

SUPPORTING INFORMATION

***In situ* synthesis of fluorescent poly(norbornene)/oxazine-1 dye loaded fluoromica hybrids: supramolecular control over dye arrangement**

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The successive and reiterated Soxhlet extractions with EtOH of the dye-clay materials, progressively decreases the low-energy band intensity peaked at 750-760 nm, related to dye aggregates emission (Figure S1), and the extracted fraction contained dye molecules.

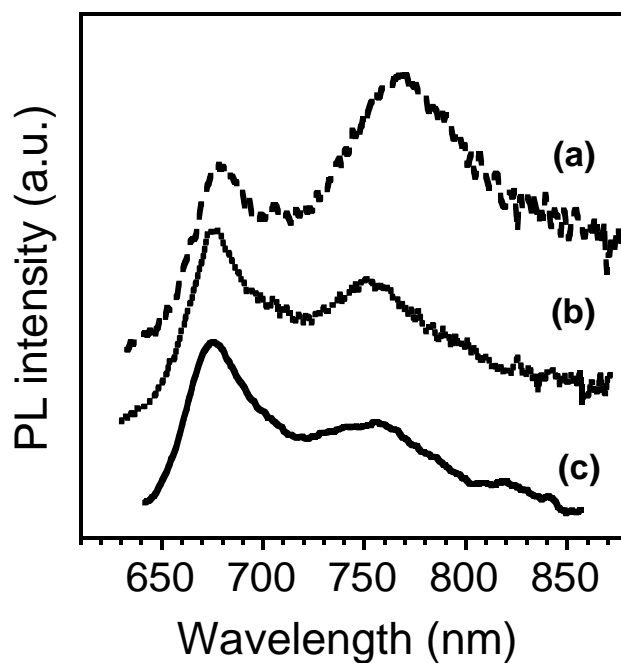


Figure S1. Normalized PL spectra of F2 powder after successive Soxhlet extractions with EtOH: (a) not extracted, (b) F2-*e* [8h], (c) F2-3*e* [24h]. Spectra are vertically shifted for clarity.

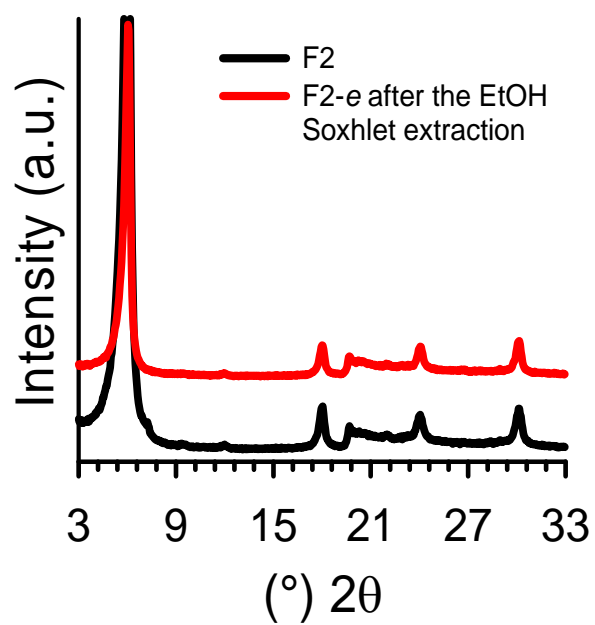


Figure S2. XRD pattern of pristine F2 and F2-*e* after the Soxhlet extraction with EtOH. Spectra are vertically shifted for clarity.

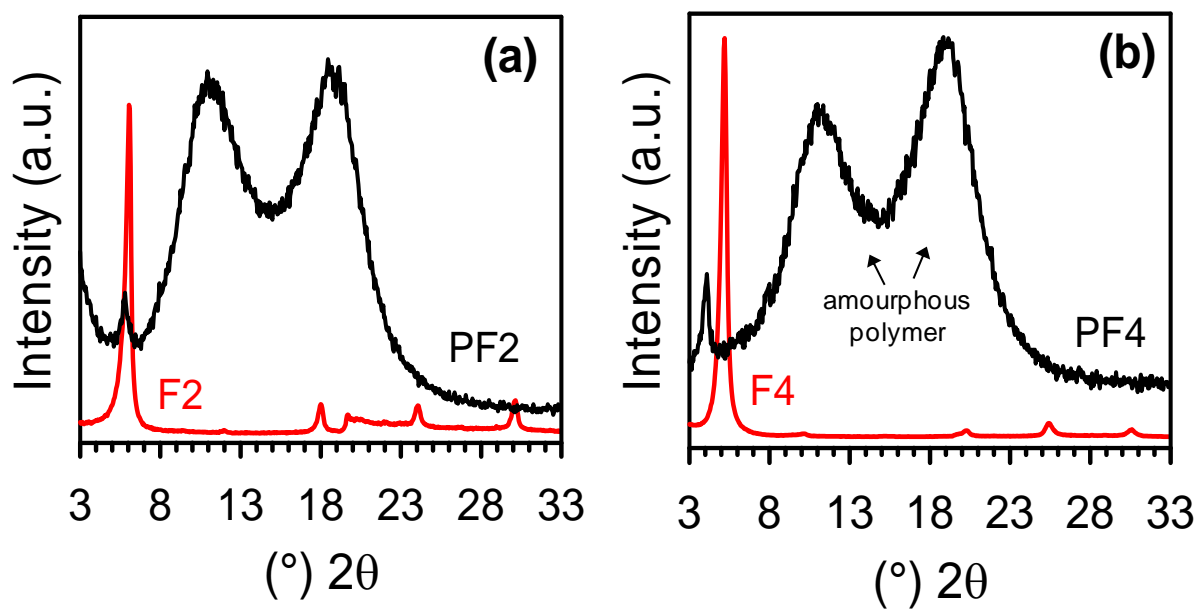


Figure S3. XRD pattern of (a) F2 and PF2 polymer hybrid, and
(b) F4 and PF4 polymer hybrid.

A narrow peak at about 722-724 nm both in PF4 absorption and PL spectra, which was not observed in the spectra of the F4 precursor (see Figure 4 in the manuscript), is observed.

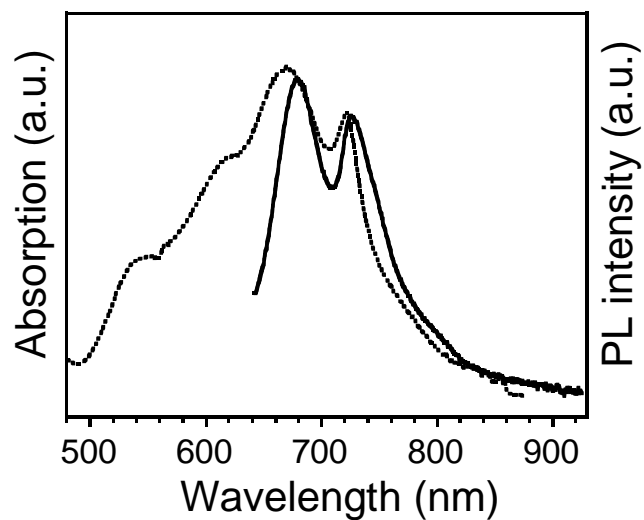


Figure S4. Normalized absorption (dotted line) and PL spectra (solid line) of PF4 film.

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 Fig.S5) upon Ox-1 aggregation in solution. The high energy absorption band at 500 nm can be assigned to large-size molecular assemblies of H-type, in agreement with the literature for similar dyes (see for example reference 47, Bujdak, J et al *Colloid Polym. Sci.* 2009, 287, 157). 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 (see Ref.s 43 and 47), well compares with the one observed in PF4 film (see Fig.S4 in ESI). 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 (Figure 6 in the manuscript), thus further supporting our assignment to J-aggregates.

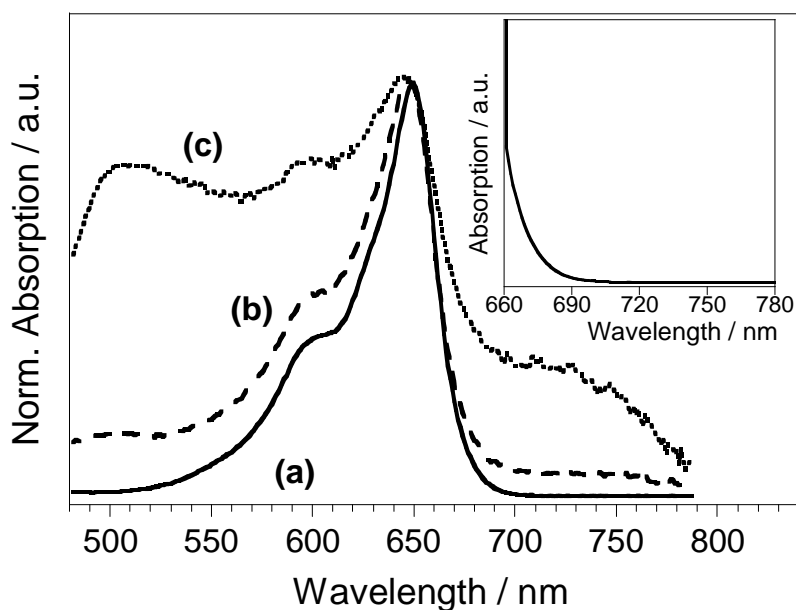
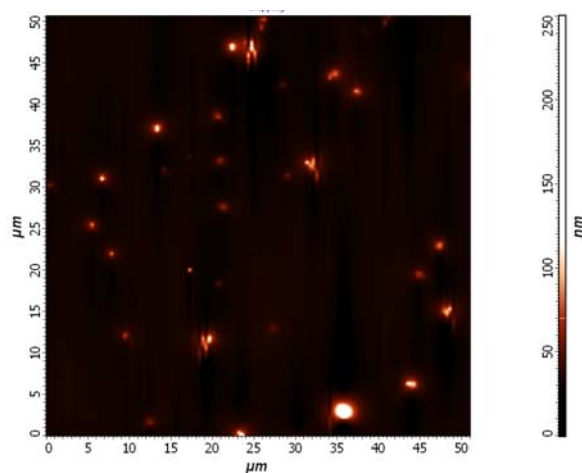


Figure S5. Normalized absorption spectra of Ox1 solution with different pentane/ethanol ratio: (a) 100 % ethanol, (b) 50/50 %, and (c) 100 % pentane. Ethanol is a good solvent for Ox1 and no aggregation is observed even at concentration of 700 μM (see inset), while pentane is a bad solvent and causes Ox1 aggregates (H- and J-Type) of different size.

AFM height images of PF2 film shows (Fig.S6a), in agreement with fluorescence image (see Figure 5 in the manuscript), homogeneously dispersed clay grains with a broad distribution of size from microns down to few nanometers. The PF2 film spin-coated on glass substrate is highly transparent ($T > 96\%$ in the range 380-720 nm) as clearly visible in the Fig.S6b.



(a)



(b)

Figure S6. AFM topography image of PF2 cast film on Si substrate (a). (b) The PF2 film spin-coated on glass substrate show an high transmittance in the visible range. The thickness of the film is about 200 nm.