Manipulating the Cavity of a Porous Material Changes the Photoreactivity of Included Guests

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

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Changing an ether to a ketone within the framework of a bis-urea macrocycle has little effect on the supramolecular assembly of this building block into porous crystals but introduces a triplet sensitizer into the framework that dramatically alters the photochemical reactions of included guests.

Supramolecular assembly deftly and efficiently creates materials with interesting structures and properties from small molecule building blocks. Some supramolecular assemblies, as well as more traditional porous materials and crystals, can be used as templates or vessels to promote chemical reactions with high regio- and stereoselectivity.¹ It is not yet possible to predict how systematic changes in these nanoreactors influence the reactants. In this paper, we examine how a change in the framework of a self-assembling macrocycle influences the UV-absorption of the macrocycle and subsequently the reaction environment of the cavity.

We have previously reported bis-urea 1 synthesized from a phenylether spacer that assembled into columnar structures that pack against each other to give porous crystals.²,³ We now report a similar macrocycle 2 that is synthesized from a benzophenone spacer and also forms porous crystals. The two macrocycles differ in their linking groups (ether 1 versus ketone 2). The homogeneous channels of the two systems have comparable diameters by gas adsorption. They absorb a similar series of guests. Despite these similarities, the new benzophenone framework of host 2 facilitates different photochemical reactions within its nanochannels. Host 1 induces the [2 + 2]-photocycloaddition of α,β-unsaturated ketones (Fig. 1), whereas host 2 is ineffective in facilitating this photocycloaddition. Conversely, only host 2 induces a rapid photoisomerization of trans-β-methylstyrene to the less stable cis-isomer (II), which is a reaction that does not proceed within host 1.

Macrocycl 1 self-assembled into columnar structures via urea–urea hydrogen bonds and aryl-stacking interactions forming crystals that display permanent porosity.³ These crystals reversibly bound guests with matched shapes and sizes and facilitated [2 + 2]-photocycloadditions of enones.⁴ We synthesized benzophenone macrocycle 2 in which the ether oxygen of host 1 was replaced with a carbonyl group. Host 2 was synthesized in two steps from the dibromide and masked urea (triazinanone).⁵ Cyclization under basic conditions yielded the urea-protected macrocycle, which crystallized as a chlororform solvate (S.I.†). Deprotection with diethanolamine followed by recrystallization of 2 from hot DMSO afforded crystals suitable for X-ray analysis.†

The crystal structure of 2 revealed the expected bis-urea structure (Fig. 2) that assembles into columnar structures similar to host 1,³ highlighting the predictability of this assembly motif. The macrocycles display strong urea–urea hydrogen bonds (Fig. 3) that extend along both sides of the tube with H···O distances from 2.17 to 2.30 Å. The individual monomers are also held together by edge to face aryl-stacking interactions. The sizeable channel of the assembly was filled with DMSO guests in a 1 : 1 (macrocycle : DMSO) ratio.

Heating removed the DMSO guest from the crystals, forming a host that maintains permanent porosity. The porosity of the empty host 2 was established by gas absorption using CO₂ at 273 K. The evacuated crystals displayed a type 1 gas adsorption isotherm (Fig. 4A), consistent with a microporous material.⁶ The Brunauer–Emmett–Teller method was applied to the isotherm at P/P₀ between 0.012 and 0.028 and the calculated surface area of 320 m² g⁻¹, comparable to the original framework 1

![Figure 1](attachment:image.png)

**Fig. 1** The characteristics of these porous nanoreactors were probed using reactive guests (3-7) in two photochemical reactions: [2 + 2]-photodadditions (I) where R, R' and n depend on the identity of the starting cyclic enone and cis-trans photoisomerization (II) of styrene 7.
forming empty host 2 to 160 structure similar to that of the single crystal. Subsequent heating in this region with a l

Host markedly different UV-absorbance spectra in DMSO (Fig. 5). Exposing of the empty host powder to guest vapour resulted in reabsorption of the guests to reform host 2. The empty host was highly crystalline by PXRD (Fig. 4B middle). Exposure of the empty host 2 powder to guest vapour resulted in reabsorption of the guests to reform host 2-DMSO, providing further evidence of the reversible nature of the absorption/desorption process. Both hosts absorbed small molecule solvents such as EtOAc, THF, and AcOH in identical host : guest ratios (S.I.†). Larger reactants 3–7 were also absorbed by both hosts.

Although they have many similarities, the two hosts exhibit markedly different UV-absorbance spectra in DMSO (Fig. 5). Host 1 has no significant absorbance in the 320–380 nm range, which is important for [2+2]-cycloadditions of enones. In comparison, the benzophenone host 2 has a strong absorbance in this region with a λmax at 339 nm, similar to what is observed for 2-cyclohexenone (λmax = 335 nm).

Previous work demonstrated that enones 4–6 underwent facile [2 + 2]-cycloaddition reactions to yield the endo head-to-tail (HT) photodimers as the major product in high conversion (Table 1). The new solid inclusion crystals (host 2 enone) were UV-irradiated using a 450 W Hannovia high pressure mercury vapour lamp at ~30 °C for 24 h. Next, each of the host–guest complexes was directly dissolved in d6-DMSO and monitored by 1H NMR spectroscopy. Only peaks that corresponded to the host macrocycle 2 and the starting enones were observed. These results are in stark contrast to the selective [2 + 2]-cycloadditions facilitated by host 1.

How is one to explain this drastic difference in observed reactivity? Both hosts load the enones with high binding ratios (2.5 : 1 for host 1 vs. 2 : 1 for host 2), yet no reaction is observed within the second host. We attribute these differences to the UV-absorption characteristics of the two hosts. Host 1 does not have any significant absorbance in the wavelength ranging from 300 to 450 nm, where most enones have strong absorption bands. Therefore, within host 1 these enones undergo the normal [2 + 2]-cycloaddition; however, host 2 displays a strong absorption in this range. Literature studies with 2-cyclopentenone in solution suggest that benzophenone transfers energy to the enone but that this triplet excited state is not conducive for the photoreaction.8

We next investigated both host 1 and host 2 as confined environments for the cis-trans photoisomerization of trans-β-methylstyrene 7 (Fig. 2, reaction II), which is a process known to require a triplet sensitizer.9 Can the covalent sensitizer of host 2 transfer energy to included guests? There are examples of sensitized photoreactions within zeolites loaded with benzophenone or in cases where acetophenone or benzophenone is covalently attached to small receptors.10

Styrene 7 (~4.3 Å × 7.7 Å) was absorbed by both hosts through vapour loading to give stable inclusion complexes after 24 h, which display similar host : guest ratios (host 1 7 (2.7 : 1 host : guest), host 2 7 (2.5 : 1 host : guest)). Prolonged exposure to the styrene 7 vapour (72 h) did not alter the
The crystals with CH$_2$Cl$_2$ and analysis by GC/MS. In the latter
removal of guests from the porous framework by washing
1 in the presence of host
3–6 binding ratios. The inclusion complex
2 followed by two methods: (A) direct dissolution of a sample in
lamp at
diated using a 450 W Hannovia high pressure mercury vapour
was observed in the host
1 2
1 cis
sensitizer in benzene solution gave a comparable percentage of
1
subjected to UV-irradiation for 30 min to 24 h. Host
5%
7
b–methylstyrene (63%) at the photostationary state (3 h). 9
These results show that small changes within the framework of
photochemical reactivity for absorbed guests. Host
1
macrocycle
2 is able to act as a triplet sensitizer for this
reaction, transferring energy to the included styrene guest.
We reported a new bis-urea macrocycle that self-assembles
self-assembled from UV-irradiation for 30 min to 24 h. Host
1 is of
subjected to UV-irradiation for 30 min to 24 h. The reaction progress was
no
trans
b–methylstyrene with benzophenone
1
b–methylstyrene.

### Notes and references


### Table 1

<table>
<thead>
<tr>
<th>Host 1 conversion (24 h)</th>
<th>Host 1 selectivity (HT)</th>
<th>Host 2 conversion (24 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I)</td>
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<tr>
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<td>no Host 1 cis (24 h)</td>
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<tr>
<td>(II)</td>
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</table>

### References

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