Supplementary material (ESI) for Journal of Materials Chemistry

Supporting Information

Fluorescence properties of H_4TPPS^{2-} in solution and in ESAM films

The fluorescence properties of H_2TPPS^{4-} and H_4TPPS^{2-}, both in the monomeric and in the aggregated forms, have been thoroughly investigated in solution [1, 2, 3, 4], while published results concerning ESAM films are limited to the free base, likely because of the pronounced fluorescence quenching induced by aggregation of the diprotonated form in ESAM [1]. Our steady-state fluorescence results for H_4TPPS^{2-} in solution agree with those reported in the literature. We observe both J_B and J_Q emissions together with a residual monomer Q emission from a solution containing the porphyrin essentially all in the aggregated form (figure S1).

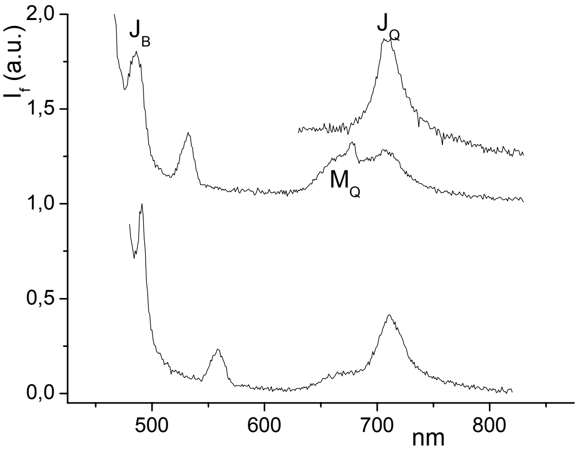

Figure S1. Normalized fluorescence emission spectra of a 10^{-6} M solution of H_4TPPS^{2-} in a 0.2 M KCl solution in water (lower curve, λ_{exc} = 470 nm) and of an ESAM with 1 PDDA / H_4TPPS^{2-} bilayer per side of the quartz plate plunged in acidified water (pH = 1) (λ_{exc} = 470 nm, intermediate curve and λ_{exc} = 489 nm, upper curve).

We therefore confirm that the aggregate has a lower fluorescence quantum yield than the monomer. The emission and excitation spectra of a PDDA/ H_4TPPS^{2-} ESAM plunged into acidified water (pH =1) are much the same as those of the solution. Fluorescence anisotropy, measured by exciting on the J_B band and observing the J_Q emission, was, again, essentially the same in solution (0.23) and for the film in water (0.25, but this result is affected by a large uncertainty, estimated to about 0.1, due to a strong contribution from highly polarized scattered light). So, the aggregates in the ESAM preserve a rotational mobility comparable to that in solution if the film is swelled by water.

Dry films exhibited a completely different fluorescence behaviour. The emission observed by exciting at 470 nm was weak and characterized by a broad spectrum (figure S2), with dominant contributions from higher transition energy traps ($\lambda > 500$ nm) and smaller ones from monomers ($\lambda > 650$ nm) and some lower transition energy traps ($\lambda > 750$ nm). Because excitation spectra were heavily deformed by a very strong light scattering, we obtained single-wavelength excitation intensities by measuring emission spectra at such excitation wavelengths, and taking the difference between the total signal at the emission maximum and the easily estimated level of scattered light. The points thus obtained follow fairly well the J-aggregate absorption profile between 360 and 480 nm, therefore suggesting that the observed emission indeed results from excitation of the H_4TPPS^{2-} aggregates.

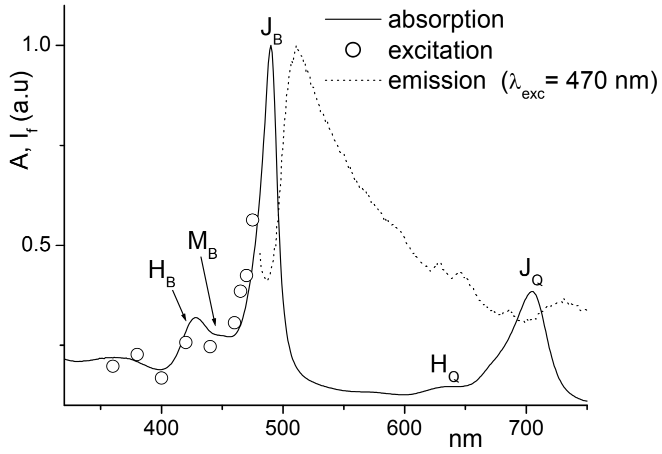

Figure S2. Absorption, emission and excitation spectra of a dry ESAM with 1 PDDA / H_4TPPS^{2-} bilayer per side of the quartz plate.

References

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[4] Pasimeni L.; Meneghetti M.; Rella R.; Valli L.; Granito C.; Troisi L. *Thin Solid Films* **1995**, *265*, 58.