



Tetraphosphonic acid functionalized perylene diimide derivative: Synthesis and pH dependent photophysical properties

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The synthesis of phosphonic acid functionalized perylene diimide (PDI) molecular architecture has been demonstrated *via* functionalization at imide position. UV-Vis absorption and fluorescence emission spectroscopic techniques have been employed to investigate the photophysical properties of the novel PDI derivative at different pH (2 to 11). These results demonstrate the fascinating photophysical characteristics based on change in pH from 7 to 2 and 7 to 11 in aqueous medium.

Keywords: Bolaamphiphile, perylene diimide, phosphonic acid, photophysical, synthesis

Perylene diimide chromophores are an important class of organic dyes. PDIs were utilized as red colorant in paints, lacquers and the vat dyeing processes¹. In recent years, PDIs have gained significant attention due to their special π -conjugated structure². PDIs are employed in the field of organic functional materials such as organic photovoltaics (OPVs), organic field effect transistors (OFET), perovskite solar cells, photodetectors, organic light emitting diodes and single molecule spectroscopy, *etc.*³ Moreover, PDIs are extensively explored in the field of biomaterials⁴. PDI chromophores exhibit good optical properties, photophysical properties, enhances thermal and photochemical stability and undergoes supramolecular self-assembly *via* π - π stacking interactions⁵. The use of PDI in aqueous media is restricted due to the aromatic core and their stacking. There have been great efforts leading towards design and synthesis of water soluble PDI derivatives⁶. Most of the PDI derivatives applications are studied in organic medium. pH responsive water soluble PDIs are promising candidates in biological and medicinal fields⁷. To the best of our knowledge there is no report on synthesis of perylene derivatives with water soluble four phosphonic acid functional groups at imide positions.

Herein, we designed and successfully synthesized perylene diimide tetraphosphonic acid (PDI-TPA) derivative using multi step reaction strategy. Furthermore, we investigated its UV-Vis and

fluorescence emission spectroscopic properties in water at different pH ranging from 0-11.

Experimental Section

All the chemicals, reagents and solvents were purchased from Sigma-Aldrich, Bengaluru, Karnataka, India and TCI, Chennai, Tamil Nadu, India. ¹H NMR were measured on Bruker Avance-400 MHz and 500 MHz spectrometers at RT. ¹³C NMR spectra were recorded at 125 MHz and ³¹P NMR spectra were measured at 162 MHz and 202 MHz. Tetramethylsilane (TMS) was used as the internal standard. FT-IR measurements were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer.

Synthesis of PDI Phosphonate, 3

In a 50 mL sealed tube were added perylene-3,4,9,10-tetracarboxylic dianhydride **1** (100 mg, 0.26 mM) and compound **2** (Ref. 8) (300 mg, 0.76 mM) in 10 mL of N,N'-dimethyl acetamide (DMA). The mixture was heated to 120°C with vigorous stirring for 48 h. The dark brown coloured reaction mixture was cooled to RT and poured into pre-cooled 50 mL of 1N aqueous HCl. The resulting suspension was extracted with dichloromethane (2×50 mL) and the organic layer was separated. The organic layer was washed with brine solution (2×30 mL), dried over anhyd. Na₂SO₄ and the solvent

evaporated using rotary evaporator to obtain crude material which was purified by column chromatography $\text{CHCl}_3:\text{MeOH}$, (95:5), to afford PDI-Phosphonate **3** as a red coloured solid (yield 70mg, 24%). ^1H NMR (500 MHz, CD_2Cl_2): δ 8.67 (s, 8H), 7.38 (s, 2H), 7.23 (s, 4H), 4.09–4.03 (m, 16H), 3.25–3.21 (d, $J=21.7$ Hz, 8H), 1.30–1.27 (t, $J=7.0$ Hz, 24H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 163.4, 135.8, 135.0, 133.6, 129.7, 128.7, 126.6, 123.5, 62.5, 34.0, 33.9, 29.7, 16.2; IR (KBr): 809, 962, 1024, 1248, 1390, 1594, 1668, 1703, 2930, 2986, 3157, 3419 cm^{-1} ; ^{31}P NMR (162 MHz, 3 \gg): δ 25.45; ESI-MS: m/z 1161 $[\text{M}+\text{NH}_4]^+$. HRMS: Calcd for $\text{C}_{56}\text{H}_{66}\text{O}_{16}\text{N}_3\text{P}_4$: 1160.3050 $[\text{M}+\text{NH}_4]^+$. Found: 1160.3380 $[\text{M}+\text{NH}_4]^+$.

Synthesis of PDI-TPA

In a 10 mL round bottom flask, TMSBr (0.168 mL, 1.28 mmol) was added drop-wise to a cooled solution of compound **3** (100 mg, 0.08 mmol) in 4 mL anhydrous acetonitrile at 0°C under nitrogen atmosphere. After 40 min stirring, the ice bath was removed and the reaction mixture was stirred at 40°C for 12 h. The solvent was evaporated under reduced pressure and 40 mL of methanol was added to the residue and stirred for 4 h at RT. The precipitates were filtered and washed with methanol to give brown coloured solid as PDI-TPA (62 mg, 76%). ^1H NMR (400 MHz, D_2O): δ 8.48 (s, 8H), 7.45 (s, 2H), 7.16 (s, 4H), 3.06 (d, $J=19.2$ Hz, 8H); ^{31}P NMR (202 MHz, D_2O): δ 20.89; IR (KBr): 989, 1124, 1258, 1365, 1401, 1594, 1660, 1696, 2925, 3136, 3416 cm^{-1} ; MALDI-TOF MS: Calcd for $\text{C}_{40}\text{H}_{30}\text{N}_2\text{O}_{16}\text{P}_4$: 918.05 $[\text{M}]^+$. Found: 918.50 $[\text{M}]^+$.

Preparation of stock solution

To prepare stock solution of PDI-TPA (1×10^{-2} M), at first it is dissolved in a small amount of dimethylsulfoxide (DMSO) and then added to Milli-Q water in measuring flask to equilibrate.

UV-Vis measurements

The UV-Vis absorption spectra were studied in a Shimadzu UV1800 spectrophotometer at RT. UV-Vis spectra of PDI-TPA were recorded at different pH ranging from 2–11 in H_2O with the quartz cell path length of 1.0 cm.

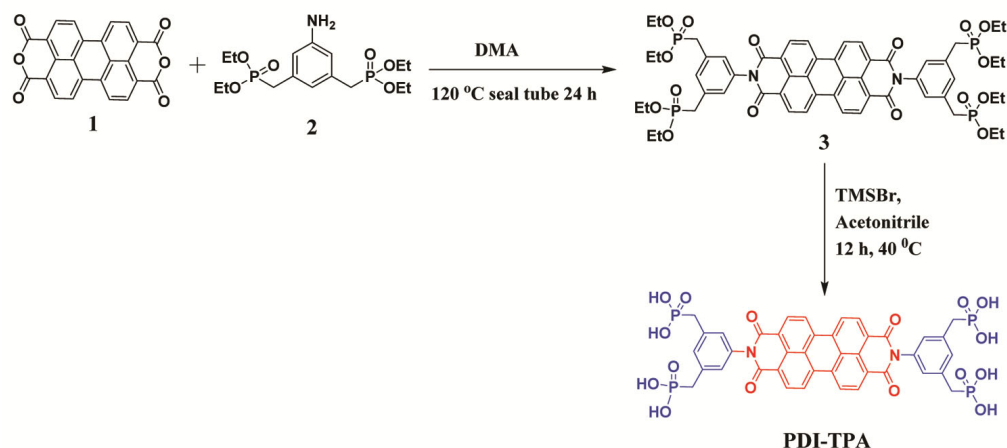
Fluorescence measurements

The fluorescence emission spectra were recorded on RF-6000 Shimadzu Fluorescence spectrofluorophotometer. The emission spectra of PDI-TPA were recorded in H_2O at RT with pH 2–10 in the quartz cell with $\lambda_{\text{ex}} = 485$ nm.

Results and Discussion

Synthesis and characterization

We designed PDI derivative PDI-TPA bearing four phosphonic acid head groups, which may enhance the solubility of PDI in aqueous media. Synthesis of PDI-TPA was achieved using multi step organic synthesis route (Scheme I). At first tetraethyl((5-amino-1,3-phenylene)bis(methylene))bis(phosphonate) **2** was synthesised starting from 5-nitroisophthalic acid in four steps followed by literature reported procedure⁸. The obtained phosphonate functional group appended aniline **2** was further reacted with PDA in dry dimethylacetamide (DMA) at 120°C in sealed tube for 24 h to yield compound **3** with 24% yield. The PDI phosphonate derivative **3** was treated with trimethylsilyl bromide in acetonitrile at 40°C for 12 h followed by protonation using methanol, resulting in to formation



Scheme I — Synthetic route of PDI-TPA from PDA

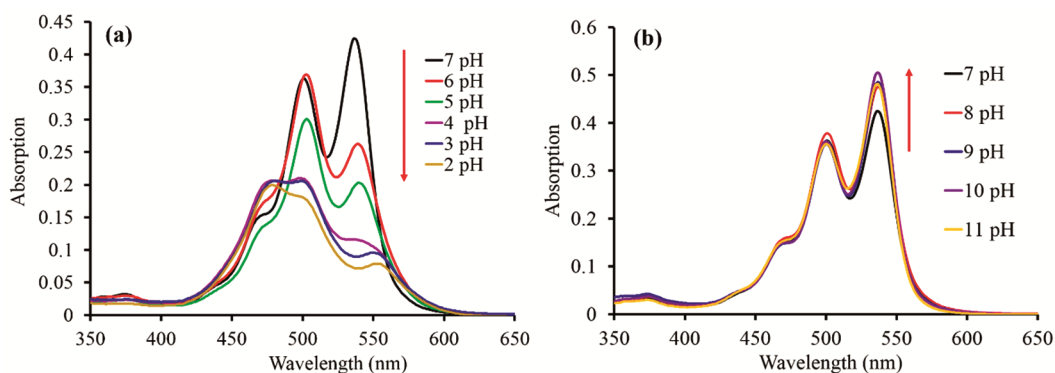


Figure 1 — UV-Vis absorption spectra of PDI-TPA in water at various *pH*, (a) 7.0 to 2.0 and (b) 7.0 to 11.0

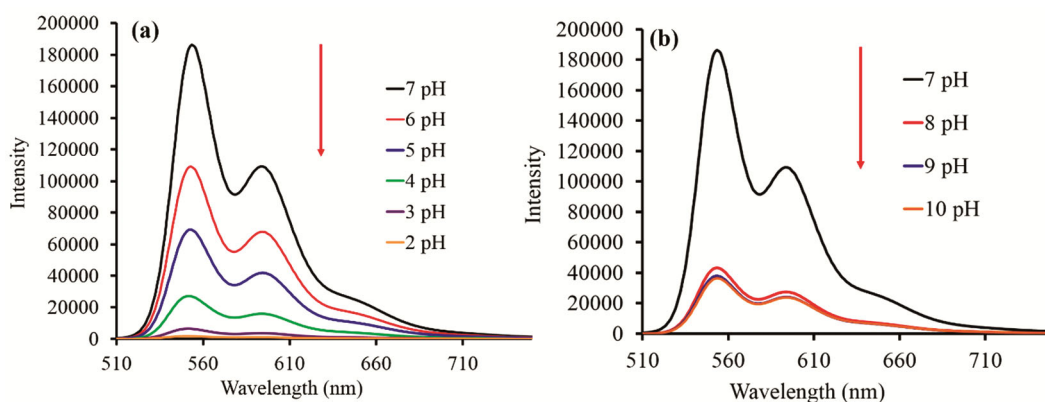


Figure 2 — Fluorescence emission spectra of PDI-TPA in water at various *pH*, (a) 7.0 to 2.0 and (b) 7.0 to 10.0

of tetraphosphonic acid functionalized PDI (PDI-TPA) with 76% yield (for spectral details see ESI[†]). The ¹H NMR peaks of compound **3** at δ 3.25-3.21 (Figure S1; ESI[†]) as doublet and at δ 1.30-1.27 (Figure S7; ESI[†]) as triplet are completely diminished in PDI-TPA. Moreover, the structure of compound PDI-TPA was confirmed by MALDI-TOF spectrum with m/z 918.50 for [M]⁺ (Figure S9; ESI[†]).

Furthermore, to know more about photophysical properties, UV-Vis absorption and fluorescence emission spectral properties of PDI-TPA were performed in water at *pH* 2-11. The obtained results are demonstrated as shown below.

UV-Vis absorption spectral study

At first UV-Vis spectroscopic technique was employed to investigate the photophysical properties of PDI-TPA in water. At *pH* 7, PDI-TPA (1×10^{-5} M) exhibited strong absorption maxima at 503 nm and 538 nm, assigned to π - π^* transition and a shoulder peak at 465 nm. The UV-Vis spectra of PDI-TPA in H₂O was greatly influenced by the change in *pH* (Figure 1a and 1b). *pH* of PDI-TPA was lowered from

7 to 5 and shows decrease in absorption peak intensities. Whereas, with further decrease in *pH* to 2, the peak at 538 nm underwent complete demise and at the same time peak at 503 nm and shoulder peak at 465 nm merged together resulting into broadening of peak along with decrease in intensity, suggesting the aggregating nature of PDI-TPA (Figure 1a). When *pH* of PDI-TPA changes from 7 to 11, the UV-Vis absorption peaks at 503 nm and 538 nm exhibits increase in intensity (Figure 1b). In acidic and basic *pH* the phosphonic functional group appended to PDI in the molecular architecture displayed the protonation and deprotonation of PDI-TPA. Thus, as illustrated in Figure 1a and 1b, the mode of protonation and deprotonation of PDI-TPA was investigated by UV-Vis titrations.

Fluorescence emission spectral study

Fluorescence spectra of PDI-TPA (1×10^{-5} M) upon excitation at 485 nm in aqueous medium at *pH* 7 exhibited two strong emission maxima at 555 nm and 595 nm. As illustrated in Figure 2a, in acidic medium *i.e.* at *pH* 6, the emission peak intensity decreased.

Further, with decrease in pH from 5 to 3, the emission peak intensities significantly decrease and at pH 2, it is completely diminished. The decreasing pH indicates the increase in aggregation state of PDI-TPA. Moreover, under basic conditions (pH 7 to 10), decrease in fluorescence peak intensity at 560 nm and 610 nm could be observed (Figure 2b). These changes in fluorescence emission spectral features indicates the formation of larger aggregates of PDI-TPA bolaamphiphile.

Conclusion

Herein, we have demonstrated the synthesis of novel PDI-TPA bolaamphiphile bearing phosphonic acid head groups. The UV-Vis absorption and fluorescence emission studied by varying pH indicates that PDI-TPA undergoes aggregation. The detailed self-assembly study is under progress in our laboratory and will be communicated very soon.

Supplementary Information

Supplementary information is available in the web site <http://nopr.niscair.res.in/handle/123456789/58776>.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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