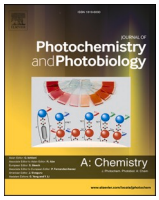
Journal of Photochemistry & Photobiology, A: Chemistry 451 (2024) 115510

Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology, A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Room temperature phosphorescence of 2-thioxo-coumarins in aqueous solution promoted by octa acid inclusion

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ARTICLE INFO

Keywords:
2-Thioxo-coumarins
Room temperature phosphorescence
Spin-orbit coupling
Intra-molecular charge transfer
Octa acid capsule

ABSTRACT

Unlike coumarins, the sulfur analogues, 2-thioxo-coumarins (TCs) have not attracted attention. Given the large energy gap between S_2 and S_1 and high spin–orbit coupling between S_1 and T_1 in these systems lack of attention is surprising. In this manuscript, we are concerned with the phosphorescence of seven TCs at room temperature. The TCs investigated here belong to two groups, one with the amino substitution at the 7-position and the other with an assorted collection of the parent, alkoxy and acetoxy substituted ones. All seven TCs show phosphorescence at 77 K while the ones with amino substitution exhibit both fluorescence and phosphorescence. The inability of phosphorescence to compete fully in this set is attributed to intramolecular electron/charge flow from the lone pair of the amino functionality. Occurrence of such a process opens opportunities to examine the solvation dynamics and TICT process in these systems. The most important result relates to the observation of room temperature phosphorescence (RTP) of these molecules in water with the help of octa acid host. TCs that are not soluble can be solubilized in water with OA capsule and this strategy suppresses self-quenching and oxygen quenching in favor of radiative process in the triplet state. When the chemical reaction is facile as in one system investigated here OA fails to bring about RTP. In our opinion, octa acid capsule can serve as an excellent medium to bring about RTP from organic molecules in water.

1. Introduction

During the last two decades, room temperature phosphorescence (RTP) of organic molecules has become an active area of investigation [1–9]. This has prompted us to present our recent results and place them along the historical evolution of this topic. We begin the presentation with a brief history: Even five hundred years ago (1600 CE), RTP was a well-known phenomenon [10,11]. At that time, most materials that showed RTP were identified to be either inorganic minerals or gems. These materials showed two types of luminescence, one with short and the other with long lifetimes. The second one was termed phosphorescence. At the early part of the last century, when electron, quantum and spin became the most important concepts, thanks to the pioneering contributions of a number of physicists and Lewis, Kasha and their co-workers a better understanding of this emission with long lifetime was reached [12–14]. By now it is common knowledge that phosphorescence originates from the triplet state of organic molecules where the ground state is a spin paired closed singlet [15].

Lewis and co-workers in their groundbreaking publications during 1941–1944 reported phosphorescence of organic molecules both at room and low temperatures [12–14]. Recognizing the importance of restricting the motions of the lumiphore, Lewis's group used boric acid glass at room temperature and EPA (ethanol/isopentane/ether mixture) glass at 77 K as the media to record phosphorescence [14]. Thus, the condition that the molecule should be rigidified to observe phosphorescence was recognized as early as 1941. In spite of this, RTP in solution was a rarity until the record-breaking independent publications of Backstrom and Parker groups reporting RTP of benzil in benzene, and benzophenone in perfluoromethylcyclohexane appeared in the early 1960s [16–18]. Examination of these and other reports [19–21] reveals that to record RTP one should avoid solvents with which excited molecules react, and the medium should be free of oxygen. Perfluorinated hydrocarbon solvents were identified to be ideal when C-H abstraction by the excited molecule (e.g., carbonyl and thiocarbonyl compounds)

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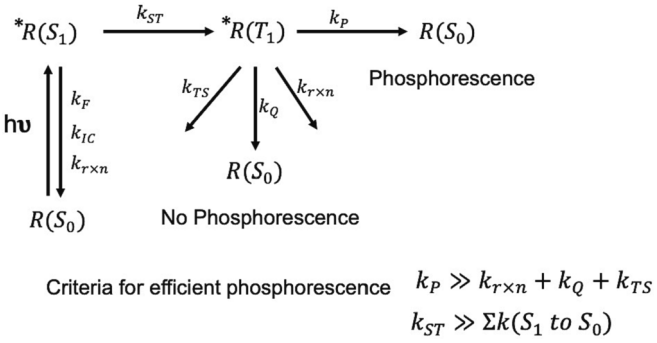
https://doi.org/10.1016/j.jphotochem.2024.115510
Received 3 December 2023; Received in revised form 26 January 2024; Accepted 30 January 2024
Available online 2 February 2024

occurs at a faster rate [22]. Up to 1972, RTP remained only an intellectual curiosity, and most workers for publications recorded phosphorescence at 77 K in an organic glass [23].

Recognition that RTP can be a valuable analytical tool for trace analysis, resulted in renaissance of interest in RTP in early 1970s [24,25]. Organic molecules adsorbed on solid surfaces of filter paper, silica gel, clays and inorganic salts such as alkali halides and acetates showed RTP [26–30]. The fact that the molecules that do not show phosphorescence in organic solvents at room temperature, do so on solid surfaces was attributed to rigidification of the lumiphore, a technique practiced by Lewis [14]. These reports prompted the search for methods to record RTP in solution, especially in aqueous media. This led to the discovery of RTP from molecules included within micelles (by Thomas et. al. and Grätzel et. al.) and cyclodextrins (by Turro et. al.) in aqueous media [31–36]. Lumiphore's isolation within micelles and cyclodextrins are thought to be the reason for RTP. RTP even from aromatic molecules with poor ISC from S_1 to T_1 could be recorded when the cations in micelles were exchanged with heavy ones such as Tl^+ [31]. Cyclodextrins (CD) also enable RTP from aromatic molecules when heavy atom bearing organic molecule such as dibromo ethane is co-included with the lumiphore [37–44]. Thus, the well-known heavy atom effect due to Kasha is important to bring about RTP [45,46]. Cline Love's group developed micellar and cyclodextrin induced RTP as a powerful analytical tool to detect trace quantities of organic molecules in water and as a HPLC detector [37–42]. Along the same line, Nocera and coworkers demonstrated that RTP from 1-bromonaphthalene can be detected when it is included within CD in presence of aliphatic alcohols. Apparently tight inclusion arrests oxygen quenching and radiationless decay. Using this technique Nocera's group developed a methodology to detect aliphatic alcohols in aqueous media [47,48]. Thus, RTP enjoyed intense activity during 1975–1990 [24,25]. During this time, importance of suppressing the oxygen quenching to record RTP was emphasized.

In fact, one of the authors of this manuscript (VR) was involved with RTP research in early 1990s [49–56]. The medium employed by his group to induce phosphorescence was alkali cation exchanged zeolites. Importantly, they were able to record RTP of aromatic molecules, olefins, diarylpolyenes and azo compounds. Especially important to note is the ability of zeolites to facilitate recording RTP of highly flexible diaryl polyenes, 1,4-diphenyl butadiene, 1,6-diphenyl hexatrience and 1,8-diphenyl octateraene. Apparently, the solid zeolite matrix suppressed the radiationless process, rotation of C = C bond and quenching by oxygen. In addition, heavy cations such as Cs^+ and Tl^+ induced ISC from S_1 to T_1 even in the case of aromatic molecules and olefins. The ability to record RTP from polyenes whose phosphorescence has never been recorded even at 77 K illustrates the power of heavy cation exchanged zeolites as matrices in the context of RTP. Extensive literature on RTP has been summarized in two valuable monographs devoted to this topic published in 1984 and 1990 [24,25]. Publications up to 2000 establish the criteria to observe RTP to be: (a) the molecule should have high rate of ISC from S_1 to T_1 ($k_{S1\ to\ T1}$), (b) high radiative rate constant (k_P), (c) low rate of internal conversion ($k_{T1\ to\ S0}$), (d) low rate of chemical reaction from T_1 and (e) low rate of quenching by oxygen (Scheme 1).

While in early 1970s recognition that RTP would be a powerful analytical tool prompted a renaissance in this area of research, in early 2010 yet another renaissance occurred when the value of RTP was recognized in bioimaging, sensing, lighting etc [57,58]. It is important to note that fundamentally there is no change in the behavior of molecules with time [15]. The availability of better instrumentation, synthetic methods and experimental methods has led to intense exploration of activity and proliferation of publications in the area of RTP directed towards applications. Conventional organic glass at 77 K has been replaced by crystals, aggregates, very viscous solutions, polymer matrices, and supramolecular hosts in water at room temperature. These media by confining the lumiphore allow phosphorescence to compete with unimolecular radiationless and bimolecular quenching processes.



Scheme 1. Competition of phosphorescence with other excited state decay pathways. Two criteria should be met for efficient RTP.

Although numerous molecules are reported to show RTP, to our knowledge the criteria listed in Scheme 1 still apply. Tremendous progress in instrumentation especially in terms of sensitivity has facilitated recording RTP of solid samples easier. In the context of the use of supramolecular hosts the principles developed with cyclodextrins, and micelles still apply [31–35]. It is our opinion, novices to this area of research would benefit by familiarizing themselves with the literature beginning with the 1941–45 publications of Lewis, Kasha and coworkers and the two monographs on phosphorimetry [12–14,24,25,45,46].

With this comprehensive introduction, we begin the presentation of our results on RTP of 2-thioxo-coumarins (TCs) in aqueous medium. The choice of (TCs) was driven by our long-standing interest in the photochemistry and photophysics of thiocarbonyl chromophores [49,59]. Given that coumarins, carbonyl analogues, serve as probes to monitor solvation dynamics and the micorpolarity of a medium [60–63], we were interested in understanding the photophysics of TCs which we believed would be equally useful as probes. Our recent interest in employing TC derivatives as phototriggers necessitated us to gain a better understanding of the dynamics of such molecules in the excited singlet and triplet surfaces [64]. To our knowledge no systematic investigation of RTP of TCs has been reported. We have shown earlier that RTP from thioketones could be recorded when they are included within cucurbiturils and octa acid (OA) capsules [59]. Results presented below form a continuation of our earlier reports on the use of OA in recording RTP [59,65,66].

2. Experimental Details

Reagents and solvents were purchased from Sigma Aldrich/Alfa Aeser/TCI/VWR. Spectrophotometric solvents (Sigma-Aldrich) were used whenever necessary unless otherwise specified. Luzchem UV quality fluorimeter cells (with a range until 190 nm) were used to record emission spectra at room temperature. For low temperature emission measurements, a quartz Dewar flask and 3-mm quartz tubes (inner diameter) were used. Synthesis and characterization of TCs are included in the Supplementary Information section (SI).

^{1}H NMR (400 MHz, 500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker NMR spectrometer at 25 °C. The complexation of guest molecules with the host (octa acid) was monitored using a 500 MHz Bruker NMR spectrometer at 25 ^{0}C. UV–Vis absorption spectra were recorded by using either UV-2600 UV–vis Spectrophotometer (Shimadzu) or Cary 300 UV–Vis spectrophotometer. Steady-state and time-resolved fluorescence measurements at room temperature were performed either on a FS920CDT Edinburgh fluorimeter or FLS1000 Photoluminescence Spectrometer (Edinburgh Instruments). All emission and excitation spectra are corrected for phototube and lamp intensity fluctuations. Phosphorescence lifetimes were recorded using FLS1000 Photoluminescence Spectrometer (Edinburgh Instruments). Time-

resolved phosphorescence measurements of TC **4** in OA at room temperature were performed on a LP980 spectrometer (Edinburgh Instruments) using a Q-switched Nd-YAG laser pumped OPO (OPOTEK) as pulsed excitation source (410 nm). The protocol for the complexation of guest molecules with octa acid for UV–vis and emission studies is detailed in SI.

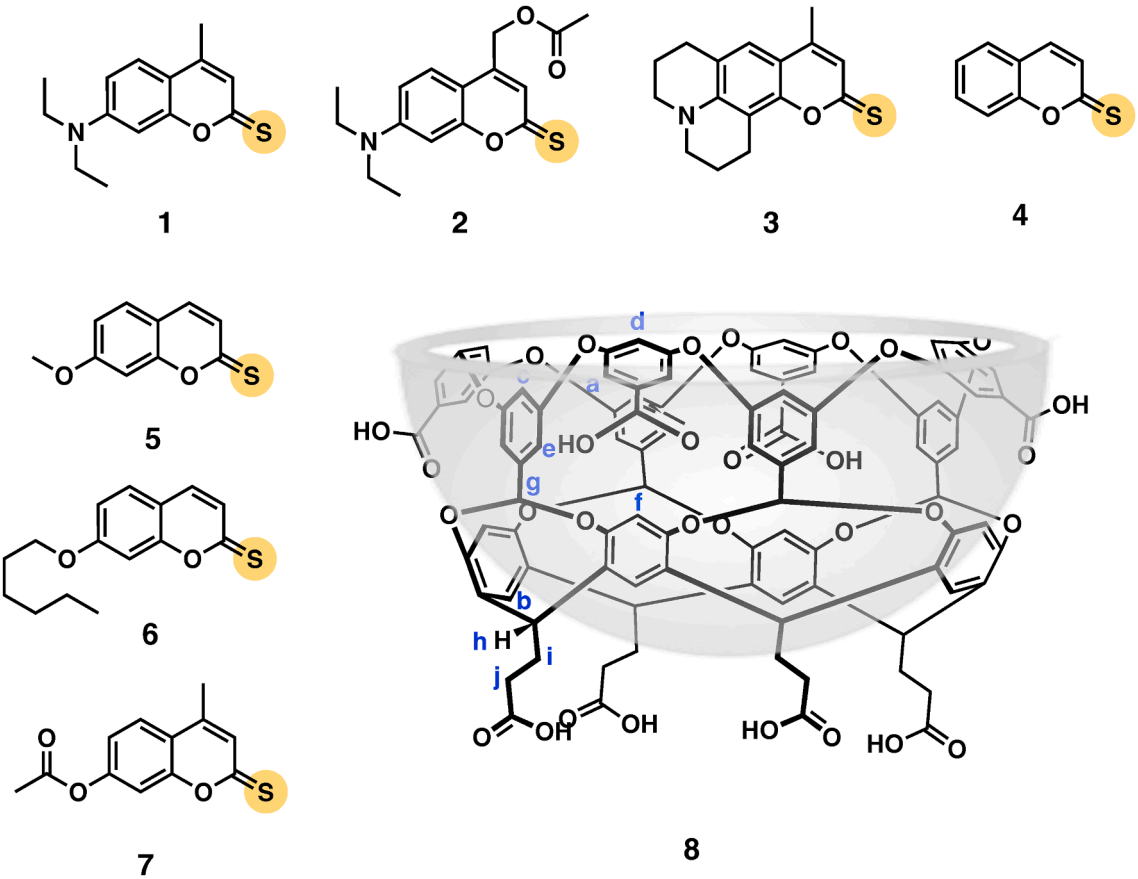
3. Results

Structures of guests TCs (**1**–**7**) whose phosphorescence spectra are reported here and the host OA are shown in Scheme 2. TCs **1**–**7** were synthesized and characterized as outlined in SI and OA was synthesized and purified as reported in the literature [67]. True to the name, the host OA contains eight acid groups and in borate buffer these ionize making it soluble in water. All studies involving OA reported here were carried out in borate buffer solution (pH = 8.7) at room temperature. In the absence of guest in solution, OA remains as free monomer. However, in presence of guests, it forms a capsular assembly including either one (host to guest ratio: 2:1) or two guest molecules (host to guest ratio: 1:1). Host to guest ratio of 1:1 could imply either a capsule formed by two molecules of OA containing two molecules of guest (capsularplex; 2:2) or a cavitand accommodating one guest molecule (cavitandplex; 1:1) [15,68–71]. In this study all complexes were capsular in nature containing either one or two guest molecules. Thus, the guests were fully protected from water and oxygen dissolved in water and remained within the non-polar interior of the host [72].

3.1. Host-guest complexation

Hydrophobic TCs **1**–**7** that are insoluble in water are readily dissolved in borate buffer in presence of OA. Inclusion of **1**–**7** within OA in borate buffer was confirmed by recording ^{1}H NMR spectra of the host–guest complexes. In Fig. 1 ^{1}H NMR spectra of free host OA (Fig. 1i) and host–guest complexes are shown (Fig. 1ii-viii). Indication of guest inclusion within OA is generally inferred from the upfield shift of the guest hydrogen signals with respect to that in $CDCl_3$, and displacement of OA signals (~δ 5.8–8.0 ppm) with respect to the free one in borate buffer [73]. In all cases except TC **4**, upfield shifted signals for the guests are evident (note the signal below δ 0 ppm). The upfield shift is attributed to diamagnetic ring current effect of the aryl framework of OA [73–76]. In case of coumarin **4** there are no alkyl substituents that would unequivocally confirm its inclusion within OA. Therefore, we depended on changes in the host signals to infer complexation. Comparison of the spectra in Fig. 1(ii-viii) with the OA spectrum in (i) reveals the distinct difference between the complexed and free OA. In the case of **4**, since the aromatic hydrogen signals are merged with the OA signals, we could not identify their signals in the spectrum (Fig. 1v).

Confirmation of its inclusion came from the ^{1}H NMR titration studies (Figs. S14–S18). Close examination of the spectra in Fig. S17 reveals that when the host:guest ratio is 1:0.5, *i.e* the ratio corresponding to a capsule with one guest molecule, signals due to free OA are visible (Fig. 2 iii). This suggested that 50 mol% of guest is not sufficient to fill all the host capsules. These signals completely disappeared only when the ratio reached 1:1 indicating that when the OA capsule is filled with two molecules, no free OA remains in solution. Similar to coumarin **4**, coumarin **5** also forms 2:2 complex with OA (Fig. 2). This is evident when one compares the titration spectra of coumarin **5** with that of coumarin **4** (Fig. 2 with Fig. S17). Similar to **4**, when the host–guest ratio reached 1:1, no longer there were signals due to free OA, and the OA signals were not split. These suggested that two molecules of guest are accommodated in a symmetrical fashion within a capsule made up of two molecules of OA. As opposed to short alkoxy chain appended **5**, the



Scheme 2. Structures of TC derivatives (**1**–**7**) and water-soluble octa acid (OA) cavitand (**8**).

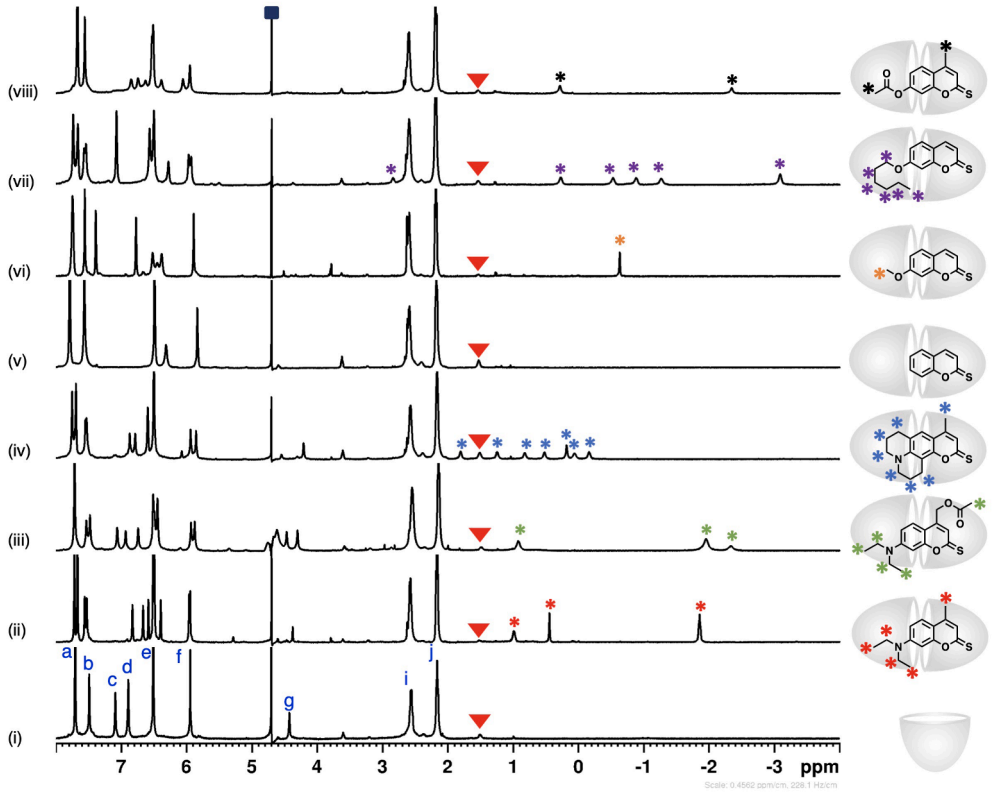


Fig. 1. ^{1}H NMR (500 MHz) spectra of guest molecules included within octa acid (OA). Bottom to top guest (i) OA, (ii) **1**@OA_2, (iii) **2**@OA_2, (iv) **3**@OA_2, (v) $\mathbf{4_2}$@OA_2, (vi) $\mathbf{5_2}$@OA_2, (vii) **6**@OA_2, and (viii) **7**@OA_2. ▼ indicates OA impurity peak; ▪ indicates the residual solvent peak (water) of D_2O. The guest signals are indicated with colored stars.

long alkoxy chain appended guest **6** (7-hexyloxy) forms 2:1 complex. In both cases, inclusion within OA capsule is confirmed by the upfield shift of the signals due to of the alkoxy chain. In the case of **5**, when the ratio of the host to the guest is 2:1, the OA signal at δ ~ 5.9 is split indicating almost half of OA molecules in solution remain uncomplexed. On the other hand, in the case of **6**, the host does not solubilize more than half equivalent of the guest indicating the formation of 2:1 complex. At this stage (Fig. 3v) the host signals are split due to unsymmetrical nature of the capsule after guest inclusion. Since the large guest molecule does not tumble within the OA capsule, identical hydrogens present in the top and bottom halves of the capsule experience different magnetic shielding [73,77]. This is the case with all guest molecules that form 2:1 complex (**1**–**3**, **6** and **7**). Based on ^{1}H NMR spectra (Figs. S14–S18 in SI) we conclude except for **4** and **5** all other TCs form 2:1 while these two forms 2:2 capsular assemblies. As will become obvious in the discussion section this is an important conclusion. Independent of how many molecules are included within OA, all TCs are protected from water molecules and dissolved oxygen by OA. In the context of RTP these are important inferences.

3.2. Absorption spectra

Focus of this manuscript is on the demonstration of RTP of **1**–**7** in aqueous medium. Spectroscopic details and intersystem crossing mechanism of these molecules will be detailed in an independent publication. The absorption spectra shown in Fig. 4 reveals that three of the seven TCs substituted with 7-amino group, exhibit solvent dependence (**1**–**3**). Similar solvatochromic properties are exhibited by the corresponding carbonyl analogs (coumarins) [78,79]. Unlike thioketones where the nπ* and ππ* absorptions are well separated (~150–200 nm) and distinctly visible as two independent bands, in TCs there is no clear absorption due to nπ* [49]. Most likely it is hidden under the strongly absorbing ππ* band extending upto ~ 475 nm in **1**–**3** and ~ 450 nm in **4**–**7** (in hexane).

3.3. Emission spectra at 77 K

To ascertain the likelihood and location of phosphoresce from **1** to **7**, emission spectra were recorded at 77 K in ethanol glass (Figs. 5 and 6) by exciting the molecule in the stronger ππ* band. The spectra on the left are steady-state emission spectra detecting the total luminescence (fluorescence and phosphorescence). The spectra on the right were recorded with pulsed excitation and gated detection, where the data collection time-window is delayed after the short-lived fluorescence has decayed to collect only phosphorescence. The long lifetime varying between 33 and 15,100 μs (Table 1) measured for the emission in the region 570–740 nm further supports their assignment to phosphorescence. It is interesting to note that of the seven TCs only **4** and **5** form 2:2 complex. Of these **5** shows two triplet lifetimes indicating that the two molecules in the cage do not have identical environments. On the other hand, TC **4** show only one lifetime. It is quite likely that smaller **4** is able to freely rotate within the capsule making the two molecules experience identical environments. The ungated spectra displayed in Figs. 5 and 6 unambiguously suggest that all three amino substituted TCs show both fluorescence and phosphorescence. However, the rest show only phosphorescence at room temperature and 77 K. This suggests that the intramolecular charge transfer (ICT and TICT) most likely play a role in decay of the excited singlet state of **1**–**3**. We are currently investigating the role of charge transfer phenomenon in TCs **1**–**3** in the context of solvation dynamics and phototriggering mechanism.

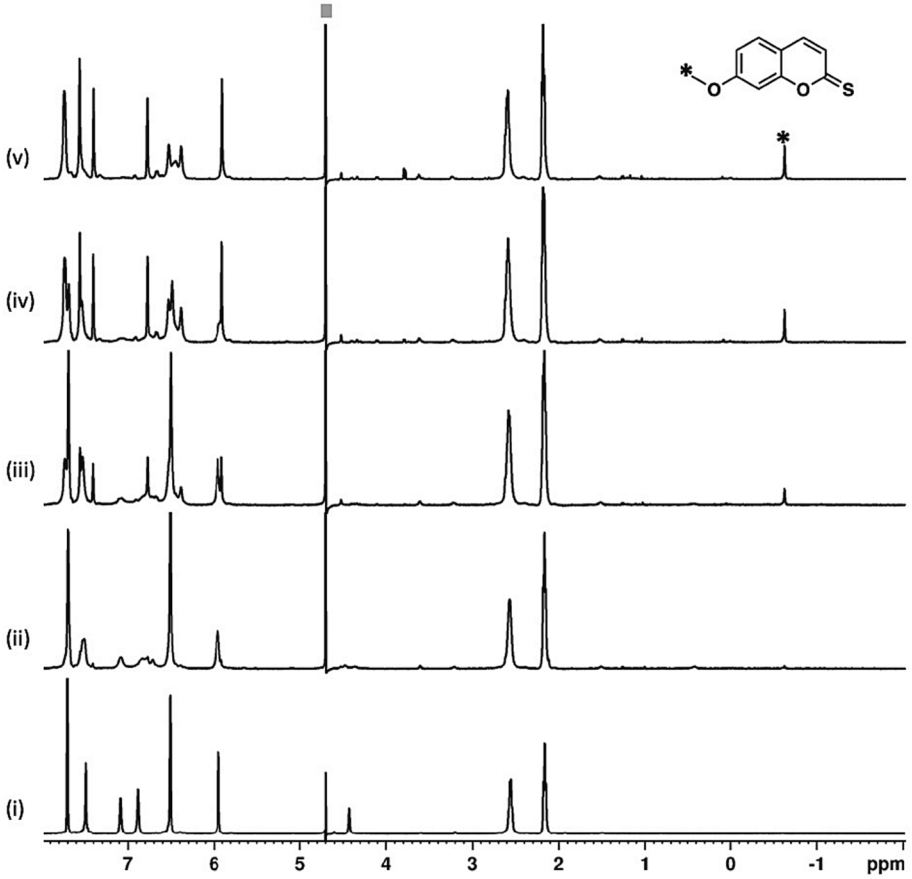


Fig. 2. ^{1}H NMR spectra (500 MHz, 10 mM $Na_2B_4O_7$ buffer/ D_2O, pH = 8.7) of (i) OA; ([OA] = 1 mM; (ii) **5**@OA; ([OA] = 1 mM and [**5**] = 0.25 mM; (iii) **5**@OA; ([OA] = 1 mM and [**5**] = 0.5 mM; (iv) **5**@OA; ([OA] = 1 mM and [**5**] = 0.75 mM; (v) **5**@OA; ([OA] = 1 mM and [**5**] = 1 mM. "*" indicates the OA-bound guest proton resonance. ■ indicates the residual solvent peak (water) of D_2O.

3.4. Emission spectra at room temperature in organic solvents and in aqueous solution

Having identified the characteristics of the phosphorescence from **1** to **7** at 77 K, we recorded the phosphoresce spectra at room temperature. Our goal was to demonstrate the value of OA in facilitating RTP from TCs. We have shown earlier that OA is a valuable host to record RTP of thioketones, benzil and pyrene [59,65,66]. The current undertaking is to establish the generality of OA as a host to record RTP of organic molecules in water. Before proceeding to present the results, it is important to note that the seven thiocoumarins **1**–**7** discussed here can be classified into four categories. Close examination of their behavior provide opportunities to test whether the OA capsule can facilitate RTP in systems undergoing a variety of competing processes: (a) TCs in general are known to undergo diffusion limited self-quenching [80–84]. Question is when there are two molecules encapsulated within a single OA capsule can RTP compete with self-quenching? TCs **4** and **5** help to address this question. (b) Excited states of TCs are well known to be quenched by oxygen both by physical and chemical processes [80,85–89]. Can encapsulation overcome this process? In fact, all systems investigated here help to answer this question. (c) Coumarins with 7-amino substituents are well-known to exhibit charge transfer behavior in the excited singlet state [60–62,78,80]. Will the charge transfer process from amino group to the excited thiocarbonyl group (ICT and TICT processes) suppress the RTP of OA encapsulated guests? TCs **1**–**3** were selected to find the answer to this question. (d) TC **2** undergoes unimolecular fragmentation process from the excited state. Can RTP compete with a fast chemical reaction?

The emission spectra at room temperature were recorded in organic solvents and in borate buffer solution. In Figs. 7 and 8 emission spectra of **1** and **2**–**7** in polar hydroxylic solvent methanol, nonpolar hexane and capsular assembly OA in borate buffer are provided. A quick glance of all spectra reveals that the phosphorescence is stronger within OA compared to that in isotropic solvents methanol and hexane. Fig. 7a and b display the absorption and emission spectra of **1**. In methanol there is fluorescence but no phosphorescence while in hexane negligible fluorescence and only weak phosphorescence is observed. On the other hand, OA encapsulated **1** in water show mostly phosphorescence. This example clearly brings out the value of OA in the context of RTP. To be sure that OA is responsible for this dramatic change in the emissive behavior, titration by gradual addition of OA to **1** in borate buffer was performed and the changes in absorption and emission were monitored. Results shown in Fig. 7c (absorption) and 7d (emission) are telling. The absorption shows a blue shift with increased addition of OA indicating **1** is being slowly encapsulated with the increased addition of OA. The encapsulation as shown in Fig. 7d shifts from fluorescence to phosphorescence with the increased addition of OA. This is more easily seen in the inset of Fig. 7d. Similar changes in absorption and emission spectra for **3** are shown in Fig. S27. As seen in Fig. 8b–f, an enhancement in phosphorescence within OA was observed for TCs **3**–**7**. As mentioned above, TC **2** undergoes facile cleavage of the Aryl-CH_2–-O(C = O)CH_3 to release CH_3COO^-. At room temperature this molecule does not show phosphorescence (Fig. 8a). The radiative process, most likely, is unable to compete with the β-cleavage process. Interestingly at 77 K this molecule phosphoresces (Fig. 5b). Probably, at this temperature the emission is able to compete with the slowed β-cleavage process. Also, to note is that this molecule does not cleave in nonpolar solvents such as hexane and ethyl acetate. In both solvents very weak phosphorescence is

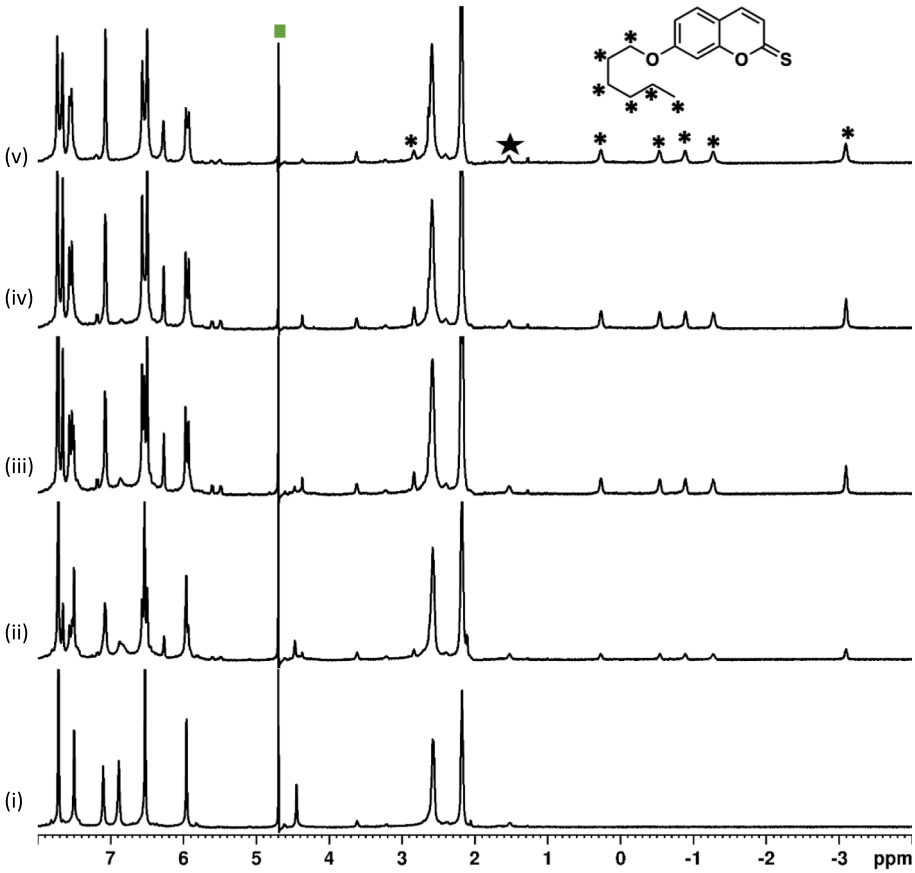


Fig. 3. ^{1}H NMR spectra (500 MHz, 10 mM $Na_2B_4O_7$ buffer/ D_2O, pH = 8.7) of (i) OA; [OA] = 1 mM; (ii) **6**@OA; [OA] = 1 mM and [**6**] = 0.125 mM; (iii) **6**@OA; [OA] = 1 mM and [**6**] = 0.25 mM; (iv) **6**@OA; [OA] = 1 mM and [**6**] = 0.375 mM; and (v) **6**@OA; [OA] = 1 mM and [**6**] = 0.5 mM. "*" indicate the OA bound guest proton resonance, ▪ indicates the residual solvent peak (water) of D_2O. indicates the OA impurity peak.

seen (Fig. S21). However, lack of RTP from OA encapsulated **2** suggests that the cleavage does occur in this environment and the radiative process is unable to compete with it. Detailed discussion of this observation will be published elsewhere. To conclude this section, we present the time gated RTP emission spectra of six of the seven TCs investigated here. These spectra unequivocally attest to the usefulness of OA as the medium to record RTP of organic molecules (Fig. 9).

3.5. Control experiments

To confirm the observed emission is not due to impurity and the emission is indeed phosphorescence, additional experiments were carried out. Results are presented in SI. The excitation spectra for **4**–**7** reproduced in Fig. S19 (SI) confirm that the phosphorescence excitation and absorption spectra overlap confirming the emission indeed arises from TCs. As expected of the phosphorescence, the emission was quenched by oxygen in organic solvents but when the coumarins are encapsulated within OA (for one example see Fig. 10 and for all see Figs. S20–S26) the quenching was inefficient. Triplet decay as followed by changes in the phosphorescence intensity are provided in Figs. S28 and S29. The decay is almost single exponential within OA at room temperature and double exponential in ethanol glass at 77 K. Microsecond lifetimes (Table 1) at room temperature, oxygen quenching of the emission, overlap of the excitation and absorption spectra and identical spectra at 77 K in ethanol glass support our conclusion that OA capsule facilitates RTP of TCs.

4. Discussion

4.1. Background

Prior to discussing the results presented above, it is useful to summarize what is known about the excited state properties of molecules possessing thiocarbonyl chromophore [22,49,90,91]. Thiocarbonyls in general have near unit quantum yield of intersystem crossing (ISC) from exited singlet (S_1) to triplet manifold and possess high inherent spin–orbit coupling, the reason for which yet to be fully understood [49,92,93]. They show phosphorescence from T_1 and fluorescence from S_2. Because of high spin–orbit coupling no external perturbation such as heavy atom effect is needed to induce ISC. This eliminates the need to suppress pathways that deactivate S_1 (Scheme 1) to observe RTP. Therefore, in principle, restraining the pathways that compete with the radiative one in the triplet manifold (k_P vs the rest in Scheme 1), should be sufficient to record RTP from molecules having C=S chromophore. Earlier we showed that RTP from several aromatic thioketones can be recorded with the help of OA and cucurbiturils as hosts in water [59]. In this article, we demonstrate that the same experimental method can be applied to TCs whose excited state properties are slightly different from thioketones. In this context, we have explored the use of OA capsule in borate buffer solution as a medium to record RTP from TCs **1**–**7** (Scheme 2) in aqueous solution.

Unlike thioketones, photochemical studies on TCs are very few [80,94–97]. Time resolved (nano to femtosecond) experiments and quantum chemical calculations on the parent TC [80,95,97] have revealed it to have unit quantum yield of ISC from $S_1(n\pi^*)$ to triplet

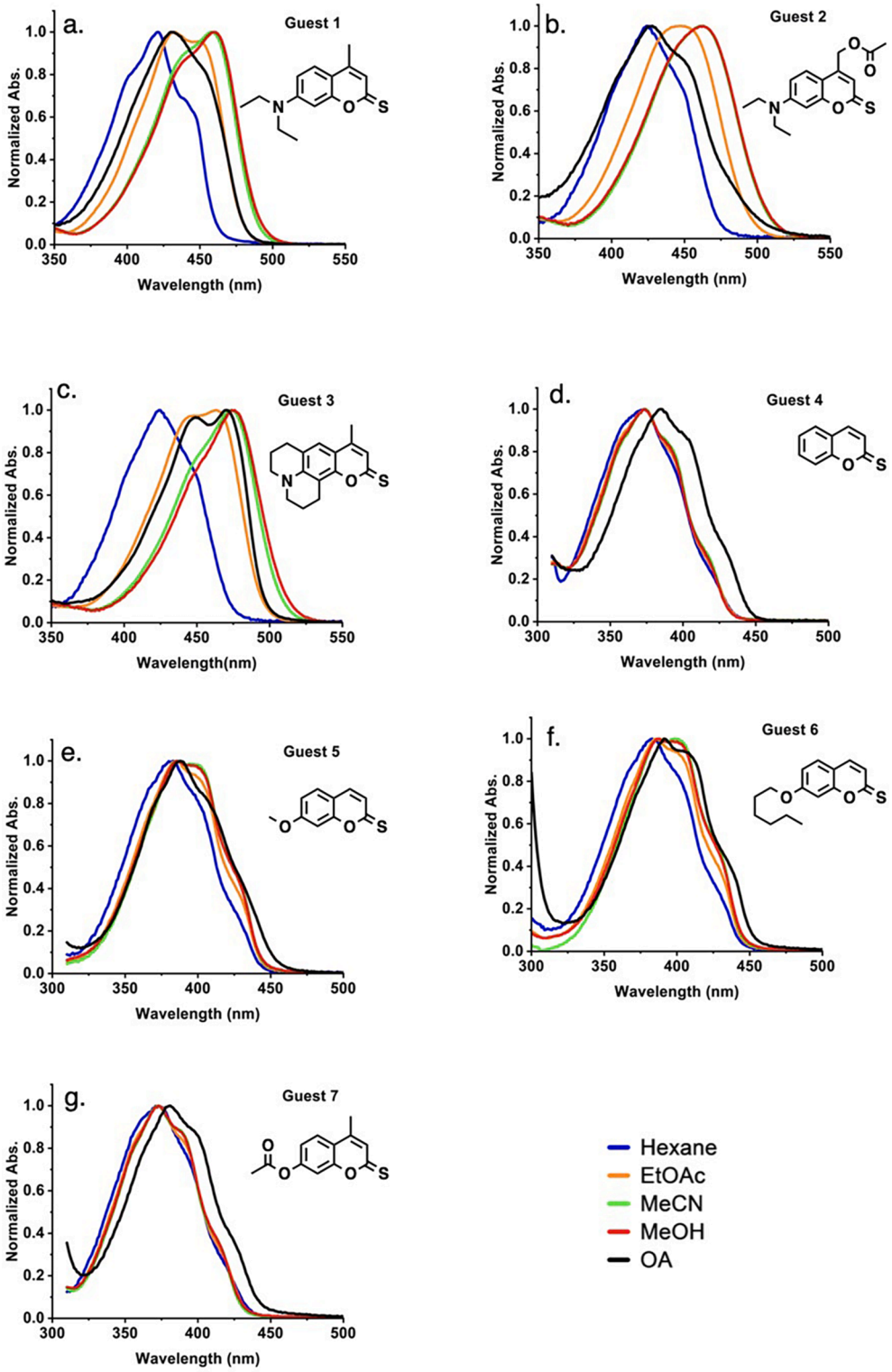


Fig. 4. Normalized absorption spectra of guests (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, (f) **6**, (g) **7** in hexane (blue), ethyl acetate (EtOAc, orange), acetonitrile (MeCN, green), methanol (MeOH, red) and OA (black) recorded at room temperature.

manifold and high spin–orbit coupling constant between S_1 to T_n (~24 cm^{-1}). Based on computational methods the parent TC is speculated to have T_1 with $\pi\pi^*$ character [94]. This is different from thioketones where the two states (S_1 and T_1) are of $n\pi^*$ in character. In TC, as compared to that in thioketones, the energy gap between S_2 and S_1 is small (~6000 cm^{-1}), which lowers the $\pi\pi^*$ triplet below $S_1(n\pi^*)$ state. Based on this it is suggested that the ISC in this system occurs from $S_1(n\pi^*)$ to $T_1(\pi\pi^*)$. This is in accordance with the El-Sayed's rule [15,98,99], which suggests that ISC between spin states of different electronic characters would be faster. Thus, high spin–orbit coupling in C=S chromophore and states involving different electronic character favor high rate of ISC in TC.

To our knowledge there is only one report of recording the phosphorescence of TC at room temperature in perfluoro-hydrocarbon

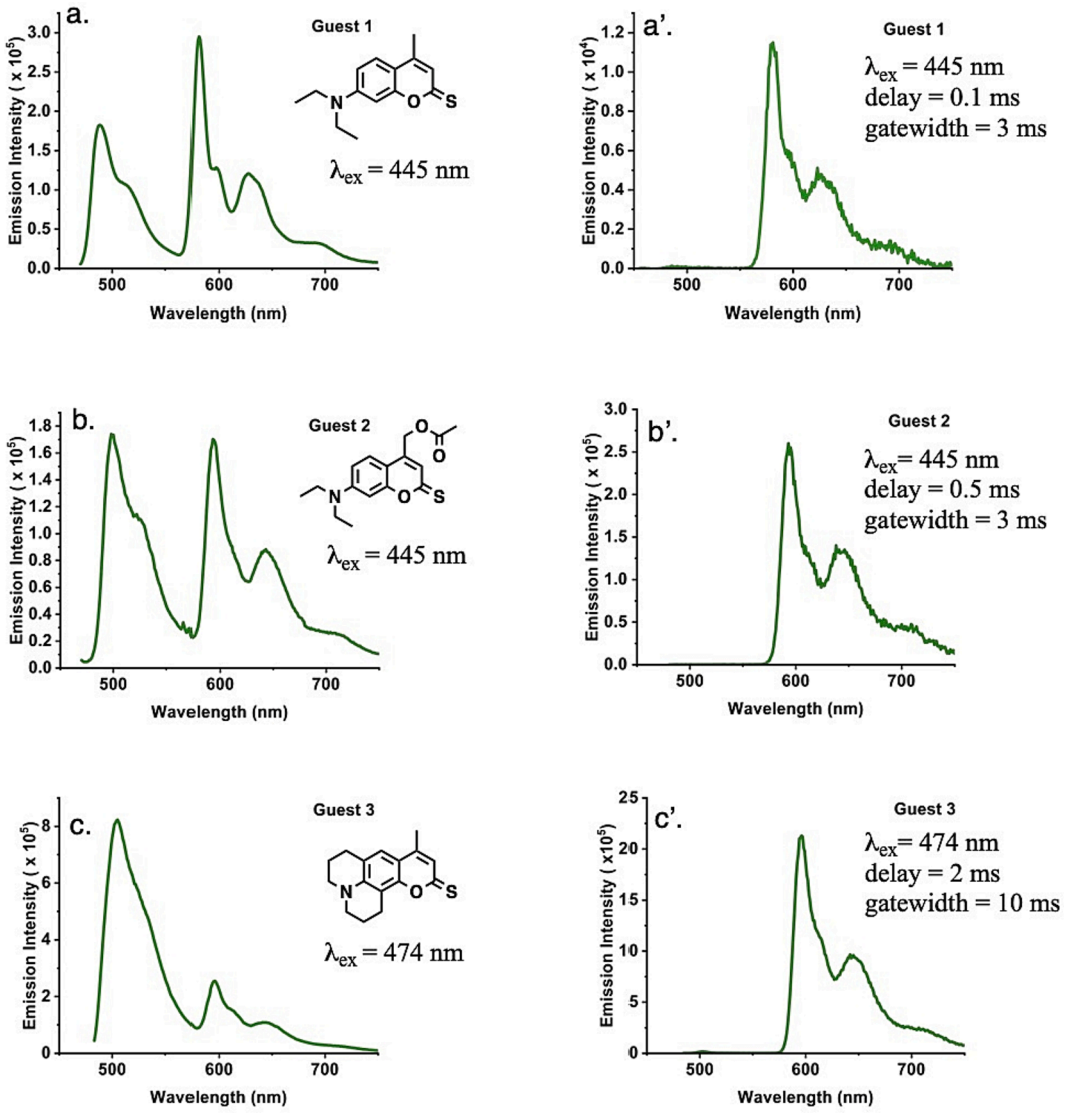


Fig. 5. Emission spectra of guests **1**–**3** without gating (left panel a-c) and with gating (right panel a'-c') in ethanol glass at 77 K.

solvent [95,97]. Even in this case the quantum yield is reported to be less than 10^{-5} indicating that one can't record RTP from TCs using readily available conventional fluorimeters. Lack of literature on RTP of TCs could be attributed to diffusion limited self-quenching and oxygen quenching in the triplet state and their facile reaction with solvent molecules, especially hydrocarbons from the triplet state [80]. Thus, the parent and substituted TCs are ideal set of molecules to test the value of OA capsule to enhance phosphorescene at the expense of self-quenching, oxygen quenching and reaction with solvent molecules. Spectra presented in the results section demonstrate that we have succeeded in this effort and have recorded RTP of several TCs. Results are discussed below in the following order: (a) OA-TCs complex (represented as TC@OA_2) formation in borate buffer (b) emission from TCs in solution at low and room temperature, (c) emission from TC@OA_2 at room temperature in borate buffer.

4.2. OA-TCs complexation in borate buffer

The focus of this investigation is to establish that OA capsule can serve as a vehicle to bring about RTP of TCs in water. Therefore, the first step is to establish the inclusion of **1**–**7** within OA capsule. Inclusion was established by monitoring the changes in the ^{1}H NMR signals of the guests and the host OA in each other's presence. The ^{1}H NMR spectra presented in Figs. 1–3 and Figs. S14–S18 in SI suggest that the inclusion indeed occurs. As discussed in the results section inclusion of guests within OA is revealed by the significant upfield shift in the ^{1}H NMR signals of the guest and moderate, yet readily seen disturbance in the signals of the host OA. Such changes confirm the inclusion of **1**–**7** within OA capsule. Also, the number of guest molecules included within OA capsule is deduced from ^{1}H NMR titration experiments (Figs. 2 and 3, and Figs. S14–S18). Except for parent TC (**4**) and 7-methoxyTC (**5**) all others formed 2:1 (host:guest) complexes. These two formed 2:2 complex resulting in exceptionally high local concentration within a capsule.

The interior of the OA capsule is established to have a polarity similar to that of benzene [72]. Therefore, the guest molecules residing within a OA capsule in aqueous medium are expected to experience a polarity similar to that of benzene rather than that of water. The absorption spectra of **1**–**3** in presence of OA confirm that these molecules reside within a non-polar environment and not in water. As shown in Fig. 4 the absorption maxima of **1**–**3** are solvent polarity dependent, the maximum being at shorter wavelength in hexane than in methanol. The absorption spectra displayed in Fig. 7(c) and Fig. S27 nicely bring out the consequence of inclusion of **1**–**3** within OA. Upon slow addition of OA to **1**–**3** in water, the absorption maximum shifts to shorter wavelength indicating that the molecule moves from polar aqueous environment to a non-polar one. Inclusion within OA results in changes in the emissive

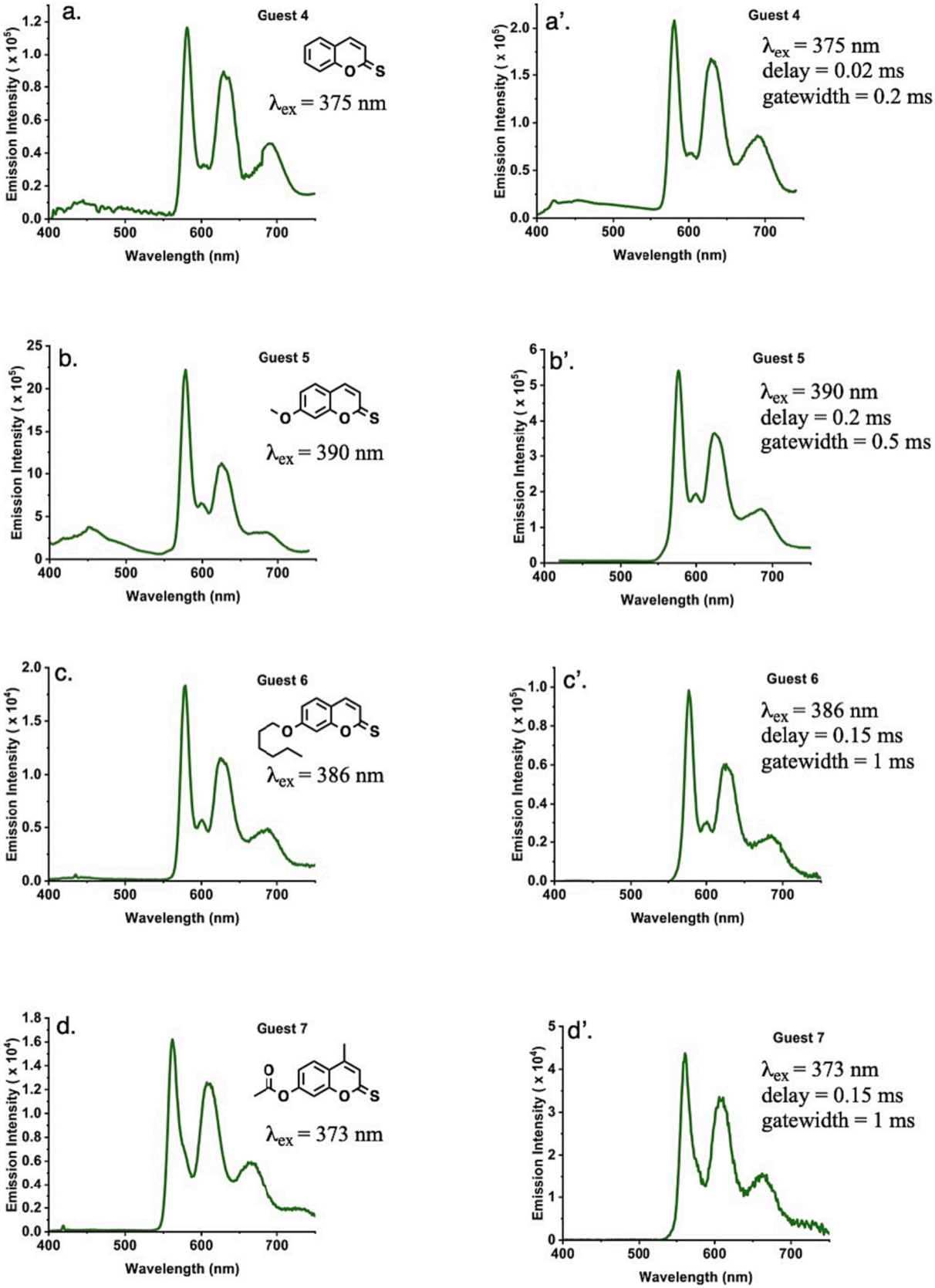
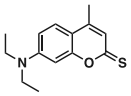
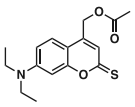
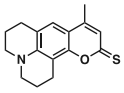
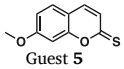
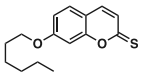
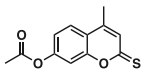


Fig. 6. Emission spectra of guests **4**–**7** without gating (left panel a-d) and with gating (right panel a'-d') in ethanol glass at 77 K.

Table 1
Triplet lifetime of guest molecules inside OA complex at room temperature and at low temperature in EtOH glass (77 K).

	Triplet lifetime in OA complex at RT (μs)	Triplet lifetime in EtOH at 77 K (μs)
 Guest **1**	τ = 123 (100 %)	τ_1 = 3800 (69 %) τ_2 = 10200 (31 %)
 Guest **2**	No phosphorescence	τ_1 = 1612 (55 %) τ_2 = 3921 (45 %)
 Guest **3**	τ = 281 (100 %)	τ_1 = 4800 (64 %) τ_2 = 15100 (36 %)
 Guest **4**	τ = 3 (100 %)	τ = 33 (100 %)
 Guest **5**	τ_1 = 6.8 (10 %) τ_2 = 21 (90 %)	τ_1 = 112 (87 %) τ_2 = 292 (13 %)
 Guest **6**	τ = 16 (100 %)	τ_1 = 117 (83 %) τ_2 = 238 (17 %)
 Guest **7**	τ = 20 (100 %)	τ = 103 (100 %)

behavior. Briefly, **1**–**3** when present in water emit only fluorescence at room temperature (Fig. 7d and Fig. S27). Upon addition of OA, the fluorescence is replaced by phosphorescence. Obviously, the emission characteristic of **1**–**3** depends on their immediate environment. Details will be discussed below.

4.3. Emission in ethanol glass at 77 K

The emission spectra at 77 K in ethanol glass displayed in Figs. 5 and 6 suggest that TCs examined here could be divided into two groups, one that emits only phosphorescence (**4**–**7**) and the other that show both fluorescence and phosphorescence (**1**–**3**). Based on the literature reports on the parent system **4** [94,95] and other thioketones [22,49], TCs are expected to show only phosphorescence. The behavior of **4**–**7** is consistent with this expectation. The fact that the **4**–**7** phosphoresce in the same region with similar vibrational pattern indicates that the emitting state in all of them probably have the same electronic character. The lifetimes of the emitting state in **4**–**7** at 77 K varies between 33 and 292 μs (Table 1). This is in the range (109–210 μs) reported earlier for pure nπ* triplet state of aryl alkyl thioketones at 77 K (EPA glass) [100]. Based on the lifetime, we surmise the emitting triplet in **4**–**7** is also nπ*. However, for **4**, based on quantum chemical calculations the lowest triplet is suggested to be ππ* [94]. Resolution of the nature of the emitting state requires further experimentation.

The unexpected observation relates to **1**–**3**. Despite expected high rate of ISC in C=S systems, these three TCs substituted with amino group at the 7-position emit both fluorescence and phosphorescence at 77 K. Comparison of the intensities of fluorescence and phosphorescence suggest that intramolecular electron/charge transfer from the electron donor 7-amino group to the excited C=S chromophore can compete with the ISC from S_1 to T_n. Comparison of the three systems reveals that the relative fluorescence in **1** and **2** is lower than that in **3**. In structural terms, the difference between the first two and **3** is mainly the flexibility of the amino group. In **3**, the amino group is constrained and planarized which would lead to better conjugation of the p-orbital on nitrogen with the π-frame of the aromatic and C=S groups. Due to steric reasons, in **1** and **2** the amino group most likely would remain rotated out of plane in ethanol glass at 77 K. This would reduce the rate of electron/charge transfer from amino group to the excited C=S group. Thus, the enhanced fluorescence in **3** is consistent with the expected difference in rates of electron/charge flow from the nitrogen lone pair to the excited C=S chromophore. Thus, the difference in emissive behavior of the two groups could be attributed to the possibility of electron/charge transfer in **1**–**3** and its absence in **4**–**7**. Similar intramolecular electron/charge transfer properties of corresponding coumarins have been extensively investigated and are used to probe solvation dynamics and mechanism of intramolecular charge transfer (ICT) and twisted intramolecular charge transfer (TICT) phenomenon [60–63,101]. We believe similar ICT and TICT experiments could be used to probe the origin of the high rate of ISC process in thiocarbonyl systems. We are currently pursuing experiments to understand these interesting aspects of **1**–**3**.

In addition, a point to note is that the triplet lifetime of these three TCs are at least an order of magnitude longer than that of **4**–**7** (range: 1612–15,100 μs; Table 1). Most likely, the emitting triplets in the two groups of molecules are not the same; in **1**–**3** the triplets may have some charge transfer character, similar to that in the singlet state while that in **4**–**7** it may be a localized nπ* or ππ*. Such a difference could lead to variation in k_p (Scheme 1) and lifetime between the two groups of TCs (Table 1). In conclusion all TCs investigated here show phosphorescence at 77 K. Interestingly the spectra including vibrational pattern are similar for all seven molecules. However, the spectra in **1**–**3** are slightly shifted to longer wavelength than in **4**–**7**.

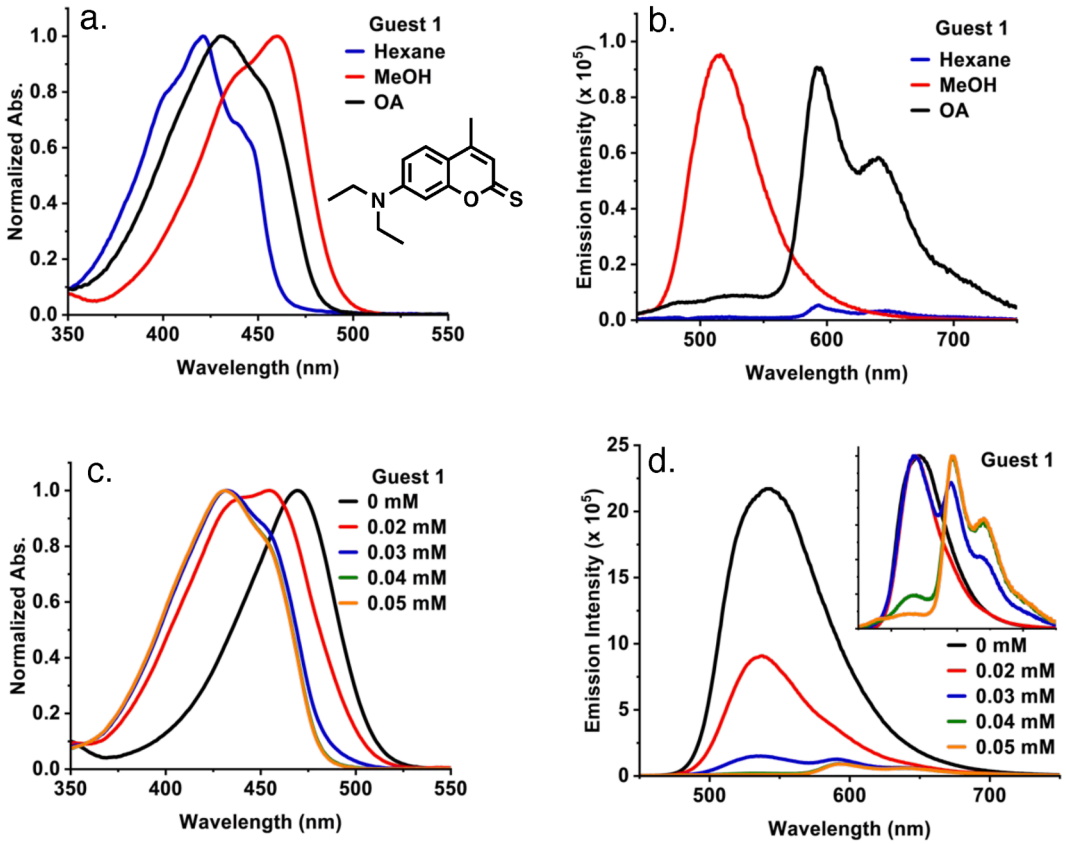


Fig. 7. (a) Absorption and (b) emission spectra of guest **1** (λ_{ex} = 430 nm) in hexane (blue), methanol (red), and OA (black), (c) absorption of guest **1** in borate buffer with addition of OA and (d) emission of guest **1** in borate buffer with addition of OA (λ_{ex} = 430 nm) (inset: normalized emission spectra of the ones shown below). Guest concentration: 0.01 mM; deoxygenated solutions (nitrogen bubbled).

4.4. Absorption and emission in isotropic solvents at room temperature

To record emission spectra we considered polar water, methanol and acetonitrile, and non-polar hexane and ethyl acetate as solvents. All TCs investigated here are practically insoluble in water and slightly soluble in hexane and methanol. Although, absorption, and emission could be recorded in water, hexane and methanol, because of solubility limits ^{1}H NMR spectra could not be recorded in these solvents. Luckily, TCs solubility in ethyl acetate and acetonitrile allows recording of ^{1}H NMR spectra in addition to absorption and emission.

The absorption spectra of **1**–**7** in methanol, acetonitrile, hexane and ethyl acetate are displayed in Fig. 4. Like the emission spectra at 77 K discussed above, the absorption characteristics also differ between the two groups, **1**–**3** and **4**–**7**. The absorption of **1**–**3** is solvent dependent, the maximum shifts towards shorter wavelength with decreasing polarity. On the other hand, the absorption spectra of **4**–**7** are relatively solvent independent. This difference suggests that the electronic character of the excited singlet states involved in transition are not identical in these two groups of molecules. In the former, charge transfer from amino lone pair may also play a role. Another feature to note is that unlike in thioketones, the nπ* and ππ* absorptions are not well separated. The former appears only as an inflection on the stronger ππ* band. The close placement of the two states suggests that both S_1 and S_2 states may have mixed nπ* and ππ* character and may not be pure states as in thioketones.

The emission spectra of **1**–**7** in various solvents under nitrogen saturated and aerated conditions at room temperature are presented in Figs. 7 to 9 and Figs. S20–S26. In all cases the phosphorescence, if at all observed was weak. As seen in Figs. 7 and 8 and Figs. S20–S22, **1–3** emit only fluorescence in polar methanol and acetonitrile. However, in nonpolar solvents such as ethyl acetate and hexane they show extremely weak phosphorescence. As expected, the latter emission is quenched in aerated solvents. Apparently, the intramolecular electron/charge transfer discussed above occurs only in polar medium and in this the ISC, a pre-requisite for phosphorescence is unable to compete with this process. In contrast to **1**–**3**, TCs **4**–**7** show weak phosphorescence both in polar and nonpolar solvents (Fig. 8). Obviously, absence of intramolecular electron/charge transfer in these media, independent of the solvent, permits ISC to compete with the decay of S_1 (Scheme 1). Results presented here suggest that TCs do show weak phosphorescence in organic solvents provided they are deoxygenated. Difference in intensities of phosphorescence between 77 K and room temperature (strong vs weak) could be attributed to diffusion limited self-quenching in isotropic solution medium. Given the early reports on the phosphorescence of benzophenone, benzil and acetophenones at room temperature in organic solvents, ability to record weak phosphorescence should not come as a surprise [16–20]. To curtail self-quenching and oxygen quenching and improve the solubility, we explored OA as the host to solubilize TCs in water.

4.5. Room temperature phosphorescence from OA encapsulated TCs (TCs@OA$_2$)

In this section we discuss the emissive behavior of **1**–**7** included within OA in borate buffer solution at room temperature. Relevant spectra are shown in Figs. 7–10 and Figs. S21–S27. TCs examined here are soluble in water only to the extent of being able to record absorption and emission spectra. However, when these TCs were added to a borate buffer solution containing OA, they readily dissolved enabling recording of absorption, emission and ^{1}H NMR spectra. Since NMR and absorption spectra that confirmed the inclusion of TCs within OA were discussed in detail in an earlier section, only emission properties are discussed below.

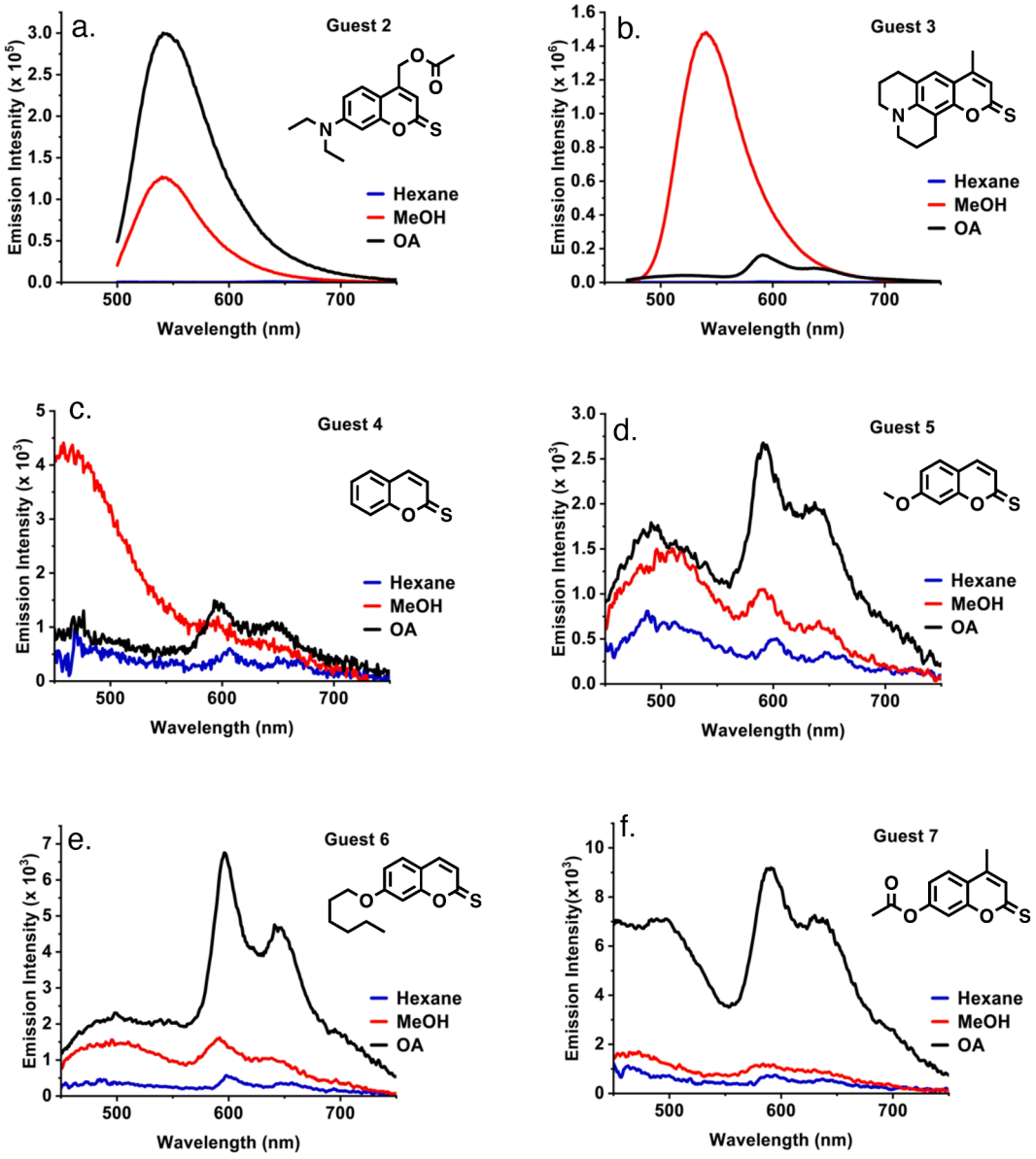


Fig. 8. Emission spectra at room temperature in deoxygenated (nitrogen bubbled) solutions of guest (a) **2** (λ_{ex} = 480 nm), (b) **3** (λ_{ex} = 450 nm), (c) **4** (λ_{ex} = 410 nm), (d) **5** (λ_{ex} = 430 nm), (e) **6** (λ_{ex} = 430 nm), and (f) **7** (λ_{ex} = 400 nm) in hexane (blue), methanol (red) and OA (black).

Remarkably, **4**–**7** showed intense phosphorescence as OA complexes in water than as free molecules in water, hexane and methanol (Figs. 7 and 8). As expected, the emission at room temperature resembles that at 77 K. Confirmation that this is indeed phosphorescence came from the overlap of absorption and excitation spectra (Fig. S19). We have earlier established that oxygen quenches the phosphorescence from OA encapsulated guest molecules provided their lifetimes are longer than 5 μs [102]. This is the minimum time required for the capsule to open-close for oxygen to reach the excited guest molecule (note that the opening-closing time could vary with the guest molecule). The emission spectra under nitrogen saturated and aerated conditions shown in Fig. 10 and Figs. S20–S26 illustrate that the phosphorescence of OA encapsulated TCs is quenched by oxygen, but much less efficiently than in free solution. For quenching by oxygen the capsule has to open at least partially for it to reach the excited TC. The lifetimes of most TC listed in Table 1 are closer to or longer than 5 μs. In this time range the capsule would be expected to open partially allowing quenching by oxygen to occur. Different amounts of quenching can be due to different lifetimes of TCs. Also, how much the capsule would open would depend on how tightly the guest resides within OA. The uniqueness of OA as a medium is brought out by the emissive behavior of **4** and **5** that form 2:2 complexes ($\mathbf{4}_2$@OA_2 and $\mathbf{5}_2$@OA_2). Based on the established behavior in solution, when two TC molecules are trapped in a small space as in OA capsule, one would expect the triplet TC to be immediately quenched by the second molecule in the ground state [49,81–83,90]. This would completely suppress the phosphorescence. Ability to record RTP from these two OA encapsulated TCs, even when two molecules are adjacent to each other, we believe, is a consequence of two molecules having very little freedom to undergo rotational and translational motions within the capsule. This restriction of mobility, likely, does not allow the excited and ground state molecules to get close in the correct geometry for quenching [81]. This observation is consistent with the behavior of OA encapsulated thioketones reported earlier [59]. The above examples illustrate that one can record RTP even from the TCs that have very little solubility in water, possess diffusion limited self-quenching and oxygen quenching.

Of the three 7-amino substituted TCs, only OA encapsulated **1** and **3** showed phosphorescence. A compelling result came during the titration

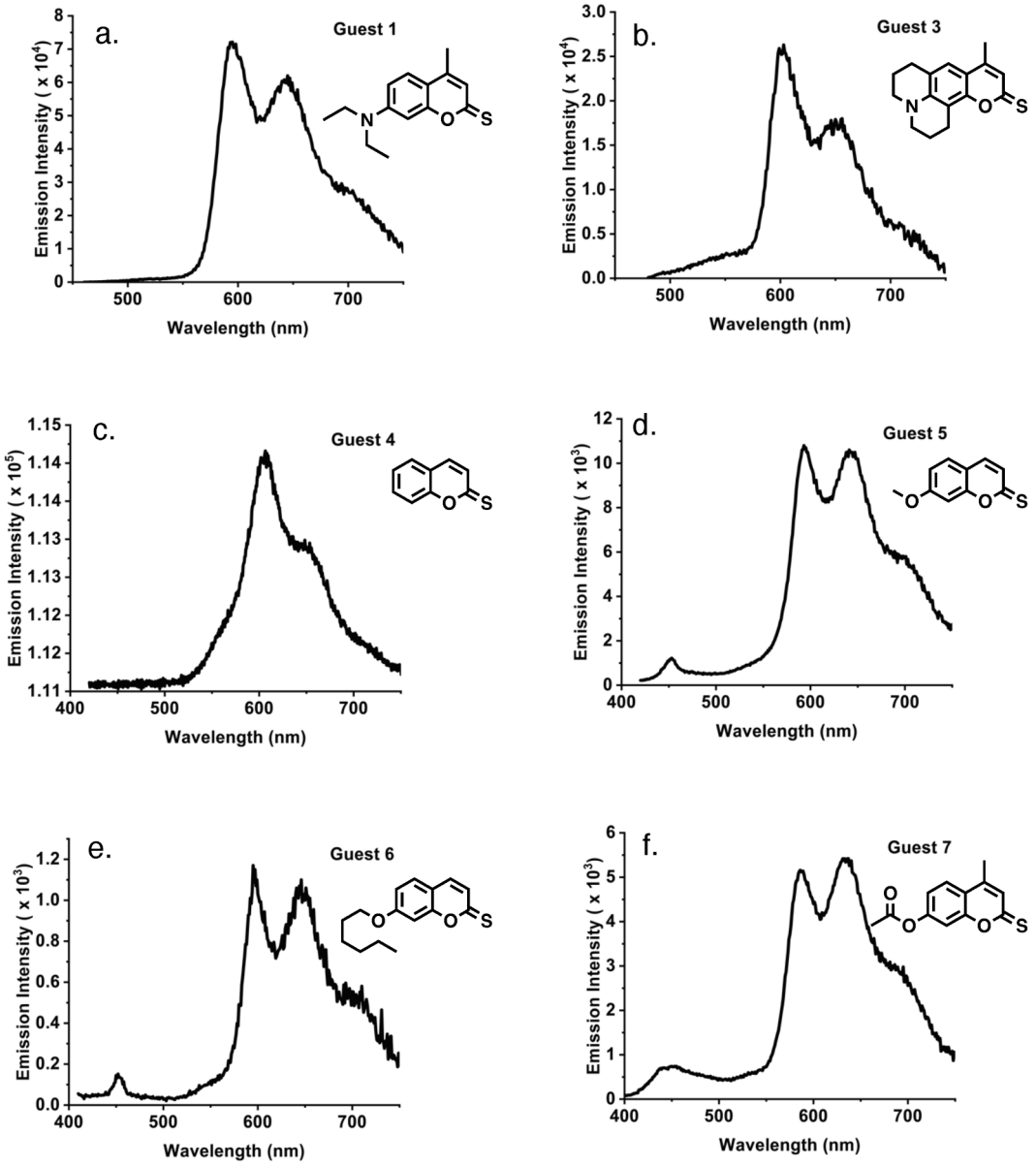


Fig. 9. Time-gated emission spectra at room temperature in deoxygenated (nitrogen bubbled) solutions of (a) **1@OA$_2$** (λ_{ex} = 430 nm, gate width 1 ms, delay 0.15 ms), (b) **3@OA$_2$** (λ_{ex} = 470 nm, gate width 1 ms, delay 0.15 ms), (c) **4$_2$@OA$_2$** (λ_{ex} = 410 nm, gate width 400 ns, delay 100 ns), (d) **5$_2$@OA$_2$** (λ_{ex} = 390 nm, gate width 1 ms, delay 0.135 ms), (e) **6@OA$_2$** (λ_{ex} = 392 nm, gate width 1 ms, delay 0.1 ms), (f) **7@OA$_2$** (λ_{ex} = 381 nm, gate width 1 ms, delay 0.14 ms).

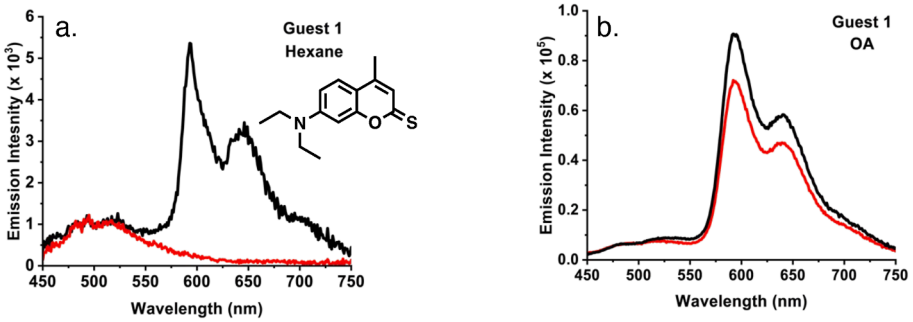


Fig. 10. Emission spectra of guest 1 in (a) hexane under aerated (red) and nitrogen saturated (black), (b) OA under aerated (red) and nitrogen saturated (black).

of OA into a borate buffer solution (pH ~ 8.5) of **1** (Fig. 7d). In water, where it is very poorly soluble, showed only fluorescence. Upon slow addition of OA into the buffer solution of **1**, the phosphorescence enhanced at the expense of fluorescence and upon complete complexation of the guest by OA there was only phosphorescence (see TOC graphics and Fig. 7d). Similar behavior was exhibited by **3** (Fig. S27).

Clearly, OA has suppressed the intramolecular electron/charge transfer that favored the fluorescence in ethanol glass at 77 K, as well as in water, methanol and acetonitrile as solvents at room temperature. The suppression of this charge/electron transfer could be attributed to the non-polar nature of the OA interior. Similar suppression of intramolecular electron/charge transfer was noticed in hexane and ethyl acetate. Thus OA is able to promote RTP even from molecules that has the potential to compete with ISC process that is needed to promote phosphorescence.

One anomaly in this set of molecules is **2** that does not show RTP even in presence of OA. However, at 77 K this molecule like the other two showed fluorescence and phosphorescence. The reason for this lies in the fact that **2** is the only one among the three that undergoes facile fragmentation of the aryl-CH_2—O-C=O bond to release the acetate anion. Such a process is well studied in coumarinyl system [103]. We are currently examining the phototriggering behavior of TC **2** and related molecules; the results will be published independently in future. Apparently, the OA is unable to suppress the reaction pathway in the excited state (probably the triplet state) although it does the electron/charge transfer pathway (in the excited singlet state). The fact that the triplet lifetimes of the two sets of molecules (**1**–**3** and **4**–**7**) are distinctly different (Table 1) indicate that the electronic nature of the emitting triplets are unlikely to be the same. This bears resemblance to their behavior in ethanol glass at 77 K.

5. Conclusion

To conclude, OA has enabled RTP from six TCs in aqueous solution. The gated spectra shown in Fig. 9 are quite clean and striking. Considering that all these molecules are only sparingly water soluble, ability to record phosphorescence in water is remarkable. Further, OA has suppressed the highly competing pathways of self-quenching in **1**–**7** and electron/charge transfer in **1** and **3**. To some extent, it has reduced the oxygen quenching compared to that in organic solvents. However, OA is unable to favor phosphorescence at the expense of a fast chemical reaction, namely C-O cleavage in the case of **2**. Thus, we have established that one can use OA as host to observe RTP of guest molecules in water. Clearly the TCs that are not capable of intramolecular electron transfer emit strongly within OA capsule. Thus, our contributions to the topic of RTP involves introducing zeolites [54] and octa acid [59] as media. The first enables recording phosphorescence even from highly flexible and photochemically reactive molecules such as polyenes in the solid-state and the latter helps to record phosphorescence in water from molecules that undergo diffusion limited quenching. Potential of these as media to record RTP from a variety of organic molecules is limitless and it is yet to be fully explored. Although the current study was restricted to TCs, most molecules that fit within the capsule are likely to show RTP.

CRediT authorship contribution statement

Sujit Kumar Ghosh: Data curation. **Lakshmy Kannadi Valloli:** Data curation. **Divya Unny:** Data curation. **Jayaraman Sivaguru:** Funding acquisition. **Steffen Jockusch:** Project administration. **Vaidhyanathan Ramamurthy:** Writing – review & editing, Writing – original draft, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

VR and JS thank the generous support of NSF (CHE-1955524, JS and CHE-2204046, VR). LKV thanks the Center for Photochemical Sciences for a McMaster fellowship. We dedicate this article to the memory of Professor Robert S. H. Liu who through his uncanny ability to identify scientific problems, and dedicated teaching and mentoring served as a role model to emulate.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jphotochem.2024.115510.

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