Aqueous phase and amorphous state room temperature phosphorescence from a small aromatic carboxylic derivative

Suman Kuila\(^1\), Swadhin Garain\(^1\), Muthusamy Eswaramoorthy\(^1,2,3\) and Subi J George\(^1,4\)\\
\(^1\) Supramolecular Chemistry Laboratory, New Chemistry Unit and School of Advanced Materials (SAMat), Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur, Bangalore 560064, India.\\
\(^2\) Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur, Bangalore 560064, India.\\
\(^3\) Authors to whom any correspondence should be addressed.\\
E-mail: george@jncasr.ac.in and eswar@jncasr.ac.in\\

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Abstract

Harvesting triplet excitons via room temperature phosphorescence (RTP) in solution or amorphous state from purely organic chromophores is a formidable challenge. Supramolecular hybrid co-assembly between a brominated aromatic carboxylic derivative (BrPhS\(^+\)) and laponite clay (LP) particles is shown to result in remarkable triplet stabilization to result room temperature phosphorescence (RTP) in aqueous solution as well as in amorphous thin films. This remarkable feature is realized by means of highly organized, rigid molecular network of the dye molecules on the inorganic scaffold which reduces the vibrational dissipations as well as limits the oxygen diffusion to facilitate the triplet harvesting under ambient conditions. The water soluble phosphor, BrPhS\(^+\) is also shown to be an excellent triplet emitter in other amorphous polymer matrices like polyvinyl alcohol (PVA) and sodium polystyrene sulphonate (PSS) with phosphorescence quantum yield over 30% in air.

1. Introduction

Purely organic room temperature phosphorescence (RTP) materials have attracted lot of attention recently as promising alternative to expensive and toxic metal based phosphorescent materials [1–5]. However, quantum yield of purely organic phosphors are affected by its poor intersystem crossing yield and high susceptibility towards vibrational as well as oxygen mediated triplet state quenching [6, 7]. As a result, most of the bright organic phosphors are known only in highly crystalline state that minimizes the non-radiative quenching of the triplet excitons by the rigid network of molecules and also by minimizing the oxygen diffusion [8–14]. However, lack of solution-processability of these crystalline phosphors limit its applications as sensors or in display devices [15]. Hence, the design of solution-processable, amorphous state or solution phase RTP is indeed challenging and significant impetus is being given in realizing RTP under ambient conditions [16]. Although, amorphous state RTP has been achieved in few organic systems by incorporating them into rigid polymer matrices [17–20] and macrocyclic hosts [21, 22], solution state RTP still remains as a formidable challenge [23–26].

In this regard, templated supramolecular organization of purely organic phosphors utilizing rigid inorganic silicate template provides a viable strategy to achieve solution phase or amorphous state RTP materials design [27, 28]. Two advantages can be envisaged with such organic-inorganic hybrid supramolecular scaffolding strategy: (a) firstly the inherent rigidity and unique nanoscale periodicity provided by the inorganic template can limit the diffusional motion of the chromophores to reduce the vibrational quenching induced non-radiative decay pathways and (b) secondly restricted oxygen diffusion through the inter-layer galleries of these layered hybrids would prevent the triplet quenching [29–32]. Very recently, we have shown that the well-structured, and negatively charged surfaces of dispersible, laponite nanodiscs can be used to organize the chromophores and to
stabilize the triplets to make solution processable luminescent hybrids. Herein we show, an ambient green phosphorescence emission from a simple water soluble brominated aromatic aldehyde salt (BrPhS (Bromo, Phenyl, Salt), figure 1(a)), using a unique organic–inorganic hybrid self-assembly approach. The electrostatic co-assembly between positively charged BrPhS and negatively charged LP particles results in efficient RTP in both aqueous state as well as solution-processable thin films. In addition, we show BrPhS also emits bright phosphorescence in rigid amorphous polymer matrices e.g. polyvinyl alcohol (PVA) and sodium polystyrene sulphonate (PSS) with excellent phosphorescence quantum yields over 30% in air, indicating the remarkable triplet yield of such a simple organic chromophores under ambient conditions.

2. Materials and methods

2.1. Materials

BrPhS was synthesized according to literature procedure [8] and also see supporting information, S1 is available online at stacks.iop.org/MRX/6/124003/mmedia. Laponite nanoparticles was obtained from Rockwood Additives Ltd, U.K. Sodium polyacrylate (MW = ~5,100) and sodium polystyrene sulphonate (MW = ~70,000) were obtained from sigma Aldrich, polyvinyl alcohol (MW = ~85,000–1,24,000 and ~90% hydrolysed) was obtained from SDFCL, India.

2.2. Methods

2.2.1. Protocol for BrPhS-LP hybrid sample preparation

A stock solution was first prepared by suspending 400 mg of LP nanoparticles in 10 ml Millipore distilled water (4 wt%) under sonication followed by addition of 16 mg of sodium polyacrylate to wrap the positive charged edges of the nanodiscs. Then 2.25 wt% samples were prepared from this stock solution and appropriate amount of BrPhS in water were added to it and sonicated for 10 min to get clear BrPhS-LP hybrid solution. For the thin film preparation, these hybrid solutions were drop-casted on clean glass substrates and dried under vacuum overnight at 60 °C.

2.2.2. Protocol for BrPhS-polymer hybrid sample preparation

First a stock solution of PVA was prepared by heating 0.5 g of the polymer in 10 ml Millipore distilled water (5 wt%) for 3 h with stirring. Another stock solution of same concentration was further prepared from PSS by sonicating at room temperature for 15 min. Required amount of BrPhS was subsequently added to these
polymer solutions to maintain the composition. For example, 1 wt% BrPhS is prepared by adding 0.5 mg of the dye to 1 ml of the stock polymer solutions containing 50 mg of either of the polymer. These solutions were then sonicated further for 5 min to get clear solutions followed by drop-casting on clean glass substrates. These samples were then dried completely under vacuum overnight at 60 °C for further photophysical measurements.

2.3. Instruments
2.3.1. NMR measurements
$^1$H and $^{13}$C NMR spectra were recorded on a BRUKER AVANCE-400 fourier transformation spectrometer with 400 and 100 MHz, respectively. The spectra are calibrated with respect to the residual solvent peaks. The chemical shifts are reported in parts per million (ppm) with respect to TMS. Short notations used are, s for singlet, d for doublet, t for triplet, q for quartet and m for multiplet, brt for broad triplet.

2.3.2. Optical measurements
Electronic absorption spectra were recorded on a Perkin Elmer Lambda 900 UV–vis-NIR Spectrometer and emission spectra were recorded at FLS1000 spectrometer, Edinburgh Instruments. UV–vis and emission spectra were recorded in 1 mm path length cuvette. Fluorescence spectra of films were recorded in front-face geometry to avoid self-absorption at high concentrations.

2.3.3. Lifetime measurements
Fluorescence lifetimes were performed on a Horiba Delta Flex time-correlated single-photon-counting (TCSPC) instrument. A 373 nm LED laser diode with a pulse repetition rate of 1 MHz was used as the light source. The instrument response function (IRF) was collected by using a scatterer (Ludox AS40 colloidal silica, Sigma-Aldrich). Phosphorescence lifetime ($\lambda_{\text{exc.}} = 350$ nm) and gated emission were measured on FLS1000 spectrometer, Edinburgh Instruments equipped with a micro flash-lamp ($\mu$F2) set-up. Quantum yield was measured using an integrated sphere in the same instrument.

2.3.4. High resolution mass spectrometry (HRMS)
HR-MS was carried out using Agilent Technologies 6538 UHD Accurate-Mass Q-TOF LC/MS.

2.3.5. Dynamic light scattering (DLS)
DLS and Zeta potential measurements were carried out using a Zetasizer Ultra (Malvern UK) employing a 633 nm laser at a back scattering angle of 173°.

3. Results and discussions

3.1. Solution and amorphous state RTP in Laponite
Here we have used water soluble laponite (LP) clay nanoparticles as the inorganic scaffold to host organic phosphors. LP clay nanoparticles are monodisperse in nature with dimensions of ~25 nm diameter and ~0.9 nm thickness (figure 1(b)) [33]. The LP nanoparticle has negatively charged surface and positively charged edges and hence strong electrostatic interaction between the particles lead to ‘house-of-cards’ packing. To prevent such organization, LP particles are efficiently exfoliated in water by neutralizing the edges with anionic polymers such as sodium polyacrylate to avoid self-absorption at high concentrations. With this basic design principle, we have synthesized a cationic aromatic carbonyl derivative, BrPhS with ammonium functional groups in its side chains. The aromatic carbonyl derivatives (e.g. benzophenone) are known for their excellent inter-system crossing (ISC) efficiency from singlet to triplet states because of good spin-orbit coupling provided by the carbonyl group [36–38]. However, they often result in poor phosphorescence quantum yield under ambient conditions. Therefore, heavy atoms like bromine or iodine are introduced in the $\pi$-conjugated framework, which, not only enhance the singlet to triplet ISC, but also facilitate the excited triplet to ground singlet state radiative transition [8, 18]. With this objective, in our molecular design we introduced both carbonyl and bromine atom for efficient triplet formation. Further, the cationic side groups were introduced for rigid molecular organizations by electrostatic interaction with charge-complementary laponite surface to reduce the vibrational dissipation and thus to promote the phosphorescence emission. BrPhS (0.1 mM) absorbs in the 250–400 nm region with absorption maxima at 268 nm ($\pi$–$\pi^*$) and 346 nm ($\pi$–$\pi^*$) in water [39], characteristic of similar benzaldehyde type chromophores (figure 2). It also shows fluorescence with a maximum at 450 nm ($\lambda_{\text{exc.}} = 350$ nm), though no phosphorescence is observed under ambient conditions in water (figures 2 and S1). Phosphorescence of BrPhS, however, could be realized by minimizing the non-radiative pathways ($\lambda_{\text{exc.}} = 350$nm, $\lambda_{\text{max.}} = 530$nm), in frozen acetonitrile solution at 77 K
The phosphorescence nature at 77 K is supported by high average lifetime ($t_{\text{avg.}} = 14.3 \text{ ms}$, $\lambda_{\text{exc.}} = 350 \text{ nm}$, $\lambda_{\text{monitored}} = 530 \text{ nm}$) as compared to fluorescence lifetime obtained in water ($t_{\text{avg.}} = 1.1 \text{ ns}$, $\lambda_{\text{exc.}} = 373 \text{ nm}$, $\lambda_{\text{monitored}} = 450 \text{ nm}$) (figures S1, S2). Thus, to harvest triplets under ambient conditions, BrPhS (0.1 mM) was first anchored with a fixed amount of LP (2.25 wt%) in water (figure 3). Interestingly, we observed appearance of a new red-shifted emission band ($\lambda_{\text{max.}} = 510 \text{ nm}$) along with the fluorescence in 350–450 nm.
region (figure 3(a)). This new band showed very high average lifetime of 4.5 ms ($\lambda_{\text{monitored}} = 530$ nm) hinting towards phosphorescence emission whereas the lower wavelength band showed much shorter lifetime in the nanosecond scale ($\lambda_{\text{monitored}} = 450$ nm, $\tau_{\text{avg.}} = 0.9$ ns) ascribing to its fluorescence nature (figure 3(b)). The phosphorescence nature was further characterized by time-gated emission (delay time $= 1$ ms) which resembles closely with the low-temperature phosphorescence band of $0.1$ mM BrPhS taken in acetonitrile at 77 K (figures 2, 3(c) and S2). Further, same laponite hybrid sample showed comparable phosphorescence emission intensity at 77 K with respect to glassy acetonitrile matrix as a result of reduced non-radiative decay (figure S2).

To get a further insight into the photophysical properties of BrPhS in presence of LP, titrations were performed by varying the concentration of BrPhS from 0.05 mM to 1.0 mM at a fixed weight percentage (2.25 wt%) of exfoliated laponite nanoparticles in water (figure 3(a)). We observed a gradual decrease in phosphorescence intensity as well as the corresponding lifetime with increasing concentration of BrPhS (figures 3(a), (b)). Decrease in RTP intensity could be due to the enhanced collisional quenching of the triplets at higher concentration range of the phosphor (>0.1 mM) (figures 3(a), (b)) [40]. We could not observe any spectral changes characteristic of inter-chromophoric interactions as observed for dicationic naphthalene diimide derivatives with large hydrophobic $\pi$-conjugated cores (figure S3) [29]. Furthermore, zeta potential and dynamic light scattering (DLS) experiments showed gradual decrease of negative charge on the LP surface with increasing concentrations of BrPhS with concomitant increase in hydrodynamic radius of the particles (figure 3(d)). This observation is a clear indication of extended electrostatic co-assembly between the LP particles and BrPhS, particularly important for creating a unique supramolecular microenvironment suitable for the generation of BrPhS-LP hybrid.
for limited oxygen diffusion and enhanced triplet stability, resulting in efficient aqueous phase phosphorescence under ambient conditions \[29\].

It was remarkable to observe that phosphorescence features were retained in the \( \text{BrPhS-LP} \) hybrid thin films, with good quantum yield \( (\Phi_P = 3.1\%) \) and average lifetime \( (2.03 \text{ ms}) \) in air, when the solutions were drop-casted on a glass substrate and dried completely (see experimental section, figure 4). Solution processability is the unique feature of the soft hybrid approach mentioned here, a property most of the ambient organic phosphor materials lack. Although, amorphous powder sample of \( \text{BrPhS} \) shows very weak phosphorescence \( (\Phi_P = 0.57\%) \) under ambient conditions, the corresponding dropcasted neat film does not show any phosphorescence reiterating the importance of scaffolding provided by inorganic LP particles (figure S4, table S1).

### 3.2. Amorphous state RTP in polymer matrices

It is evident that \( \text{BrPhS} \) can act as an excellent phosphor, when the vibrational dissipations and oxygen mediated triplet quenching are minimized in supramolecular microenvironments. In an attempt to reproduce the ambient RTP even in amorphous state and solid matrix, we have used two water-soluble polymers polyvinyl alcohol \( (\text{PVA}) \) and sodium polystyrene sulphonate \( (\text{PSS}) \). \text{PVA} is known to interact with various small organic chromophores via ion-dipole and H-bonding interactions and result in phosphorescence under inert atmosphere \[19\]. On the other hand, \text{PSS}, an anionic polymer matrix rarely explored for RTP applications, is expected to have strong electrostatic interaction with cationic chromophores like \( \text{BrPhS} \) to reduce the vibrational quenching of the triplets. With these objectives, \( \text{BrPhS} \) is first solubilized in \text{PVA} or \text{PSS} solutions in water (1 wt% of \( \text{BrPhS} \) in \text{PVA} or \text{PSS}).

Resulting solutions were then drop-casted on glass substrate and dried completely at 60°C for 12 h, under vacuum. Remarkably, the resulting transparent thin films show highly efficient RTP emission with excellent quantum yields \( (\Phi_P = 33.6\% \text{ in } \text{PVA} \text{ and } \Phi_P = 8.7\% \text{ for PSS hybrids}) \) and long average phosphorescence lifetime \( (6.6 \text{ ms and } 6.3 \text{ ms} \text{ for PVA and PSS hybrids, respectively}) \) in air at 530 nm (figure 5). The corresponding excitation spectra monitored at phosphorescence wavelength (530 nm) show nearly identical feature as compared to the solution state excitation spectrum collected at fluorescence wavelength (450 nm), hinting
towards an excellent isolation of the BrPhS molecules in the polymer matrices (figure S5) [19]. Increasing the BrPhS content in fixed amount of polymer show a decrease in phosphorescence intensity, which could be due to self-quenching of highly concentrated chromophores in less amount of polymer host [8, 41].

4. Conclusions

In conclusion, we have shown an efficient supramolecular hybrid co-assembly approach to harness triplet excitons via RTP in aqueous solution and solution processed thin films. Controlled organisation of heavy (Br)-atom substituted BrPhS derivative on inorganic LP surfaces lead to a unique supramolecular microenvironment which not only reduces the vibrational dissipations of the triplets, but also prevents oxygen mediated quenching. Similar spectroscopic features were also retained in corresponding solution-processed thin films, further widening the application scope of characteristics even in other rigid and amorphous matrices like sodium polystyrene sulphonate (PSS) and polyvinyl alcohol (PVA) with high quantum yields over 30% in air. The supramolecular strategy presented here to attain solution state as well as amorphous state RTP is rarely reported and we envisage potential applications in sensing and bio-imaging applications [39, 40].

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ORCID iDs

Subi J George © https://orcid.org/0000-0003-4429-5237

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