A Light Controlled Cavitand Wall Regulates Guest Binding

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Electronic Supplementary Information

1. General Information

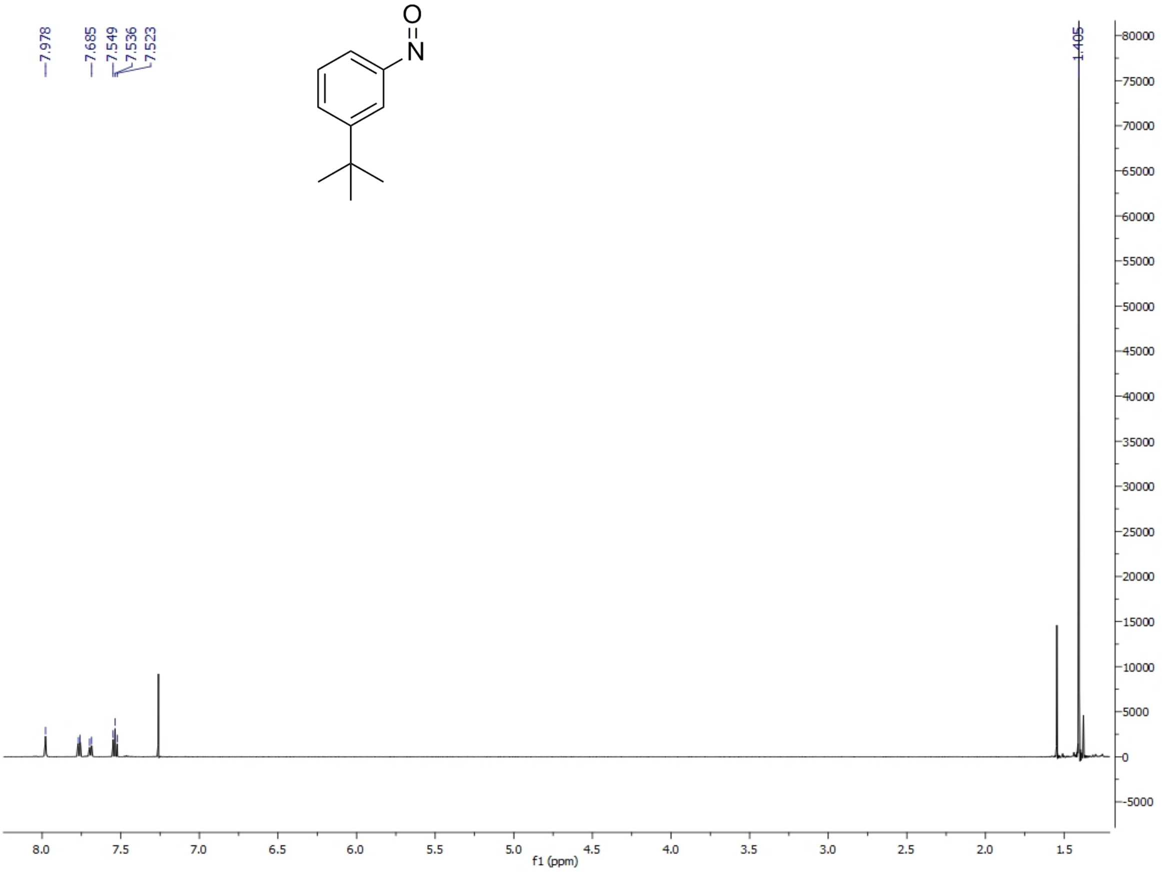
All materials were obtained from TCI-America, Sigma-Aldrich, Acros and Strem and used as received unless otherwise noted. All glassware was dried in an oven at 150 °C or flame dried immediately prior to use. Nuclear Magnetic Resonance ^{1}H NMR spectra were recorded on a Bruker DRX 600 spectrometer with a 5 mm QNP probe. Chemical shifts (δ) are expressed as ppm downfield from tetramethylsilane using either the residual solvent peak as an internal standard ($CDCl_3$ ^{1}H: 7.26 ppm), or using $CDCl_3$ spiked with 1% trimethylsilane for the ^{1}H NMR spectra. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc., Andover, MA, and used without further purification. Signal patterns are indicated as b, broad; s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants (J) are given in hertz. Photo-isomerization to the *cis* cavitands was performed with a Blak-Ray Long Wave Ultraviolet Lamp, Model B-100 AP after passing filtering out all light above 400 nm with a filter obtained from Andover Corporation. For the reverse isomerization process a High Intensity Discharge – Quartz Metal Halide light was used (GE Multi-Vapor Quartz Metal Halide ED37) after filtering all light below 450 nm with a filter obtained from Andover Corporation.

2. Syntheses and Characterization Data

2.1 Nitroso Arene synthesis

3-*tert*-butyl nitrosobenzene

Procedure adapted from known literature preparation of 2-methyl nitrosobenzene.[i] To a round bottom flask was added 3-*tert*-butylaniline (0.200 ml, 1.340 mmol) and MeOH (2.00 ml). H_2O (0.600 ml) was added to the reaction flask followed by 30% H_2O_2 (0.600 ml). The resulting orange solution was cooled to 0 °C and MoO_3 (0.0203 g, 0.141 mmol) was added resulting in a gray suspension. NaOH (2M, 0.100 ml) was added and the reaction was stirred at 5 °C for 1 day. A 1:1 mixture of DCM:H_2O (60 ml) was added and the aqueous layer was extracted 3 × with DCM. The organic layer was dried with Na_2SO_4 and concentrated down to a brown/green oil which solidified in the freezer overnight. The crude reaction mixture was purified by column chromatography through silica gel (95:5 hexanes:DCM). The green fractions were collected and concentrated down to a green oil/yellow solid (0.112 g, 49% yield). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.98 (s, 1H), 7.76 (d, *J* = 6.7 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H) 7.53 (t, *J* = 7.8 Hz, 1H), 1.40 (s, 9H).

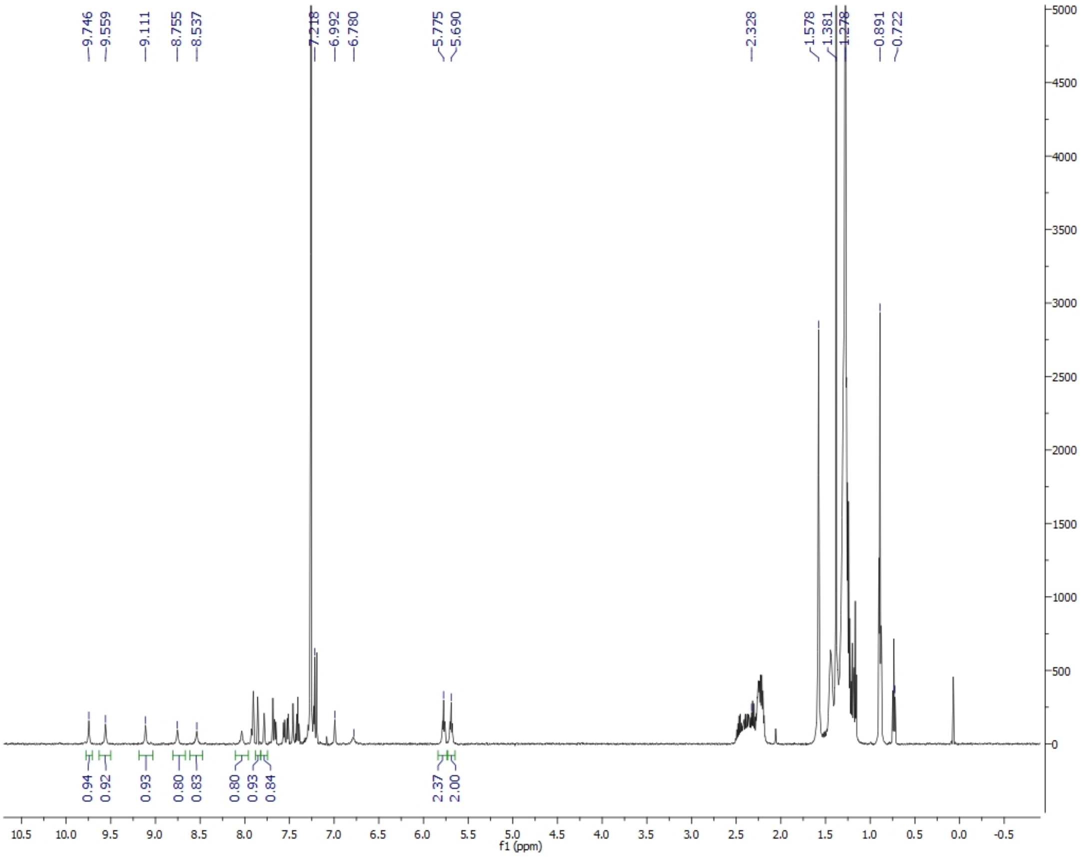


2.2 Cavitand Synthesis

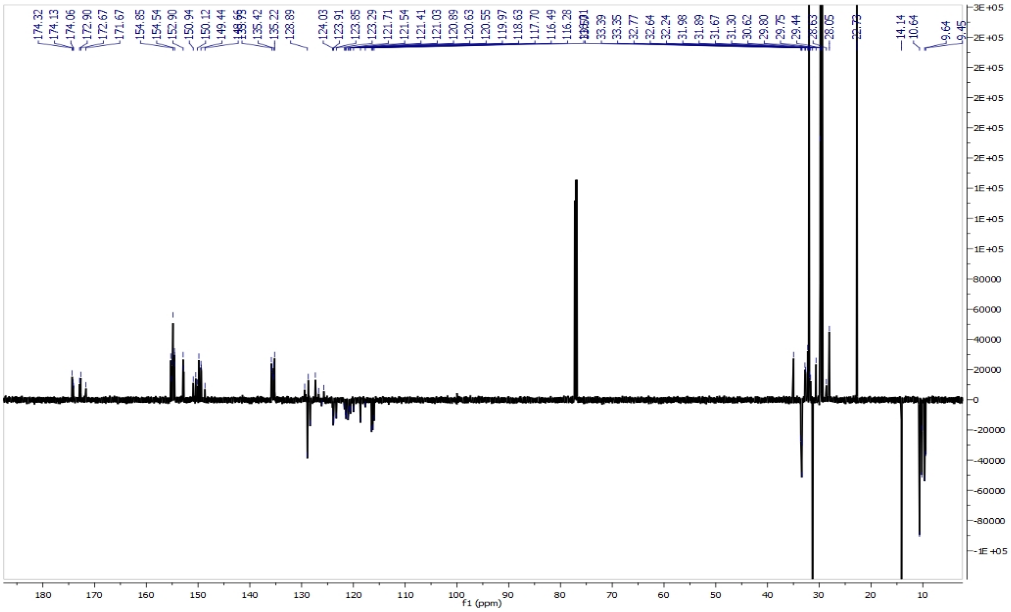
Cavitand 1

3-*tert*-butyl nitrosobenzene (0.075 g, 0.460 mmol) was dissolved in glacial acetic acid (3 ml). The resulting green solution was transferred to an oven dried round bottom flask (50 ml) and stored under a blanked of N_2. In a separate flask hexa-amido C_{11} monoamine cavitand **3**[ii] (0.175 g, 0.0923 mmol) was dissolved in glacial acetic acid (10 ml). This solution was transferred to the reaction vessel and stirred at room temperature under N_2. After stirring for 6 days pure product was filtered off as an orange solid (0.103 g, 56% yield) after filtering and washing with minimal glacial acetic acid. For *trans*-**1** ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.75 (b, 1H), 9.56 (b, 1H), 9.11 (b, 1H) 8.75 (b, 1H) 8.54 (b, 1H), 8.04 (b, 1H), 7.91 (b, 2H), 7.86 (s, 1H), 7.78 (s, 1H), 7.66 (m, 2H), 7.56 (d, J = 7.2 Hz, 1H), 7.52 (d, J = 6.6 Hz, 1H), 7.46 (s, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.20 (d, J = 13.8 Hz, 2H), 6.99 (b, 1H), 6.782 (b), 5.77 (t, J = 8.4 Hz, 2H), 5.69 (t, J = 8.4 Hz, 2H) 2.35 (m), 1.58 (m), 1.38, (s, 9H), 1.28 (m), 0.89 (t, J = 5.4 Hz, 14H), 0.734 (t, J = 7.8 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ = 174.32, 174.13, 174.06, 172.90, 172.67, 171.67, 155.28, 155.17, 154.98, 154.85, 154.57, 154.54, 154.52, 152.90, 152.79, 150.94, 150.45, 150.12, 149.84, 149.44, 149.36, 148.66, 135.85, 135.73, 135.61, 135.42, 135.37, 135.22, 129.41, 128.89, 128.71, 128.36, 127.35, 126.71, 126.15, 125.71, 124.03, 123.91, 123.85, 123.29, 121.71, 121.54, 121.41, 121.03, 120.89, 120.63, 120.55, 119.97, 118.63, 117.70, 116.49, 116.28, 116.01, 34.97, 33.57, 33.39, 33.35, 32.77, 32.64, 32.24, 31.98, 31.89, 31.67, 31.30, 30.62, 29.80, 29.75, 29.44, 28.63, 28.05, 22.73, 14.14, 10.64, 10.19, 10.11, 9.64, 9.45. MALDI-TOF (THAP): m/z: 1988.21 ($[MH]^+$, $C_{124}H_{163}N_8O_{14}^+$, calc. 1988.23)

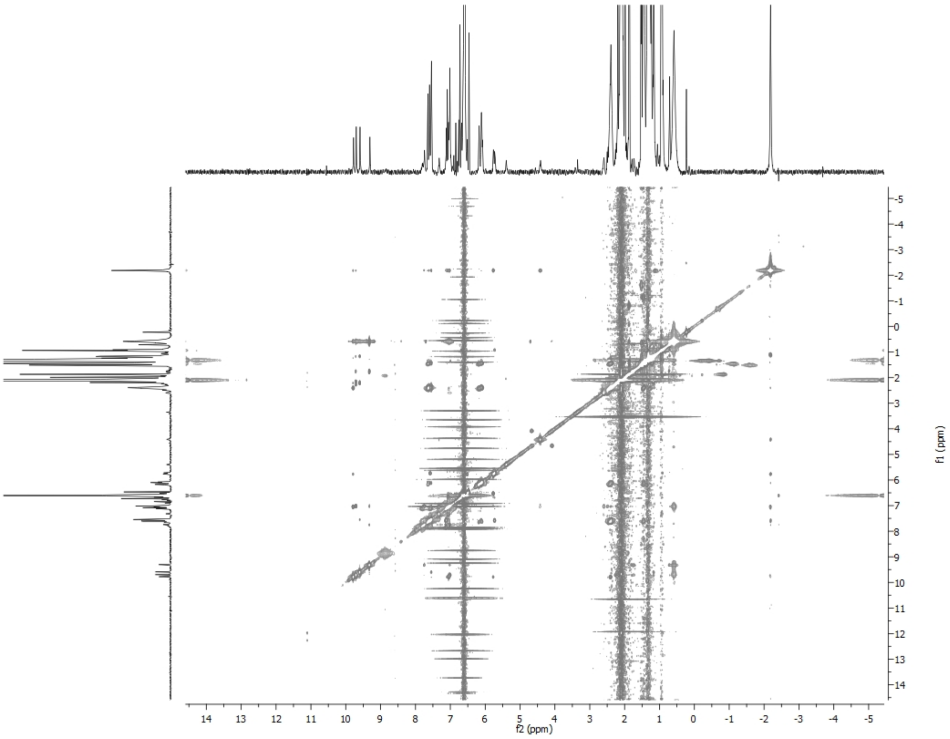
^{1}H NMR of *trans*-**1** in $CDCl_3$



^{13}C NMR of *trans*-**1** in $CDCl_3$

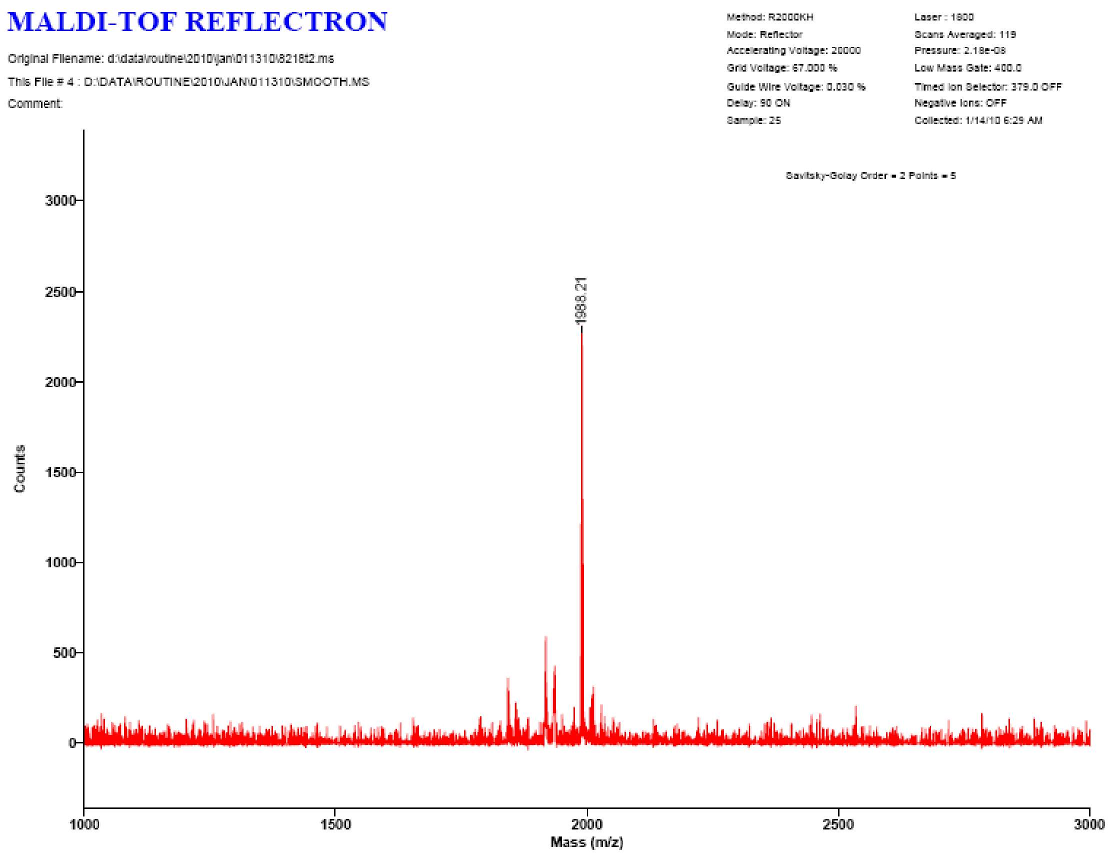


NOESY spectrum of *cis*-**1** in d_{12}-mesitylene



NOESY NMR studies corroborate the self-contained configuration of *cis*-**1**. NOE's are observed between the *tert*-butyl signals and the aromatic H's of the cavitand while no enhancement is seen with the externally directed methine protons

MALDI-TOF of **1**



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Savitsky-Golay Order = 2 Points = 5

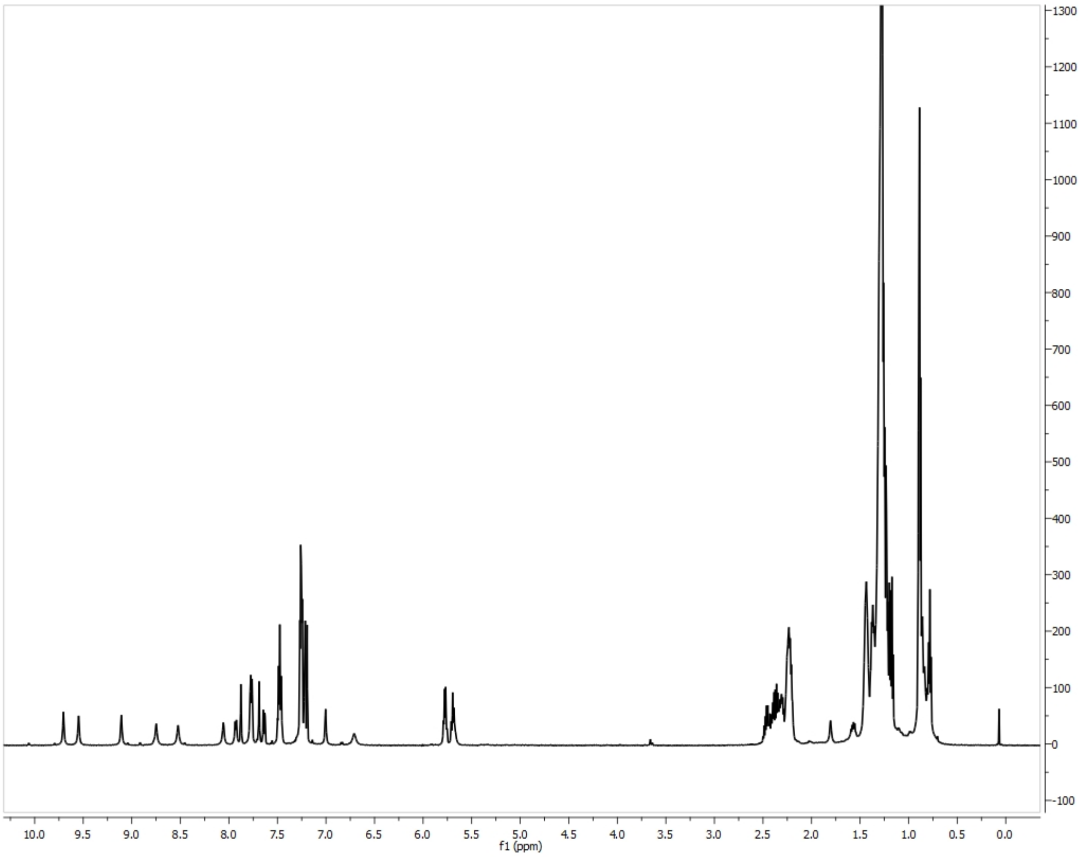
Cavitand 2

nitrosobenzene (0.078 g, 0.728 mmol) was dissolved in glacial acetic acid (2 ml) and filtered. The resulting green solution was transferred to an oven dried round bottom flask (50 ml) and stored under a blanked of N_2. In a separate flask hexa-amido C_{11} monoamine cavitand **3**[ii] (0.132 g, 0.0694 mmol) was dissolved in glacial acetic acid (3 ml). This solution was transferred to the reaction vessel and stirred at room temperature under N_2. After stirring for 8 days pure product was isolated as an orange solid after filtering and washing with glacial acetic acid. Additional product could be obtained by concentrating down the acetic acid from the reaction and purifying the resulting red oil by silica gel column chromatography (6:1 toluene:EtOAc) (0.0460 g for a combined yield of 34%). For *trans*-**2** ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.72 (b), 9.55 (b), 9.11 (b) 8.73 (b) 8.54 (b), 8.06 (b), 7.94 (m, 1H), 7.87 (s, 1H), 7.89 (b, 2H), 7.77 (s, 2H), 7.77 (s, 1H), 7.65 (dd, *J* =

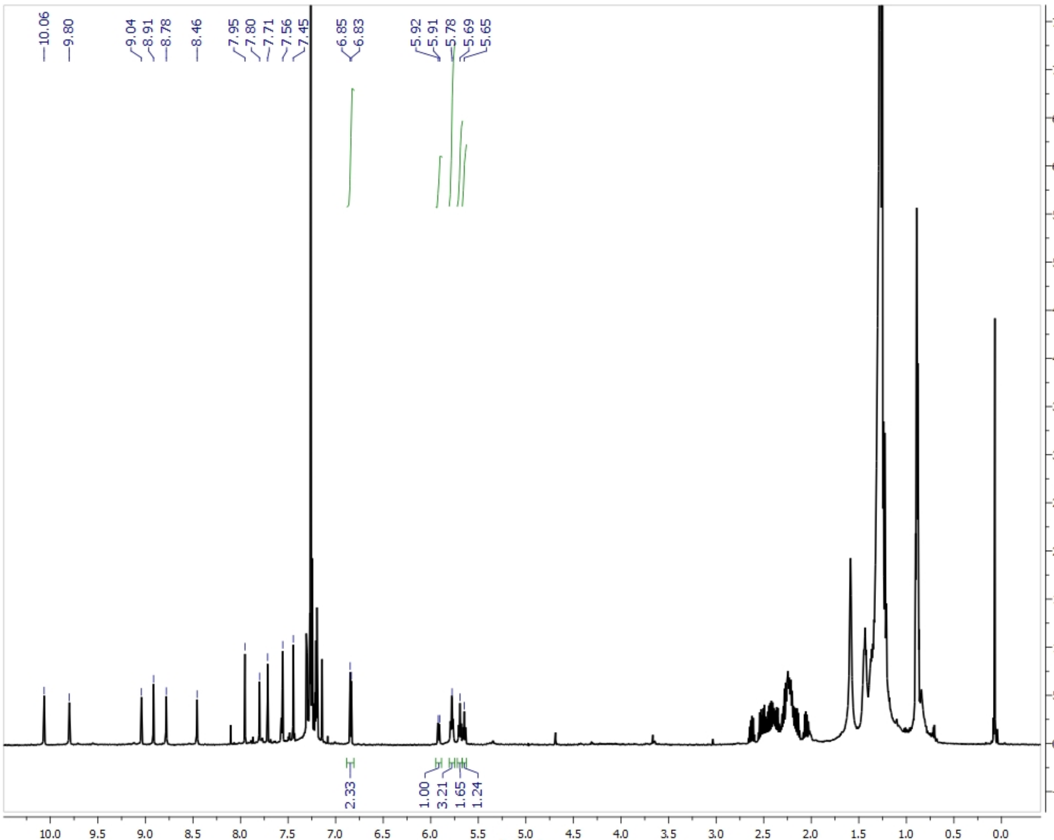
6.6 Hz, 1H), 7.49 (m, 4H), 7.00 (b), 6.87 (b), 5.78 (m, 2H), 5.69 (t, *J* = 8.4 Hz, 2H), 2.37 (m), 1.60 (b), 1.28 (m), 0.89 (m), 0.78 (m).

^{13}C NMR (151 MHz, CDCl3) δ = 174.53, 174.30, 174.24, 173.06, 172.85, 171.75, 155.49, 155.46, 155.13, 155.04, 154.97, 154.79, 154.76, 153.05, 151.20, 150.66, 150.36, 149.99, 149.75, 149.52, 148.74, 136.08, 135.98, 135.74, 135.57, 135.47, 131.27, 129.48, 128.95, 127.52, 124.27, 124.08, 124.01, 123.52, 122.82, 122.28, 121.69, 121.56, 120.86, 120.16, 117.60, 116.68, 116.46, 116.20, 100.20, 33.74, 33.60, 33.55, 32.89, 32.74, 32.59, 32.46, 32.18, 32.11, 31.92, 30.88, 30.07, 30.05, 30.00, 29.95, 29.64, 29.05, 28.30, 28.26, 28.20, 22.93, 14.34, 10.87, 10.39, 10.32, 9.85, 9.65. MALDI-TOF (THAP): m/z: 1954 ([MNa]$^{+}$, $C_{120}H_{154}N_8O_{14}Na^{+}$, calc. 1954); m/z: 1970 ([MK]$^{+}$, $C_{120}H_{154}N_8O_{14}K^{+}$, calc. 1970).

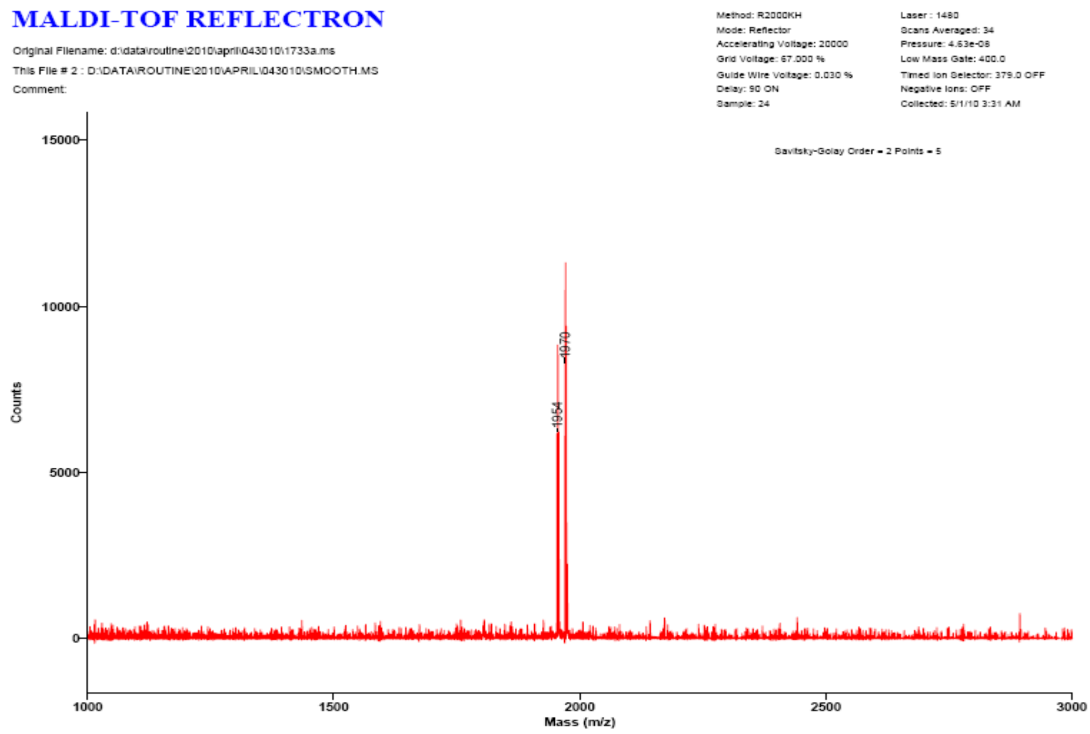
^{1}H NMR of *trans*-**2** in $CDCl_3$



^{1}H NMR of *cis*-**2** in $CDCl_3$



MALDI-TOF of **2**



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Laser : 1480
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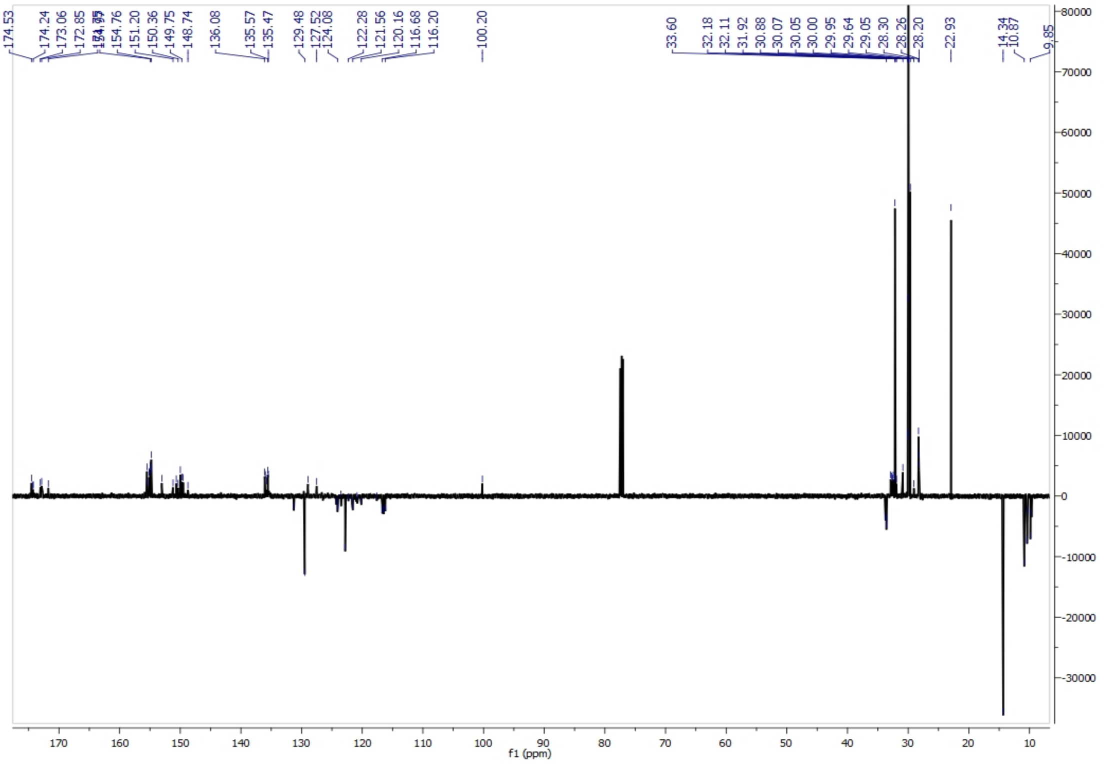
Savitsky-Golay Order = 2 Points = 5

^{13}C NMR of *trans*-**2** in $CDCl_3$



3. Kinetics of Photo-isomerization Without Guest

Cis-**1** and *cis*-**2** can be converted back to their *trans* configurations by applying heat or light. For example, heating the *cis*-**1** sample to 164 °C for 5 minutes reverts it to exclusively *trans*-**1**. Similarly, irradiating *cis*-**1** with 450+ nm light for 20 minutes converts it to *trans*-**1** and it reaches a photo-stationary state of 69% *trans*-**1** under these conditions. This switching cycle was repeated 5 times without degradation of the system.

***Trans* to *cis* photo-isomerization of cavitand 1**

Cavitand **1** (0.003 g, 0.00151 mmol) was dissolved in d_{12}-mesitylene (0.600 ml) and transferred to a NMR tube. The sample was heated to reflux with a heat gun for 5 minutes and allowed to cool after wrapping the sample in aluminum foil. A ^{1}H NMR spectrum was acquired after 3 hours. The sample was subsequently subjected to UV light for 10 minutes and another spectrum was acquired. To complete the isomerization process the sample was subjected to UV light for 5 additional minutes and monitored by ^{1}H NMR spectroscopy. Complete isomerization was determined by the disappearance of the *trans*-**1** amide signals at approx. 8.2 ppm.

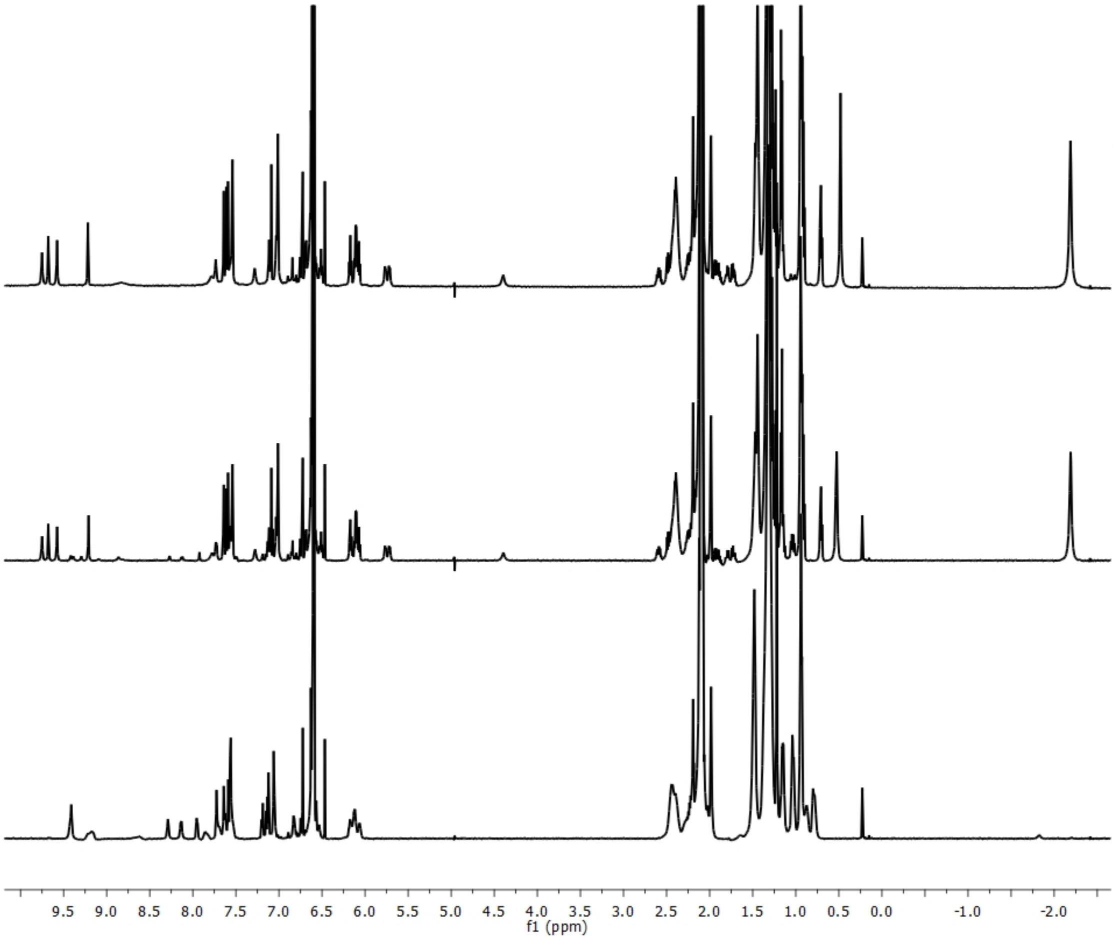


Figure S1. *Trans* to *cis* photo-isomerization of cavitand **1**; ^{1}H NMR spectra after heating to reflux for 5 minutes and cooling in the dark (bottom), after irradiating with UV light for 10 minutes (middle) and after irradiating with UV light for 15 minutes (top).

***Cis* to *trans* photo-isomerization of cavitand 1**

Cavitand **1** (0.003 g, 0.00151 mmol) was dissolved in d_{12}-mesitylene (0.600 ml) and transferred to a NMR tube. The sample was irradiated with UV light for 30 minutes. The sample was subsequently subjected to visible light and ^{1}H NMR spectra were acquired after 20, 40, 80 and 120 minutes. The completion of the isomerization was determined by comparing the integration of the methine signals at 6.23 to 6.04 ppm versus the *cis*-*tert*-butyl signal at -2.2 ppm. Photostationary state = 79% *trans*-**1** after 20 minutes.

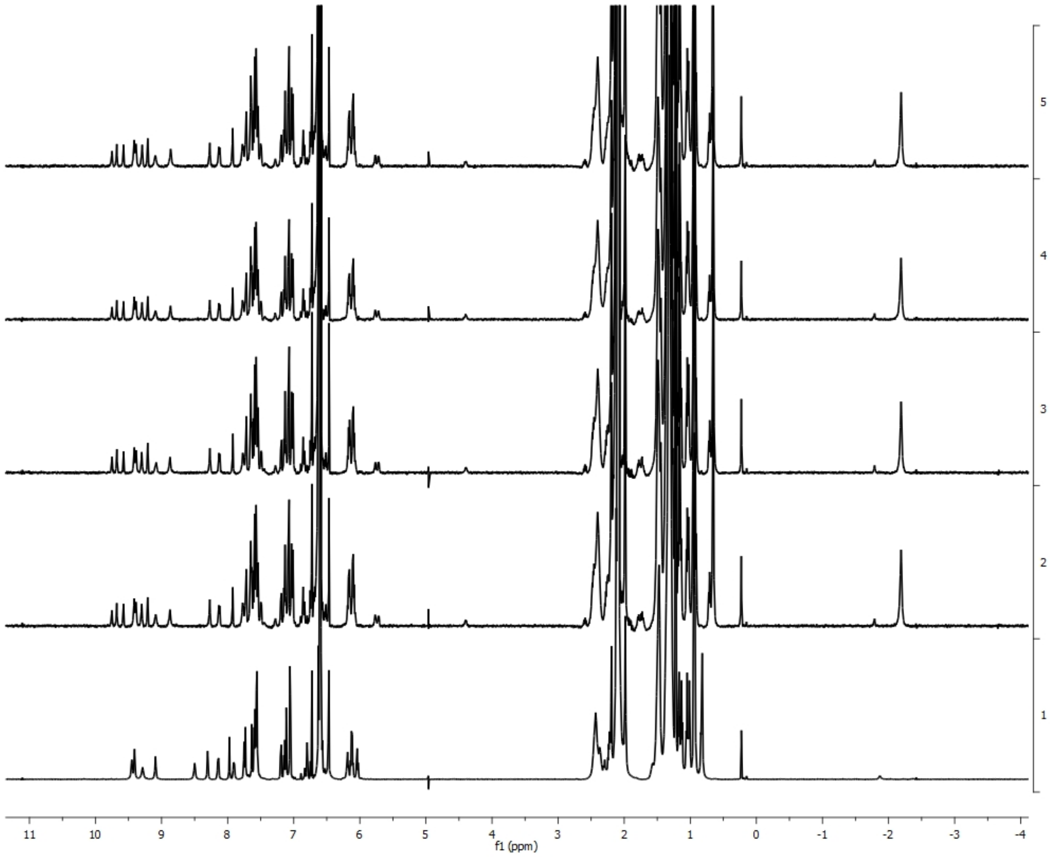


Figure S2. *Cis* to *trans* photo-isomerization of cavitand **1** without guest present; ^{1}H NMR spectra after dissolving **1** and heating to reflux for 5 min (bottom, 1), after irradiating with visible light for 20 minutes (middle, 2), after irradiating with visible light for 40 minutes (middle, 3), after irradiating with visible light for 80 minutes (middle, 4) and after irradiating with visible light for a total of 120 minutes (top, 5).

Trans **to** ***cis*** **photo-isomerization of cavitand 2**

Cavitand **2** (0.0036 g, 0.00186 mmol) was dissolved in d_{12}-mesitylene (1.075 ml) and transferred to a NMR tube. The sample was heated to reflux with a heat gun for 5 minutes and allowed to cool after wrapping the sample in aluminum foil. A ^{1}H NMR spectrum was acquired after 3 hours. The sample was subsequently subjected to UV light for 10 minutes and another spectrum was acquired. To complete the isomerization process the sample was subjected to UV light for 5 additional minutes and monitored by ^{1}H NMR spectroscopy. Complete isomerization was determined from the disappearance of the *trans*-**2** amide signal at 8.6 ppm.

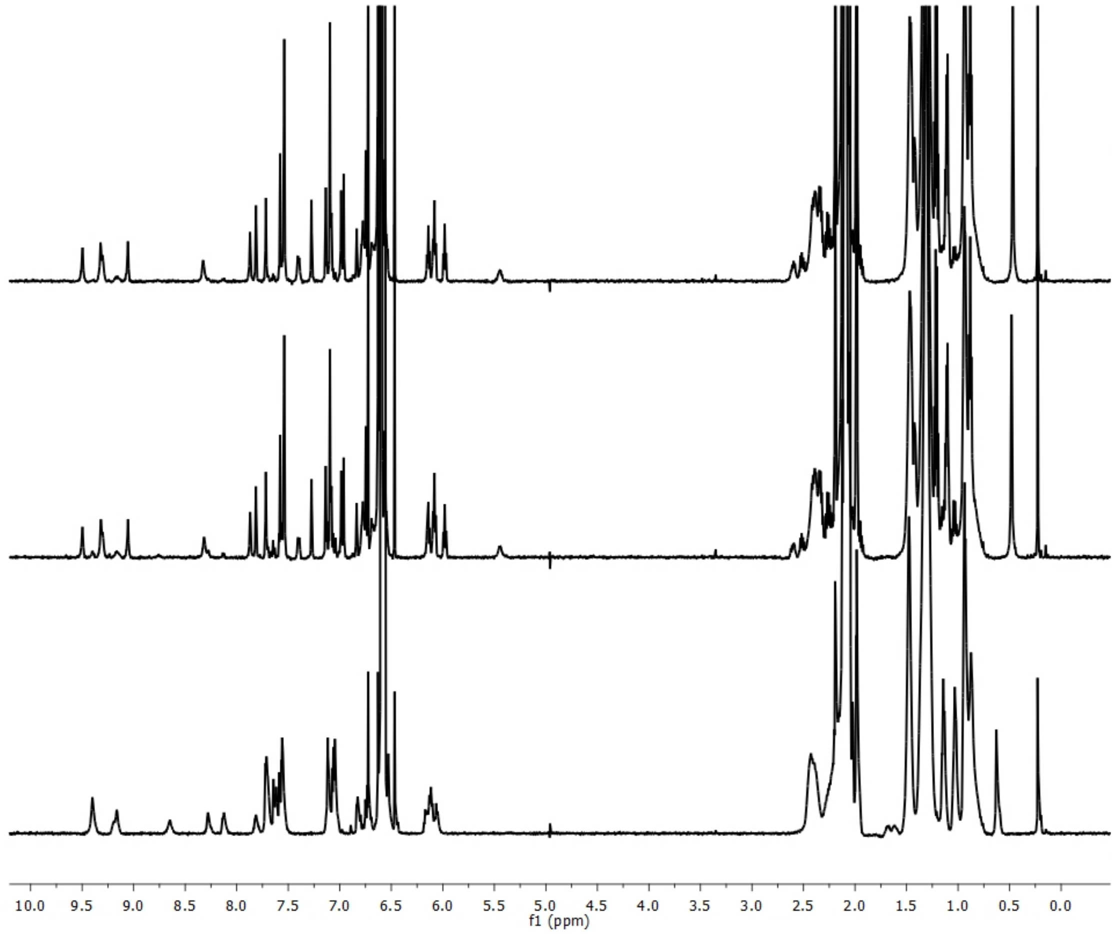


Figure S3. Kinetics of photo-isomerization of cavitand **2**; ^{1}H NMR spectra after heating to reflux for 5 minutes and cooling in the dark (bottom), after irradiating with UV light for 10 minutes (middle) and after irradiating with UV light for 15 minutes (top).

***Cis* to *trans* photo-isomerization of cavitand 2**

Cavitand **2** (0.0036 g, 0.00186 mmol) was dissolved in d_{12}-mesitylene (1.075 ml) and transferred to a NMR tube. The sample was irradiated with UV light for 30 minutes. The sample was subsequently subjected to visible light and ^{1}H NMR spectra were acquired after 20, 40, 80 and 120 minutes. The completion of the isomerization was determined by comparing the integration of the methine signals at 6.20 to 6.05 ppm versus the *cis* methine signal at 5.98 ppm. Photostationary state = 70% *trans*-**2** after 20 minutes.

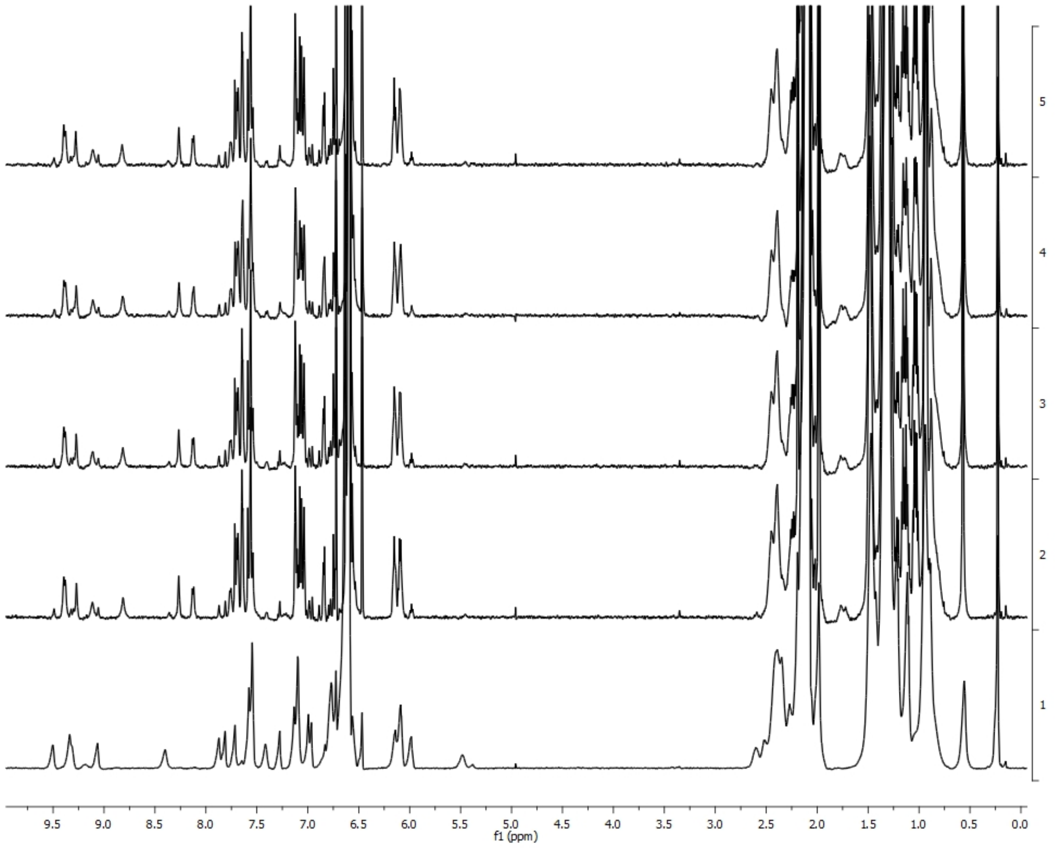


Figure S4. *Cis* to *trans* photo-isomerization of cavitand **2** without guest present; ^{1}H NMR spectra after irradiating with UV light for 30 minutes (bottom, 1) after irradiating with visible light for 20 minutes (middle, 2), after irradiating with visible light for 40 minutes (middle, 3), after irradiating with visible light for 80 minutes (middle, 4) and after irradiating with visible light for a total of 120 minutes (top, 5).

4. Binding and Guest Release Studies

Table. Association constants of **1** and **2** with guests **4-8**.[a,b]

Guests	**1**	**2** K_a (M^{-1})
1-adamantanemethanol (**4**)	5	6
1-chloroadamantane (**5**)	37	45
1-adamantaneamine (**6**)	166	145
1-adamantanecarbonitrile (**7**)	311	226
2-adamantanone (**8**)	653	703

[a] Reported K_a (M^{-1}) values are the average of 3-6 experiments with errors estimated at 20% see discussion below. [b] All experiments were performed in *d*$_{12}$-mesitylene at 300 K, with initial [**1**] or [**2**] = 2.3 to 5.8 mM.

General: Cavitand **1** or **2** (~0.003 g) was dissolved in *d*$_{12}$-mesitylene (0.600 ml) and transferred to a NMR tube. A guest stock solution was prepared by dissolving adamantane guest (**4-8**) (0.005 g) in *d*$_{12}$-mesitylene (1 ml). ^{1}H NMR spectra were recorded after adding aliquots from the guest stock solution (0.025 to 0.100 ml) to the NMR tube and mixing for 30 seconds. One to three spectra were recorded for each sample and the average association constants were reported. Association constants were determined using the following equation; K_a = [cavitand•guest]/[cavitand][guest]. To determine the concentrations of each species in solution the methine protons on the host were integrated relative to the (upfield) guest signals. The free cavitand concentration was determined by subtracting the quantity of bound guest (cavitand•guest) from the total amount of cavitand in solution. Similarly, the free guest was determined by subtracting the amount of bound guest from the total guest added to the solution. It was observed that changing pulse delay from the default of 1 second did not affect the integration of bound guest.

Error Estimation: The most significant source of error for the determination of K_a values in this system is the integration of the NMR spectra. To estimate the magnitude of error in the experiment 10 integrations of the bound guest region were performed on a representative spectrum (cavitand **1** + 2-adamantanone (**8**)). These values ranged from 0.53 to 0.58. An association constant was determined for each integration and the variability of the calculated K_a values is reported as the estimated error, 20% (lowest value = 560 M^{-1}, highest value = 702 M^{-1}).

Cavitand 1 + 2-adamantanone (8)

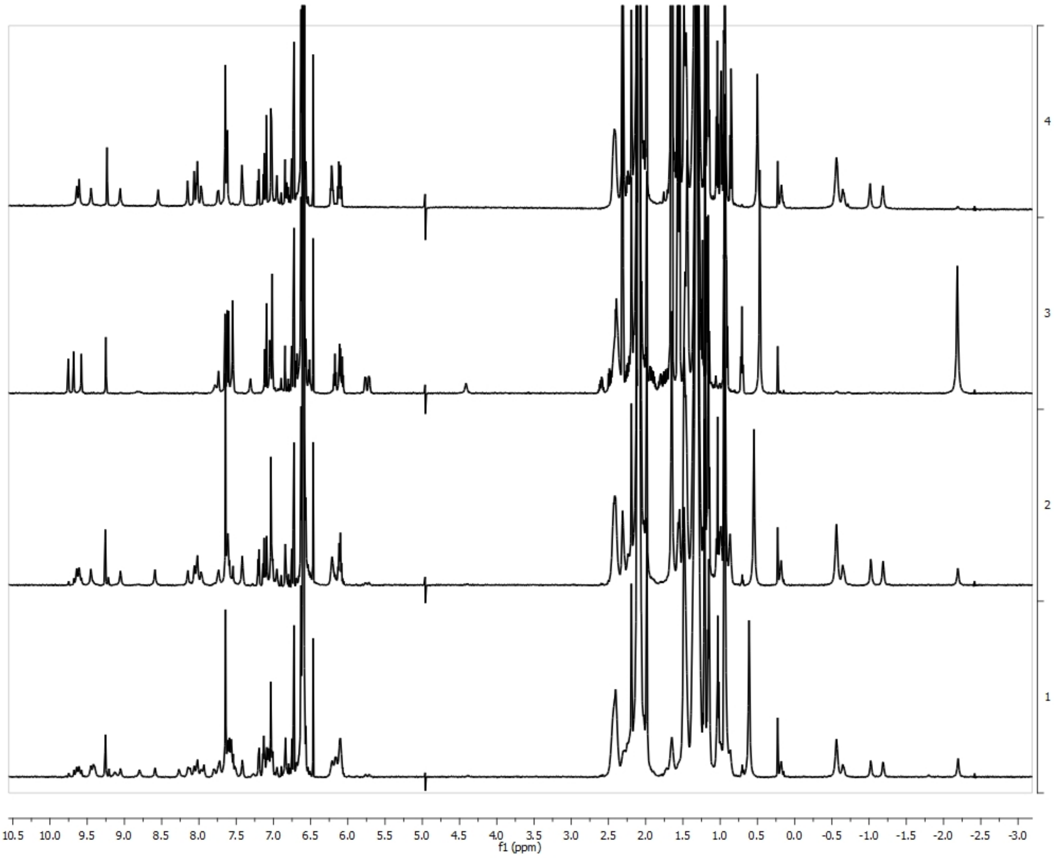


Figure S5. Titration of 2-adamantanone into cavitand **1** and subsequent guest release and uptake; ^1H NMR spectra after adding 0.025 ml guest stock (1), after adding 0.075 ml guest stock (2), after adding 0.375 ml guest stock solution and irradiating with UV light for 1 hour and 10 minutes (3), after refluxing for 5 minutes (4).

Cavitand	tBu Azo **1**	Amt H (g)	Vol in NMR tube (L)	[H]initial
mw	1988.66	0.0031	0.00060	0.0026

Guest	2-adamantanone	Amt G (g)	Vol guest Stock (L)	[G] stock (M)
mw	150.22	0.0049	0.0010	0.033

Trial 1

amount G added (L)	[G] (M)	$[H]_o$ (M)
0.000025	0.0013	0.0025

Norm Integral	# Hs on guest	HG Ratio	H Ratio
0.6	2	0.3	0.7

[HG] (M)	[H] (M)	[G] (M)
0.00075	0.0017	0.00056

Ka
770

Trial 2

amount G added (L)	[G] (M)	$[H]_o$ (M)
0.000075	0.0036	0.0023

Norm Integral	# Hs on guest	HG Ratio	H Ratio
1.1	2	0.55	0.45

[HG] (M)	[H] (M)	[G] (M)
0.0013	0.0010	0.0024

Ka
520

Trial 3	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000025	0.0013	0.0025	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.57	2	0.29	0.72
	[HG] (M)	[H] (M)	[G] (M)	
	0.00071	0.0018	0.00059	
	Ka			
	671			

ave Ka	653

Cavitand 1 + 1-adamantanecarbonitrile (7)

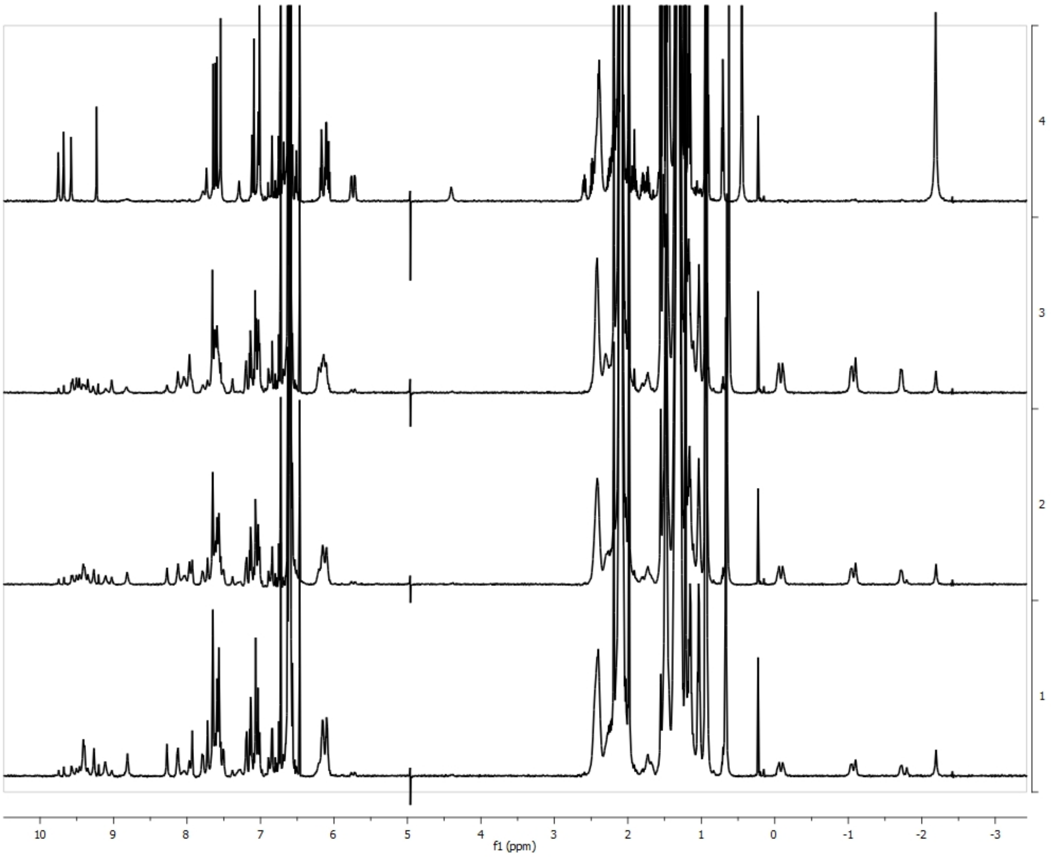


Figure S6. Titration of 1-adamantanecarbonitrile into cavitand **1** and subsequent guest release and uptake; ^{1}H NMR spectra after adding 0.020 ml guest stock (1), after adding 0.040 ml guest stock (2), after adding 0.090 ml guest stock solution (3), after adding 0.190 ml guest stock and irradiating with UV light for 20 minutes (4).

Cavitand	tBu Azo **1**	Amt H (g)	Vol in NMR tube (L)	[H]initial
mw	1988.66	0.0029	0.00060	0.0024
Guest	1-adamantanecarbonitrile	Amt G (g)	Vol guest Stock (L)	[G] stock (M)
mw	161.24	0.0045	0.0010	0.028

Trial 1	amount G added (L)	[G] (M)	[H]$_o$ (M)	
	0.000020	0.00090	0.0024	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.94	6	0.16	0.84
	[HG] (M)	[H] (M)	[G] (M)	
	0.00037	0.0020	0.00053	
	Ka			
	349			

Trial 2	amount G added (L)	[G] (M)	[H]$_o$ (M)	
	0.000040	0.0017	0.0023	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	1.63	6	0.27	0.73
	[HG] (M)	[H] (M)	[G] (M)	
	0.00062	0.0017	0.0011	
	Ka			
	331			

Trial 3	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000090	0.0036	0.0021	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	2.47	6	0.41	0.59
	[HG] (M)	[H] (M)	[G] (M)	
	0.00087	0.0012	0.0028	
	Ka			
	253			

ave Ka 311

Cavitand 1 + 1-adamantaneamine (6)

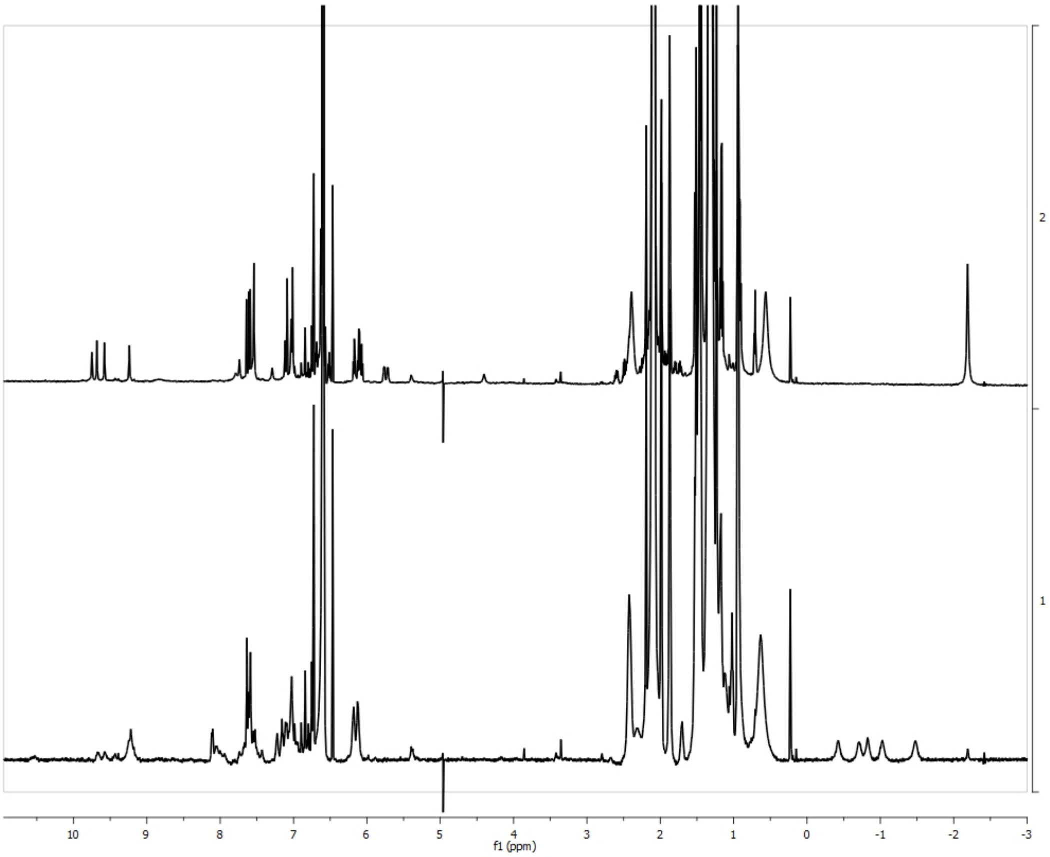


Figure S7. Addition of 1-adamantaneamine into cavitand **1** and subsequent guest release; ^{1}H NMR spectra after adding 0.050 ml guest stock (1), after irradiating with UV light for 1 hour and 50 minutes (2).

Cavitand	tBu Azo **1**	Amt H (g)	Vol in NMR tube (L)	[H]initial
mw	1988.66	0.007	0.00060	0.0059
Guest	1-adamantaneamine	Amt G (g)	Vol guest Stock (L)	[G] stock (M)
mw	151.25	0.0104	0.0010	0.069

Trial 1	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000050	0.0053	0.0054	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	1.12	3	0.37	0.63
	[HG] (M)	[H] (M)	[G] (M)	
	0.0020	0.0034	0.0033	
	Ka			
	182			

Cavitand	tBu Azo	Amt H (g)	Vol in NMR tube (L)	[H]initial
mw	1988.66	0.0038	0.0006	0.003184724
Guest	1-adamantaneamine	Amt G (g)	Vol guest Stock (L)	[G] stock (M)
mw	151.25	0.0053	0.0010	0.035

Trial 2	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.00010	0.0050	0.0027	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	1.17	3	0.39	0.61
	[HG] (M)	[H] (M)	[G] (M)	
	0.0011	0.0017	0.0039	
	Ka			
	162			

Trial 3	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.00020	0.0088	0.0024	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	3.2	6	0.53	0.47
	[HG] (M)	[H] (M)	[G] (M)	
	0.0013	0.0011	0.0075	
	Ka			
	153			

ave Ka 166

Cavitand 1 + 1-chloroadamantane (5)

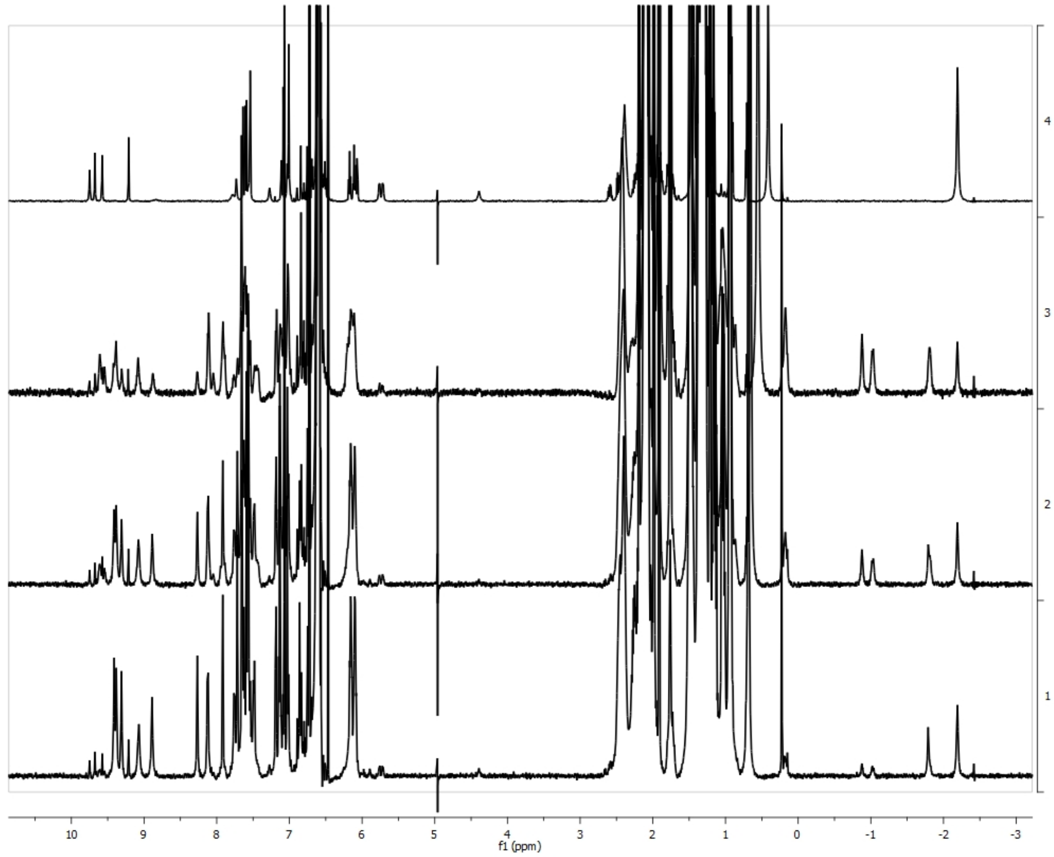


Figure S8. Titration of 1-chloroadamantane into cavitand **1** and subsequent guest release; ^{1}H NMR spectra after adding 0.025 ml guest stock (1), after adding 0.075 ml guest stock (2), after adding 0.500 ml guest stock solution (3), after irradiating with UV light for 1 hour (4).

Cavitand	tBu Azo **1**	Amt H (g)	Vol in NMR tube (L)	[H]initial
mw	1988.66	0.0031	0.00060	0.0026
Guest	1-chloroadamantane	Amt G (g)	Vol guest Stock (L)	[G] stock (M)
mw	170.68	0.0052	0.0010	0.030

Trial 1	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000025	0.0012	0.0025	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.11	3	0.037	0.96
	[HG] (M)	[H] (M)	[G] (M)	
	0.000091	0.0024	0.0011	
	Ka			
	34			

Trial 2	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.00010	0.0044	0.0022	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.43	3	0.14	0.86
	[HG] (M)	[H] (M)	[G] (M)	
	0.00032	0.0019	0.0040	
	Ka			
	41			

Trial 3	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.00050	0.014	0.0014	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.95	3	0.32	0.68
	[HG] (M)	[H] (M)	[G] (M)	
	0.00045	0.00097	0.014	
	Ka			
	35			

ave Ka 37

Cavitand 1 + 1-adamantanemethanol (4)

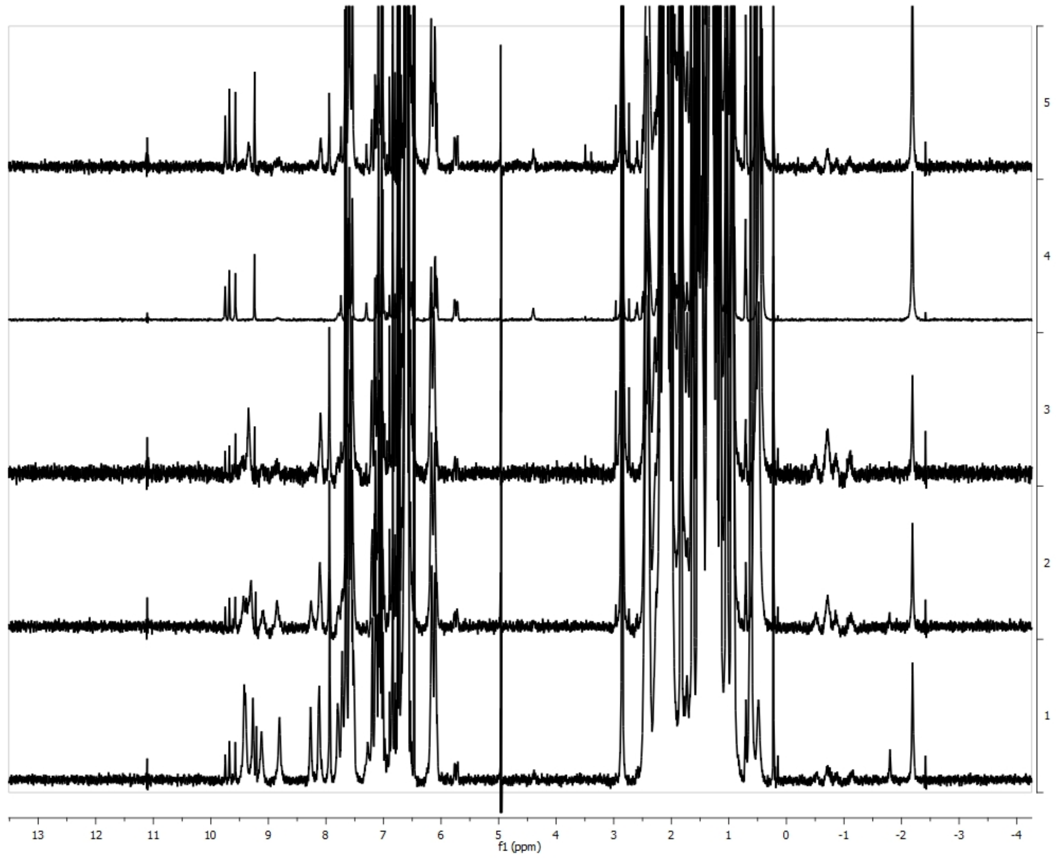


Figure S9. Titration of 1-adamantanemethanol into cavitand **1** and subsequent guest release and uptake; ^{1}H NMR spectra after adding 0.075 ml guest stock (1), after adding 0.275 ml guest stock (2), after adding 0.775 ml guest stock solution (3), after irradiating with UV light for 1 hour and 10 minutes (4); after irradiating with visible light for 1 hour and 20 minutes (5).

Cavitand	tBu Azo **1**	Amt H (g)	Vol in NMR tube (L)	[H]initial
mw	1988.66	0.0028	0.00060	0.0023
Guest	1-adamantanemethanol	Amt G (g)	Vol guest Stock (L)	[G] stock (M)
mw	166.26	0.0049	0.0010	0.029

Trial 1	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000075	0.0032	0.0021	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.07	3.0	0.023	0.98
	[HG] (M)	[H] (M)	[G] (M)	
	0.000049	0.0020	0.0032	
	Ka			
	7.4			

Trial 2	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000275	0.0093	0.0016	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.10	3.0	0.033	0.97
	[HG] (M)	[H] (M)	[G] (M)	
	0.000053	0.0016	0.0092	
	Ka			
	3.7			

Trial 3	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000775	0.017	0.0010	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.17	3.0	0.057	0.94
	[HG] (M)	[H] (M)	[G] (M)	
	0.000058	0.00097	0.017	
	Ka			
	3.6			

ave Ka 4.9

Cavitand 2 + 2-adamantanone (8)

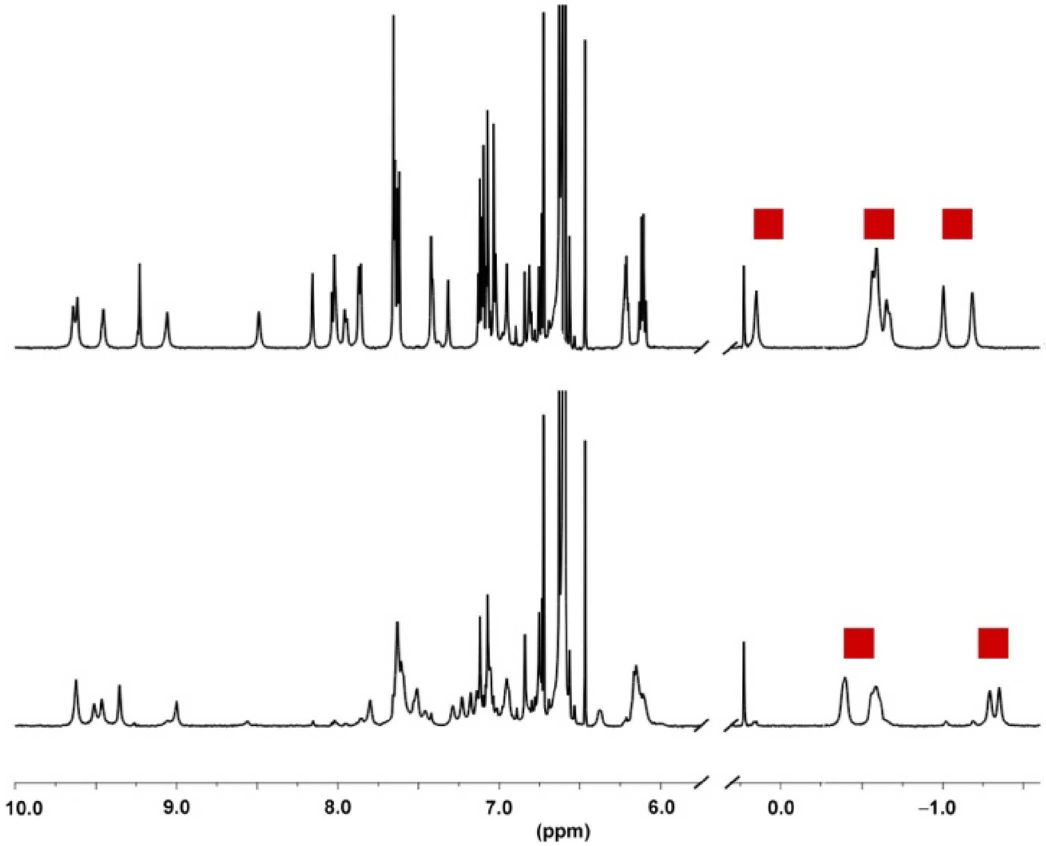


Figure S10. ^{1}H NMR spectra in d_{12}-mesitylene showing cavitand **2** binding 2-adamantanone (**8**, 9.3 eq.) both in the *trans* configuration (top) and *cis* configuration (bottom). The guest remains bound when cavitand **2** is in either configuration and the guest signals are marked with red squares.The broadened ^{1}H NMR spectrum observed for *cis*-**2** is due to the multiple *cis* conformations that cavitand **2** can adopt when a guest molecule is present. The rate of the switching process is nearly independent of the presence of guest molecules although it is slightly retarded and can be achieved by heating or application of light. UV light converts *trans*-**2** adamantane complexes to the *cis*-**2** complexes after 30 minutes. The reverse *cis* to *trans* process with heat is fast (<5 minutes), while visible light reverses this process in 20 minutes reaching a photostationary state of 95% *trans*-**2**.

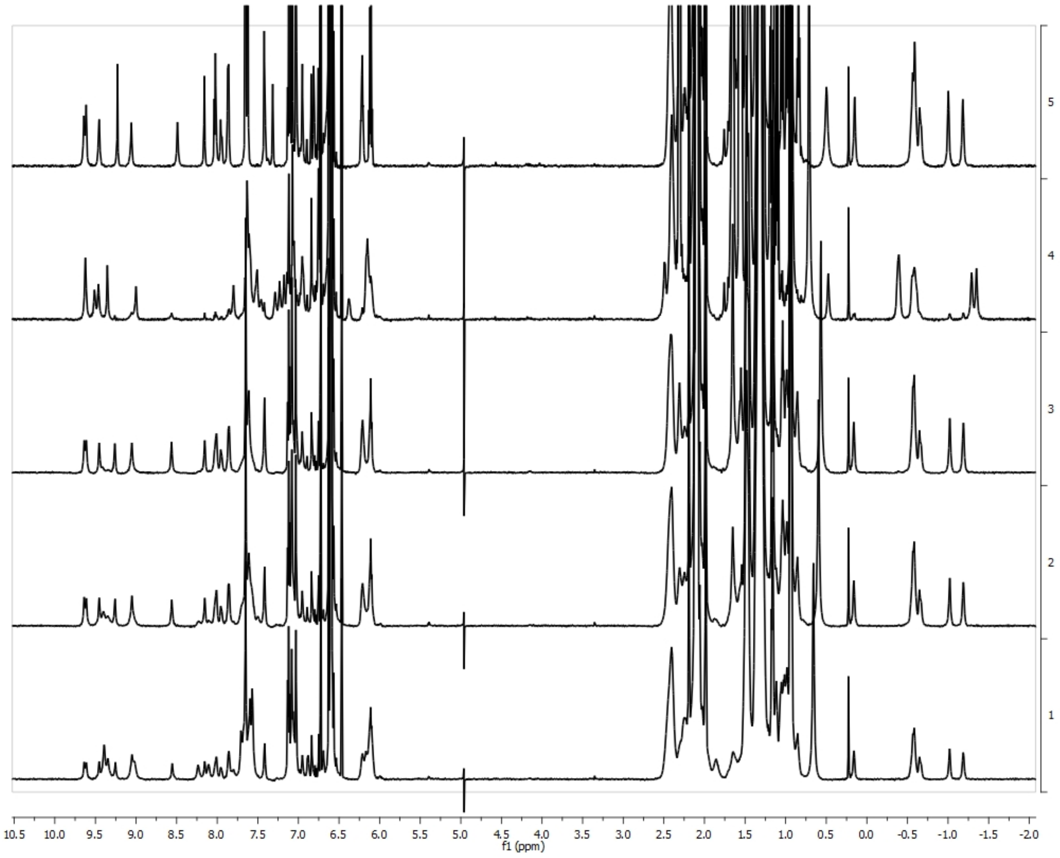


Figure S11. Titration of 2-adamantanone into cavitand **2** and subsequent isomerization; ^{1}H NMR spectra after adding 0.025 ml guest stock (1), after adding 0.050 ml guest stock (2), after adding 0.075 ml guest stock solution (3), after adding 0.475 ml guest stock solution and irradiating with UV light for 1 hour and 25 minutes (4); after heating to 164.7 °C for 5 minutes (5).

Cavitand	PhenylAzo **2**	Amt H (g)	Vol in NMR tube (L)	[H]initial
mw	1932.55	0.00345	0.00058	0.0031
Guest	2-adamantanone	Amt G (g)	Vol guest Stock (L)	[G] stock (M)
mw	150.22	0.0053	0.0010	0.035

Trial 1	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000025	0.0015	0.0030	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.60	2.0	0.30	0.70
	[HG] (M)	[H] (M)	[G] (M)	
	0.00089	0.0021	0.00057	
	Ka			
	748			

Trial 2	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000050	0.0028	0.0028	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	1.0	2.0	0.51	0.50
	[HG] (M)	[H] (M)	[G] (M)	
	0.0014	0.0014	0.0014	
	Ka			
	745			

Trial 3	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000075	0.0040	0.0027	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	1.2	2.0	0.60	0.40
	[HG] (M)	[H] (M)	[G] (M)	
	0.0016	0.0011	0.0024	
	Ka			
	623			

Cavitand	tBu Azo	Amt H (g)	Vol in NMR tube (L)	[H]initial
mw	1932.55	0.0031	0.0006	0.0027

Guest	2-adamantanone	Amt G (g)	Vol guest Stock (L)	[G] stock (M)
mw	150.22	0.0049	0.001	0.033

Trial 4	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000025	0.0013	0.0026	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.59	2	0.30	0.71
	[HG] (M)	[H] (M)	[G] (M)	
	0.00076	0.0018	0.00055	
	Ka			
	764			

Trial 5	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.00005	0.0025	0.0025	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	1	2	0.50	0.50
	[HG] (M)	[H] (M)	[G] (M)	
	0.0012	0.0012	0.0013	
	Ka			
	784			

Trial 6	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000075	0.0036	0.0024	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	1.12	2	0.56	0.44
	[HG] (M)	[H] (M)	[G] (M)	
	0.0013	0.0010	0.0023	
	Ka			
	555			

ave Ka	703

Cavitand 2 + 1-adamantanecarbonitrile (7)

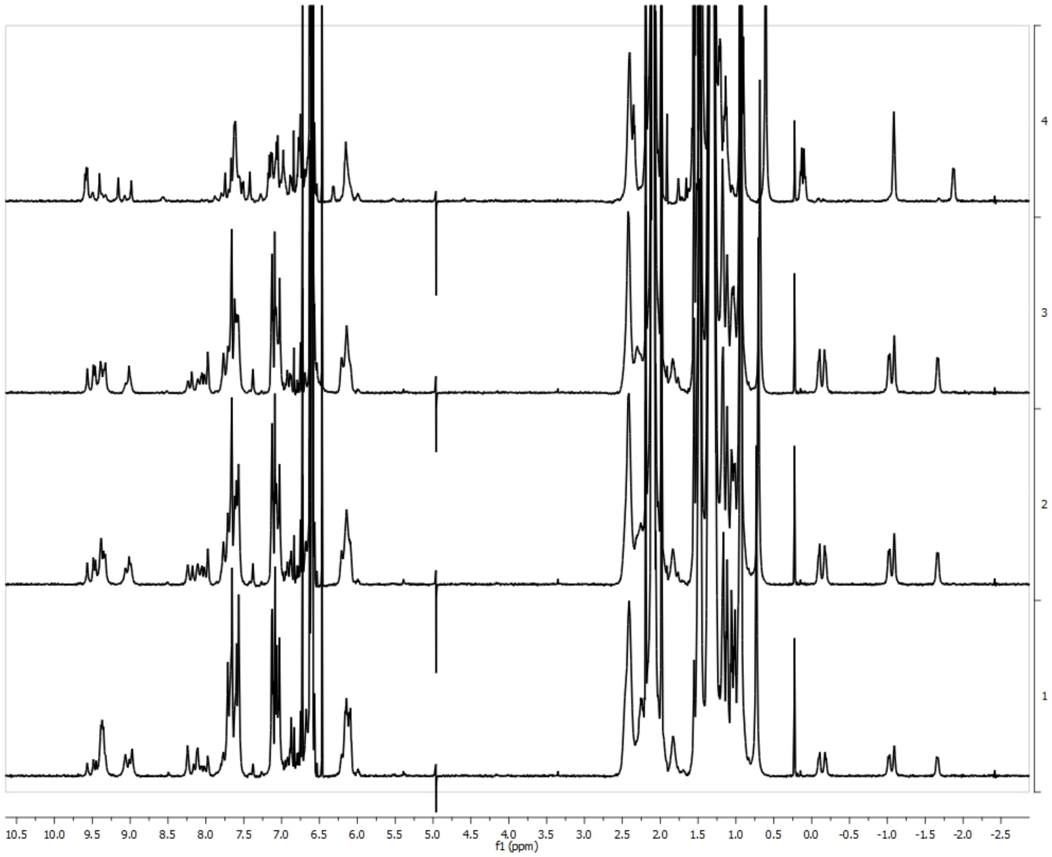


Figure S12. Titration of 1-adamantanecarbonitrile into cavitand **2** and subsequent isomerization; ^{1}H NMR spectra after adding 0.025 ml guest stock (1), after adding 0.050 ml guest stock (2), after adding 0.075 ml guest stock solution (3), after adding 0.575 ml guest stock and irradiating with UV light for 1 hour and 25 minutes (4).

Cavitand	PhenylAzo **2**	Amt H (g)	Vol in NMR tube (L)	[H]initial
mw	1932.55	0.0035	0.00060	0.0030
Guest	1-adamantanecarbonitrile	Amt G (g)	Vol guest Stock (L)	[G] stock (M)
mw	161.24	0.0054	0.0010	0.033

Trial 1	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000025	0.0013	0.0029	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.50	3.0	0.17	0.83
	[HG] (M)	[H] (M)	[G] (M)	
	0.00048	0.0024	0.00086	
	Ka			
	232			

Trial 2	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000050	0.0026	0.0027	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.87	3.0	0.29	0.71
	[HG] (M)	[H] (M)	[G] (M)	
	0.00080	0.0019	0.0018	
	Ka			
	230			

Trial 3	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000075	0.0037	0.0026	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	1.1	3.0	0.37	0.63
	[HG] (M)	[H] (M)	[G] (M)	
	0.00099	0.0017	0.0027	
	Ka			
	218			

ave Ka 226

Cavitand 2 + 1-adamantaneamine (6)

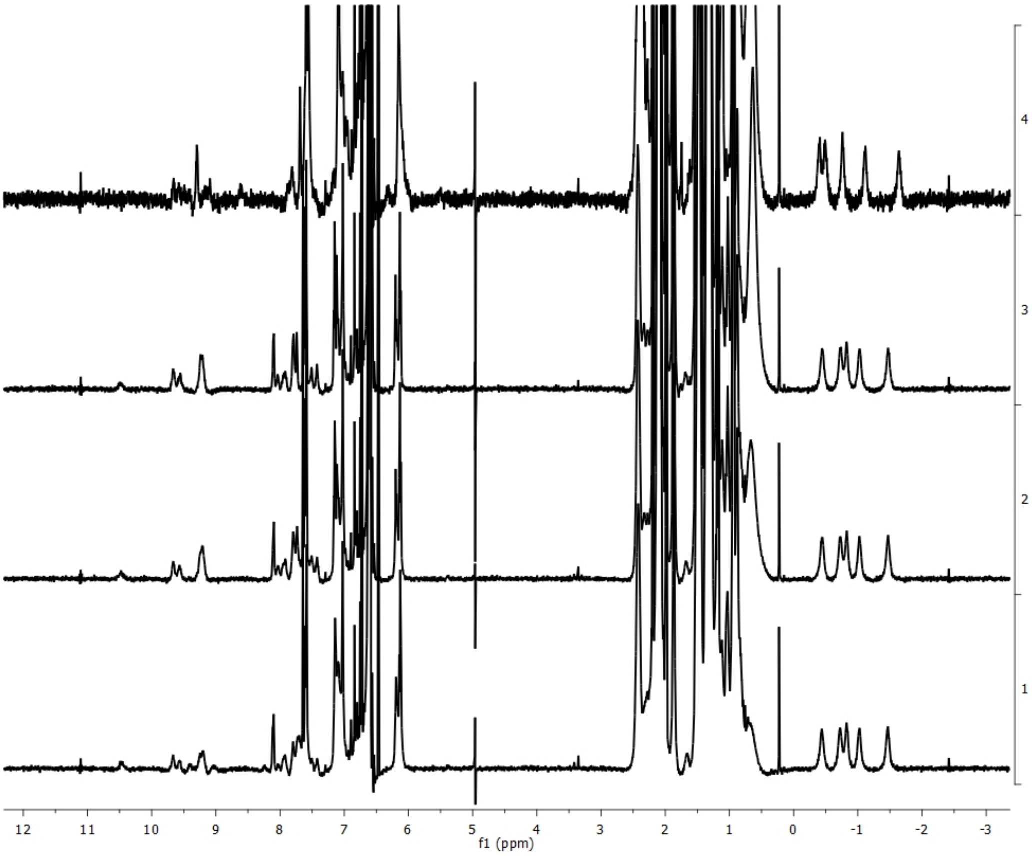


Figure S13. Titration of 1-adamantaneamine into cavitand **2** and subsequent isomerization; ^{1}H NMR spectra after adding 0.100 ml guest stock (1), after adding 0.200 ml guest stock (2), after adding 0.300 ml guest stock solution (3), after irradiating with UV light for 35 minutes (4).

Cavitand	PhenylAzo **2**	Amt H (g)	Vol in NMR tube (L)	[H]initial
mw	1932.55	0.0031	0.00060	0.0027
Guest	1-adamantaneamine	Amt G (g)	Vol guest Stock (L)	[G] stock (M)
mw	151.25	0.0052	0.0010	0.034

Trial 1	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.00010	0.0049	0.0023	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	1.3	3.0	0.42	0.58
	[HG] (M)	[H] (M)	[G] (M)	
	0.00096	0.0013	0.0039	
	Ka			
	183			

Trial 2	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.00020	0.0086	0.0020	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	1.5	3.0	0.51	0.49
	[HG] (M)	[H] (M)	[G] (M)	
	0.0010	0.00098	0.0076	
	Ka			
	139			

Trial 3	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.00030	0.011	0.0018	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	1.6	3.0	0.54	0.46
	[HG] (M)	[H] (M)	[G] (M)	
	0.00097	0.00081	0.010	
	Ka			
	113			

ave Ka	145

Cavitand 2 + 1-chloroadamantane (5)

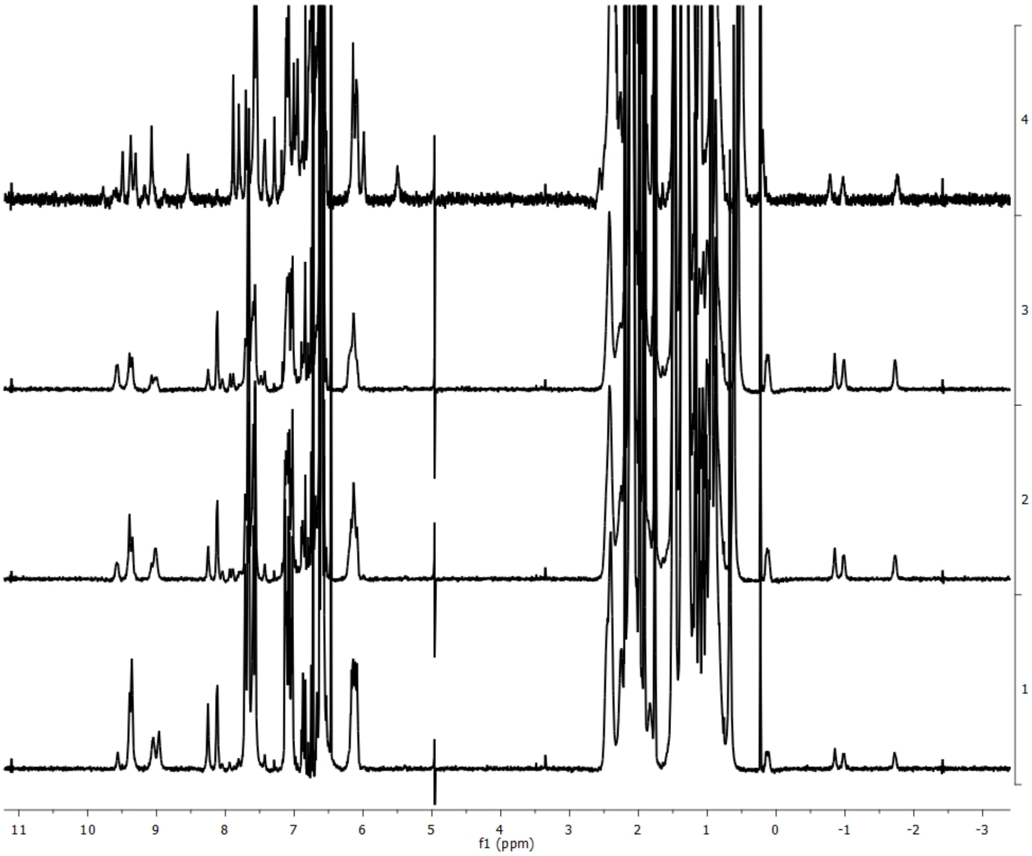


Figure S14. Titration of 1-chloroadamantane into cavitand **2** and subsequent isomerization; ^{1}H NMR spectra after adding 0.050 ml guest stock (1), after adding 0.150 ml guest stock (2), after adding 0.350 ml guest stock solution (3), after irradiating with UV light for 35 minutes (4).

Cavitand	PhenylAzo **2**	Amt H (g)	Vol in NMR tube (L)	[H]initial
mw	1932.55	0.0031	0.00060	0.0027
Guest	1-chloroadamantane	Amt G (g)	Vol guest Stock (L)	[G] stock (M)
mw	170.68	0.0052	0.0010	0.030

Trial 1	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.000050	0.0023	0.0025	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.28	3.0	0.093	0.91
	[HG] (M)	[H] (M)	[G] (M)	
	0.00023	0.0022	0.0021	
	Ka			
	49			

Trial 2	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.00015	0.0061	0.0021	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.60	3.0	0.20	0.80
	[HG] (M)	[H] (M)	[G] (M)	
	0.00043	0.0017	0.0057	
	Ka			
	44			

Trial 3	amount G added (L)	[G] (M)	$[H]_o$ (M)	
	0.00035	0.011	0.0017	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.91	3.0	0.30	0.70
	[HG] (M)	[H] (M)	[G] (M)	
	0.00051	0.0012	0.011	
	Ka			
	41			

ave Ka 45

Cavitand 2 + 1-adamantanemethanol (4)

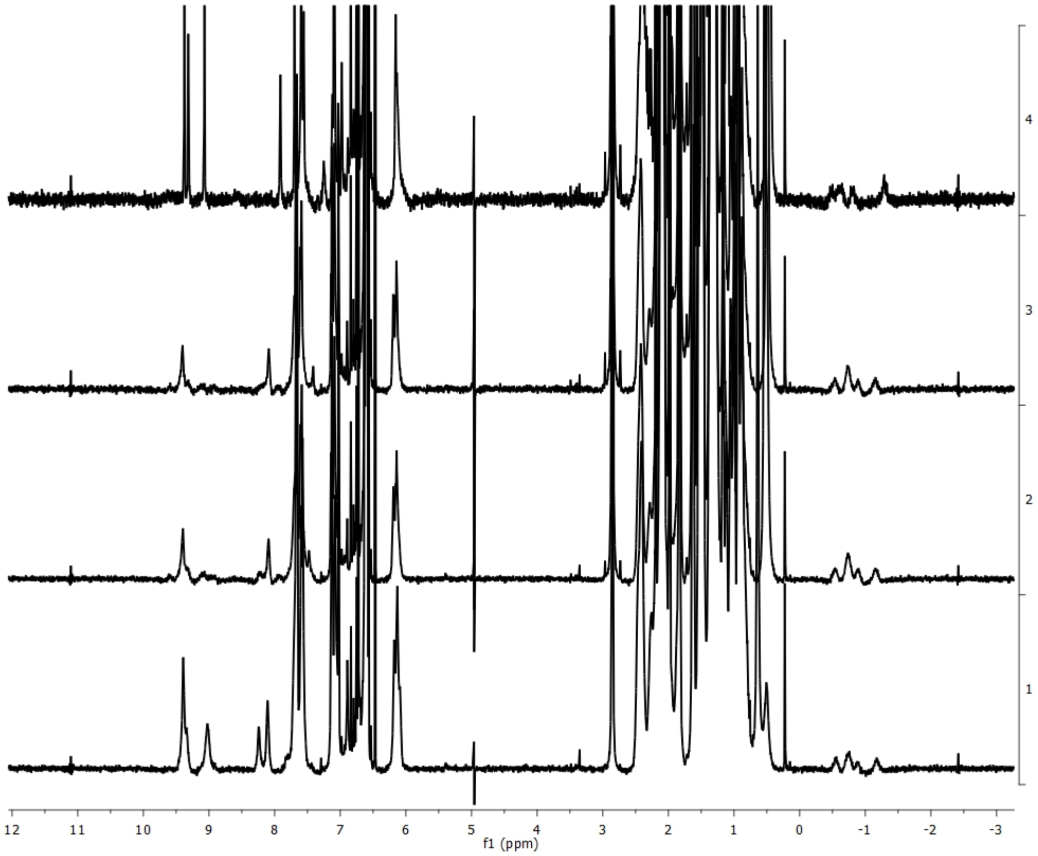


Figure S15. Titration of 1-adamantanemethanol into cavitand **2** and subsequent isomerization; ^{1}H NMR spectra after adding 0.100 ml guest stock (1), after adding 0.400 ml guest stock (2), after adding 0.700 ml guest stock solution (3), after irradiating with UV light for 35 minutes (4).

Cavitand	PhenylAzo **2**	Amt H (g)	Vol in NMR tube (L)	[H]initial
mw	1932.55	0.0036	0.00060	0.0031
Guest	1-adamantanemethanol	Amt G (g)	Vol guest Stock (L)	[G] stock (M)
mw	166.26	0.0056	0.0010	0.034

Trial 1	amount G added (L)	[G] (M)	[H]$_o$ (M)	
	0.00010	0.0048	0.0027	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.080	3.0	0.027	0.97
	[HG] (M)	[H] (M)	[G] (M)	
	0.000071	0.0026	0.0047	
	Ka			
	5.8			

Trial 2	amount G added (L)	[G] (M)	[H]$_o$ (M)	
	0.00040	0.013	0.0019	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.20	3.0	0.067	0.93
	[HG] (M)	[H] (M)	[G] (M)	
	0.00012	0.0017	0.013	
	Ka			
	5.4			

Trial 3	amount G added (L)	[G] (M)	[H]$_o$ (M)	
	0.00070	0.018	0.0014	
	Norm Integral	# Hs on guest	HG Ratio	H Ratio
	0.29	3.0	0.097	0.90
	[HG] (M)	[H] (M)	[G] (M)	
	0.00014	0.0013	0.018	
	Ka			
	5.9			

ave Ka 5.7

5. Kinetics of Photo-isomerization With Guests

Trans to *cis* photo-isomerization of cavitand 1 in the presence of 2-adamantanone (8)

Cavitand **1** (0.0031 g, 0.00156 mmol) was dissolved in d_{12}-mesitylene (0.600 ml) and transferred to a NMR tube. A stock solution of 2-adamantanone (0.0046 g, 0.0306 mmol) in d_{12}-mesitylene (1 ml) was prepared and 0.375 ml of this stock solution were transferred to the NMR tube and mixed. The sample was heated to reflux with a heat gun for 5 minutes and allowed to cool after wrapping the sample in aluminum foil. A ^{1}H NMR spectrum was acquired after 3 hours. The sample was subsequently subjected to UV light for 10 minutes and another spectrum was acquired. To complete the isomerization process the sample was subjected to UV light for 5 additional minutes and monitored by ^{1}H NMR spectroscopy. Complete isomerization was determined by the disappearance of the bound guest signals at -1.0 ppm.

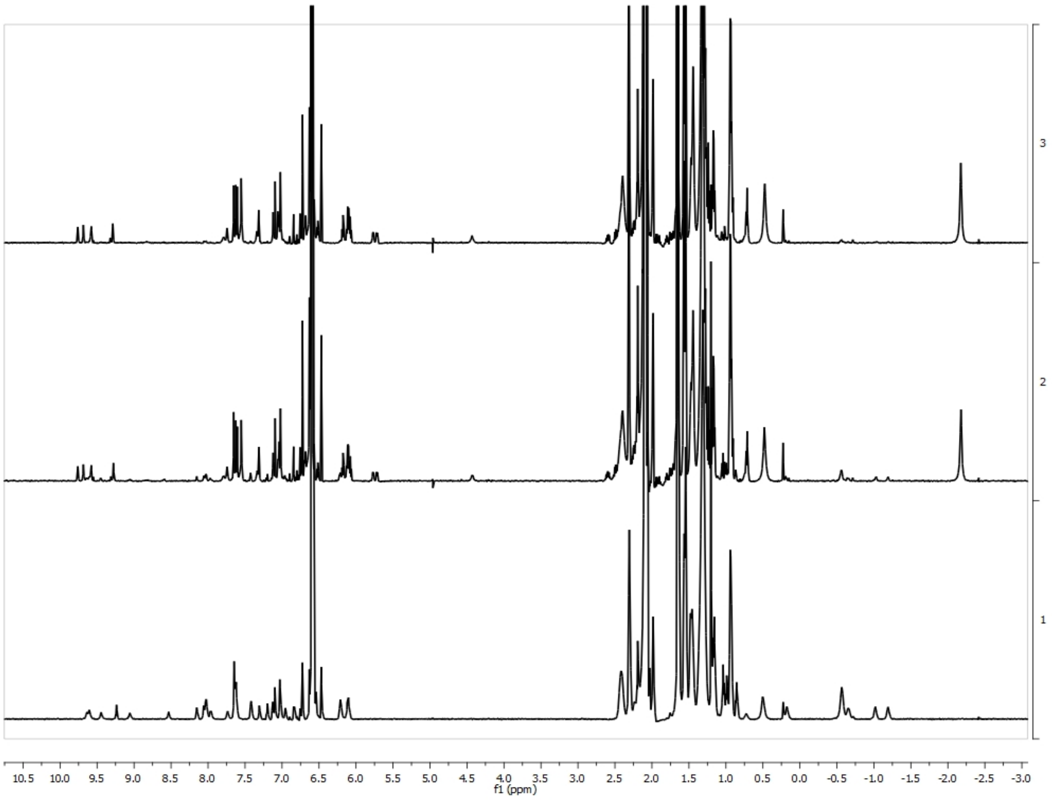


Figure S16. *Trans* to *cis* photo-isomerization of cavitand **1** in the presence of 2-adamantanone; ^{1}H NMR spectrum after heating to reflux for 5 minutes and cooling in the dark (bottom), after irradiating with UV light for 10 minutes (middle) and after irradiating with UV light for 15 minutes (top).

Cis **to *trans* photo-isomerization of cavitand 1 in the presence of 2-adamantanone (8)**

Cavitand **1** (0.0031 g, 0.00156 mmol) was dissolved in d_{12}-mesitylene (0.600 ml) and transferred to a NMR tube. A stock solution of 2-adamantanone (0.0046 g, 0.0306 mmol) in d_{12}-mesitylene (1 ml) was prepared and 0.375 ml of this stock solution was transferred to the NMR tube and mixed. The sample was irradiated with UV light for 30 minutes. The sample was subsequently subjected to visible light and ^{1}H NMR spectra were acquired after 20, 40, 80 and 120 minutes. The completion of the isomerization was determined by comparing the integration of the methine signals at 6.23 to 6.04 ppm versus the *cis*-*tert*-butyl signal at -2.2 ppm. Photostationary state = 80% *trans*-**1** after 20 minutes.

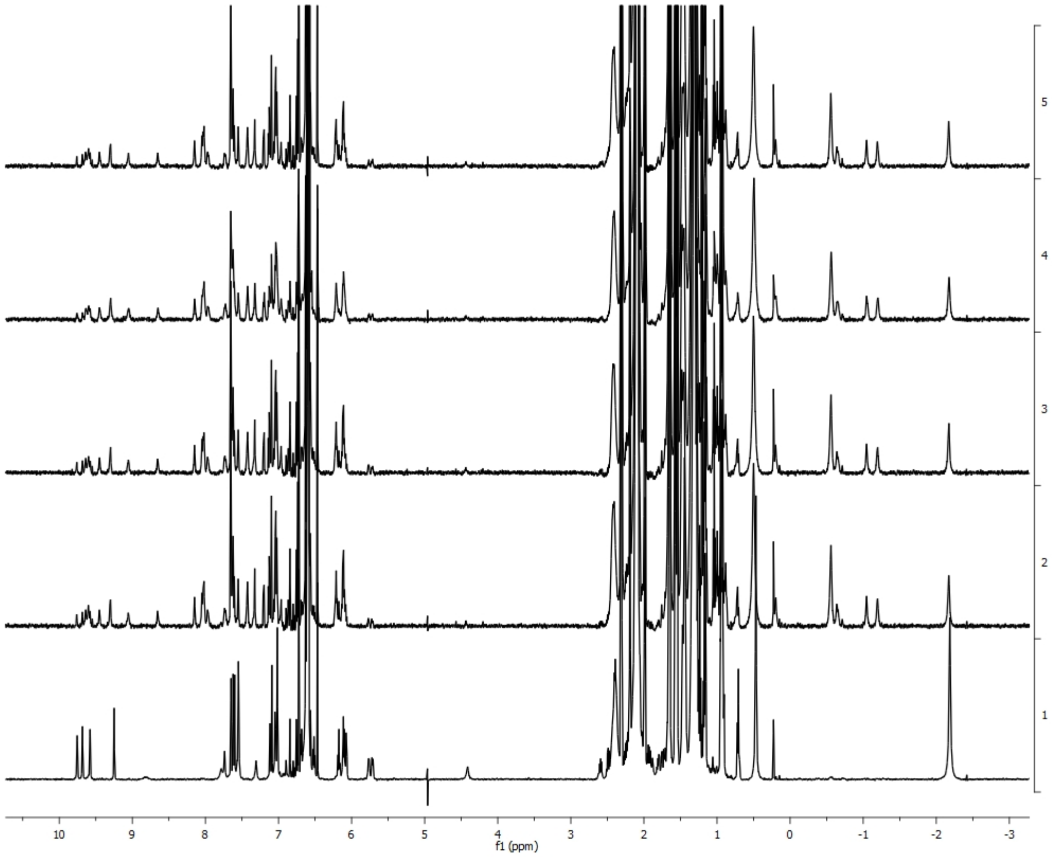


Figure S17. *Cis* to *trans* photo-isomerization of cavitand **1** in the presence of 2-adamantanone; ^{1}H NMR spectra after irradiating with UV light for 30 minutes (bottom, 1) after irradiating with visible light for 20 minutes (middle, 2), after irradiating with visible light for 40 minutes (middle, 3), after irradiating with visible light for 80 minutes (middle, 4) and after irradiating with visible light for a total of 120 minutes (top, 5).

<u>*Trans* to *cis* photo-isomerization of cavitand 2 in the presence of 2-adamantanone (8)</u>

Cavitand **2** (0.0035 g, 0.00181 mmol) was dissolved in d_{12}-mesitylene (0.600 ml) and transferred to a NMR tube. A stock solution of 2-adamantanone (0.0053 g, 0.0353 mmol) in d_{12}-mesitylene (1 ml) was prepared and 0.475 ml of this stock solution was transferred to the NMR tube and mixed. The sample was heated to reflux with a heat gun for 5 minutes and allowed to cool after wrapping the sample in aluminum foil. A ^{1}H NMR spectrum was acquired after 3 hours. The sample was subsequently subjected to UV light for 10 minutes and another spectrum was acquired. Another spectrum was acquired after 15 minutes and to complete the isomerization process the sample was subjected to UV light for 5 additional minutes and monitored by ^{1}H NMR spectroscopy. Complete isomerization was determined by the disappearance of the *cis*-**2** bound guest signals at -1.01 ppm.

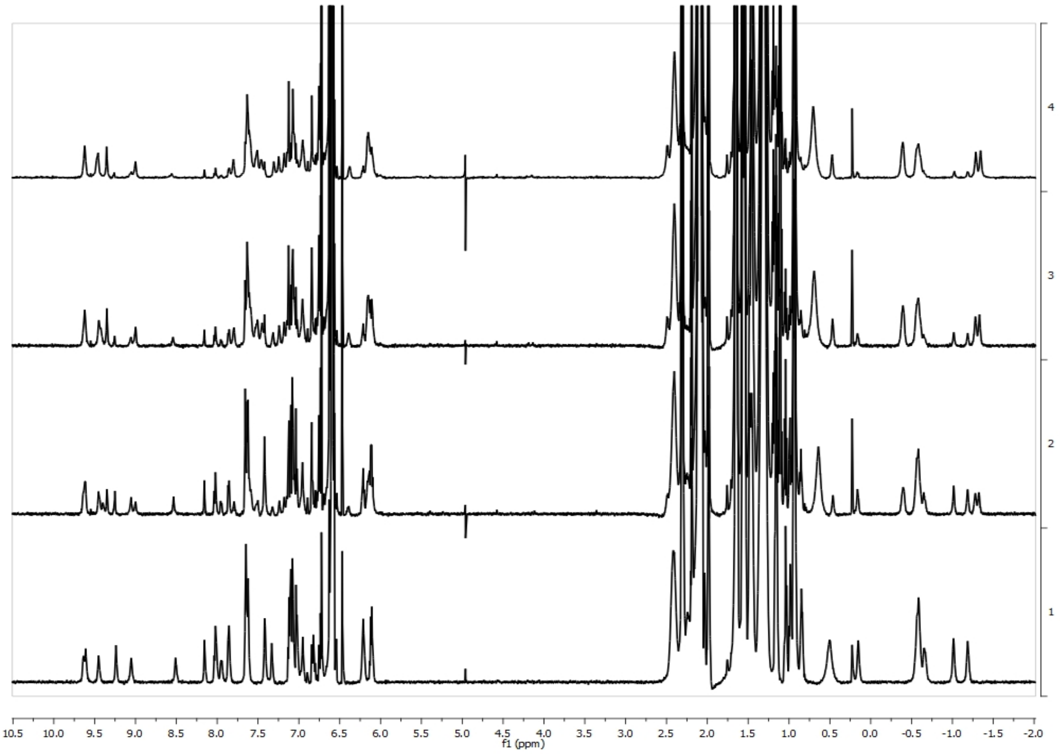


Figure S18. Kinetics of photo-isomerization of cavitand **2** in the presence of 2-adamantanone; ^{1}H NMR spectra after heating to reflux for 5 minutes and cooling in the dark (bottom), after irradiating with UV light for 10 minutes (middle, 2), after irradiating with UV light for 15 minutes (middle, 3) and after irradiating with UV light for 20 minutes (top).

Cis to *trans* photo-isomerization of cavitand 2 in the presence of 2-adamantanone (8)

Cavitand **2** (0.0035 g, 0.00181 mmol) was dissolved in d_{12}-mesitylene (0.600 ml) and transferred to a NMR tube. A stock solution of 2-adamantanone (0.0053 g, 0.0353 mmol) in d_{12}-mesitylene (1 ml) was prepared and 0.475 ml of this stock solution was transferred to the NMR tube and mixed. The sample was irradiated with UV light for 30 minutes. The sample was subsequently subjected to visible light and ^{1}H NMR spectra were acquired after 20, 40, 80 and 120 minutes. The completion of the isomerization was determined by comparing the integration of the methine signals at 6.21 and 6.11 ppm versus the *cis*-bound guest signals at -1.29 and -1.35 ppm. Photostationary state = 95% *trans*-**2** after 20 minutes.

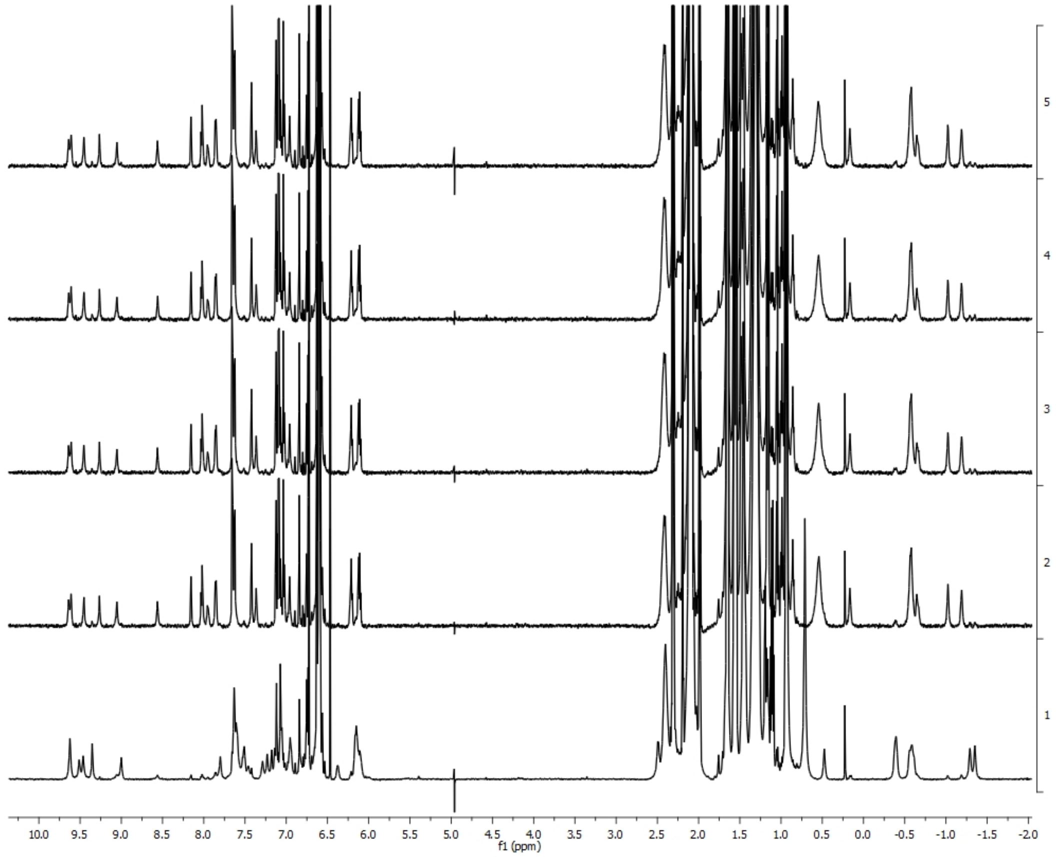


Figure S19. *Cis* to *trans* photo-isomerization of cavitand **2** in the presence of 2-adamantanone; ^{1}H NMR spectra after irradiating with UV light for 30 minutes (bottom, 1), after irradiating with visible light for 20 minutes (middle, 2), after irradiating with visible light for 40 minutes (middle, 3), after irradiating with visible light for 80 minutes (middle, 4) and after irradiating with visible light for a total of 120 minutes (top, 5).

6. Computational Studies

AM1 minimizations were performed with the CAChe software package.[iii]

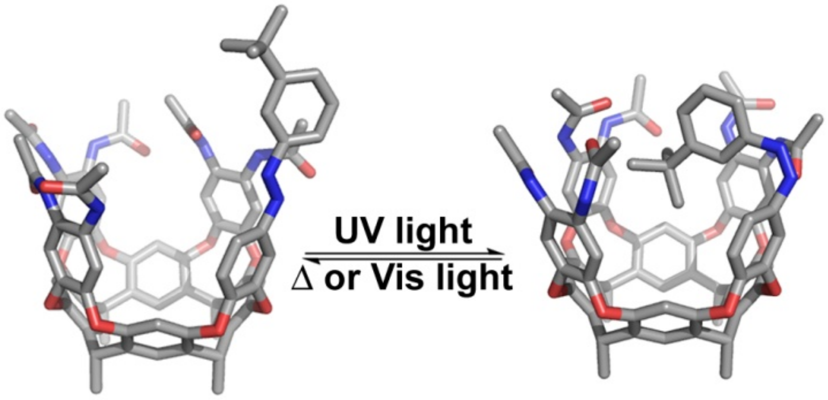


Figure S20. AM1 minimizations of azo-cavitand **1** illustrating the open configuration of *trans*-**1** (left) and the self-contained configuration *cis*-**1** (right). Hydrogens and alkyl chains have been removed.

7. References

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