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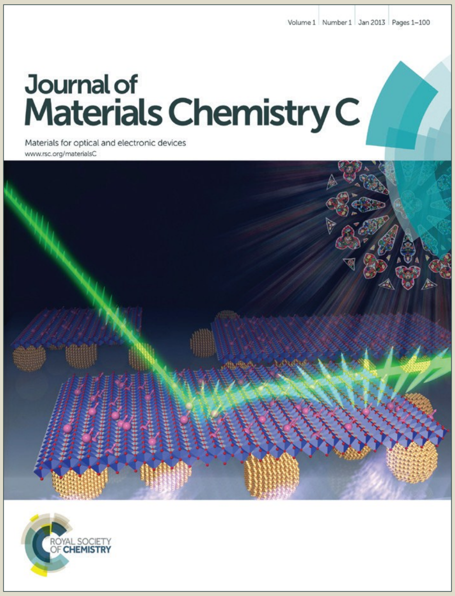

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Light Induced *in-situ* post-modification of clay-chromophore hybrids for multiple white light emissions

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This work uses soft clay chromophore hybrids to demonstrate a photo-modification strategy in which a white light standard can be converted into another via *in situ* generation of blue emitting chromophore. This strategy has been used to obtain various white light standards , post formulation, via simple irradiation.

Supramolecular design of white light emitting materials has been one of the major research frontiers in organic opto-electronics.[1,2] Various supramolecular designs have been explored such as organogels and organic inorganic hybrids for light harvesting and white light emission.[3-8] However, most of these materials have shown single white light emission and require re-mixing of ingredients for multiple color lights. Getting colors closer to multiple white light standards is therefore a challenging and tedious task in these materials. The general concept of white light emission revolves around creating a broad emission spectrum in the visible range which has been achieved either by mixing dyes with different colour emissions in appropriate amounts or as in case of single molecule white light emitters, carefully adjusting the molecular parameters. In either case for achieving a particular colour, mixture proportions are to be standardized individually. The advantageous strategy therefore could be to modulate the mixture such that various colours can be achieved from a single mixture. This strategy will be particularly useful if one were to apply it and achieve multiple white light standards from a single concoction.[9] Herein we show the first report of a light induced post-modification of clay chromophore hybrids where same mixture of chromophores with color pertaining to a white light standard can be converted into a another.

In recent years we have been working on amino-clay based soft hybrids for light harvesting.[10-12] In addition we have also shown that on amino-clay (**AC**) hybrids a tetraphenylethylene derivative (**TPTS**) which shows aggregation induced emission (AIE)[13] can be converted into di-hydro phenanthrene derivative **PhP** photo-chemically (Fig.1).[14] Spectroscopically speaking during photo conversion the maxima of the emission spectra changes from 475 nm to 410 nm, and thus creates a blue emitting component (Fig. S1-2). In this current report we wish to take advantage of this photo generation of the blue component and modify, post formulation, the clay hybrid containing green and red component (**TPTS** and **SRG** respectively) (Fig. 1). Therefore by controlling the irradiation time we would have a control on the concentration of blue chromophore and hence the effective colour of the hybrid. The complete synthesis and characterization of **TPTS** has been reported in our previous work.[14]

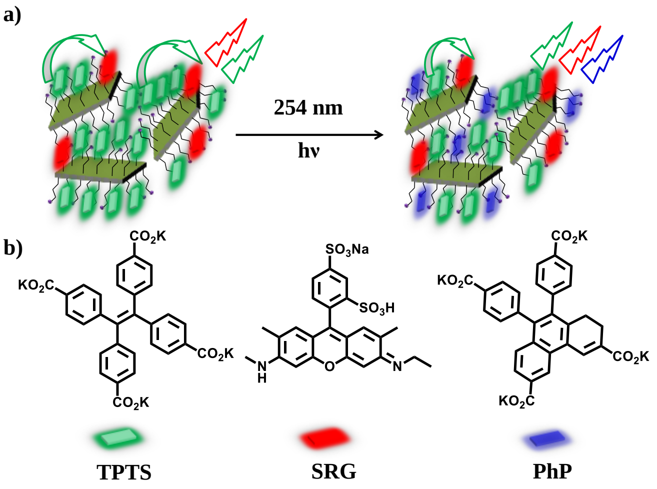

Fig. 1 (a) Schematic showing the strategy for photo-modulation of the clay hybrids, (b) Molecular structures of the **TPTS**, **SRG** and TPTS photoproduct (**PhP**).

We first investigated the amino-clay (**AC**) hybrid assembly with **TPTS** and **SRG** chromophores. To an aqueous dispersion containing 0.4 wt% **AC** and 10^{-4} M **TPTS** we varied the percentage of **SRG** from 0% to 12%. With a concomitant

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Electronic Supplementary Information (ESI) available:. See DOI: 10.1039/x0xx00000x increase in **SRG**% we saw a decrease in **TPTS** emission at 475 nm (Fig 2a). This observation could be attributed to the partial Förster resonance energy transfer (FRET) from **TPTS** to **SRG**. To further strengthen this conclusion we performed excitation spectra at 570 nm which is attributed to the **SRG** emission region and monitored it between 300 to 410nm which corresponds to the **TPTS** absorption region (Fig S3). As expected in cases with FRET the increase in acceptor percentage increased the intensity of excitation spectra in **TPTS** region suggesting the **SRG** emission increase is majorly contributed to energy transfer from **TPTS**. We also performed Time correlated single photon counting (TCSPC) experiments on the hybrids to further investigate the FRET process. With 6% SRG we could clearly see a decrease in lifetime of the donor **TPTS** (λ_{mon} = 474 nm, λ_{exc} = 380 nm) and an increase in acceptor **SRG** lifetime (λ_{mon} = 560 nm, λ_{exc} = 380 nm) (Fig S4).

It is worth noting that extent of energy transfer decreases after 9% of **SRG** as seen in Fig 2 (a), S3. To investigate this we did control experiments containing **AC** with varying amounts of **SRG** (Fig. S5). The excitation spectra at 570 nm suggested that **SRG** has a tendency to aggregate at higher percentages hence explaining the decrease in energy transfer efficiency.

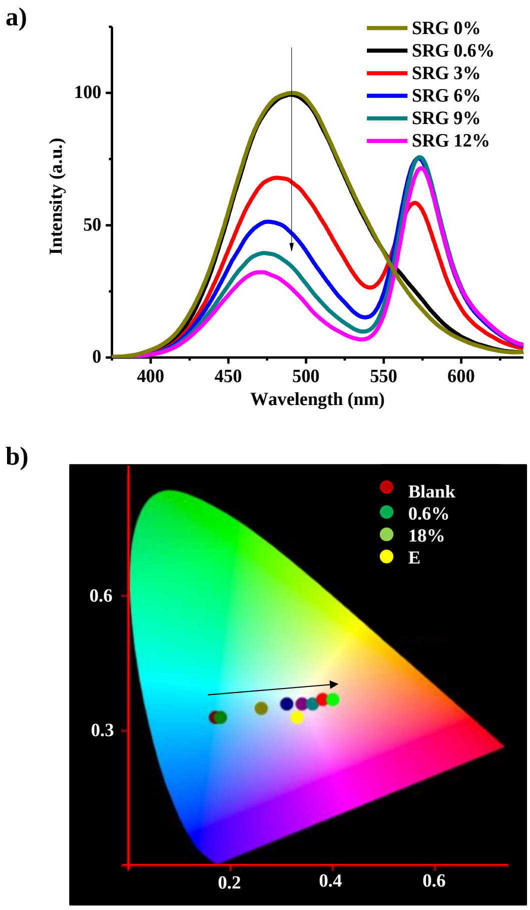

Fig. 2 (a) Emission spectra of **TPTS**+**AC** hybrid (10^{-4}M **TPTS**, 0.4 wt% **AC**, H_2O) with varying percentages of **SRG** (0% to 12%) excited at 330 nm, 2 mm cuvette, (b) 1931 CIE coordinates for respective hybrids with varying **SRG** percentage (0% to 18%) with equal energy white light (E, (0.33,0.33)) noted for reference.

Moreover, as one investigates the emission colour of these hybrids it is clear that the 1931 CIE co-ordinates of the mixture lie just above the perfect white region and need a blue component to bring it to those co-ordinates (Fig 2b, S10, S13). However it is worth noting that even though the emission of hybrids is not in the pure white region they still lie close to other white standards. The above point is evident from the fact that **AC** hybrid with 10^{-4} M **TPTS** and 9% **SRG** has the CIE co-ordinates (0.34,0.36) close to D50 standard, and 15 (0.38,0.37)and 18% **SRG** (0.40,0.37) have it closer to F11 and F3 standard respectively (Fig S10).

Having established the optical properties of two component hybrid assemblies we irradiated these dispersions with 254 nm to generate the blue component into the hybrids (Fig. 3). The samples were irradiated for total 4 mins in time periods of 30 secs. As hypothesized with prolonged irradiation the peak at 475 nm changed to 410 nm signifying the formation of **PhP** *in situ* (Fig. 4a-b,S6). Concomitant with the **PhP** generation is the decrease in **SRG** emission at 570 nm. TCSPC study of 6% **SRG** with 10^{-4} M **TPTS** in 0.4% **AC** after 4 mins of irradiation under 254 nm light showed that it is due to decrease in FRET as a result of the depleting concentration of **TPTS.** Moreover, **PhP** does not undergo FRET with **SRG**. For a sample containing 6% **SRG** we monitored the fluorescence lifetime at 410 nm (**PhP** region) and 560 nm (**SRG** region) and observed almost no change in the lifetimes compared to the individual control samples, hence confirming this hypothesis (Fig. S7). As a result of these photo-modifications the emission colour of the dispersions moved towards lesser CIE co-ordinates due to the addition of the blue component (Fig. 3, S10-13). The drop casted films of these dispersions also followed this trend (Fig. S8-9).

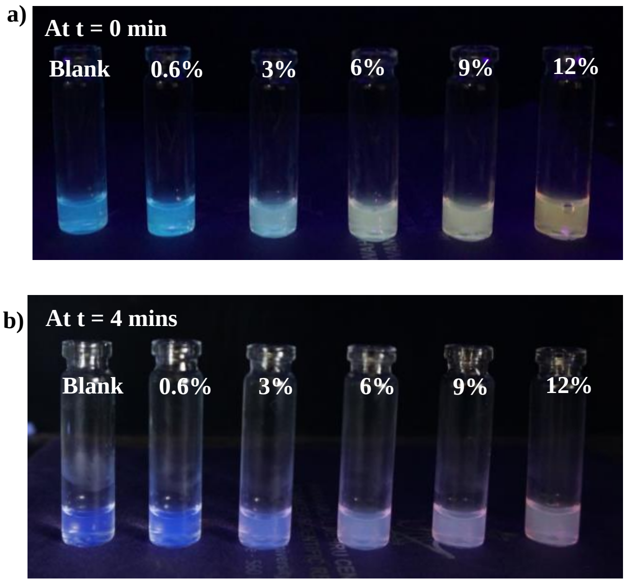

Fig. 3 (a) and (b) Photographs under 365 nm illumination of 254 nm irradiation progression over 4 mins of **TPTS**+**AC** hybrid.

We further calculated the 1931 CIE co-ordinates from the emission spectra of these dispersions and as we expected the generation of blue chromophore inside the mixture photo-tuned into various other white standards. The D50 standard of 9% **SRG** at t = 0 could be converted to nearly D55 (0.33, 0.34) after 30 secs of irradiation. Moreover, the 12% **SRG** dispersion which had (0.36, 0.36) as CIE co-ordinates at t = 0, changed to (0.35, 0.35) after 30 secs of exposure which is closer to F10, F8 and B white standards. Further irradiation converted it to (0.34, 0.33) and (0.33, 0.32) after 1 and 1.5 mins of irradiation, respectively.

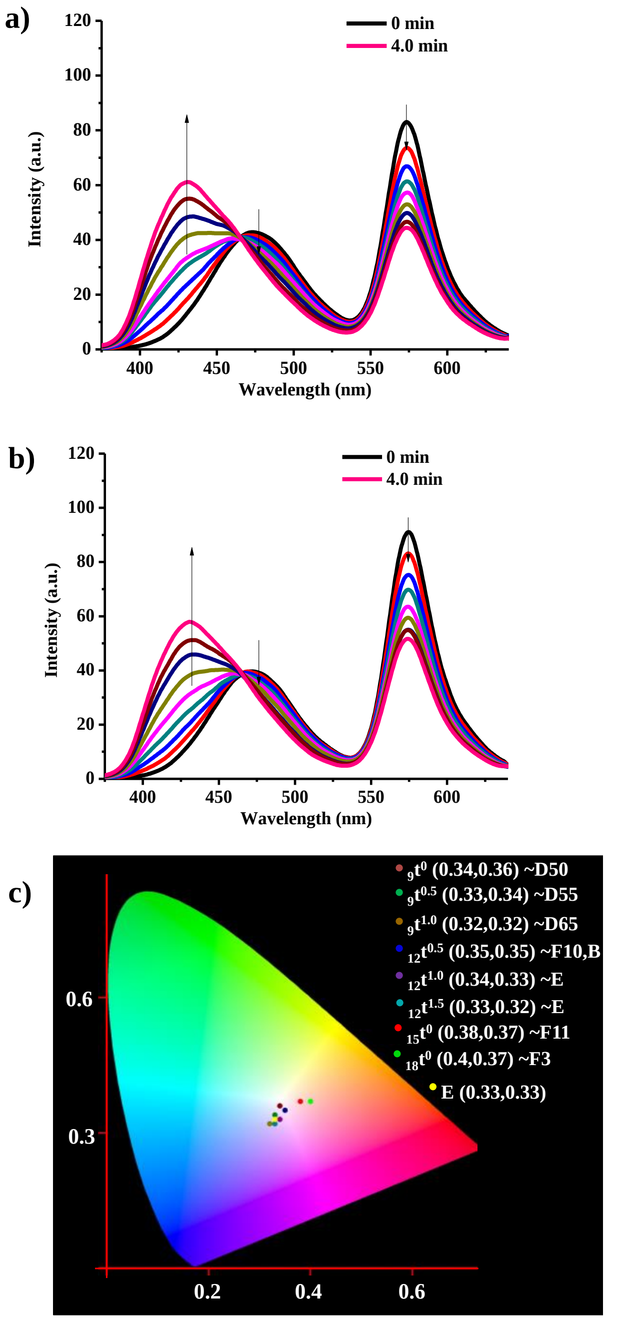

Fig. 4 (a) and (b) emission spectra of **TPTS+AC** hybrid containing 9% and 12% **SRG** respectively under 254 nm irradiation over time(λ_{exc} = 330 nm, *l* = 2mm). (c) 1931 CIE co-ordinates of the various white lights obtained (notation of the legend $_x t^y$, x denotes the % of **SRG** and y denotes the time of 254 nm irradiation in minutes. The quantities in parentheses are the CIE co-ordinates and the notations next to it denote the white light standard they resemble)

These co-ordinates are very close to the equal energy white light standard E (Fig. 4c,S11). To the best of our knowledge this is the first report showing light mediated modification of materials to achieve excellent control over white light emission. These results thus show the photo-modulation of clay hybrids, post formulation, gives an added advantage that for various white lights we need not make different formulations due to interconversion of colors via this approach.

We further tried and evaluated the stability of these hybrids in visible light. On a 9% **SRG** hybrid with 10^{-4} M **TPTS** in 0.4% **AC** we alternatively irradiated with 254 nm and visible light for 30 secs each and the emission spectra trend was followed at 400 nm. The trend clearly showed that the change occurred only during 254 nm illuminations and not during visible light illumination hence showing that these hybrids are stable to visible light and only photo-convert on 254 nm illuminations (Fig. 5,S14). We also exposed the dispersion to diffused daylight and the hybrid showed sparing changes hence proving their stability (Fig. 5).

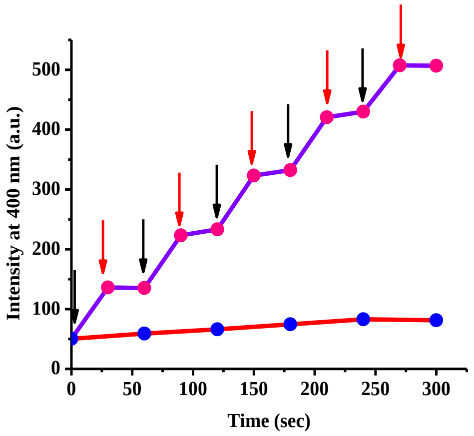

Fig. 5 Emission spectra of 9% **SRG** with 10^{-4}M **TPTS** and 0.4 wt% **AC** monitored at 400 nm. For pink dots: (Black arrow suggests 254 nm illumination "ON" and visible light illumination "OFF". Red arrow suggests visible light illumination "ON" and 254 nm illumination "OFF"). For blue dots: illumination under diffused sunlight over time.

Conclusions

In conclusion we show an unprecedented control over the white light region via photo-modification of clay based hybrids. We take advantage of the *in situ* generation of blue emitting photoproduct and modify the colour of these hybrids via subsequent irradiations. This approach leads to interconversion of various white light emissions as various white lights standards can be achieved via mere irradiation which could have otherwise taken a painful route of mixture optimization. Moreover, we also prove that these hybrids are stable to visible light. We believe that this work is a proof of concept showing the strength of photo modification as a route to achieve subtle changes in optical properties of hybrids.

Acknowledgements

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Graphical abstract:

This work uses soft clay chromophore hybrids to demonstrate a photo-modification strategy in which a white light standard can be converted into another via *in situ* generation of blue emitting chromophore.