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Supporting Information for

Surfactant-Induced Alterations in Optoelectronic Properties of Perylene Diimide Dyes: Modulating Sensing Responses in Aqueous Environments

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EXPERIMENTAL SECTION

1.1 General: Perylene tetracarboxylic bisanhydride(99%), imidazole(98%), L- alanine(99%), All chemicals (solvents, reagents, and chemicals) were purchased from best-known local chemical suppliers (Sigma-Aldrich, TCI chemicals, Avra synthesis pvt. Limited, Alfa Aesar Chemicals) and used without further purification. Solvents were distilled and dried prior to use. On the other hand, ¹H NMR and ¹³C NMR spectra were recorded with a Bruker Advance DRX 400 spectrometer operating at 400 and 100 MHz for ¹H and ¹³C NMR spectroscopy, respectively. Chemical shifts were reported in ppm downfield from the internal standard, tetramethylsilane (TMS). Mass spectra were recorded on Micromass Q-TOF LC-MS.

1.2 Spectroscopic studies: The UV–vis spectroscopic studies were recorded on a Shimadzu model 2100 spectrometer. The slit width for the experiment was kept at 5 nm. The stock solution for $Fe(NO_3)_3.9H_2O$ and Heparin was 10mM and 10 mM respectively. Sensing was carried out by adding requisite amounts of cations (Ag⁺, Al⁺³, Cd⁺², Co⁺², Cu⁺², Cr⁺³, Hg⁺², Fe⁺³, Mg⁺², Ni⁺², Pb⁺², Zn⁺² etc.) to water (1% DMSO) solutions of **PDI-Ala** (1 × 10⁻⁵ M). On the other hand, fluorescence experiments were performed in an Eclipse spectrofluorimeter. The slit-width for the fluorescence experiment was kept at 5 nm (excitation) and 5 nm (emission), and the excitation wavelength was set at 480 nm. For preparation of the surfactant solution, stock surfactants Cetyltrimethylammonium bromide (CTAB) were prepared in water medium.

1.4 Detection limit determination: The method used for the calculation of the detection limit is known as the blank variability method. In this method, the calibration curve was prepared by recording fluorescence spectra of in different amounts of $Fe(NO_3)_{3.9}H_2O$ and Heparin.

From the equation obtained from the calibration plot, the added iron & heparin concentrations were calculated. Then another calibration curve was drawn between the C_{real} (added Fe⁺³, Heparin, μ M) vs. C_{calc} (Calculated amount of Fe⁺³, Heparin, μ M). This afforded a value of the slope (b).

The fluorescence spectra of **PDI-Ala** were taken as blank reading. A total 10 replicates of the blank were measured. The standard deviation from the blank readings was calculated by fitting the fluorescence reading into the equation obtained from the first calibration curve (titration spectra). Using this standard deviation value, we calculated decision limit by this following equation.

 $L_{\rm C} = t_{\rm C} \times s \times (1 + 1/N)1/2$ (1)

where, N = the number of blank replicates taken; the value of t_c for 10 blank readings is 1.833; and s = the standard deviation value.

The detection limit (L_D) was calculated as the double of the decision limit obtained,

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$l_{\rm ID} = 2 l_{\rm I}$	17	1
$L_{\rm D} = 2 L_{\rm c}$	(~	,

In concentration term, the detection limit appeared as,

 $x_D = 2 \times C = 2 L_C / b$ (3)

where, b = slope of the second calibration curve (Creal vs. Ccalc.).

1.5 ¹H NMR Studies: ¹H NMR titration studies of **PDI-Ala** (5 mM) were performed with Fe⁺³ (1.0 equ.) in DMSO-d₆. The spectra were recorded using identical parameters.

1.6 Scanning Electron Microscopy: Solution of **PDI-Ala** (concentration 10 μ M) in water, then consecutively Fe+3, C-TAB was added with Comp-1. All three samples were drop casted over double-sided tapes attached onto the brass stubs and air-dried for 48 h. The samples were then coated with gold vapor and analysed on a Quanta 200 SEM operated at 15 kV.

1.7 Dynamic Light Scattering Studies (DLS): DLS measurements were done using a Malvern Zetasizer NanoZS particle sizer (Malvern Instruments Inc., MA) instrument. Samples (**PDI-Ala** and **PDI-Ala**-CTAB 10µM) were prepared in water and examined under dust free conditions. Reported mean hydrodynamic diameters were obtained from Gaussian analysis of the intensity weighted particle size distributions.

1.8 Life time measurements: Lifetime measurements were performed using Horiba Delta flex.

Modular fluorescence lifetime system with following instrumental parametres:440 nm Nano LED excitation source and peak preset 1000 counts.

Synthesis and Characterization of PDI-Ala

PDI-Ala was synthesized according to the procedure reported in literature. (1) Perylene tetracarboxylic bisanhydride (1 mmol, 1 equiv.), the L- alanine (2 equiv.) and imidazole (40 equiv.) were mixed in a flask which was flooded with argon gas for 15 minutes. The mixture was heated to 120 °C for 30 minutes and then cooled to 85 °C. The pH value of the reaction mixture was adjusted to 3 - 4 with 1 N HCl. The precipitate was collected by suction filtration, washed with water and dried in high vacuum.

Characterization

1H NMR (400 MHz, DMSO) δ 8.46 (d, *J* = 8.3 Hz, 4H), 8.33 (d, J=8.3 Hz, 4H), 5.58 (q, *J* = 6.9 Hz, 2H), 1.64 (d, J=7.0 Hz,6H).

References

(1) T. H. Rehm, M. R. Stojković, S. Rehm, M. Škugor, I. Piantanida and F. Würthner, *Chem. Sci.*, 2012, **3**, 3393-3397.

ADDITIONAL SPECTROSCOPIC DATA



Figure S1. Change in fluorescence intensity of **PDI-Ala** (10 μ M, λ ex = 480 nm) with different metal ions (0.05 mM) in water medium.



Figure S2. Normalized fluorescence spectra of **PDI-Ala-**CTAB (10 μ M, 1:20, λ ex = 480 nm) with Fe³⁺ (0.5 mM) in water medium.



Scheme S1. Concentration-dependent interaction of PDI-Ala with CTAB in water medium.



Figure S3. (a) UV-visible spectra of **PDI-Ala** (10 μ M) in water and Brij-58 micelle. (b) Fluorescence spectra of **PDI-Ala** (10 μ M, λ ex = 480 nm) in water and Brij-58 micelle