

# Closed Nanocontainer Enables Thioketones to Phosphoresce at Room Temperature in Aqueous Solution<sup>†</sup>

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Thiocarbonyl compounds possess unusual photophysical properties: they fluoresce from  $S_2$ , phosphoresce from  $T_1$  only at extremely low concentrations in solution at room temperature, have unit quantum yield of intersystem crossing from  $S_1$  to  $T_1$ , undergo self-quenching at diffusion-controlled rates, and are quenched by ground-state oxygen leading to self-destruction. In this article, we are concerned with finding a new method to observe phosphorescence from thioketones at room temperature in aqueous solution at high concentrations. To achieve this goal, one needs to find ways to eliminate diffusion-limited self-quenching and oxygen quenching. We present here a general strategy that has allowed us to record phosphorescence from a number of thioketones in aqueous solution at room temperature. The method involves encapsulation of thioketone molecules within a “closed nanocontainer” made up of two cavitand molecules known by its trivial name as octa acid. In these supramolecular complexes, despite two thiocarbonyl compounds being present in close proximity, no self-quenching occurs within the confined space due to curtailment of their rotational freedom. Although phosphorescence could also be observed when these thioketones are included in open containers, such as cucurbiturils and cyclodextrins, the closed container made up of octa acid is found to be the best medium to observe phosphorescence from thioketones whose excited state chemistry is essentially controlled by self-quenching.

## Introduction

This article presents results of our studies on phosphorescence at room temperature in aqueous solution of thioketones included in water-soluble containers. Lewis and Kasha, in their pioneering publication in 1945 connecting emission from organic molecules at low temperatures in an organic glass to their lowest triplet state, included thiobenzophenone as an example.<sup>1</sup> The emission in the region of 650–820 nm, although correctly assigned by these workers to be phosphorescence, caused confusion in the literature as to whether the emission was fluorescence from  $S_1$  or phosphorescence from  $T_1$ . In 1972, de Mayo and co-workers showed conclusively that a number of dialkyl and diaryl thioketones emit from their triplet state at 77 K.<sup>2,3</sup> Strong spin-orbit coupling of the thiocarbonyl group allows observation of weak  $S_0$ -to- $T_1$  absorption and  $T_1$ -to- $S_0$  phosphorescence from thioketones. Thus, thioketones exhibit photophysics and photochemistry that are distinctly different from their functional group analogues, ketones.<sup>4–7</sup> The large energy gap between the  $S_1$  ( $n, \pi^*$ ) and  $S_2$  ( $\pi, \pi^*$ ) states allows thioketones to emit from the  $S_2$  state and provides pure  $n, \pi^*$  character to the lowest emitting triplet state.

Although the presence of strong spin-orbit coupling allows thioketones to possess larger radiative rate constants for phosphorescence from  $T_1$ , unfortunately, diffusion-limited self-quenching of phosphorescence at room temperature occurs in solution at concentrations above  $10^{-5}$  M.<sup>8–14</sup> In addition to self-quenching, triplets of thioketones suffer from diffusion-

controlled oxygen quenching.<sup>15–18</sup> Singlet oxygen generated by this process reacts with thioketones, resulting in their destruction.<sup>19,20</sup> Therefore, to be able to record phosphorescence from thioketones at room temperature at higher concentrations, a new method to eliminate diffusion-limited self-quenching and oxygen quenching needs to be identified. This report presents such a method.

In the past, there has been considerable interest in developing methods that allow the ready observation of phosphorescence from aromatic molecules at room temperature.<sup>21</sup> In general, the radiative rate needed to be selectively increased while the radiationless rate and oxygen quenching must be suppressed. Novel methods have been adopted to achieve these goals.<sup>22</sup> Use of micelles, cyclodextrins, and zeolites coincided with non-reactive heavy atom/cation-containing cohosts resulted in selective enhancement of radiative rate constants of aromatic hydrocarbon molecules and olefins at room temperature, and encapsulation in a confined space helped to reduce oxygen quenching.<sup>23–27</sup> Thioketones pose a different set of challenges: they have a high radiative rate constant, and therefore, no external stimuli is needed to phosphoresce. However, in the case of thioketones, self-quenching must be suppressed. Previous studies have alleviated the problem of self-quenching to some extent with the use of micelles in water and with cyclodextrin, calixarene, and cellulose as hosts in the solid state.<sup>28–35</sup> We demonstrate in this report that a cavitand known by the trivial name octa acid (OA), which has not been explored previously in the context of room temperature phosphorescence, performs a far better job than any of the organic hosts explored thus far. We also compare the performance of OA as a container to enhance phosphorescence from thioketones at room temperature

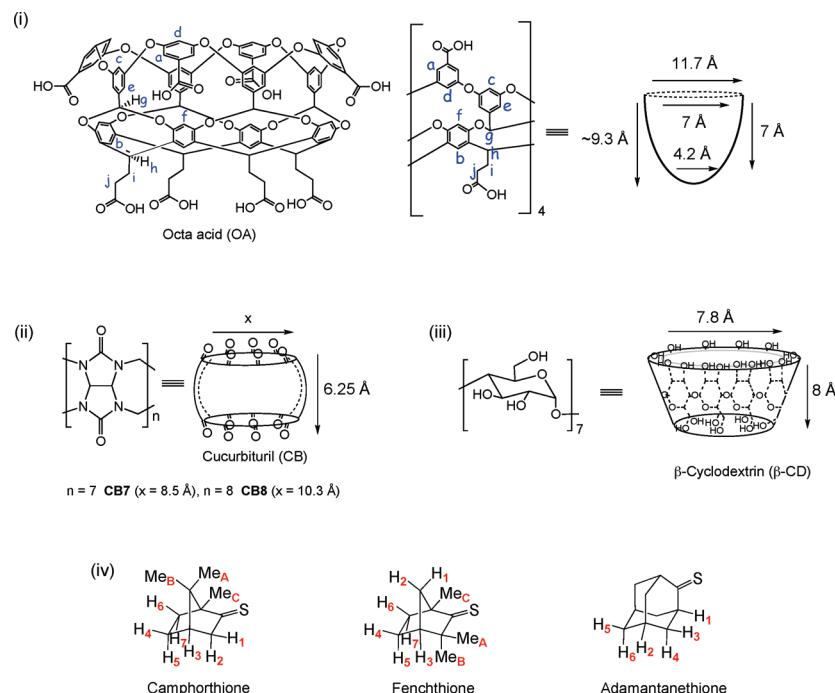
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**SCHEME 1:** Structures of the Hosts (i) Octa Acid (OA), (ii) Cucurbiturils (CB), (iii)  $\beta$ -Cyclodextrin ( $\beta$ -CD), and Guest (iv) Thioketones Investigated<sup>a</sup>



<sup>a</sup> The distances refer to atom-to-atom and do not include van der Waals radii.

with the more common water-soluble organic hosts cucurbiturils and cyclodextrins.

Structures of three dialkyl thioketones used as guests and three water-soluble hosts employed to solubilize and isolate the guests in water are provided in Scheme 1. Phosphorescence emission and excitation spectra of the three thioketones investigated in this study are completely consistent with the literature reports, confirming that the observed emission is from  $T_1$ .<sup>2,7</sup>

One of the host molecules employed in this investigation is a deep-cavity cavitand known by the trivial name octa acid.<sup>36</sup> The eight carboxylic acids on both the top and bottom rims of this host make it water-soluble under basic ( $\text{pH} \sim 9.0$ ) conditions. The dimensions of OA cavity are provided in Scheme 1. In the presence of a suitable guest (or guests), two molecules of OA assemble in aqueous solution to form a supramolecular closed capsule that we call a “closed nanocontainer”.

The second host molecule belongs to a family of hosts known as cucurbiturils (CB).<sup>37</sup> The two cucurbiturils employed in this investigation are CB[7] (cavity diameter  $\sim 8.5 \text{ \AA}$ ) and CB[8] (cavity diameter  $\sim 10.3 \text{ \AA}$ ). Cucurbiturils are moderately water-soluble under neutral conditions. Unlike OA, CB when complexed with guests exists as an “open nanocontainer”.

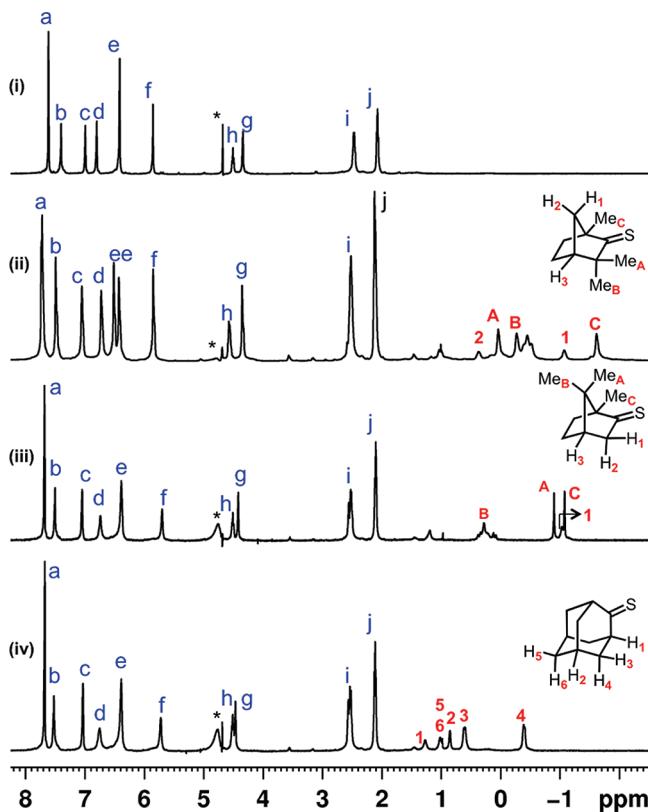
For the purpose of comparison, a third host, a well-known host  $\beta$ -cyclodextrin, was also briefly investigated, the results of which are presented in the Supporting Information.<sup>38</sup>

## Results and Discussion

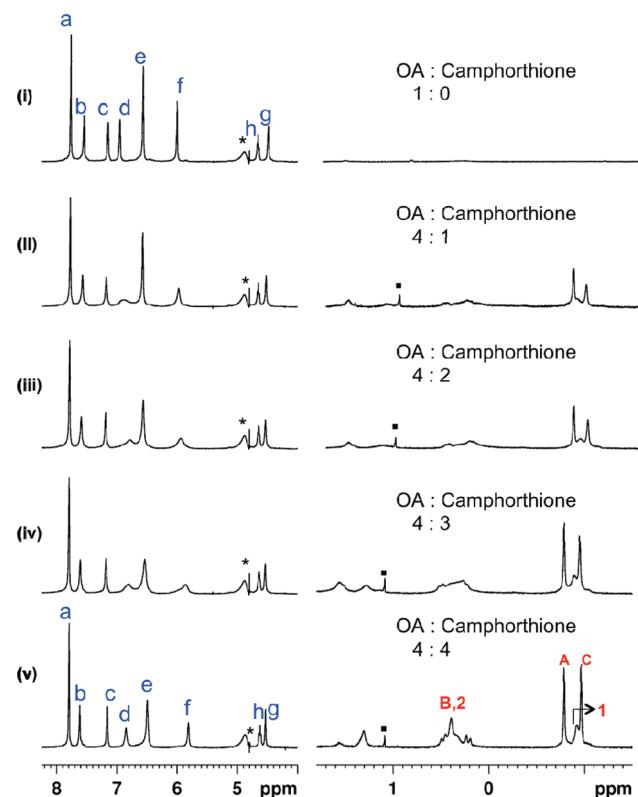
**Octa Acid As a Container to Enhance Phosphorescence from Thioketones at Room Temperature in Water.** Inclusion and orientation of guest thioketone molecules within the closed nanocontainer made up of two OA molecules was inferred from  $^1\text{H}$  NMR, COSY, and NOESY data.  $^1\text{H}$  NMR titration data as well as diffusion constants measured by  $^1\text{H}$  NMR experiments were employed to determine host–guest stoichiometry. We discuss  $^1\text{H}$  NMR results of camphorthione in detail below. Following the same reasoning adopted in the case of camphor-

thione, conclusions on the orientation of fenchthione and adamantanethione within the OA container were arrived at from their  $^1\text{H}$  NMR data. To conserve space,  $^1\text{H}$  NMR titration spectra for the latter two thioketones and all COSY data are included as Supporting Information and are only briefly mentioned here.  $^1\text{H}$  NMR signals assigned to various hydrogens of OA and guest molecules through COSY are marked in displayed figures in the text and Supporting Information. Numbering of hydrogens for thioketones and OA are included in Scheme 1. It is important to note that for all three host–guest systems,  $^1\text{H}$  NMR signals corresponding to free guests were seen only when the guest was in excess of 1:1 ratio, which suggests that they form a complex of 1:1 stoichiometry. During titration experiments,  $^1\text{H}$  NMR chemical shifts of the OA-bound guests remained constant, independent of the host concentration in the solution (host concentration was varied between 0 and 1.2 equiv of the guest), which suggests a lack of equilibrium between the complexed and free guest molecules (or larger  $K_{\text{assoc}}$ ). This precluded determination of the binding constants of host–guest complexes.

Inclusion of camphorthione, fenchthione, and adamantanethione within OA ( $10^{-3} \text{ M}$  OA in  $10^{-2} \text{ M}$  borate buffer/ $\text{D}_2\text{O}$ ) was evident from the upfield shifted guest  $^1\text{H}$  NMR resonances (note the presence of signals below  $\delta 0 \text{ ppm}$  for a few of the hydrogens in each of the three thioketones in Figure 1) due to paramagnetic shielding by the four phenyl rings present at the base of the OA capsule.<sup>39,40</sup>  $^1\text{H}$  NMR titration experiments performed by the gradual stepwise addition of 0.25 equiv of camphorthione to a  $10^{-3} \text{ M}$  OA solution helped us infer the stoichiometry of the thioketone–OA complex (Figure 2). At early stages of addition (when excess OA is present in the solution), the signals due to  $\text{H}_d$  and  $\text{H}_e$  of OA and  $\text{Me}_B$  and  $\text{H}_2$  of the guest were slightly broad (Figure 2 ii, iii, and iv), suggesting the host–guest complex to be weak under these conditions. However, all peaks sharpened when the host/guest



**Figure 1.**  $^1\text{H}$  NMR (500 MHz,  $\text{D}_2\text{O}$ ) spectra of complexes of thioketones (1 mM) with OA (1 mM) at a 1:1 ratio in 10 M borate buffer. (i) Absence of thioketone, (ii) thiophenone, (iii) camphorthione, and (iv) adamantanethione.



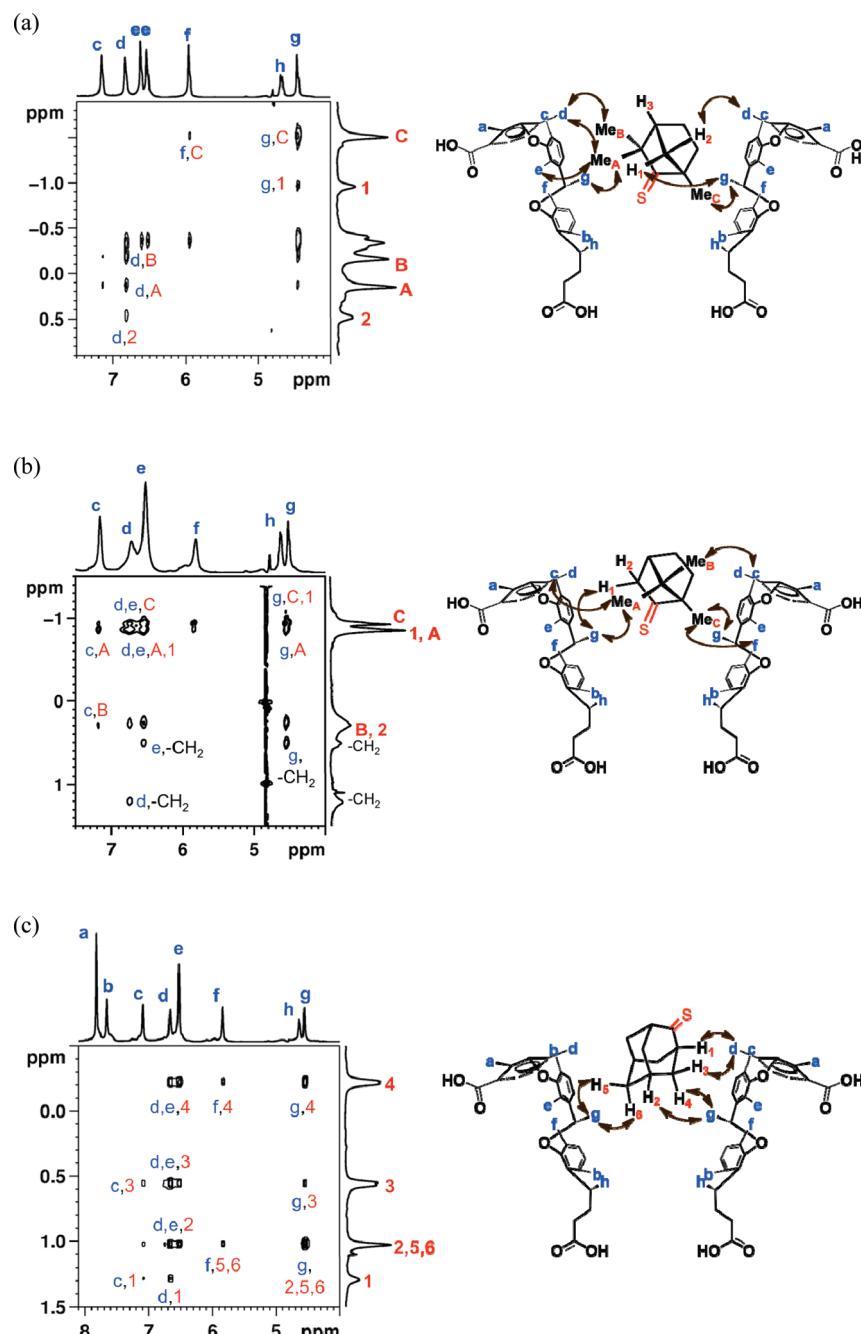
**Figure 2.**  $^1\text{H}$  NMR (500 MHz,  $\text{D}_2\text{O}$ ) spectra of camphorthione within OA at different OA–camphorthione ratios: [OA] = 1 mM, borate buffer 10 mM. \*, residual water resonances; ■, an impurity in OA.

ratio reached 1:1 (Figure 2v). Further addition of the guest resulted in no change in the spectra except for the presence of

signals due to free camphorthione in solution. On the basis of the titration spectra, we believe that camphorthione formed a complex with OA in a stoichiometry of 1:1 (more precisely, a  $(1:1)_n$ , which could represent a complex of either 1:1 or 2:2 ratio; i.e., thioketone@OA or thioketone<sub>2</sub>@OA<sub>2</sub>). Similar conclusions were drawn from NMR titration spectra of fenchthione and adamantanethione with OA; see the Supporting Information for titration spectra). Measured diffusion constants for complexes of camphorthione, fenchthione, and adamantanethione with OA,  $1.58 \times 10^{-6}$ ,  $1.55 \times 10^{-6}$ , and  $1.56 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , respectively, were smaller than that for free OA ( $1.88 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ). For a hydrodynamic radius of 1:1 complex being closer to that of free OA, one would expect the diffusion constant for free OA and the 1:1 complex to have a similar value.<sup>39,40</sup> On the basis of this logic, the measured diffusion constants being smaller than for free OA, we believe that thioketones form a 2:2 rather than 1:1 complex with OA.

On the basis of the above data and reasoning, we believe that two independent OA–guest supramolecules assemble to form a closed nanocontainer (2:2 complex). When there are two thioketone molecules within the OA container, depending on their arrangement in the two halves of the container, the host–guest complex as a whole could be either symmetrical or unsymmetrical, and importantly relative to the issue of self-quenching, the two C=S groups could be in each other's proximity or some distance from one another. Analysis of the  $^1\text{H}$  NMR spectrum of the complex corresponding to the host region should provide information concerning the overall symmetry of the container. The OA host (Scheme 1) is made up of four identical panels containing 10 sets of chemically nonequivalent hydrogens (total number of hydrogens: 14) giving a maximum of 10 NMR signals in the region  $\delta$  2–8 (Figure 1i). When the guest occupation on the top and bottom halves of the capsule is identical, only 10 host signals are expected. On the other hand, when the guest occupation on the top and bottom halves of the capsule is not identical, one could expect more than 10 signals for the host. However, in the presence of chiral camphorthione and fenchthione, diastereotopic  $\text{H}_e$  and  $\text{H}_a$  could become magnetically nonequivalent and result in additional signals. In the case of fenchthione, signals due to  $\text{H}_e$  were split, but all other signals appeared as a single peak. Despite camphorthione's being chiral, diastereotopic  $\text{H}_e$  and  $\text{H}_a$  were not split, and still, only 10 signals for the host were observed. In the case of achiral adamantanethione, no signals were split. On the basis of the above  $^1\text{H}$  NMR data, we conclude that two thioketone molecules in all three cases are symmetrically placed (on an average) in the two halves of the container.

To be able to predict whether OA encapsulation would reduce self-quenching, we needed to identify the orientation of two thiocarbonyl chromophores within the container. If they face the broader midregion, there is a good possibility that two thiocarbonyl chromophores would most likely interact during the triplet lifetime, leading to self-quenching. On the other hand, if two thiocarbonyl groups face the narrower end of the container, the two chromophores would have difficulty interacting during the excited state lifetime. The former arrangement would not favor phosphorescence, but the latter would. Detailed analyses of the  $^1\text{H}$  NMR spectra and NOESY data (recorded at a standard mixing time of 300 ms) provided an insight into the guest orientation within the OA capsule. The NOESY correlation spectra of regions of interest to the discussion for camphorthione<sub>2</sub>@OA<sub>2</sub>, fenchthione<sub>2</sub>@OA<sub>2</sub>, and adamantanethione<sub>2</sub>@OA<sub>2</sub> are provided in

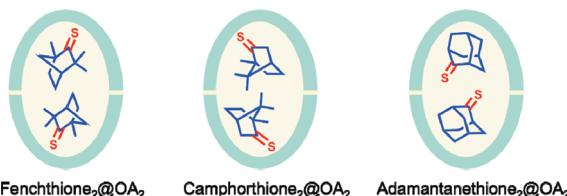


**Figure 3.** Select regions of 2D-NOESY spectra of thioketone<sub>2</sub>@OA<sub>2</sub> (500 MHz, D<sub>2</sub>O, [OA] = 5 mM in 50 mM borate buffer, [thioketone] = 5 mM: (a) fenchthione, (b) camphorthione, and (c) adamantanethione.

Figure 3. For easy visualization, the figure also includes the correlations between the host and guest molecules in a schematic fashion.

In the case of camphorthione, the most upfield shift (in comparison to D<sub>2</sub>O) was noted for the  $\alpha$ -methylene hydrogens (H<sub>1</sub> and H<sub>2</sub>) adjacent to the thiocarbonyl chromophore ( $\Delta\delta$  −3.3 ppm) (Figure 1). This suggested that this part of camphorthione molecule is at the narrower end of the container where four phenyl groups converge. Consistent with this postulate, among the three methyl groups, the one  $\alpha$  to the thiocarbonyl chromophore (Me<sub>C</sub>) was shifted most ( $\Delta\delta$  −2.01 ppm), and the bridgehead methyl (Me<sub>B</sub>) facing away from the thiocarbonyl chromophore shifted the least ( $\Delta\delta$  −0.51 ppm). NOESY correlations shown in Figure 3b also supported the above arrangement. Two methyl groups marked A and C of the guest correlated with H<sub>g</sub> and H<sub>d</sub> of the host that are present at a deeper

part of the cavity. In addition,  $\beta$ -hydrogen marked H<sub>3</sub> of the guest showed correlation with H<sub>g</sub> of OA. These correlations are consistent with orientation of camphorthione shown in Figure 3b. Similar analyses of fenchthione<sub>2</sub>@OA<sub>2</sub> led us to conclude that fenchthione also adopts an orientation similar to camphorthione within the container (Figure 3a). The correlations noted for adamantanethione are quite different. In this case, all hydrogens (H<sub>5</sub>, H<sub>6</sub>, H<sub>2</sub>, and H<sub>4</sub>) present at the bottom part of the adamantane unit correlated with H<sub>g</sub> (located at the narrower end) of OA. Furthermore, H<sub>1</sub>, and H<sub>3</sub> present closer to the thiocarbonyl chromophore correlated with H<sub>d</sub> (present at the rim) of OA. These correlations are consistent with the model shown in Figure 3c. On the basis of the above NOESY data, possible orientations of the three thioketones within the OA container are illustrated in Figure 4. Thus, in a closed container made up of two OA molecules, the thiocarbonyl chromophores



**Figure 4.** A cartoon representation of the orientation of two thioketone molecules within the closed nanocontainer made up of OA cavitand, based on NOESY analysis.

of two fenchthione molecules and camphorthione molecules would be farther apart, whereas in adamantanethione, they would be closer and face each other. Thus, the arrangement of adamantanethione would favor self-quenching, whereas that in fenchthione and camphorthione would not favor self-quenching.

In Figure 5, phosphorescence emission spectra of camphorthione<sub>2</sub>@OA<sub>2</sub>, fenchthione<sub>2</sub>@OA<sub>2</sub>, and adamantanethione<sub>2</sub>@OA<sub>2</sub> recorded at room temperature in borate buffer in water ( $10^{-4}$  M) are displayed. For comparison, in each case, the very weak phosphorescence spectra in perfluoro-1,3-dimethylcyclohexane recorded under identical conditions are included. Although these thioketones are soluble in water up to  $10^{-3}$  M, no phosphorescence could be observed in the concentration range  $10^{-3}$ – $10^{-5}$  M. Clearly, inclusion within the closed nanocontainer made up of OA molecules resulted in remarkable phosphorescence in all three thioketones. Even more important is the measured lifetime of the triplet of the thioketones trapped within the closed nanocontainer in D<sub>2</sub>O. The lifetime was measured by monitoring the phosphorescence decay after exciting the thioketone with a microsecond flash lamp (254 nm) or pulsed Nd:YAG laser (266 nm). Measured lifetimes at  $1.25 \times 10^{-5}$  M of thioketone<sub>2</sub>@OA<sub>2</sub> complexes are provided in Table 1. For comparison, lifetimes at infinite dilution in perfluorodimethylcyclohexane taken from the literature are included.<sup>7</sup> It is important to note that at  $10^{-5}$  M used for our studies, the expected lifetimes (assuming diffusion-controlled self-quenching) for these thioketones in perfluorodimethylcyclohexane would be shorter than 10  $\mu$ s. Interestingly, lifetimes for camphorthione<sub>2</sub>@OA<sub>2</sub> and fenchthione<sub>2</sub>@OA<sub>2</sub> are longer than in perfluorodimethylcyclohexane at infinite dilution.<sup>7</sup> For example, the triplet lifetime of fenchthione in the OA container is 187  $\mu$ s, and that in perfluorodimethylcyclohexane at infinite dilution is 154  $\mu$ s. In the case of camphorthione, in the OA container, the lifetime is 65  $\mu$ s, but in perfluorodimethylcyclohexane at infinite dilution, it is 46  $\mu$ s. In all cases, the nature of the lowest emitting triplet state has been established to be of nπ\* character. Enhanced triplet lifetime and emission intensity suggest that no self-quenching occurs between excited and ground-state thioketone molecules, despite the two molecules being present in the same container. We attribute the lack of self-quenching to the lack of mobility and the arrangement of two thioketone molecules within the OA container (Figure 4). Supramolecular steric interaction between the host and the guest molecules, most likely, does not permit rotation of the two thioketones within the nanocontainer during the triplet lifetime. Yet another factor to note is that although in perfluorodimethylcyclohexane the triplet lifetime was dependent on the concentration of the thioketone, no such dependence was found in the concentration range  $10^{-3}$ – $10^{-5}$  M for thioketone<sub>2</sub>@OA<sub>2</sub> complexes.

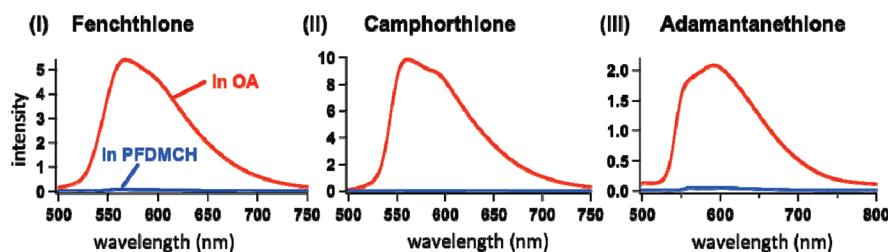
Oxygen quenching that occurs at a diffusion-limited rate in solution is much lower when thioketone molecules are present in a closed container. The rate constants of oxygen quenching of the triplets for the three thioketones are included in Table 1. They are at least 2 orders of magnitude lower than that in

common solvents. We have recorded phosphorescence at 1270 nm from singlet oxygen upon quenching of the thione triplet by triplet oxygen. As indicated above, thioketone molecules remain isolated within the container during its entire triplet lifetime, and therefore, most likely, oxygen is unable to undergo direct bimolecular quenching interaction with the triplet states. Had the excited guest escaped the container or the container opened fully so that oxygen could have free access, the quenching rate constant would be similar to that in solution. From the reduced oxygen-quenching rate constant, we also draw the conclusion that the container does not fully open and close in the time scale of the triplet lifetime ( $\sim 2$ –200  $\mu$ s) of the thioketones.

On the basis of the orientation deduced from NOESY experiments of adamantanethione molecules within the OA container (Figure 4c), one would expect this molecule to show a reduced level of phosphorescence resulting from self-quenching. Adamantanethione<sub>2</sub>@OA<sub>2</sub> exhibits strong phosphorescence in aqueous solution, demonstrating the lack of effective self-quenching. Interestingly, the lifetime of the triplet of adamantanethione<sub>2</sub>@OA<sub>2</sub> was shorter than that for adamantanethione in perfluoro-1,3-dimethylcyclohexane at infinite dilution (17.2 vs 43.3  $\mu$ s). This difference can be understood on the basis of the orientation of adamantanethione molecules within the OA container shown in Figure 4. Unlike in the case of camphorthione<sub>2</sub>@OA<sub>2</sub> and fenchthione<sub>2</sub>@OA<sub>2</sub>, in adamantanethione<sub>2</sub>@OA<sub>2</sub>, self-quenching must be contributing to the reduction in lifetime, although not to the same extent as in solution. Two molecules being so close would have resulted in no emission in solution. The fact that there is emission and lifetime is still 40% that in solution suggests that the mobility of the two adamantanethioketone molecules within the OA container is restricted and that the orientation of the C=S group determines the effectiveness of self-quenching. It is known from classical investigations of reactions of ketones that the rate constant of triplet quenching depends strongly on the orientation of ketone triplets and reactants.<sup>41,42</sup> Clearly, within the confined space, despite the two thiocarbonyl chromophores' being so close, they are unable to reach the geometry required for self-quenching. From the results presented above, it is clear that self-quenching could be suppressed with the help of the OA container, and how much it could be suppressed depends on the orientation of guest thioketones. With the present knowledge, one cannot predict a priori the orientation of guest molecules within the OA container.

We close this section by drawing attention to Figure 6, which displays the emission titration curve for camphorthione. With increasing addition of OA, the phosphorescence intensity continuously increased, but beyond a 1:1 ratio, there was no further increase, supporting our conclusion that camphorthione forms a complex with a (1:1)<sub>n</sub> stoichiometry. A similar observation was made with the other two thioketones. One should also note that the phosphorescence enhancement and prolonged lifetime is also due to the fact that the OA container lacks any abstractable hydrogens and water. Both are known to quench the triplet of thioketone.<sup>40,43</sup> Thus, a combination of factors facilitates room temperature phosphorescence from thioketones included in the OA container.

Having established that forming a complex as a closed nanocontainer can suppress self- and oxygen quenching of thioketone triplets and thereby enhance phosphorescence emission at room temperature, we were also interested in examining how effective an “open” 1:1 nanocontainer would be. In this context, we examined the use of cucurbiturils (Scheme 1ii) that

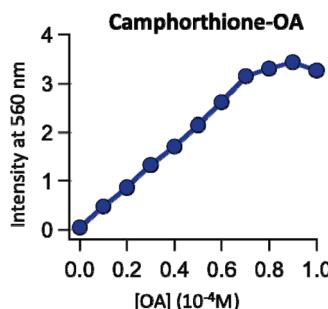


**Figure 5.** Phosphorescence spectra of thioketones in perfluoro-1,3-dimethylcyclohexane (PFDMCH) (blue) and in 2:2 OA/thioketone capsular assemblies (red): [thioketone] = 0.1 mM, [OA] = 0.12 mM in 10 mM sodium tetraborate buffer (10 mM),  $\lambda_{\text{excitation}} = 254$  nm; under aerated conditions. See Figure 4 for structures of thioketone complexes.

**TABLE 1: Triplet Lifetime and Rate Constant of Oxygen Quenching for Thioketones Included in Three Different Containers and Extrapolated Lifetime in Solution**

guests	$\tau^0_T$ ( $\mu\text{s}$ ) <sup>a</sup>	CB[7] <sup>b</sup>			CB[8] <sup>b</sup>			OA <sup>b</sup>		
		H:G <sup>c</sup>	$\tau_T$ ( $\mu\text{s}$ ) <sup>d</sup>	$k_{q,\text{O}_2}(\text{M}^{-1}\text{s}^{-1})$	H:G <sup>c</sup>	$\tau_T$ ( $\mu\text{s}$ ) <sup>d</sup>	$k_{q,\text{O}_2}(\text{M}^{-1}\text{s}^{-1})$	H:G <sup>c</sup>	$\tau_T$ ( $\mu\text{s}$ ) <sup>d</sup>	$k_{q,\text{O}_2}(\text{M}^{-1}\text{s}^{-1})$
fenchthione	154	1:1	150	$(3.4 \pm 0.3) \times 10^6$	1:1	40	$(3.0 \pm 0.3) \times 10^8$	2:2	187	$(1.6 \pm 0.4) \times 10^6$
camphorthione	46.3	1:1	10	$(1.3 \pm 0.1) \times 10^8$	1:1	14	$(1.7 \pm 0.2) \times 10^8$	2:2	65	$(2.4 \pm 0.1) \times 10^7$
adamantanethione	43.3	1:1	— <sup>e</sup>	— <sup>e</sup>	1:1	5	$(2.1 \pm 0.1) \times 10^8$	2:2	17.2	$(2.8 \pm 0.1) \times 10^7$

<sup>a</sup>  $\tau^0_T$  = extrapolated lifetime (lifetime at infinite dilution) in perfluoro-1,3-dimethylcyclohexane (PFDMCH).<sup>7</sup> <sup>b</sup> CB[7] = cucurbit[7]uril, CB[8] = cucurbit[8]uril, and OA = octa acid. <sup>c</sup> Host/guest concentrations, experiments with CB7: [thioketone] =  $1.0 \times 10^{-4}$  M, [CB7] =  $4.2 \times 10^{-4}$  M. Experiments with CB8: [thioketone] =  $1.0 \times 10^{-5}$  M, [CB8] =  $1.0 \times 10^{-4}$  M. Experiments with OA: [thioketone] =  $1.25 \times 10^{-5}$  M, [OA] =  $1.5 \times 10^{-5}$  M in 10 mM sodium tetraborate. <sup>d</sup> Triplet lifetime measured in deoxygenated D<sub>2</sub>O solutions. <sup>e</sup> No phosphorescence emission was observed.  $\lambda_{\text{excitation}} = 266$  nm.



**Figure 6.** Intensity of camphorthione phosphorescence at 560 nm at different OA concentrations. [Camphorthione] =  $1 \times 10^{-4}$  M; 10 mM borate buffer;  $\lambda_{\text{excitation}} = 254$  nm.

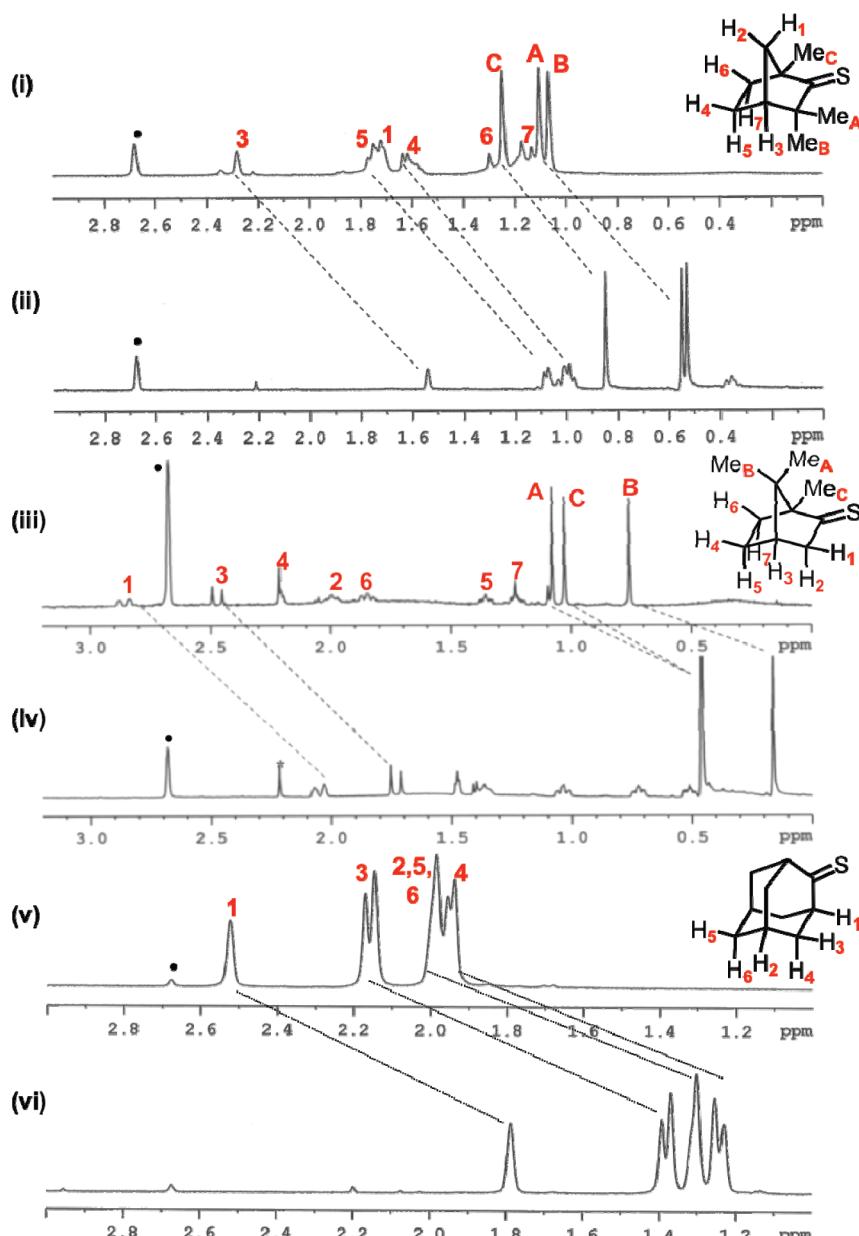
are soluble in water under neutral conditions. Cucurbit[7]uril with smaller cavity dimensions formed a better complex than cucurbit[8]uril with the three thioketones examined here. Poor solubility of the CB[8] complex resulted in poor quality NMR spectra. Therefore, most of our NMR studies were restricted to cucurbit[7]uril.

Complexation of cucurbit[7]uril with all three thioketones was evident from their <sup>1</sup>H NMR spectra, displayed in Figure 7. In every case, the guest signals were upfield-shifted, indicating their location to be within the CB cavity. At 1:1 ratio of thioketone to CB[7] ( $1.5 \times 10^{-3}$  M), no free guest signals were evident in the NMR spectra, indicating that at this concentration, all guest molecules reside within the host. On the basis of the phosphorescence titration spectra, the binding constant for fenchthione with CB[7] was determined to be  $2 \times 10^5 \text{ M}^{-1}$  (see the Supporting Information for details). We assume that the binding constant for both camphorthione and adamantanethione with CB[7] must be in the same range. Due to a lack of hydrogens at the interior of the CB cavity, NOESY experiments were not helpful to draw conclusions regarding the orientation of guest molecules within CB.

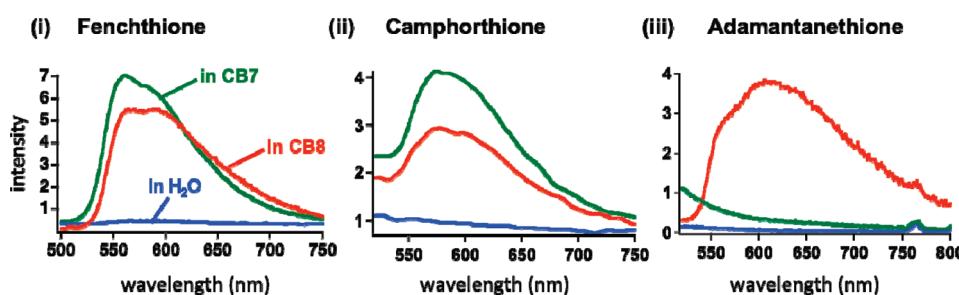
Phosphorescence spectra of fenchthione, camphorthione, and adamantanethione in water, in the presence of CB[7] and CB[8] are displayed in Figure 8. Since emission studies required a much lower concentration than NMR, we did not face any

problem in recording phosphorescence in the presence of CB[8]. The spectra recorded at various host/guest ratios for fenchthione in CB[7] and CB[8] suggest that the emission reaches its maximum with 1.2 equiv of CB[7], whereas in the case of CB[8], a much higher ratio (>6 equiv) is required (Figures 9 and 10). This is consistent with the conclusions drawn from <sup>1</sup>H NMR studies that CB[7] formed a stronger complex than CB[8] with thioketones. The lifetimes of the triplets and oxygen quenching rate constants measured by time-resolved techniques are included in Table 1.

Examination of Figure 8 and Table 1 leads to the following conclusions: (a) Both fenchthione and camphorthione included in CB[7] provide moderately enhanced phosphorescence with respect to that in water. However, adamantanethione upon inclusion within CB[7] did not show any enhancement with respect to water. (b) The triplet lifetime of fenchthione@CB[7] was close to that of free fenchthione at infinite dilution in perfluorodimethylcyclohexane but shorter than that of fenchthione<sub>2</sub>@OA<sub>2</sub>. However, the triplet lifetime of fenchthione@CB[8] was much shorter than fenchthione@CB[7]. (c) Camphorthione had a shorter lifetime when included both within CB[7] and within CB[8], suggesting that this molecule is only partially protected by cucurbiturils. (d) Although the rate constants for oxygen quenching in all cases were slightly reduced compared to that in water, the reduction is not as dramatic as in OA. (e) Most importantly, adamantanethione included in CB[7] did not show any phosphorescence. Given the fact that both fenchthione and camphorthione included in CB[7] showed enhanced phosphorescence, the lack of phosphorescence in the case of adamantanethione@CB[7] is surprising. However, weak phosphorescence was recorded when it was included within CB[8]. A majority of the above observations suggest that a closed nanocontainer OA<sub>2</sub> is a much better medium than an open nanocontainer CB[n] to observe phosphorescence from systems such as thioketones that readily undergo self- and oxygen quenching. When an open nanocontainer, as in the case of CB[8], is slightly larger, the complexation is weak, enabling the emitting molecule to escape the container during its triplet lifetime to be quenched by another molecule of its own variety or oxygen.



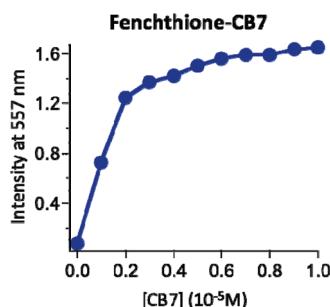
**Figure 7.** <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O) spectra of free thioketones and in the presence of CB[7]. (i) Fenchthione (1.5 mM in D<sub>2</sub>O), (ii) CB[7]/fenchthione (1:1) ([CB7] = [fenchthione] = 1.5 mM), (iii) camphorthione (1.5 mM), (iv) CB[7]/camphorthione (1:1) ([CB7] = [camphorthione] = 1.5 mM), (v) adamantanethione (1.5 mM)/ and (vi) CB[7]:adamantanethione (1:1) (CB[7] = [adamantanethione] = 1.5 mM). \*, an impurity; •, residual proton resonances from DMSO-d<sub>6</sub>.



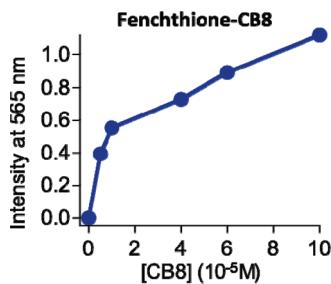
**Figure 8.** Phosphorescence spectra of thioketones in water (blue), CB[7]@thioketone complexes (green), and CB[8]@thioketone complexes (red) under deaerated conditions. (i) [Fenchthione] = 1 × 10<sup>-5</sup> M, CB[7] = 1 × 10<sup>-5</sup> M, and CB[8] = 6.0 × 10<sup>-5</sup> M; (ii) [camphorthione] = 1 × 10<sup>-5</sup> M, CB[7] = 1 × 10<sup>-5</sup> M, and CB[8] = 1.2 × 10<sup>-5</sup> M; (iii) [adamantanethione] = 1 × 10<sup>-5</sup> M, CB[7] = 1 × 10<sup>-5</sup> M, and CB[8] = 1 × 10<sup>-5</sup> M.  $\lambda_{\text{excitation}} = 254$  nm.

The difference in emission behavior between fenchthione and adamantanethione included in CB[7] could be the result of the difference in orientation of the two thioketones within

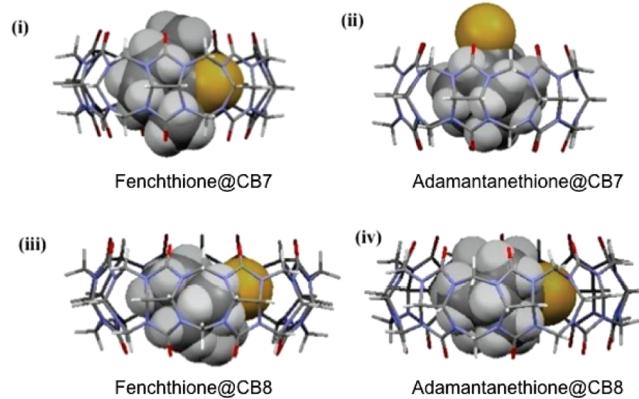
CB[7]. Since NMR experiments were not helpful for gaining insight into the orientation of the guest molecules within CB, we optimized several structures of these complexes at the



**Figure 9.** Intensity of fenchthione phosphorescence in water solution at 560 nm at different CB[7] concentrations. [fenchthione] = 10  $\mu$ M; 10 mM borate buffer;  $\lambda_{\text{excitation}} = 254$  nm.



**Figure 10.** Intensity of fenchthione phosphorescence in water solution at 560 nm at different CB[8] concentrations. [fenchthione] = 10  $\mu$ M;  $\lambda_{\text{excitation}} = 254$  nm.



**Figure 11.** BLYP/6-31G(d,p) energy-minimized structures of fenchthione and adamantanethione within CB[7] and CB[8].

BLYP/6-31G(d)<sup>44,45</sup> level using the Gaussian D3, revision D.01 program.<sup>46</sup> The final energies of the optimized structures were improved by performing single-point calculations using the 6-311+G(d) basis set of the triple- $\zeta$  quality. The dielectric effect of the surrounding water molecules was taken into account using the self-consistent reaction field IEF-PCM method.<sup>47</sup> Of the various structures generated for fenchthione and adamantanethione complexes with CB[7] and CB[8], the ones with the lowest energy in each case are presented in Figure 11. It is gratifying to note that the optimized structures aptly reflect the difference in the emission characteristics of fenchthione@CB[7] and adamantanethione@CB[7]. Whereas the thiocarbonyl chromophore of fenchthione reside within the CB cavity, that of adamantanethione faces water. In the latter case, the thiocarbonyl chromophore is exposed to water as well as to any other quenchers, including another adamantanethione@CB[7]. Thus the triplet of adamantanethione@CB[7] is subjected to self-quenching, oxygen quenching, and quenching by water molecules. Under such conditions, the absence of phosphorescence from adamantanethione@CB[7]

is not surprising. That adamantanethione@CB[8] is phosphorescent (Figure 8) is also readily understood from the computed structure for the same. In this case, the thiocarbonyl chromophore is buried within the CB[8] cavity, thus protecting it from quenchers.

On the basis of the results with CB, it is clear that a closed container (made up of OA) is a better medium to control the diffusion-limited self-quenching process than an open container. To make sure that this is, indeed, the case, we also examined the phosphorescence of the above three thioketones included in  $\beta$ -cyclodextrin that has dimensions similar to cucurbit[7]uril and has less tendency to form a closed capsule. In presence of  $\beta$ -cyclodextrin, phosphorescence of fenchthione and camphor-thione enhanced only by ~20%, as compared to that in water, and in the case of adamantanethione, no emission was observed (for spectra see the Supporting Information). In the past, a substantial increase in phosphorescence from arylthioketones has been reported in solid complexes of  $\beta$ -cyclodextrin.<sup>32–35</sup> However, in an aqueous solution, emission is weak, and apparent switch in the emissive state is speculated. It is quite likely that in solution,  $\beta$ -cyclodextrin does not protect the arylthioketone from self- and oxygen quenching. From our studies, we conclude that cucurbiturils is a better medium in aqueous solution than cyclodextrins.

## Summary

Results presented in this report suggest that the closed nanocontainer formed by two OA molecules is the best choice to observe room temperature phosphorescence in solution from molecules whose radiative rate constant is strong but not strong enough to compete with diffusion-limited quenching processes. Interestingly, despite having two thioketone molecules in a single OA container (effective concentration > 3 M), self-quenching did not inhibit phosphorescence emission. Orientation of guest molecules within the container plays an important role in controlling the self-quenching process. To make further progress in controlling the excited state chemistry of guest molecules, one needs to acquire knowledge of the factors that control the orientation of molecules within confined space, which we hope to achieve in the coming years.

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**Supporting Information Available:** Experimental details, synthetic procedures, photophysical data, and additional NMR and emission spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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