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Self-assembled Nano rods of Bay functionalized perylenediimide: Cu²⁺ based 'turn on' response for INH, complementary NOR/OR and TRANSFER logic functions and fluorosolvatochromism

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Self-assembled nanorods of bay functionalized perylenediimide with ICT/PET features shows disassembly of nanorods and inhibition of ICT/PET process with Cu²⁺ for developing INH, TRANSFER and complimentary OR/NOR logic functions and fluorosolvatochromism for differentiating organic solvents.



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Page 2 of 10

Self-assembled Nano rods of Bay functionalized perylenediimide: Cu²⁺ based 'turn on' response for INH, complementary NOR/OR and TRANSFER logic functions and fluorosolvatochromism

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We design and synthesized mono bay functionalized perylenediimide (PDI) derivative PDI-DMEA which undergoes selfassembly to form Nano rods morphology. The diameter of these Nano rods are in the range of 150-300 nm and length extended up to µm range. These Nano rods on interaction with Cu2+ ions transformed into spherical aggregates having diameter of 350-600 nm in consonance with DLS studies. In solution, PDI-DMEA shows blue shift of the internal charge transfer (ICT) absorption band from 605 to 570 nm along with hyperchromic effect at 570 nm, in the presence of 0.7 equiv. of Cu²⁺ ions. The addition of 2 equiv. of Cu²⁺ ions result in complete disappearance of ICT band at 570 nm and appearance of normal absorption band of PDI at 515 nm (visual colour change from colourless to yellow). On the other hand PDI-DMEA shows strong fluorescence 'turn-on' response at 537 and 573 nm on addition of higher equiv. of Cu²⁺ ions. Thus, PDI-DMEA represent several examples of molecular switches such as 'OFF-ON-OFF' and 'ON-OFF-ON' at 570/515 nm (Cu²⁺, absorbance); 'OFF-ON' at 570 nm (Fe²⁺ absorbance) and 537 nm (Cu²⁺, fluorescence) and thus offers the possibility for developing NOR, OR, INH and TRANSFER logic and complimentary logic circuits. Moreover, PDI-DMEA and PDI-DMEA-Cu²⁺ complex show fluorosolvatochromism which help to develop colour array for differentiating organic solvents. The detailed mechanism of interaction of Cu²⁺ and Fe²⁺ with PDI-DMEA, confocal laser scanning microscopic studies, dynamic light scattering, ¹H NMR titration and reversibility are discussed.

INTRODUCTION

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Perylenediimides (PDIs) are well documented class of intensively coloured organic dyes with interesting photophysical properties.¹ Moreover, their chemical and thermal stabilities, high molar extinction coefficient and fluorescence quantum yields, possibilities of functionalization at imide and bay positions with various substituents has led to wide spread interest of PDI in supramolecular chemistry²⁻⁸ dyes and pigment industries⁹ and optoelectronic based devices. $^{10\text{-}13}$ Due to presence of planar $\pi\text{-}conjugated$ core, PDI has high propensity for aggregation in aqueous medium via π - π stacking, hydrogen bonding, electrostatic and solvation interactions. In literature we have seen various reports where self-assembled nanostructures can be generated after modification of N-terminal position¹⁴⁻¹⁵, however self-assembly

- ⁺ Footnotes relating to the title and/or authors should appear here.
- Electronic Supplementary Information (ESI) available: [Structural data, self-

of bay substituted PDIs are scarcely reported.¹⁶⁻¹⁷ It could be attributed that due to presence of bulky substituents at bay position of PDIs results in deviation of perylene backbone from planarity and so the examples of self-assembled PDIs are lesser known.

From literature point of view, PDIs are considered as promising materials for various optoelectronic devices, however, the full exploitation of bay functionalized PDIs scaffold for molecular recognition of metal ions and anion in organic and aqueous medium has not been achieved. In this regard, recently, we reported bay functionalized PDI as deaggregation based intracellular PDI probe for ClO₄⁻ ions.² Moreover, we have also reported new class of PDI as an integral part of ethylenediaminetetraacetic acid (EDTA) as PET sensor for trivalent metal cation in water and DMSO^{3a} and PDI based dual chemosensor which allow ratiometric sensing of Cu²⁺ ions and subsequently PDI-Cu²⁺ complex was utilized for sensing of CN⁻ ions.^{3b} In the literature PDI functionalized with dipyridine amine or picolinamide units at bay position were utilized as chemosensor for detection of the Cu²⁺ ions.⁴ Zhu et al utilized displacement approach using ensemble (perylene bisimide- AuNPs) for detection of Cu²⁺ ions^{5a} whereas Li et al, reported PDI-dipeptide conjugate as chemosensor for Cu²⁺ ions.^{5b} The PDI functionalized with dithioacetal^{6b}, Salen^{7a} and oligo thymine sequence^{7b} were utilized as chemosensor for

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assembly and photophysical including spectroscopic data of PDI-DMEA and control molecules and additional information]. See DOI: 10.1039/x0xx00000x

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 Hg^{2+} ions. PDI derivatives functionalized with O-/N-propargyl groups were utilized as chemosensor for Pd^{2+}/Pd^{0} ions.⁸

Although several organic fluorophores have potential to mimic molecular analogs of AND, OR, NOR, XOR, INHIBIT and NAND logic gates along with half subtractor, half adder, full adder and full subtractor¹⁸⁻¹⁹, however description of perylenediimide based logic gate and molecular switches such as "ON-OFF-ON" and "OFF-ON-OFF" are rare in the literature.²⁰ Additionally, most of the reported Cu²⁺ chemosensors show quenching of the fluorescence emission,²¹⁻²² whereas examples of fluorescence enhancement as a result of copper ion binding always favoured.²³⁻²⁴ In these and other context, designing of perylenediimide based chemosensor which possess charge-transfer (CT) characteristics and applications in electronics, molecular recognition would be a case of interest.

In continuation of our interest in design and synthesis of bay functionalized PDIs for generating self-assembled nanostructure and their application in molecular recognition, here in we report self-assembled Nano rods morphology for mono bay functionalized PDI derivative (PDI-DMEA). The Nano rods respond to Cu²⁺ ions to generate spherical structures. In solution, **PDI-DMEA** on interaction with Cu^{2+} results in inhibition of ICT band at 605 nm with concomitant increase in the absorption band at 515 nm (absorbance) and significant fluorescence enhancement ('turn-on' behaviour). Moreover, the applications of PDI-DMEA and its copper complex for developing "ON-OFF-ON", "OFF-ON-OFF" and "OFF-ON" molecular switches; INH, OR, NOR, TRANSFER logic gates, Complementary logic circuits and fluorosolvatochromism properties for differentiating various organic solvents would be delineated.

Experimental

Materials and Methods

Chemicals and solvents were of reagent grade and used without further purification unless otherwise stated. All reactions were performed under N₂ atmosphere. All solvents used for photophysical studies were of HPLC grade. Chromatographic purification was done with silica gel 60-120 mesh. TLC was performed on aluminium sheets coated with silica gel 60 F254 (Merck, Darmstadt). NMR spectra were recorded on Bruker (operating at 500 and 400 for ¹H; 125 and 100 MHz for ¹³C, respectively). The peak values were obtained as ppm (δ), and referenced to the TMS in ¹H NMR and deutrated solvent in ¹³C NMR spectra. Abbreviations used for splitting patterns are s = singlet, bs = broad singlet, t = triplet, q = quartet, m = multiplet. SEM measurements were performed on a ZEISS SUPRA[™]55 operating at an acceleration voltage of 10 KV with tungsten filament as electron source. Sample of PDI-DMEA was dissolved in CH_3CN and 6 μL aliquot was deposited on glass surface using drop cast method. After drying and gold plating of the sample, the glass surface was imaged. Wide angle X-ray diffraction (WXRDs) were recorded using a Rigaku diffractometer with CuK α (λ = 1.54 Å) emission and spectra were recorded in the (2 θ) range of 5-50°. The radiation used was with a Ni filter and a data collection was carried out using flat holder in Bragg Brentano geometry. Dynamic Light Scattering measurements were performed at 25.0 ± 0.1°C using a light-scattering apparatus (Zetasizer Nano ZS Malvern Instrument Ltd., U.K.). The solutions were filtered with a Millipore membrane filter (Acrodisc syringe filter, 0.2 µm Supor membrane) before measurements. The samples were thermally equilibrated for 10 min before each measurement, and an average of 10 measurement runs were considered to be data. The temperature was controlled to an accuracy of ±0.1 °C using an inbuilt Peltier device. Data was analyzed using the standard algorithms. Confocal laser scanning microscopy (CLSM) imaging was performed on NIKON AIR machine using laser with excitation at 488 nm. Imaging was done with 60X objective lens with oil-emersion. The absorption spectra were recorded on Shimadzu-2450 spectrophotometer from Shimadzu equipped with Peltier system as temperature controller. Quartz cells of appropriate length were used for sample measurement. The spectral bandwidth and the scan rate were fixed at 2 nm and 140 nm min⁻¹, respectively. The fluorescence titrations were performed on Varian Carey Eclipse fluorescence spectrophotometer with excitation at 490 nm, unless otherwise stated. Fourier transform infrared (FT-IR) spectra were recorded on Perkin Elmer 92035. High resolution mass spectra were recorded on a BRUKER DALTONIK micrOTOF-Q11 spectrometer. ¹H NMR titration of **PDI-DMEA** against $Cu(ClO_4)_2$ was performed in CDCl₃ on Bruker 500 MHz spectrometer. All absorption and fluorescence scans were saved as ACS II files and further processed in Excel[™] to produce all graphs shown. The spectral data were analyzed through curve fitting procedures by using non-linear regression analysis SPECFIT 3.0.36 to determine the stability constants and the distribution of various species. PDI $\mathbf{1}^{25}$, $\mathbf{2}^{25}$ PDI $\mathbf{3}^{26}$ and PDI-NH $_2^{26}$ have been synthesized by following the literature methods.

Synthesis of PDI-DMEA

The mixture of PDI 1 (0.2 g, 0.280 mmol) and N,N'dimethylethylenediamine (7.42 ml, 6.71 mmol) were heated under N₂ atmosphere at 110°C for 4 hrs. After completion of the reaction (tlc), the reaction mixture was extracted with chloroform and organic layer was concentrated under reduced pressure to obtain crude product which was further purified by column chromatography (SiO₂, chloroform/methanol) to isolate pure PDI-DMEA, bluish-black colour solid, yield 140 mg (0.22 mmol, 78.2%); R_f = 0.5 (MeOH:CHCl₃ 2:8). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ 8.88 (d, 1H, J = 8.0, perylene-ArH), 8.37-8.63 (m, 5H, perylene-ArH), 8.16 (s, 1H, perylene-ArH), 7.08 (bs, 1H, NH), 5.00-5.10 (m, 2H, cyclohexyl), 3.50 (bq, J = 5.0, 2H, CH₂), 2.78 (t, J = 5.5 Hz, 2H, CH₂), 2.53-2.63 (m, 4H, cyclohexyl), 2.33 (s, 6H, N-CH₃), 1.91-1.93 (m, 4H, cyclohexyl), 1.73-1.79 (m, 4H, cyclohexyl), 1.27-152 (m, 8H, cyclohexyl), ppm; ¹³C NMR (125 MHz, CDCl₃, 25 °C): δ 25.6, 26.7, 29.3, 29.4, 41.6, 45.0, 53.0, 54.1, 57.2, 119.9, 121.0, 121.5, 121.6, 122.7, 123.1, 123.6, 124.0, 126.7, 127.8, 128.4, 130.0, 131.2, 131.7, 132.4, 135.4, 136.5, 140.0, 147.7, 164.2, 164.4 ppm; IR (ATR): v 3300, 2926, 2852, 2777, 1691, 1650, 1588, 1481, 1341, 1259, 1114, 748 cm⁻¹. HR-MS: *m/z* found 663.4618; calcd. 663.2942 for C₄₀H₄₀N₄O₄Na. UV/Vis (CH₃CN): λ_{max} = 515, 605 nm; fluorescence: λ_{max} = 537, 575 nm.

Results and discussion

Synthesis of PDI derivatives

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The **PDI-DMEA** was prepared by reacting pure 1,7-Br-PDI (PDI 1) with N,N-dimethylethylenediamine at 110°C for 8h (scheme 1). Unfortunately only mono-bay substituted derivative was isolated due to reductive debromination of other bromine under this reaction condition.^{4a} The presence of NCH₂ signals at δ 2.08 and 3.52 ppm, signature signals for mono-bay substituted PDIs and signals due to cyclohexyl groups confirm the formation of **PDI-DMEA** (Fig. S1, ESI). The presence of broad peak in wide angle X-ray diffraction (WXRD) shows amorphous nature of **PDI-DMEA** (Fig. S2, ESI).

In order to provide insight into the mechanism of **PDI-DMEA** towards metal ions, control compound PDI-NH₂ was also synthesized. For this purpose, first nitration of PDI **2** has been performed according to modification of the literature procedure. Briefly, PDI **2** was treated with ceric ammonium nitrate (CAN) with immediate addition of H₂SO₄-HNO₃ mixture at room temperature to afford PDI **3** in 10 min (according to literature report at least 2h was required for nitration).²⁶ Subsequently, PDI **3** was reduced in the presence of Zn dust and acetic acid mixture at room temperature to isolate PDI-NH₂. The presence of NH₂ signal at δ 5.17 ppm, signature signals for mono-bay substituted PDIs and signal due to cyclohexyl groups confirm the formation of PDI-NH₂ (Fig. S3-S4, ESI).



The self-assembly of PDI-DMEA in CH₃CN was checked by performing dynamic light scattering (DLS) experiments. The stock solutions of **PDI-DMEA** $(1x10^{-4} \text{ M}, \text{CH}_3\text{CN})$ and $\text{Cu}(\text{CIO}_4)_2$ were filtered through 0.02 micron filter membrane to remove any interfering impurities. The particle size analysis of the solution of PDI-DMEA (10 µM) in CH₃CN revealed the formation of aggregates with hydrodynamic diameter in the range of 150-300 nm (Fig. 1a). Further, we anticipated that due to presence of DMEA unit, there is a possibility for interaction of PDI-DMEA with Cu²⁺ ions. To verify this idea, we have also performed DLS experiment of PDI-DMEA-Cu²⁺ (1:5) complex in CH₃CN solution. From particle size analysis we observed that the size of the aggregates drastically increased with hydrodynamic diameter in the range of 350-600 nm and thus this preliminary data supports the complexation of PDI-DMEA with Cu²⁺ ions (Fig. 1b).

Self-assembly of PDI-DMEA

The self-assembly of **PDI-DMEA** and **PDI-DMEA**+Cu²⁺ (1:2) complex has been also investigated using scanning electron microscopic (SEM) technique. The SEM images of thin films on TLC plate prepared by drop cast method from solution of **PDI-DMEA** in CH₃CN shows presence of 3D nano rods morphology all over the surface. The diameter of these nano rods is in the range of 200-350 nm in consonance with DLS experiment in solution form (Fig. 2a-d), whereas the length of the nano rods extended up to several μ m. During scanning of the surface of deposited sample we observed that nano rods are jumbled in such a manner that superficially the nanostructure looks like nest of '*Baya weaver bird*' (Fig. 2a and Fig. S5-6).

The SEM Images of **PDI-DMEA**+ Cu^{2+} (1:5) complex show that addition of 2 equivalents of Cu^{2+} ions caused the complete disintegration of nano rods into spherical aggregates.



Scheme 1 Synthesis of PDI-DMEA; reagents and conditions: (a) Br_2 , H_2SO_4 , I_2 ; (b) NMP, Acetic acid, cyclohexylamine; (c) N,N'-dimethylethylenediamine, $110^{\circ}C$, 8h; (d) Imidazole, cyclohexylamine, $140^{\circ}C$, 4h; (e) ceric ammonium nitrate, H_2SO_4 -HNO₃ mixture, RT, 10 min; (f) Zn dust, CH₃COOH, THF, RT, 24h.

PDI 3

Fig. 1 (a) DLS analysis of PDI-DMEA (10 $\mu M)$ and (b) DLS analysis of PDI-DMEA (10 $\mu M)$ on addition of Cu(ClO₄)₂ (50 $\mu M)$ in CH₃CN solution.

PDI 2

PDI-NH₂

ARTICLE



Fig. 2 Self-assembly of **PDI-DMEA** (10 μ M) and morphological changes in **PDI-DMEA** upon the addition of Cu(ClO₄)₂ in CH₃CN solution; (a,c) normal and (b,d) magnified view of Nano rods of **PDI-DMEA** extending into several μ m as observed in the SEM; (e, f) SEM images of **PDI-DMEA** on addition of Cu(ClO₄)₂ showing the disintegration of Nano rods.

The average diameter of the spherical aggregates is in the range of 450-600 nm (Fig. 2e-f), in consonance with DLS data. We attribute that DMEA unit on PDI interact intermolecularly with each other to form a rod-like self-assembly and probably, on addition of Cu^{2+} ions, the DMEA unit of PDI-DMEA interacts with Cu^{2+} ions and results in breaking of self-assembled nano rods into spherical structures (Fig. 2f and Fig. S7 shows presence of few nanorods which are in mid-way of disintegration).

Photophysical properties of PDI-DMEA

The unsubstituted PDI **2** shows well defined vibronic bands with λ_{max} at 525 nm due to S_0 - S_1 electronic transition^{3b} whereas PDI-NH₂ shows broad absorption band with λ_{max} at 560 nm due to ICT transition from HOMO of the NH₂ to the LUMO of the PDI core. On the other hand **PDI-DMEA** shows absorption bands that covers almost whole visible range (Fig. 3, Inset). The characteristic absorption bands present in the visible region with λ_{max} at 478 and 515 nm are due to perylene dimide moiety, whereas absorption band extended to red region with λ_{max} 605 nm is due to ICT transition from HOMO of the N,N'-dimethylethylenediamine (DMEA) to the LUMO of the PDI core indicating interaction of electron rich DMEA moiety



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Fig. 3 UV-Vis absorbance and fluorescence spectra of PDI-DMEA, PDI-NH₂ and PDI 2 recorded in CH₃CN; λ_{ex} = 490 nm; slit width (Ex = 2 nm/2 nm, Em = 1 nm/1 nm).

with electron deficient-PDI core to make stronger push-pull electronic system.

Based on these observations, we speculate that broad CT band of **PDI-DMEA** at 605 nm might have contribution of two transition, i:e, from HOMO of the –NH group (2° amine of lateral DMEA unit –**NH**CH₂CH₂N(CH₃)₂ to the PDI core and from HOMO of the –N(CH₃)₂ group (3° amine of lateral DMEA unit – NHCH₂CH₂N(CH₃)₂ to the PDI core.

The emission spectrum of **PDI-DMEA** and PDI-NH₂, show emission intensity at 537 and 521 nm respectively, when recorded in CH₃CN solution (λ_{ex} = 490 nm). On the other hand, emission spectrum of **PDI 2** shows high emission intensity at 537 and 572 nm in CH₃CN solution (λ_{ex} = 490 nm) (Fig. 3).

Spectroscopic response of PDI-DMEA

The absorption spectrum of **PDI-DMEA** (25 μ M) in CH₃CN on addition of Cu(ClO₄)₂ (as source of Cu²⁺ ions, 250 μ M) shows complete disappearance of ICT band at 605 nm with concomitant increase (10 times) in the intensity of the normal absorption band at 515 nm (Fig. 4a) and consequently exhibit naked eye colour change from colourless to yellow (Fig. 4c), whereas addition of all other metal ions (as their perchlorate salt) viz. Fe²⁺, Hg²⁺, Zn²⁺, Ni²⁺, Pb²⁺, Ba²⁺, Sr²⁺, Cs²⁺ and Co²⁺ (250 μ M) to the solution of **PDI-DMEA** causes only the blue shift of the ICT band from 605 nm to 570 nm as well as insignificant naked eye colour change (Fig. 4a, c and Fig. S8).

The emission spectrum of **PDI-DMEA** (5 x 10^{-8} M) on addition of Cu²⁺ ions resulted in enhancement of fluorescence intensity at 537 nm and consequently weakly emissive solution of **PDI-DMEA** (25 µM) becomes fluorescent bright yellow colour solution when illuminated using 365 nm UV lamp (Fig. 4b,d). Although as expected enhancement in the fluorescence intensity was observed in the emission spectrum of **PDI-DMEA** on addition of all other metal ions (250 µM) however, visibly (under 365 nm UV lamp) weak enhancement was seen except Fe²⁺ where light greenish fluorescence was observed (Fig. 4d). Journal Name



Fig. 4 (a) UV-Vis spectra of PDI-DMEA (25 μ M) on addition of metal ions (250 μ M); (b) Fluorescence spectra of PDI-DMEA (5x10⁻⁸ M) on addition of metal ions (5x10⁻⁷ M); (c) Photographs of naked eye colour change of PDI-DMEA (25 μ M) and (b) fluorescence images of PDI-DMEA (25 μ M) after addition of various metal ions (250 μ M) under illumination at 365 nm UV lamp. All spectra were recorded in CH₃CN. λ_{ex} = 490 nm; slit width (Ex/Em = 10/10 nm).

UV-Vis and Fluorescence spectroscopy

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In the UV-Vis titration of **PDI-DMEA** (25 μ M, CH₃CN) with Cu²⁺ ions, we observed immediate blue shift of the CT band from 605 to 570 nm and then intensity of CT band gradually increased to its limiting value up to 0.7 equivalent (17.5 μ M) of Cu²⁺ ions. On further addition of Cu²⁺ ions CT band at 570 nm slowly decreases and finally it vanish at 2 equivalent (50 μ M) of Cu²⁺ ions and then it achieves the plateau. On the other hand, normal absorbance band at 515 nm continuously increase predominantly to its limiting value up to 2.0 equivalent (50 μ M) of Cu²⁺ ions and then it achieves the plateau (Fig. 5, Inset). The isosbestic point appeared at 533 nm. The spectral fitting of the titration data by using non-linear regression analysis programme (SPECTFIT-32) shows log $\beta_{\text{PDI}(Cu^{2+})} = 8.35 \pm 0.2$ (PDI:Cu²⁺; 2:1).

The fluorescent titration of PDI-DMEA (5x10⁻⁸ M) shows that on addition of Cu²⁺ ions, the emission bands at 537 and 573 nm slowly increase with increase in the concentration of Cu^{2+} ions and then achieve the plateau at 200 equivalent (10 $\mu M)$ of Cu^{2+} ions. This constitutes a 'turn-on' sensor for detection of Cu²⁺ ions with nearly 310% increase in the emission intensity (Fig. 6). These results could be attributed to inhibition of electron transfer (PET) from DMEA to PDI due to Cu²⁺ complexation. The fluorescence quantum yield^{27a} increases from 0.035 (for PDI-DMEA alone) to 0.29 (PDI-**DMEA**-Cu²⁺ complex). The spectral fitting of these data shows the formation of 1:1 and 2:1 (PDI:Cu²⁺) stoichiometric complexes with stepwise stability constant of log $\beta_{PDI(Cu2+)}$ = 5.81 \pm 0.11 (PDI:Cu^{2+}, 1:1) and log $\beta_{\text{PDI}(\text{Cu}2+)}$ = 13.6 \pm 0.18 (L:Cu²⁺, 2:1). The fluorescence intensity plot demonstrates two steps of linear change between 1x10⁻⁸ M - 2.5x10⁻⁷ M and



Fig. 5 UV-Vis spectra of PDI-DMEA (25 μ M) recorded in CH₃CN on addition of the Cu²⁺ ions; Inset: plot of absorbance vs conc. of Cu²⁺ ions at 515 and 605 nm; magnified view of absorption spectra showing blue shift from 605 to 570 nm on addition of 0.7 equivalent of Cu²⁺ ions.



Fig. 6 Fluorescence spectra of **PDI-DMEA** (5x10⁻⁸ M) recorded in CH₃CN on addition of the Cu²⁺ ions; Inset: plot of fluorescence intensity (FI) vs conc. of Cu²⁺ ions at 537 nm; λ_{ex} = 490 nm; slit width (Ex/Em = 10/10 nm).

 2.6×10^{-7} M – 9.5×10^{-6} M concentration of Cu²⁺ ions (Fig. 6, Inset). The detection limit is found to be 20 nM which is sufficiently low to detect the nano-mloar concentration of Cu²⁺. The association constant (K) of the **PDI-DMEA** with Cu²⁺ determined by Benesi-Hildebrand plot is found to be 2.1×10^{5} M⁻¹. The Job's plot^{27b} shows a maxima at the mole fraction of 0.4 with an unsymmetrical peak shape which suggests the formation of 2:1 **PDI-DMEA**-Cu²⁺ complex along with other complexes (Fig. S9, ESI).

Mechanism of interaction of PDI-DMEA toward Cu^{2^+} and other metal ions

After close inspection of structure of **PDI-DMEA**, we could argue that in our **PDI-DMEA**, the 3° nitrogen atom at lateral appendage is more basic in comparison to 2° nitrogen atom which is directly attached with electron deficient PDI core. So, the probability of 3° nitrogen to undergo complexation or

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protonation is much higher in comparison to 2° nitrogen and accordingly we proposed binding mode II and III as more probable form of complexes for interaction of Cu²⁺ with **PDI-DMEA** in the UV-Vis titration (Fig. 7).

Initially in the binding mode II, probably only 3° nitrogen atoms interact with Cu²⁺, while 2° nitrogen atoms are still capable of undergoing ICT process and as a consequence PDI-DMEA show blue shift from 605 to 570 nm. This assumption was further verified by looking at the UV-Vis spectrum of PDI-NH₂ which shows absorption maxima at 560 nm (Fig. 3). So, as the contribution of ICT from 3° nitrogen to PDI core decreases, the ICT from 2° nitrogen to PDI core increases and thus justified concomitant increase in the absorbance of CT band at 570 nm. As soon as the concentration of Cu²⁺ ions reaches >0.7 equivalent, the binding mode III becomes more preferred one which involves participation of both nitrogen atoms and accounts for drastic decrease of ICT band at 570 nm and appearance of normal absorption band of PDI core at 515 nm. This complexation of **PDI-DMEA** with Cu²⁺ was further confirmed by UV-Vis titration of PDI-NH₂ (taken as control compound) with Cu²⁺ ions. We observed that when solution of Cu^{2+} ions was added into the solution of PDI-NH₂ (25 μ M, CH₃CN), the ICT absorption band at 560 nm continuously decreased up to 3 equiv. (75 μ M) concentration of Cu²⁺ ions along with slight increase in the absorption intensity of normal band at 511 nm (Fig. S10, ESI).

Although fluorescence experiments were performed at much lower concentration in comparison to absorption experiments, however initially we propose binding mode III as the probable mode for complexation where both nitrogen atoms of two PDIs undergo interaction with Cu²⁺ and results in sharp increase in fluorescence intensity (FI) which corresponds to 22% of the total increase in the FI (first step of linear change highlighted with circle in Fig. 6). Later on the contribution of binding mode I simultaneously increase and fluorescence enhancement effectively slows down as the conc. of Cu²⁺ increases from 2.5x10⁻⁷ to 9.5x10⁻⁶ M which accounts for 73% of the total increase in FI (second step of linear change) (Fig. 6). This fact was further supported by looking at fluorescence titration of PDI-NH₂ with Cu^{2+} , where the emission band at 521 nm progressively increased showing 62% fluorescence enhancement up to addition of 10 equivalents of Cu²⁺ ions (Fig. S11, ESI).

Although we have seen insignificant naked eye colour change (absorbance) and 'turn-on' (emission) response on



Fig. 7 The probable binding modes of PDI-DMEA with Cu²⁺ as observed in the UV-visible and fluorescence titrations.

addition of all other metal ions, however observance of blue shift in ICT band from 605 to 570 nm on addition of >125 μ M (in comparison to 17 μ M of Cu²⁺) and 'turn-on' emission profile with 0.5 μ M to 1 μ M (in comparison to 10 μ M of Cu²⁺ ions) concentrations of other metal ions prompted us to investigate the **PDI-DMEA** response for other metal ions and perchloric acid. On gradual titration of **PDI-DMEA** (25 μ M, CH₃CN) with Fe²⁺, Hg²⁺ (taken as representative metal ions) and perchloric acid we observed that CT band undergoes immediate blue shift from 605 to 570 nm and then it achieves the plateau. Interestingly, the weak absorbance of normal band of **PDI-DMEA** at 515 nm was not affected to greater extent. Similarly, the fluorescence titration of **PDI-DMEA** (5x10⁻⁸ M) with these metal ions and perchloric acid caused increase in the emission intensity (Fig. S12-15).

Surprisingly, when optical titrations of PDI-NH₂ were performed with these metal ions (Fe²⁺, Hg²⁺) and perchloric acid, we observed insignificant changes in the absorbance and emission spectrum of PDI-NH₂ (Fig. S16-17). Based on these results, we propose that most of these metal ions under studies interact with more basic 3° amine via complexation (due to the high lewis acidity of some of the transition metals) or due to protonation to inhibit the ICT or PET from 3° amine to PDI core and consequently blue shift from 605 to 570 nm was observed whereas, due to least basicity of -NH group of PDI-DMEA (in line with PDI-NH₂ derivatives), it shows least interaction via protonation. Moreover, based on hard soft acid base (HSAB) principle, Fe²⁺, Hg²⁺ etc. are incompetent to bind the soft ligating sites of DMEA as effectively as Cu²⁺ can do. So, the inhibition of ICT band and fluorescence enhancement on addition of Cu²⁺ ions is due to the true complexation of PDI-**DMEA** with Cu²⁺ ions rather than protonation.

Molecular switches and Logic functions

As described above, the charge transfer (CT) band of PDI-DMEA undergoes distinctive changes on gradual addition of Cu²⁺ ions in the absorption spectrum (Fig. 5) and thus PDI-DMEA could represent rare example of "OFF-ON-OFF" molecular switch at 570 nm, if the initial absorbance value at 570 nm considered as thresh hold value for this particular case. Initially the absorbance at 570 nm for PDI-DMEA is in the low state ('OFF') when $[Cu^{2+}] = 0 \mu M$. The absorbance at 570 nm rapidly increased with the addition of $[Cu^{2+}] = 17.5 \ \mu M$, indicating high state ('ON') and again the absorbance at 570 nm rapidly decreased with $[Cu^{2+}] = 50 \ \mu M$ (representing low state, 'OFF'). Interestingly, we can visualize 'ON-OFF-ON' molecular switch, if the absorbance were monitored at 570 and 515 nm. For the working of this 'ON-OFF-ON' molecular switch, we shall considered absorbance at 570 nm as high ('ON' state) at $[Cu^{2+}] = 0 \mu M$ and then after addition of $[Cu^{2+}] =$ 50 μ M, although the absorbance at 570 nm decreases ('OFF' state), however the absorbance at 515 nm concomitantly increased ('ON') state. Alternatively, 'ON-OFF-ON' molecular switch can be imagined as combination of 'ON-OFF' switch at 570 nm and 'OFF-ON' switch at 515 nm and thus PDI-DMEA offer dual signalling windows for Cu²⁺ ions.²⁸ Conversely. PDI-DMEA behave only as 'OFF-ON' molecular switch at 570 nm on

6 | J. Name., 2012, 00, 1-3

View Article Online DOI: 10.1039/C6TC00422A ARTICLE

Journal Name

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addition of $[Fe^{2^+}] = 175 \ \mu M$ in the absorbance mode and thus provide an advantage to distinguish between different transition metals.

Besides using absorption channel as output, there is a possibility to check functioning of molecular switch using emission channel as output. As we also observed 'turn-on' response in the emission spectrum on addition of either Cu^{2+} , and Fe^{2+} ions, so **PDI-DMEA** represent 'OFF-ON' switch when fluorescence was monitored at 537 nm. As molecular switches and logic gates obey close analogy due to similar intrinsic protocols for conversion of input stimulation into output signals, so these molecular switches discussed above could be transformed into following logic gates.

We visualized that **PDI-DMEA** behave as NOT gate at 605 nm (absorbance) and becomes Cu^{2+} driven YES logic at 515 nm (absorbance). The emission spectrum of **PDI-DMEA** exhibit 3.5 and 2.3 times increase in the intensity of emission band at 537 nm on addition of 10 μ M concentrations of Cu^{2+} or 0.5 μ M concentrations of Fe^{2+} ions, or even when both Cu^{2+} and Fe^{2+} were added, we also observed 3.5 time increase in the emission intensity of **PDI-DMEA** at 537 nm and thus these inputs can be used for developing two inputs based OR logic gate at 537 nm (Fig 8). Moreover, the molecular computation in present scenario rely on multiple inputs-one output combination, so we can extend the present two inputs based OR gate into four inputs based OR gate using Cu^{2+} , Hg^{2+} , Fe^{2+} ions and perchloric acid as four inputs and measuring the output at 537 nm.

The other demonstration of molecular information was based on a photonic NOR logic function. The absorbance at 610 nm could be at a high value only when inputs of Fe^{2+} , Cu^{2+} or both are absent (Fig 8).

(a)	Inputs		Outputs			
	Cu ²⁺ Fe ²⁺		Absorbance			Fluorescence
			A ₅₁₅	A ₅₇₀	A ₆₁₀	F ₅₃₇
	0	0	0	0	1	0
	1	0	1	0	0	1
	0	1	0	1	0	1
	1	1	1	0	0	1
	Logic		TRANSFER	INH	NOR	OR
(b)	Cu ²⁺ Fe ²⁺ A ₅₇₀ INH					
) — A	610 NOR

Fig. 8 (a) Truth table for various logic functions (NOR, INH, OR) fabricated for PDI-DMEA using Cu^{2+} and Fe^{2+} ions as inputs and absorption/emission as outputs at different wavelengths; (b) Pictorial representation of combinatorial circuit from NOR, OR and INH logic gate using absorption/emission as output mode.

The absorption band at 610 nm shift to 515 nm in the presence of the Cu^{2+} (50 μ M) alone or in the presence of Cu^{2+} and Fe^{2+} (50 µM each), whereas the absorption band at 610 nm shift to 570 nm in the presence of the Fe^{2+} (50 μ M) and thus all these outputs could be labelled as an 'OFF' state at 610 nm. We also observed that solution of PDI-DMEA exhibit new ICT band at 570 nm on addition of Fe^{2+} ions (50 μ M). However the presence of Cu^{2+} ions (50 μ M) to the solution of PDI-DMEA+Fe²⁺ or PDI-DMEA alone shows an output signal 515 nm and thus inhibits the outputs signal caused due to Fe²⁺ ions in the absorbance mode. So an INHIBIT function (AND gate when one input is reversed) at 570 nm (absorbance) was observed (Fig. 8). According to the truth table given in figure 8, the absorbance at 515 nm corresponds to 'TRANSFER' logic because the output is low when either both inputs are low or one input is low and output is high when either both inputs are high or one input is high. In our case, the absence of Cu²⁺ and Fe^{2+} inputs (entry 1, Fig 8a) or presence of Fe^{2+} (entry 3), the absorbance at 515 nm was low, whereas in the presence of Cu^{2+} and Fe^{2+} (entry 4) or presence of Cu^{2+} (entry 2), the absorbance at 605 nm vanish and high absorbance value was observed at 515 nm.

By operating the OR and the NOR logic functions at 537 nm (Fluorescence mode) and 610 nm (absorbance mode) in parallel, a sequential logic circuit such as complementary output logic circuit can be fabricated. The complementary logic circuit is based on the phenomena of two parallel working logic gates that have output exactly opposite to each other as a response to the two working inputs. Such combinations that have been used in electronic devices are the combinations of IMPLICATION/INHIBT, YES/NOT, OR/NOR and AND/NAND gates.^{29,30} This sequential logic circuit has added advantages of less power requirement, higher working speed, a lower physical space requirement for fabrication and negligible time lag between two outputs with respect to each other as two optical outputs can be recorded at the same time.

Fluorosolvatochromism for differentiating organic solvents

We have also explored ICT and PET properties of **PDI-DMEA** and their modulation in the presence of Cu²⁺ ions (**PDI-DMEA** + Cu²⁺ complex) to develop colour array to differentiate organic solvents based on its response with organic solvents in terms of physical or chemical interactions.³¹ A pattern of colour changes were generated through comparison of colour as observed in different flask in paint software (Fig. 9).

PDI-DMEA exhibit naked eye bluish and brownish colour in toluene and DCM respectively; brick red in CHCl₃; greenish colour in DMSO and **PDI-DMEA** is colourless in CH₃CN solution. However, **PDI-DMEA**+Cu²⁺ complex shows brown and yellow colour in THF and CH₃CN solvents respectively; orange colour in DCM and light brown colour in acetone.

Similarly, **PDI-DMEA** shows fluorescent pink and blue colour in CHCl₃ and ethanol respectively; light green in DMSO when visualized under 365 nm UV lamp, whereas **PDI-DMEA**+Cu²⁺ complex shows fluorescent bright yellow and dark green colour when visualized under 365 nm UV lamp (Fig. S18, ESI).

ARTICLE





Fig. 9 Patterns of (A) PDI-DMEA (25 µM) and (B) PDI-DMEA-Cu²⁺ (1:10) complex obtained in response to various organic solvents for application to develop colourimetric (upper) and fluorometric (lower) colour array. For visualization colour range as observed in different flask were transformed to different colour range in paint software.

Confocal Laser Scanning Microscopic Studies

Thin films of **PDI-DMEA** (1x10⁻⁵ M) were prepared by drop cast method and analyzed by using confocal laser scanning microscope (CLSM). Thin films of **PDI-DMEA** do not show any fluorescence in CLSM which could be attributed due to aggregation induced quenching via π - π stacking of PDI chromophore in solid state.¹ However, when 20 µL solution of **PDI-DMEA** (1x10⁻⁵ M) in CH₃CN was placed on glass slide and imaged under CLSM, we observed weak emission in solution phase (Fig. 10, a-b) which changes to bright green fluorescence on addition of Cu²⁺ ions (5 equiv.) which truly support complexation of **PDI-DMEA** with Cu²⁺ (Fig. 10, c-d).



Fig. 10 Images from confocal laser scanning microscopy (CLSM) of PDI-DMEA (10 μ M); (a-b) non-fluorescent nature of PDI-DMEA (c-d) addition of 5 equivalents of copper perchlorate to the solution of PDI-DMEA results in 'switching on' of fluorescence.

¹H NMR titration of PDI-DMEA with Cu²⁺

The complexation behaviour of **PDI-DMEA** with Cu²⁺ was also proved through ¹H NMR titration experiments. Due to less solubility of **PDI-DMEA** in CD₃CN or DMSO- d_6 at such high concentration (5 mM), we prefer CDCl₃ solvent for ¹H NMR titration (Fig. S19). Upon addition of Cu²⁺, the proton signals of the perylene aromatic core shows ~0.02-0.03 ppm downfield shift along with signal broadness. Moreover, we also observed ~0.015-0.02 ppm downfield shift of the DMEA protons (-CH₂ and -NH). These results could be attributed to complexation of **PDI-DMEA** with Cu²⁺ ions.

Reversibility and dual sensing

To check the reversibility of the Cu²⁺ recognition process, the EDTA solution was added to the solution of PDI-DMEA-Cu²⁺ complex and optical measurements were carried out. We observed that the fluorescence intensity of PDI-DMEA-Cu²⁺ complex decreases slowly however it has not reached to its initial value. Similarly, addition of EDTA to the solution of PDI-DMEA-Cu²⁺ (1:2) complex only marginally regenerate the ICT band at 605 nm, however we observed drastic decrease in the normal absorption band at 515 nm. We also observed colour change from yellow to very light-yellow (visible) and bright fluorescent parrot colour to weekly emissive sea green colour (under 365 nm UV lamp) on addition of EDTA (Fig. S20-22, ESI). We also exploited **PDI-DMEA**-Cu²⁺ complex for sensing of CN ions via displacement assay, however we observed similar response as observed with EDTA (only 50% recovery of fluorescence at 537 nm and absorption band at 515 nm without affecting the ICT band) (Fig. S20,22 ESI). Therefore, the aggregates of PDI-DMEA forms very strong complex with Cu²⁺, which finds difficulty in decomplexation on addition of EDTA or CN⁻ ions.

Effect of coexisting ions

To evaluate the selectivity and sensitivity of **PDI-DMEA** towards Cu^{2+} , we also carried out several competition experiments. We observed that the optical changes which were observed in **PDI-DMEA** in the presence of Cu^{2+} (inhibition of ICT band and fluorescent enhancement) were retained even in the presence of other metal ions (selectivity). On the other hand, no change in optical properties of **PDI-DMEA** were observed in the presence of other competitive metal ions, however addition of Cu^{2+} in the same solution immediately cause the disappearance of CT band and fluorescence enhancement (sensitivity) (Fig. S23, ESI).

Conclusions

In conclusion, we report Nano rods self-assembly of bay functionalized perylenediimide derivative (**PDI-DMEA**) and its response towards Cu^{2+} in solid and solution form. On interaction with Cu^{2+} , the Nano rods disintegrate to form spherical nanostructures whereas in solution the Cu^{2+} complexation results in restriction of ICT absorption band at 605 nm (absorbance) and significant enhancement of the

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Journal Name

emission intensity at 537 nm (fluorescence and CLSM studies). The multiple outputs obtained using Cu^{2+} and Fe^{2+} as inputs were elaborated for developing various logic functions and circuits. **PDI-DMEA** also showed fluorosolvatochromism phenomena through modulation of its ICT/PET properties in the absence and presence of Cu^{2+} to develop the colour array as observed under sunlight or after 365 nm UV illumination for differentiating the organic solvents.

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