Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information (SI)

A Probe with Aggregation Induced Emission Characteristics for Screening of Iodide

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1. Experimental

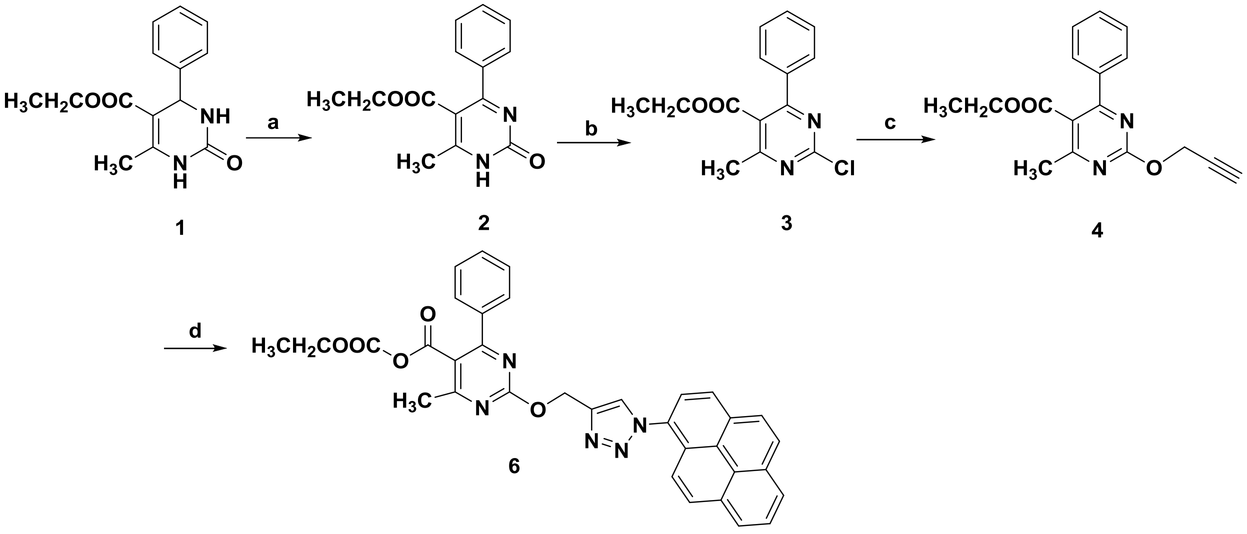
1.1 Materials and reagents

All liquid reagents were dried/ purified following recommended drying agents and/ or distilled over 4 Å molecular sieves. CH_3CN was dried by refluxing over P_2O_5. K_2CO_3 was dried overnight in furnace. 1-Aminopyrene was bought from SIGMA ALDRICH and used as such.

1.2 Instrumentation

Fluorescence studies were carried out using Perkin Elmer LS 55 Fluorescence Spectrometer at emission slit width= 3.5 nm and excitation slit width= 12 nm. Time resolved fluorescence studies were carried out using Edinburgh FL920 Fluorescence Life Time Spectrometer. A pulse diode laser at 375 nm is used as excitation source. τ calculated using FAST software. Quality of fit judged by $\chi^2<1$. UV-visible studies were carried out using UV-1800 SHIMADZU UV-Spectrophotometer. The pH titrations were carried out using Equip-Tronics Digital pH meter model –EQ 610 and electrode was calibrated using standard buffers of pH 4.0, 7.0 and 9.2. Dynamic Light Scattering was carried out using MALVERN Zetasizer Nano ZS instrument. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Biospin Avance III HD at 500 MHz, with TMS as internal standard using $CDCl_3$ as deuterated solvent. Data are reported as follows: chemical shift in ppm (δ), integration, multiplicity (s=singlet, d=doublet, t=triplet, m=multiplet), coupling constant *J* (Hz). SEM images were taken at ZEISS Supera 55 Scanning Electron Microscope. The purity of the products was checked by elemental analysis performed on a Thermoelectron FLASH EA1112 CHNS analyzer and within ±0.4% of the theoretical values. IR spectrum was recorded on Perkin-Elmer FTIR-C92035 Fourier-transform spectrophotometer in range 400–4000 cm^{-1}using KBr as medium. All reported yields are isolated yields. 1-

Azidopyrene was synthesized using literature reported procedure.[1] Melting points were determined in open capillaries and are uncorrected. For column chromatography silica gel (60–120 mesh) was employed and eluents were ethyl acetate/hexanes mixtures.



Scheme 1: Synthesis of **6**: (a) PCC, DCM, 24 h, 89%; (b) $POCl_3$, 105 °C, 95%; (c) 2-propyn-1-ol (propargyl alcohol), K_2CO_3, CH_3CN, 94%; (d) 1-azidopyrene **5**, $CuSO_4.5H_2O$, (sodium-L-ascorbate), EtOH: H_2O (9:1 *v/v*), 92%.

Ethyl 4-methyl-6-phenyl-2-(prop-2-ynyloxy)pyrimidine-5-carboxylate **4**: White solid (94%) yield. Rf: (0.5, 30% ethyl acetate/ hexane.); Mp 65-67 °C (DCM/Hexane); IR (KBr): ν_{max} 1533, 1552, 1708, 2985, 3250 cm^{-1}; ^1H (500 MHz, $CDCl_3$, 25°C): δ 1.07 (t, *J* = 5.0 Hz, 3H, C5-CH_3), 2.5 (t, *J* = 2.5 Hz , 1H, CCH), 2.61 (s, 3H, C6-CH_3), 4.18 (q, *J* = 10.0 Hz, 2H, OCH_2), 5.11 (d, *J* = 2.5 Hz, C2-OCH_2) 7.44-7.69 (m, 5H, C_6H_5); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): 13.62, 22.77, 55.15, 61.75, 74.76, 78.29, 120.53, 128.36, 128.43, 130.25, 137.54, 163.06, 166.36, 168.13, 168.97; Anal. Calcd. (%) for $C_{17}H_{16}N_2O_3$: C, 68.92; H, 5.41; N, 9.46; Found: C, 68.95; H, 5.44; N, 9.49; HRMS: *m/z* 296.1489 (M^+).

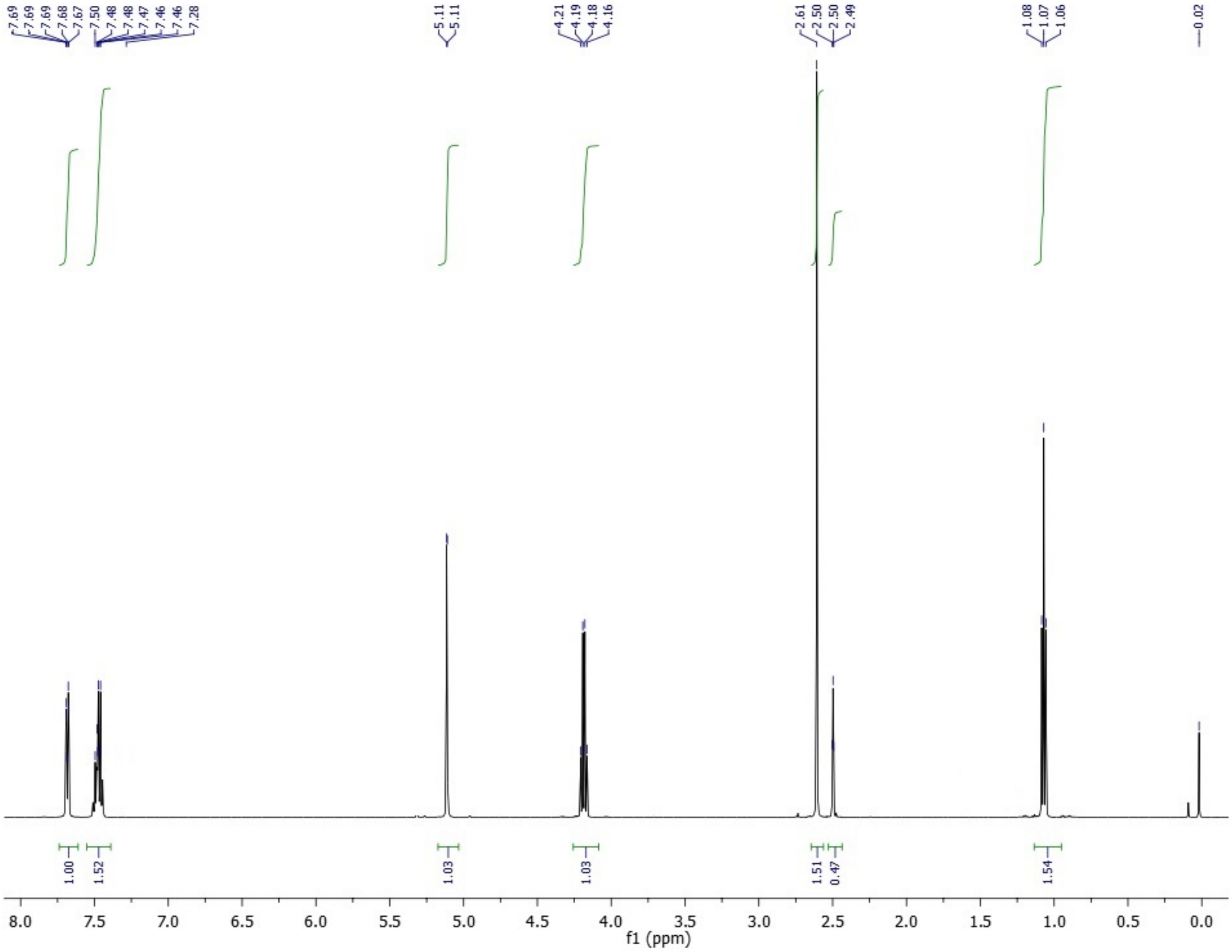


Fig. S1 ^{1}H NMR (500 MHz, CDCl$_3$) of **4**.

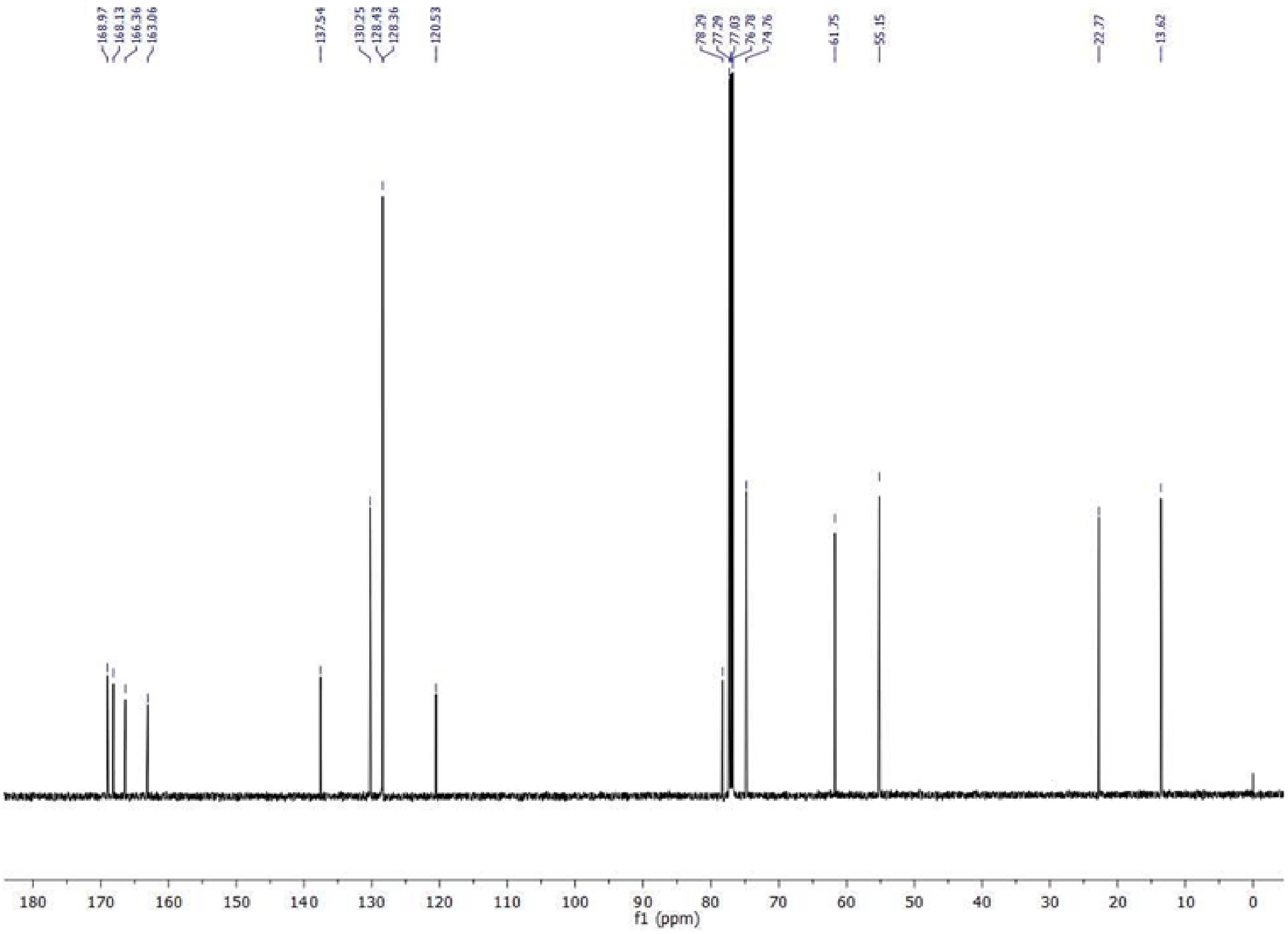


Fig. S2 ^{13}C NMR (125 MHz, CDCl$_3$) of **4**.

Ethyl 4-methyl-6-phenyl-2-((1-(pyren-1-yl)-1*H*-1,2,3-triazol-4-yl)methoxy)pyrimidine-5-carboxylate **6:** Brown solid (92%) yield. Rf : (0.3, 50% ethyl acetate/hexane); Mp 120-122 °C (DCM/Hexane); IR (KBr): ν_{max} 1547, 1601, 1729, 2967, 3137 cm^{-1}. ^{1}H (500 MHz, CDCl$_3$, 25°C): δ 1.08 (t, *J* = 5.0 Hz, 3H, C5-CH$_3$), 2.65 (s, 3H, C6-CH$_3$), 4.19 (q, *J* = 10.0 Hz, 2H, C5-OCH$_2$), 5.9(s, 2H, C2-OCH$_2$), 7.47-8.31 (m, 15H); ^{13}C NMR (125 MHz, CDCl$_3$, 25°C): 13.63, 22.85, 61.41, 61.77, 120.48, 121.07, 123.37, 124.15, 124.72, 125.02, 126.13, 126.16, 126.43, 126.48, 126.78, 126.98, 128.34, 128.49, 129.00, 129.77, 130.27, 130.33, 130.66, 131.12, 132.3, 137.62, 143.64, 163.62, 166.64, 168.16 and 169.02; Anal. Calcd. (%) for $C_{33}H_{25}N_5O_3$: C, 73.47; H, 4.64; N, 12.99; Found: C, 73.42; H, 4.58; N, 12.82; HRMS: *m/z* 540.2272 (M+1).

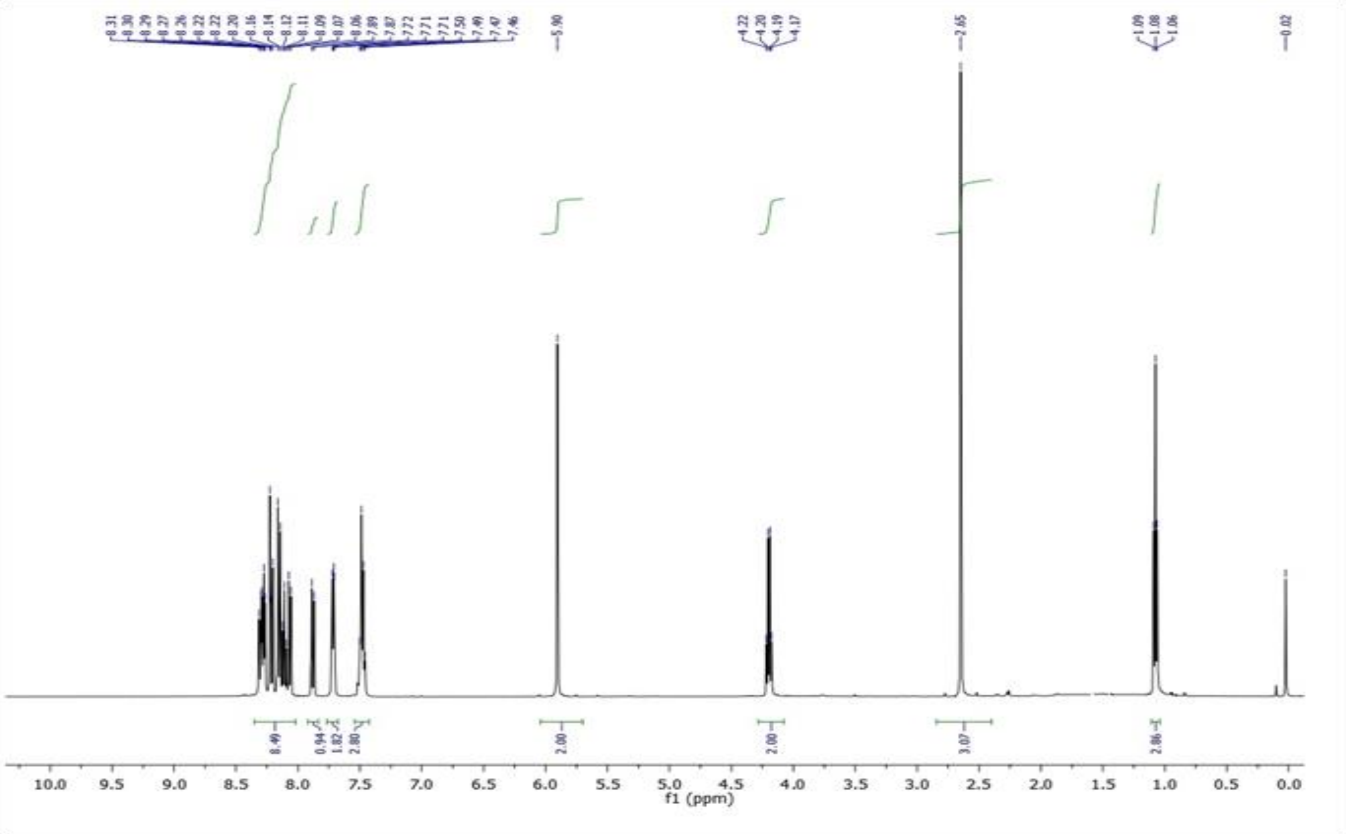


Fig. S3 ^{1}H NMR (500 MHz, CDCl$_3$) of **6**.

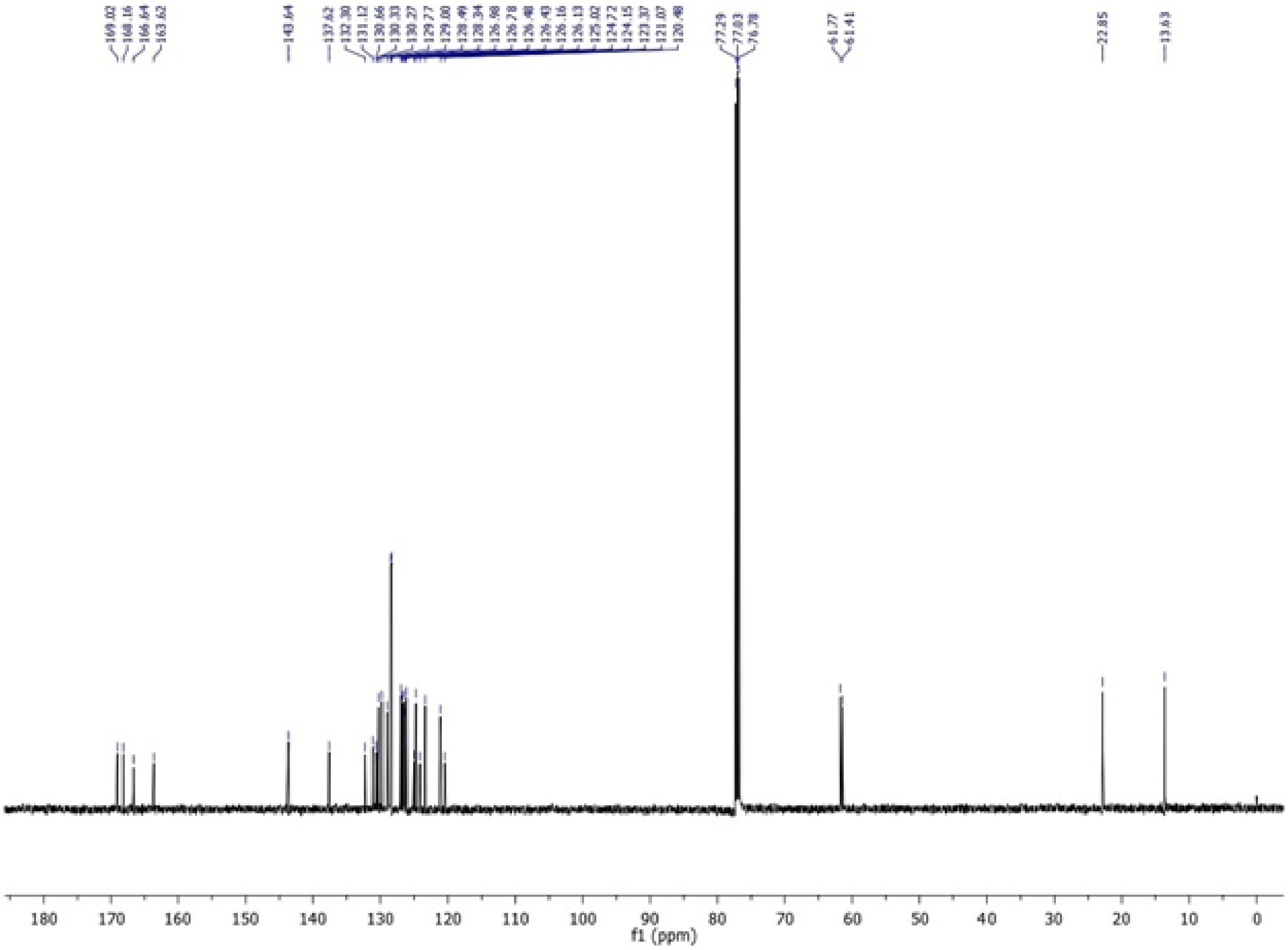


Fig. S4.^{13}C NMR (125 MHz, CDCl$_3$) of **6**.

Quantum yield calculations:

The fluorescence quantum yields were measured with respect to 9, 10-diphenylanthracene as standard having quantum yield of 0.86 in cyclohexane.[2]

$\Phi_u = \Phi_s \cdot F_u.(1\text{-}10^{-A_sL_s}).\eta_u^2/(1\text{-}10^{-A_uL_u}).\ F_s.A_u.\eta_s^2$

Φ = quantum yield

F = Integrated fluorescence intensity

A = Absorbance

η = refractive index of solvent

L= length of cell. (1.0 cm for standard and sample)

s = standard i.e. 9, 10-diphenylanthracene

u = sample

Computational details:

All theoretical calculations were carried out by using the Gaussian 09 suite of programs.[3] The molecular geometries of the chromophores were optimized at the DFT method employing the hybrid B3LYP[4] functional. 6-31G* basis set was used. The same model chemistry was used for the calculation of the properties of the chromophores. The first 50 excited states were calculated by using time-dependent density functional theory (TD-DFT calculations). The molecular orbital contours were plotted using Gauss view 5.0.9.

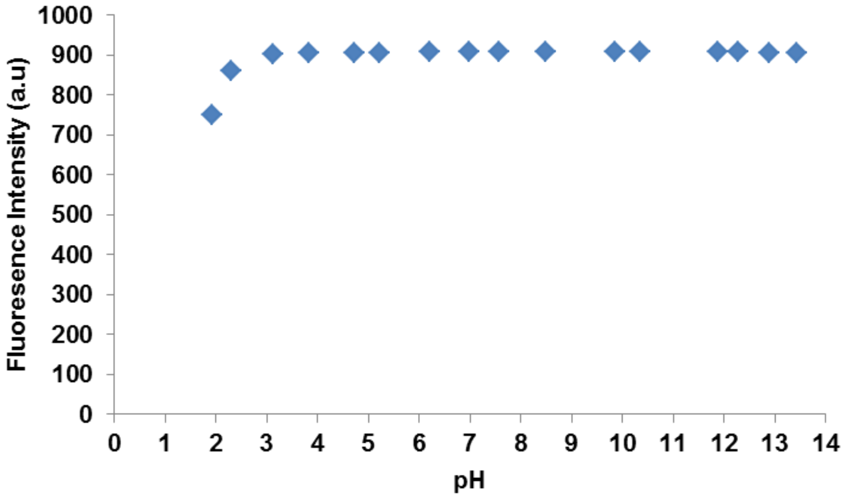


Fig. S5 Change in emission intensity of **6** (1 x 10^{-5} M) in 50:50 *v/v*, THF:HB fraction, pH 6.99, at 380 nm on changing pH.

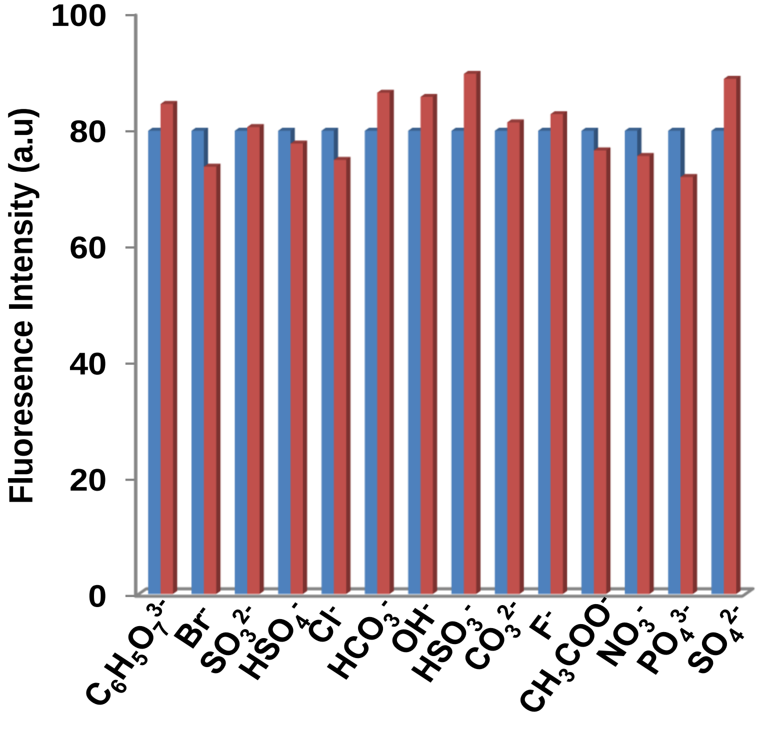


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Fig. S6 Change in emission intensity of **6** (1 x 10^{-5} M) in 50:50 *v/v*, THF:HB fraction, pH 6.99, $\lambda_{exc.}$= 342 nm, on addition of iodide (3.71 x 10^{-4} M) in the presence of various anions (3.71 x 10^{-4} M) in H_2O.

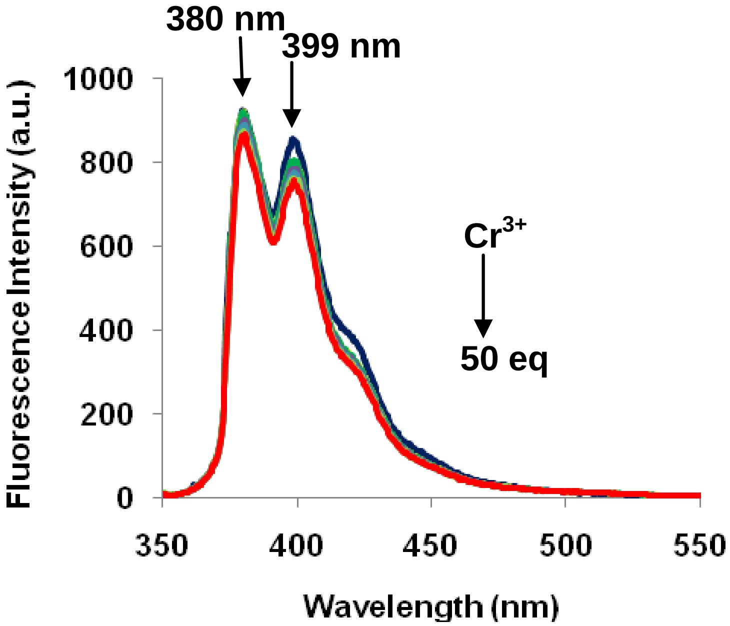

Fig. S7a. Changes in emission spectra of **6** (1×10^{-5} M) in 50:50 *v/v*, THF:HB fraction, pH 6.99, $\lambda_{exc.}$= 342 nm upon incremental additions of Cr^{3+}(upto 5.00×10^{-4} M), in H_2O, added as $Cr(ClO_4)_3$.

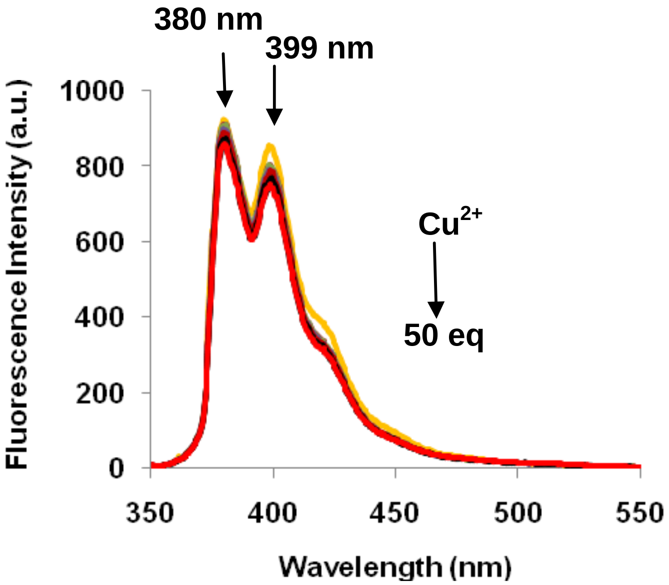

Fig. S7b. Changes in emission spectra of **6** (1×10^{-5} M) in 50:50 *v/v*, THF:HB fraction, pH 6.99, $\lambda_{exc.}$= 342 nm upon incremental additions of Cu^{2+}(upto 5.00×10^{-4} M), in H_2O, added as $Cu(ClO_4)_2$.

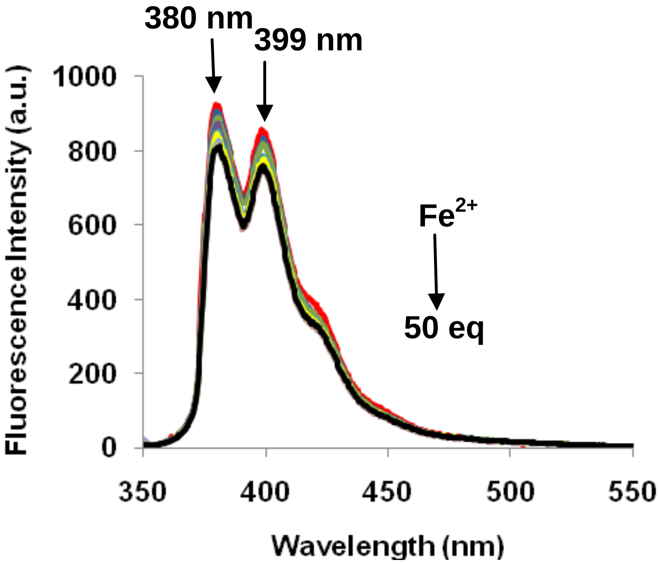

Fig. S7c. Changes in emission spectra of **6** (1 x 10^{-5} M) in 50:50 *v/v*, THF:HB fraction, pH 6.99, $\lambda_{exc.}$= 342 nm upon incremental additions of Fe^{2+}(upto 5.00 x 10^{-4} M), in H_2O, added as $Fe(ClO_4)_2$.

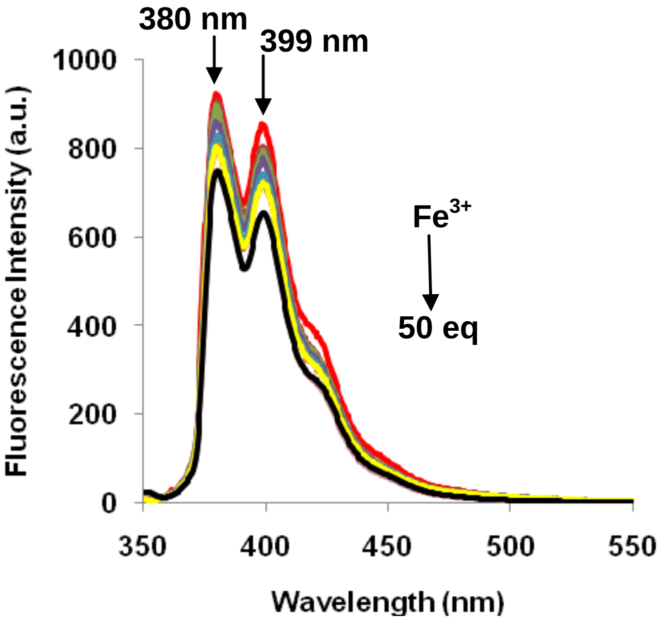

Fig. S7d. Changes in emission spectra of **6** (1 x 10^{-5} M) in 50:50 *v/v*, THF:HB fraction, pH 6.99, $\lambda_{exc.}$= 342 nm upon incremental additions of Fe^{3+}(upto 5.00 x 10^{-4} M), in H_2O, added as $Fe(ClO_4)_3$.

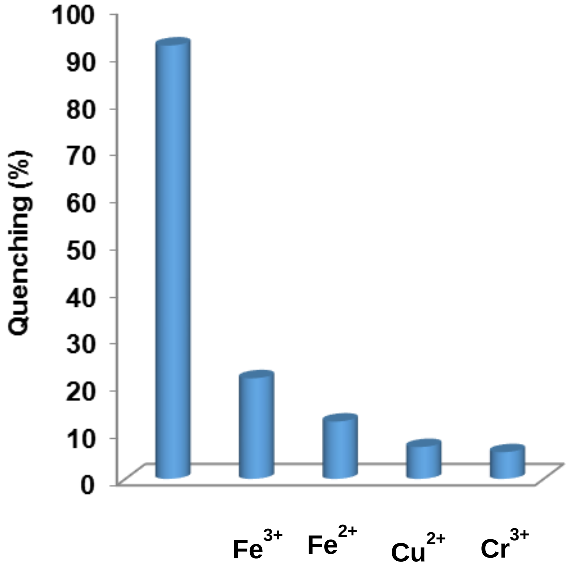

Fig. S7e. Percentage fluorescence quenching observed upon addition of (5.00×10^{-4} M) aqueous solution of various cations and iodide to a solution of **6** (1×10^{-5} M in 50:50 *v/v*, THF:HB fraction, pH 6.99, $\lambda_{exc.}$= 342 nm) $\lambda_{em.}$= 380 nm.

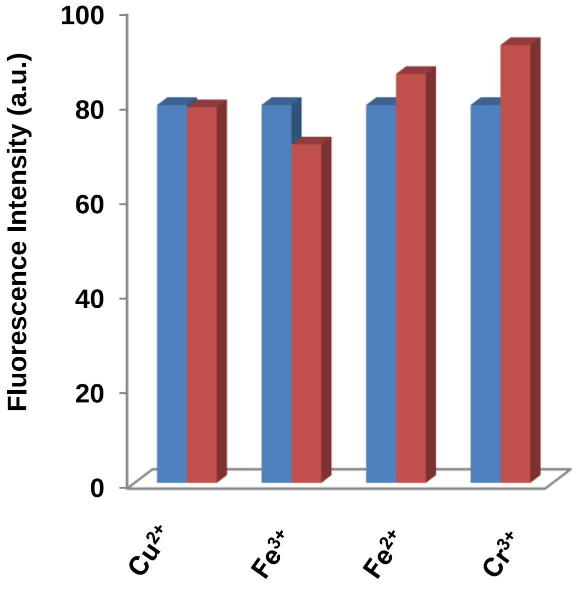

Fig. S7f. Change in emission intensity of **6** (1×10^{-5} M) in 50:50 *v/v*, THF:HB fraction, pH 6.99, $\lambda_{exc.}$= 342 nm, on addition of iodide (3.71×10^{-4} M) in the presence of various cations (3.71×10^{-4} M) in H_2O.

Analysis of iodide in urine sample:

To a given solution of **6** (1 x 10^{-5} M) in 50:50 *v/v*, THF:HB fraction, 3.5 ml was added 20 µl urine sample and emission spectra was recorded for **6**.

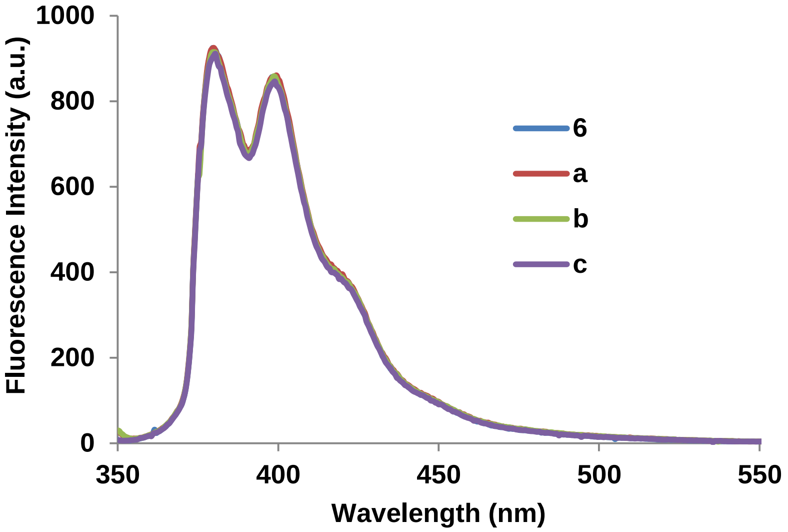

Fig. S8 Change in emission spectra of **6** (1 x 10^{-5} M) in 50:50 *v/v*, THF:HB fraction, pH 6.99, $\lambda_{exc.}$= 342 nm, on addition of (a) 20 µl urine, (b) and (c) 7 µl iodide solution (1 x 10^{-3} M) in H_2O.

Concentration of iodide in urine sample is calculated utilizing following equation.

y = -2e+ 06 x + 919.39.

y = Emission intensity.

x = Concentration of iodide

Now to the above solution was added 7 µl iodide solution of concentration (1 x 10^{-3} M) was added successively and again emission spectra was recorded.

Recovery (%) = (Conc. of iodide found/Total conc. of iodide) x 100.

Calculation of detection limit:

The detection limit was calculated on the basis of the fluorescence titration. The fluorescence emission spectrum of **6** was measured 6 times, and the standard deviation of blank measurement was achieved. To gain the slope, the ratio of emission intensity at 380 nm was plotted as a concentration of Iodide ion. The detection limit was calculated using the following equation.

$$\text{Detection limit} = 3 \times \sigma/K$$

σ = Standard deviation of blank measurement = 0.30602

K = Slope between the ratio of emission intensity versus $[I^-]$ = -2364326

= 3 x 0.30602/2364326 = 3.88 $\times 10^{-7}$M = 49.30 µg.

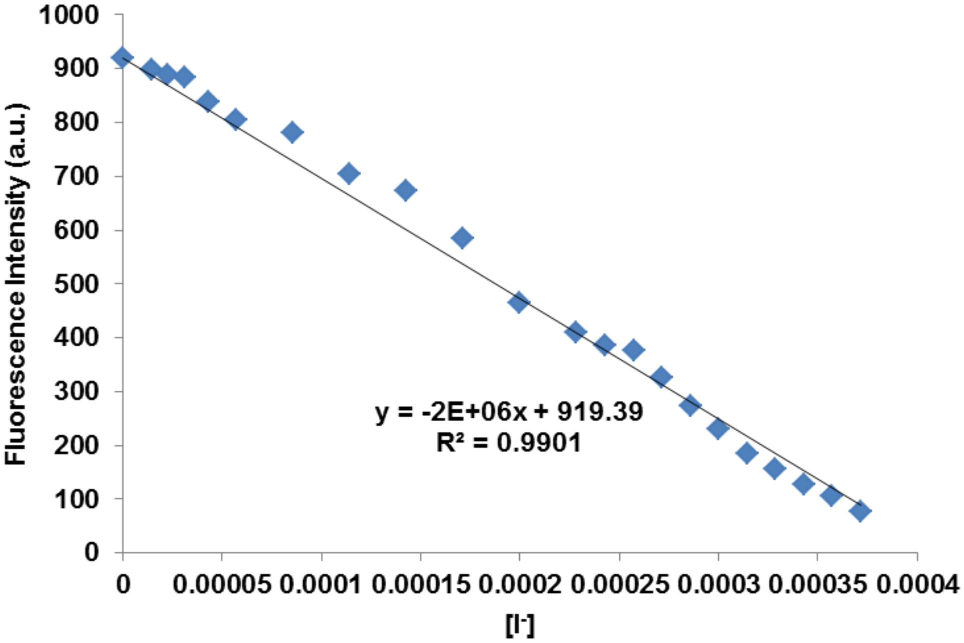

Fig. S9 Plot of emission intensity of **6** (1×10^{-5} M) in 50:50 *v/v*, THF:HB fraction, pH 6.99, $\lambda_{exc.}$= 342 nm with iodide (3.71×10^{-4} M) in H_2O.

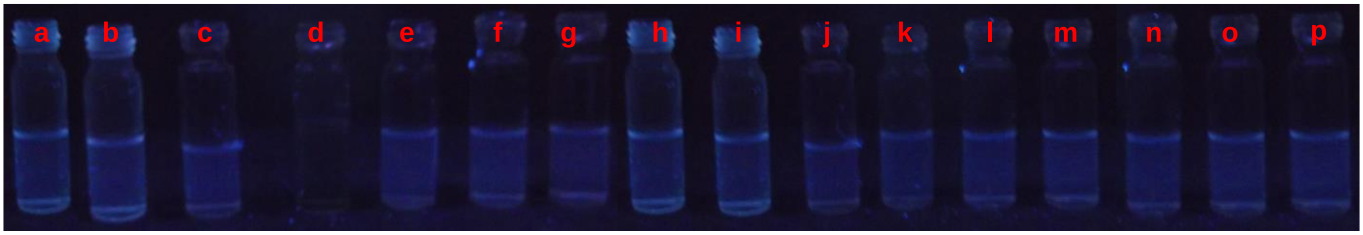

Fig. S10 Visually perceived change in emission intensity of **6** (1×10^{-5} M) in 50:50 *v/v*, THF:HB fraction, pH 6.99, in the presence of various anions (3.71×10^{-4} M) in H_2O (a) **6**, (b) Cl^-, (c) Br^-, (d) I^-, (e) F^-, (f) HSO_4^-, (g) $C_6H_5O_7^{3-}$, (h) SO_3^{2-}, (i) HCO_3^-, (j) PO_4^{3-}, (k) CO_3^{2-}, (l) HSO_3^-, (m) SO_4^{2-}, (n) CH_3COO^-, (o) OH^- and (p) NO_3^-.

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(3) Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

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