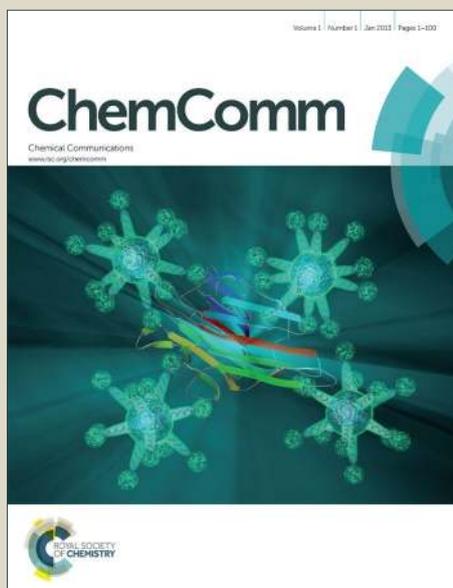


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## Pure White Light Emission from Organic Molecules Using *Solvent Induced Selective Self-Assembly*

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Generating pure white light emission from organic materials have attracted considerable attention in recent times due to their potential applications in lighting and display devices. We have used anthracene carboxylic acid (AnA) and anthracene carbaldehyde (AnC) to generate white light using *Solvent Induced Selective Self-Assembly* (SISSA). Mechanistically, SISSA prevents a fast intersystem crossing of AnC monomer and generates an emissive state from the self-assembled AnC. While AnA emits in the blue region, self-assembled AnC emits in the greenish yellow region with identical emission intensity. CIE coordinates (0.33, 0.33) of pure white light has been achieved by incorporating orange emitting rhodamin B. More importantly, the pure white light formation has been demonstrated at desired temperatures in both aqueous medium as well as in agar-agar hydrogel.

Design and synthesis of materials which emit white light have gained considerable attention due to the ever-growing demand for white light sources in areas such as lighting and display systems.<sup>1a-1d</sup> A variety of materials based on organic molecules,<sup>2a-2g</sup> polymers,<sup>3a-3c</sup> inorganic complexes,<sup>4</sup> metal-organic frame work,<sup>5a-5b</sup> graphene quantum dots,<sup>6</sup> inorganic quantum dots<sup>7</sup> and natural resources<sup>8</sup> have been utilized for generating white light emission.

Study of organic molecule for white light emission has received significant attention because of tuneable emission property and high emission quantum yield, which make them potential candidates for organic light emitting diodes (OLEDs).<sup>9</sup> There are several strategic approaches reported regarding white light generation from organic molecules.<sup>3a</sup> For example, ratiometric emission from organic fluorophores has been utilised to generate white light, where desired emission was achieved by tuning the abundance of one of the molecular system by an external stimuli. White light has been generated through single molecular Excited State Intramolecular Proton Transfer

(ESIPT), where ultrafast ESIPT leads two tautomer excited states emitting complementary colours.<sup>10a-10c</sup> Self-assembly of organic dyes has been used for generating white light through partial energy transfer.<sup>2b,2c</sup>

From an application point of view, white light emission from organo/hydro gels has attracted considerable attention. White light emission has been achieved through partial energy transfer in organogels, which contain multi-components with emissions in the blue, green and yellow regions.<sup>11a-11d</sup> White light emission in hydrogel (agar-agar gel) has also been achieved by incorporating blue emitting quinazolinidone, green emitting riboflavin and orange emitting rhodamine B.<sup>12</sup> Presently, achieving pure white light emission (achieving CIE coordinates 0.33, 0.33) from organic molecules/molecular systems remains a challenging task. One of the major issues is to design molecules with identical or comparable emission quantum yields. In order to achieve comparable emission intensities, structurally similar compounds with complementary emission colours are required. Here in, we achieve this by invoking selective aggregation of one of the structurally similar compounds using the solvent, leading to complementary emission from the aggregate with identical emission intensity to that of the monomer analogue.

We have selected two anthracene derivatives to implement this strategy: anthracene carboxylic acid (AnA) and anthracenecarboxaldehyde (AnC). It has been reported in the literature that AnA in acetonitrile emits from its singlet state, where it exists as a hydrogen bonded dimer. Conversely, AnC does not emit from its singlet state due to a fast intersystem crossing process. We hypothesized that addition of water in to a mixture of AnA and AnC will have opposing effect on the aggregation properties of the anthracene derivatives. For example, water can compete with the hydrogen bonded dimers of AnA, leading to the formation of AnA monomer, whereas presence of water can promote aggregation of AnC, preventing its fast intersystem crossing from the monomer singlet state.<sup>13</sup> Thus, the *solvent induced selective aggregation* of the anthracene derivatives could result in the emission from

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AnA monomer (blue) and emission from AnC aggregate (green to yellow).

Absorption spectra of AnC in several solvents such as acetonitrile, methanol, ethanol, and propanol show characteristic  $S_0-S_1$  transition and  $S_0-S_2$  transitions. Addition of water to above mentioned solvents results in a red shift in the absorption spectra. As the fraction of water increase from 0 to 0.96 ( $\phi_0$  to  $\phi_{0.96}$ ), the absorption band shifts from 260 nm to 290 nm (Figure S1-S4, ESI). This suggests formation of J type aggregates in the system.

Next, the concentration of AnC is varied from 6  $\mu\text{M}$  to 120  $\mu\text{M}$ , by keeping the water fraction at 0.96 ( $\phi_w 0.96$ ). As [AnC] increases, an additional shoulder absorption band at 290 nm arises, as observed previously, and the peak intensity at 260 nm decreases concomitantly (Figure 1). The molar absorption coefficient at 290 nm gradually increases up to 50  $\mu\text{M}$  concentration of AnC and undergoes a sudden rise with further increase in [AnC]. This indicates that aggregate formation takes place when [AnC] > 50  $\mu\text{M}$ .

Further confirmation of aggregate formation by AnC was obtained from dynamic light scattering (DLS) experiments. The DLS experiments were performed in acetonitrile-water mixture at  $\phi_w 0.96$  and the results corroborate with that of UV experiments. While aggregate formation was not visible in DLS at 30 mM of AnC, it was evident at 60  $\mu\text{M}$  and 90  $\mu\text{M}$  concentrations. More importantly, angular dependent DLS experiments results in different aggregate size, which indicates the non-spherical nature of aggregate (Figure 2a). Additional evidence of AnC aggregation has been obtained from variable concentration NMR experiments. NMR experiments were performed in  $\text{CD}_3\text{CN}-\text{D}_2\text{O}$  solvent mixture with  $\phi_D 0.1$  ( $\text{D}_2\text{O}$ ), in a range of AnC concentrations (6-42 mM). In addition, NMR experiments were also performed with varying the solvent ratios at fixed concentration of AnC (12 mM). As shown in figure S5,S6 ESI, an up field shift was observed for aromatic protons for both the cases, suggesting aggregation due to  $\pi-\pi$  interaction.

In order to verify whether the aggregation leads to a self-assembled structure of AnC, scanning electron microscopy (SEM) has been utilized. The SEM images shows flat ribbon like self-assembled structures of the anthracene derivative (60  $\mu\text{M}$ ) in acetonitrile-water mixture (04:96), unequivocally proving the *solvent induced self-assembly* in the system. The

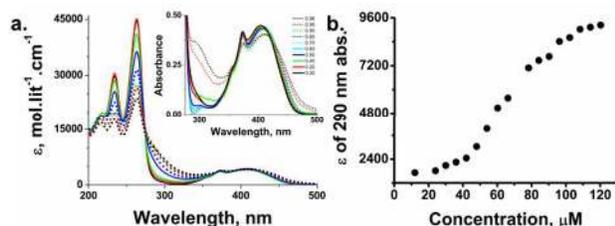


Figure 1: a. UV-visible absorption spectra of AnC in acetonitrile-water at  $\phi_w 0.96$  at variable concentrations of AnC; 1a inset: Absorption spectra of AnC in propanol-water mixture [AnC=60  $\mu\text{M}$ ] at variable [water]; 1b: plot of molar absorption coefficient at 290 nm vs concentration of AnC.

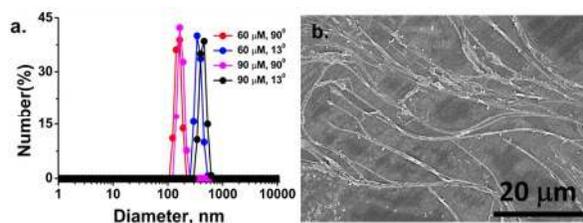
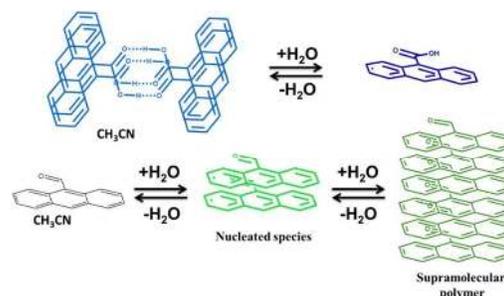


Figure 2: a. Aggregate size distribution of AnC in acetonitrile-water from DLS study; b. SEM image of AnC self-assembly in acetonitrile-water. ( $\phi_w = 0.96$ ). [AnC] = 60  $\mu\text{M}$

ribbons are of 500-1000 nm in width and about several tens of micrometres in length. However, when the concentration of AnC was increased (120  $\mu\text{M}$ ), the width of the fibres was found to be further increased (0.50-2.5 micrometers) (Figure 2b, Figure S7, ESI). Subsequently, the effect of water addition on the monomer-aggregation equilibrium of AnA was investigated in acetonitrile-water mixture. AnA did not aggregate in presence of water, up to  $\phi_w 0.96$  of water. This was evident from the absorption and emission spectra of AnA, where structured peaks, identical to anthracene monomer, have been observed in presence of water (Figure S8-S12, ESI). This corroborates our hypothesis that competence for hydrogen bonding between the AnA...AnA and AnA...water leads to shift the equilibrium towards monomer side.<sup>14</sup> Further, results from NMR experiments of AnA (12 mM) in  $\text{CD}_3\text{CN}$  with increasing concentration of  $\text{D}_2\text{O}$  suggest a conversion from dimer to monomer (Figure S13, ESI). We have carried out DLS studies with a wide range of AnA concentrations in acetonitrile-water and no aggregation has been observed. The results taken together indicates that *solvent induced selective self-assembly* results in the formation of anthracene monomer from AnA, and anthracene nucleated species as well as self-assembled structures from AnC, as shown in Scheme 1.

As mentioned before, fluorescence was absent from monomer AnC in solvents such as acetonitrile, methanol, ethanol etc. due to fast intersystem crossing. However, upon addition of water, AnC exhibits excimer emission. The excimer emission intensity increases as water concentration increases up to  $\phi_w 0.9$  and further addition of water results in a decrease in the emission intensity (Figure S14-S18, ESI). The emission maxima show small red shift at higher concentrations of water, presumably due to the increased polarity. The fluorescence quantum yield values of AnA and AnC in presence of water are given in table S1, ESI.

Scheme 1: Impact of water on the aggregation of AnA and AnC in acetonitrile-water mixture. (nucleated species are represented as dimer for simplicity)



Time correlated single photon counting (TCSPC) experiments were carried out to determine the excited state lifetime of the emitting species from AnC (60  $\mu\text{M}$ ) in presence of different mole fractions of water. The lifetime decays were mono exponential, with a value of  $1.58 \pm 0.03$  ns when mole fraction of water ( $\phi$ ) is 0.96 and above (Figures S19-20 and Table S2-5, ESI). From the emission maximum and lifetime values, it is concluded that the emitting species from the system is anthracene excimer, formed from the nucleated species. The decrease in the average lifetime values (1.56 ns to 0.64 ns) as the amount of water is decreased ( $\phi_w$  0.96 to  $\phi_w$  0.60) could be presumably due to the existence of varied types of anthracene excimers in the system (Figure S21, ESI).<sup>15a,15b</sup>

Upon increasing the concentration of AnC from 6-120  $\mu\text{M}$ , the emission intensity from the system increases initially (ie., up to 50  $\mu\text{M}$  of AnC) and then results in the quenching of emission intensity (Figure 3a). A similar trend in the emission intensity from AnC is observed as a function of temperature as well. The emission intensity increases as the temperature is decreased from 90  $^\circ\text{C}$  to 40  $^\circ\text{C}$  and then decreases as the temperature is further decreased (figure S22-S25, ESI).

The variations of absorption and emission intensity as a function of water content and concentration can be explained based on the aggregation mechanism of AnC in acetonitrile-water mixture. As depicted in Scheme 1, the initial step in the aggregation processes is nucleation. As a result of this, an absorption maximum is red shifted and emission intensity of the excimer peak increases. The nucleated species are further self-assembled to a supramolecular structure upon increasing the concentration or water content. The onset of a drastic change in the absorption spectra indicates the sudden process of supramolecular polymerization (Figure 3b). In the emission spectra, the supramolecular polymerization results in a decrease in the emission intensity (Figure S26, ESI), as the number of nucleated species is decreased, due to supramolecular polymerization. Among the two mechanistic possibilities of supramolecular polymerization, namely, isodesmic or cooperative pathway, results indicate that the AnC system follows a cooperative pathway for self-assembly.<sup>16a,16b</sup> The data from the absorption experiments were best fitted by cooperative model with a cooperativity ( $\sigma$ ) value of 0.001 (Figure 3b). From the Figure, it can be concluded that the nucleation equilibrium constant ( $K_2$ )

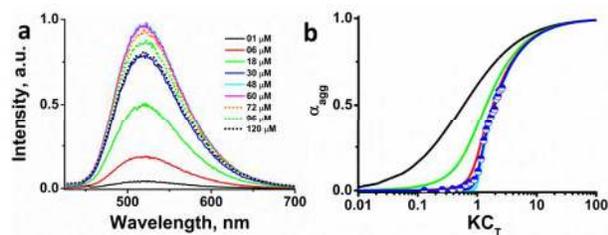


Figure 3: a. Variable concentration emission spectra of ANC in acetonitrile-water at  $\phi_w$  0.96 b. Plot of fraction of aggregated molecules ( $\alpha_{agg}$ ) vs  $KC_T$  for different values of  $\sigma$  (the values of  $\sigma$  are: 1 (black line), 0.1 (green line), 0.01 (red line), 0.001 (blue line), 0.0001 (cyan line) and blue sphere represents the experimental data points from figure 1b)

value is  $21.45 \pm 1.1 \text{ M}^{-1}$  and elongation equilibrium constant ( $K$ ) value is  $21.45 \pm 1.1 \times 10^3 \text{ M}^{-1}$ .<sup>17a,17b</sup>

Initial attempts to achieve white light emission were performed by mixing AnA and AnC in acetonitrile-water, under varied concentrations and excitation wavelengths (Figure S27-28 and Table S6, ESI). The best CIE coordinates obtained were (0.22, 0.31), when [AnC] and [AnA] was 60 mM and 36 mM, respectively at  $\phi_w$  0.96 and  $\lambda_{exc}$  at 380 nm. In order to improve the quality of the white light, a commonly available dye (rhodamin B) was mixed with the mixture of AnA and AnC. We have carried out a titration experiment to optimize the concentrations of the three components for pure white light emission, by keeping RhB and AnC concentration constant (10  $\mu\text{M}$ , 60  $\mu\text{M}$ ) and changing the concentration of AnA. We have achieved pure white light emission with CIE (0.33, 0.33) for the mixture of when the [AnA] is 16 mM (Figures 4 a,b; Table S7 ESI).

To verify whether partial energy transfer play a role in the mechanism of white light emission from the system, TCSPC measurement was performed. Fluorescence lifetime for the individual fluorophores were mono exponential in nature with excited state lifetime of 1.24 ns (AnA), 1.56 ns (AnC) and 1.61 ns (RhB) (Figure S29-S38, ESI). The excited state lifetimes of the fluorophores did not change in the mixture, suggesting the absence of resonance energy transfer in the system. The white light emission observed is the result of emission of blue, green and orange colours from the three components with comparable emission intensity (Figure 4c). The emission intensity from the components, which is an important factor in generating quality white light, matches in the case of AnA and AnC due to the structural similarity of the components.

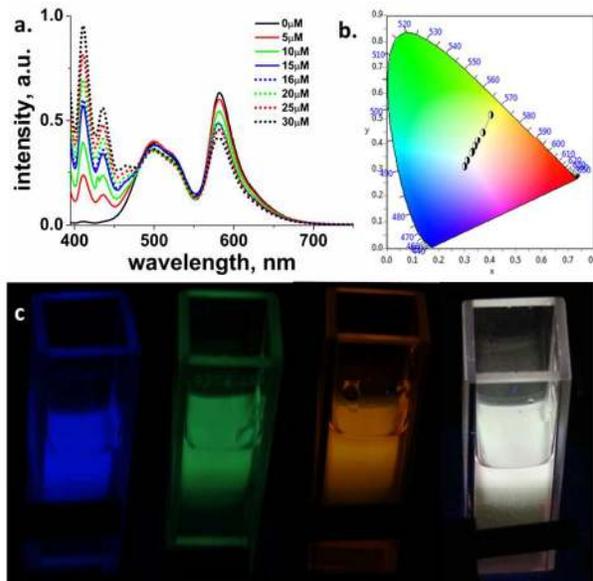


Figure 4: a. Emission spectra of the mixture of AnA, AnC (60  $\mu\text{M}$ ) and RhB (10  $\mu\text{M}$ ) in acetonitrile-water ( $\phi_w$  0.9) with various concentrations of AnA; b. corresponding CIE diagram; c. UV illuminated photographs of AnA (blue), AnC (green), RhB (orange) and the mixture (white) in acetonitrile-water ( $\phi_w$  0.9). [AnA] in the mixture = 16  $\mu\text{M}$

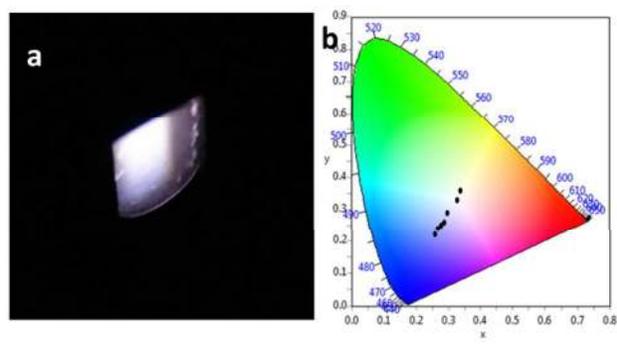


Figure 5: a. UV illuminated photograph of a gel containing AnA (11  $\mu\text{M}$ ), AnC (60  $\mu\text{M}$ ) and RhB (10  $\mu\text{M}$ ) ( $\lambda_{\text{exc}}=380\text{ nm}$ ); b. CIE diagram of gel for various concentrations of AnA with AnC (60  $\mu\text{M}$ ) and RhB (10  $\mu\text{M}$ ). Pure white light was obtained for [AnA] = 11  $\mu\text{M}$

Since the emissions we generate are from supramolecular assemblies, temperature dependency of the white light generation has been examined in a range from zero degree to 90  $^{\circ}\text{C}$ . The results suggest that white light can be generated at a desired temperature, by regulating the amount of one of the concentrations of the trimer. While the white light was generated at room temperature in the above example, data from the temperature dependant study indicate that white light can also be generated at 20, 40 and 45  $^{\circ}\text{C}$  from the same system, provided AnA concentration can be varied from 16  $\mu\text{M}$  to 20  $\mu\text{M}$ , 17  $\mu\text{M}$  and 15  $\mu\text{M}$ , respectively (Figure S39-42 and Table S8-9, ESI). The increased temperature leads to disruption of the hydrogen bonded assemblies and hence alter the emission intensity from AnA. Hence, comparable emission intensities required for white light generation is achieved at a different mole ratio between the three components.

White light generation will have increased practical applications if it can be generated in gels or solid state, compared to that in solution. In this context, we have used agar-agar hydrogel as medium where the three components (AnA, AnC and RhB) were mixed to get white light emission from the gel medium. The fluorescence properties of the molecules and aggregates were retained in gel medium, except that the intensity from AnC and RhB has marginally decreased, compared to identical conditions in solution. In the present study, 1.5 (wt %) agar-agar was used for gelation in acetonitrile-water mixture with  $\phi_w$  0.9. The results suggest that CIE of 0.33, 0.33 has been obtained from the mixture of AnA (11  $\mu\text{M}$ ), AnC (60  $\mu\text{M}$ ) and RhB (10  $\mu\text{M}$ ) in the gel medium (Figure 5 and Figure S43, Table S10-11, ESI).

In summary, white light emission in aqueous medium and hydrogel has been achieved with CIE of 0.33, 0.33, using commonly available anthracene derivatives and rhodamin B dye. The mechanistic studies clearly indicate that solvent induced selective self-assembly plays a crucial role in generating emission from AnC aggregates, which otherwise undergoes a fast intersystem crossing resulting in fluorescence quenching. The complementary emissions from the anthracene derivatives with comparable intensity, along with the emission from RhB, generate white light in solution as well as agar-agar gel. The supramolecular assembly was sensitive to

temperature, which has been utilized to generate white light at a desirable temperature by regulating the concentrations of the components.

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