Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

AIEE effect and Two-Photon Absorption (TPA) enhancement induced by polymerization: synthesis of a monomer with ICT and AIE effects and its homopolymer by ATRP and a study of their photophysical properties

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^{1}H NMR spectra

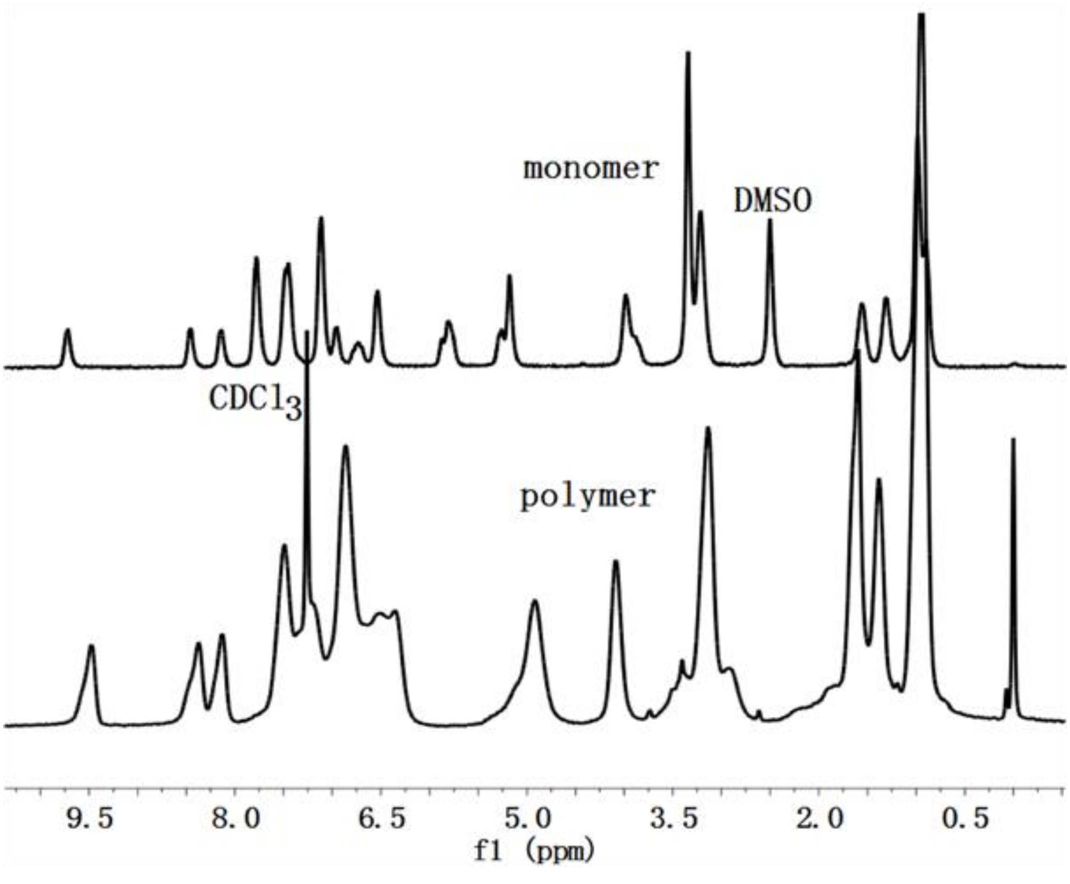
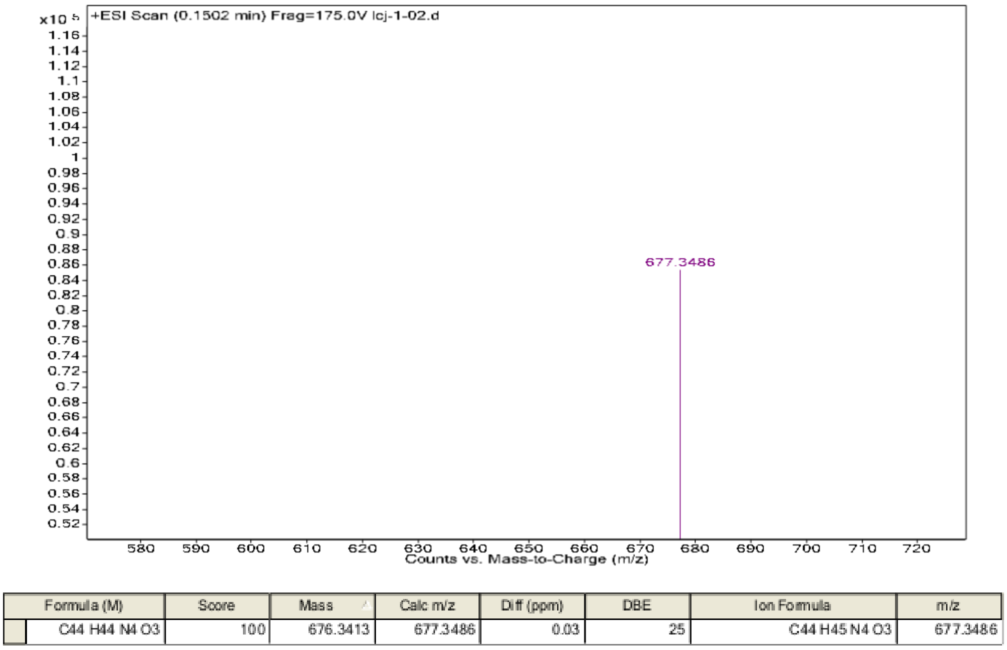


Figure S1. ^{1}H NMR spectra of monomer (*DMSO-d_6*) and polymer (*$CDCl_3$*) at r.m.



Formula (M)	Score	Mass	Calc m/z	Diff (ppm)	DBE	Ion Formula	m/z
C44 H44 N4 O3	100	676.3413	677.3486	0.03	25	C44 H45 N4 O3	677.3486

Figure S2. HRMS-ESI spectra of StTPP-NI

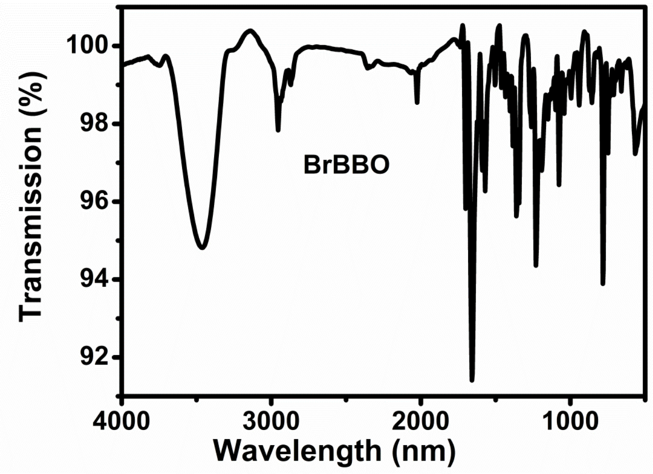


Figure S3. FT-IR profile of compound BrBBO

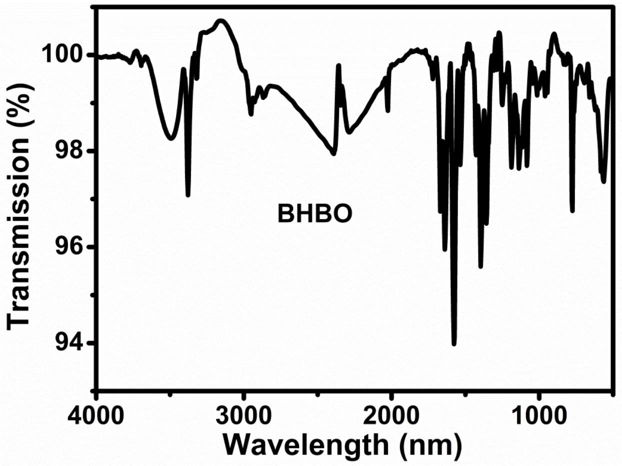


Figure S4. FT-IR profile of compound BHBO

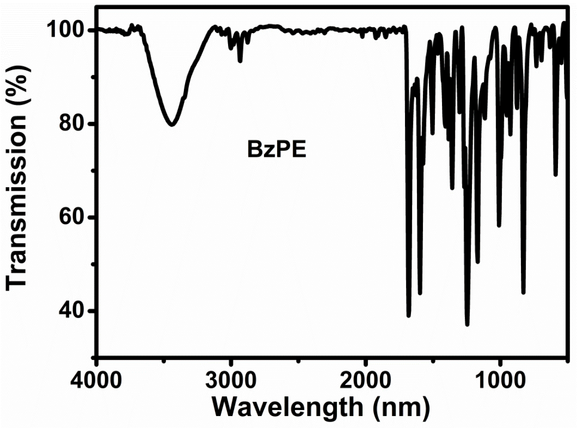


Figure S5. FT-IR profile of compound BzPE

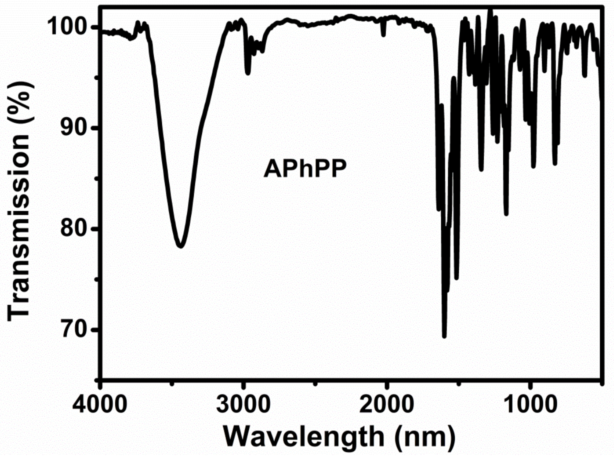


Figure S6. FT-IR profile of compound APhPP

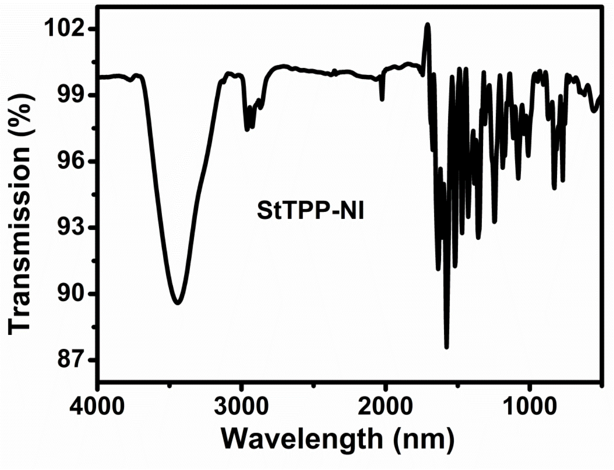


Figure S7. FT-IR profile of compound StTPP-NI

TGA and DSC

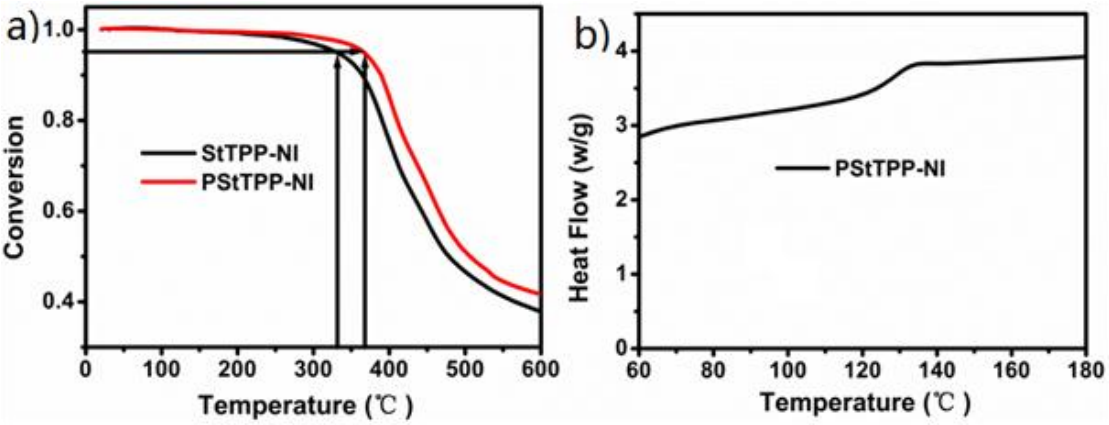


Figure S8. a) TGA curve of StTPP-NI and PStTPP-NI collected under N_2 at a heating rate of 10 ˚C min^{-1}; b) DSC curve of PStTPP-NI collected under N_2 at a scanning rate of 10 ˚C min^{-1}.

Absorption and emission spectrum

To see whether there was any correlation between the optical properties of the PL and the solvent polarity, the Lippert-Mataga model was used in a series of solvents with a broad range of polarities. The solvent polarity parameters (Δf) were expressed by the following equation:

$$\Delta f = f(\varepsilon) - f(n^2) = (\varepsilon\text{-}1/2\varepsilon+1) - (n^2 - 1/2n^2+1) \qquad (1)$$

where ε and n are the permittivity (or dielectric constant) and the refractivity (or refractive index) of the solvent, respectively.

In a non-polar solvent of cyclohexane (Δf = 0.004), the monomer shows a sharp emission band at 496 nm with an apparent shoulder band at around 525 nm. The sharp λ em and shoulder can be attributed to the local excited (LE) state and the ICT state, respectively. The emission spectrum is sensitively affected by solvent polarity. Thus, although the Δf value (0.014) of toluene is only slightly higher than that of cyclohexane, the λ em is already red-shifted to 540 nm and the shoulder peak disappears, with a concomitant decrease in the emission intensity. In the high polar solvents of THF (Δf = 0.21) and DMF (Δf = 0.28), the emission almost quenched due to the strong ICT effects. In addition, the emission quench of STPP-NI in polar solvents could be recovered when a certain amount of solvents with less polarity was added. For example, emission of StTPP-NI in THF solution was enhanced but blue-shifted when cyclohexane was added, and showed characteristic emission spectra that were 45-fold higher than those in pure THF solution when fraction of cyclohexane (f_{CH}) is 99 % (see Figure S9). This illustrated that molecule-solvent interaction should play an important role in emission tuning and the ICT character was the key point of emission quenching.

Previous studies of conformation on pyrazolines have revealed that a planar conformation is favored in a crystalline environment and the twist conformation is preferred in the isolated state. The strong intermolecular interactions were aroused in the planar π-conjugated chromophores, which induce the formation of excimer complex leading to the fluorescence quenching. However, according to the DFT calculation, such a twisted conformation of the pyrazoline ring and naphthalimide ring restricted the parallel face-to-face intermolecular interactions in aggregates and avoided emission quenching.

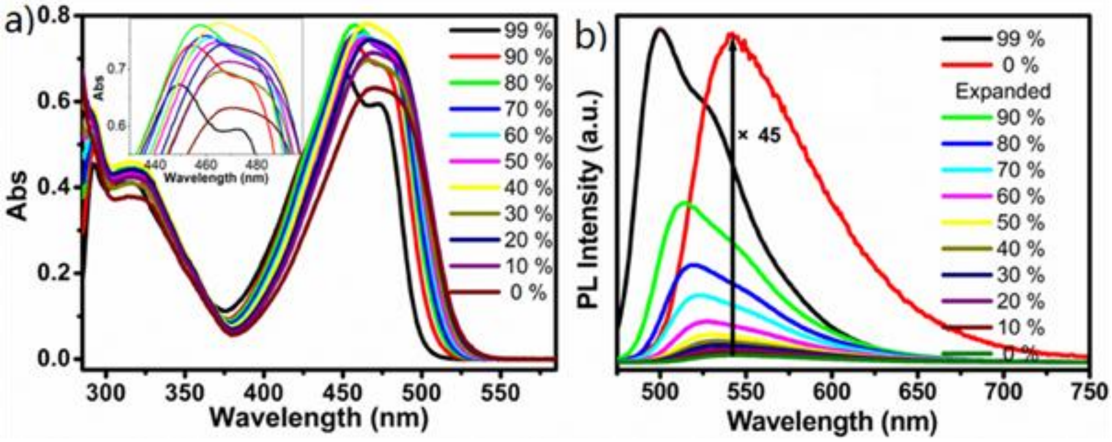


Figure S9. a) UV/Vis absorption spectra and b) emission spectra of StTPP-NI in the THF/cyclohexane mixtures (10^{-5} mol L^{-1}, λ ex = 467 nm).

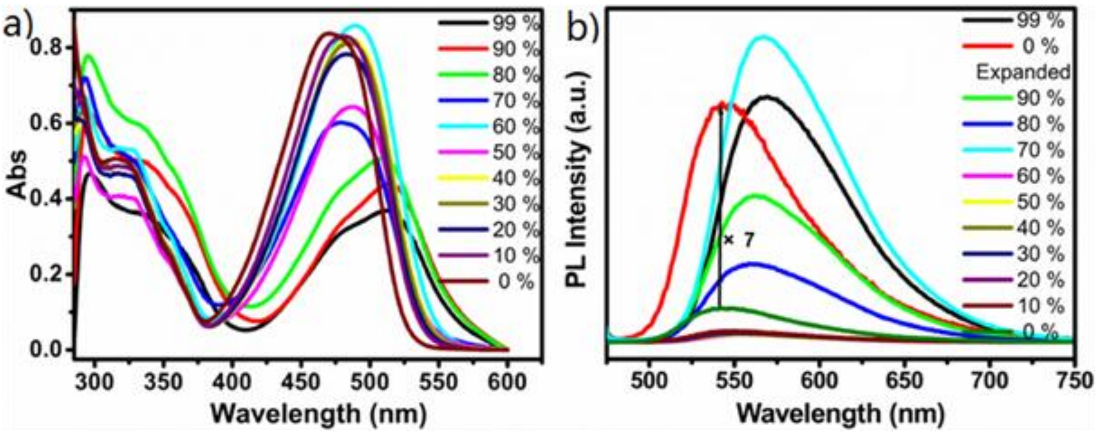


Figure S10. a) UV/Vis absorption spectra and b) emission spectra of StTPP-NI in the THF/water mixtures (10^{-5} mol L^{-1}, λ_{ex} = 467 nm).

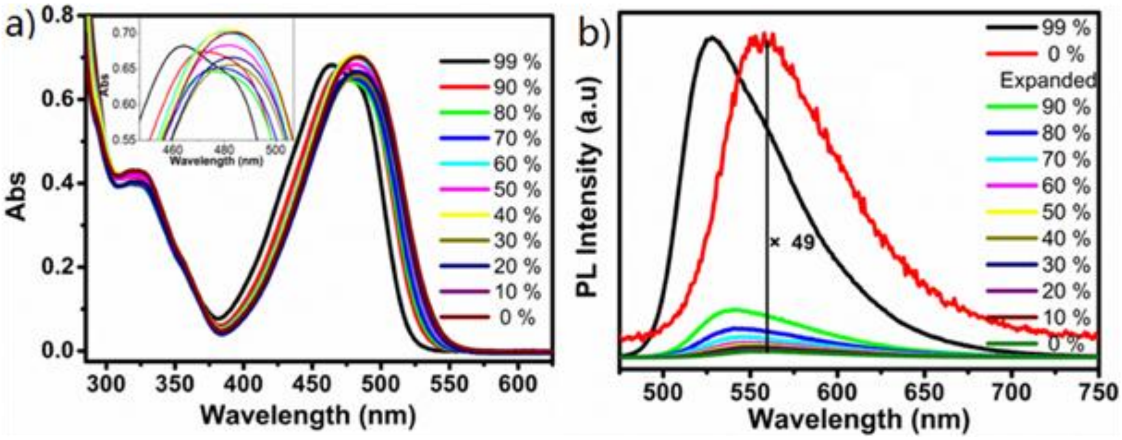


Figure S11. a) UV/Vis absorption spectra and b) emission spectra of StTPP-NI in the DMF/toluene mixtures (10^{-5} mol L^{-1}, λ_{ex} = 467 nm).

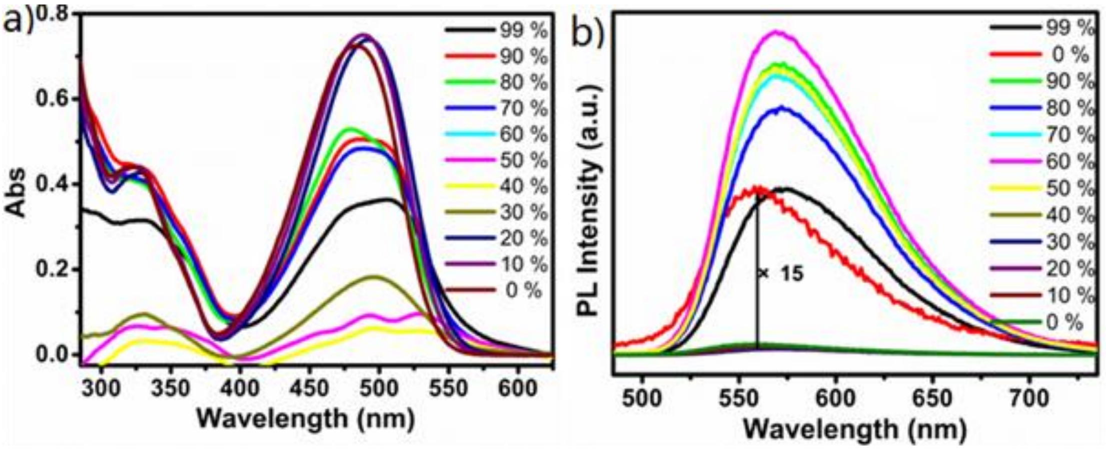


Figure S12. a) UV/Vis absorption spectra and b) emission spectra of StTPP-NI in the DMF/water mixtures (10^{-5} mol L^{-1}, λ_{ex} = 467 nm).

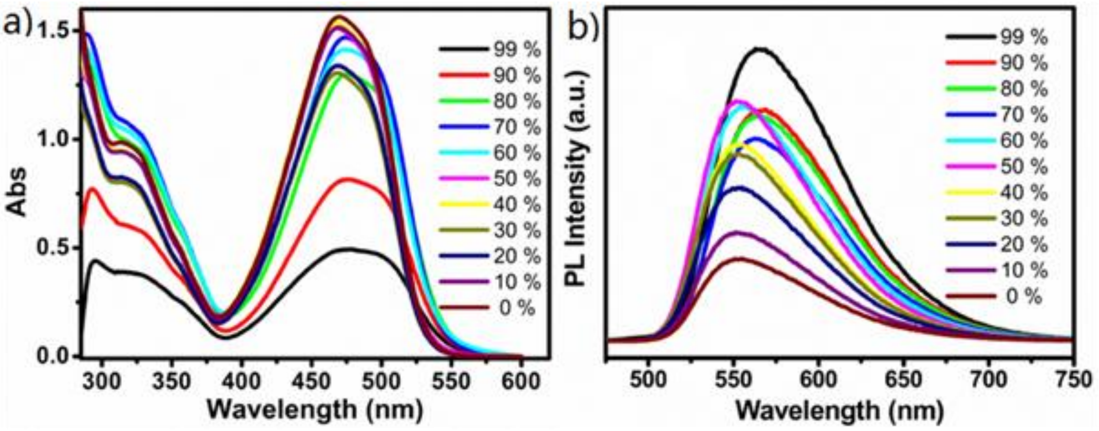


Figure S13. a) UV/Vis absorption spectra and b) emission spectra of PStTPP-NI in the THF/cyclohexane mixtures (10^{-6} mol L^{-1}, λ_{ex} = 467 nm).

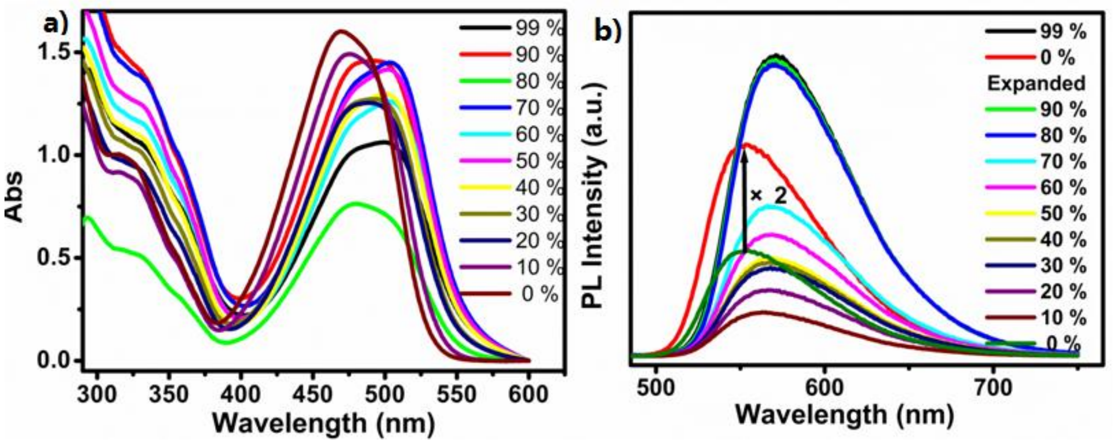


Figure S14. a) UV/Vis absorption spectra and b) emission spectra of PStTPP-NI in the THF/ethanol mixtures (10^{-6} mol L^{-1}, λ_{ex} = 467 nm).

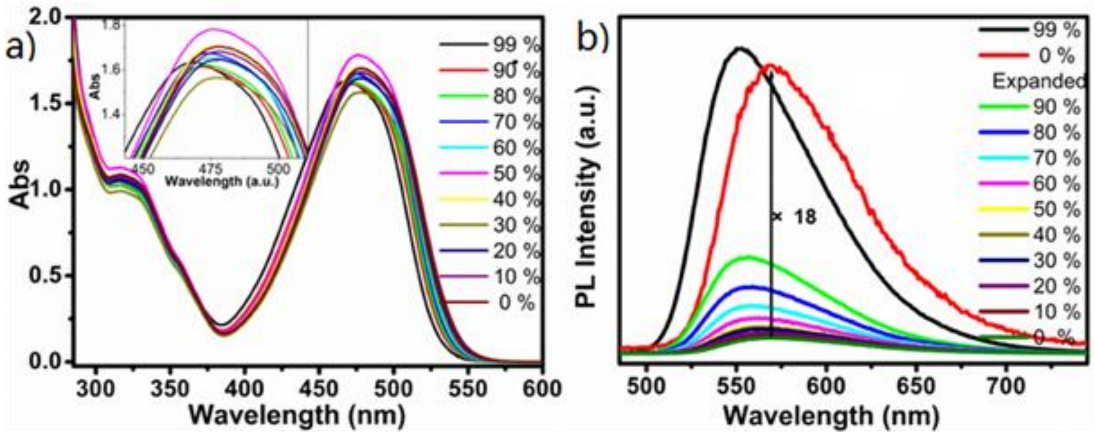


Figure S15. a) UV/Vis absorption spectra and b) emission spectra of PStTPP-NI in the DMF/toluene mixtures (10^{-6} mol L^{-1}, λ_{ex} = 467 nm).

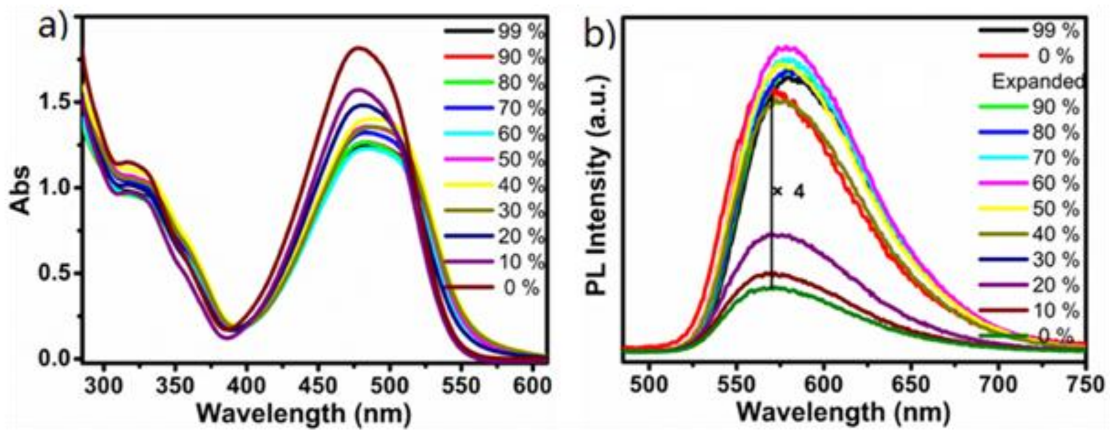


Figure S16. a) UV/Vis absorption spectra and b) emission spectra of PStTPP-NI in the DMF/ethanol mixtures (10^{-6} mol L^{-1}, λ_{ex} = 467 nm).

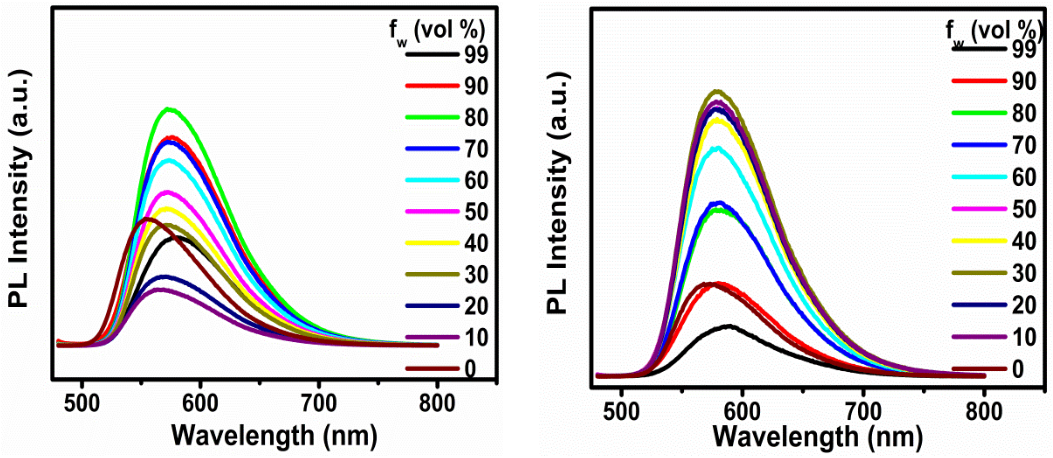


Figure S17. Emission spectra of PStTPP-NI in the THF/water (left) and DMF/water (right) mixtures (10^{-6} mol L^{-1}, λ ex = 467 nm).

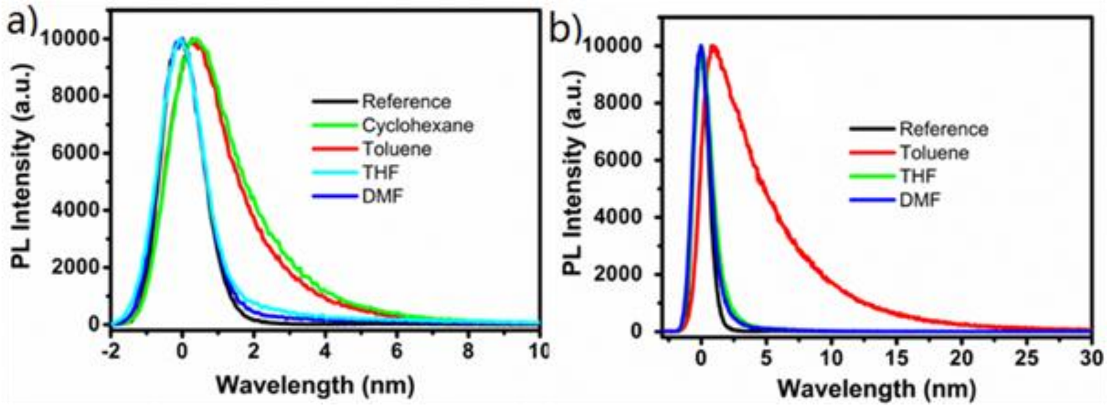


Figure S18. Typical fluorescence decay curves associated with lamp profile for StTPP-NI (a) and PStTPP-NI (b) in ambient environment. Excitation wavelength is constant at 300 nm.

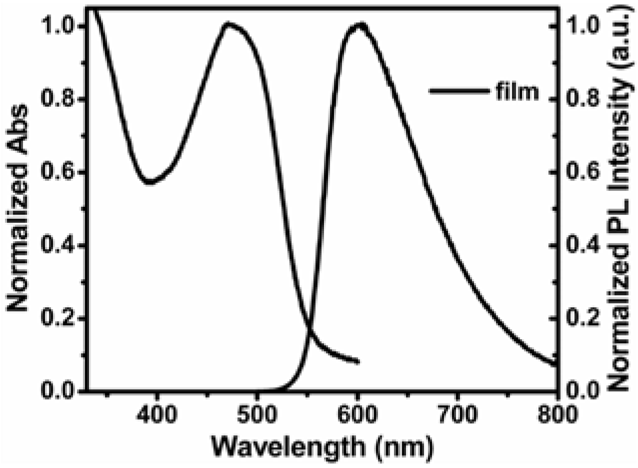


Figure S19. UV/Vis absorption spectra and emission spectra of PStTPP-NI in the film state (λ ex = 467 nm).

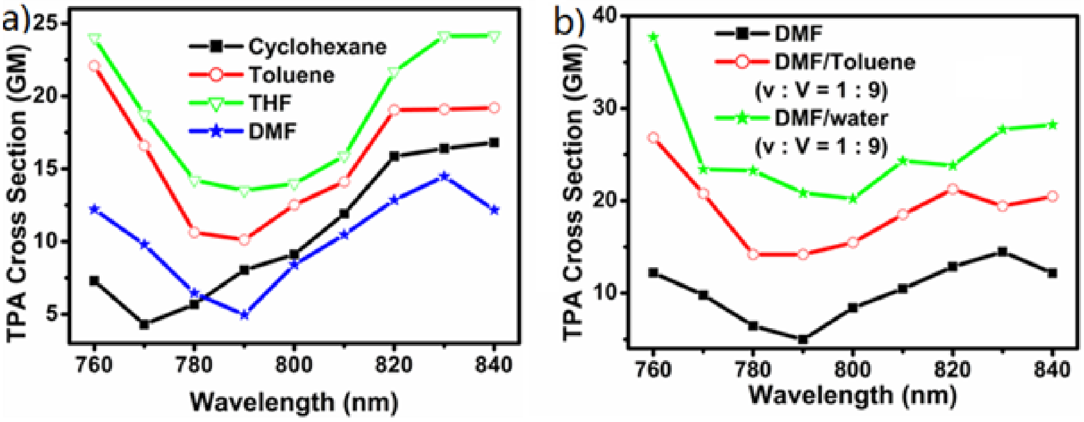


Figure S20. TPA cross section of StTPP-NI in different solvents (a) and in the aggregation state (b).

SEM images of monomer and polymers in aggregates

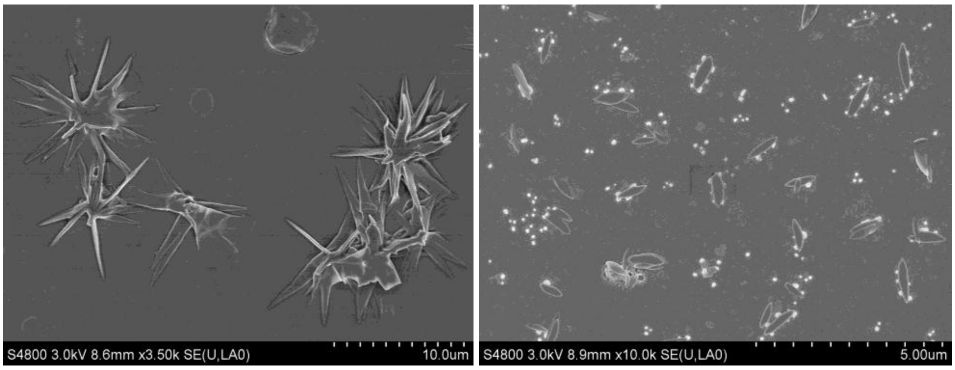


Figure S21. SEM images of monomer formed in THF\water (3: 7 (left) and 2 : 8 (right) by volume). Scale bar is 10 um and 5 um.

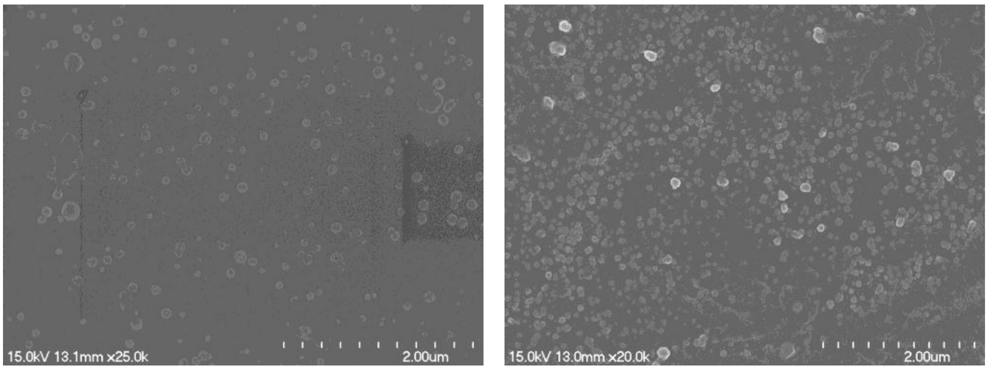


Figure S22. SEM images of monomer formed in THF\water (1 : 9, by volume, left) and DMF\water (1 : 9, by volume, right) mixtures. Scale bar is 2 μm.

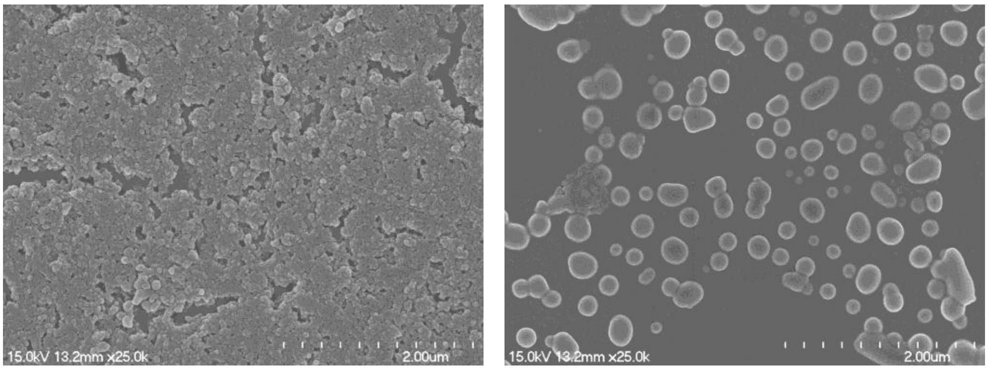


Figure S23. SEM images of polymer formed in THF\CH (1 : 9, by volume, left) and DMF\toluene (1 : 9, by volume, right) mixtures. Scale bar is 2 um.

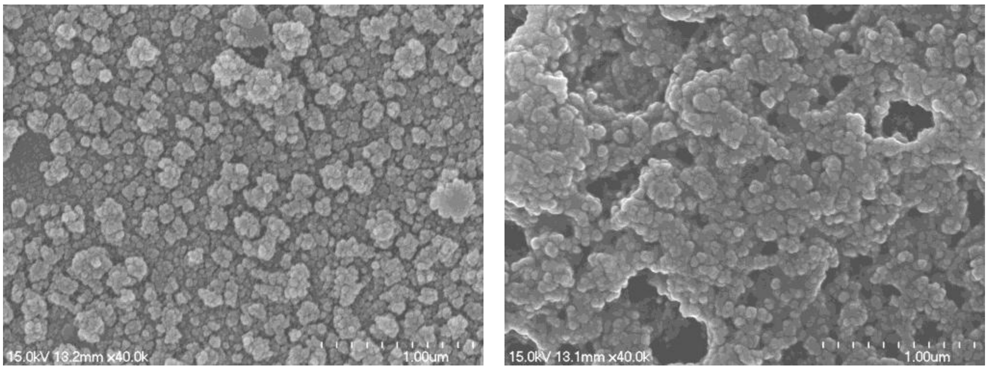


Figure S24. SEM images of polymer formed in THF\ethanol (1 : 9, by volume, left) and DMF\ethanol (1 : 9, by volume, right) mixtures. Scale bar is 1 um.