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Aqueous Phase Phosphorescence: Ambient Triplet Harvesting of Purely Organic Phosphors via Supramolecular Scaffolding

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Dedicated to Professor M. V. George on the occasion of his 90th birthday

Abstract: Ambient solution and amorphous state room temperature phosphorescence (RTP) from purely organic chromophores is rarely achieved. Remarkable stabilization of triplet excitons is realized to obtain deep red phosphorescence in water and in amorphous film state under ambient conditions by a unique supramolecular hybrid assembly between inorganic laponite clay and heavy atom core substituted naphthalene diimide (NDI) phosphor. Structural rigidity and oxygen tolerance of the inorganic template along with controlled molecular organization via supramolecular scaffolding are envisaged to alleviate the unprecedented aqueous phase phosphorescence.

Room temperature phosphorescent materials based on purely organic molecules have attracted much attention recently as an alternative to expensive, rare and toxic metal based organometallic phosphors.[1] However, most of the organic systems are not efficient phosphors as they are susceptible to vibrational and oxygen-mediated quenching of their triplets.[2] This point thus also explains the fact that most efficient organic RTP have been reported in crystal state which minimizes the non-radiative quenching of triplet excitons by providing a rigid network and a barrier for oxygen diffusion.[3] However it poses concerns over the solution processability of these phosphorescent materials for applications in display devices and sensors. In this respect, organic RTP materials which are either solution processable or emissive in solution phase would be beneficial.[4] With this objective, amorphous organic RTP materials have been recently designed by the incorporation of triplet phosphors into polymeric[5] and cage-like hosts.[6]

A supramolecular scaffolding approach,[7] with controlled and rigid organization of organic phosphors can be envisaged to be an efficient, alternative approach for the design of processable RTP materials. In this respect, co-assembly of organic phosphors with an inorganic silicate template would be advantageous as latter's structural rigidity and nanoscale periodicity can lead to well-organized chromophores with limited diffusional motion of both the components to minimize the vibrational quenching of triplets.[8] Further, oxygen tolerance of the inter-layer galleries of such organic-inorganic hybrids would be an added benefit to harvest phosphorescence under ambient conditions.[9] We envision that a supramolecular hybrid co-assembly approach between soluble organic and inorganic components in solution would render soft-hybrids with processability or amorphous nature.[10] Herein we report an ambient red phosphorescence from a core-substituted naphthalenediimide (NDI) derivative (**BrNDI**, Figure 1), using a unique organic-inorganic supramolecular scaffolding approach. An electrostatically driven co-assembly of NDI phosphor with a water soluble inorganic silicate based nano-template (Laponite, **LP**) gives RTP both in solution and solution-processed, transparent thin films. Remarkably, by virtue of the oxygen barrier characteristics of the microenvironments in these supramolecular assemblies, an unprecedented stabilization of phosphorescence in aqueous solution is observed.

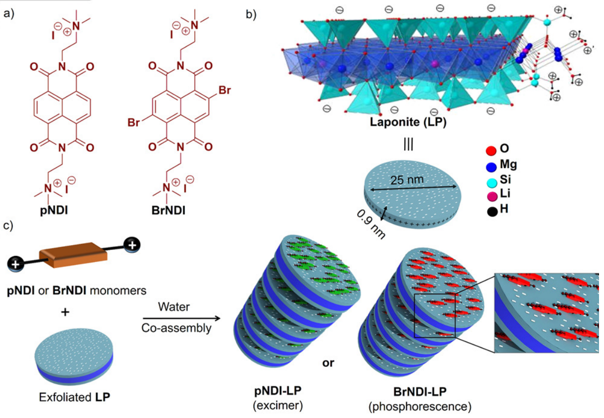

Figure 1. a) Molecular structures of **pNDI** and **BrNDI** and b) schematic diagram of Laponite (**LP**) structure. c) Schematic of the proposed ionic hybrid self-assembly of exfoliated **LP** nanoplates (by the wrapping of anionic polymer shown in blue color along the edges) and cationic chromophores in water.

We have used water soluble laponite (**LP**) clay nanoplates as the inorganic scaffold, with monodisperse dimensions of 25 nm diameter and 0.9 nm thickness.[11] These inorganic particles have a unique structure with orthogonally charged surfaces and edges, having negative and positive charges, respectively (Figure 1b). **LP** particles can be exfoliated in aqueous solutions by neutralizing the positively charged edges with anionic polymer such as sodium polyacrylate, which prevent the electrostatically driven ''House of Cards'' packing of **LP** particles.[11] As a result the negatively charged surface of **LP** can be used further for the electrostatic

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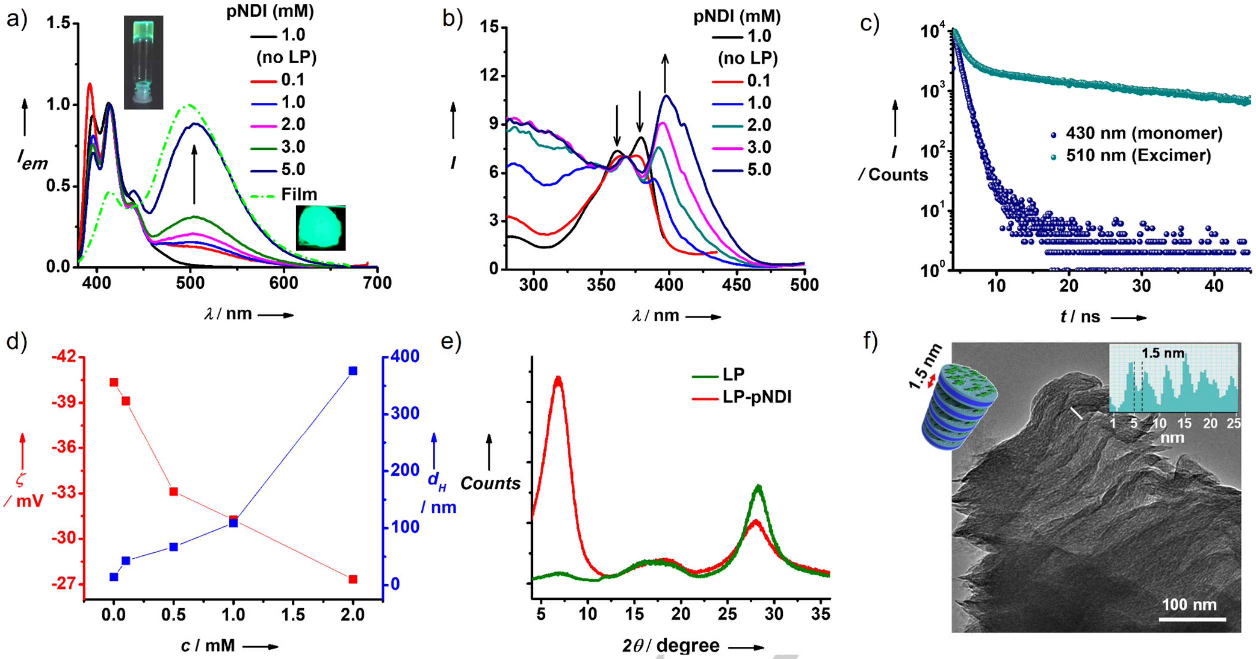

Figure 2. Normalized a) emission and b) excitation spectra of **pNDI-LP** hybrids (**LP** = 2.25 wt. %, λ_{exc} = 365 nm) in solution. Inset of a) shows the photographs of **pNDI-LP** hybrids in the gel state (top left) and film state (bottom right) under 365 nm UV irradiation ([**pNDI**] = 5.0 mM). c) Fluorescence lifetime profiles of **pNDI-LP** hybrids monitored at monomer (430 nm) and excimer wavelengths (510 nm) in water ([**pNDI**] =1.0 mM, **LP** = 2.25 wt. %, λ_{exc} = 373 nm). d) Zeta potential and DLS measurements of **pNDI-LP** hybrids in water during the titration (**LP** = 2.25 wt. %). e) PXRD pattern of films made from 5.0 mM **pNDI-LP** hybrids along with blank **LP** (**LP** = 2.25 wt. %). f) TEM image of **pNDI-LP** xerogels ([**pNDI**] = 5.0 mM, **LP** = 2.25 wt. %) and inset shows the electron density profile of the white line.

anchoring and co-assembly of complementary positively charged chromophores (Figure 1c).[12] Hence in order to promote an ionic self-assembly cationic NDI derivatives with ammonium functional groups were designed. Although NDI and its core-substituted derivatives have been well-studied for their remarkable fluorescence properties, their phosphorescence properties are rarely explored despite good ISC efficiencies in some derivatives.[13] Parent NDI derivative, **pNDI**, without any core substitution is used as a model cationic system to investigate the hybrid co-assembly, whereas core-heavy atom substituted **BrNDI-LP** is designed to stabilize the triplets (See Supporting Information for synthesis).

First we investigated the hybrid co-assembly between **pNDI** and **LP** nanoplates and the resultant modulations in the molecular organization of NDI chromophores using spectroscopic and light scattering experiments. Detailed titrations were performed in water by increasing the concentration of **pNDI** from 0.1 mM to 5.0 mM at a constant weight percentage of **LP** (2.25 wt.%). With increasing concentration, a decrease in the intensity of **pNDI** monomer emission (λ_{max} = 430 nm) with concomitant appearance of new broad emission centered at 510 nm is observed (Figure 2a). Time-resolved fluorescence decay profiles of this new emission showed a major long-lived component with a lifetime of 28.9 ns, characteristic of excimer formation between NDI chromophores (Figure 2c and Table S2).[14] Further, the excitation spectra collected at 510 nm showed a 20 nm red-shifted peak at 398 nm with respect to the monomer absorption (λ_{max} = 378 nm), suggesting that excimer-like emission is originated from the assembled chromophores in the ground state (Figure 2b and Figure S1). These results indicate the pre-organization of NDI chromophores in a J-type slipped manner templated by the inorganic **LP** scaffold. Zeta potential and Dynamic Light Scattering (DLS) studies showed that, negative charge on **LP** particles decreases along with simultaneous increase in the hydrodynamic radius, when the concentration of **pNDI** is increased in the hybrids (Figure 2d), signifying an extended hybrid co-assembly of **LP** and chromophores directed by electrostatic interactions. Formation of extended assembly is further evident from the hydrogel formation at high concentrations (>3.0 mM, inset, Figure 2a).

Solutions and hydrogels of **pNDI-LP** hybrids could also be transferred onto glass substrates without affecting the molecular organization as evident from the J-aggregated spectral features and excimer emission retained in the film state. The emission spectrum of film made from **pNDI-LP** hybrid hydrogel (5.0 mM-**pNDI**) showed major amount of excimer emission at 500 nm with a lifetime of 25.3 ns (Figure 2a and inset, Figure S2 and Table S2).These films are highly transparent and showed more than 99% transmittance above 550 nm where these dyes do not have an absorbance (Figure S3). This validates the efficient supramolecular scaffolding of the chromophores by the **LP** templates and also the excellent solution processability of these hybrids with homogeneous organization.

Powder X-ray diffraction (PXRD) pattern of the **LP** film showed two peaks at 17º and 28º characterisitc of the crystalline lattice planes of **LP** particle. Absence of any peak at the low angle region in the PXRD pattern ruled out the stacking of **LP** particles at this concentration. Remarkably, a strong low angle peak (2θ = 6.4º) corresponding to a d-spacing of ~1.4 nm was observed for the **pNDI-LP** hybrid films suggesting an extended organization by the alternating co-assembly of **LP** templates and **pNDI** linkers via eletcrostatic intreactions (Figure 2e). Since the observed d-

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spacing is less than that expected from **pNDI** with a molecular dimesion of 1.48 nm and **LP** particles with 0.9 nm thickness, we envisage a tilted slipped stacking of the chromophores in the interlayer galleries. The extended organization is further supported by transmission electron microscopy (TEM) of the corresponding hybrid xerogels, which showed nanoscale striations with alternating bright and dark contrasts due to the organic-inorganic layered co-stacking (Figure 2f).

Inspired by the organization of **pNDI** chromophores by the the **LP** nanoplates, we have further attempted the triplet state stabilization using similar approach. However to harness triplet excitons, an efficient intersystem crossing (ISC) is crucial and internal heavy atom effect is considered to be the most viable strategy to achieve the same.[1,3a,4a] Hence **pNDI** design is modified to **BrNDI**, with two Br as the heavy atoms substituted at the core. Time-dependent density functional theory (TDDFT) calculations using B3LYP exchange-correlation functional were performed to get a qualitative understanding on the ISC efficiency of **pNDI** and **BrNDI** molecules (Figures S4-S5 and Table S1). The ISC rate is determined by the spin-orbit coupling (SOC) strength, whose quantitative estimate can be obtained by calculating the SOC matrix element (SOCME) between S_1 and T_n states.The main contributing channel for ISC is found to be S_1 (π-π*) to T_3 (n-π*) in both the molecules and this corroborates with the El Sayed's rule, which forbids SOC between S_1 (π-π*) and T_1 (π -π*)/T_2 (π -π*) states. Accordingly, for **BrNDI** (**pNDI**) the SOCME between T_1 and T_2 with S_1 are found to be 0.12 (0.00) cm^{-1} and 0.06 (0.01) cm^{-1}, respectively. The SOCME between T_3 and S_1 is higher in **BrNDI** (21.03 cm^{-1}) compared to **pNDI** (0.15 cm^{-1}) owing to the presence of heavy Br atoms in the former. Strong SOC in **BrNDI** not only leads to faster ISC to improve the triplet yield, but also allows the spin-forbidden $T_1 \rightarrow S_0$ transition to facilitate room temperature phosphorescene, provided other non-radiative pathways are minimized.

In an attempt to harness the triplets of **BrNDI** as ambient phosphorescence, supramolecular hybrids with **LP** was synthesized similar to **pNDI** (*vide supra*). Owing to the increased hydrophobicity of Br substituted NDI core, the solubility of **BrNDI** decreases and hence its photophysical properties could not be explored beyond 1.0 mM concentration. Red-shift in the absorption (411 nm to 418 nm) and fluorescence (437 nm to 445 nm) spectra with increased fluorescence lifetime of **BrNDI** on interaction with **LP** suggests the J-aggregation of chromophores similar to **pNDI** molecules (Figure 3a and Figure S6). Corresponding increase in the DLS signifies the extended hybrid co-assembly (Figure S7). Interestingly, a new emission band with a maximum at 613 nm was observed in these **BrNDI-LP** hybrid assemblies (**LP** = 2.25 wt. %) (Figure 3a and Figure S6). Average lifetime of the new red-shifted emission was found to be 347 μs compared to the short lifetime of 0.34 ns corresponding to the monomer fluorescence, suggesting the phosphorescence nature of the emission (Figure 3c, Figure S6 and Tables S3-S4). We envisage that reduced vibrational motions and less oxygen content provided by the supramolecular microenvironments in the organic-inorganic hybrid galleries facilitate the triplet emission even in water. To the best of our knowledge this is the first report of an aqueous state stabilized RT red phosphorescence under ambient conditions with high lifetime (Tables S4 and S6). Remarkably, corresponding solution processed hybrid films showed enhanced room temperature phosphorescence emission (Φ_P = 3.5 %) with a lifetime of 523 μs and corresponding fluorescence emission is significantly quenched as evident from the gated spectrum with a time delay of 50 μs (Figures 3b-c and Table S4).

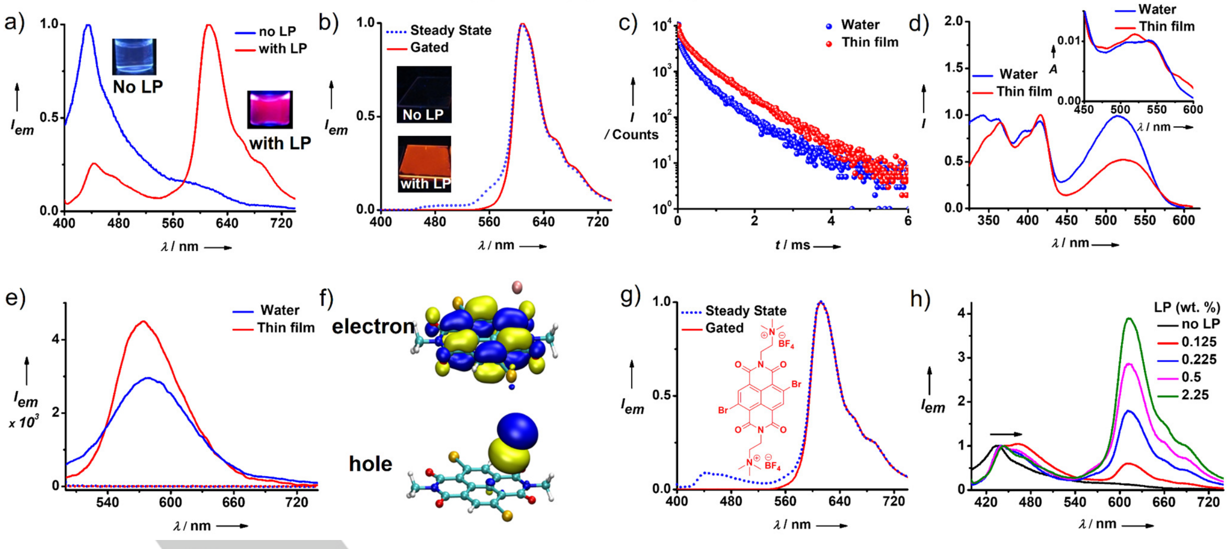

Figure 3. a) Normalized emission spectra of **BrNDI-LP** hybrids in water ([**BrNDI**] = 0.1 mM, λ_{exc} = 380 nm). Inset: shows the photographs of **BrNDI-LP** hybrids under 365 nm UV irradiation. b) Steady state and gated emission spectra of **BrNDI-LP** hybrid ([**BrNDI**] = 1.0 mM, λ_{exc} = 380 nm) in solid state. Inset: Photographs of **BrNDI-LP** in film state under 365 nm UV-lamp. c) Phosphorescence lifetime decay spectra of **BrNDI-LP** hybrids in water and thin film (λ_{exc} = 380 nm, $\lambda_{monitored}$ = 615 nm). d) Excitation spectra (monitored at 625 nm) of **BrNDI-LP** hybrids in water and thin film ([**BrNDI**] = 1.0 mM). Inset : Corresponding absorption spectra showing anion-π CT absorption. e) Steady state emission spectra of **BrNDI-LP** hybrids in water and thin film by exciting at the CT band and dotted lines shows corresponding gated emission spectra, suggesting no phosphorescence component ([**BrNDI**] = 1.0 mM, λ_{exc} = 480 nm). (In all cases **LP** = 2.25 wt. % and delay time of 50 μs for gated emission) f) Natural transition orbitals (NTOs) of dibromo NDI and iodide complex, calculated using TD-CAM-B3LYP/6-31+g(d) level of theory. g) Steady state and gated emission spectra of **BrNDI-BF4-LP** hybrids ([**BrNDI-BF4**] = 0.1 mM, **LP** = 2.25 wt. %) in water. Inset: Molecular structure of **BrNDI-BF4**. h) Emission spectra of **BrNDI** with increasing wt. % of **LP** in water ([**BrNDI**] = 0.1 mM, λ_{exc} = 380 nm).

Increased phosphorescence intensity with enhanced lifetime under vacuum and at lower temperatures further proves the triplet character of the emission (Figure S8 and Table S4). In order to explain the remarkable stabilization of triplets in aqueous and ambient conditions by the supramolecular scaffolding strategy we further investigated the spectroscopic properties in detail. A closer look at the absorption spectra of the **BrNDI** and **BrNDI-LP** hybrids in solution showed a weak, broad absorption in the 450-580 nm range apart from the high energy locally excited transitions (inset, Figure 3d and Figure S6a).[13a] These spectral features are characteristic of the charge-transfer (CT) interaction between iodide counter anion and NDI core, as reported for anion-π complexes of electron deficient NDIs with externally introduced anions.[15] Interestingly, selective excitation of this red-shifted absorption band at 480 nm of both **BrNDI** and its **LP** hybrids show an emission with maxima at 580 nm (Figure 3e and Figures S9a-c). High lifetime (4.75 ns) of this new emission band and the excitation spectra (collected at 625 nm) hints towards an anion-π induced CT emisison,[16] although it is rarely explored in NDI systems (Figure S9d-e). Presence of CT interaction between NDI core and the counter iodide ions is further supported by TDDFT calculations where NTO (natural transition orbital) analysis shows a CT transition between counter anion (donor) and NDI core (acceptor) (Figure 3f). Since CT states are known to play important role in promoting the ISC process we further explored this aspect.[16] In order to resolve the contributions of overlapping anion-π mediated CT and phosphorescence emissions, we have performed gated excitation spectra at 625 nm (Figures S9c and S9f). Although steady state excitation spectra of the hybrids collected at 625 nm in solution and film states showed a strong band corresponding to this CT absorption in the 450-580 nm range, a gated excitation spectra (50 µs time delay) did not show any CT absorption; instead showed only peaks corresponding to the locally excited NDI absorption (Figure 3d, Figures S9e and S9f). In addition, no phosphorescence emisison was observed when the CT band is selectively excited at 480 nm, thus ruling out a CT mediated ISC (Figure 3e). Moreover, exchanging the iodide counter anions with BF$_4^-$ does not affect the phosphorescence of the resulting **BrNDI-BF4-LP** hybrids, further suggesting the absence of external heavy atom effect from the counter ions and CT mediated triplet emission in our system (Figure 3g, Figure S10 and Table S5). On the other hand, titration of **BrNDI** (0.1 mM) with laponite showed an increased aggregation of the chromophore with concomitant increase in the phosphorescence intensity, which hints toward the role of aggregation in fostering ISC efficiency and phosphorescence, as shown previously in the case of H-aggregated RTP crystals (Figure 3h).[3c,f]

In conclusion we have demonstrated a unique organic-inorganic hybrid self-assembly for the controlled molecular organization of chromophores. In the case of **pNDI** without heavy atom substitution, pre-organization of chromophores results in green excimer-like emission. On the other hand, **BrNDI** hybrids showed red-emitting RT phosphorescence as a result of heavy atom effect. The structural rigidity and oxygen tolerance of the inorganic clay particles further minimize the molecular vibrations and triplet quenching of organic phosphors, which in turn stabilizes the phosphorescence in solution phase (water) and films under ambient conditions. Red emitting phosphors with visible light excitation and ambient stability in water are seldom reported and would be of potential use in bio-imaging and sensors.

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Keywords: Non-covalent interactions• Naphthalenediimide• Organic-inorganic hybrid composites• Room Temperature Phosphorescence • Self-Assembly

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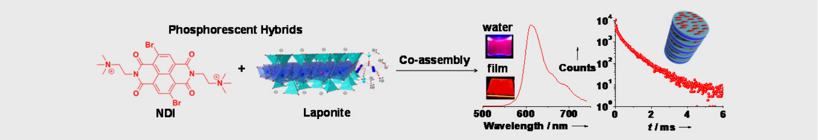

Aqueous Phosphorescence*: An unprecedented organic-inorganic hybrid co-assembly approach is proposed to obtain aqueous state as well as amorphous red-emitting room temperature phosphorescence. Heavy-atom effect in the NDI derivative along with its J-aggregation enhance the intersystem crossing efficiency whereas rigid and oxygen tolerant laponite templates stabilizes the triplets.*

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