Oxazine-1 J-aggregates in Polymer Nanohybrids

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Supplementary Information

The optical characterization of Ox1 dye in solution and film is reported in the figure below.

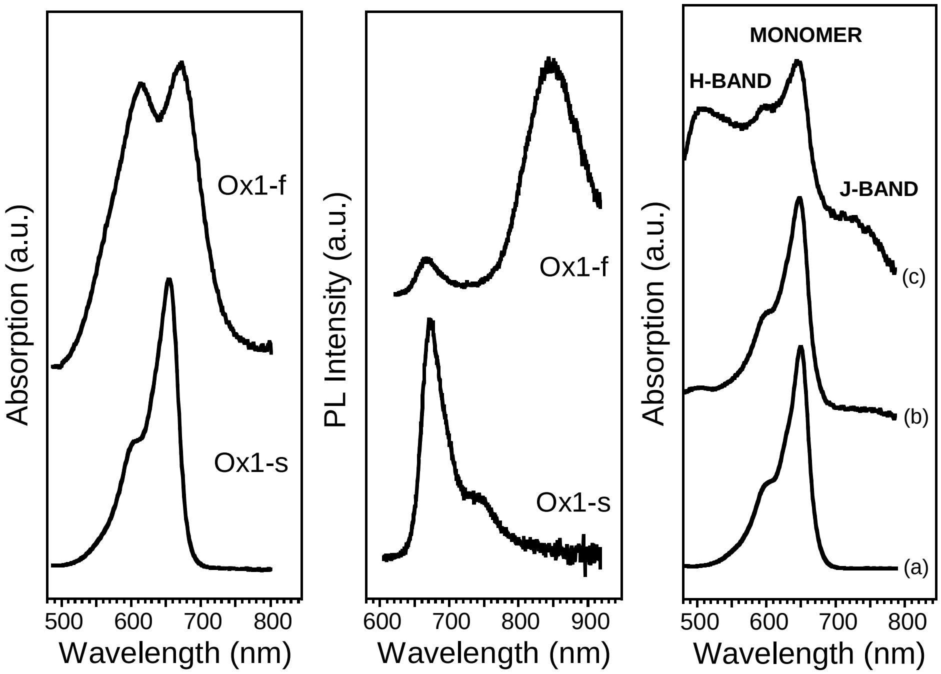

Figure S1. Normalized absorption (left) and PL spectra (middle) of Ox1 diluted toluene solution (Ox1-s), Ox1 film (Ox1-f), PL spectra are obtained by exciting with 514 nm laser radiation. Normalized absorption spectra (right) of Ox1 solution with different Pentane/ethanol ratio: (a) 100 % ethanol, (b) 50/50 %, and (c) 100 % pentane. Ethanol is a good solvent for Ox1 and no aggregation is observed even at high concentration (700 µM), while pentane is a bad solvent and causes Ox1 aggregates (H and J-Type) of different size. Spectra are vertically shifted for clarity.

We studied the neat oxazine-1 dye dissolved in ethanol (good solvent) and pentane (bad solvent) mixtures. New bands appear in the absorption spectra at both low and high energies (see Figure S1 - right) upon Ox-1 aggregation in solution. The high energy emission band at 500 nm can be assigned to large-size molecular assemblies of H-type, in agreement with the literature for similar dyes [2]. The shoulder near 600 nm may arise from either solvent-dye or dye-dye (H-dimer) interaction. Furthermore, a low energy broad band in the range of 700–760 nm was observed. This band, previously assigned to J-aggregation, well compares with the one observed in PF4 film. The much narrower band of the PF4 composite is related to a better control over the aggregates size than in the solution. Moreover, this absorption band overlaps with the emission peak at 724 nm observed in PF4 polymer composite, thus further supporting our assignment to J-aggregates.

Absorption and steady-state PL spectra of PF4 solution and film at room temperature, reported in Fig. S2, show both monomer and J-aggregate features. The solutions are preferred for pump-probe measurement for the reduced light scattering.

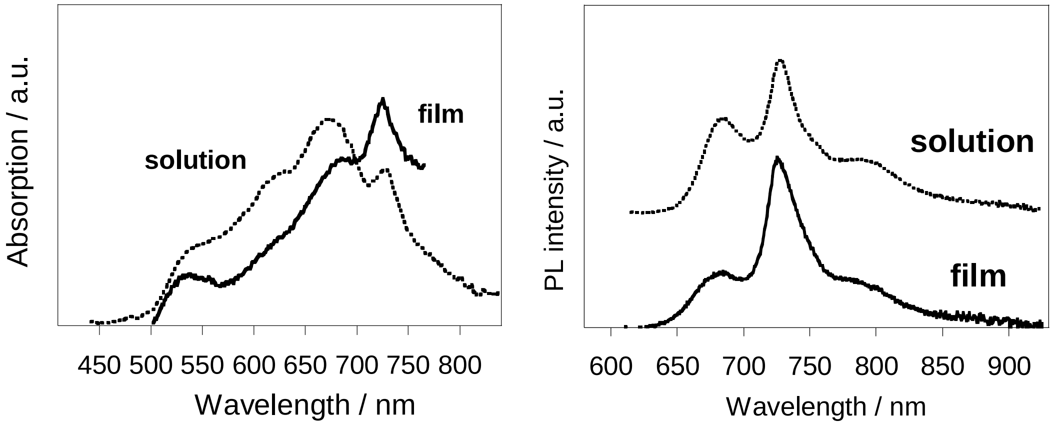

Figure S2. Absorption (left) and PL spectra (right) of PF4 solution (dotted line) and film (solid line) at room temperature excited with 514 nm laser. The 725 nm J-aggregates peak is present in both solution and solid-state of PF4.

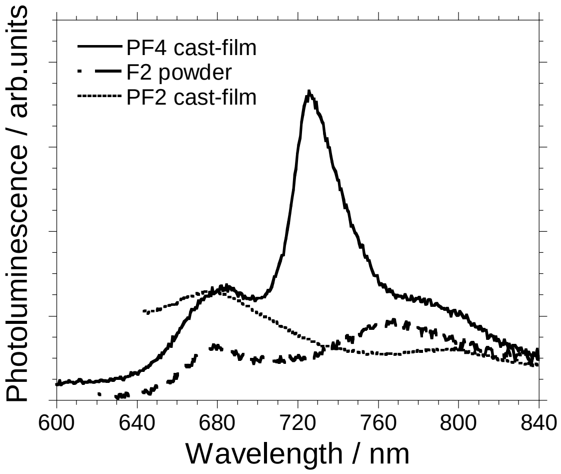

Figure S3. PL spectra of PF2, PF4 cast-film and F2 crystalline powder

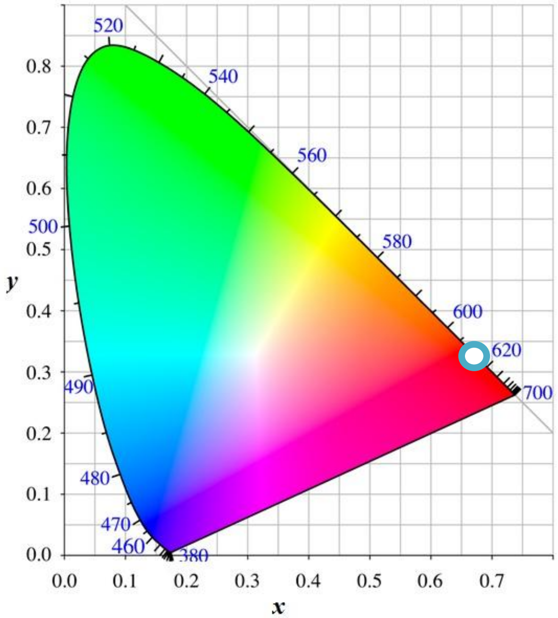

Figure S4. CIE 1931 chromaticity diagram, with deep red (0.67; 0.33) coordinates of PF4 film emission.

References

1 (a) Leone, G.; Giovanella, U.; Porzio, W.; Botta, C.; Ricci, G. *J. Mater. Chem.* 2011, **21**, 12901-12909; (b) Leone, G.; Boglia, A.; Boccia, A. C.; Taglialatela Scafati, S.; Bertini, F.; Ricci, G. *Macromolecules* 2009, **42**, 9231–9237

2 see for example Bujdak, J et al *Colloid Polym. Sci.* 2009, **287**, 157