

Supporting Information

Strongly Red-Shifted Photoluminescence Band Induced by Molecular Twisting in Cyanine (Cy3) Dye Films

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Non-emissive dimers

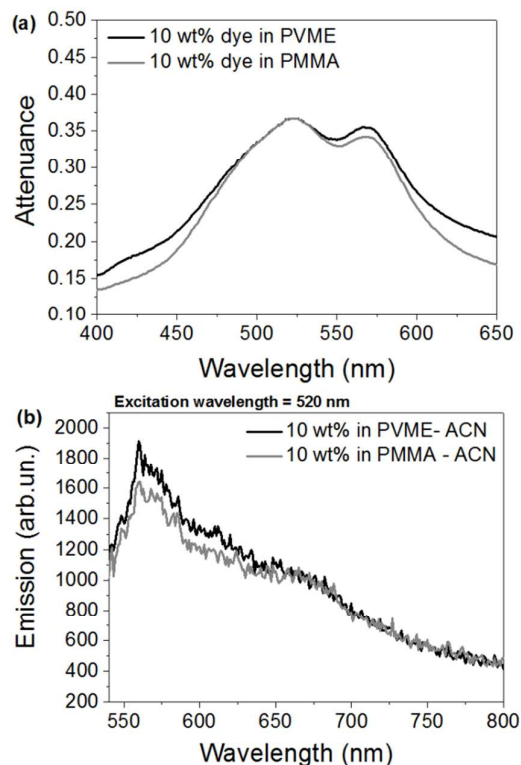


Figure S1. Attenuance (a) and emission (b) of non-emissive dimers

Structural motifs dictate the molecular packing thereby influencing the dimer emission. This is because of the well-known reasoning that modifying the quinoline ring in a cyanine dye can affect the aggregation nature.¹⁻² To verify this, we studied a Cy3 benzooxazol dye, where the dimethyl group is replaced by oxygen in the quinoline ring. The film forming properties of this dye are very poor, for that we dispersed the dye in a PVME polymer. In that matrix the dye shows even stronger dimer absorption (Figure S1a) compared to the other Cy3 dyes shown earlier in this study. When excited at the dimer wavelength (520 nm), the film shows a small monomer emission but no second emission was observed (Figure S1b). Introducing oxygen in the motif will decrease the steric hindrance for parallel alignment of the dye molecules, thereby reducing the torsional angle between dimers, prohibiting potential emission from the dimer.

Conversely, we can say that the presence of hydrocarbon chains induces strong dimer emission. This goes in hand with the observation by Sorokin et.al.,³ where a long hydrocarbon tail in the DiI dye has shown a strong dimer emission. This observation looks still valid, on comparing the LB films studied by Debnath et.al.,⁴ where excimers are observed even in a monolayer film. From this observation, we argue that long hydrocarbon chains can have strong interaction with the neighboring dye molecules, leading to more unique way of packing the molecules. To see whether changing the polymer matrix can help in dispersing this dye, we chose PMMA, which has better dispersion properties than PVME. It can be seen from Fig. S1b, the dispersing matrix has no effect in tuning the second emission. Furthermore, this point was verified by choosing another dye by replacing oxygen with sulphur (benzothiazol), which confirms that the non-emissivity is not due to internal quenching. Therefore, we can conclusively say that structural motifs can influence the dimer emission.

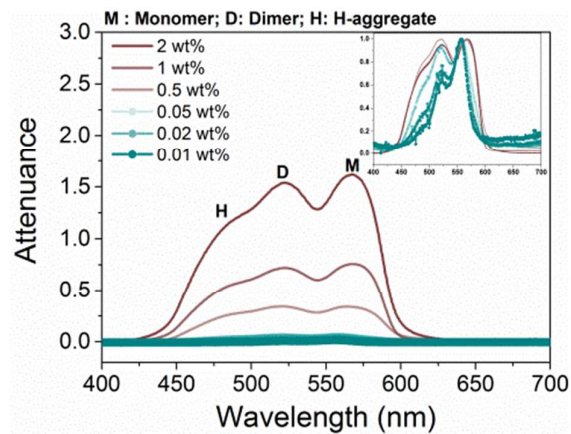


Figure S2. Attenuance for different concentrations of Cy3-P dye dispersed in a PVME matrix.

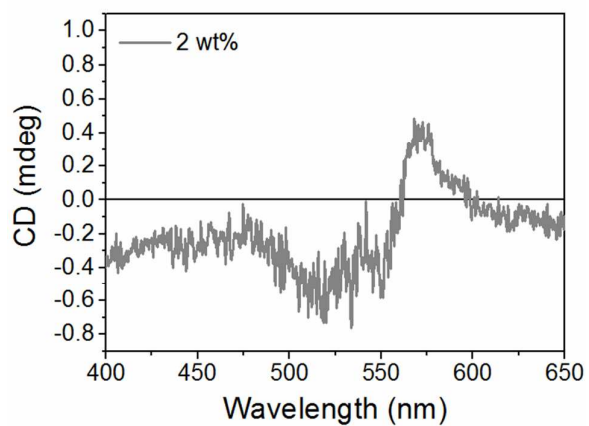


Figure S3. Circular dichroism (CD) spectroscopy for 2 wt% of Cy3-P dye dispersed in the PMMA matrix.

Stability of monomer and dimer emission in the influence of light and oxygen

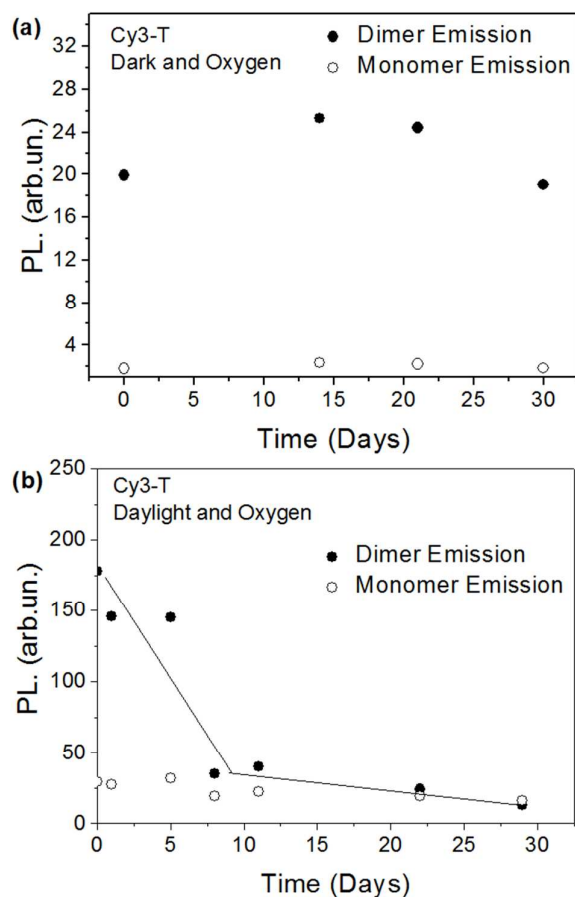


Figure S4. Stability study of the dimer and monomer emission peak from Cy3-T dye films monitored for 30 days when preserved in dark (a) and in daylight (b) in the presence of oxygen. The line is guide to the eye.

Having said that the second emission peak obtained in the film can have longer lifetime than a monomer emission, the atmosphere in the film storage can also influence the lifetime. If this is due to a triplet emission, atmospheric oxygen can also quench the fluorescence. To investigate this, the films were stored in dark and in daylight in the presence of oxygen. The monomer and dimer emission were monitored periodically for 30 days. It was observed that when samples were preserved in dark and in the presence

of oxygen, the emission measured for 30 days is almost within the standard deviation of the light signal of the instrument (Figure S4a). We can say that the second emission signal is stable in the presence of oxygen, which again disowns the role of triplet state. However, when exposed to daylight and in the presence of oxygen, the intensity of both monomer and dimer decreases (Figure S4b). This can be due to accelerated photo-bleaching of cyanine dyes in the presence of oxygen and light. Finally, this shows that samples preserved in dark has a stable dimer emission.

SI References

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