

# Self-Assembled Benzophenone Bis-urea Macrocycles Facilitate Selective Oxidations by Singlet Oxygen

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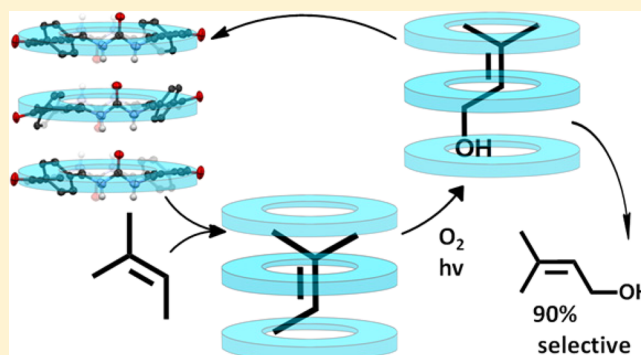
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## S Supporting Information

**ABSTRACT:** This manuscript investigates how incorporation of benzophenone, a well-known triplet sensitizer, within a bis-urea macrocycle, which self-assembles into a columnar host, influences its photophysical properties and affects the reactivity of bound guest molecules. We further report the generation of a remarkably stable organic radical. As expected, UV irradiation of the host suspended in oxygenated solvents efficiently generates singlet oxygen similar to the parent benzophenone. In addition, this host can bind guests such as 2-methyl-2-butene and cumene to form stable solid host–guest complexes. Subsequent UV irradiation of these complexes facilitated the selective oxidation of 2-methyl-2-butene into the allylic alcohol, 3-methyl-2-buten-1-ol, at 90% selectivity as well as the selective reaction of cumene to the tertiary alcohol,  $\alpha,\alpha'$ -dimethyl benzyl alcohol, at 63% selectivity. However, these products usually arise through radical pathways and are not observed in the presence of benzophenone in solution. In contrast, typical reactions with benzophenone result in the formation of the reactive singlet oxygen that reacts with alkenes to form endoperoxides, dioxetanes, or hydroperoxides, which are not observed in our system. Our results suggest that the confinement, the formation of a stable radical species, and the singlet oxygen photoproduction are responsible for the selective oxidation processes. A greater understanding of the mechanism of this selective oxidation could lead to development of greener oxidants.



## INTRODUCTION

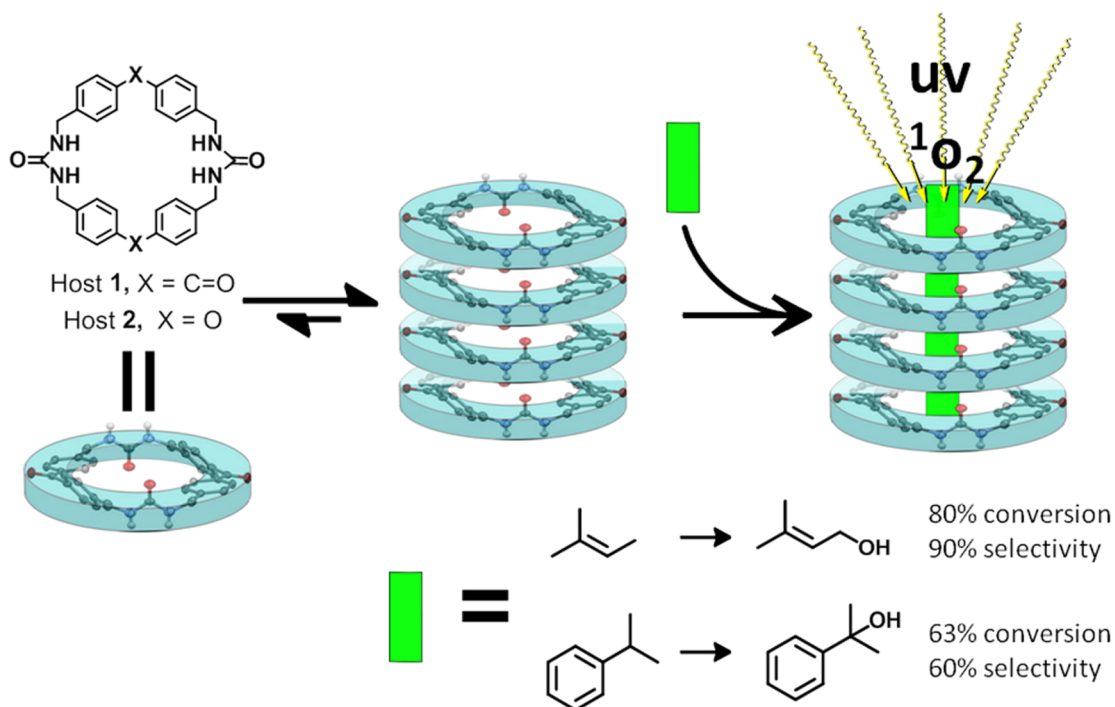
Oxidations of small-molecule alkenes are of importance in the synthesis of pharmaceuticals<sup>1</sup> as feedstock for industrial chemistry<sup>2</sup> and have important repercussions in biological systems.<sup>3–5</sup> Typical oxidants include potassium permanganate, selenium dioxide, and strong acids such as chromic and nitric acid, which are highly reactive and toxic and generate stoichiometric amounts of waste. An alternative and more environmentally friendly oxidation method would incorporate molecular oxygen, the smallest conceivable oxidant. The first excited electronic state of molecular oxygen, also known as singlet oxygen, is produced by irradiation of ground state triplet oxygen (g) with light in the presence of a triplet sensitizer such as Rose Bengal, TPP (5,10,15,20-tetraphenyl porphyrin), or benzophenone.<sup>6–8</sup> Our group has developed bis-urea macrocycles (**1** and **2**) that assembled into columnar nanotubes, which have accessible intrinsic channels for binding guests.<sup>9–12</sup> A phenylether bis-urea macrocycle (host **2**) was used to facilitate the selective reaction of enones such as cyclohexenone and methyl cyclopentenone to afford their [2 + 2] cycloadducts in the solid state.<sup>13,14</sup> Herein, we investigate the photophysical properties of a bis-urea macrocycle **1** that has two

benzophenone units in its framework and show that this self-assembled host generates an unusually stable radical under ambient light and atmospheric conditions. When UV-irradiated in oxygenated solutions or under an oxygen atmosphere, this self-assembled host also acts as a sensitizer to generate single oxygen. We report the use of the bis-urea host **1** as a porous material to absorb small molecule guests and to facilitate the selective oxidation of the encapsulated guest upon UV irradiation in an oxygen atmosphere (Figure 1).

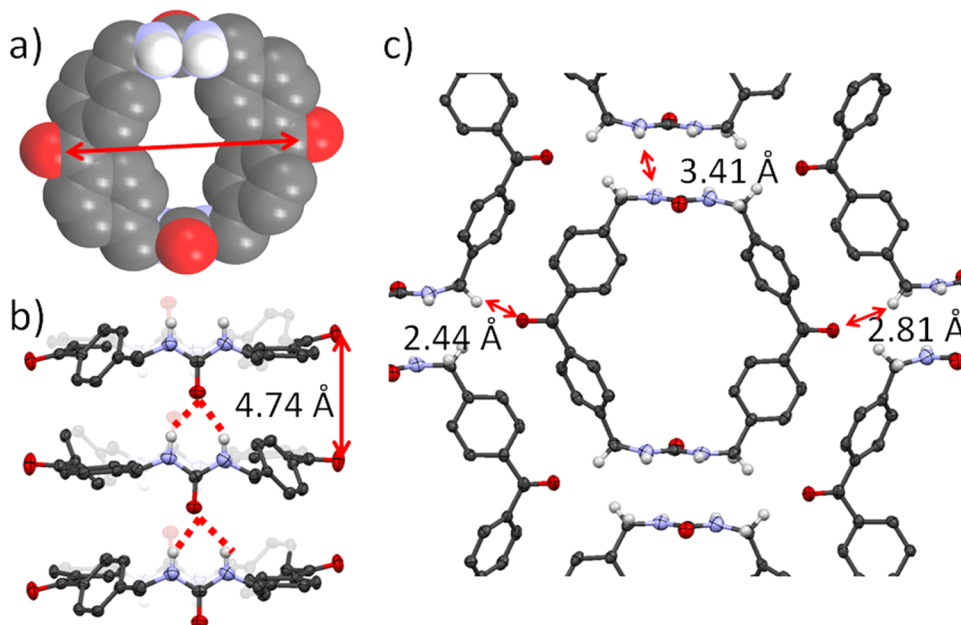
The small size and high reactivity of singlet oxygen often leads to unselective oxidation reactions. In order to tune the selectivity and regiochemistry of the oxidation, researchers have investigated the use of molecular containers such as porous polymers,<sup>16,17</sup> zeolites,<sup>18–22</sup> and microemulsions.<sup>23</sup> For example, Arumugam reported the use of sodium infused Nafion beads as a microenvironment for the oxidation of 1,2-dimethyl cyclohexene with singlet oxygen at high yields (85%) and high conversion (90%) to selectively afford the endocyclic allylic peroxide, 1,2-dimethyl cyclohex-2-ene peroxide (89:11, en-

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**Figure 1.** Host 1, a benzophenone containing bis-urea macrocycle, self-assembles into crystalline columnar structures that can absorb small guests.<sup>15</sup> UV-irradiation of these solid complexes under an oxygen atmosphere affords selective oxidations.



**Figure 2.** Views from the crystal structure of host 1.<sup>15</sup> (a) Space-filling model of a single macrocycle highlighting the cavity. The distance between the carbonyl carbons of benzophenone is 6.84 Å accounting for van der Waals radii. (b) View along a single column illustrates the three-centered urea hydrogen bonding motif, which controls the average distance between neighboring benzophenone carbonyls (C...C) to 4.74 Å (ellipsoids shown at 60% probability level and some hydrogens have been omitted for clarity). (c) Crystal packing showing select close contacts between one macrocycle and its nearest neighbors.

do:exo).<sup>17</sup> Ramamurthy et al. facilitated the selective oxidation and “*cis*”-hydrogen abstraction of alkenes in a Na–Y dye-supported zeolite.<sup>18,22</sup> Tung et al. observed hydrogen abstraction from the largest branch of the alkene during oxidation in the presence of a ZSM-5 zeolite.<sup>20</sup> Work by Griesbeck demonstrated the use of SDS microemulsions to convert a tertiary peroxide into an epoxy enone.<sup>23</sup> These examples showed that confinement is an effective way to

control the reactivity and selectivity of molecular oxygen and inspired us to design a system that incorporated a sensitizer, such as benzophenone, into the spacer group of our bis-urea macrocycles.

Benzophenone is an efficient triplet sensitizer, with an intersystem crossover quantum yield from the singlet excited state to the triplet state that is unity and a crossover rate of 10<sup>11</sup> s<sup>-1</sup>.<sup>24</sup> Benzophenone has been used for systems such as

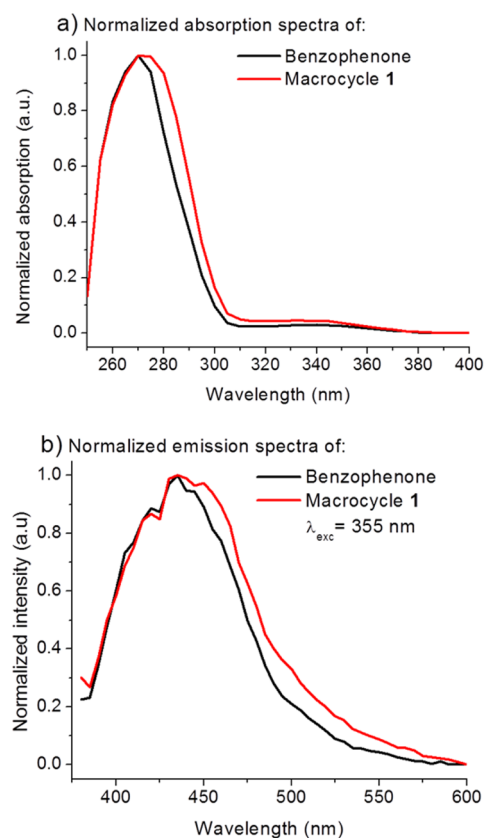
photoinitiators in polymerizations,<sup>25,26</sup> as a substrate for the oxidation of environmental pollutants,<sup>27</sup> and as antimicrobial coatings.<sup>28,29</sup> Our tailored photosensitizer **1** (Figure 2) preorganizes two benzophenone groups close in space within a small macrocycle.<sup>15</sup> These sensitizers are separated by urea and two methylene units, and the X-ray structure shows that the two benzophenone carbonyl carbons within a single macrocycle are separated by  $\sim 7$  Å accounting for van der Waals radii. Macrocycle **1** self-assembles through typical three centered urea hydrogen bonding assisted by aryl stacking interactions to give host **1**. This porous host has been used to absorb *trans*- $\beta$ -methylstyrene and facilitated the *cis*-*trans* isomerization under UV irradiation, a process that requires a triplet sensitizer.<sup>15</sup> This manuscript investigates the effect of the proximity of the benzophenones in host **1** on its photophysical properties including absorption and emission spectroscopy, phosphorescence quantum yield, and radical generation. The solid-state emission quantum yield and lifetimes of host **1** were observed to be considerably less/shorter than that of benzophenone itself. Under ambient conditions, we observed a remarkably stable organic radical with host **1** in contrast to the radical of benzophenone, which can only be observed through radical trapping or at low temperatures.<sup>30–33</sup> UV irradiation of **1** suspended in oxygenated  $\text{CDCl}_3$  gave singlet oxygen, which was identified by its emission in the near IR.<sup>1,7</sup> We then studied the uptake of a series of small molecules by host **1** to form stable solid inclusion complexes. Finally, we investigated the oxidation of the guest in these crystalline complexes and observed that 2-methyl-2-butene and cumene afforded selective oxidation reactions, while other guests were unreactive. Our hypothesis is that oxidation of these two guests proceeds through a confinement-assisted radical and singlet oxygen-mediated mechanism (auto-oxidation) in the presence of host **1**.

## RESULTS AND DISCUSSION

The bis-urea benzophenone macrocycle (host **1**) was synthesized as previously reported.<sup>15</sup> The 4,4'-dibromomethylbenzophenone was cyclized with triazinanone under basic conditions. The triazinanone protecting groups were removed by heating in an acidic aqueous/methanol (1:1 v/v) solution of diethanol amine to afford the bis-urea macrocycle **1**. Upon crystallization from DMSO, compound **1** self-assembled into columnar structures through strong directional urea-urea hydrogen bonding assisted by edge-to-face aryl-aryl stacking to give host **1**.<sup>15</sup> Inspection of the crystal structure of host **1** shows the resulting columnar structure with an internal cavity having  $6.84$  Å (urea carbonyl...urea carbonyl minus van der Waals)  $\times$   $4.68$  Å (aryl...aryl minus van der Waals) dimensions (Figure 2a). In the assembled structure, the benzophenone groups on neighboring macrocycles (above and below) are close in space with an average distance of  $4.74$  Å (Figure 2b). Individual columns pack together into a hexagonal array. Figure 2c illustrates the close contacts between the neighboring tubes with respect to the benzophenone carbonyl and the urea groups. The benzophenone carbonyl oxygen forms a close interaction with the acidic methylene CH's on the adjacent column with O...H(C) distances of  $2.44$  and  $2.81$  Å. The urea groups of the neighboring columns are also close packed with a N...N distance of  $3.41$  Å. In solution, the parent benzophenone is a monomer and an efficient triplet sensitizer. Our first question was how the incorporation of two benzophenone monomers into a cyclic small molecule would affect its

photophysical properties? To probe the photophysical properties of host **1**, we examined its absorption and emission (phosphorescence) spectra and determined its phosphorescent quantum yield in solution where it is not assembled. Next, we address the effects of assembly and crystal packing on the photophysical properties by characterizing its phosphorescent quantum yield and its excited state lifetime in the solid-state. These studies were carried out in solution, where the macrocycle is not assembled and in the solid state, where the assembly is expected to further impact the photophysical properties.

The absorption and emission of monomer **1** (unassembled) was analyzed to determine if the incorporation into the cyclic system effected the generation of the triplet state of benzophenone. The host was only soluble in DMSO, an aggressive solvent that precludes self-assembly. UV-vis and fluorescence studies were conducted on a  $0.025$  mM solution of benzophenone and the macrocycle **1** in DMSO. Figure 3a

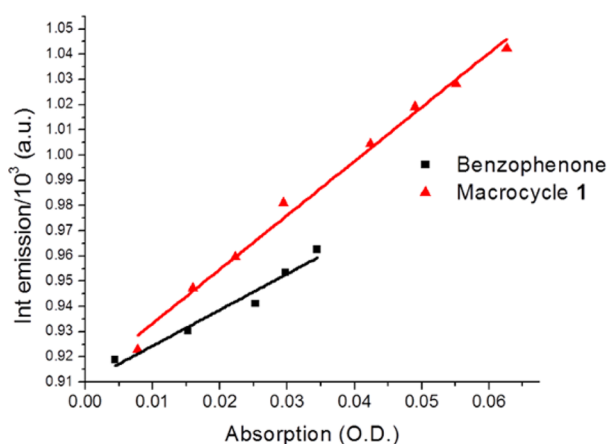


**Figure 3.** Normalized absorption and emission spectra of host **1** (red) versus benzophenone (black) in DMSO: (a) UV-vis absorption of  $2.5 \times 10^{-5}$  M solution of benzophenone (black) and macrocycle **1** (red) in DMSO; (b) normalized emission spectra of the same solutions excited at 355 nm.

shows the adsorption and fluorescence of macrocycle **1** (red) and benzophenone (black). Comparing the two spectra, we see that macrocycle **1** retains the major spectroscopic properties that are observed with benzophenone. The absorption spectra both show the typical bands for  $\pi$ - $\pi^*$  excitation at  $\lambda_{\text{max}} \sim 270$  nm, and the  $n$ - $\pi^*$  excitation at  $\lambda_{\text{max}} \sim 345$  nm. No additional bands are apparent, suggesting that the proximity of the two benzophenones within a macrocycle has little effect on the absorption. Macrocycle **1** has a molar absorptivity coefficient of

$\epsilon = 622 \pm 20 \text{ M}^{-1} \text{ cm}^{-1}$  in DMSO, approximately twice that of benzophenone ( $\epsilon = 342 \pm 60 \text{ M}^{-1} \text{ cm}^{-1}$ ). Next, both benzophenone and macrocycle **1** DMSO solutions were excited at 355 nm. The emission of **1** and benzophenone were similar with a  $\lambda_{\text{max}}$  at 435 nm. The broadening of the peaks is due to the polarization effect of DMSO. These studies suggest that the cyclization did not influence the photophysical character of the benzophenone and allows us to compare the emission quantum yields of the two compounds.

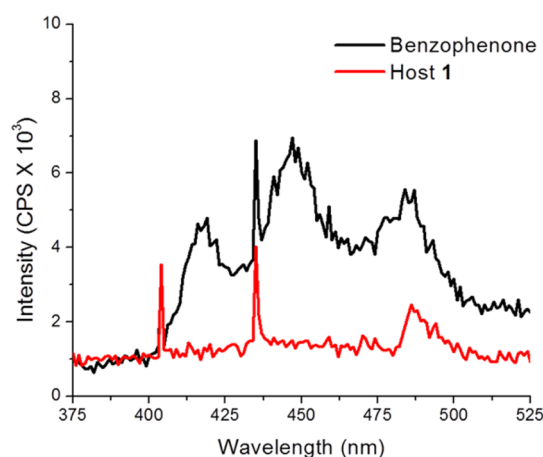
To study the phosphorescence quantum yields, a series of five solutions of benzophenone (concentrations = 0.012–0.070 mM) and eight solutions of macrocycle **1** (benzophenone concentrations (two per cycle) = 0.012–0.091 mM) were prepared in argon-degassed DMSO. For each solution, the absorption and the integrated emission were recorded on a Molecular Devices Spectra Max M2 fluorimeter. This was plotted and fitted using a linear relation method (Figure 4).



**Figure 4.** Plot of the absorption vs integrated emission of macrocycle **1** (red) vs benzophenone (black). The ratio of the linear plots slopes was 1.5.

Analysis of Figure 4 demonstrated that in the concentration range of 0.012–0.070 mM the cyclization of two benzophenones within host **1** resulted in a 50% increase of the quantum yield relative to the free benzophenone in DMSO.

Emission quantum yields are effected by solvent polarity,<sup>34,35</sup> proximity, or availability of quencher,<sup>36,37</sup> and assembly or aggregation.<sup>24</sup> Thus, we were interested if the increase in quantum yield observed in solution was retained upon assembly in the solid state. Host **1** was prepared by crystallization from a slow cooled solution in DMSO. A 10 mg powder sample of benzophenone and 10 mg of freshly evacuated crystals of host **1** were used to measure the quantum yield. The quantum yield was measured on a Horiba Fluorolog 3 with the fiber optic and Quanta- $\phi$  accessories. Figure 5 shows the resulting spectra with the expected phosphorescent peaks for benzophenone (black) with a quantum yield of 0.5% at ambient conditions. Surprisingly, the emission of the host **1** crystals (Figure 5 red) was not detected by the instrument, which indicates a quantum yield of <0.1%. Such difference between the liquid and the solid-state emission behaviors of benzophenone and the host **1** suggests that the close proximity of benzophenone moieties within the assembled host **1** system significantly increases the quenching of the excited states. In light of these results, we next evaluated the lifetimes of the two samples.

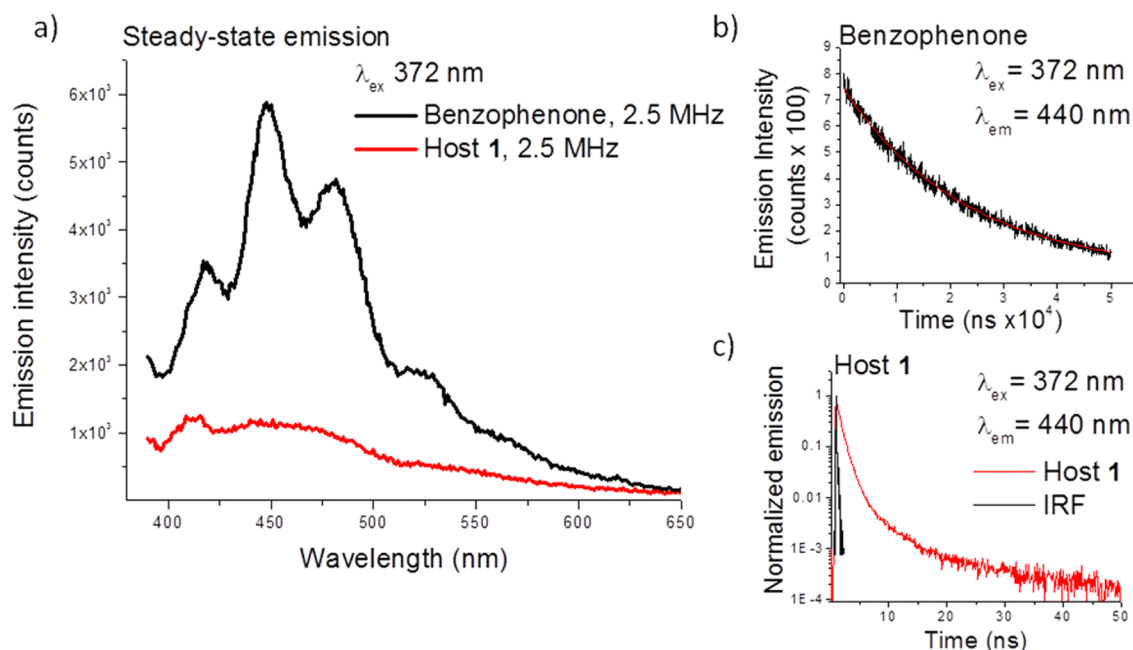


**Figure 5.** Emission spectra of solid host **1** and benzophenone showing the phosphorescent peaks between 375 and 525 nm ( $\lambda_{\text{ex}} = 355 \text{ nm}$ ). The measurements were taken in a Horiba Quanta- $\phi$  integrating sphere at ambient conditions.

Crystalline powder samples of the benzophenone and host **1** system were sandwiched between two quartz slides, and the samples were excited at 372 nm with a picoseconds pulsed diode laser (LDH-P-C-375) with a repetition rate of 1 kHz for the benzophenone sample and 2.5 MHz for the host **1** sample (Figure 6). The solid state room temperature phosphorescent lifetimes of benzophenone showed a single exponential decay with the expected lifetime of  $22.6 \pm 0.3 \mu\text{s}$ . This value compares well to literature values.<sup>38</sup> The solid-state emission of the host **1** crystals had similar steady-state spectra to benzophenone, but the lifetime decay was markedly shorter. The phosphorescence decay showed a multiexponential character independent of the observation wavelength (430–640 nm). Table 1 shows that the decays ranged from 36 ps ( $\tau_1$ ) to 4.3 ns ( $\tau_4$ ) with the weighted average lifetime of 320 ps. Such dramatic decrease in the solid-state quantum yield and lifetime of host **1** suggests that the assembly/packing of benzophenone within the host **1** solid-state structure makes the benzophenone more accessible to quenching or nonradiative relaxation than that of the compact structure of benzophenone in the solid-state.

Our absorption/emission studies suggested that in solution, host **1** has similar photophysical properties to benzophenone and may have an increased phosphorescent quantum yield. In contrast, in the solid state, the lifetime of host **1** appears to be significantly shortened. Our primary interest in these self-assembled macrocycles is to produce functional materials for controlling reactivity. Thus, we proceeded to test if host **1** could facilitate the production of singlet oxygen in spite of its diminished emission lifetime and quantum yield. Therefore, freshly prepared crystals of host **1** were suspended in oxygenated  $\text{CDCl}_3$  and excited at 345 nm ( $\lambda_{\text{max}}$  absorption of host **1**) and the emission in the near IR was monitored. A strong emission at 1270 nm was observed corresponding to the phosphorescence of the  $^1\text{O}_2$  species (Figure 7).<sup>24</sup> Comparison of IR spectra (Supporting Information, Figure S43 and Table S5) and  $^1\text{H}$  NMR spectra in  $\text{DMSO}-d_6$  of the host **1** crystals before and after UV irradiation in the presence of oxygen showed no change, suggesting that the host is stable during the process of generating singlet oxygen and does not react with singlet oxygen. However, it is possible that a reactive oxygen species could be formed reversibly in the host's cavity. Such a



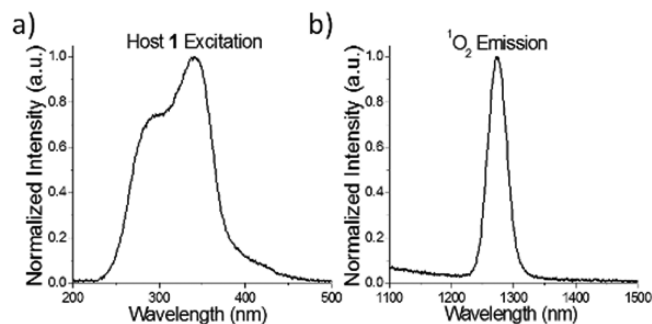


**Figure 6.** (a) Steady-state emission spectra ( $\lambda_{ex} = 372$  nm) of benzophenone and host **1** samples taken on TCSPC (time-correlated single photon counting) system. (b) Phosphorescence decay of benzophenone showing single exponential decay fit with lifetime of 22.6  $\mu$ s. (c) Phosphorescence decay of host **1**.

**Table 1. Time Constants ( $\tau_i$ ) and Normalized (to 1) Pre-exponential Factors ( $A_i$ ) of the Multi-exponential Function Fitting the Emission Transients of Solid-State Host **1** at Room Temperature ( $\lambda_{ex} = 372$  nm)**

lifetime ( $\tau$ , ns) <sup>a</sup>	pre-exponential factor ( $A$ ) <sup>b</sup>
0.036	0.64
0.33	0.14
1.0	0.21
4.3	0.01

<sup>a</sup>The fit quality was inspected using the weighted residuals and the values of  $\chi^2$  which in all cases were <1.1. <sup>b</sup>All amplitudes are normalized in the following way:  $\sum_{i=1}^n A_i = 1$ .

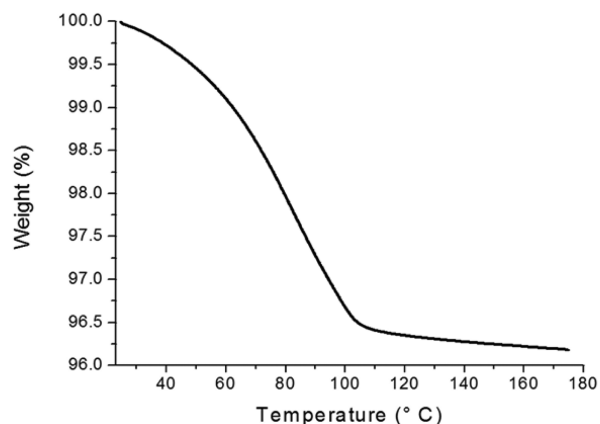


**Figure 7.** Absorption spectra of host **1** suspended in oxygenated CDCl<sub>3</sub>: (a) absorption spectra of host **1** crystal suspension showing a  $\lambda_{max}$  of 345 nm; (b) near IR emission spectra of singlet oxygen produced from the excitation of the host **1** crystals at  $\lambda_{max}$ .

species could also influence the selectivity and efficiency of an oxidation reaction that occurs within the host's channel.

Work done by Adams, Clennen, and others,<sup>1,7,40–43</sup> suggested that simple alkenes react with singlet oxygen to form peroxides and are then subsequently reduced to the corresponding alcohols. Would host **1** also mediate the


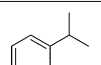

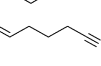

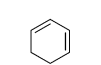

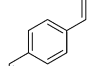

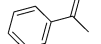
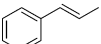
oxidation of small molecules with singlet oxygen? We selected alkenes based on their size and shape, mindful of the size of our hosts' cavity, which forms a linear channel that runs the length of the crystals and has a dimension of  $\sim 7 \times 4$  Å. We then examined the loading of these alkenes into the host **1** crystals. First, crystals of **1** were soaked in neat liquid guests for 18 h and vacuum filtered. The loading of guests was monitored by TGA analysis and <sup>1</sup>H NMR. No loading was observed for the alkane such as hexanes and cyclohexanes. Thus, we used hexanes to transfer and to rinse the other crystalline complexes to remove any surface absorbed guests. The crystals were allowed to set on the filter apparatus for 10 min to remove excess hexanes. The loading of 2-methyl-2-butene (**3**) was monitored by TGA and showed a single step desorption curve at 75 °C which corresponded to a 3.5% weight loss (Figure 8). Assuming this weight loss is due to the loss of 2-methyl-2-butene (**3**), we



**Figure 8.** TGA graph with a single-step desorption of 2-methyl-2-butene (**3**) from the host/guest complex showing to 3.5% weight loss, which corresponds to a 3:1 binding of 2-methyl-2-butene (**3**) with host **1**.

calculated the host:guest stoichiometry in the complex as 3:1 (Table 2). An independent assessment of the host:guest ratio

**Table 2. Absorption of Guests by Host 1**

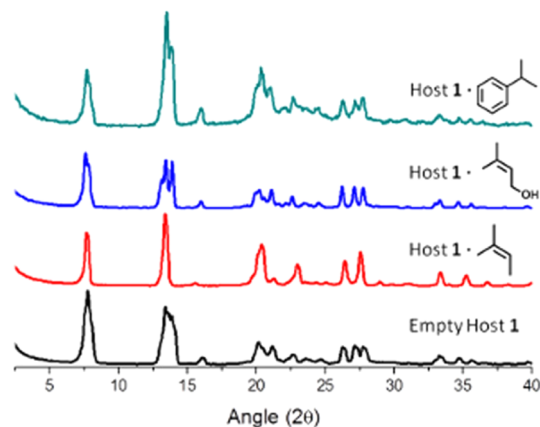
Alkene	Guest	Loading (host:guest) <sup>a</sup>	Loading (host:guest) <sup>a</sup>
		3.0:1	5.6:1
		4.0:1	5:1
		4.0:1	2:1
		5.0:1	3.5:1
		2.7:1	3:1
			2.5:1

<sup>a</sup>All host/guest ratios are an average of at least three separate loading experiments by TGA.

was also done by dissolving a sample of the complex (2 mg) in DMSO-*d*<sub>6</sub>. Integration of the <sup>1</sup>H NMR spectra gave a host:guest ratio of 3.2:1, similar to the TGA experiment. Table 2 summarizes the host/guest loading for a series of guests as determined by TGA. The reported values are an average of at least three binding experiments. In general, the smaller more compact alkenes were loaded in higher ratio with cyclohexadiene (8) affording a complex with 2:1 host/guest stoichiometry, while the styrenes (12 and 13), *trans*-2-pentene (11), and 2-methyl-2-butene (3) formed complexes with ~3:1 stoichiometry. The 2,3-dimethylbutene (5) and 3-methyl-2-buten-1-ol (7) displayed a ~4:1 host/guest ratio. Cumene (4) and 2-methyl-2-pentene (9) loaded at the lowest ratios and showed 6:1 and 5:1 host/guest ratios, respectively. No loading was observed for methylcyclopentene, methylcyclohexene, and 1,2-dimethylcyclohexene.

Preorganization of guests inside the cavity of our system appears to be a key feature for inducing selectivity inside bis-urea host systems,<sup>11,13,44</sup> although selectivity can also be enhanced by the fit of the products as seen with coumarins in the phenylethynylene host.<sup>12</sup> We tested the effect of guest encapsulation on the crystallinity of host 1. Host 1 crystals freshly recrystallized from DMSO, which typically gave microcrystals of ~150 μm × 10 μm as assessed by SEM, which were too small for single-crystal analysis, although larger crystals were occasionally observed. Both sizes of crystals were subjected to TGA or heated to 180 °C for 2 h to remove the DMSO solvent and afford the “empty host”. Unfortunately, upon removal of solvent, the large single crystals were not of quality for single-crystal analysis. Host 1-DMSO crystals were ground to a powder and examined by powder X-ray diffraction (PXRD) experiments to monitor structural changes upon absorption/desorption of guests. As observed previously, the PXRD pattern of the ground crystals was similar to the theoretical pattern, generated from the single crystal structure, suggesting that the ground powder was of single phase with a similar structure (Figure S19, Supporting Information). The DMSO was removed by heating and the powder submitted for PXRD. The “empty” host 1 crystals show a distinct and well-

defined pattern that suggests a highly crystalline and ordered system (Figure 9, bottom). The host 1 powder was treated with



**Figure 9.** Comparison of PXRD patterns of host 1 empty, host 1-2-methyl-2-butene (3) complex, host 1-3-methyl-2-buten-1-ol complex (7), and host 1-cumene (4).

2-methyl-2-butene (3) as described to give the complex with 3:1 host:guest stoichiometry and examined by PXRD (Figure 9). While qualitatively the two patterns appear similar, we observed differences which include but are not limited to shifts in low angle peaks (7.75 to 7.65 in the complex), a sharpening of the broad band at 13.4, and disappearance or shifting of the 16.10 to a new band at 15.50. The 2-methyl-2-butene (3) guest was removed by TGA (25–180 °C, heating rate 10 °C/min), which gave a pattern nearly identical to the empty host, suggesting that absorption and desorption of guests does not irreversibly change the host structure. Treatment of host 1 with 3-methyl-2-buten-1-ol (7) afforded a 4:1 host:guest complex, and treatment of host 1 with cumene (4) resulted in a 5.6:1 host guest complex. Both of these complexes were also highly crystalline (Figure 9, top). Comparison of the four patterns in Figure 9 suggest that there are some changes in the structure of the host but that each complex is well-ordered and highly crystalline.

Next, we tested if host 1 could facilitate the oxidation of these guests within each of these complexes. Host 1-guest complex crystals (10 mg) were loaded into a quartz test tube and purged with dry oxygen for 5 min. The crystals were then irradiated in a Rayonet RPR-200 UV reactor equipped with RPR-3500 lamps for 0–18 h. Samples (2 mg) of the host-guest complexes were removed at intervals, dissolved in DMSO-*d*<sub>6</sub>, and analyzed by NMR spectroscopy. Integration of the <sup>1</sup>H NMR spectra gave estimates of conversion. Complexes that showed reaction were further analyzed by extracting the guest from the complex with deuterated solvents (sonication 2 × 10 min in CD<sub>2</sub>Cl<sub>2</sub> or CD<sub>3</sub>CN) and subsequent analysis by GC/MS, <sup>1</sup>H NMR and GC/FID to monitor conversion and product distribution. Interestingly, no quenching or neutralization step was used, yet no peroxides were detected. In most cases, UV-irradiation of the complexes did not facilitate any reaction, and the starting materials (alkenes (5, 8, 9, 11),  $\alpha$ -methylstyrene (12), divinylbenzene (10), and hex-5-enitrile (6)) were simply reisolated from each complex. UV irradiation of host 1- $\beta$ -methyl styrene (13) afforded benzaldehyde, which is the typical product under singlet oxygen.<sup>6,45,46</sup>

UV irradiation of the host 1-2-methyl-2-butene (3) complex facilitated a selective oxidation and gave a product distribution

## Scheme 1. Oxidation of 2-Methyl-2-butene under Selected Reaction Conditions

Conditions	% conversion	Selectivity				
Host 1	80	--	--	--	90	10
Host 2	--	--	--	--	--	--
Benzophenone/ benzene CH <sub>3</sub> CN <sup>a</sup>	68	12	23	65	--	--
Zeolite/thionin <sup>b</sup>	75	72	28	--	--	--

<sup>a</sup>Conversion after 3.5 h = 68%. <sup>b</sup>Isolated yields 65–75% no time reported.<sup>39</sup>

## Scheme 2. Oxidation of Cumene under Selected Reaction Conditions

Conditions	% conversion	Selectivity		
Host 1 Ru <sup>IV</sup> O <sup>2+</sup> / CH <sub>3</sub> CN <sup>a</sup>	69	71	4	25
CuO nanoparticles	44.2	93	2.5	4.5

<sup>a</sup>Along with trace amounts of 2-phenylpropanal and 2-phenylpropenal.<sup>55</sup> <sup>b</sup>Zhang et al.<sup>56</sup>

that differs from what is typically observed with oxygen/triplet sensitizer conditions.<sup>6,47</sup> After 30 min of UV irradiation in an oxygen-rich atmosphere, we observed 50% conversion of 2-methyl-2-butene (3) as estimated by integration of the <sup>1</sup>H NMR spectra in DMSO-*d*<sub>6</sub>. <sup>1</sup>H NMR spectra showed the emergence of four new peaks, 1.58 (s), 1.66 (s), 3.90 (t), and 5.25 (t) ppm consistent with the formation of an allylic alcohol. Upon increase of the irradiation time, we observed increased conversion (60% at 1 h and 80% at 2 h). Longer irradiation times gave no further conversion. The GC/MS trace showed the extract contained two products, which were identified by coinjection with commercial standards. GC/FID also suggested an 80% conversion at 2 h. The first product was the allylic alcohol, 3-methyl-2-buten-1-ol (7), which was formed in 90% selectivity. The second product corresponded to 3-methyl-2-buten-1-al (8) (10%), which represents the further oxidation of the initial alcohol to the corresponding aldehyde. In comparison, reaction of 2-methyl-2-butene (3) in oxygenated benzene/CH<sub>3</sub>CN with benzophenone as a sensitizer give 68% conversion at 3.5 h to afford the oxirane (16) as the major product (65% selectivity) from the [2 + 2]-cycloaddition as well as two oxygen-ene products, 3-methyl-3-buten-2-ol (14) and 2-methyl-3-buten-2-ol (15), in ~1:2 ratio (Scheme 1 entry 3).<sup>6,47</sup> We repeated our experiments at 0 °C to examine the effect of temperature and observed similar selectivity and conversion. No reaction was observed when host 1:2-methyl-2-butene (3) was UV irradiated under argon (g) atmosphere. The product of the oxidation of the guest in the host 1:2-methyl-2-butene complex is one that could arise through a radical mechanism, which is also referred to as an autoxidation.<sup>24</sup> This product is also observed upon oxidation of 2-methyl-2-butene (3) using selenium dioxide, where the selenium dioxide coordinates with the alkene and then through a [1,3] sigmatropic rearrangement forms the allylic selenium ester.

Subsequent hydroxylation of the ester then results in the allylic alcohol with efficient selectivity of the *E* isomer.<sup>48–51</sup>

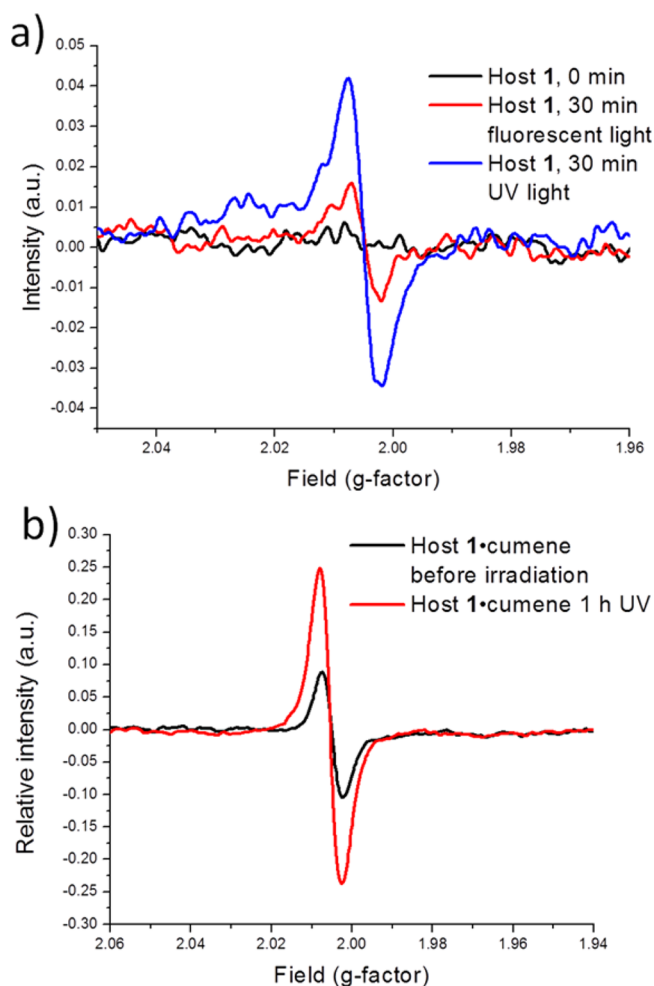
Given the unusual product observed in the oxidation of 2-methyl-2-butene (3) in the complex, we next tested if the host 1 could be used as a catalyst to mediate the oxidation of the alkene in solution. We looked at water, acetonitrile, and water/acetonitrile mixtures due to the relatively short lifetime of singlet oxygen in these solvents ( $\tau^1\text{O}_2 \sim 3.5 \mu\text{s}$  in H<sub>2</sub>O versus 54  $\mu\text{s}$  in CH<sub>3</sub>CN). In addition, water and 1:9 acetonitrile/water should favor absorption of the alkene by the host.<sup>53,54</sup> The host (1 mg, 5 mol %) was suspended in oxygenated alkene solutions (10 mM, 5 mL). The suspensions were then irradiated under UV light in a Rayonette reactor for 2 h. A sample of the products was extracted and worked up with excess triphenyl phosphine to reduce any peroxides, and the products were monitored by GC/FID with phenol as an internal standard. The retention times were compared with known standards of the products. We observed no selectivity for 3-methyl-2-buten-1-ol (7), suggesting that only a low percentage of the reaction occurred in confinement. We observed 25% conversion upon 2 h of UV irradiation in water and acetonitrile/water to give only two products. The products in 1:9 acetonitrile/water were 3-methyl-3-buten-2-ol (14) (53%) and 2-methyl-3-buten-2-ol (15) (47%), which are the typical products when benzophenone is used as a sensitizer. No oxirane (16) was formed, which is not surprising since the host is not soluble. None of the primary allylic alcohol (7) was observed, which in contrast was the major product for the solid host/guest complex. In acetonitrile after 2 h of UV irradiation, the reaction reached 50% conversion affording 14 (47%), 15 (44%), and the primary allylic alcohol, 3-methyl-2-buten-1-ol (7) (9%). Our hypothesis is that 7, a primary allylic alcohol, was produced when the reaction occurred in confinement. Studies are being conducted to optimize the reaction conditions with other solvent systems such as acetone and acetone/acetonitrile mixtures to promote

the catalytic activity. If this process can be further developed and optimized, it might yield a greener catalyst for the formation of pharmaceutical and industrial feedstock.

In order to elucidate the reaction pathway further, we examined the other substrates. Thus, we turned to guests known to oxidize through the radical pathway such as 1,2-dimethyl cyclohexene and cumene (**4**).<sup>55,56</sup> The autoxidation of **4** to the benzyl alcohol has been well developed and is known to proceed through a radical mechanism with an initiator to afford  $\alpha,\alpha'$ -dimethylbenzyl alcohol, an important industrial product (Scheme 2). Our host did not absorb 1,2-dimethylcyclohexene even upon prolonged (24 h) soaking in the liquid; however, cumene (**4**) was absorbed to form a 5.6:1 host/guest complex as seen by TGA and <sup>1</sup>H NMR. The host 1-cumene complex was similarly irradiated (0–18 h) under either oxygen or argon, samples were removed at intervals, extracted in CD<sub>2</sub>Cl<sub>2</sub>, and monitored by <sup>1</sup>H NMR and GC/MS. Analysis by GC/MS of the reaction carried out under oxygen showed 69% conversion of cumene (**4**) to three products:  $\alpha,\alpha'$ -dimethylbenzyl alcohol (**19**) (71%), acetophenone (**20**) (25%), and  $\alpha$ -methylstyrene **12** (4%). The product formation from the oxidation of cumene **4** inside the host **1** system suggests that the oxidation is proceeding through a radical mechanism.<sup>55,56</sup> No reaction was observed when host 1-cumene was UV irradiated under argon (g) atmosphere.

Given that host **1** facilitates the production of singlet oxygen, binds guests, and affords oxidation products that are usually observed through radical-mediated mechanisms, we next investigated if the host itself might afford radicals. The formation of a stable host radical during the UV-irradiation might also explain our observations of the curiously shortened phosphorescence lifetime in solid host **1**. The literature provides examples where the parent benzophenone radical is observed; however, it is certainly not long-lived and has not been observed at room temperature. The benzophenone radical has been detected through radical trapping with nitroxides,<sup>31,57</sup> through H-abstraction,<sup>58</sup> at low temperatures (2 or 77 K)<sup>30,32,59</sup> or through time-resolved ESR measurements in the nano-second time scale.<sup>33,60,61</sup> In the case of host **1**, our experiments suggest that such a radical formed after UV irradiation might be significantly stabilized and detected at room temperature by electron paramagnetic resonance (EPR). Freshly evacuated crystals of host **1** (10 mg) were loaded into an EPR tube and kept in the dark for a week. The sample was purged with argon gas for 30 min in the dark, and the EPR spectra was recorded (Figure 10a, black line), which shows no signal. The sample was then left on the benchtop for 30 min under typical room lights (fluorescent). Surprisingly, the EPR spectra (Figure 10a, red line) shows a peak, indicative of a radical with a g-factor of 2.0049, which is in the range for a lone unpaired electron in an organic substrate.<sup>62</sup> Next, the sample was exposed to UV radiation in a Rayonet reactor equipped with 16 × 120 W lamps (350 nm) for 30 min. The EPR spectra shows a single peak with  $g = 2.0051$ . Benzophenone was also similarly treated, and as expected, no radical was observed at room temperature.

We next tested if the host **1** radical could be generated under ambient air. Host **1** was irradiated (1 h) in Rayonet reactor, and we then observed similar EPR spectra with an identical g-factor (Figure S37, Supporting Information). We kept the sample in the dark and monitored the EPR over the following week to estimate the time needed for the radical to be completely quenched. The EPR signal persisted for days, suggesting that host **1** generates an unusually stable radical that is not



**Figure 10.** Generation of radicals from host **1** crystals as monitored by EPR: (a) host **1** was kept in the dark for 1 week (black line) followed by exposure to fluorescent lighting (30 min, red line) and finally UV-irradiated (30 min, blue line). (b) EPR spectra of host **1**-cumene complex before (black) and after (red) UV irradiation.

quenched by oxygen, nitroxide, or hydroxide radicals from the atmosphere. Stable radicals are of interest for their material properties, in catalysis and for living polymerizations. Stable or persistent families of organic radicals include nitroxide and nitronyl nitroxide radicals,<sup>63</sup> heterocyclic thiazyls,<sup>64</sup> triphenylmethyl,<sup>65</sup> and verdazyl radicals.<sup>66</sup>

Our hypothesis is that selective oxidation of cumene (**4**) and 2-methyl-2-butene (**3**) facilitated by our host may proceed via a radical process. Could the radical be similarly observed in the corresponding solid host-guest complexes? Figure 10b compares the EPR spectra obtained for the host **1**-cumene complex and host **1** after each of these solids were UV irradiated for 1 h at rt under oxygen. In each case, a strong signal was observed at  $g = 2.0051$ . The same experiment was carried out on host **1**-2-methyl-2-butene complex and also showed an identical EPR signal (Figure S39, Supporting Information). Taken together, the data from the EPR experiments suggests that the incorporation of benzophenone into a cyclic bis-urea assembled host has a stabilizing effect on the ketyl radical that is typically formed in the excitation of benzophenone and produces a stable radical at room temperature. The lack of splitting of the peaks suggests that there is no strong coupling with neighboring radicals or nuclei



and that the radical is stabilized either through resonance or fast exchange H abstraction or a combination of the two.<sup>60,67,68</sup> The presence of a radical host species might serve to enhance the formation of singlet oxygen or to initiate or facilitate radical pathways for the oxidation of the guest. A collaborative effort is underway to investigate the nature of this radical computationally to understand its origin and explain its stability. We surmise that the assembled system gives rise to a distorted geometry that might account for both the surprisingly stable radical and the lack of coupling. We are currently investigating if radical polymerizations might be facilitated by this host.

## CONCLUSION

Incorporation of benzophenone into a cyclic bis-urea system resulted in a macrocycle that forms crystalline columnar assemblies through the self-assembly of the ureas. The resulting macrocycle monomer showed an increase in its phosphorescent quantum yield in solutions and dramatic quenching upon assembly into the columnar structures in the solid-state. Studies of the solid-state lifetime of our host displayed a subnanosecond decay time suggesting the solid-state structure was more prone to quenchers such as molecular oxygen and atmospheric water or to nonradiative pathways such as formation of a stabilized radical. Indeed, EPR studies demonstrated that host **1** does give a stable radical when UV-irradiated under argon or at atmospheric conditions. Even ambient fluorescent light was enough to generate the radical, which was stable for days. In contrast, the parent benzophenone did not form a stable radical under ambient conditions. Our hypothesis is that it is the supramolecular assembly that gives rise to this stabilized radical. Other supramolecular assemblies, such as thin films of 1,4,5,8-naphthalene diimides and zirconium also show persistent radicals.<sup>69,70</sup> We are currently using computations to investigate the structure of radicals within the columnar assembly.

Despite its low quantum yield and short lifetime, we found that host **1** could be used to readily generate singlet oxygen both in solution and also when the solid host was irradiated under oxygen atmosphere. Although host **1** crystals readily absorbed small molecule guests to form complexes, only some of these complexes were reactive. The complexes were UV irradiated under an oxygen atmosphere at room temperature and then extracted into deuterated solvent without any additive to neutralize peroxides normally observed in singlet oxygen-ene reactions. In most cases, UV-irradiation of the complexes did not facilitate any reaction, and the starting materials were reisolated. However, three complexes facilitated the oxidation of guests in the solid state. Host **1**· $\beta$ -methylstyrene afforded benzaldehyde, which is the typical product under singlet oxygen. Host **1**·2-methyl-2-butene complex facilitated a selective oxidation in 80% conversion to afford the primary allylic alcohol, 3-methyl-2-butene-1-ol, in 90% selectivity. This product is not typically observed using organic sensitizers. Furthermore, host **1**·cumene complex was oxidized in 69% conversion under conditions similar to those of  $\alpha,\alpha'$ -dimethylbenzyl alcohol at 71% selectivity. After these reactions, the host was recovered without loss, and no changes were observed in the host by IR and <sup>1</sup>H NMR spectroscopy. Cumene is known to undergo autoxidation via a radical process. Thus, the evidence suggests that host **1** acts through a dual role of singlet oxygen sensitization and radical formation to selectively oxidize 2-methyl-2-butene and cumene within host:guest complexes.

Because host **1** displays a long-lived radical by EPR, it is possible that the oxidation proceeds by a mechanism similar to the type I mechanism proposed by Foote et al.<sup>3,71,72</sup> that would involve hydrogen abstraction from the guest to the host **1** to give a resonance-stabilized radical. Subsequent reaction of these radicals with singlet oxygen and reabstraction of the hydrogen from the host could yield the alcohol. Further testing is in progress to determine whether it is the production of singlet oxygen or the formation of the radical that is responsible for the selectivity observed in this host or if it is some combination of the two pathways. Current studies are focused on exploring the mechanism of this transformation. We will also explore the ability for this system to sensitize the oxidation of other small molecules and to mediate radical polymerizations of encapsulated monomers. Future studies will investigate the optimization of conditions (solvent, temperature, etc.) to see if this process can be made both selective and catalytic.

## EXPERIMENTAL SECTION

**General Procedures.** Chemicals were used as received without further purification. <sup>1</sup>H and <sup>13</sup>C NMR were recorded on 300 and 400 MHz NMR. GC-FID analyses were performed on a 30 m capillary column (Rtx-5). A typical oven temperature program was as follows: start at 50 °C, hold for 2 min, ramp to 300 °C at 10 °C/min. The thermometer for melting point was not calibrated.

**Synthesis of 4,4'-Bis(bromomethyl)benzophenone.** Commercially available 4,4'-bis(methyl)benzophenone (10.27 g, 49 mmol) was reacted with *N*-bromosuccinimide (NBS) (18.26 g, 103 mmol) and 2,2'-azobis(isobutyronitrile) (AIBN) (0.080 g, 0.488 mmol) in refluxing carbon tetrachloride (130 mL) for 18 h. The product was purified by flash chromatography (1:9 ethyl acetate/hexanes) to afford a pale yellow solid (16.41 g, 91%): <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>)  $\delta$  = 7.78 (4H, d, *J* = 8.1), 7.51 (4H, d, *J* = 8.4), 4.54 (4H, s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 195.5, 142.5, 137.5, 130.8, 129.3, 32.4; HRMS (EI) [*M*<sup>+</sup>] calcd for C<sub>15</sub>H<sub>12</sub>Br<sub>2</sub> 365.9255, found 365.9244.

**Synthesis of Triazinanone-Protected Bis-urea Benzophenone Macrocycle.** All glassware was dried by heating under vacuum. Triazinanone (1.00 g, 6.36 mmol) and NaH (60% suspension in mineral oil, 0.916 g, 38.16 mmol) were heated to reflux in freshly distilled dry THF (300 mL) under nitrogen atmosphere for 1.5 h. Then the suspension was cooled to room temperature, and a solution of 4,4'-bis(bromomethyl)benzophenone (2.34 g, 6.36 mmol) in dry THF (200 mL) was added dropwise over 1 h. The reaction mixture was heated to reflux for 48 h. Upon completion, the reaction mixture was cooled to room temperature, and excess NaH was neutralized with 1 N HCl (10 mL) and distilled water (100 mL). The reaction mixture was reduced to ~100 mL in vacuo, and the crude product was extracted with methylene chloride (3 × 100 mL). The combined organic layers were washed with brine and dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub>. The product was purified by flash chromatography with methanol/ethyl acetate (1:9) eluent as a white solid (0.694 g, 15%): mp = 230–233 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.81 (8H, d, *J* = 8.4), 7.45 (8H, d, *J* = 8.1), 4.36 (8H, s), 1.10 (18H, s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 196.0, 155.7, 143.5, 136.6, 131.0, 127.4, 63.0, 54.4, 49.2, 28.5; HRMS (EI) [*M* + H<sup>+</sup>] calcd for C<sub>44</sub>H<sub>51</sub>N<sub>6</sub>O<sub>4</sub> 727.3972, found 727.3981.

**Deprotection of Bis-urea Benzophenone Macrocycle (Host 1).** Triazinanone-protected bis-urea macrocycle **1** (0.200 g, 0.275 mmol) was heated to reflux in 1:1 20% diethanolamine (pH ~2 with concd HCl)/water/methanol solution (100 mL) for 48 h. The product precipitated out of solution as a white powder. The powder was vacuum filtered, washed with 1 N HCl (20 mL) and distilled water (3 × 100 mL), and then dried in vacuo (0.144 g, 98%): mp 340 °C dec; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  = 7.73 (8H, d, *J* = 8.1), 7.41 (8H, d, *J* = 8.1), 6.81 (4H, t), 4.36 (8H, d, *J* = 5.4); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  = 196.0, 155.7, 143.5, 136.6, 131.0, 127.4, 63.0, 54.4, 49.2, 28.5; IR (neat)  $\nu$  3317, 1634, 1588, 1426, 1314, 1281, 1172, 1058, 931, 787, 749, 634, 493, 465, 448 cm<sup>-1</sup>; HRMS (EI) [*M*<sup>+</sup>] calcd

for C<sub>32</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub> 532.2111, found 532.2096. CCDC reference numbers for previously reported host 1 (684400).

**Recrystallization and Preparation of Host 1 Crystals.** Host 1 (50 mg) was stirred in hot DMSO (20 mL) in a pressure tube. The mixture was heated to 130 °C until all was dissolved. The solution was then allowed to slow cool at a rate of 1 °C h<sup>-1</sup> to room temperature. The colorless needle crystals were vacuum filtered and heated to 180 °C for 1–2 h to remove any residual DMSO solvent. The crystals were then stored in a desiccator until use.

**Phosphorescence Study of Host 1.** The concentrations of all solutions during quantum yield measurements were such that the absorbance of the band at 310–380 nm was never above 0.1 abs. The concentrations of all solutions were prepared from a stock solution of 0.10 mM benzophenone or host 1 in argon-degassed DMSO. Solutions measured were made by addition of sequential aliquots of 20 μL of the stock solution to 1.5 mL of DMSO, and the absorbance and emission were recorded after each addition. The solid-state phosphorescence was measured on 10 mg sample of host 1 or benzophenone in a spectrometer equipped with an integrating sphere.

**Lifetime Studies.** Samples were prepared by sandwiching 2 mg of powdered benzophenone or crystals of host 1 between two quartz slides and centering the sample in the excitation beam. Phosphorescence lifetimes of the solid-state benzophenone and host 1 crystal samples were measured using a time-correlated single photon counting (TCSPC) system. The system used a 372 nm picosecond pulsed diode laser with laser pulse of 110 ps (fwhm). The detection system consisted of a high speed MicroChannel Plate PhotoMultiplier Tube and TCSPC electronics. The repetition rate varied from 1 kHz for benzophenone to 2.5 MHz for host 1.

**Singlet Oxygen Generation.** A suspension of host 1 crystals were suspended in oxygenated deuteriochloroform. The suspension was irradiated at 345 nm under continuous stirring and the phosphorescence recorded with spectrometer equipped with an air-cooled InP/InGaAs PMT detector.

**General Loading Procedures.** Host 1 crystals were loaded into a vial and then soaked in 0.50 mL of neat alkene for 18 h. The crystals were vacuum filtered and rinsed with 1.5 mL of hexanes (0.5 mL × 3). The crystals were then allowed to sit on the filtering apparatus for 10 min to allow any excess solvent to evaporate. The guest binding was monitored by TGA and <sup>1</sup>H NMR.

**TGA Desorption Studies.** Guest desorption studies were carried out on 10–20 mg of guest absorbed sample. The TGA analysis was done under high purity helium at a heating rate of 10 °C min<sup>-1</sup> from 25 to 180 °C with an isotherm at 180 °C for 5 min. Samples were recollected after analysis for further characterization.

**<sup>1</sup>H NMR Loading Analysis.** All <sup>1</sup>H and <sup>13</sup>C NMR analysis were conducted on a 300 and 400 MHz NMR spectrometer. Host 1-guest complexes (~2 mg) were dissolved in DMSO-*d*<sub>6</sub> (0.500 mL), and the ratios were determined by integration of the resultant peaks.

**Powder X-ray Diffraction Studies.** Empty host 1 crystals as well as freshly loaded crystals of host1-guest were ground to a powder and examined by PXRD. Diffraction data was collected on a powder X-ray diffractometers using Cu K $\alpha$  radiation. The step-scans were collected at +0.05° steps at an angular range of 2–40° 2 $\theta$  at ambient conditions.

**General Oxidation Procedures.** Each solid crystal inclusion complex, such as host 1-alkene complex crystals (10 mg), were loaded into a quartz test tube and purged with dry oxygen for 5 min. The crystals were then irradiated in a UV reactor equipped with 16 × 350 nm lamps for 2 h. A 1–2 mg sample of the host-guest complex was separated from the sample and dissolved in DMSO-*d*<sub>6</sub> to examine the product <sup>1</sup>H NMR peaks with respect to the host peaks. The remaining sample products were extracted from the host 1 complex with deuterated methylene chloride or deuterated acetonitrile and analyzed by GC/mass, <sup>1</sup>H NMR, and GC/FID.

**Solutions.** All solvents were aerated with dry oxygen prior to use by bubbling oxygen through the solvent during sonication (30 min). Host 1 crystals (5 mg) were suspended in the aerated solvent in a quartz test tube. Then 10 molar equiv of the alkene were added. The suspension was then irradiated in a UV reactor equipped with 16350 nm lamps (120 W each) for 2 h. The suspension was worked up with excess

triphenylphosphine and filtered. The filtrate was analyzed by GC/mass, GC/FID, and <sup>1</sup>H NMR. The crystals were dissolved in DMSO-*d*<sub>6</sub> and analyzed by <sup>1</sup>H NMR to check for bound products.

**EPR Studies.** EPR experiments were conducted on 10–30 mg of empty or guest absorbed sample. EPR spectra were recorded on a EPR equipped with an X-band microwave bridgehead.

**Dark Experiment.** Freshly evacuated host 1 crystals (10 mg) were loaded into an EPR tube that was wrapped in aluminum foil and stored in the dark until no EPR signal was observed (~5 days). The sample was then purged with argon gas (99.99% purity) in the dark, and the EPR was recorded. Then the sample was allowed to sit on the benchtop under fluorescent lighting (GE Ecolux) for 30 min and the EPR recorded. The sample was irradiated in a Rayonet UV reactor equipped with 3500 nm bulbs for 30 min, and the EPR was recorded.

**Empty Experiments.** Benzophenone (20 mg) and host 1 crystals (freshly evacuated, 20 mg) were loaded into separate EPR tubes, and the individual spectra were recorded. The host 1 sample was then transferred to the UV reactor and irradiated for 1 h, and the spectra were recorded.

**Loaded Experiments.** Crystals of host 1 (20–30 mg) were loaded as previously reported, and the EPR was recorded. After initial spectra were recorded, the sample was transferred in the sealed EPR tube to the UV reactor and irradiated for 1 h. After irradiation, the sample was transferred back to the EPR to record the spectra.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

CCDC reference numbers for previously reported host 1 (684400). Includes absorption/emission spectra, quantum yields, phosphorescence lifetime studies, GC traces and MS of oxidation products, IR, NMR, and PXRD. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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