

Organic Porphyrin Nanoparticles with Induced optical Activity: Ion-Based Synthesis from Achiral Chromophore and Chiral Counterions

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HOMO and LUMO of TRISPHAT

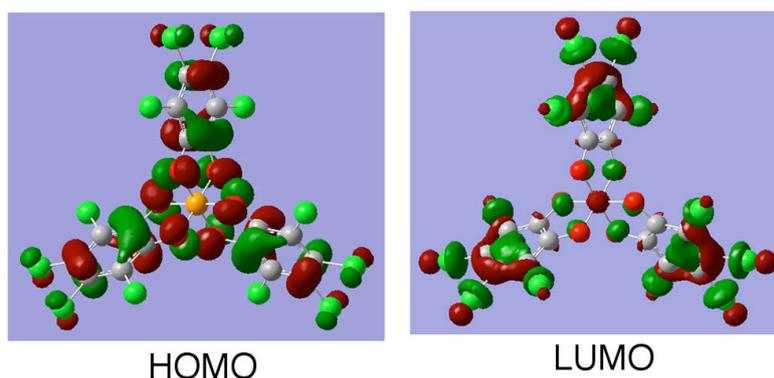


Figure S1. DFT calculations of HOMO and LUMO of TRISPHAT. The orange, red, and green balls are phosphorous, oxygen, and chlorine atoms, respectively. The dark-gray and light-gray balls are carbon and hydrogen atoms, respectively.

We calculated the molecular orbitals of TRISPHAT by applying time-dependent density functional theory (TD-DFT) approach using B3LYP functional and a 6-31+G* basis set. Figure S1 shows the calculated HOMO and LUMO. The HOMO has electron density principally in the vicinity of oxygen atoms of the phosphate, but the LUMO has electron density primarily around the outer aromatic region, suggesting that the HOMO–LUMO transition can be ascribed to the $n-\pi^*$ transition. In addition, we found that the lowest excitation is originated from the HOMO–LUMO transition with very small electric and large magnetic transition dipoles,

suggesting that the HOMO–LUMO transition is electrically forbidden ($f = 0.0004$) but magnetically allowed, in agreement with the $n-\pi^*$ transition.

Polarized-Light Microscopy for Solid Products Prepared with TMPyP and TRISPHAT or BINPHAT at the Net Charge Ratio of Unity

To check whether the solid products (TMPyP/TRISPHAT or TMPyP/BINPHAT precipitates) are crystalline or amorphous, polarized-light microscopy (PLM) is effective since structural anisotropy displays birefringence with contrast-enhancing imaging. Figure S2 shows typical optical micrographs of these samples without (left-side images) and with (right-side images) cross polarizers. Then PLM was performed with a BXP optical microscope (Olympus). If the specimen is optically anisotropic or crystalline, we can visualize the object; however, from Figure S2, the complete absence of the PLM images indicates that the solid products of TMPyP/TRISPHAT and TMPyP/BINPHAT are amorphous.

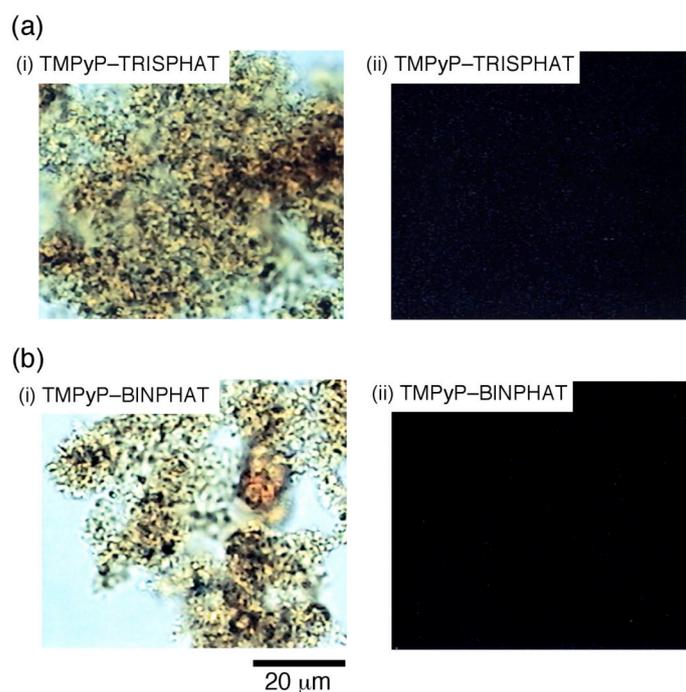


Figure S2. Representative optical micrographs of the solid-state products of (a) TMPyP/TRISPHAT and (b) TMPyP/BINPHAT. The left- and right-side images correspond to those observed without and with cross polarizers, respectively.

Fluorescence Spectra of TMPyP monomer and Nanoparticle Samples

Figure S3 shows the typical fluorescence spectrum of TMPyP monomer along with those of TMPyP-T and TMPyP-B nanoparticle samples in water/methanol (9/1) mixture excited at 550 nm. For the fluorescence of nanoparticle samples, the corresponding absorption spectra are shown in Figure 4 in the main text. The fluorescence spectra of all TMPyP nanoparticles exhibited a red shift compared to that of the monomeric species in the water/methanol solution. The large Stokes shifts (~ 18 nm) of $Q(0,0)$ fluorescence bands observed in both nanoparticle samples prove the absence of self-aggregation into J-aggregates, since the J-aggregates exhibit almost no Stokes-shifted fluorescence.¹ In addition, similarity in their fluorescence spectral shapes also corroborates the absence of the J-aggregate in the nanoparticles.

References

- (1) Kobayashi, T. ed., *J-Aggregates*, 1996, World Scientific, Singapore.

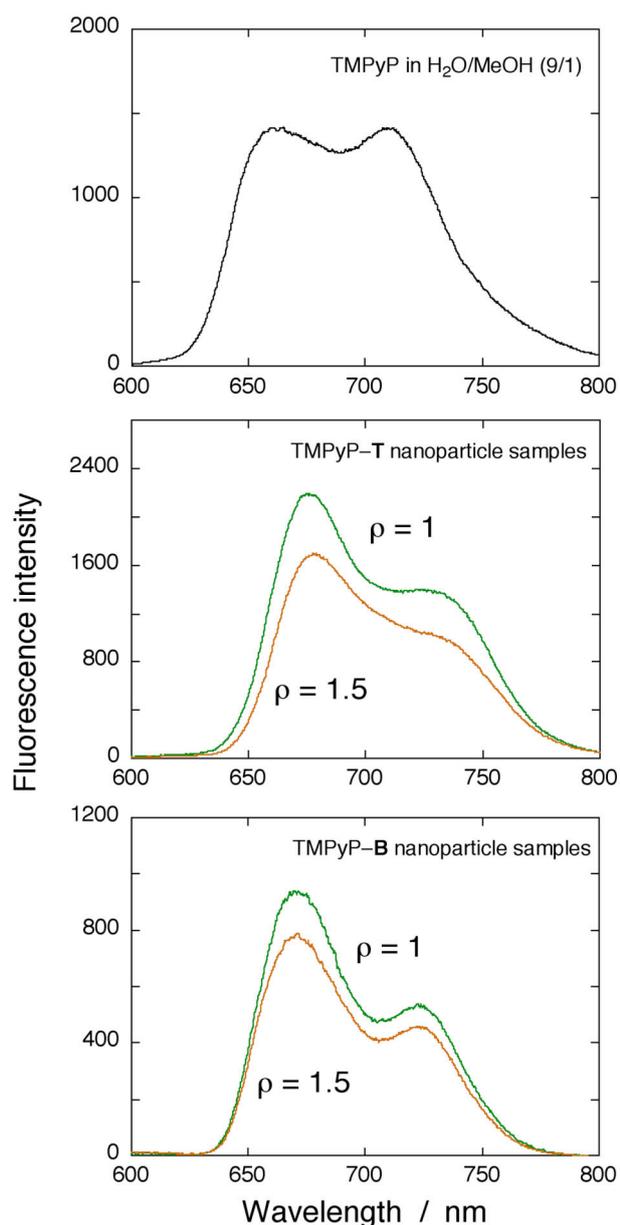


Figure S3. Fluorescence spectra in water/methanol (9/1) mixture. Upper; monomeric TMPyP, middle; TMPyP-T nanoparticle samples, lower; TMPyP-B nanoparticle samples.