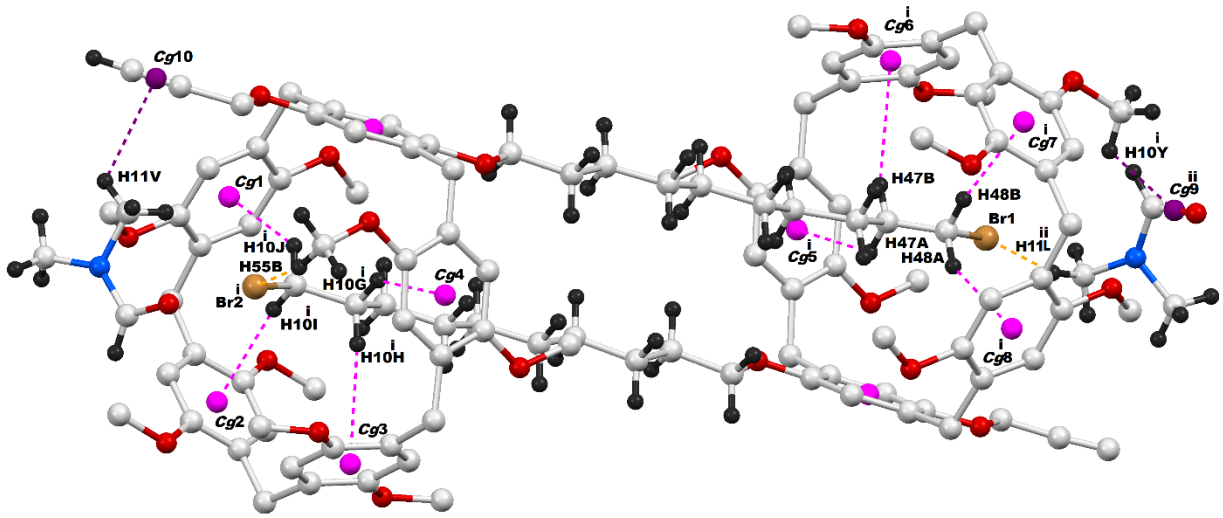

Figure S7. Possible noncovalent interactions in the crystal of **Pillar-D2**.

Table S4. Intermolecular non-bonding interactions (Å, °) in the **Poly(Pillar-D2)** crystals which facilitated the formation of polymeric threaded dimer.

A-B···C	**A-B**	**B···C**	**B···C**	**A-B···C**
C47-H47A···*Cg*5^{i}	0.99	3.062	3.702	123.59
C47-H47B···*Cg*6^{i}	0.99	2.994	3.949	162.24
C48-H48A···*Cg*8^{i}	0.99	2.707	3.608	151. 51
C48-H48B···*Cg*7^{i}	0.99	2.686	3.668	171.56
C113^{iii}-H11L^{iii}···Br1	0.98	2.822	3.76(2)	161.2
C103-H10G···*Cg*4^{ii}	0.99	2.956	3.735	136.40
C103-H10H···*Cg*3^{ii}	0.99	2.952	3.939	174.71
C104-H10I···*Cg*2^{ii}	0.99	2.844	3 .812	166.19
C104-H10J···*Cg*1^{ii}	0.99	2.779	3.504	130.59
C55^{ii}-H55B^{ii}···Br2	0.979	3.118	3.977(9)	147.2
C109-H10Y···*Cg*9^{iv}	0.98	2.827	3.382	116.72
C114-H11V···*Cg*10	0.98	2.800	3.411	121.08

*Cg*1 – *Cg*8 are the centroid of the pillararene phenyl rings constitute C8-C13, C15-C20, C22-27, C29-C34, C64-C69, C71-C76, C78-C83 and C85-C90 respectively; *Cg*9 & *Cg*10 are the centroids of C115=O21 and C37=C38 double bonds respectively. Symmetry code: (i) -1+x, -y, z; (ii) 1+x, y, z (iii) -1+x, 1-y, ½+z (iv) x, 1-y, ½+z

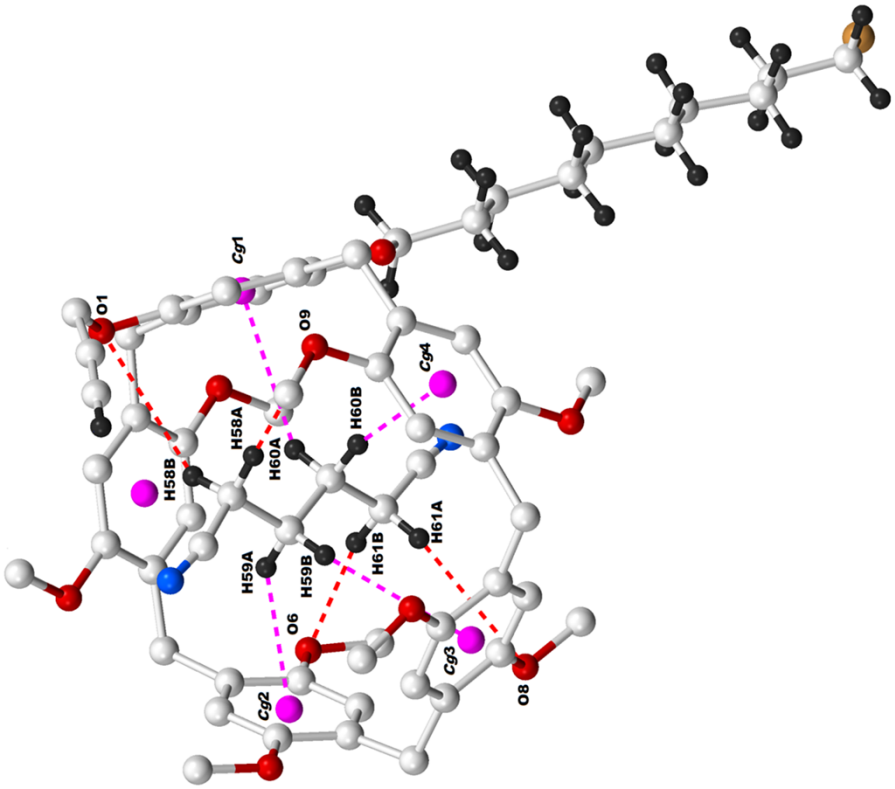

Figure S8. Possible noncovalent interactions between Pillararene host and encapsulated adiponitrile in the crystal of [**Pillar** ⊃ **ADN2**]. *Cg*1 - *Cg*4 are the centroid of the pillararene phenyl rings constitute C1-C6, C15-C20, C22-27 and C29-C34 respectively.

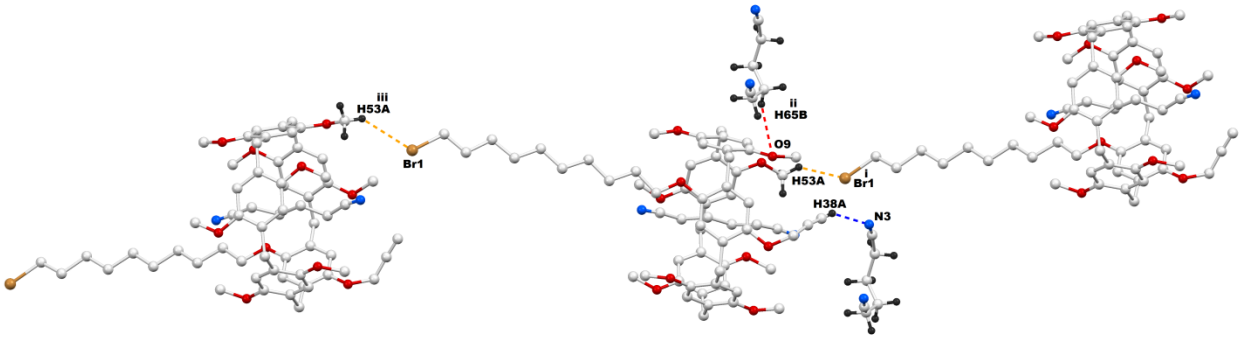

Figure S9. Possible noncovalent interactions of pillararene with adjacent pillararenes and the void filling adiponitrile molecules in the crystal of [**Pillar** ⊃ **ADN2**]. Symmetry code: (i)1/2+x, 1/2-y, 1/2+z; (ii)1.5-x, -1/2+y, 1.5-z. (iii)-1/2+x, 1/2-y, -1/2+z.

Table S6. Intermolecular non-bonding interactions in the [**Pillar** ⊃ **ADN2**] crystals (Å, °) observed in the Pillar-Adiponitrile and Pillar-Pillar bonds.

A-B···C		**A-B**	**B···C**	**B···C**	**A-B···C**
C58	H58A···O9	0.99	2.936	3.92(1)	171.3
C58	H58B···O1	0.99	3.103	3.90(1)	138.2
C59	H59A···*Cg*2	0.99	3.072	3.928	145.51
C59	H59B···*Cg*3	0.99	3.084	3.982	151.69
C60	H60A···*Cg*1	0.99	3.087	3.765	126.90
C60	H60B···*Cg*4	0.99	2.939	3.890	161.29
C61	H61A···O8	0.99	3.012	3.87(1)	145.7
C61	H61B···O6	0.99	3.110	4.07(1)	164.2
C38A	H38A···N3	0.95	1.96	2.61(2)	124
C53	H53A···Br1^{i}	0.98	3.027	3.817(7)	138.6
C65^{ii}	H65B^{ii}···O9	0.99	2.724	3.56(2)	141.8

*Cg*1 - *Cg*4 are the centroid of the pillararene phenyl rings constitute C1-C6, C15-C20, C22-27 and C29-C34 respectively; Symmetry code: (i)1/2+x, 1/2-y, 1/2+z; (ii)1.5-x, -1/2+y, 1.5-z.

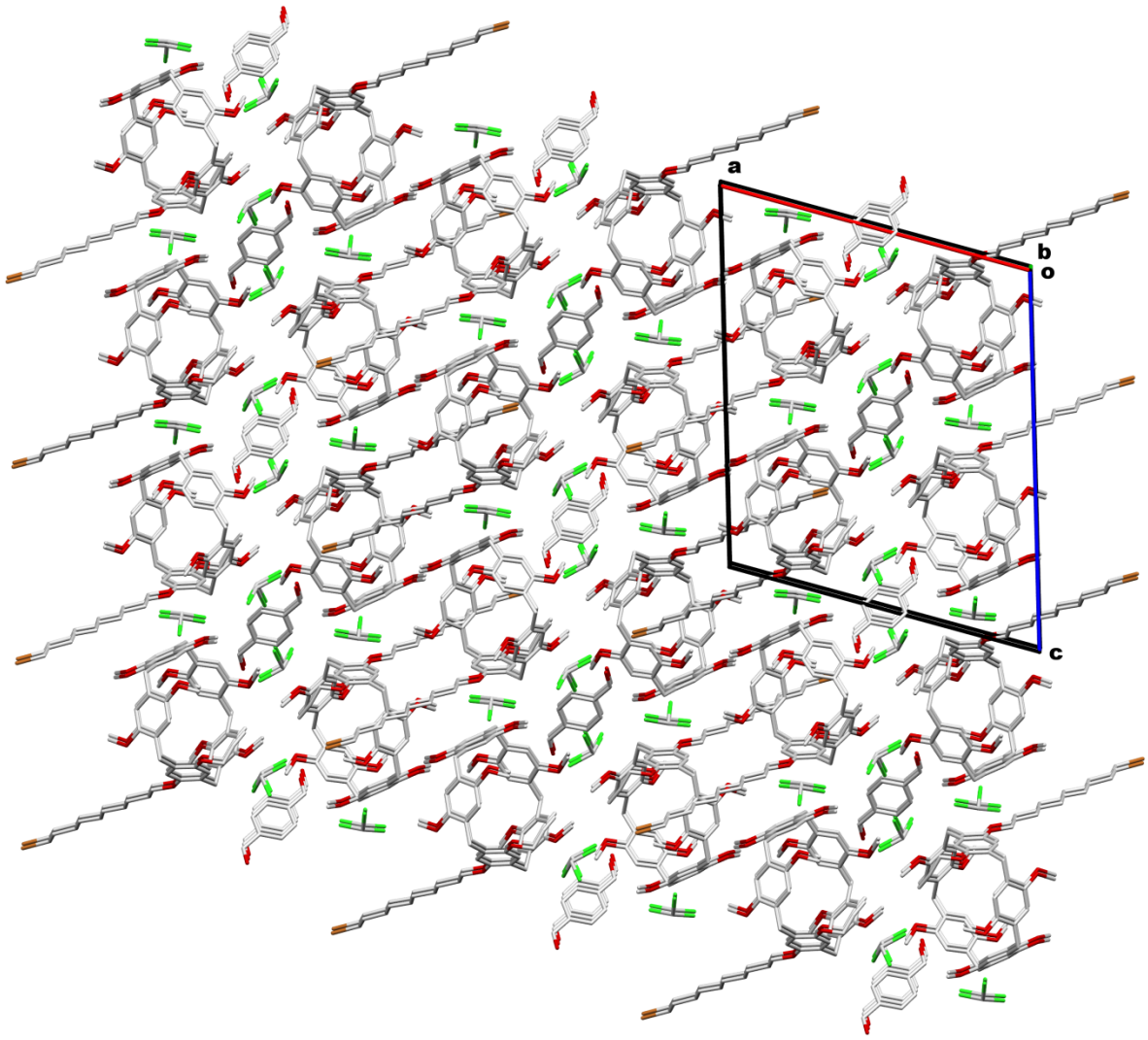

Figure S10. Packing diagrams of **Pillar-D1**

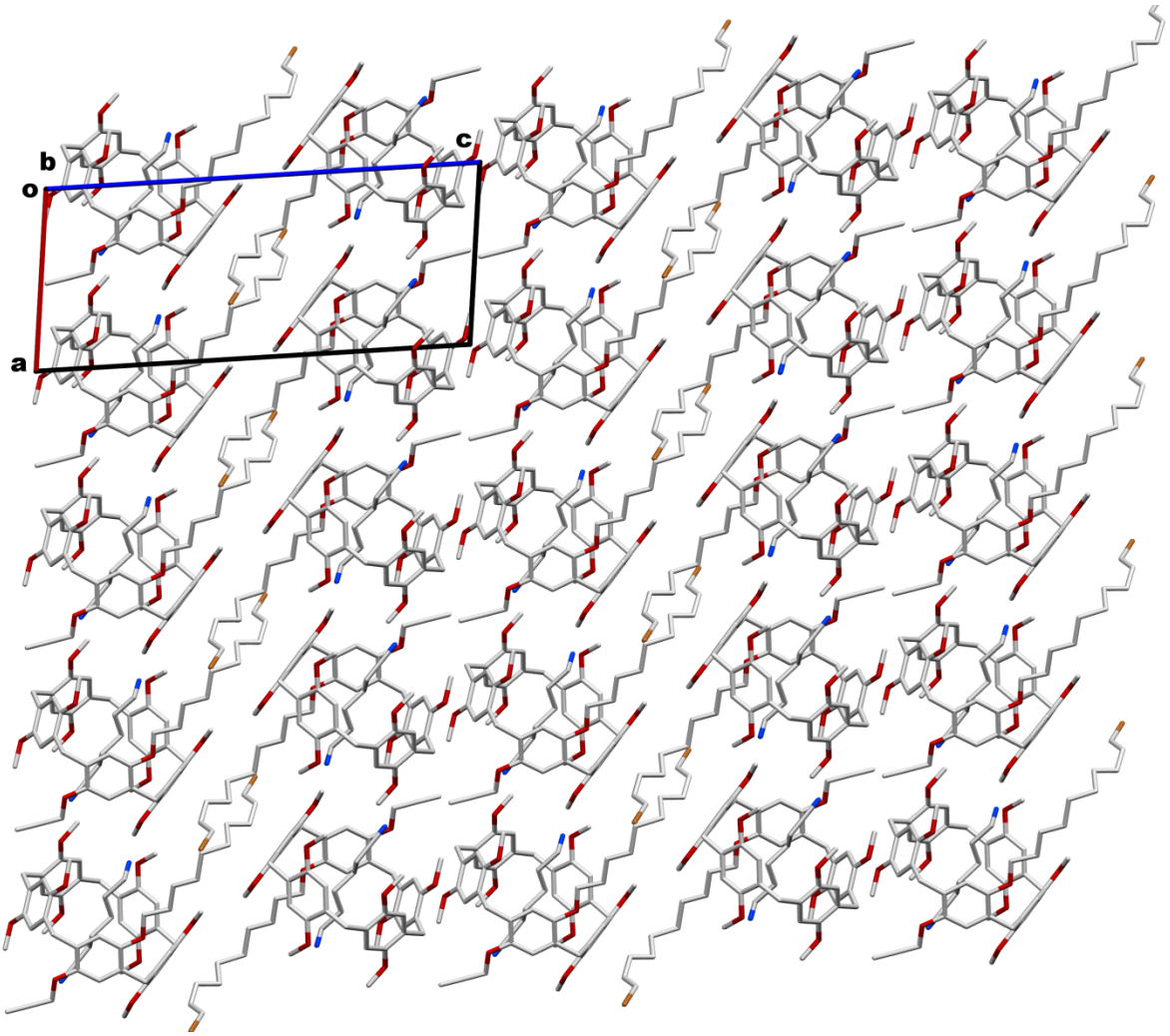

Figure S11. Packing diagrams of **Pillar-ADN1**

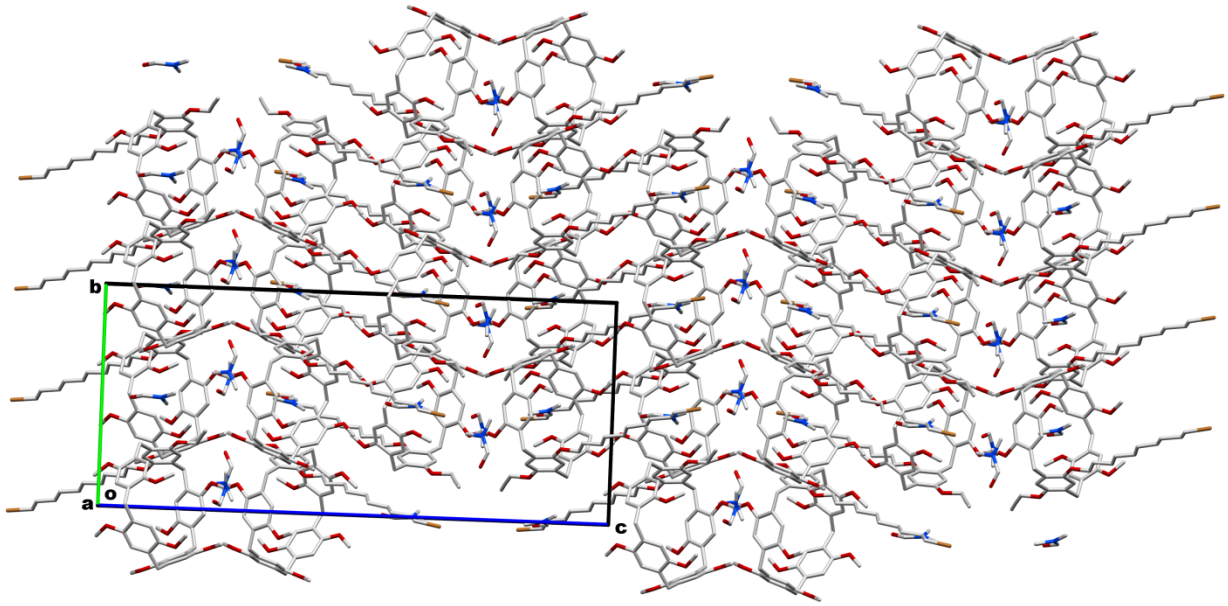

Figure S12. Packing diagrams of **Pillar-D2**

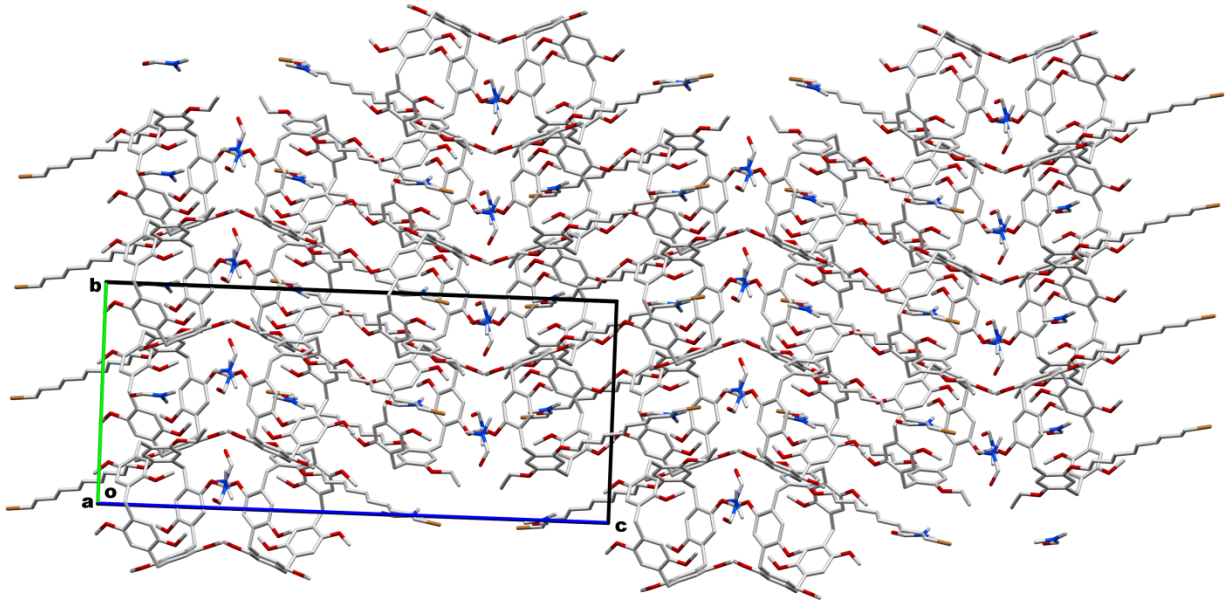

Figure S13. Packing diagrams of **Pillar-ADN2**

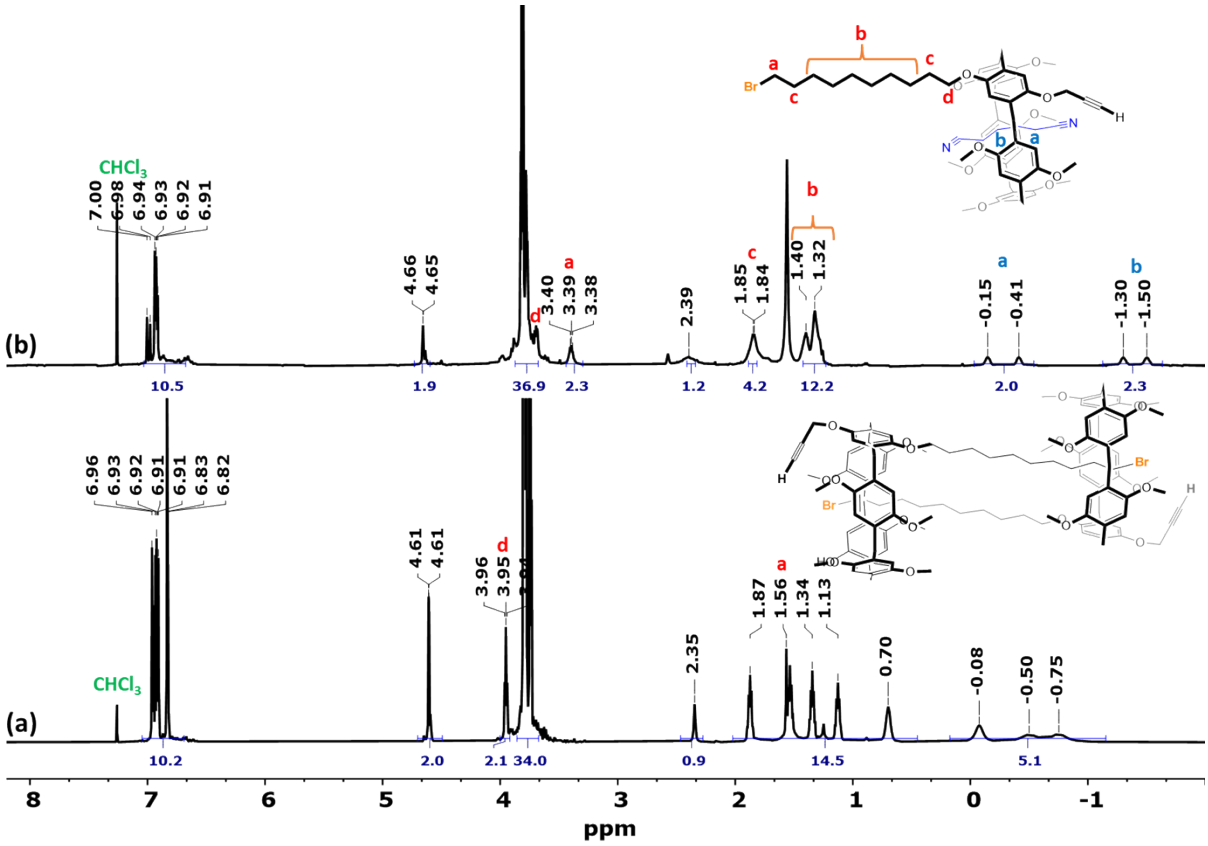

Figure S14. ^{1}H NMR spectra (600 MHz, $CDCl_3$ at 298 K) of **Pillar-D1** (a), and [**Pillar** ⊃ **ADN1**] (b).

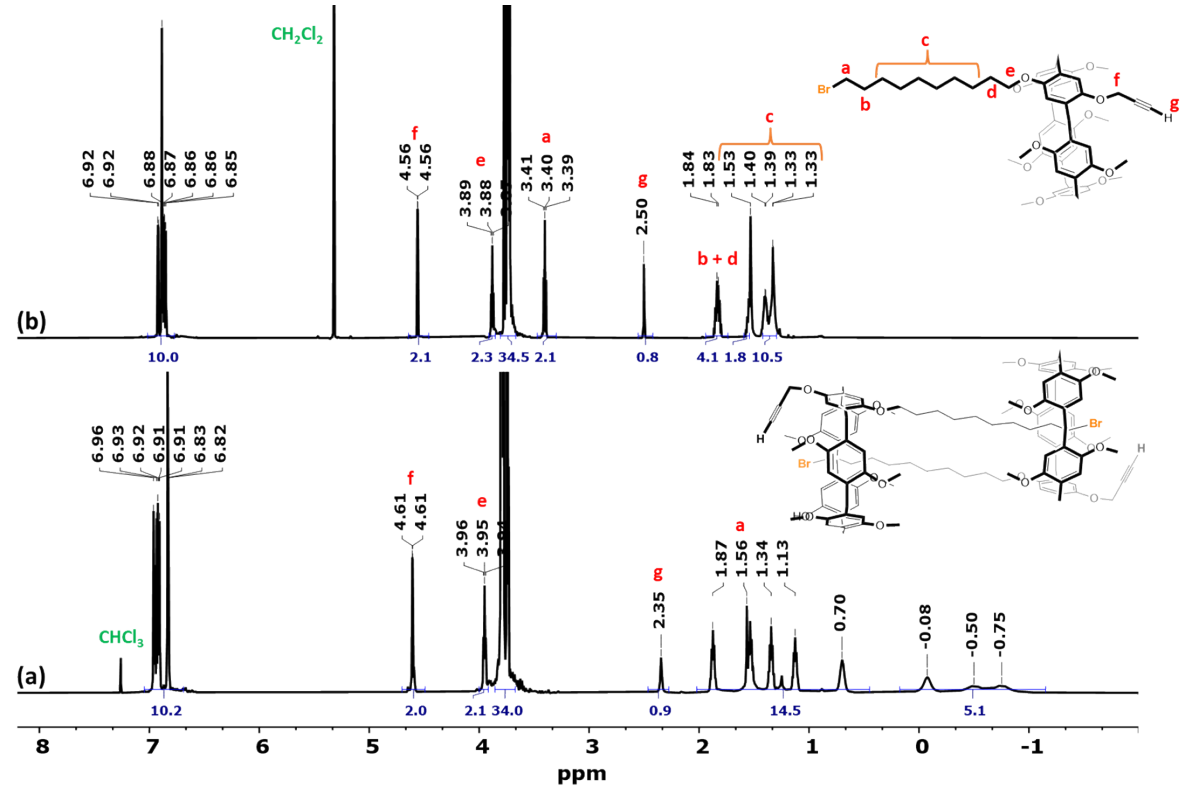

Figure S15. ^{1}H NMR spectra (600 MHz, 298 K) of the **Pillar-D1** [2c] daisy chain recorded in (a) $CDCl_3$ and (b) CD_2Cl_2.

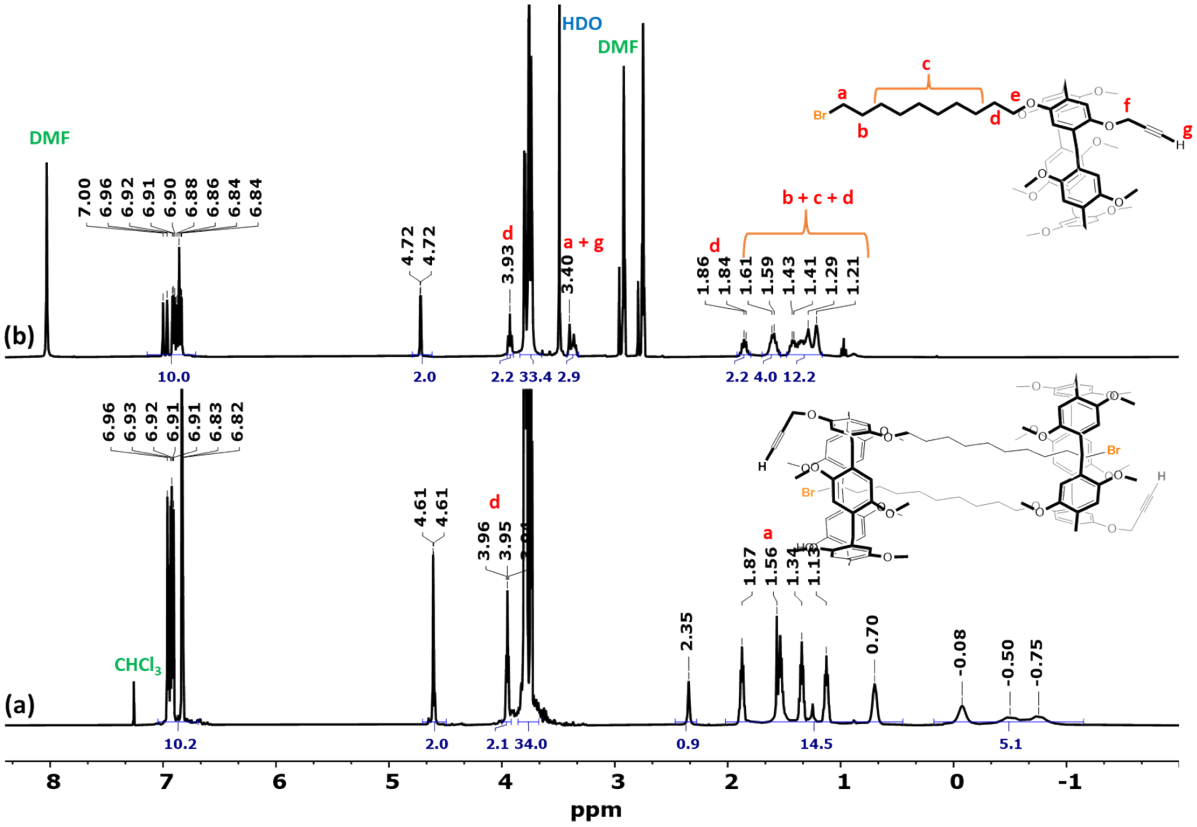

Figure S16. ^{1}HNMR (600 MHz, 298 K) spectra of **Pillar-D1** in $CDCl_3$ (a), and DMF-d_7 (b).

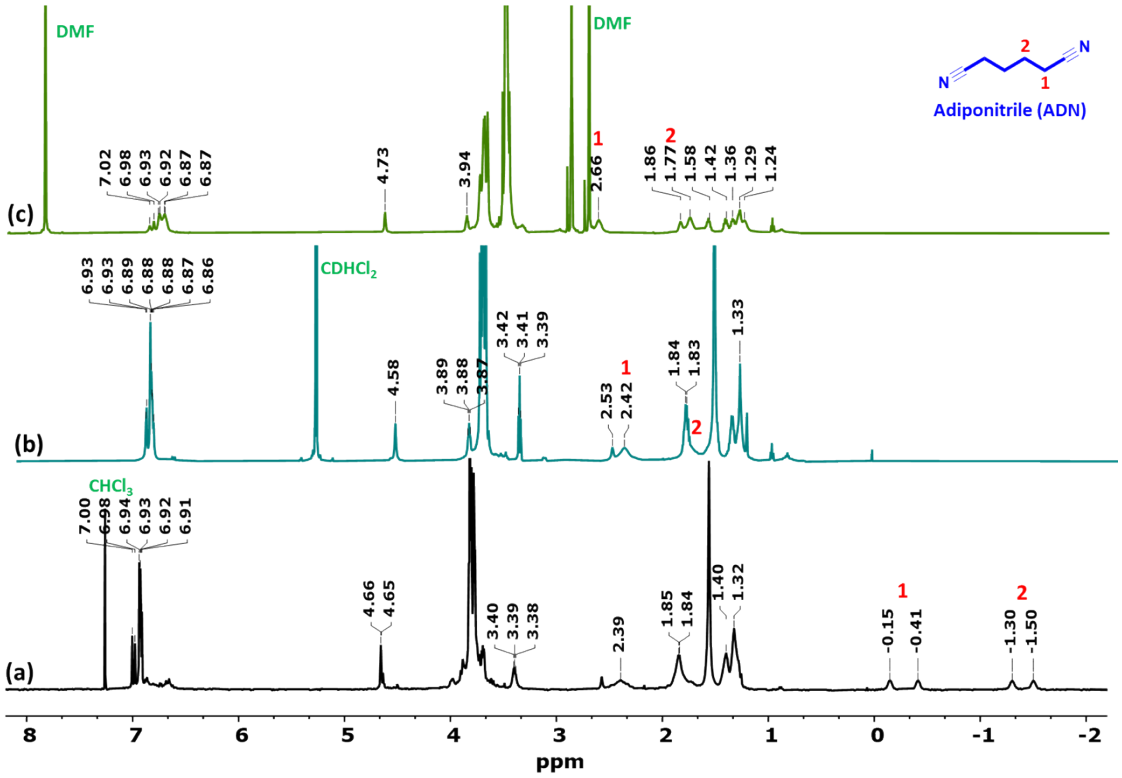

Figure S17. [1]HNMR (600 MHz, 298 K) spectra of equimolar solution of **Pillar** with adiponitrile (**AND**)in $CDCl_3$ (a), CD_2Cl_2 (b) and DMF-d_7 (c).

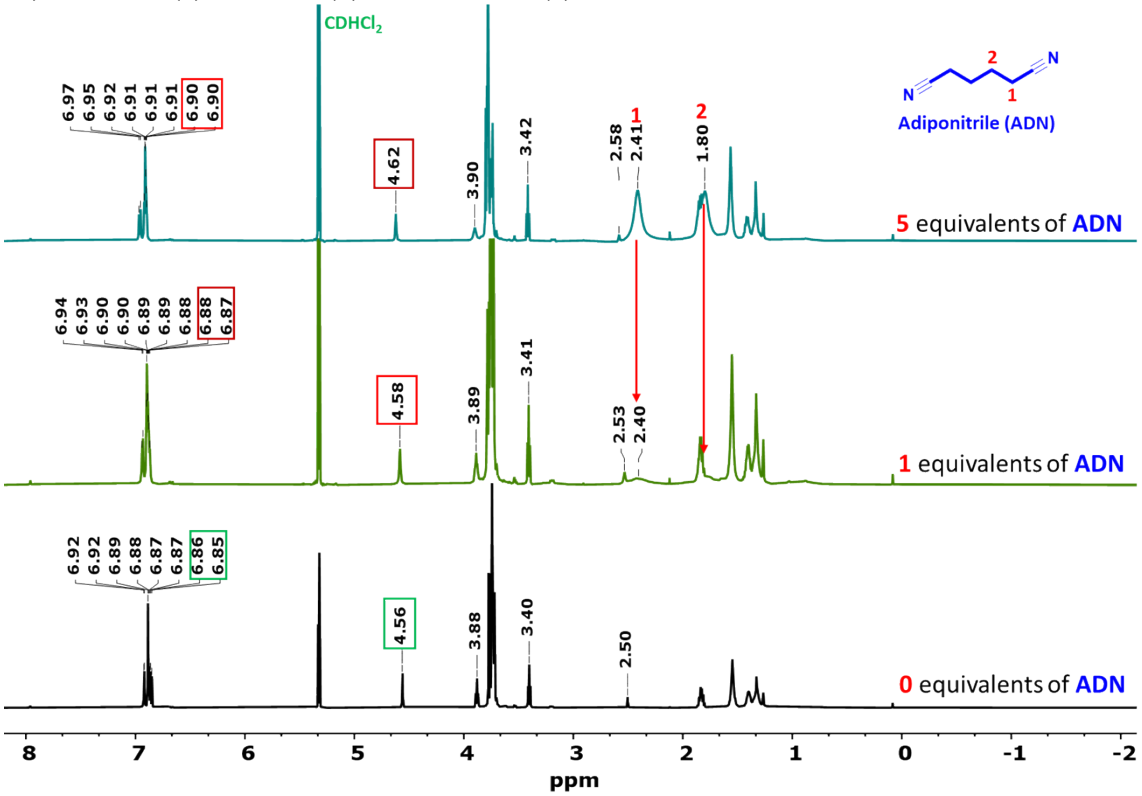

Figure S18. [1]HNMR (600 MHz, CD_2Cl_2 at 298 K) spectra of **Pillar** with different concentrations of adiponitrile (**AND**).

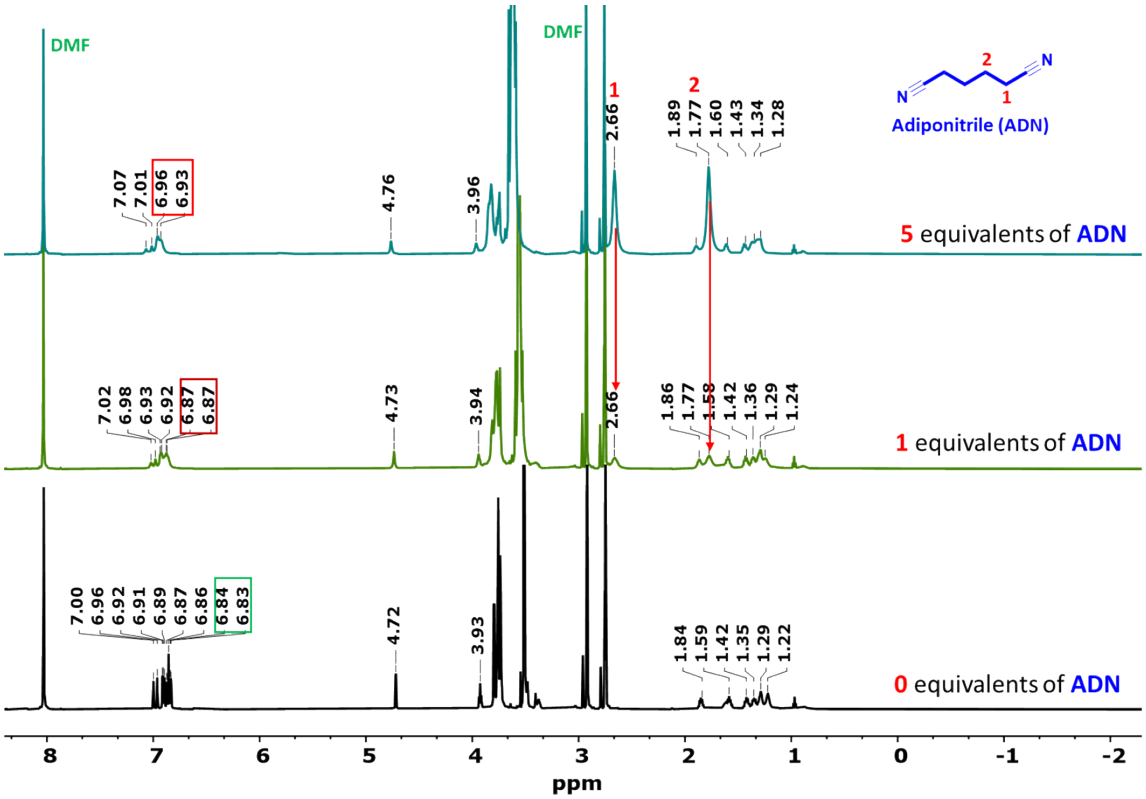

Figure S19. [1]HNMR (600 MHz, DMF-d_7 at 298 K) spectra of **Pillar** with different concentrations of adiponitrile (**AND**).

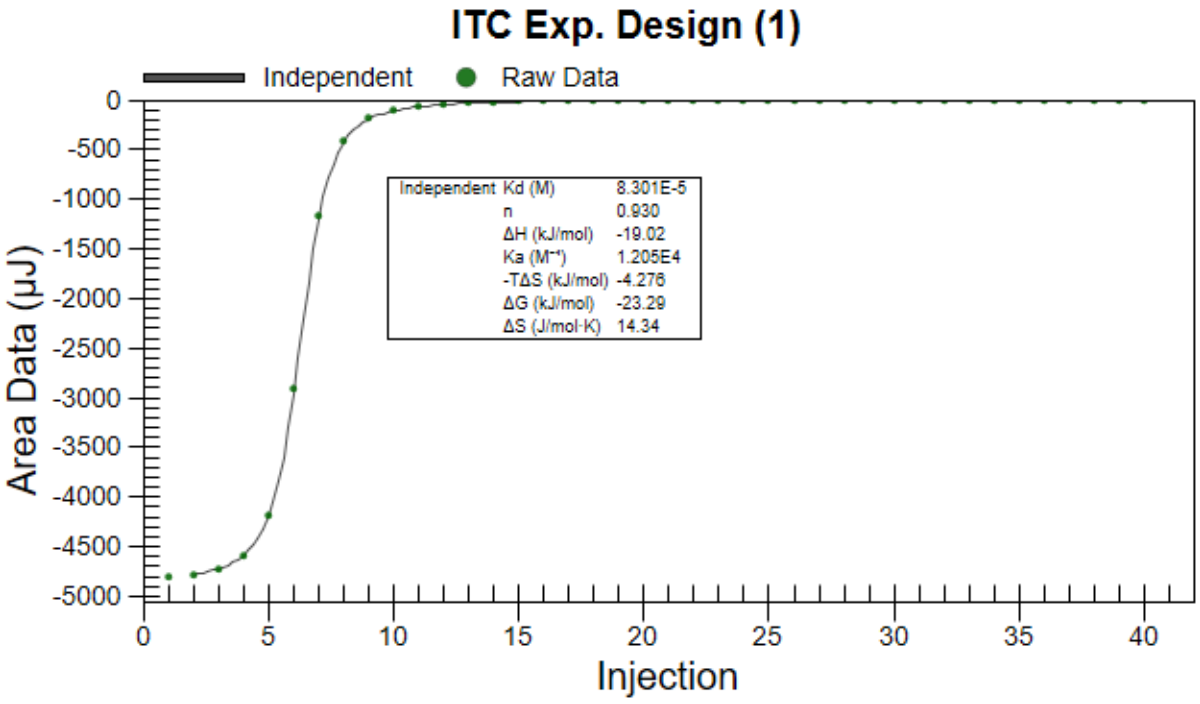

Figure S20. Net heat of complexation in **chloroform** of 10 mM solution of **Pillar** with **adiponitrile** as a function of injection after subtracting heat of dilution.

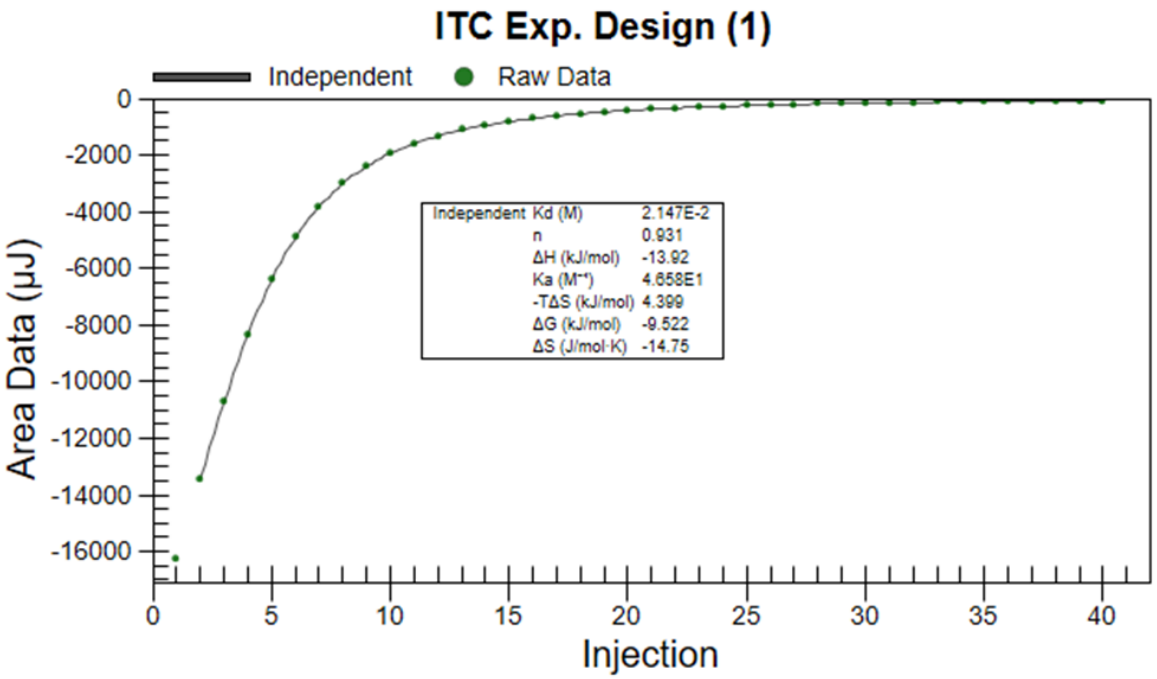

Figure S21. Net heat of complexation in ***N*, *N*-dimethylformamide** (**DMF**) of 10 mM solution of **Pillar** with **adiponitrile** as a function of injection after subtracting heat of dilution.

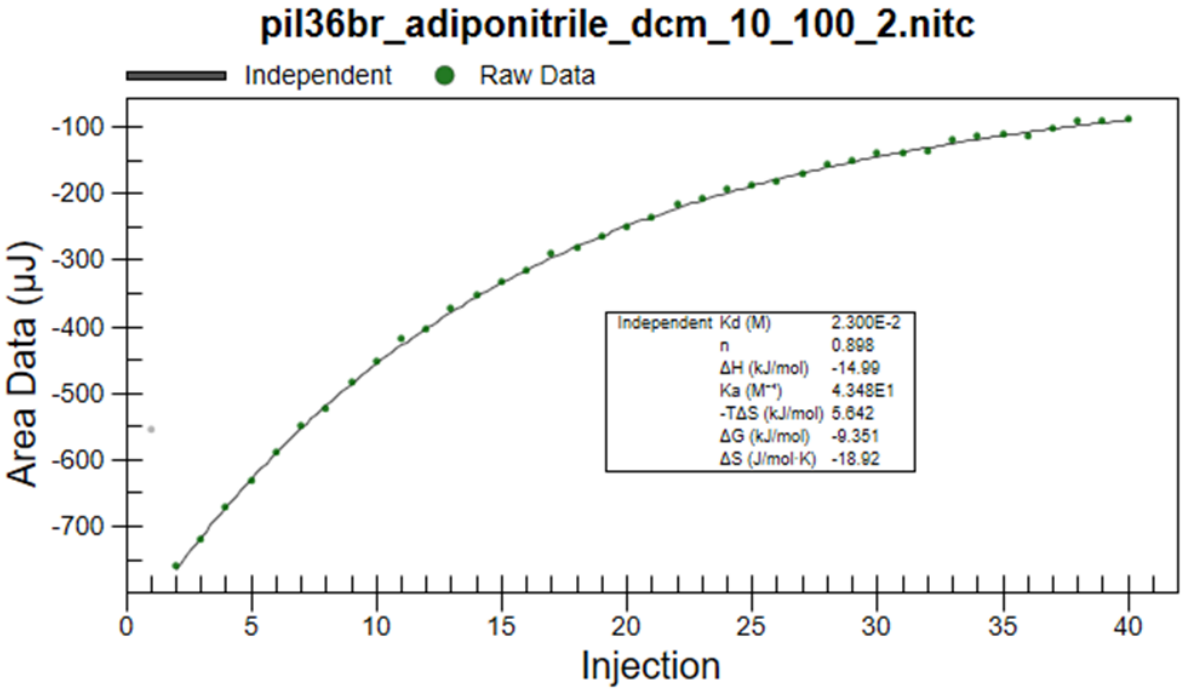

Figure S22. Net heat of complexation in **dichloromethane** (**DCM**) of 10 mM solution of **Pillar** with **adiponitrile** as a function of injection after subtracting heat of dilution.

References

1. G. M. Sheldrick, *Acta Cryst*. 2015, C**71**, 3-8.