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Reversible Photochemically Gated Transformation of a Hemicarcerand to a Carcerand**

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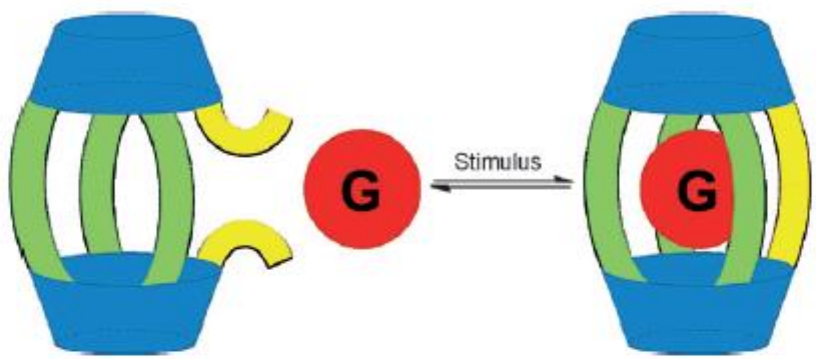
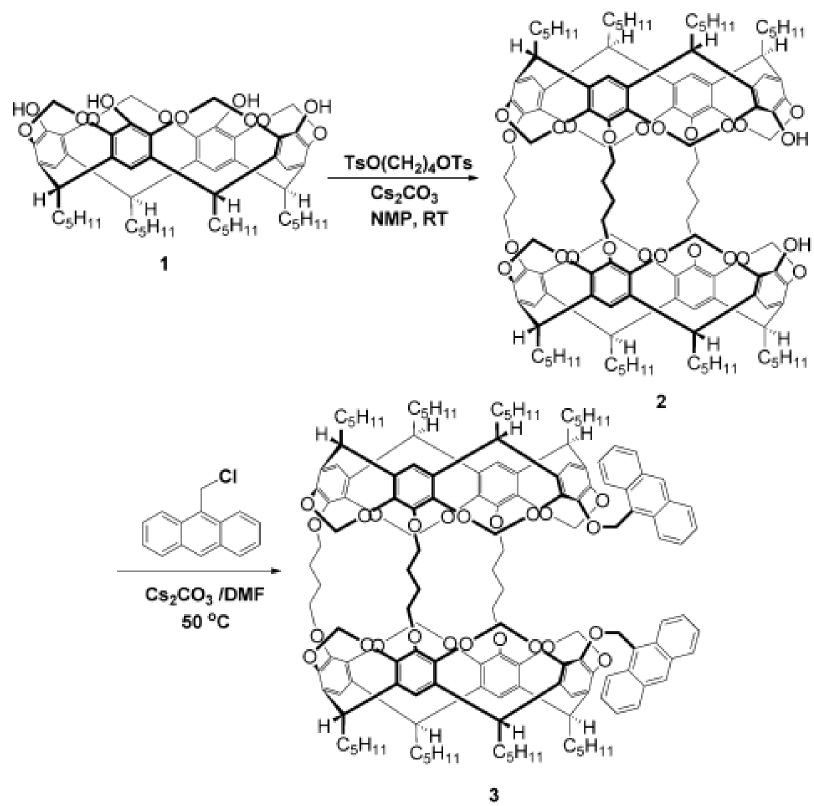
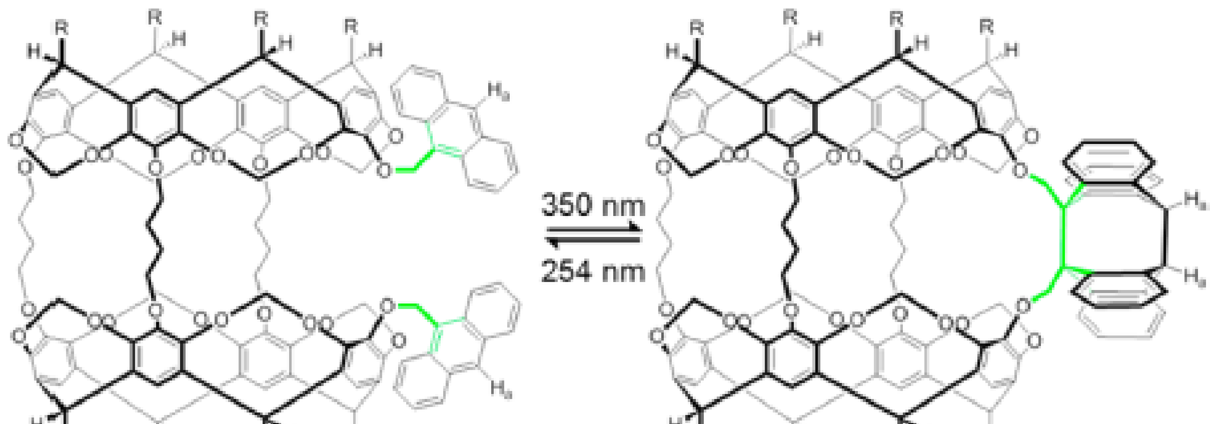
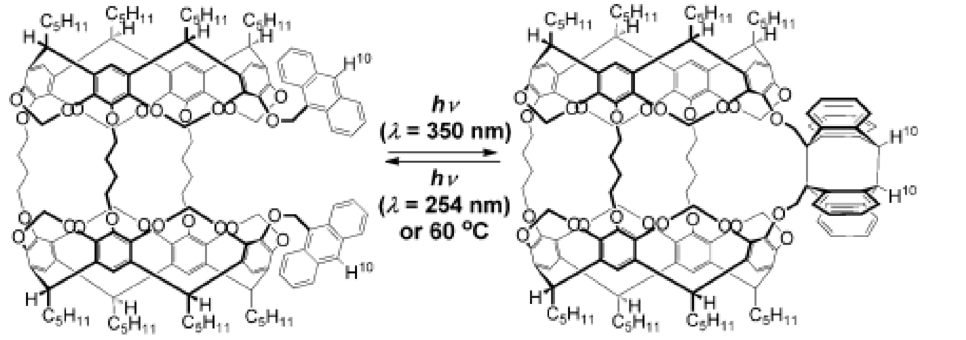


Figure 1. Gating in container molecules converts a hemicarcerand (left) into a carcerand (right).


TsO(CH2)4OTs
Cs2CO3
NMP, RT
Cl
Cs2CO3 /DMF
50 oC
C5H11
1
2
3



6a. R = pentyl
6b. R = Me



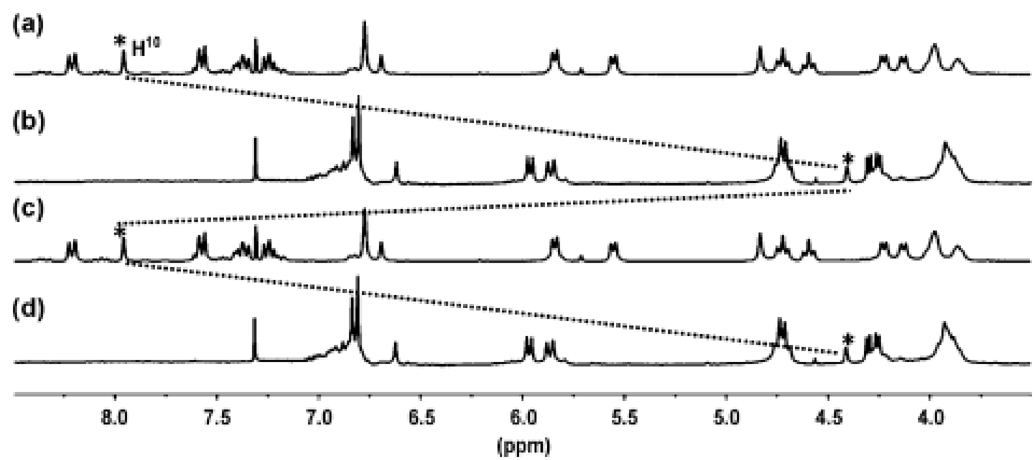
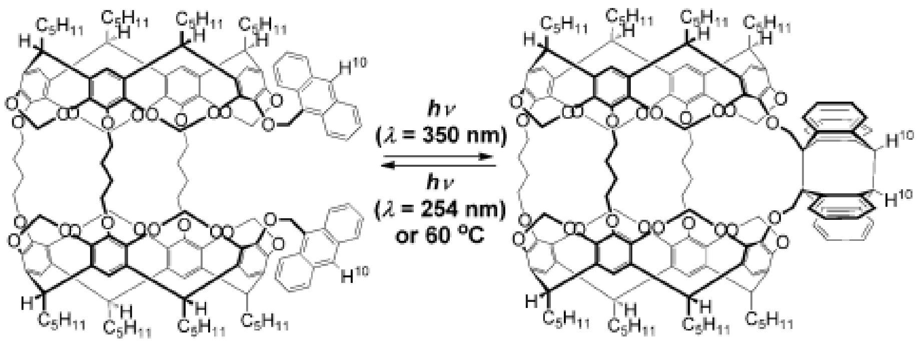
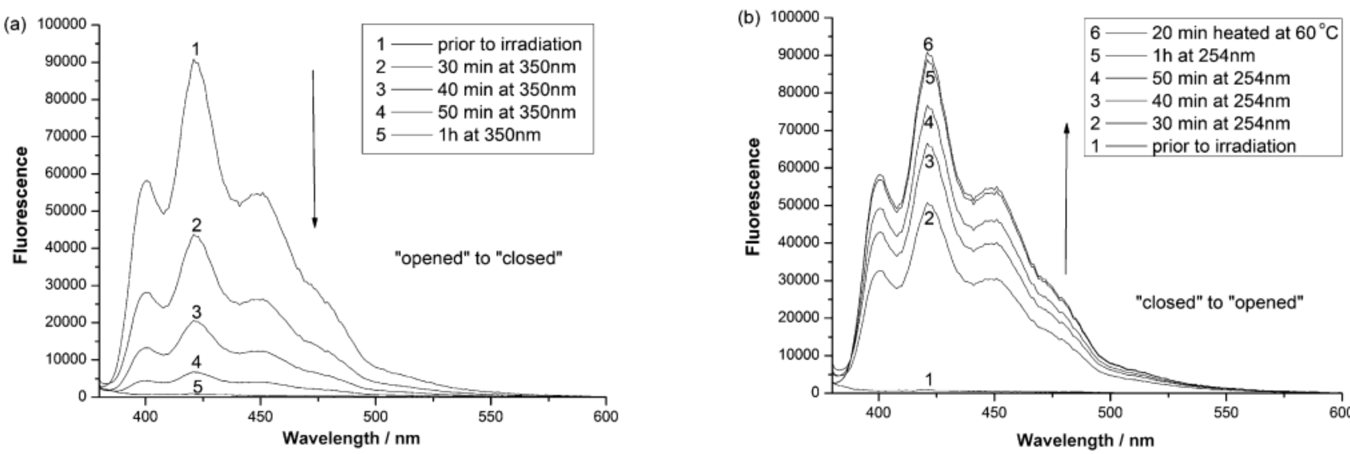


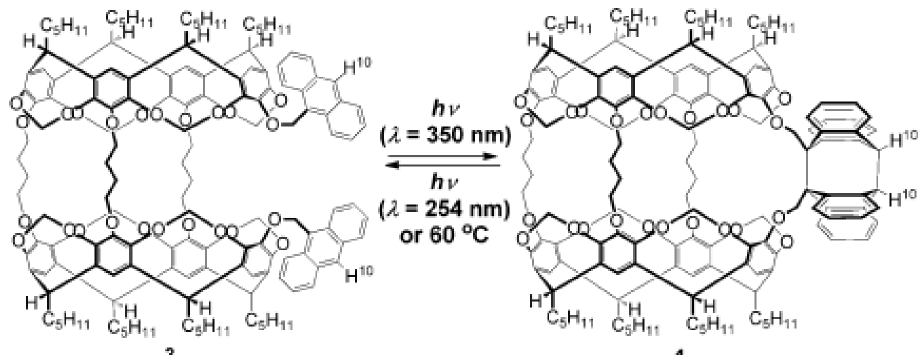
Figure 3. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$) of a) host **3** b) irradiation of host **3** with light at 350 nm for 1 h, c) irradiation of b with light at 254 nm for 1 h or heating at 60 °C for 20 min, d) irradiation of c with light at 350 nm for 1 h.



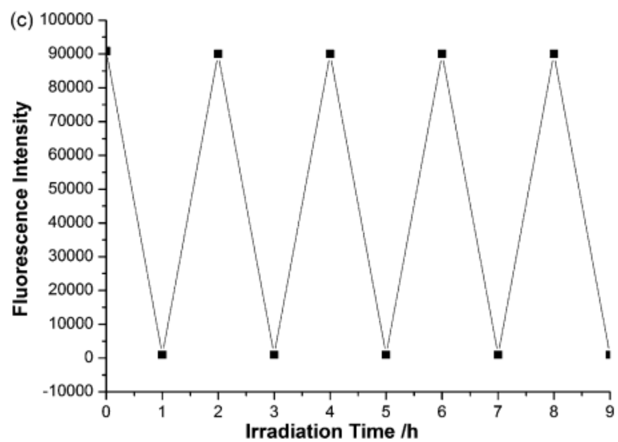
hν
(λ = 350 nm)
hν
(λ = 254 nm)
or 60 °C
C5H11
H
H10
O



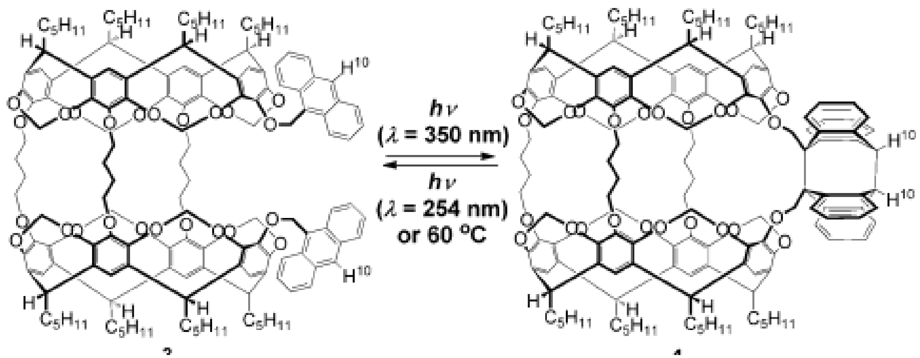
(a)
1 prior to irradiation
2 30 min at 350nm
3 40 min at 350nm
4 50 min at 350nm
5 1h at 350nm
"opened" to "closed"
Fluorescence
Wavelength / nm
(b)
6 20 min heated at 60 °C
5 1h at 254nm
4 50 min at 254nm
3 40 min at 254nm
2 30 min at 254nm
1 prior to irradiation
"closed" to "opened"
Fluorescence
Wavelength / nm



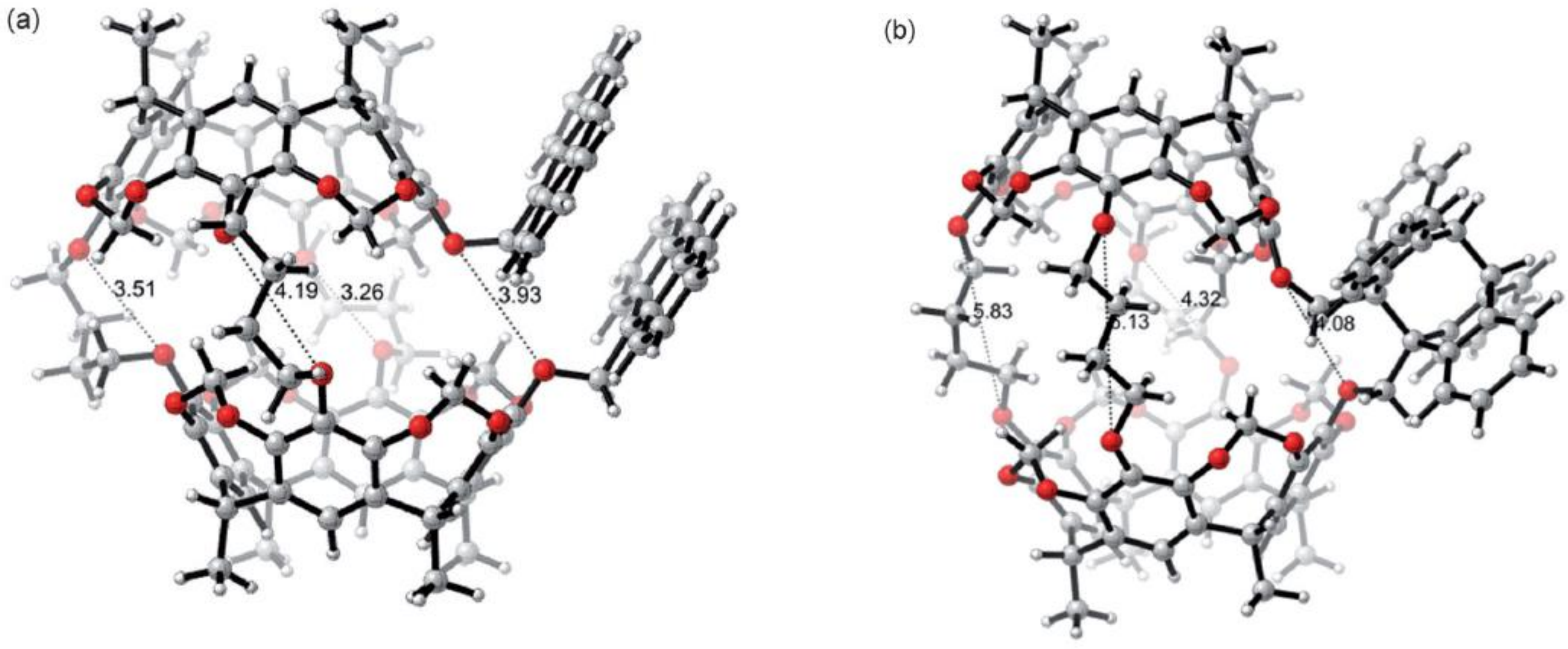
hν
(λ = 350 nm)
hν
(λ = 254 nm)
or 60 °C

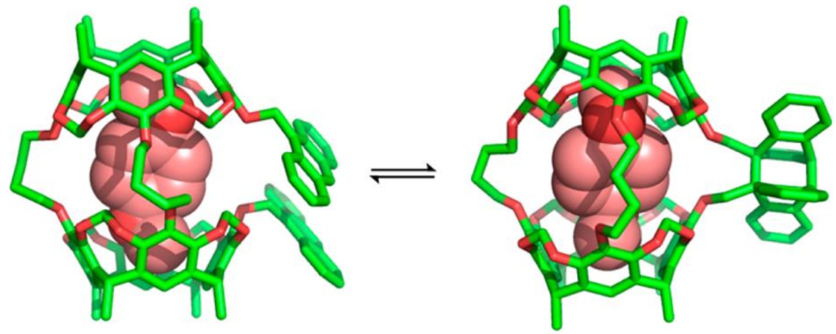


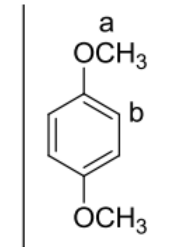
(c)
Fluorescence Intensity
Irradiation Time /h



The progress of the photodimerization was also monitored by thin-layer chromatography, which showed only one band after completion of the photodimerization. Photodimer 4 was purified after photolysis at 350 nm. In the high-resolution mass spectrum the molecular ion of photoproduct 4 has the same mass as the parent open-state host 3.


(a)
3.51
4.19
3.26
3.93
(b)
5.83
4.32





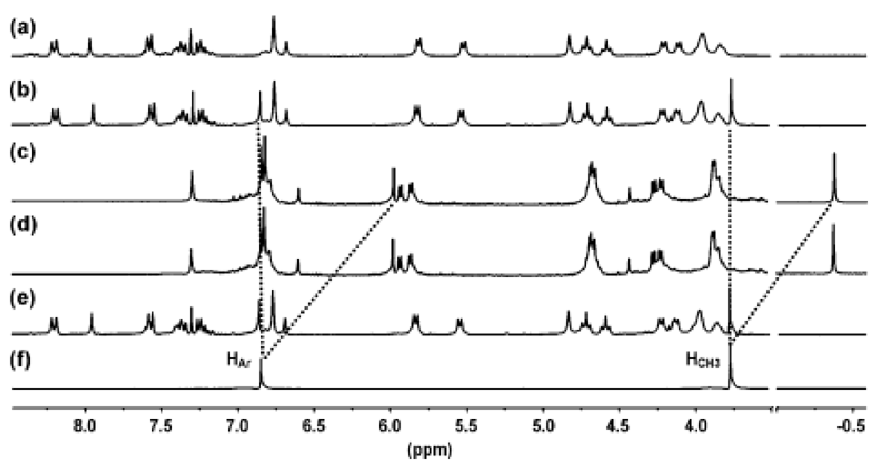
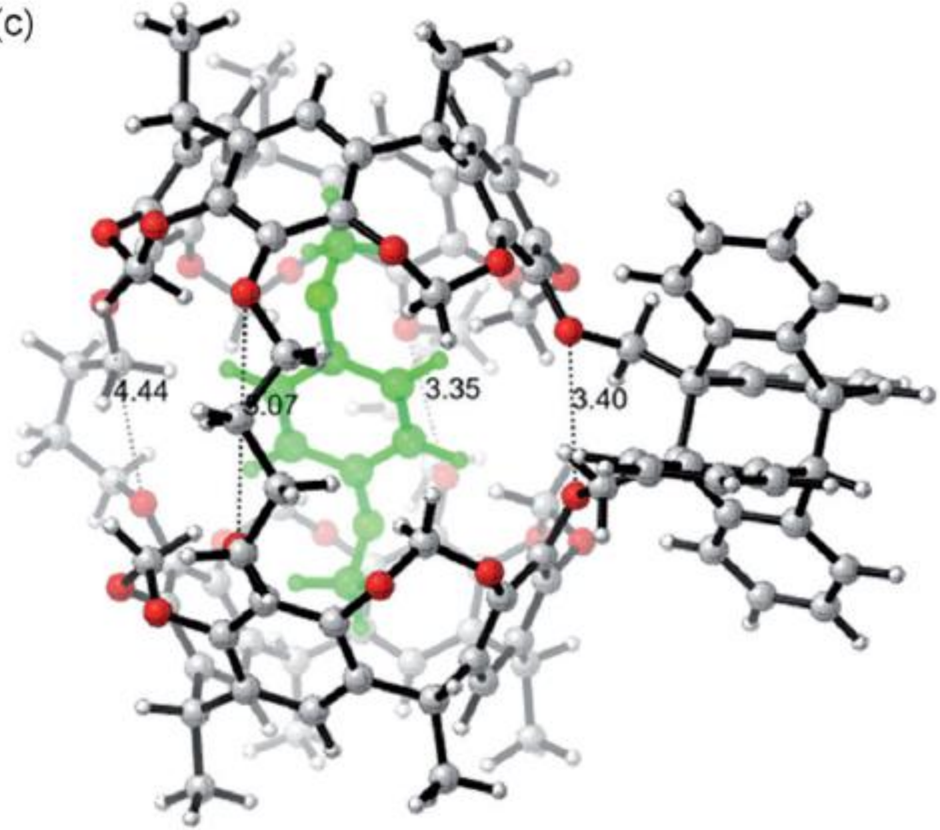


Figure 6. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$) of a) host **3** b) addition of 1 equiv of 1,4-$(MeO)_2C_6H_4$ into host **3** solution without irradiation, c) **4**⊙1,4-$(MeO)_2C_6H_4$,[16] d) c after 4 weeks in dark and RT, e) irradiation of c with light at 254 nm for 1 h or heating at 60 °C for 20 min, f) guest 1,4-$(MeO)_2C_6H_4$.

(c)



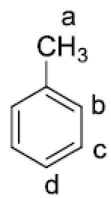
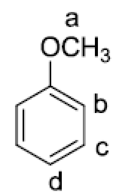
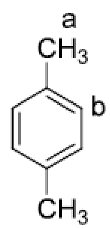
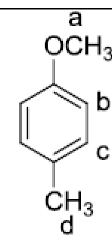
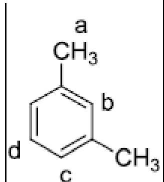
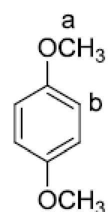
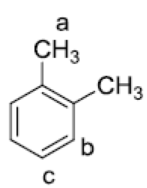
Guest	H	Δδ (ppm)	Guest	H	Δδ (ppm)
	H_a	3.96		H_a	3.87
	H_b	1.53		H_b	1.60
	H_c	1.85		H_c	1.95
	H_d	3.35		H_d	3.30
	H_a	4.17		H_a	4.01
	H_b	1.06		H_b	0.84
				H_c	0.98
				H_d	4.21
	H_a	3.17		H_a	4.15
	H_b	hidden		H_b	0.85
	H_c	1.86			
	H_d	hidden			
	H_a	2.34	CH_aCl_2—$CHCl_2$	H_a	0.95
	H_b	1.54	CH_aBr_2—$CHBr_2$	H_a	1.02
	H_c	1.95			

Table S1: Complexation of **4** with various guest molecules and the chemical shift changes of corresponding Hs (before and after complexations) on the guests.

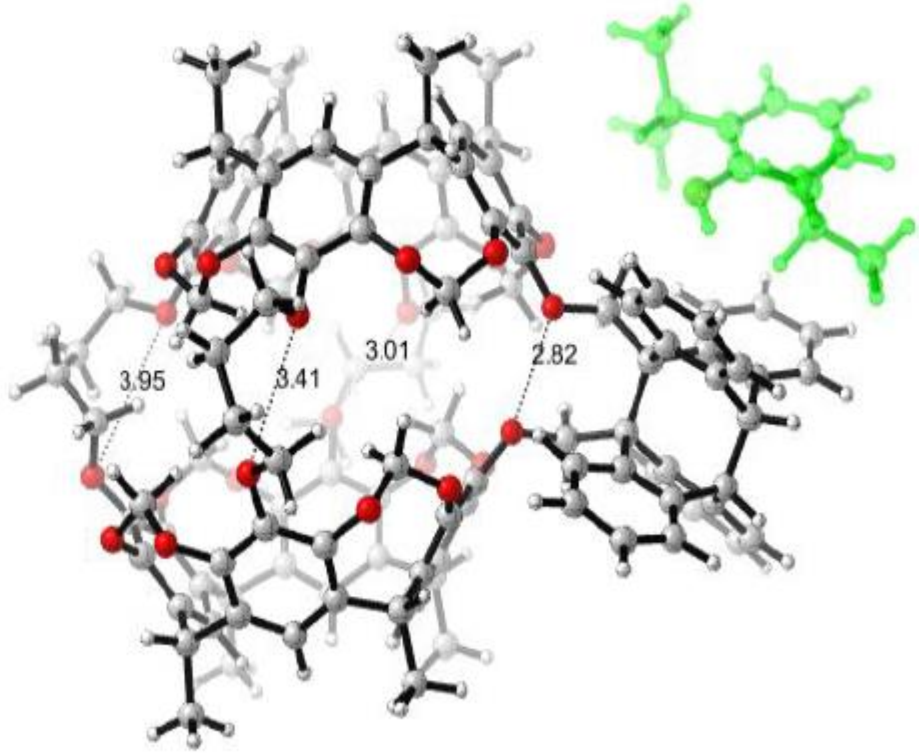


Figure S2: Molecular modelling of complexation of **4** with propofol (2,6-diisopropylphenol) using Schrödinger Macromodel (OPLS_2005, GB/SA $CHCl_3$). (The geometry began with the guest inside the host; the guest came out of the host after the minimization)

In summary, a new reversible photoswitchable gated hemicarcerand containing two anthracene groups was designed and synthesized. The photochemical properties of this system were studied by ^{1}H NMR and fluorescence spectroscopy. The photoswitchable cycle between the open (hemicarcerand) and closed (carcerand) states of the host is well controlled by radiation of different wavelengths, and controlled encapsulation and release of the guest molecules such as 1,4-dimethoxybenzene was observed. We are currently working on enlarging the cavity size of the host as well as increasing the water solubility of the host.