A EUROPEAN JOURNAL

CHEMPHYSCHEM

OF CHEMICAL PHYSICS AND PHYSICAL CHEMISTRY

Accepted Article

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To be cited as: *ChemPhysChem* 10.1002/cphc.201601053

Link to VoR: http://dx.doi.org/10.1002/cphc.201601053

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ChemPubSoc Europe

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www.chemphyschem.org

10.1002/cphc.201601053

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FULL PAPER

A Viologen-Perylenediimide Conjugate as an Efficient Base Sensor with Solvochromic Property

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Dedication ((optional))

Abstract: A viologen-perylenediimide conjugate, termed as PDEV, is prepared for efficient base sensing. The conjugate is showing solvatochromic behavior as well. The base-sensitivity of viologen is purposefully coupled with the emission property of perylenediimide (PDI) in order to lower the detection limit. PDEV has shown base sensing ability in the ppb level which is at least three orders of magnitude lower than the previously reported sensors. The probe is sensitive toward solvent polarity and generates different shades of colors based on the polarity of the medium (solvent). The photo-physical properties follow a linear correlation with the solvent polarity and thus making it an efficient solvatochromic agent. On the other hand, the generation of viologen cation radicals by bases affect the aggregation and consequently the absorption and emission behavior of the PDI core. The effect of bases can also be visualized as the probe generates different colors in presence of bases both under normal as well as under UV light. Organic amines can be detected even in the crystalline state as dark red color of the PDEV crystals change to purple in a reversible fashion upon exposure to amine vapors. An easy and practical paper based tool is also created using the probe which can efficiently be used to detect solvent polarity as well as presence of bases optically.

Introduction

Solvents and bases are the two extremely important constituents of modern day chemical industry which are used or produced in huge quantities. However, the inherent cytotoxicity and volatility of these chemicals leave an adverse impact on environment and effective ways to sense these toxic chemicals are essential.[1,2] Compounds which show dependence of color on solvent polarity are generally employed as solvatochromic sensors.[3] Pyridinium N-phenolate betaine dyes are considered as the standard to estimate the polarity of a solvent.[4] Though this dye shows the most pronounced solvatochromism, the synthesis of this molecule is somewhat expensive and tedious.[4] On the other hand, various methods such as single molecule and array sensors, enzymes, molecularly imprinted polymers, fluorescent sensors etc. have been developed and used successfully for sensing bases.[5-9] However, requirement of sophisticated instrumental facilities significantly limits the practical applicability of these methods. In this regard, though many sensors have been developed that allow detection of these chemicals by naked eye through color change but many of them lack proper sensitivity.[10-12] Detectors showing efficient visual sensing of solvent polarity as well as bases are therefore of great importance.

In this regard, owing to the redox controlled and charge transfer complexation induced color change, viologens (Scheme 1A) have found its use as base sensors.[10,11] One important feature of viologens is their electron deficient nature which makes them very good electron acceptors.[13-15] Viologens undergo a fast and reversible two step redox process and are capable of forming three different species like, a dication, a radical cation, and the neutral species (Scheme 1A).[16-18] The optical charge transfer between N^{1+} and N^{0} of the radical cation species makes them intensely colored.[16-18] Using this phenomenon, Ma et al. reported a benzyl-substituted viologen based sensor for amines.[11] Similarly, Zhu and co-workers recently enhanced the efficiency of the viologen based sensors by delocalization of the radical generated by bases.[10] Detectable color change was observed at 1×10^{-5} M sensor concentration in presence of 10 equivalents of base and the sensitivity was in ppm level. Notably, all these viologen based sensors rely on the absorbance behavior of viologen and related species generated by the redox reactions which decreases the overall sensitivity of the systems in solution phase detection.

We envisioned that the sensitivity of viologen towards bases can be amplified by conjugating viologen units with a suitable fluorophore which will also act as an alternative for common solvatochromic probes. In this regard, perylenediimides (PDI) are a well-studied class of fluorophore with excellent electronic, optical, and redox properties.[19,20] PDI have recently emerged as a very efficient moiety to prepare fluorescent sensors for a variety of species especially because of their outstanding photochemical stability and high quantum yields.[21-23] In addition, the PDI chromophores have added advantage in the design of sensors because of their inclination towards self-assembly through π–π stacking, electrostatic and solvation interactions.[21-23] The presence of planar π-conjugated core leads to the formation of both J- and H- type aggregates depending upon the functionalization at the imide positions as well as the medium (solvent).[24-27] The aggregation of the PDIs is associated with

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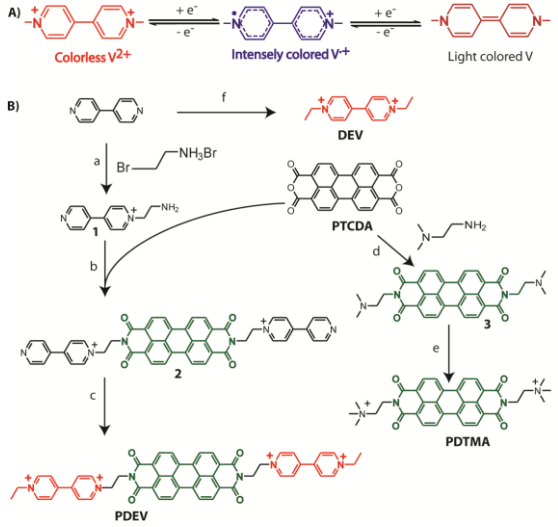
drastic influence on their photophysical properties.[21-27] The aggregation of PDIs and consequently the changes in their photophysical properties are highly influenced by the medium and thus with appropriate conjugation, PDIs can be solubilized in solvents with a wide range of polarity and can be used as a solvatochromic agent.[28,29]

As a proof of concept, we have selected PDI as the emissive component of our molecule and a viologen-PDI conjugate has been prepared (PDEV, Scheme 1). This bola-amphiphilic viologen-PDI conjugate showed solvatochromic property by generating distinguishable colors in different solvents. As expected, the presence of two viologen units at the two terminals of PDI make this molecule an effective sensor for bases. Incorporation of the fluorophore significantly enhanced the base sensing efficiency (sensitivity ~1-77 ppb for various bases) compared to that of the previously reported viologen based base sensors in solution phase (sensitivity ~130-1880 ppb for various bases)[10] as well as in solid crystalline phase.



Scheme 1. A) Redox induced chromic process of viologens; B) Synthetic routes to DEV, PDEV and PDTMA, a) ACN, 81 °C, 12 h; b) imidazole, DMAP, 1,2-dichlorobenzene, 80 °C, 12 h; c) Et-Br, ACN, reflux,12 h; d) DMF, 130 °C, 5 h; e) MeI, DCM, 8 h; f) Et-Br, 80 °C, 24 h.

Results and Discussion

The absorption spectra of PDEV in aqueous medium showed several absorption bands generated from the viologen (253 nm) and PDI chromophores (Fig. S1). As PDI core is mainly responsible for the aggregation and the emission, for clarity, absorption region (400-800 nm) corresponding to the PDI core is shown in Figure 1A. In this region, two prominent vibronic bands at 534, 494 and a shoulder at 464 nm attributed to the 0-0, 0-1 and 0-2 vibrational transitions were observed.[30,31] The concentration dependent absorption spectra results in a continuous increase in the absorption for all three transitions with a change in the slope at 2.6×10^{-5} M. Above this concentration, the intensity order changes from 0-0> 0-1 to 0-1 > 0-0 and this order reversal is characteristic of aggregation of the PDI core. In this process, the $A_{0\text{-}0}/A_{0\text{-}1}$ ratio decreased from 1.54 (0.1×10^{-6} M) to 0.85 (2.6×10^{-5} M or above). Thus, this particular concentration (2.6 × 10-5 M) can be considered as the minimum aggregation concentration (MAC, Table 1). The emission spectrum of PDEV in water is the mirror image of the absorption spectrum with a Stokes shift of 12 nm. The fluorescence spectra showed three emission peaks at 549, 588, and 639 nm (Figure 2A).[32] Notably, the concentration dependent emission pattern also showed a drastic change at 2.6×10^{-5} M. The initial linear enhancement of the intensities with increase in PDEV concentration suddenly took a negative slope above 2.6×10^{-5} M. Above a concentration of 1×10^{-4} M, no measurable emission intensity was observed. The decrease in the emission intensity and complete loss of emission can presumably be explained in terms of self-quenching by stacked arrangement of molecules. The inflection point at 2.6×10^{-5} M is very similar to the MAC obtained from absorption spectra and can be considered as the concentration above which all the molecules remain in aggregated form.

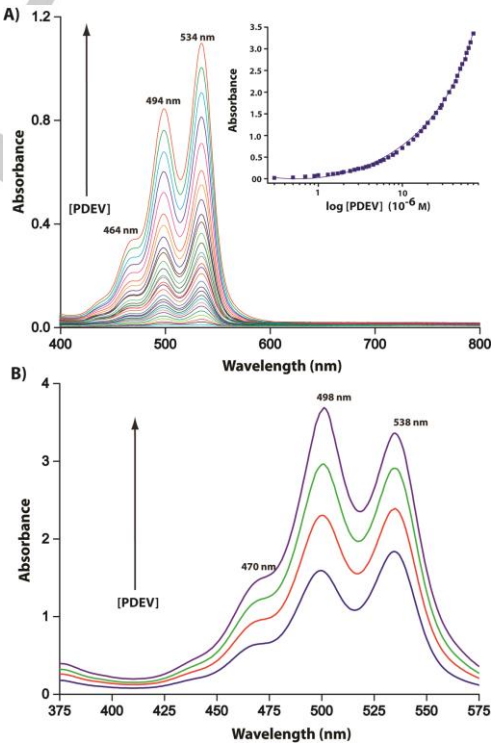


Figure 1. Absorption spectra of PDEV in water with varying concentrations. A) up to 2.6×10^{-5} M and B) above 2.6×10^{-5} M showing the reversal of order of 0-0, 0-1 transitions above this concentration. Inset of A) absorbance at 534 nm vs log [PDEV] plot showing the inflection point.

PDEV has a fairly high solubility in water, dimethylformamide (DMF), dimethylsulfoxide (DMSO), methanol (MeOH), ethanol (EtOH), acetonitrile (ACN), and acetone. Concentration dependent study in these solvents showed similar behavior to that in case of water (Figures S2-S8). Though a sudden change in the

Table 1. Photophysical Parameters of PDEV in Different Solvents

Solvent	$E_T(30)$ (kcal mol^{-1})	E_T^N	λ_{abs} (nm)	ν_{abs} (cm^{-1})	λ_{em} (nm)	ν_{em} (cm^{-1})	$\Delta\nu$ (cm^{-1})	Φ_ϕ	MAC (× 10^{-6} M)
Water	63.1	1	534	18727	549, 588	18215	512	0.06	26
MeOH	55.4	0.762	530	18868	536, 574	18656	212	0.04	32
EtOH	51.9	0.654	528	18939	537, 575	18622	317	0.08	12
ACN	45.6	0.46	526	19011	533, 572	18762	249	0.06	12
DMSO	45.1	0.444	524	19084	539, 577	18553	531	0.06	20
DMF	43.2	0.386	523	19120	542, 581	18450	670	0.08	8.2
Acetone	42.2	0.355	522	19157	523, 562	19120	37	0.03	5.2

absorption in all these solvents was observed above a particular concentration, no peak reversal was observed in any of these organic solvents. As in case of water, the fluorescence intensities increased with increase in concentration and after a certain concentration, a sharp decrease was observed. The inflection points in both absorption and emission spectra were obtained at very similar concentrations for a particular solvent.

The UV-Vis and fluorescence spectra of PDEV in different solvents at low concentration (1 × 10^{-6} M), under which aggregation does not occur (below MAC), are shown in Figure 3. With increasing solvent polarity, a clear bathochromic shift was observed in the peaks generated from 0-0, 0-1 and 0-2 vibrational transitions (Figure 3A). The absorption maxima of PDEV displays good linear correlation with the $E_T(30)$ values (parameter indicative of solvent polarity and hydrogen bond donating ability) of the solvents and found to shift to lower energies as the $E_T(30)$ value increases. This can presumably be attributed to the presence of dicationic viologen units at both ends of PDEV which stabilizes the excited states with increasing solvent polarity.[22] The emission of PDEV in these solvents except DMF and DMSO (hydrogen bond accepting solvents) also show similar changes in the emission band positions. A red shift was observed for all the peaks when moved from the nonpolar to polar solvents (Figure 3B and inset).[34,35] However, the quantum yield (Φ) values of PDEV in these solvents using rhodamine 6G as the standard could not reveal any correlation with the solvent polarity (Table 1).

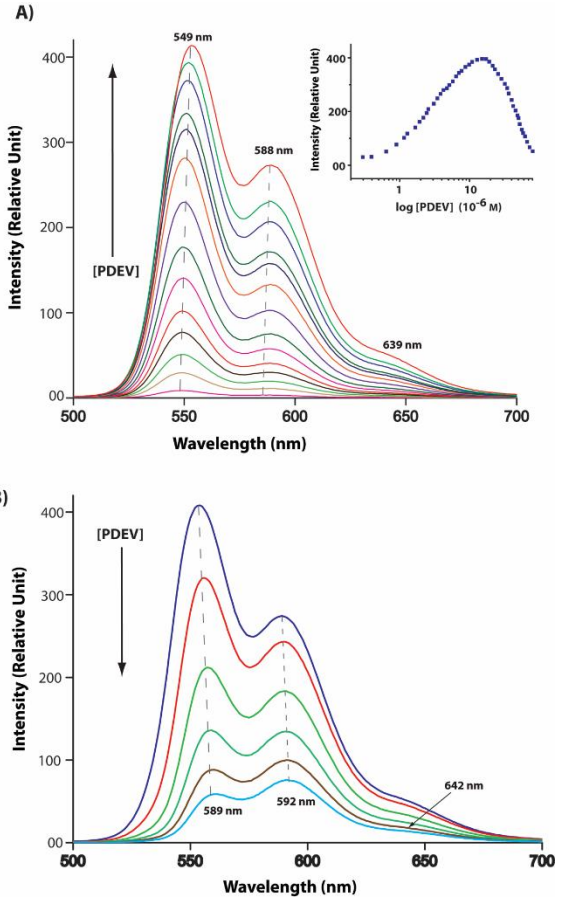


Figure 2. Emission spectra of PDEV in water with varying concentration A) up to 2.6 × 10^{-5} M and B) above 2.6 × 10^{-5} M showing the decrease in emission intensities after this concentration. Inset of A) Intensity at 549 nm vs log [PDEV] plot showing the inflection point.

Interestingly, the solutions of PDEV generate different colors in these solvents (Figure 4) indicating its solvatochromic behavior. The aqueous solution of PDEV was reddish orange in color while the color changes to pale straw yellow to dark straw yellow in ACN and DMSO respectively. Under UV-light (365 nm), the same solutions fluoresce differently as can be expected from the emission studies. As we move from water to less polar acetone, the color of the emitted light changes from dark orange (water) to fluorescent yellow (ACN) to fluorescent greenish yellow (acetone).

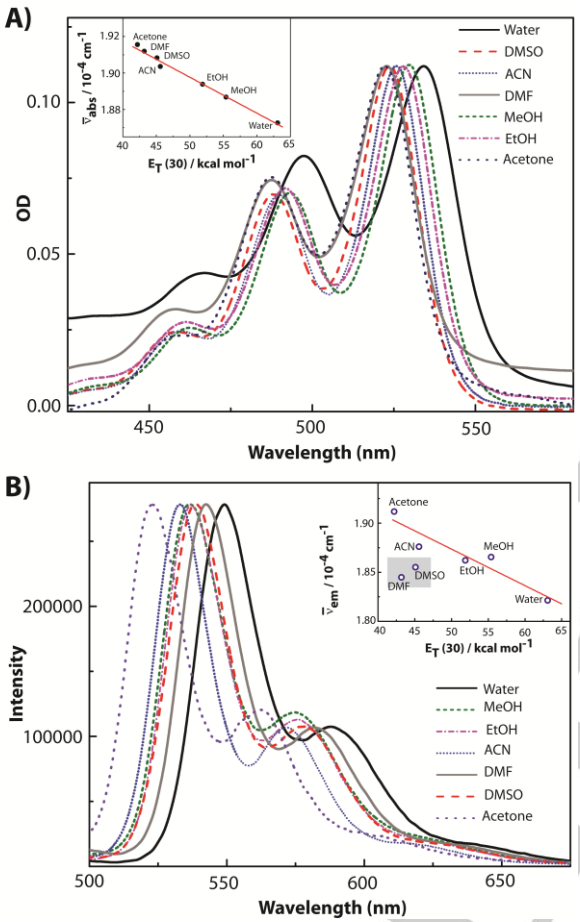


Figure 3. A) Normalized absorption and B) normalized emission spectra of PDEV in different solvents. [PDEV] = 1 × 10^{-6} M. Inset of A) $\bar{\nu}_{abs}$ vs $E_T(30)$ of solvents and Inset of B) $\bar{\nu}_{em}$ vs $E_T(30)$ of solvents plots.

To test the base sensitivity of PDEV, six different amines (diisopropylethylamine (DIPEA), N, N-dimethyl-4-aminopyridine (DMAP), pyridine, piperidine, triethylamine (TEA) and triisopropylamine (TPA)), and NaOH were used. As seen in Figure 5, solutions of PDEV changed color dramatically upon addition of amine/base. PDEV can act as a fast detector of amines to the naked eye. This prominent changes in color can be detected even at a concentration of 5 × 10^{-6} M and that too in presence of 1-2 equivalent bases which makes PDEV a far superior and efficient visual base sensor than other viologen based sensors.[10,11] Under influence of UV light (365 nm), these solutions emit differently, and notably, the visual detection limit further dropped to 5 × 10^{-7} M of PDEV which is the lowest ever reported to the best of our knowledge.

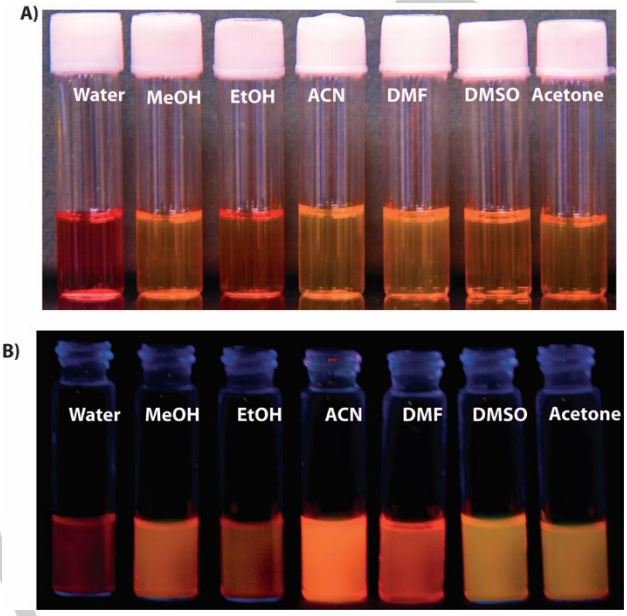


Figure 4. Photographic images of PDEV (1 × 10^{-6} M) in different solvents, A) under normal light, and B) under UV light (λ = 365 nm).

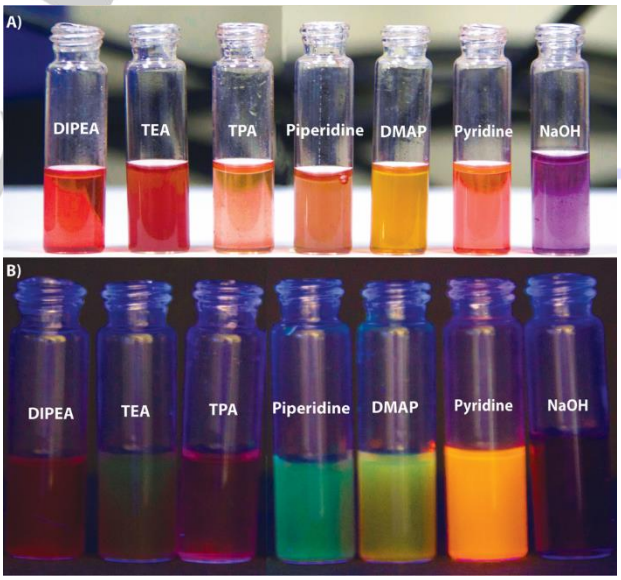


Figure 5. Photographic images of PDEV in presence of different bases (2 equivalents), A) under normal light [PDEV] = 5× 10^{-6} M and B) under UV light (λ = 365 nm), [PDEV] = 5 × 10^{-7} M. Photographs were taken two minutes after the addition of aqueous (NaOH) or ACN (amines) solutions to an aqueous solution of PDEV and mixing.

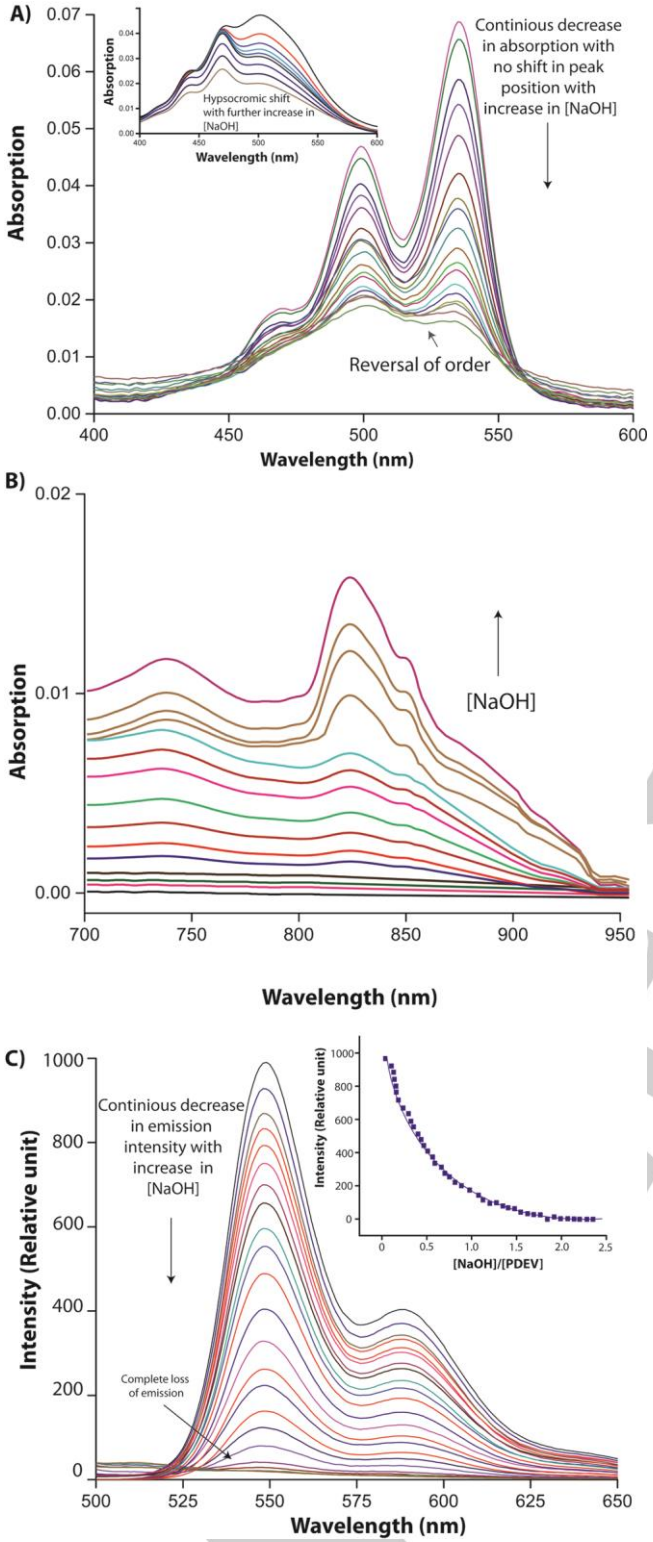


Figure 6. A) Absorption spectra of PDEV in water with increase in concentration of NaOH upto 2 eq. of NaOH; Inset: with higher amount of NaOH showing the hypsocromic shift and broadening of the peaks; B) same in the higher wavelength region showing the appearance of the viologen radical cation peaks; C) emission spectra of PDEV in water with increase in concentration of NaOH; Inset: Intensity vs molar ratio of NaOH/PDEV plot. [PDEV] = 1×10^{-6} M.

In order to gain an insight into the possible reason behind such changes in color, we did examine the absorption and emission behaviors of PDEV in presence of various bases. When titrated with NaOH, the absorption profile of PDEV showed a decrease in intensity up to an equimolar ratio of NaOH (Figure 6). Above this concentration, the absorption corresponding to the 0-1 transition becomes higher than that of the 0-0 transition, signifying the aggregation. With further increase in NaOH concentration (> 2 equivalents), the absorption bands blue shifted significantly along with broadening of the peaks. A similar absorption profile was observed at high pH as well (Figure S9). Along with these changes in the UV-visible region, new bands started appearing in the NIR region at higher mole ratio (3-4 equivalents, Figure 6B). The new bands in NIR region and deep blue coloration suggest the radical cation formation.[16,17] Above this concentration, the material precipitated. The microscopic image of the precipitate showed extremely ordered flower like arrangements (Supporting Information S10). It is worth mentioning that the aqueous solution of PDEV at a concentration below MAC showed no prominent morphology while above MAC, a highly ordered arrangement of brick like structures were found.

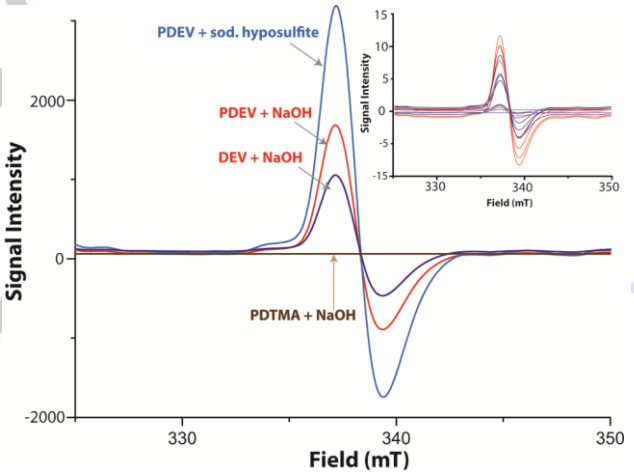


Figure 7. EPR spectra of PDEV, DEV and PDTMA in presence of NaOH or sodium hyposulfite. Inset: EPR spectra of PDEV in presence of various amines. For all measurements, the following parameters were used, temperature: 295 K, power: 0.995 mw.

As expected, the fluorescence intensity decreased with increase in NaOH concentration without any significant change in the emission pattern (Figure 6C). The intensity vs concentration plot shows an inflection point when one equivalent NaOH was added. At higher equivalence of NaOH (> 2), the emission property vanishes completely. The blue shift of the absorption bands and complete loss of emission suggests H-type aggregation of the PDI core.[35] Excitation spectra of the 1:2 PDEV-NaOH solution collected at 575 nm, produced a broad, structure-less band centered at 535 nm suggesting the formation of H-type aggregates (Figure S11). Notably, in case of PDTMA, under similar condition, only ~ 25%

decrease (Figure S12) in emission intensity with no change in the solution color detected. The absorption spectra of PDTMA in presence of NaOH also did not show the appearance of any new peak in the NIR region (Figure S13). Additionally, treatment of DEV with NaOH produces a strong blue color and the peaks corresponding to viologen radical cations in the NIR region (Figure S14). These results conclusively point the effect of the presence of viologen units in PDEV. Under strong basic medium, the formation of viologen radical cations leads to aggregation and consequently affect the emission of the PDI core.

Table 2. Absorption Maxima of PDEV in Presence of Various Bases, Base Sensitivity at Δ_{abs} = 0.01 and Δ_{em} = 10% of a 1.0 × 10^{-6} M Aqueous Solution of PDEV Measured at Absorbance and Emission Maxima (588 nm).

Base	λ_{abs} (nm)	Base Sensitivity (ppb)	
		Δ_{abs} = 0.01	Δ_{em} = 10%
NaOH	535	1.01	1.89
DIPEA	533	19.95	12.27
DMAP	522	29.10	14.68
Piperidine	524	17.78	3.69
Pyridine	523	36.76	17.45
TEA	533	77.41	41.01
TPA	521	40.84	18.91

In case of the organic bases, due to solubility issue, acetonitrile solutions of the amines were used for the titration. In all cases, the absorption corresponding to all three transitions decreased with increase in the base concentration but no reversal of the peak intensities was detected in any case (Figures S15-20). Also in the emission spectra, a continuous decrease in the emission intensity was noted with increase in the base concentration. Owing to the weak nature of the organic bases, no noticeable absorption band in the NIR region was detected.

The EPR spectra of PDEV, PDTMA and DEV showed no measurable signal (Figure 7). When treated with NaOH, intense signals were observed only in case of PDEV and DEV. As a standard, the EPR spectra of PDEV in presence of a strong reducing agent (sodium hyposulfite) was monitored for comparison purpose. Though the signal position remained same, the intensity was found to be much higher than that of the other samples at similar PDEV concentration. These observations along with the appearance of absorption bands in the NIR region in case of NaOH treated PDEV samples clearly indicate the formation of viologen radical cations.[17] However, presence of various amines resulted in extremely low signals which indicate a minor population of the radical cation in these cases (Inset of Figure 7).

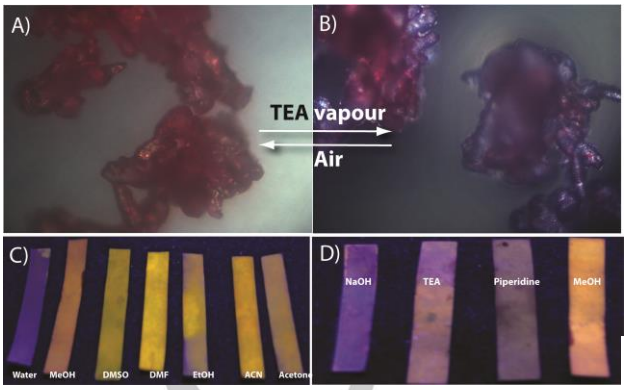


Figure 8. A-B) Photographs of PDEV crystals A) before and B) after exposure to amine vapor; C-D) photographs of test papers soaked in PDEV solution and then exposed to different C) solvents and D) bases. C-D) images were taken under UV light (365 nm).

Base sensitivity of PDEV in solution phase was quantified using both absorbance and fluorescence. Only the absorbance and fluorescence changes of the PDI core is considered as it is not directly affected by the bases. The changes in absorption and emission intensities against the equivalence of bases in all cases follow a linear trend up to 2 equivalents of bases (Figure 6 and S15-20). These linear plots can be considered as a calibration curve in order to quantitatively estimate the amount of bases present. However, concentrations of bases required to change the absorbance by 0.01 (Δ_{abs} = 0.01) and emission intensity by 10% (Δ_{em} = 10%) in the initial linear part of these calibration plots are considered to calculate the sensitivity (Table 1). Remarkably, the sensitivities were found in ppb level or less. The sensitivity observed in the present case was in the range of 1-77 ppb whereas the previously reported best viologen-containing sensor showed sensitivity in the order of 130-1880 ppb.[10] Overall, the sensitivity is observed to be three orders of magnitude lower than the previously reported viologen based sensors.[10,11] To the best of our knowledge, these results suggest that PDEV is the most sensitive base sensor both qualitatively and quantitatively.

In addition to the solution based detection, for a practical colorimetric detection, it would be preferred if the compound shows color change in solid state upon exposure to amines. For that purpose, the tetrafluoroborate (BF_4^-) salt of PDEV was prepared and crystallized from acetonitrile. Upon exposure to amine vapors, the dark red crystals immediately changed to purple (Figure 8 A, B). When kept under ambient condition, the color of the crystals slowly returned to its original dark red color. Unfortunately, the obtained crystals could not be analyzed by X-ray crystallography owing to poor diffraction.

For another practical application, a paper based sensor was developed for in situ on-site detection of both solvents as well as bases. A strip of filter paper was immersed in methanol (for base sensing) or aqueous (for solvents) solutions of PDEV and

air dried. As can be seen in Figure 8, papers from the aqueous solution did not fluoresce under UV light (365 nm) while the same from methanol solution emits strongly. Upon exposure to various solvents, the test papers from aqueous medium showed different colors (Figure 8C). Spraying dilute solutions of different bases on the test papers (methanol) quench the emission (Figure 8D) completely. These results show that PDEV can be used to prepare efficient and easy paper based sensors for both solvents and bases.

Conclusions

In summary, the conjugation of PDI unit with viologen allowed us to prepare an efficient base sensor as well as a solvatochromic probe. PDEV shows linear dependence of photophysical properties on solvent polarity and generates distinguishable colors in different solvents. In presence of bases, viologen radical cations are produced which affect the photophysical behavior of the PDI core and thus allowing optical sensing of bases. The bases can be detected by PDEV in ppb level in solutions as well as in crystalline state. For a practical application, a paper strip based technique is developed which allows to detect bases and solvents through color changes. These findings will certainly open up the possibility to create new base and solvent sensors with higher efficacy.

Experimental Section

General: All the chemicals and reagents used were obtained from Sigma-Aldrich (USA) and used without further purification. All solvents were procured from Merck, India and Spectrochem, India. Amberlite IR 400 anion exchange resin was obtained from Merck, India. To prepare samples, Milli-Q water with a conductivity of less than 2 $\mu S \cdot cm^{-1}$ was used. ^{1}H NMR and ^{13}C NMR were recorded either on a Bruker Ascend 600 MHz (Bruker, Coventry, UK) or on an Oxford AS400 (Varian) spectrometer and referenced to deuterated solvents. ESI-MS was measured using a Q-tof-Micro Quadrupole mass spectrophotometer (Micromass). UV visible data was recorded using a PerkinElmer Lambda 750 spectrometer. Fluorescence measurements were obtained using a Carry Eclipse spectrophotometer (Agilent). All emission spectra were recorded by exciting the sample at 485 nm. Unless otherwise mentioned, all studies were performed at room temperature. Samples were prepared by casting a drop of the solution on a silicon wafer and dried under ambient conditions. Standard 10 mm path quartz cuvettes were used for all spectroscopic measurements.

Sample Preparation: The stock solutions of PDEV, PDTMA, and DEV were prepared in a 10 mL of volumetric flasks in different solvents. These stock solutions were diluted to desired concentration as required for the experiments. For amine sensitivity, the organic bases were dissolved in acetonitrile at high concentration and appropriate amounts from these stocks were added to the aqueous solutions of PDEV. In order to avoid any effect from added acetonitrile, only 0.1% v/v of the base solutions were added. An appropriate control experiment carried out by adding exactly the same amount of acetonitrile in aqueous solution of PDEV resulted in no observable change in the absorption as well as emission spectra.

Electron paramagnetic resonance (EPR): For EPR measurements, prior to the addition of the bases, all the samples were degassed by purging argon gas for 10 mins. After the addition of bases, Argon was flushed thoroughly and the sample tubes were sealed properly to prevent any areal oxidation. All measurements were carried out with 1×10^{-6} M samples (PDEV, PDTMA, DEV) with 2 equivalents of bases/reducing agent on a JES-FA200 instrument from JEOL.

Quantum Yield Measurements: The fluorescence quantum yields of PDEV in different solvents were determined by using Rhoamine-6G as a standard fluorophore following equation (1),

$$\Phi_u = (A_s F_u n_u^2)/ (A_u F_s n_s^2)\Phi_s \quad (1)$$

where, Φ_s is the quantum yield of the reference (Rhodamine, 0.95) in ethanol, Φ_u is the quantum yield of PDEV, A_s and A_u are the absorbance of Rhodamine and PDEV at the excitation wavelength, F_s and F_u are the area of integrated fluorescence intensity of the Rhodamine and PDEV sample when excited at the same excitation wavelength. The refractive indices of the solvents for the PDEV and Rhodamine are denoted by n_u and n_s respectively. To minimize the reabsorption of the fluorescence light passing through the samples their absorption maximum was kept 0.1.

Calculation: The initial linear parts of the absorption (at absorption maximum) or emission intensity (at 588 nm) vs concentration of added bases are considered. The concentration of base required ([base conc.]) to change the absorbance by 0.01 (Δ_{Abs} = 0.01) or initial emission intensity by 10% (Δ_{em} = 0.01) used in equation 2 to calculate the base sensitivity.[10]

$$\text{Sensitivity (ppb)} = MW \times [\text{base conc.}] \times 1000000 \quad (2)$$

Synthesis: All the compounds were synthesized following the routes shown in Scheme 1B.

Compound 1: To a stirring solution of 4, 4-bipyridyl (1 g, 6.4 mmol) in acetonitrile (10 mL), 2-bromoethylamine hydrobromide (262 mg, 1.28 mmol) was added and was refluxed. After 12 h, the reaction mixture

was cooled to room temperature and volatiles were removed under reduced pressure. The crude product was then washed several times with ether to get the white solid. Yield: 300 mg (83%). ^{1}H NMR (600 MHz, D_2O) δ = 9.09 (d, J = 6.6 Hz, 2H), 8.80 (d, J = 4.8 Hz, 2H), 8.53 (d, J = 6.6 Hz, 2H), 7.96 (d, J = 4.8 Hz, 2H), 5.07 (t, J = 6.6 Hz, 2H), 3.79 (t, J = 3.6 Hz, 2H) ppm; Anal calcd. for $C_{12}H_{14}N_3Br$: C, 51.44; H, 5.04; N, 15.00. Found: C, 51.42; H, 5.09; N, 15.07; HRMS (ESI) *m/z* calcd. for $C_{12}H_{14}N_3$: 200.1184; found 200.1174 $[M\text{-}Br^-]^+$.

Compound 2: Perylene-3, 4, 9, 10-tetracarboxylic anhydride (PTCDA, 100 mg, 0.255 mmol), compound 1 (184 mg, 0.501 mmol), and imidazole (68 mg, 1 mmol) were taken in 1, 2-dichlorobenzene (8 mL), 4-N, N-dimethylaminopyridine (56 mg, 0.5 mmol), and was heated at 80 °C with stirring for 12 h. The reaction mixture was then cooled to room temperature and the precipitate was collected by centrifugation. The collected red solid was dissolved in water (50 mL) and washed with dichloromethane (DCM) to remove water insoluble residues. The volume of the aqueous layer was lowered by removing water on a rotory evaporator and to it was added a portion of saturated aqueous ammonium hexafluorophosphate (NH_4PF_6) solution (10 mL). The resulting red precipitate was collected by filtration and dried under vacuum. Yield: 166 mg (62%). ^{1}H NMR (400 MHz, DMSOd_6): δ = 9.37 (d, J = 5.6 Hz, 4H), 8.87 (d, J = 4.4 Hz, 4H), 8.72 (d, J = 8 Hz, 4H), 8.63 (d, J = 6 Hz, 4H), 8.35 (d, J = 8 Hz, 4H), 8.04 (d, J = 4 Hz, 4H), 5.0 (s, 4H), 4.70 (s, 4H) ppm; Anal calcd. for $C_{48}H_{32}N_6O_4P_2F_{12}$: C, 55.08; H, 3.08; N, 8.03. Found: C, 55.10; H, 3.04; N, 8.06; HRMS (ESI) *m/z* calcd. for $C_{48}H_{32}N_6O_4$: 378.1237; found 378.1227 $[M\text{-}2PF_6^-]^{2+}$.

PDEV: A mixture of **2** (100 mg, 0.09 mmol) and ethyl bromide (104 mg, 0.9 mmol) in acetonitrile was refluxed for 12 h. After cooling to room temperature, the resulting precipitates were collected by centrifugation and washed with acetonitrile several times before drying it under reduced pressure. The material was then taken in water and subjected to ion exchange by passing the solution through a column of bromide functionalized amberlite IR 400 anion exchange resin. The fractions containing the compound was freeze dried and crystalized from methanol-diethyl ether solvent mixture to get the desired compound. Yield: 62 mg (63 %). ^{1}HNMR (600 MHz, DMSOd_6): δ = 9.58 (d, J = 5.4 Hz, 4H), 9.44 (d, J = 5.4 Hz, 4H), 8.92 (d, J = 7.2 Hz, 4H), 8.85 (q, J = 5.4, 6.0 Hz, 8H), 8.47 (d, J = 7.2 Hz, 4H), 5.10 (s, 4H), 4.74 (t, J = 7.8 Hz, 8H), 1.61 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, DMSOd6) δ = 163.17, 162.91, 148.79, 148.13, 146.68, 145.68, 134.18, 131.08, 126.54, 126.18, 125.61, 124.28, 122.63, 56.53, 40.95, 16.33 ppm; Anal calcd. for $C_{52}H_{42}N_6O_4Br_4$: C, 55.05; H, 3.73; N, 7.41. Found: C, 55.04; H, 3.74; N, 7.43; MS (MALDI-TOF, DHB matrix) *m/z* calcd. for $C_{52}H_{42}N_6O_4$: 814.3246; found 814.3510 [M-4Br].

Compound 3: A suspension of PTCDA (500 mg, 1.27 mmol) and N, N-dimethylaminoethylamine (1.5 mL, 13.7 mmol) in dimethyl formamide (10 mL) was heated at 130 °C under stirring for 5 h. After cooling to room temperature, 25 mL tetrahydrofuran (THF) was added and the resulting precipitate was collected by suction filtration and washed with 3 ×10 mL THF. Drying the residue in vacuum oven at 40 °C overnight yielded the title compound as a dark purple solid. Yield: 610 mg (90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.676 (s, 4H,), 8.62 (s, 4H) 4.37(s, 4H), 2.70 (s, 4H), 2.37(s, 12H) ppm; Anal. calcd. for $C_{32}H_{28}N_4O_4$: C, 72.17; H, 5.30; N, 10.52. Found: C, 72.14; H, 5.34; N, 10.55. HRMS (ESI) *m/z* calcd. for $C_{32}H_{29}N_4O_4$: 533.2183; found 533.2183 $[M+H]^+$.

PDTMA: Compound 3 (50 mg, 0.094 mmol), iodomethane (58 µL, 0.94 mmol) were taken in DCM and the mixture was stirred for 8 h. The reaction mixture was centrifuged and the precipitate was washed with DCM, finally with THF. The resulting red precipitates were dried under vacuum. Yield: 65 mg (84 %). 1H NMR (600 MHz, DMSOd_6) δ = 9.02 (d, J = 7.8, 4H), 8.64 (d, J = 7.8 Hz, 4H), 4.51(t, J = 7.2 Hz, 4H), 3.67 (t, J = 7.2 Hz, 4H), 3.24 (s, 12H) ppm; 13C NMR (125 MHz, DMSOd_6) δ = 162.69, 133.93, 130.92, 128.36, 125.26, 124.21, 122.36, 61.89, 52.56, 33.76 ppm; Anal calcd. for $C_{34}H_{34}N_4O_4Br_2$: C, 56.52; H, 4.74; N, 7.75. Found: C, 56.55; H, 4.71; N, 7.73. HRMS (ESI) *m/z* calcd. for $C_{34}H_{34}N_4O_{42}$: 281.1284; found 281.1280 $[M\text{-}2I^-]^{2+}$.

DEV: DEV was prepared following a previously reported protocol.[36] In brief, excess (10 equivalent) ethyl bromide was mixed with 4, 4′ -dipyridyl in a glass tube and the mouth of the tube was sealed. The tube was heated to 80 ° C for 24 h. After being cooled to room temperature, the seal was broken and the material was concentrated on a rotory evaporator, and the residue was crystallized three times from methanol-diethyl ether to get a yellow solid (Yield: 35%). ^{1}H NMR (400 MHz, D_2O) δ = 9.15 (d, J = 7.2 Hz, 4H), 8.56 (d, J = 7.2 Hz, 4H), 4.77 (m, 4H), 1.73 (t, J = 8.0 Hz, 6H) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 150.17, 146.12, 129.21, 57.92, 15.91 ppm; Anal calcd. for $C_{14}H_{18}N_2Br_2$: C, 44.95; H, 4.85; N, 7.49. Found: C, 44.98; H, 4.86; N, 7.43; HRMS (ESI): *m/z* calcd. for $C_{14}H_{18}N_2Br$: 293.0648, found: 293.0651 $[M\text{-}Br^-]^+$.

Acknowledgements

We want to thank BRNS, India (BRNS/2013/RP/37C/60), CSIR India (01(2757)/13/EMR-II), and SERB, DST, India (SR/FT/CS-154/2011) for financial support. DD wants to thank AvH foundation for instrument grant and Dr. A. Dasgupta for helpful discussion.

Keywords: Sensors • Viologen • Solvatochromism • Base • Fluorescence

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10.1002/cphc.201601053

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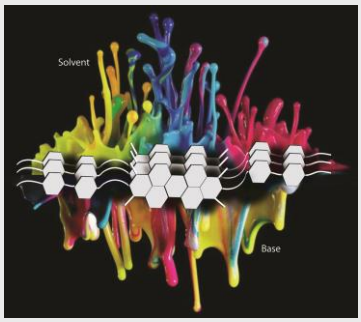
Base sensing

A Viologen-PDI conjugate with efficient base sensing ability and solvatochromic behavior



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