

Perylene Diimide Appended with 8-Hydroxyquinoline for Ratiometric Detection of Cu^{2+} Ions and Metal Displacement Driven “Turn on” Cyanide Sensing

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Abstract Perylene diimide (PDI) 3 and 4 appended with 8-hydroxyquinoline derivatives have been synthesized and their photophysical and spectroscopic properties have been experimentally determined. Moreover, PDIs 3 and 4 show ratiometric behavior to detect Cu^{2+} colorimetrically with visible color change from coral red to light pink, whereas 3 and 4 show “turn-off” behavior in fluorescence with lowest limit of detection 5×10^{-7} M. The PDI 3 could be further utilized for ratiometric CN^- detection colorimetrically and as “turn-on” sensor for CN^- detection fluorometrically with lowest limit of detection 8×10^{-6} M. The comparison of spectroscopic properties of PDI 1-4 highlights the importance of linking 8-hydroxyquinoline units on the PDI core at bay position for achieving Cu^{2+} recognition event into ratiometric signal.

Keywords Perylene diimide · Dyes · Ratiometric · Fluorescent sensor · Copper ions · Cyanide

Introduction

Perylene diimide (PDI) derivatives are intensively colored with high molar extinction coefficient, fluorescence

quantum yields and exceptional thermal, chemical and photochemical stability [1, 2]. Although literature reports have considered PDIs as promising materials for various optoelectronic devices [3–6], we have witnessed slow growth in considering PDIs as chromo-fluorescent probes for sensing applications. So far, only a few reports on PDIs based fluorescent probes for cations [7–17] and anions [18, 19] have been reported and few of these were for Cu^{2+} [13–15] and CN^- ion [19]. Jinsong and co-workers utilized dipicolylethylenediamine moiety at N-terminal of the PDI for detection of the Cu^{2+} ion [13]. Zhu and co-workers shows displacement of gold nanoparticles (AuNPs) from the ensemble (perylene bisimide-AuNPs) by Cu^{2+} ions [14] whereas, Li and co-worker shows that the addition of Cu^{2+} into PDI-dipeptide conjugate leads to aggregation induced fluorescence quenching followed by pyrophosphate sensing via disassembly of the PDI-dipeptide- Cu^{2+} complex and thus consequently recovery of the fluorescence [15]. For last few years, research has focused on developing chromo-fluorescent sensors as a safeguard for global ecosystem, for monitoring of toxic, carcinogenic metal ions and anions that impose serious human and environmental health hazards [20, 21]. Moreover, during analysis of any analyte concentration, the ratios between the two intensities (either two absorption intensity or emission intensity) are useful as it nullifies the environmental effects [22].

Copper is a significant pollutant, despite being an essential element in biological systems. It has a toxic impact on the microorganisms and is harmful to humans at higher concentrations being associated with neurodegenerative diseases [23, 24]. Cyanide is also considered as most toxic of all anions and considered lethal to humans. It inactivates the active site of cytochrome c and blocks the electron transport chain resulting

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in inhibition of cellular respiration. Various industrial processes and agriculture sector require copper and cyanide ions and moreover cyanide has been used as chemical warfare agent which thus ultimately leads to environmental contamination [25, 26]. Therefore, easy and affordable methods for detection of Cu^{2+} and CN^- to control the environmental pollution are of great importance. We have taken the advantage of bidentate chelating effect of 8-hydroxyquinoline [27, 28], for the selective sensing of Cu^{2+} ions. To the best of our knowledge, there is no report on the synthesis of ratiometric chromo-fluorescent probe based on PDIs, bay functionalized with 8-hydroxyquinoline for detection of Cu^{2+} ions, followed by metal displacement driven “turn on” sensing of cyanide anion.

Herein we describe the synthesis, photophysical and spectroscopic properties of 8-hydroxyquinoline (8-HQ) appended PDIs. These PDIs show ratiometric sensing of Cu^{2+} ions with blue shift (20 nm) in absorption maxima and visible color change from coral red to light pink. Simultaneously, the emission from the perylene diimide undergoes quenching due to formation of Cu^{2+} complex. The quenching of the fluorescence intensity of the 8-HQ linked PDI by the Cu^{2+} ions opens the possibility to use non-fluorescent PDI- Cu^{2+} complex as a “turn on” fluorescent assay for the CN^- ions via metal displacement assay.

Materials and Methods

Experimental

General Procedures

Chemicals and solvents were reagent grade and used without further purification unless otherwise stated. All reactions were performed under N_2 or Ar atmosphere. N-Methylpyrrolidine (NMP) was dried over 4 Å molecular sieves. Chromatographic purification was done with silica gel 60-120 and 230-400 mesh. TLC was performed on aluminium sheets coated with silica gel 60 F254 (Merck, Darmstadt). NMR spectra were recorded on Bruker-400 and JEOL-300 (operating at 400 and 300 for ^1H ; 100 and 75 MHz for ^{13}C , respectively). The peak values were obtained as ppm (δ), and referenced to the TMS as reference in ^1H NMR and deuterated solvent in ^{13}C NMR spectra. Abbreviations used for splitting patterns are s=singlet, bs=broad singlet, t=triplet, q=quartet, m=multiplet. Fourier transform infrared (FT-IR) spectra were recorded on Perkin Elmer 92035. The fluorescence spectra were recorded by excitation at 500 nm. The fluorescence titrations were performed on Varian Carey Eclipse fluorescence spectrophotometer using slit width (excitation=10 nm, emission=2.5 nm), unless otherwise stated. The life-time studies were performed on BH-CHRONOS spectrophotometers and absorption spectra were recorded on Shimadzu-2450

spectrophotometer from Shimadzu. The solutions of PDIs 1-4 were prepared in chloroform (HPLC grade). The solutions of metal perchlorates and tetrabutylammonium cyanide were prepared in acetonitrile (HPLC grade) and were added in microliter quantities so that the amount of acetonitrile remained less than 1% in chloroform. 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. The details of synthesis of PDI 1 and PDI 5 are reported in supporting information.

Synthesis

Synthesis of *N,N'*-bis(Cyclohexyl)

Perylene-3,4,9,10-Tetracarboxylic Acid Diimide PDI 1

The perylene dianhydride (PTCDA) (250 mg, 0.637 mmol) and imidazole (346 mg, 5.09 mmol) were placed in 100-mL round bottomed flask and mixture was heated to 120 °C for 0.5 h [29]. This was followed by the addition with stirring of cyclohexylamine (148 mg, 1.49 mmol). After addition, temperature was raised to 140 °C. The reaction mixture was stirred continuously for additional 4 h at 140 °C. After this time interval, the mixture was first diluted with ethanol before complete cooling, then 2M HCl was added and reaction mixture was kept for 1 h. The precipitates were filtered, washed with water, then dried to give 380 mg of PDI 1 which was further purified by column chromatography (SiO_2 , ethylacetate/chloroform) to isolate pure PDI 1 as red solid, yield 270 mg (0.48 mmol, 71%); $R_f=0.5$ (chloroform/ethyl acetate 99:1). ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 1.30-1.96 (m, 16H, cyclohexyl), 2.52 (m, 4H, cyclohexyl), 5.08 (m, 2H, cyclohexyl), 8.79 (s, 8H, perylene-ArH); IR (ATR): $\nu=3082, 2923, 2851, 1692, 1656, 1592, 1488, 1335, 1265, 1160, 960 \text{ cm}^{-1}$.

Synthesis of *N, N'*-bis(Cyclohexyl)-1,7-bis(Phenoxy)

Perylene-3,4,9,10-Tetracarboxylic Acid Diimide PDI 2

The mixture of phenol (16 mg, 0.170 mmol) and K_2CO_3 (36 mg, 0.026 mmol) was stirred in N-methyl-2-pyrrolidine (NMP) at room temperature. Then compound 5 (50 mg, 0.070 mmol) was added under N_2 . The reaction mixture was stirred at 85 °C for 7 h. After cooling to RT, the reaction mixture was poured into ice and precipitates were filtered, washed with water, then dried to get 68 mg of PDI 2 which was further purified by column chromatography (SiO_2 , chloroform/hexane) to isolate pure PDI 2 as red solid, yield 35 mg (0.047 mmol, 68%); $R_f=0.6$ (chloroform/hexane 70:30). ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 1.25-1.86 (m, 16H, cyclohexyl), 2.50 (m, 4H, cyclohexyl), 5.00 (m, 2H,

cyclohexyl), 7.17 (d, $J=8.1$ Hz, 4H, phenoxy), 7.26 (s, this signal merged with CDCl_3 signal, 2H, phenoxy), 7.46 (t, $J=7.8$ Hz, 4H, phenoxy), 8.29 (s, 2H, perylene-ArH), 8.58 (d, $J=8.4$ Hz, 2H, perylene-ArH), 9.58 (d, $J=8.4$ Hz, 2H, perylene-ArH) ppm; IR (ATR): $\nu=3075, 2922, 2850, 1699, 1654, 1593, 1489, 1328, 1260, 1196, 1074, 750\text{ cm}^{-1}$.

Synthesis of N, N'-bis(Cyclohexyl)-1,7-bis(8-Quinoloxyl)Perylene-3,4,9,10-Tetracarboxylic Acid Diimide PDI 3

Procedure as described in Section "Synthesis of N, N'-bis(Cyclohexyl)-1,7-bis(Phenoxy)Perylene-3,4,9,10-Tetracarboxylic Acid Diimide PDI 2". was followed. The reaction of 8-hydroxyquinoline (51 mg, 0.351 mmol) with compound 5 (100 mg, 0.140 mmol) using K_2CO_3 (72 mg, 0.521 mmol) as base in NMP as solvent gave 132 mg of PDI 3 which was further purified by column chromatography (SiO_2 , chloroform/ethyl acetate) to isolate pure PDI 3 as violet color solid, yield 85 mg (0.101 mmol, 65%); $R_f=0.4$ (chloroform/ethyl acetate 96:4). $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25 °C): δ 1.23–1.43 (m, 6H, cyclohexyl), 1.66–1.69 (m, 6H, cyclohexyl), 1.82–1.85 (m, 4H, cyclohexyl), 2.40–2.49 (m, 4H, cyclohexyl), 4.90–4.96 (m, 2H, cyclohexyl), 7.32 (dd, $J_1=7.6$ Hz, $J_2=1.0$ Hz, 2H, 8-HQ), 7.45–7.56 (m, 4H, 8-HQ), 7.75 (dd, $J_1=8.2$ Hz, $J_2=1.0$ Hz, 2H, 8-HQ), 8.24 (s, 2H, Perylene-ArH), 8.30 (dd, $J_1=8.4$ Hz, $J_2=1.6$ Hz, 2H, 8-HQ), 8.50 (d, $J=8.4$ Hz, 2H, perylene-ArH), 8.96 (dd, $J_1=4.2$ Hz, $J_2=1.6$ Hz, 2H, 8-HQ), 9.90 (d, $J=8.4$ Hz, 2H, Perylene-ArH) ppm; $^{13}\text{C NMR}$ (75 MHz, TFA: CDCl_3 (1:9), 25 °C): δ 25.2, 26.3, 28.8, 55.0, 120.4, 122.0, 123.00, 124.8, 125.7, 126.1, 129.0, 129.3, 131.3, 132.6, 145.0, 146.1, 147.6, 153.2, 163.7, 164.1 ppm; IR (ATR): $\nu=2923, 2854, 1690, 1654, 1599, 1469, 1330, 1248, 1188, 1094, 907\text{ cm}^{-1}$ (Fig 1).

Synthesis of N, N'-bis(Cyclohexyl)-1,7-bis(5-Chloro-8-Quinoloxyl)Perylene-3,4,9,10-Tetracarboxylic Acid Diimide PDI 4

The reaction of 5-chloro-8-hydroxyquinoline (75 mg, 0.418 mmol) with compound 5 (100 mg, 0.140 mmol) using K_2CO_3

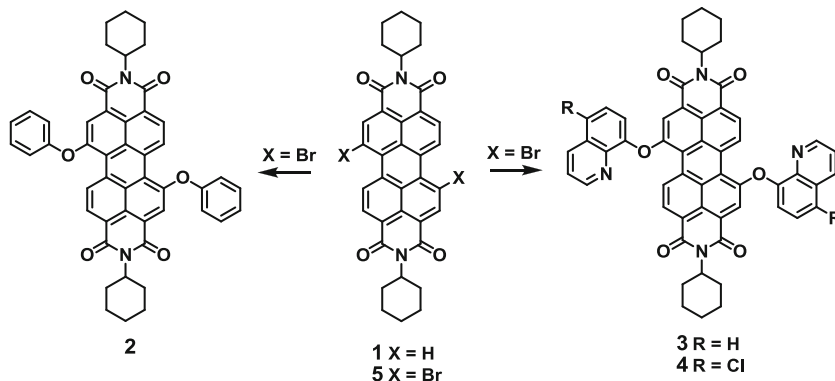
(86 mg, 0.631 mmol) as base in NMP as solvent gave 126 mg of PDI 4 which was further purified by column chromatography (SiO_2 , chloroform/methanol) to isolate pure PDI 4 as violet color solid, yield 88 mg (0.097 mmol, 70%); $R_f=0.7$ (chloroform/methanol 99.5:0.5). $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25 °C): δ 1.33–1.42 (m, 6H, cyclohexyl), 1.66–1.69 (m, 6H, cyclohexyl), 1.82–1.86 (m, 4H, cyclohexyl), 2.36–2.48 (m, 4H, cyclohexyl), 4.90–4.96 (m, 2H, cyclohexyl), 7.27 (d, $J=8.0$ Hz, 2H, HQ), 7.60 (d, $J=8.0$ Hz, 2H, HQ), 7.65 (dd, $J_1=8.0$ Hz, $J_2=4.0$ Hz, 2H, HQ), 8.19 (s, 2H, Perylene-ArH), 8.50 (d, $J=8.0$ Hz, 2H, perylene-ArH), 8.68 (dd, $J_1=8.0$ Hz, $J_2=1.6$ Hz, 2H, HQ), 8.98 (dd, $J_1=4.0$ Hz, $J_2=1.4$ Hz, 2H, HQ), 9.83 (d, $J=8.0$ Hz, 2H, perylene-ArH) ppm; $^{13}\text{C NMR}$ (75 MHz, TFA: CDCl_3 (1:9), 25 °C): δ 25.3, 26.3, 28.9, 54.4, 120.5, 123.4, 125.1, 125.9, 128.3, 129.3, 132.5, 134.4, 141.4, 146.8, 147.7, 153.3, 163.2, 163.6 ppm; IR (ATR): $\nu=3083, 2924, 2852, 1693, 1655, 1591, 1461, 1330, 1264, 1193, 1055, 809\text{ cm}^{-1}$.

Results and Discussion

Photophysical Properties of PDI 1-4

The absorption and emission spectra of the PDI 1-4 in chloroform are displayed in Fig. 2. We observed that the maximum absorption peak of PDI 1 is at 525 nm. However, the absorption maxima for PDI 2-4 were shifted to 541–546 nm, due to presence of two aryloxy groups at 1 and 7-positions of PDI core. Similarly, the emission maxima of PDI 2-4 in chloroform on excitation at 500 nm were shifted to 574–579 nm in comparison to the maxima at 538 nm in case of PDI 1. The bathochromic shifts in both UV-vis and fluorescence spectra are in consonance with increasing electron donating strength of the substituents. PDI 2-4 display larger stokes shift in comparison with that of PDI 1. The fluorescence quantum yields as well as first order radiative (K_f) decay constants decreased as we moved from PDI 1 to 4 (Table 1). The decrease in fluorescence quantum yields could be attributed to charge transfer character in the excited state of the PDI

Fig. 1 Synthesis of perylene diimide PDIs 1-4



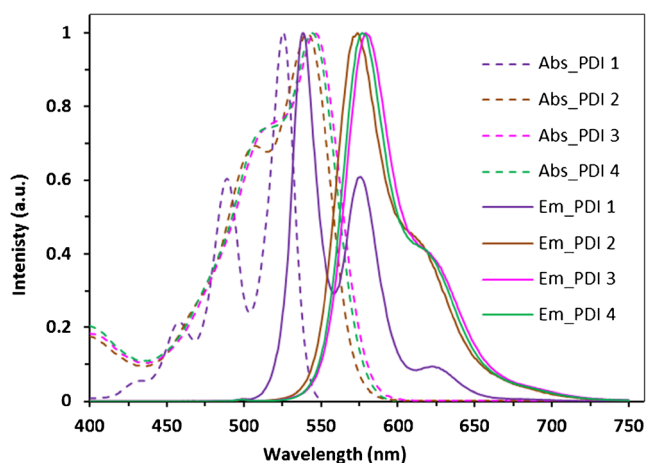


Fig. 2 Normalized UV-Vis absorption and emission spectra of PDI 1-4 in chloroform

molecules comprising electron-donating side groups and electron-deficient nature of the PDI core. The absorption domain for 8-hydroxyquinoline moiety lies at 270-350 nm range with λ_{\max} at 302 nm.

Optical Response of PDIs 3 and 4 Towards Cu^{2+}

The effect of various metal ions such as Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , Na^+ , K^+ , Ca^{2+} and Mg^{2+} (100 μM) on the UV-vis and emission spectrum of PDI 3 (10 μM) in chloroform was studied. We observed that the addition of only Cu^{2+} to the solution of PDI 3 resulted in >50% decrease in the absorbance intensity with concomitant blue shift of the absorbance band and >90% quenching of the fluorescence intensity on addition of 50 μM . Other metal ions did not modulate the absorption spectrum, however addition of Zn^{2+} and Na^+ , Ca^{2+} , Mg^{2+} (100 μM) caused only 40% and (10-15%) fluorescence quenching, respectively (Fig. SI 1). These preliminary results point to strong ground and excited state interaction of PDI 3 with Cu^{2+} .

On gradual addition of Cu^{2+} to the solution of PDI 3, the absorption band at 546 nm decreased with concomitant appearance of the new band at 526 nm which increased prominently to the limiting value, thus allowing ratiometric sensing of Cu^{2+} ions (Fig. 3a and Fig. SI 2). The isosbestic point appeared at 535 nm and the plateau was achieved at 5.0 equivalents (50

μM) of Cu^{2+} ions. The plot of ratios of absorbance intensities *i.e.* A_{526}/A_{546} vs. Cu^{2+} ion concentration shows a linear increase between 0-16 μM of Cu^{2+} ion. The spectral fitting of the titration data by non-linear regression analysis (SPECFIT-32) shows $\log \beta_{\text{L}(\text{Cu}^{2+})} = 10.23 \pm 0.04$ (L: Cu^{2+} , 1:2).

The fluorescent titration of PDI 3 in chloroform showed that on addition of Cu^{2+} ions, the emission band at 579 nm decreases up to 1.8 equiv. (18 μM) of Cu^{2+} ions and then a new blue shifted emission band centered at 553 nm was observed whose intensity increased 1.7 times up to 3.0 equiv. (30 μM) of Cu^{2+} and then achieved the plateau (Fig. 3b, Fig. SI 3). The isosbestic point appeared at 561 nm. The formation of new blue shifted emission band could be attributed to the formation of a PDI 3- Cu^{2+} complex. The chelation induced fluorescent quenching (CHEQ) may be due to paramagnetic effect of Cu^{2+} ions. The fluorescence quantum yield decreased from 0.96 (for PDI 3 alone) to 0.11 (PDI 3- Cu^{2+} complex). The spectral fitting of these data shows the formation of 1:1 and 1:2 (L:M) stoichiometric complex with $\log \beta_{\text{L}(\text{Cu}^{2+})} = 6.61 \pm 0.08$ (L: Cu^{2+} , 1:1) and $\log \beta_{\text{L}(\text{Cu}^{2+})} = 13.17 \pm 0.14$ (L: Cu^{2+} , 1:2). The association constant (K) of the PDI 3 with Cu^{2+} determined by Benesi-Hildebrand plot was found to be $0.8 \times 10^5 \text{ M}^{-1}$. The Job's plot shows a maxima at the mole fraction of 0.5 with an unsymmetrical peak shape which suggests the formation of 1:1 PDI 3- Cu^{2+} complex along with other higher order complexes. The minimum detection limit of Cu^{2+} was found to be $5 \times 10^{-7} \text{ M}$. The PDI 3 showed fluorescence life time $\tau_f = 4.92 \text{ ns}$, whereas, after addition of Cu^{2+} (30 μM), it shows fluorescence life time $\tau_{f(1)} = 4.80 \text{ ns}$ (for free PDI 3) and $\tau_{f(2)} = 0.73 \text{ ns}$ (for Cu^{2+} bound PDI 3). The HRMS spectrum of the complex between PDI 3 and Cu^{2+} showed the appearance of peak at m/z 1002.1729 (theor. 1002.1710), assignable to $[3+\text{Cu}^{2+}+\text{ClO}_4^-]$ which further confirms the formation of 1:1 complex. The Stern-Volmer plot follows the linear relation between 0-6 μM Cu^{2+} but at higher concentrations of Cu^{2+} the quenching process becomes non-linear (Fig. 3b, Fig. SI 4). The Stern-Volmer constant value (K_{sv}) was $1.54 \times 10^5 \text{ M}^{-1}$. The quenching rate constant (K_q) of 1 for Cu^{2+} was calculated to be $1.12 \times 10^{-4} \text{ sM}^{-1}$.

Similarly, on gradual addition of Cu^{2+} to the solution of PDI 4, the intensity of the absorption band at 544 nm remained unaffected till addition of 1.0 equivalents (10 μM) of Cu^{2+}

Table 1 Spectroscopic and photophysical characteristics of PDI 1-4 in chloroform

	Absorption λ_{\max}/nm	Emission λ_{\max}/nm	Quantum Yield ^a (ϕ_f)	Stoke shift ($\nu_A - \nu_F$) (cm^{-1})	Life time τ/ns	K_f^b (10^8 s^{-1})	K_{nr}^c (10^8 s^{-1})
PDI 1	458, 489, 525	538, 576, 622s	0.32	460.2	4.86	0.66	1.39
PDI 2	507s, 541	574, 620s	0.29	1062.7	4.83	0.59	1.48
PDI 3	515s, 546	579, 625s	0.27	1062.7	4.92	0.55	1.48
PDI 4	508s, 542	577, 615s	0.18	1119.2	4.92	0.37	1.66

^a Fluorescence quantum yield. The fluorescence quantum yields (ϕ_f) were determined using rhodamine B [33] as a reference with the known $\phi_f = 0.5$ in ethanol; slit width (excitation=5 nm, emission=2.5 nm). ^b Radiative decay constant $K_f = \phi_f/\tau_f$. ^c Non-radiative decay constant $K_{\text{nr}} = (1/\phi_f - 1)K_f$ [34]

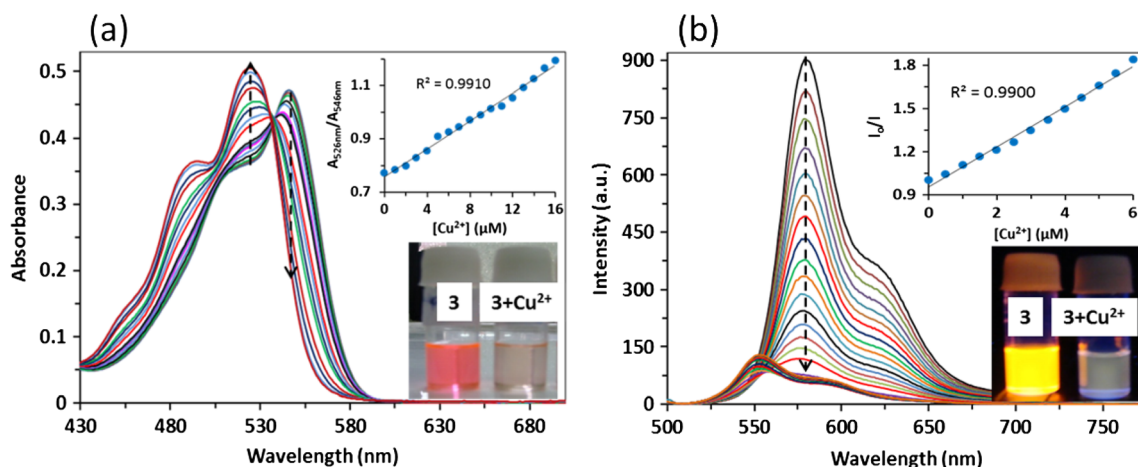


Fig. 3 (a) UV-Vis and (b) fluorescence spectra of PDI **3** (10 μM) recorded in chloroform on addition of the Cu^{2+} ions; Excitation at 500 nm. Inset: (a) ratiometric plot of $A_{526\text{ nm}}/A_{546\text{ nm}}$ vs conc. of Cu^{2+} ions; the color changes of PDI **3** (10 μM) and **3**+ Cu^{2+} ions (50 μM). Inset: (b)

Stern-Volmer plot at 579 nm corresponding to fluorescence titration; fluorescence of PDI **3** (10 μM) before and after addition of Cu^{2+} ions (20 μM) under illumination at 365 nm

ions and at higher concentrations of Cu^{2+} it decreased gradually with concomitant appearance of the new band at 528 nm and achieved the plateau after addition of 2.0 equivalents (20 μM) of Cu^{2+} ions. The fluorescent titration of PDI **4** in chloroform showed that on addition of Cu^{2+} ions, the emission band at 577 nm decreased gradually and plateau was achieved after addition of 15 equivalents (150 μM) of Cu^{2+} (Fig. SI 5, 6). The fluorescence quantum yield decreased from 0.65 (for PDI **4** alone) to 0.017 (PDI **4**- Cu^{2+} complex). Spectral fitting of these titration data shows the formation of 1:1 stoichiometric complex with $\log \beta_{L(\text{Cu}^{2+})} = 5.18 \pm 0.11$ (L: Cu^{2+} , 1:1) (absorption) and $\log \beta_{L(\text{Cu}^{2+})} = 4.75 \pm 0.01$ (L: Cu^{2+} , 1:1) (fluorescence). The limit of detection of Cu^{2+} was 1×10^{-6} M. The Stern-Volmer plot shows that the quenching process is non-linear with respect to Cu^{2+} concentration. The Stern-Volmer constant value (K_{sv}) was calculated to be $5.24 \times 10^4 \text{ M}^{-1}$ (Fig. SI 7). Therefore, in PDI **3**, both alkoxy quinoline units form complex with one Cu^{2+} each, but in PDI **4**, the two

quinoline units cooperate to form complex with one Cu^{2+} only. Probably the decreased co-ordination ability of quinoline oxygen due to the presence of electron withdrawing chlorine atom in PDI **4**, leads to stabilization of Cu^{2+} through co-ordination with two nitrogen atoms of two quinoline units.

To check further the practical applicability of PDI **3** as Cu^{2+} selective fluorescent sensor, we carried out competition experiments. We observed that the fluorescence quenching caused by Cu^{2+} was retained with Cd^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} , Mg^{2+} , Ca^{2+} , Na^+ and K^+ (200 μM) (Fig. SI 8), however small emission enhancement was observed for Zn^{2+} , Co^{2+} and Ni^{2+} in comparison to PDI **3**- Cu^{2+} complex.

Optical Response of PDI **1** and **2** Towards Cu^{2+}

We have chosen 8-HQ as a binding unit because to achieve charge transfer response we need to incorporate the donor units with strong binding capacity. Therefore, the Cu^{2+}

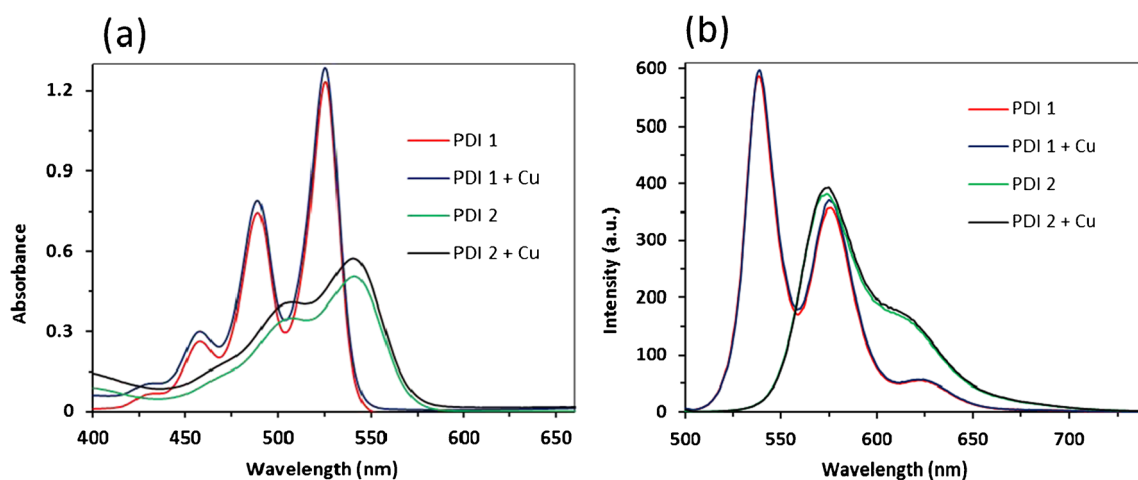


Fig. 4 (a) UV-Vis and (b) fluorescence spectra of PDI **1** and **2** (10 μM) recorded in chloroform after addition of the Cu^{2+} ions (100 μM , 10 equiv). (For complete titration see the ESI)

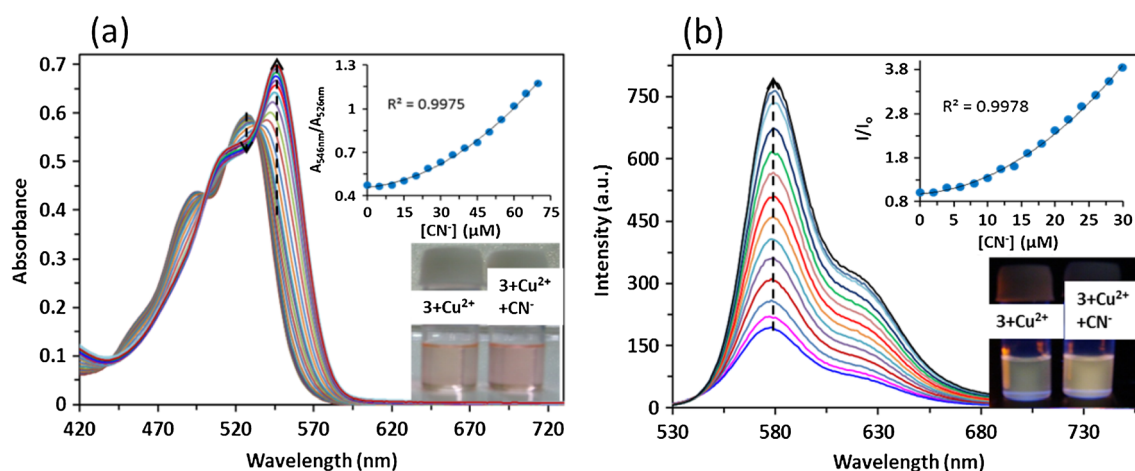


Fig. 5 (a) UV-Vis and (b) fluorescence spectra of PDI 3- Cu^{2+} ($10 \mu\text{M}$) recorded in chloroform on addition of the CN^- ions; Excitation at 500 nm . Inset: (a) ratiometric plot of $A_{546 \text{ nm}}/A_{526 \text{ nm}}$ vs conc. of CN^- ions; the color changes of PDI 3- Cu^{2+} (1:5) complex on addition of CN^- ions (50

μM). Inset: (b) Stern-Volmer plot at 579 nm corresponding to fluorescence titration; fluorescence of PDI 3- Cu^{2+} (1:2) complex before and after addition of CN^- ions ($20 \mu\text{M}$) under illumination at 365 nm

recognition event in PDI 3 and 4 is being converted into a ratiometric signal. Furthermore, we also studied the photophysical behavior of PDI 2 (having a phenoxy substituent at 1,7-position of PDI core) and PDI 1 (without any binding motif) towards Cu^{2+} in chloroform. We observed that the addition of even $100 \mu\text{M}$ Cu^{2+} to the solution of PDI 2 resulted in $<13\%$ increase in the absorbance intensity without appearance of any blue shifted absorbance band, whereas in the emission spectrum, the addition of $100 \mu\text{M}$ Cu^{2+} shows merely 2% decrease in the fluorescence intensity. Similarly, the addition of Cu^{2+} ions ($100 \mu\text{M}$) to the solution of PDI 1 caused insignificant change in absorbance and emission intensities of PDI 1 (Fig. 4, Fig. SI 9, 10).

These results indicate that (i) 8-HQ acts as a bidentate chelating ligand to encapsulate the Cu^{2+} selectively, (ii) phenoxy substituent in PDI 2, does not have sufficient ligating sites to bind Cu^{2+} , and (iii) these results exclude the possibility

of surface complexation of Cu^{2+} with perylene diimide (PDI 1) core only.

Optical Response of PDI 3- Cu^{2+} Complex Towards CN^- Ions

It is well known that CN^- has strong complexation ability towards Cu^{2+} [30]. In this “context” sensor utilizing copper-cyanide affinity [31, 32] becomes paradigm for detection of CN^- ions even though various other analytical methods are available in the literature for detection of CN^- ions. So, there is possibility to exploit the present PDI 3- Cu^{2+} complex as ensemble system for sensing the CN^- ions. We observed that the addition of CN^- ions ($100 \mu\text{M}$) to the solution of PDI 3- Cu^{2+} (1:5) complex gradually caused bathochromic shift (20 nm) of the absorption band from 526 nm to 546 nm and then achieves the plateau. It was also associated with color change from light pink to carmine pink. The poorly fluorescent complex PDI 3- Cu^{2+} (1:1.8) ($\phi_f=0.14$), on addition of CN^- ($<40 \mu\text{M}$) shows increase in fluorescence intensity at 579 nm ($\phi_f=0.88$) and then it achieve the plateau (Fig. 5, Fig. SI 11). In this respect, PDI 3 could be utilized for ratiometric CN^- sensing with lowest limit of detection $1 \times 10^{-5} \text{ M}$ (colorimetrically) and as “turn-on” sensor for CN^- with lowest limit of detection $8 \times 10^{-6} \text{ M}$ (fluorometrically). The newly formed absorption and emission band by the addition of the CN^- ions to a solution of PDI 3- Cu^{2+} complex were found to be the same as that of PDI 3 alone. These results indicate that cyanide causes decomplexation of Cu^{2+} from PDI 3- Cu^{2+} complex to give free PDI 3. These results were further supported by the fact that on individual titration of PDI 3 with CN^- , the absorption and emission spectra of the PDI 3 remains unchanged on addition of CN^- ions ($0 \mu\text{M} - 100 \mu\text{M}$).

The Cu^{2+} induced blue shift observed in the absorption and fluorescence spectra of PDI 3, which could be attributed to the

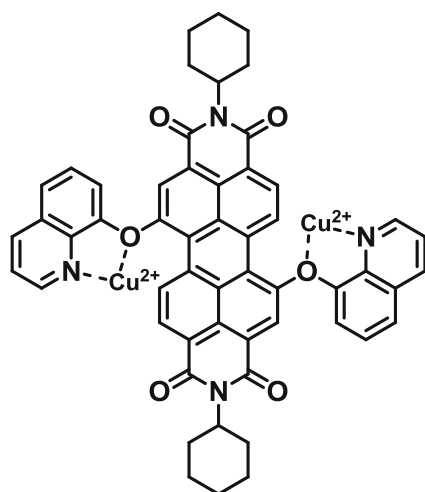


Fig. 6 Proposed structure of the complex PDI 3 - Cu^{2+}

inhibition of the ICT phenomena. In general when electron donating group (such as 8-HQ in our case) attached to electron acceptor (such as PDI in our case), then ICT from the donor to the acceptor upon excitation was expected. Therefore, selective binding of the Cu^{2+} ions with the chelating 8-HQ group inhibits the ICT phenomena thus leading to hypsochromic shift in the absorption spectrum and decrease in the fluorescence intensity. Addition of the CN^- ions to this PDI 3- Cu^{2+} complex results in the displacement of the metal ion from the complex due to higher association constant of the $[\text{Cu}(\text{CN})_x]$ complex, causing revival of the absorption and emission band to its original position and constitutes ‘turn on’ CN^- sensing fluorometrically.

Conclusion

We have synthesized two new perylene diimide based chromo-fluorescent sensors PDI 3 and 4 for the detection of Cu^{2+} and cyanide ions. The PDI 3 and 4 show ratiometric behavior to detect Cu^{2+} colorimetrically with visible color change from coral red to light pink whereas it shows “turn-off” behavior in fluorescence with minimum detection limit 5×10^{-7} M (PDI 3) and 1×10^{-6} M (PDI 4). The PDI 3 could be further utilized for ratiometric CN^- detection (1×10^{-5} M) colorimetrically and as “turn-on” sensor for CN^- detection (8×10^{-6} M) fluorimetrically.

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