Supplementary Material (ESI) for Chemical Communications

Supplementary Data

Manipulating the cavity of a porous material changes the photoreactivity of included guests

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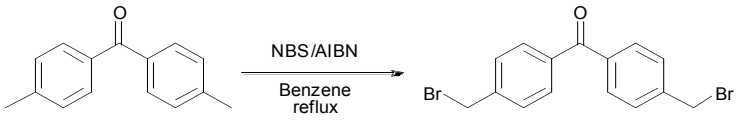
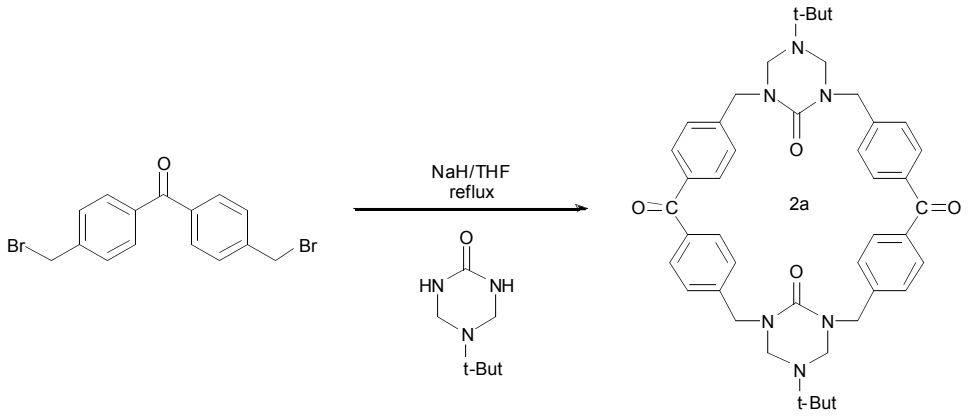
Materials and Instruments: All chemicals were purchased from Aldrich and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Mercury/VX 300 & VX 400. The IR data were collected on Shimadzu 8400 FT-IR spectrometer in KBr cells of 0.2 mm to 1 mm path length. The electron spray mass spectra were obtained with Micromass Q-TOF I mass spectrometer. The GC-MS spectra were obtained with Micromass VG70S magnetic sector mass spectrometer, Column: Restek RTX-5, 30 m X 0.25 mm, 0.25 _m film thickness. The thermometer for melting point was not calibrated. The Scanning Electron Microscopy image was recorded on Quanta 200 ESEM with accelerating voltage 30 kV. Photoisomerizations were carried out using a Hanovia medium-pressure 450 W mercury arc lamp cooled in a borosilicate immersion well, and the entire apparatus was placed in a UV shielded and refrigerated reaction chamber. The starting temperature was 0 ^{o}C and the final temperature did not increase above 30 ^{o}C. The X-ray powder diffraction data were collected on a Rigaku Dmax-2100 & 2200 powder X-ray diffractometers using a Bragg-Brentano geometry with CuK_ radiation. The step scans covered the angular range 2-40^{o} 2_ in steps of 0.05^{o}. Thermogravimetric analysis for the guest desorbtion studies were carried out on 5-10 mg of absorbed sample using on a TA Instruments SDT-2960 simultaneous DTA-TGA at a heating rate of 4 ^{o}C/min from 25 to 160 ^{o}C under helium.



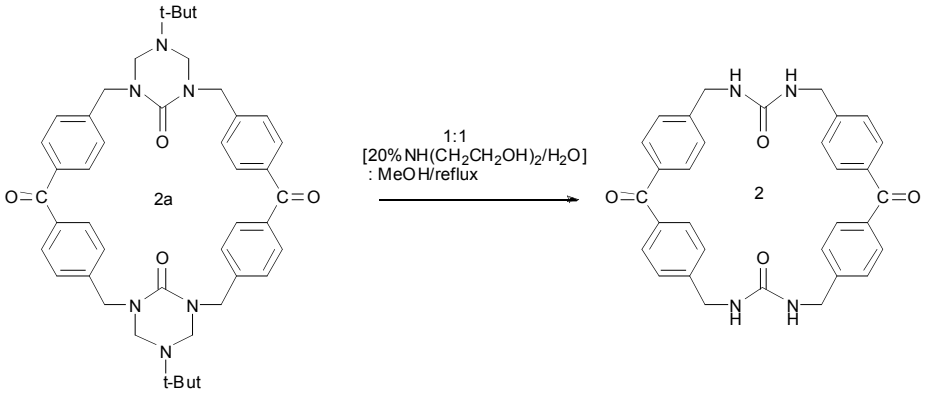
Scheme S1. synthesis of 4,4'-bis (bromo methyl) benzophenone

4,4'-bis (bromo methyl) benzophenone : 4,4' Dimethyl benzophenone (10.27 g, 49 mmol) was refluxed in benzene (122 mL) for 30 min. Then N-bromo succinamide (18.26 g, 103 mmol) and 2,2'-azobis(2-methylpropionitrile) (AIBN) (0.080 g, 4.88 x 10^{-1} mmol) were added to the solution. The reaction mixture was cooled to the room temperature and refluxed overnight. Upon completion the solvent was evaporated *in vacuo* and the crude reaction mixture was purified by flash chromatography in ethyl acetate : hexanes (1 : 9) eluent to obtain the product as pale yellow solid (4.2 g, 81.1%).; **^{1}H-NMR**: $_{H}$(300 MHz; $CDCl_3$; Me_4Si) 7.78(4H, d, *J* 8.1, C*H*), 7.51(4H, d, *J* 8.4, C*H*), 4.54(4H, s, CH_2Br); **^{13}C-NMR**: δ_C(75 MHz, $CDCl_3$, Me_4Si) 195.46, 142.52, 137.45, 130.75, 129.25, 32.43; **HRMS (EI)**: [M^+] Calculated for formula $C_{15}H_{12}$[79]Br_2O: 365.9255 Found: 365.9244, *m/z* 368(15%) 287(100%), 180(60%), 104(25%), 90(30%); **IR**: $_{max}$($CHCl_3$)/cm^{-1} 1658, 1608, 1315, 1278, 929, 694, 679; mp 106-108 °C (from CH_2Cl_2).



Scheme S2. **S**ynthesis of triazinanone protected bis-urea macrocycle

Triazinanone protected bis-urea macrocycle (2a) : Triazinanone (0.869 g, 5.44 x 10^{-1} mmol) and NaH (0.823 g, 22 mmol) were heated to reflux in freshly distilled dry THF (100 mL) for 45 min. Then the solution was cooled to room temperature and 4,4' bis (bromomethyl) benzophenone (2.00 g, 5.44 x 10^{-1} mmol) dissolved in dry THF (172 mL) was added drop wise over 45 min. then the reaction mixture was refluxed for 48 h. Upon completion the reaction was quenched with 1N HCl (5 mL) and H_2O (16 mL) then reduced *in vacuo* to 75 mL. The solution was diluted with 1N HCl (26 mL) and H_2O (86 mL) then extracted with chloroform (100 mL three times). Combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, and crude reaction mixture was purified by flash chromatography with methanol : ethyl acetate (1 : 9) eluent to obtain the product as white solid (0.216 g, 5.5%).; **^{1}H-NMR**: δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.81(8H, d, *J* 8.4,C*H*), 7.45(8H, d, *J* 8.1, C*H*), 4.36(8H, s, CH_2), 1.10(18H, s, CH-CH_3); **^{13}C-NMR**: _$_C$ (75 MHz, $CDCl_3$, Me_4Si) 196.02, 155.69, 143.52, 136.62, 131.00, 127.35, 62.99, 54.35, 49.24, 28.45; **HRMS (EI)**: [M^+] Calculated for formula $C_{44}H_{50}N_6O_4$: 727.3972 Found: 727.3981 ,*m/z* 642(23%), 525(82%), 484(48%), 411(61%), 385(29%), 364(81%), 322(23%); **IR**: _$_{max}$($CHCl_3$)/ cm^{-1} 2977, 1635, 1608, 1506, 1413, 1284, 929, 705, 694,678; mp 230-233 °C (from $CHCl_3$).



Scheme S3. Deprotection of triazinanone protected bis-urea macrocycle

Bis-urea macrocycle (2): Triazinanone protected bis-urea macrocycle (**2a**) (0.290 g, 3.99 x 10^{-1} mmol) was heated to reflux in 1:1 20% [$NH(CH_2CH_2OH)_2/H_2O$] pH ~ 2 with Conc. HCl : MeOH (90 mL) for 48 h. The white precipitate was cooled to room temperature, suction filtered and washed with 45 mL 1N HCl and 45 mL H_2O. The filtrate was dried *in vacuo* to obtain the product as white powder (0.218 g 98.1%).; **^{1}H-NMR**: δ_H (300 MHz, DMSO, Me_4Si) 7.73(8H, d, *J* 8.1 C*H*), 7.41(8H, d, *J* 8.1 C*H*), 6.81(4H, t, CH_2-N*H*) 4.36(8H, d, *J* 5.4 C*H*$_2$-NH); **^{13}C-NMR**: _$_C$ (75 MHz, $CDCl_3$, Me_4Si) 196.02, 155.69, 143.52, 136.62, 131.00, 127.35, 62.99, 54.35, 49.24, 28.45. **HRMS (EI)**: [M^+] Calculated for formula $C_{32}H_{28}N_4O_4$ 532.2111, Found: 532.2096, *m/z* 532(10%),292(50%), 266(34%), 160(100%), 149(80%),119(35%). **IR**: _$_{max}$(KBr)/cm^{-1} 305, 2920, 1645, 1596, 1284, 1056, 931, 790, 746, 638. Macrocycle **2** • DMSO decomposes at 343 ºC.

Recrystallization: Macrocycle **2** (50 mg) was stirred in DMSO (20 mL) in a pressure tube. The mixture was heated (at 130 _C) for 2 h. The oil bath was ramped to cool at a rate 1 _C/h to room temperature. Colorless needles of self-assembled macrocycle **2** crystallized.

Guest loading: DMSO guest from self-assembled crystals of **1** were removed by heating up to 160 °C to form the empty host. The crystalline host **2** (5 – 25 mg) was taken in vial, then the vial was placed in a sealed guest chamber (chamber was wrapped with aluminum foil) for 1 to 4 days. Host : guest binding ratios were analyzed by ^{1}H NMR and thermogravimetric analysis (TGA).

TGA desorption studies: Guest desorption was monitored by TGA. TGA analysis was carried out using TA instruments SDT 2960 simultaneous DTA-TGA instrument with a 5-10 mg crystalline material. The material was heated at 4°C/min from 25 to 160 °C under Helium gas. Upon completion, the material was collected for the next absorption-desorption study. All host guest binding ratios were calculated from a minimum three adsorption/desorption cycles using the formulas below.

$$\text{\# mols of host} = \frac{\text{Final weight g}}{\text{532.59 g/mol}}$$

$$\text{\# mols of guest} = \frac{\text{(Initial weight-final weight)}}{\text{Guest molecular weight g / mol}}$$

$$\text{Host : Guest} = \frac{\text{\# of mols of host}}{\text{\# of mols of guest}}$$

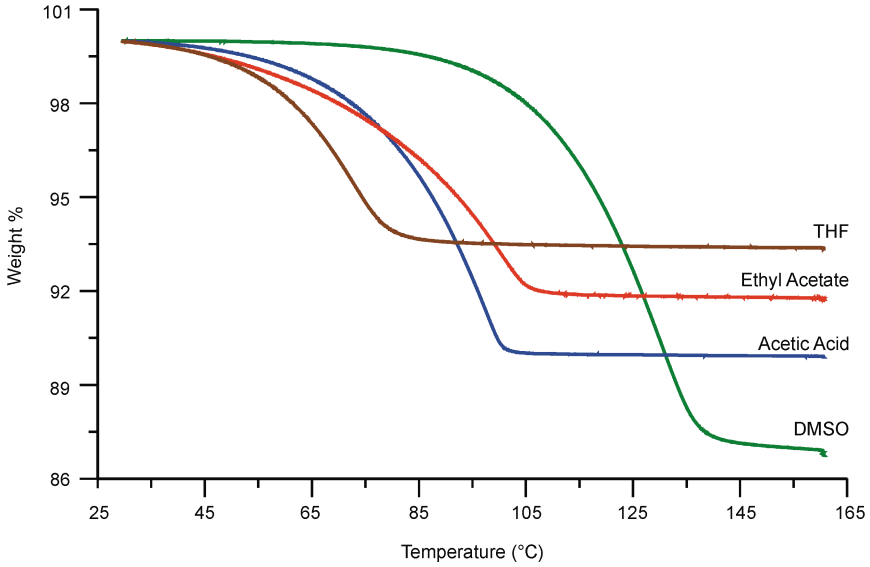


Figure S1. Guest desorption by TGA in Host **2**

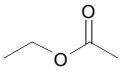
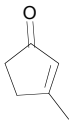
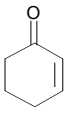
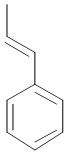
guest	host **1** : guest	host **2** : guest
	2 : 1	2 : 1
	2 : 1	2 : 1
	1 : 1	1 : 1
	2.5 : 1	2 : 1
	1 : 1.5	2.3 : 1
	2.5 : 1	2 : 1
	1 : 1.5	2 : 1
	2.7 : 1	2.5 : 1

Table S1. Hosts **1** & **2** bind similar guests

Micropore analysis: BET analysis was performed by Quantachrome Instruments, 1900 Corporate drive, Boynton Beach, FL 33426. Solvent guest molecules were removed from freshly recrystallized material by TGA and sent to Quantachrome for analysis. A clean and dry sample cell (6mm, large bulb) was measured on the balance. Approximately 0.0474 g of sample was transferred into the cell and recorded the weight again. The sample containing cell was transferred to an Autoadsorb degassing unit. Sample was degassed for 24 h at 130 °C. After outgassing completed the cell was disconnected and reweighed on the balance and recorded the weight. Then sample cell was transferred to the analysis station of the Physisorption instrument. CO_2 gas was used as adsorbate and the isotherm was generated at 0 °C (273 K). In analysis parameters P_0 value of 760 mm/Hg was entered by using "user entered" option. This tells the instrument to measure in the range of absolute pressure up to 760 mm. After the analysis, and before the data reduction process, this value was changed in the Analysis Information panel to the correct value (P_0=26,115 torr for CO_2 at 273 K. An isotherm with 40 points in adsorption and 20 in desorption was measured in a pressure range of 0.05 to 0.995. In fact the actual relative pressure range was from 0.0003 to 0.03 after correcting the P_0 value at 273K. The volume pressure data thus obtained was reduced using Autosorb software for surface area, total pore volume and pore size distribution calculations.

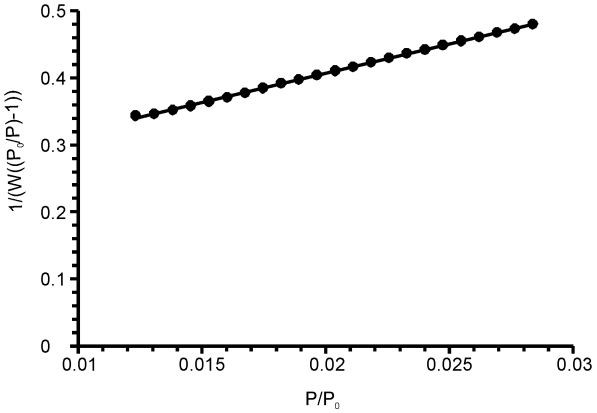


Figure S2. BET plot

^{1}H NMR data analysis: Inclusion crystals in NMR tube were dissolved in d_6-DMSO solvent. Next the macrocycle:guest ratios were determined by ^{1}H NMR integration using a 400 MHz Mercury Varion NMR spectrometer. Recovery delay times were optimized for integration. Host : Guest ratios (±5%) were calculated from proton integration using formula below.

$$\text{Host : Guest} = \frac{\text{Average } ^1\text{H integration for macrocycle}}{\text{Average } ^1\text{H integration for guest after bound}}$$

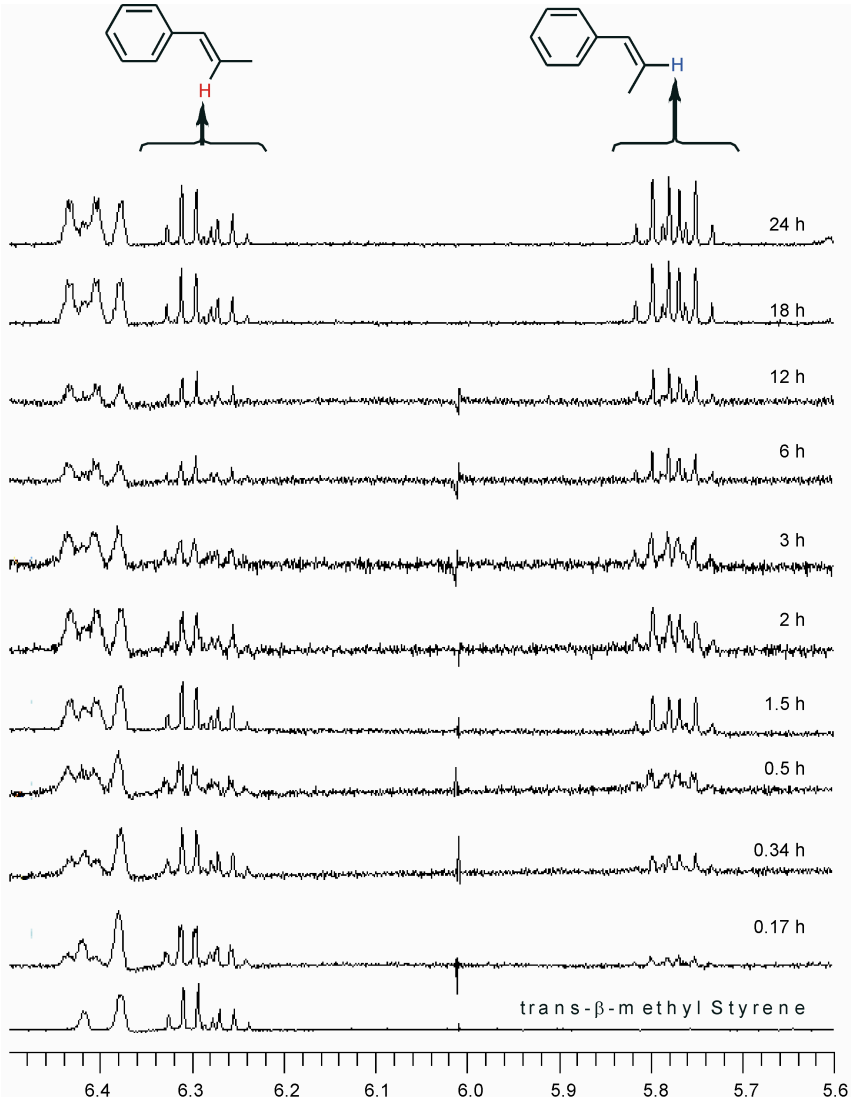


Figure S3. Photoisomerization of **7** in presence of host **2** followed by ^{1}H NMR

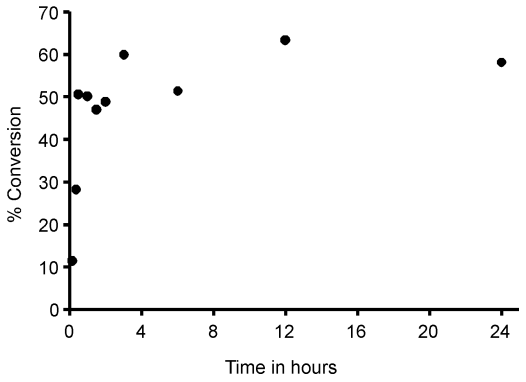


Figure S4. % of *trans* isomer converted to *cis* over time.

Scanning electron microscopy (SEM) Freshly recrystallized assembled **1** was loaded dropwise on a silicon waffle using a micropipette. The sheet was dried by evaporation. The Scanning Electron Microscopy image was recorded on Quanta 200 ESEM with accelerating voltage 30 kV.

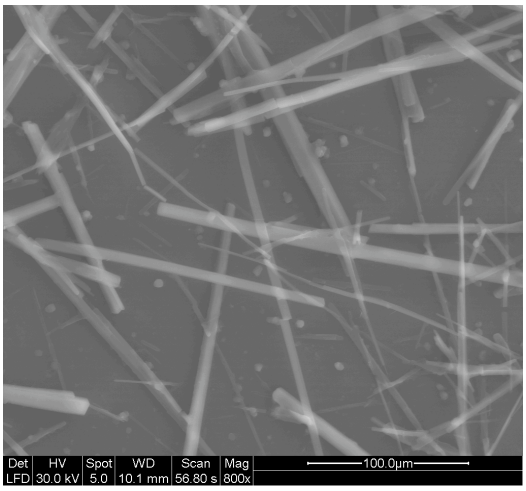


Figure S5. Scanning electron microscope image of the host **2** • DMSO crystals

Powder X-ray diffraction (PXRD): Both freshly recrystallized crystals as well as empty crystals of **1** were ground to a powder and examined by PXRD. X-ray powder diffraction data was collected on a Rigaku DMAX-2100 & DMAX-2200 powder X-ray diffractometers using CuKα radiation. The step-scans data were collected at +0.05° steps in the angular range 2-40° 2θ at ambient temperature

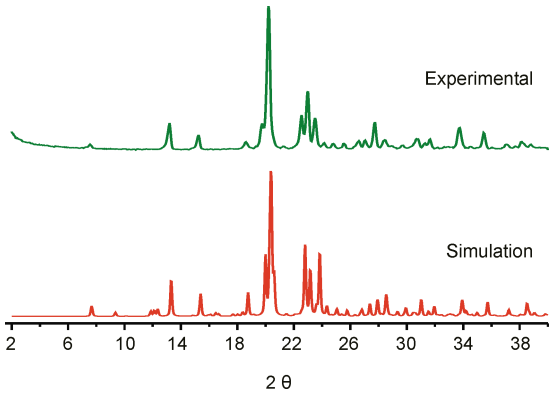


Figure S6. Experimental and simulated PXRD patterns for host **2** with DMSO included

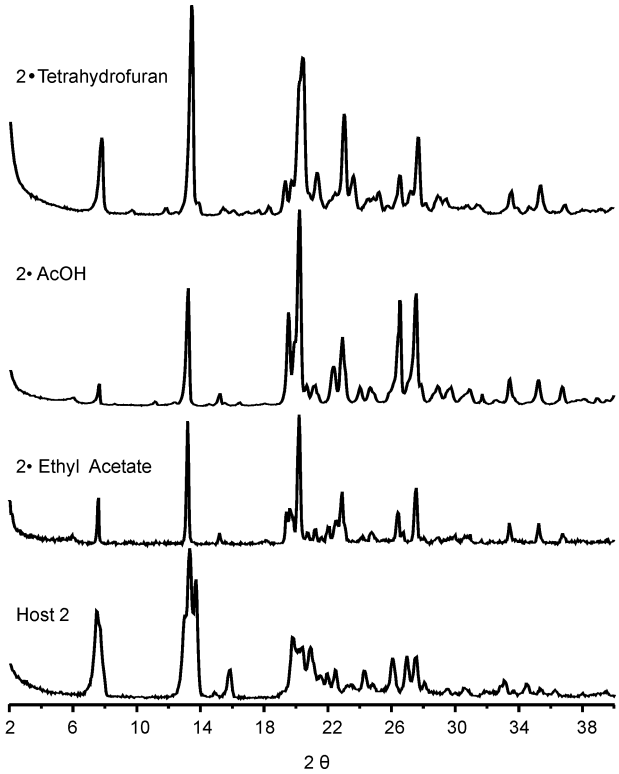


Figure S7. Host **2** • guest complexes are highly crystalline

Photoisomerisation of *trans*-_-methylstyrene: Host **2** (25 mg) was loaded with *trans*-_-methylstyrene (see loading procedure pg # S3). Host guest binding ratio was monitored by dissolving 2 mg samples of the material in d_6-DMSO and integrating the ^{1}H NMR spectra. Then the vial was taken out of the chamber, the crystals from the vial were transferred into a new vial with septum. Then the vial was flushed with N_2 gas for 15 min before subjecting to UV irradiation. After 24 h UV irradiation products were extracted with dichloromethane and analyzed by GC/MS.

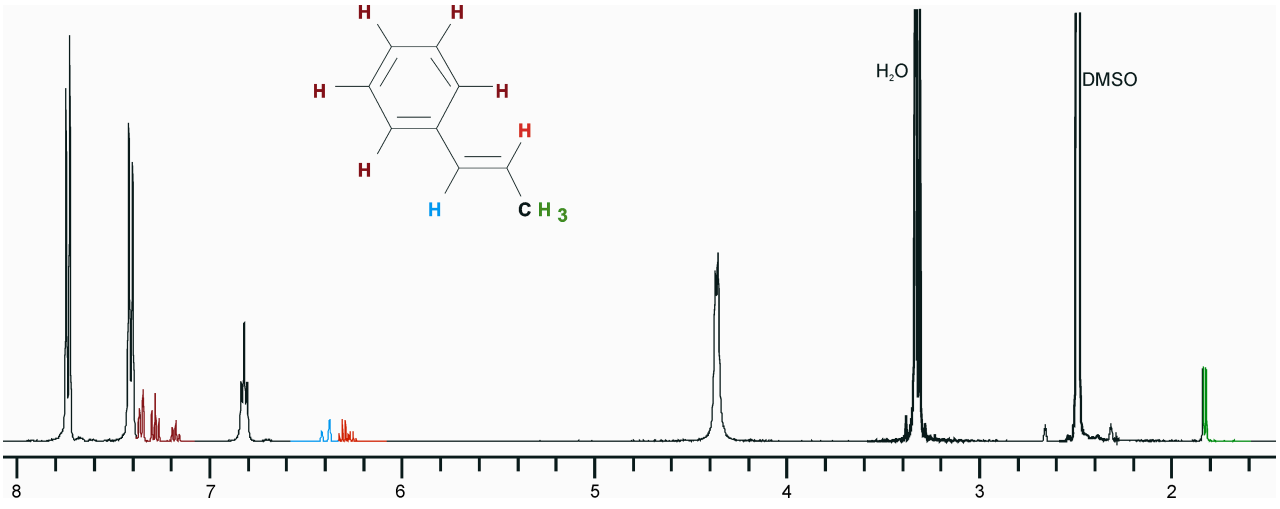


Figure S8. HNMR of *trans*-_-methylstyrene binding in host **2**

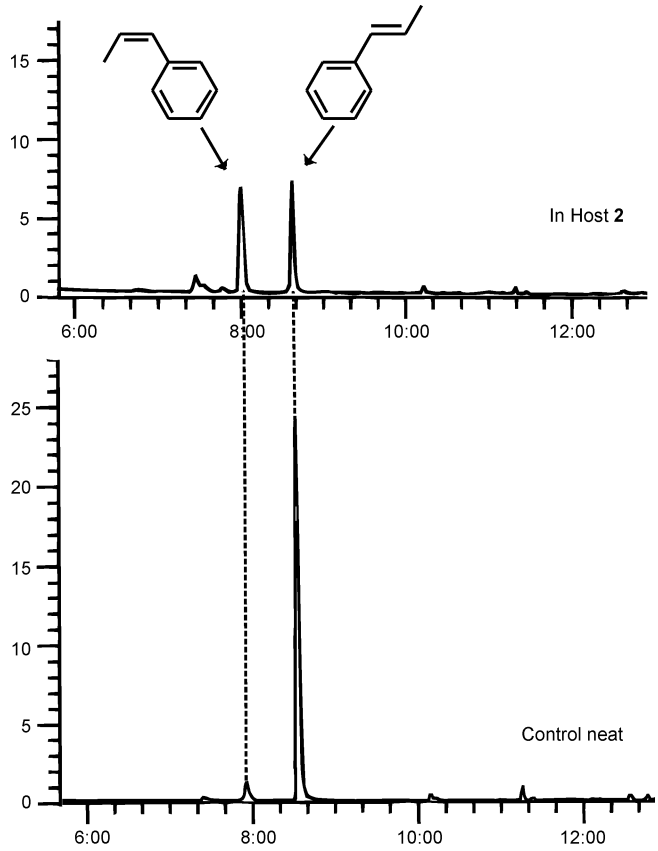


Figure S9. GC/MS analysis of isomerization of *trans*-_-methylstyrene

X-Ray Structure Determination of Triazinanone protected bis-urea macrocycle (2a) ($C_{44}H_{50}N_6O_4$_$2CHCl_3$): X-ray diffraction intensity data from a colorless plate crystal were measured at 150(1) K on a Bruker SMART APEX diffractometer (Mo Kα radiation, λ = 0.71073 Å).[1] Raw area detector data frame integration was performed with SAINT+.[1] No appreciable scattering was observed above 2_ ca. 45° and the data were truncated at this value. Final unit cell parameters were determined by least-squares refinement of 2163 strong reflections from the data set. Analysis of the data showed negligible crystal decay during collection. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL.[2]

The compound crystallizes in the space group $P2_1/c$ as determined uniquely by the pattern of systematic absences in the intensity data. The asymmetric unit consists of half of a $C_{44}H_{50}N_6O_4$ molecule located on a crystallographic inversion center, and one $CHCl_3$ molecule. The $CHCl_3$ molecule is disordered equally over two closely separated positions. A total of 30 C-Cl and Cl-Cl distance restraints were used to assist in modeling the disorder. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference maps before being placed in geometrically idealized positions and included as riding atoms.

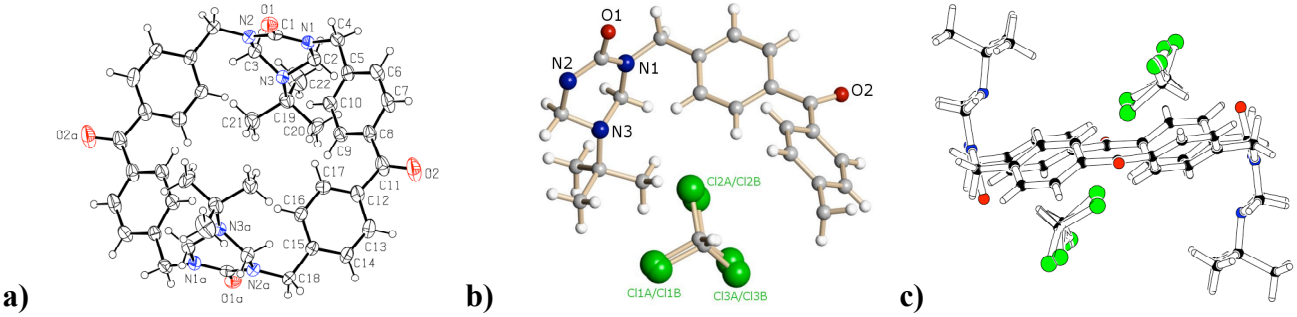


Figure S10. X-ray crystal structure of Triazinanone protected bis-urea macrocycle (**2a**); a) Ellipsoid plot of cycle with hydrogens, displacement ellipsoids drawn at the 40% probability level cycle on crystallographic inversion center, atoms labeled with suffix (lowercase) "a" related to equivalent atoms by symmetry operation 1-x, 1-y, 1-z; b) Asymmetric unit of the crystal. Half of a cycle located on a crystallographic inversion center and a disordered $CHCl_3$ c) Vertical orientation of macrocycle.

Table S2. Crystal data and structure refinement for Triazinanone protected bis-urea macrocycle (**2a**) ($C_{44}H_{50}N_6O_4\_2CHCl_3$):

Identification code	md01066	
Empirical formula	C46 H52 Cl6 N6 O4	
Formula weight	965.64	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.4583(6) Å	α= 90°.
	b = 22.4576(12) Å	β= 104.5050(10)°.
	c = 9.6210(5) Å	γ = 90°.
Volume	2396.8(2) $Å^3$	
Z	2	
Density (calculated)	1.338 Mg/m^3	
Absorption coefficient	0.407 mm^{-1}	
F(000)	1008	
Crystal size	0.30 x 0.10 x 0.05 mm^3	
Theta range for data collection	1.81 to 22.54°.	
Index ranges	-12<=h<=12, -24<=k<=24, -10<=l<=10	
Reflections collected	19646	
Independent reflections	3152 [R(int) = 0.0780]	
Completeness to theta = 22.54°	100.0 %	
Absorption correction	None	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3152 / 30 / 307
Goodness-of-fit on F^2	0.910
Final R indices [I>2sigma(I)]	R1 = 0.0484, wR2 = 0.1021
R indices (all data)	R1 = 0.0842, wR2 = 0.1148
Largest diff. peak and hole	0.277 and -0.216 e.Å^{-3}

X-Ray Structure Determination of bis-urea macrocycle 2 ($C_{32}H_{26}N_4O_4$_$(CH_3)_2SO$): X-ray diffraction intensity data from a colorless block crystal were measured at 150(1) K on a Bruker SMART APEX diffractometer (Mo Kα radiation, λ = 0.71073 Å).[1] All available crystals were small in size and scattering power. For the selected data crystal, no appreciable diffraction was observed above 2_ ca. 45°, and the data were truncated at this value. Raw area detector data frame integration was performed with SAINT+.[1] Final unit cell parameters were determined by least-squares refinement of 2019 strong reflections from the data set. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL.[2]

The compound crystallizes in the space group $P2_1/c$ as determined uniquely by the pattern of systematic absences in the intensity data. The asymmetric unit consists of half each of two $C_{32}H_{26}N_4O_4$ cycles, both located on inversion centers, and a total of one DMSO molecule. The DMSO is disordered equally over two independent positions. All non-hydrogen atoms were refined with anisotropic displacement parameters except the carbon atoms of the disordered DMSO molecules (isotropic). Hydrogen atoms were clearly located in difference maps before being placed in geometrically idealized positions and included as riding atoms. Examination of the final difference maps showed a pattern of residual electron peaks in the vicinity of both independent urea groups corresponding to the opposite orientation of these urea groups. This is likely due to minor orientational disorder of the cycles. No attempt was made to model this disorder due to its small fraction (ca. 10% based on trial refinements). The cycle disorder and the weak scattering power of the data crystal are the reasons for the high R-factors.

Table S3: Crystal data and structure refinement for bis-urea macrocycle 2.

Identification code	md2007m	
Empirical formula	C34 H34 N4 O5 S	
Formula weight	610.71	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.4680(6) Å	α= 90°.
	b = 23.0549(15) Å	β= 92.765(2)°.
	c = 13.3023(9) Å	γ = 90°.
Volume	2900.3(3) Å^3	
Z	4	

Density (calculated)	1.399 Mg/m^3
Absorption coefficient	0.163 mm^{-1}
F(000)	1288
Crystal size	0.16 x 0.10 x 0.08 mm^3
Theta range for data collection	1.77 to 22.54°.
Index ranges	-10<=h<=10, -24<=k<=24, -14<=l<=14
Reflections collected	21351
Independent reflections	3813 [R(int) = 0.0801]
Completeness to theta = 22.54°	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3813 / 0 / 413
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0675, wR2 = 0.1722
R indices (all data)	R1 = 0.1044, wR2 = 0.1907
Largest diff. peak and hole	0.610 and -0.210 $e.Å^{-3}$

1. SMART Version 5.630, SAINT+ Version 6.45. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.
2. Sheldrick, G. M. SHELXTL Version 6.14; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.

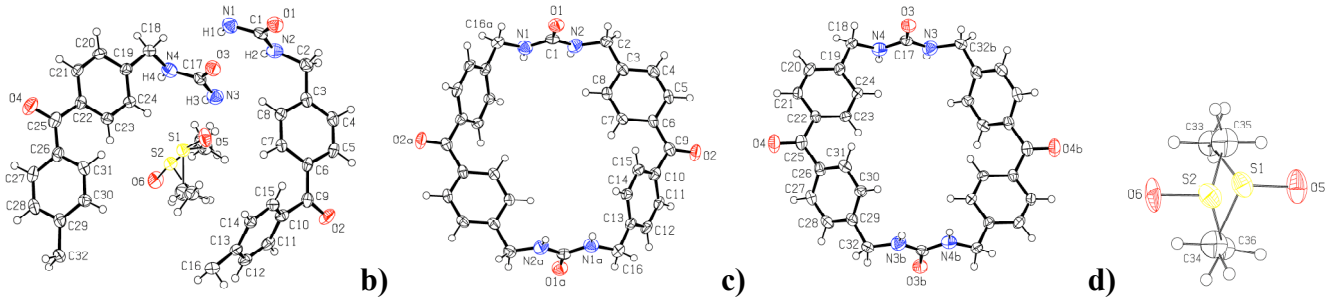


Figure S11: X-ray crystal structure bis-urea macrocycle **2**; a) Ellipsoid plot of atoms of the asymmetric unit. Half each of two crystallographically independent cycles, both on inversion centers, and a disordered DMSO molecule. Displacement ellipsoids drawn at the 50% probability level. Some atom labels omitted for clarity; b) The crystallographically independent cycle, atoms labeled with suffix "a" related to equivalent atoms by symmetry operation 1-x, 1-y, 1-z; c) Another crystallographically independent cycle, atoms labeled with suffix "b" related to equivalent atoms by symmetry operation -x, 1-y, 1-z; d) The DMSO disorder in the crystal. Displacement ellipsoids drawn at the 50% probability level.