Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Covalent Functionalization of Two-Dimensional Black Phosphorus Nanosheets with Porphyrins and Its Photophysical Characterizations

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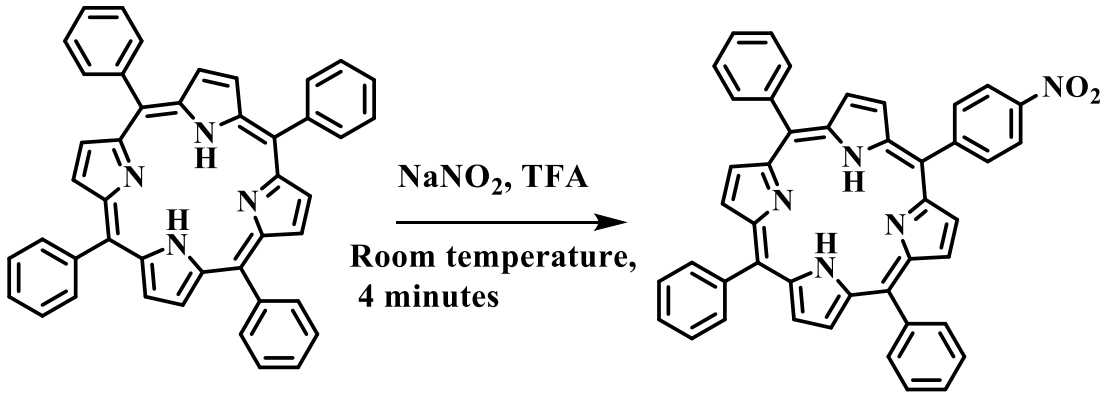
Synthesis of TPP-NO_2

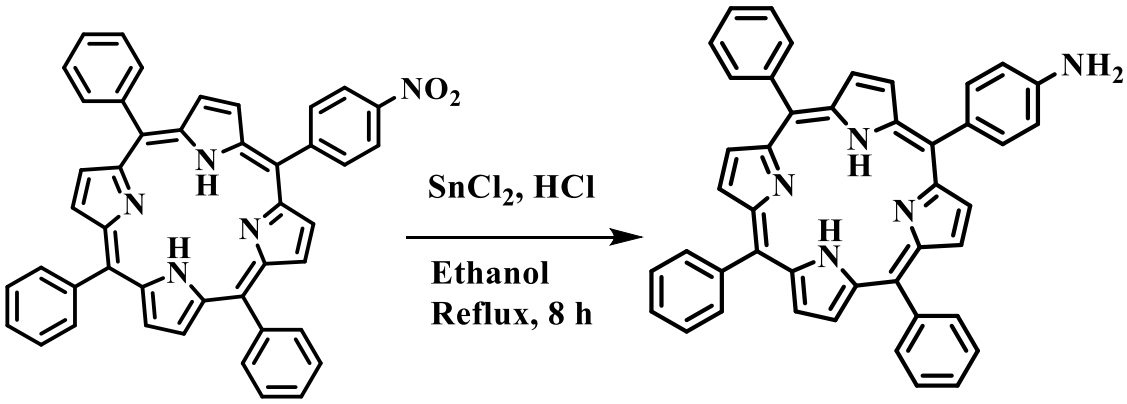
Tetraphenyl porphyrin (TPP) (250 mg, 0.407 mmol, 1eq), trifluoro acetic acid (TFA) (20 mL) and sodium nitrite ($NaNO_2$) (50.5 mg, 0.732 mmol, 1.8 eq) were stirred at room temperatue for 4 minutes under nitrogen atmosphere. The reaction mixture was poured into distilled water (100 mL) and the pH was adjusted to 7. The organic phase was collected by extraction using dichloromethane and the combined organic layer was dried under rotary evaporator. The crude sample was purified by column chromatography using 20% chloroform-petroleum ether solvent mixture followed by a recrystallization step using chloroform-methanol solvent mixture (1:5 volume ratio). Yield: 40%, ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.90 (d, 2H, J = 4 Hz), 8.86 (s, 4H), 8.75 (d, 2H, J = 8 Hz), 8.65 (d, 2H, J = 8 Hz), 8.41 (d, 2H, J = 8 Hz), 8.22 (d, 6H, J = 8 Hz), 7.78 (m, 9H), -2.78 (s, 2H).

Synthesis of TPP-NH_2

TPP-NO_2 (100 mg, 0.152 mmol, 1eq), $SnCl_2 \cdot 2H_2O$ (171mg, 0.76 mmol, 5eq), and concentrated hydrochloric acid (2.2 mL) were added into ethanol (20 mL) in a three-necked flask. The mixture was refluxed for 8 h under nitrogen atmosphere. After cooling to room temperature, the mixture solution was poured into deionized water (150 mL), followed by adjusting the pH to basic using NaOH solution. The solution was extracted with chloroform and then washed with water. The combined organic layer was dried under rotary evaporator. The crude was purified by column chromatography using 80% chloroform-hexane solvent mixture on silica. After column, TPP-NH_2 was further purified by recrystallization using a chloroform-methanol (1:5) solvent mixture. Yield: 46%, ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.94 (s, 2H), 8.83 (s, 6H), 8.22 (m, 6H), 8.01 (d, 2H, J = 8Hz), 7.76 (m, 9H), 7.08 (d, 2H, J = 8 Hz), 4.03 (s, 2H), -2.76 (s, 2H).



Scheme S1 Synthesis of TPP-NO_2.



Scheme S2 Synthesis of TPP-NH_2.

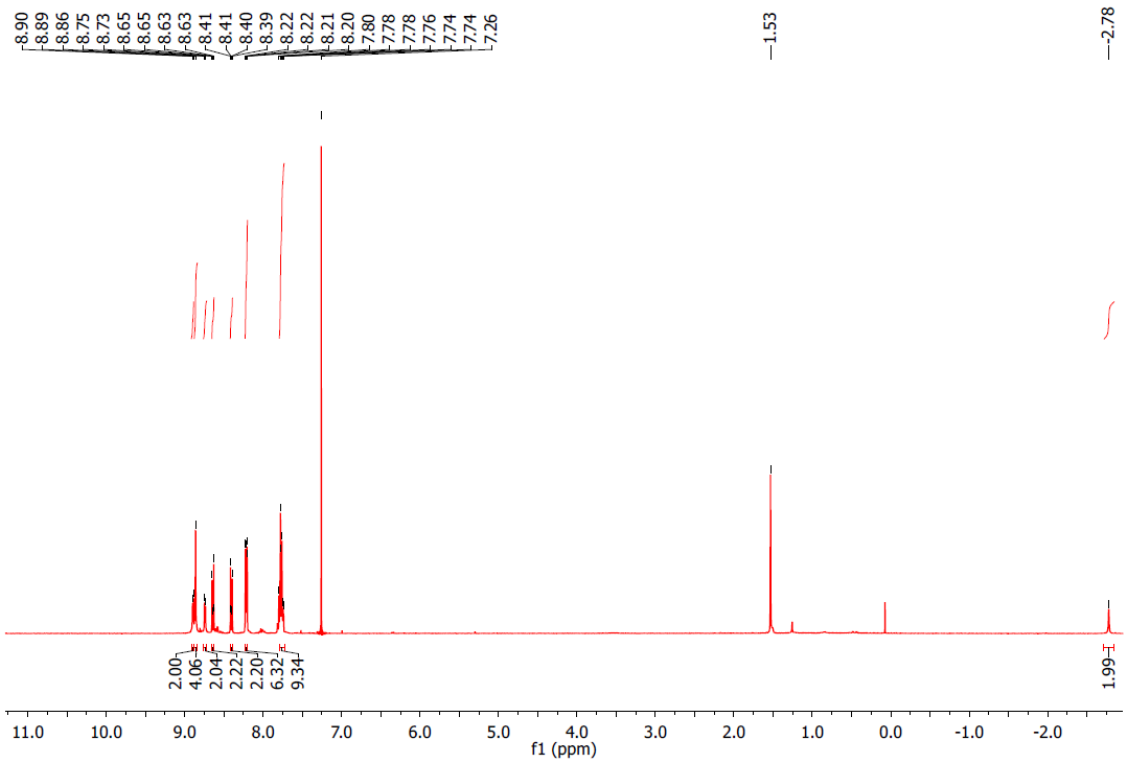


Fig. S1 ^{1}H NMR spectrum of TPP-NO_2.

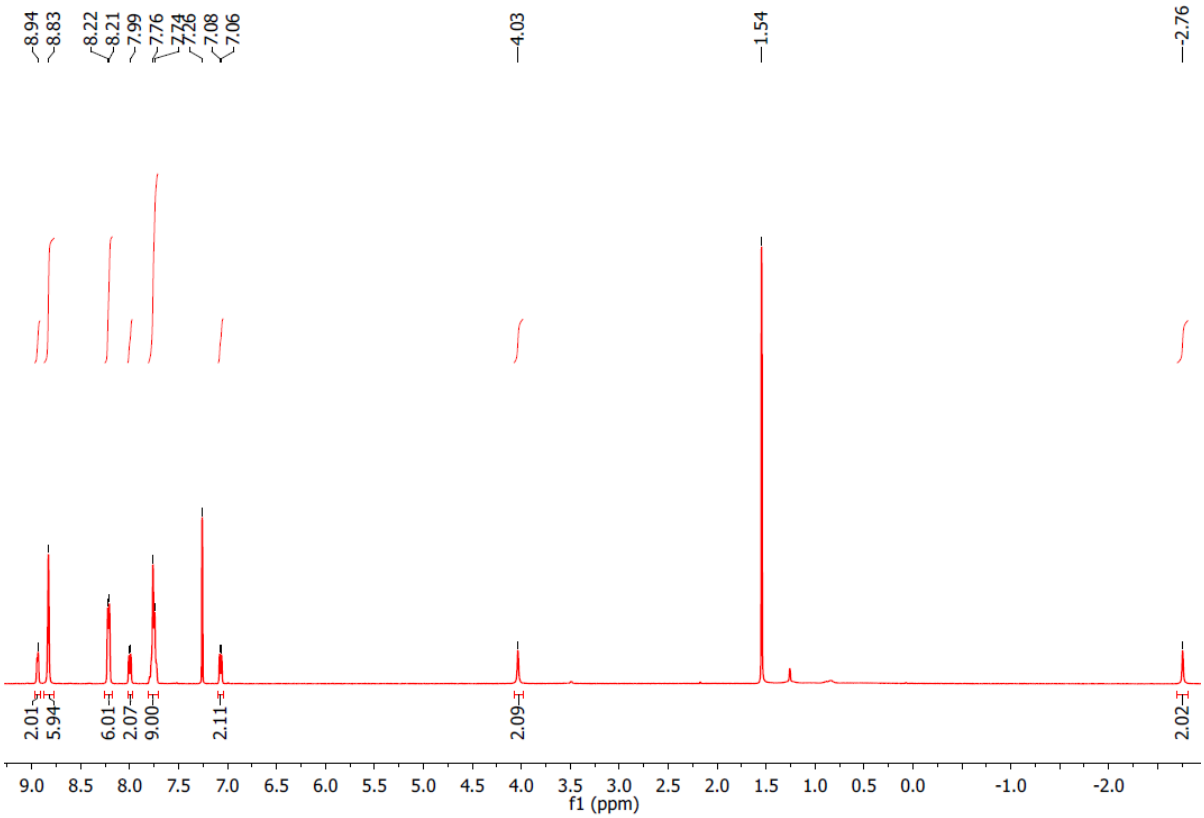


Fig. S2 ^{1}H NMR spectrum of TPP-NH_2.

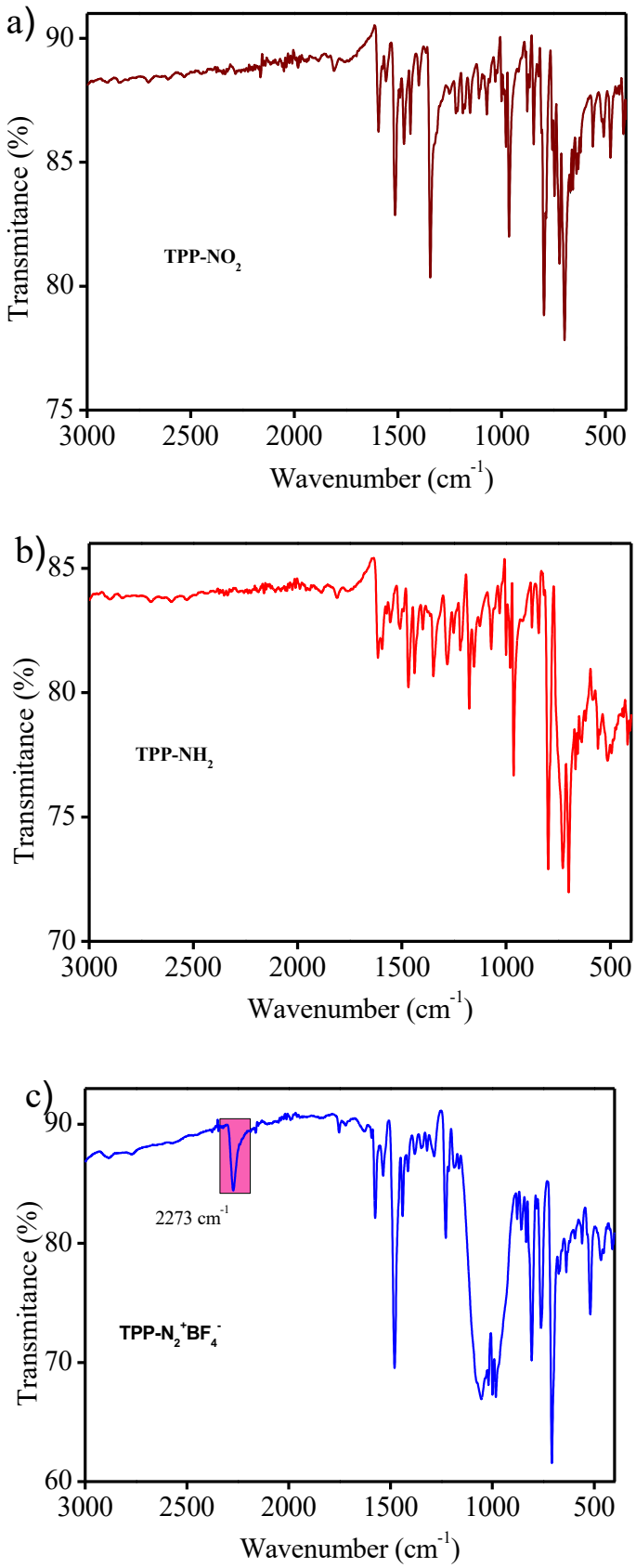


Fig. S3 FTIR spectra of (a) TPP-NO_2, (b) TPP-NH_2 and (c) TPP-$N_2^+BF_4^-$.

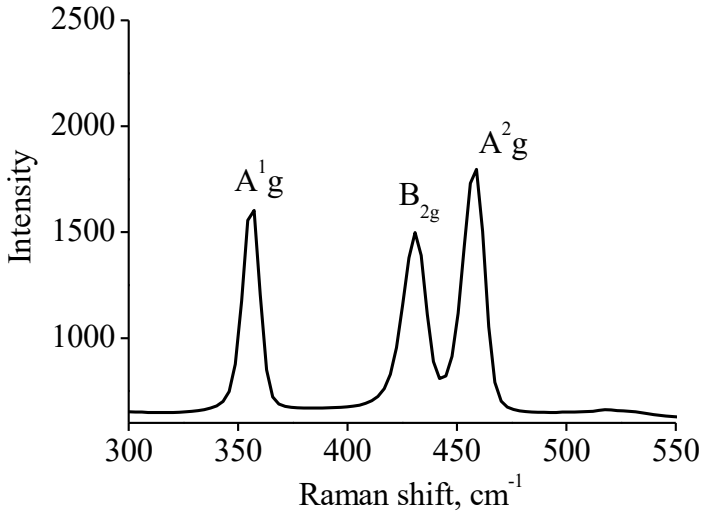


Fig. S4 Mean Raman spectrum of the control sample measured using a 532 nm laser excitation.

Compared with BPNSs-TPP, the mean Raman spectrum of control sample showed Raman bands at 357 cm^{-1} (A^1g), 431 cm^{-1} (B_{2g}) and 460 cm^{-1} (A^2g), similar to the bare BPNSs. This further indicates the covalent functionalization of BPNSs in the BPNSs-TPP hybrid.

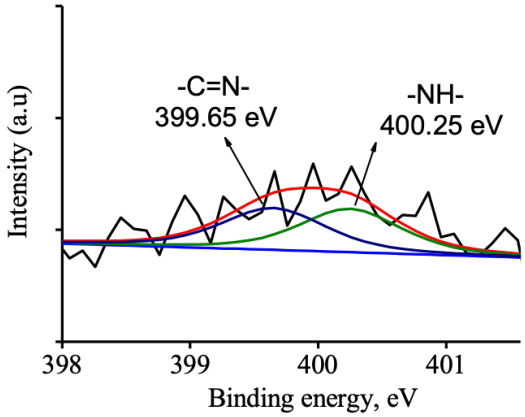


Fig. S5 N1s spectrum of BPNSs-TPP, which can be deconvoluted to two peaks. One peak is at 399.65 eV and the other one is at 400.25 eV, corresponding to -C=N- and -NH- nitrogen, respectively.[1]

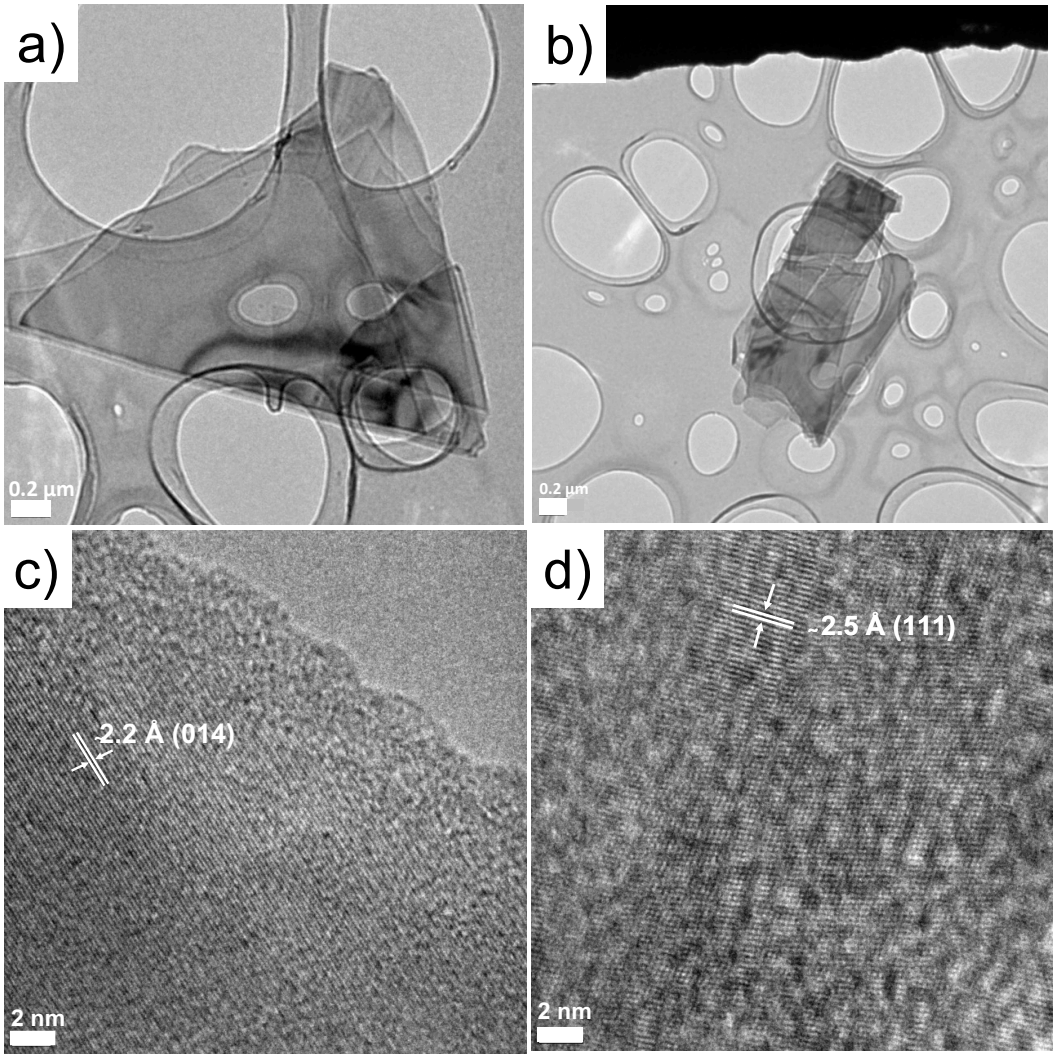


Fig. S6 (a, b) TEM and (c, d) HRTEM images of BPNSs.

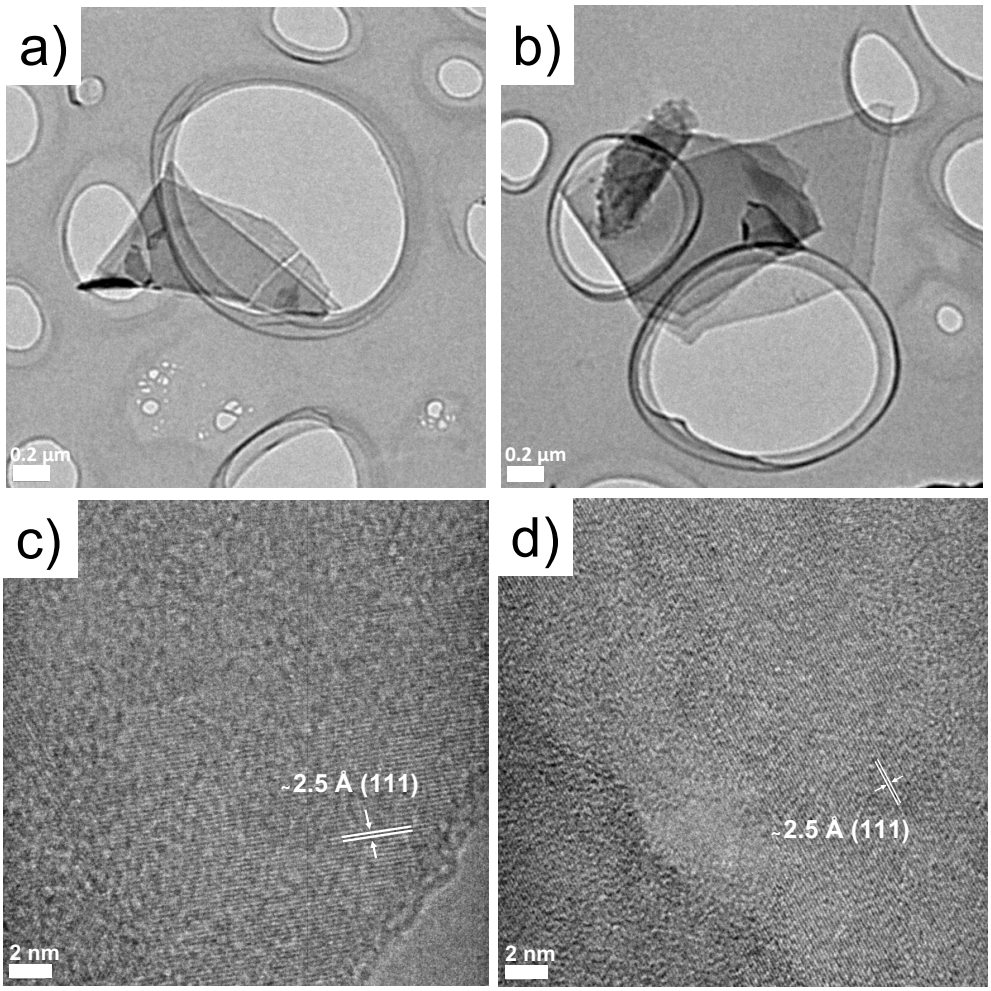


Fig. S7 (a, b) TEM and (c, d) HRTEM images of BPNSs-TPP.

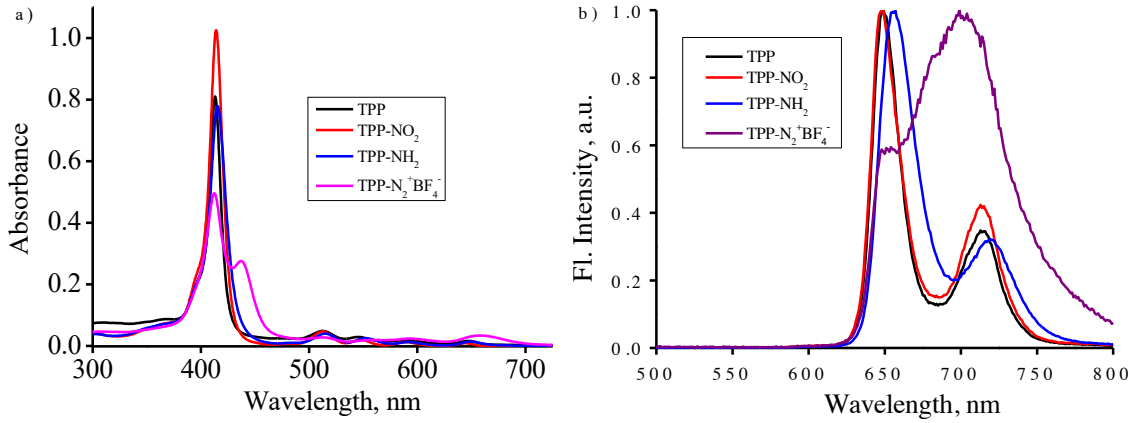


Fig. S8 (a) Absorption and (b) fluorescence spectra of TPP, TPP-NO_2, TPP-NH_2 and TPP-$N_2^+BF_4^-$ in acetonitrile solution.

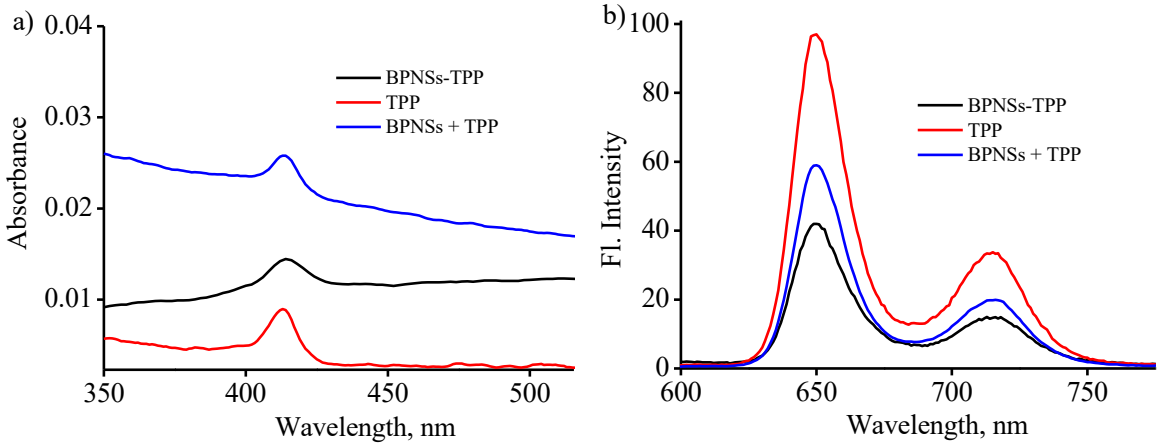


Fig. S9 (a) UV-Vis absorption and (b) fluorescence spectra of BPNSs-TPP, TPP and a physical mixture of BPNSs and TPP (BPNSs + TPP) with matching the optical density (OD) values.

1 J. R. Eskelsen, Y. Wang, Y. Qui, M. Ray, M. Handlin, K. W. Hipps and U. Mazur, Protonation state of core nitrogens in the meso-tetra(4-carboxyphenyl)porphyrin impacts the chemical and physical properties of nanostructures formed in acid solutions, *J. Porphyr. Phthalocyanines*, 2012, **16**, 1233-1243.