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Multi-functionalized MOFs with Large-Pore Apertures as Luminescent Probes for Efficient Sensing of Quinones

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1. Experimental Section

1.1 Materials and Methods

All reagents for the syntheses and analysis were commercially available and used as received. The infrared spectra were recorded on a Nicolet Fourier Transform IR, Nicolet 100 spectrometer in the range 500-4000 cm^{-1} using the KBr disk technique. Crystallographic measurement for TMU-84 was undertaken on the MX1 beamline at the Australian Synchrotron, part of ANSTO,[1] and TMU-85 at 175(1) K for TMU-85 using Rigaku XtaLabPro mm003 Pilatus 200, delivering, MoK_α (λ = 0.71073 Å) radiation. Melting points were measured on an Electrothermal 9100 apparatus. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromated Co-K_α (1.78897 Å)

radiation. Elemental analyses were collected on a CHNS Thermo Scientific Flash 2000 elemental analyzer. The molecular structure scheme and simulated XRD powder pattern based on single crystal data were prepared using Mercury software. Details relating to the crystals and the structural refinements are presented in Table S1. Full details of crystals data and structure refinements, in CIF format, are available as Supplementary Information CCDC 1864216 and 2084352 for TMU-84 and TMU-85 respectively.

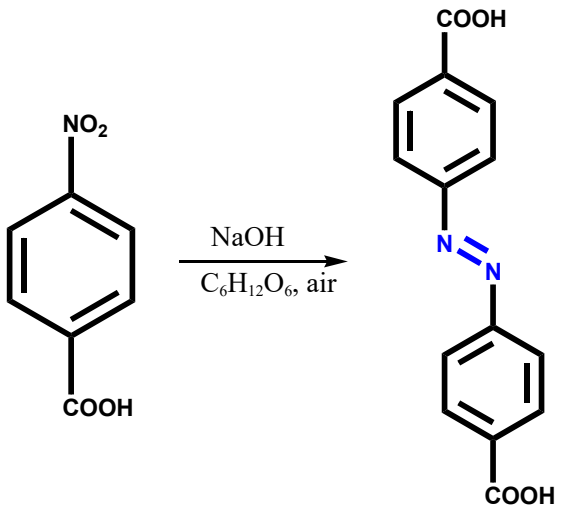
1.2 Synthesis of azine and azobenzen based ligands

The azobenzene-4,4-dicarboxylic acid was synthesized according to the reported procedure. In summary, 12 mmol of 4-nitrobenzoic acid (2.0 g) and 144 mmol NaOH (5.75 g) were dissolved in 30 mL of distillated water. By adding 20 mL of glucose (13.0 g, 72 mmol) aqueous solution (70 ˚C), a yellow precipitate formed which was vigorously stirred and upon further addition of glucose a brown solution resulted. The mixture was refluxed overnight under a stream of air. The light brown precipitate was dissolved in water, and the pH adjustment in range of 5-6 was done by acetic acid. The light pink precipitate was filtered and washed several times by water and dried in vacuum to give azobenzene-4,4-dicarboxylic acid (Scheme S1). Yield: 65%. ^{1}H NMR (500 MHz, DMSO-d6) d (ppm): 8.3 (d, 4H, J = 8.4 Hz), 8.15 (d, 4H, J = 8.4 Hz). Synthesis of 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (4-bpdh) linker also was done based on literature methods.

X-ray crystallography: TMU-84 was measured at the Australian Synchrotron on the MX1 macromolecular beamline, data integration was completed using XDS[2] software programs. Structural solutions were obtained by charge flipping[3] methods and refined using full-matrix least-squares methods against F2 using SHELX2015, [3] in conjunction with Olex2 [3] graphical user interface. All hydrogen atoms were placed in calculated positions using the riding model.

Table S.1. Crystals data and structure refinements of TMU-84 and TMU-85.

Identification code	TMU-84	TMU-85
Chemical formula	C_{28} H_{22} Cd N_6 O_4,1.5(C_3 H_7 N O),O	C21 H15 N4 O4 Zn
computing_structure_refinement	SHELXL-2018/3	SHELXL-2018/3
Chemical formula weight	700.01	775.29
T(K)	100.2	293.2
Crystal syst	Monoclinic	Triclinic
Space group	P 2/n	P -1
a (°A)	9.6230(19)	17.0853(7)
b (°A)	12.319(3)	17.0996(6)
c (°A)	30.374(6)	18.1213(7)
α (deg)	90	93.078(3)
β (deg)	91.18(3)	102.821(3)
γ (deg)	90	105.231(3)
V (Å^3)	3599.94	4945.4
Z	4	4
F(000)	1648	1597
R(int)	0.1064	0.0830
Goodness-of-fit on F^2	1.369	1.086
wR factor	0.2667	0.2337
CCDC number	1864216	2084352



Scheme 1. Schematic representation of the production of $adcH_2$ ligand.

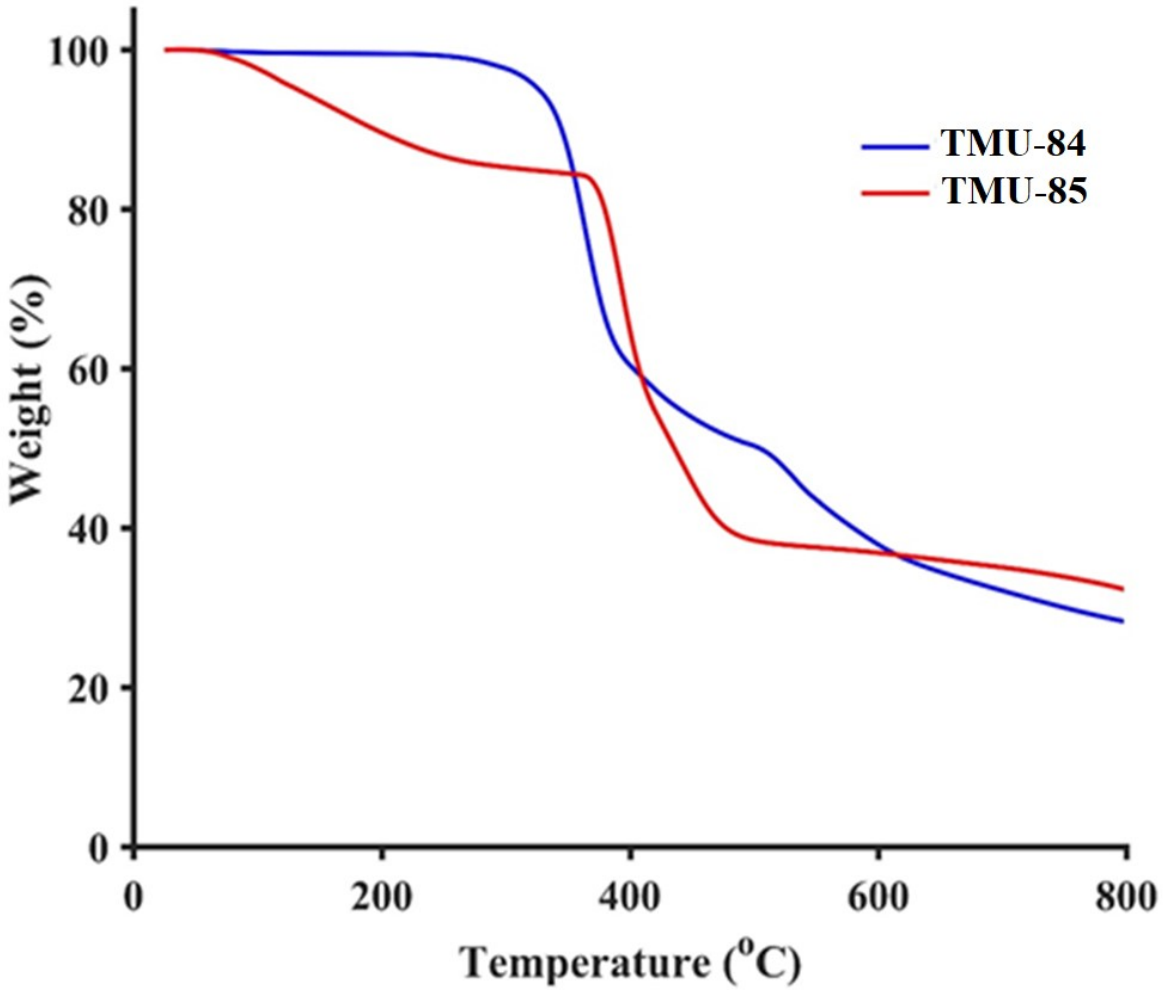


Figure S1. Thermogravimetric analysis of TMU-84 and TMU-85.

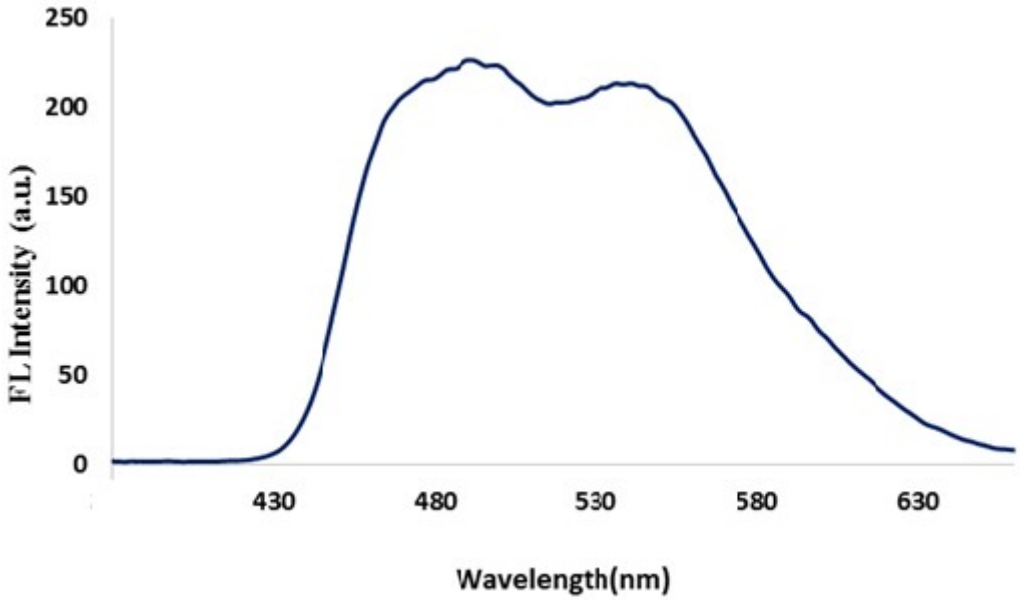


Figure S2: Fluorescence emission spectra of hydroxyanthraquinone

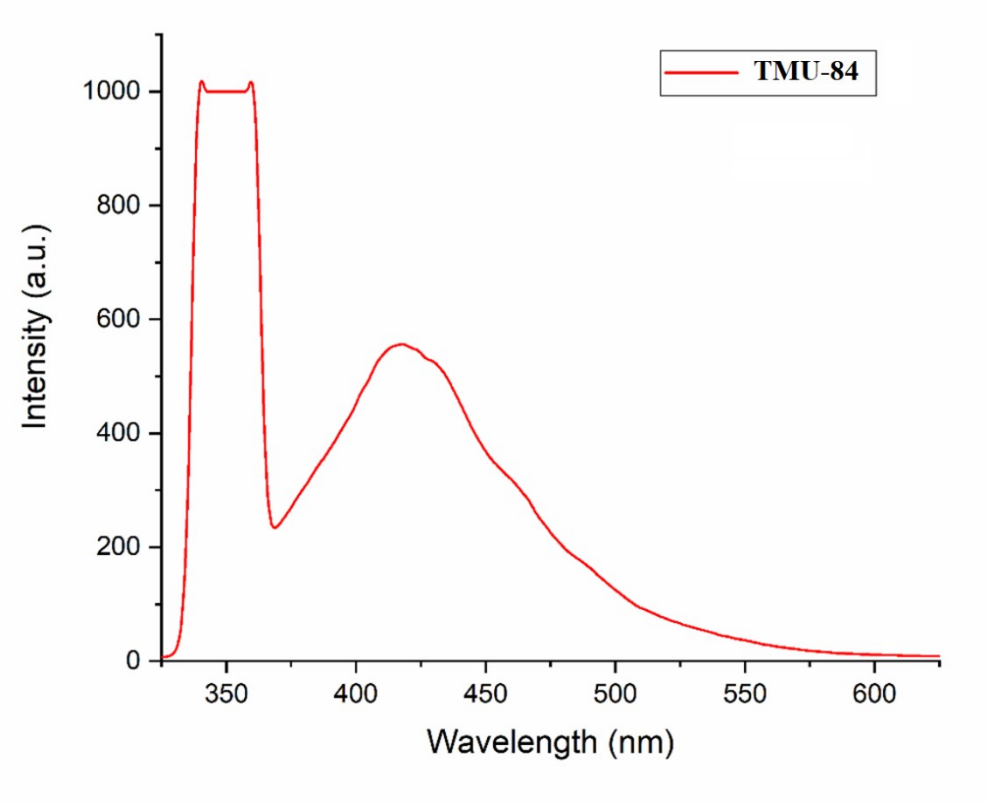


Figure S3: Fluorescence excitation and emission spectra of TMU-84

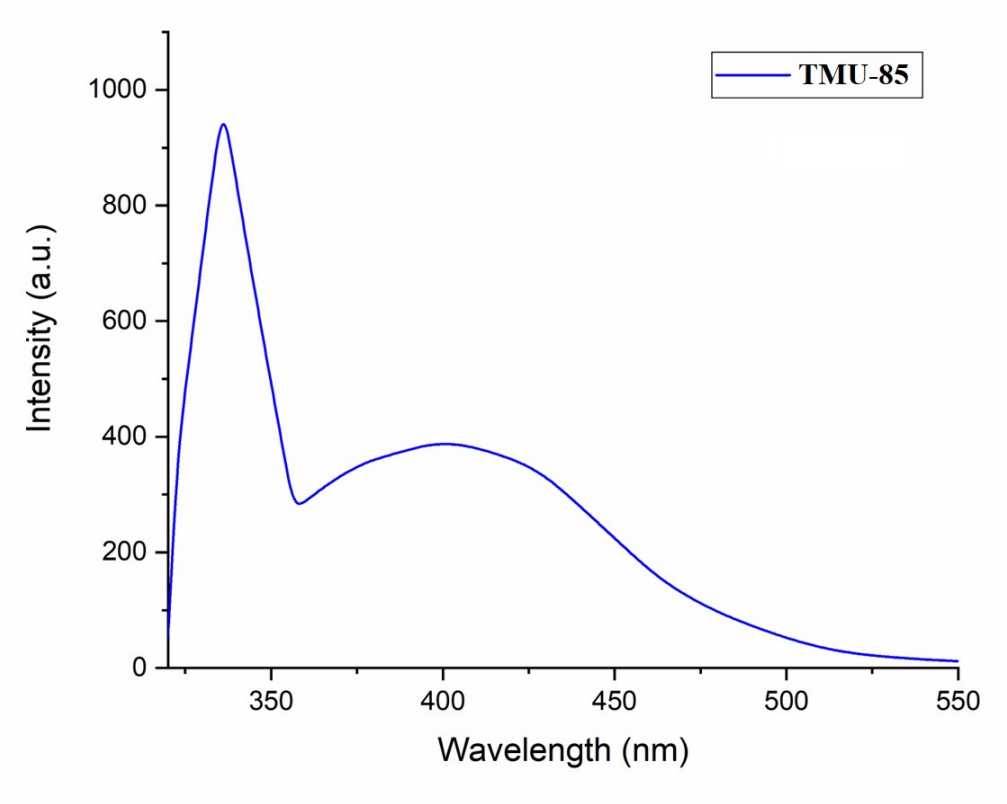


Figure S4: Fluorescence excitation and emission spectra of TMU-84

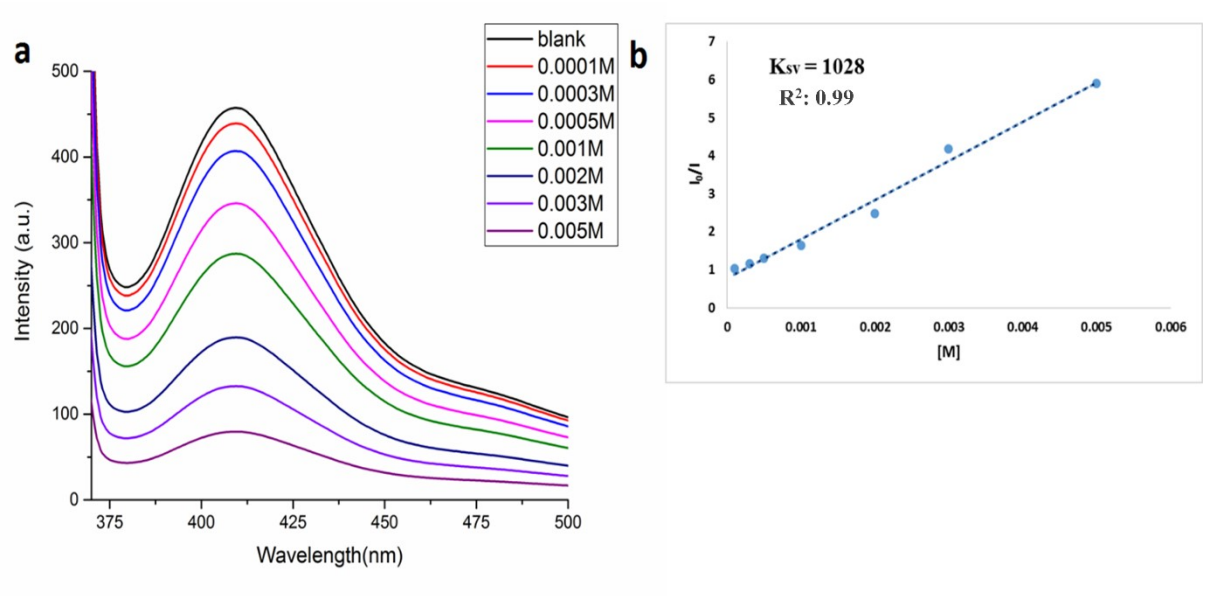


Figure S5: Fluorescence emission spectra of TMU-84 dispersed in EtOH solution of Naphthoquinone at different concentrations, (a). Stern–Volmer (SV) plots in the presence of 3 mg of TMU-84 in different Naphthoquinone (b)

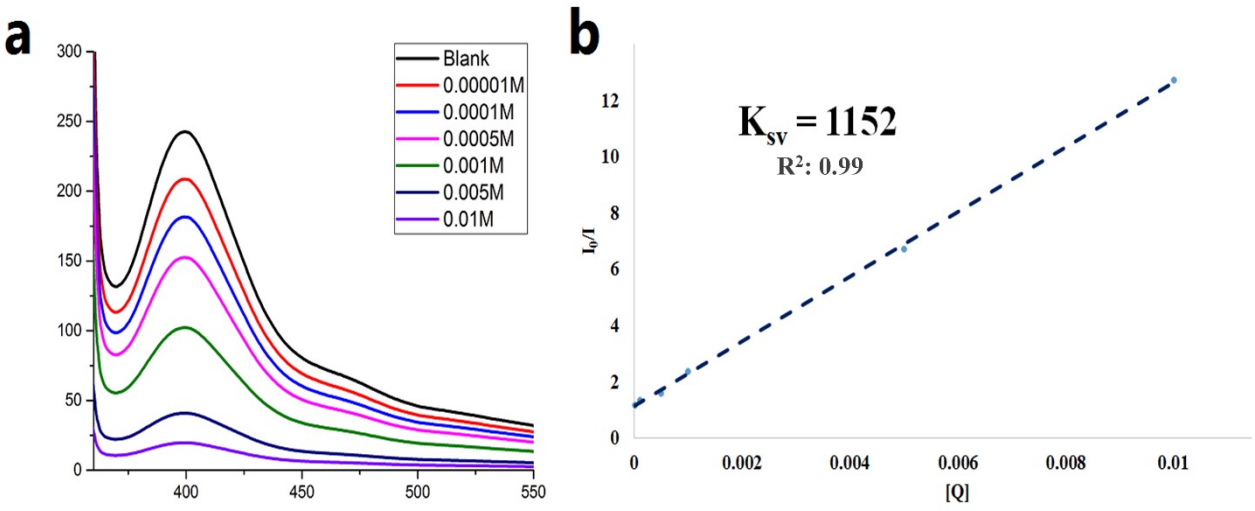


Figure S6: Fluorescence emission spectra of TMU-85 dispersed in EtOH solution of Naphthoquinone at different concentrations, (a). Stern–Volmer (SV) plots in the presence of 3 mg of TMU-85 in different Naphthoquinone (b)

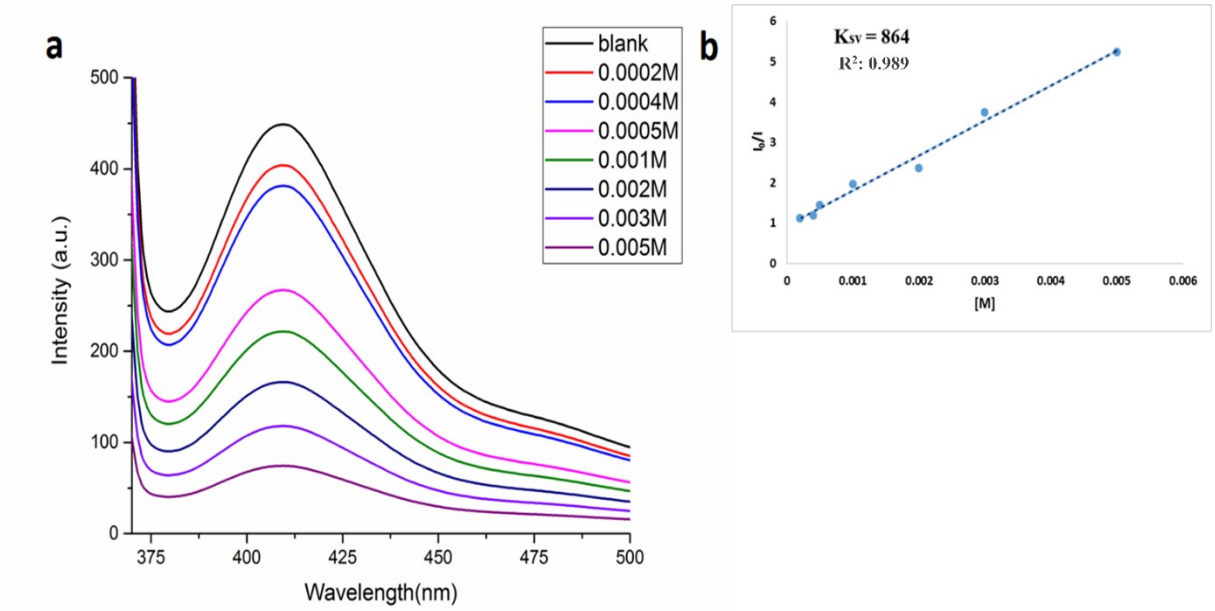


Figure S7: Fluorescence emission spectra of TMU-84 dispersed in EtOH solution of anthraquinone at different concentrations, 3(a). Stern–Volmer (SV) plots in the presence of 3 mg of TMU-84 in different anthraquinone (b)

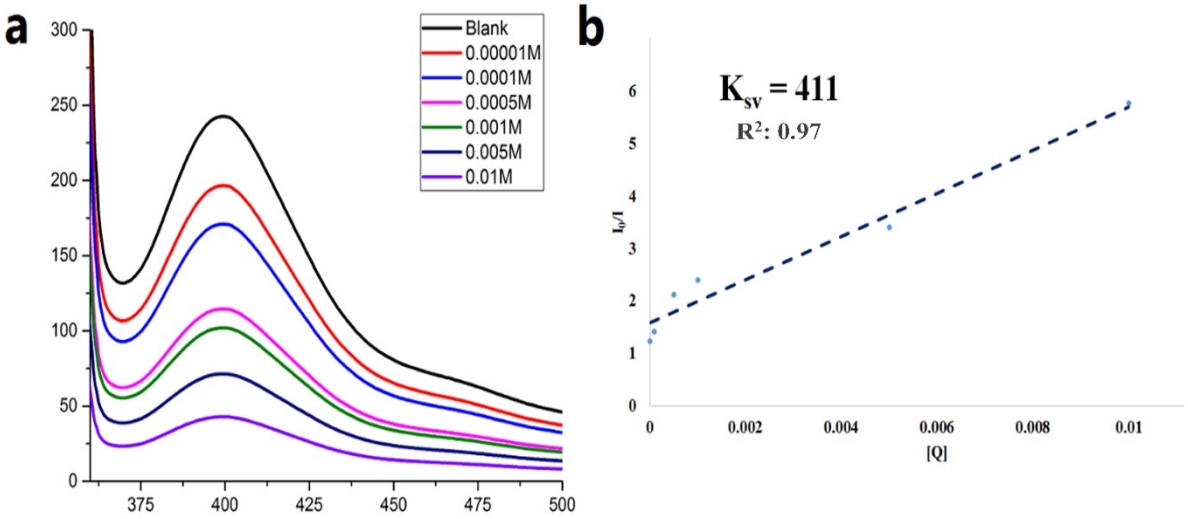


Figure S8: Fluorescence emission spectra of TMU-85 dispersed in EtOH solution of anthraquinone at different concentrations, (a). Stern–Volmer (SV) plots in the presence of 3 mg of TMU-85 in different anthraquinone (b)

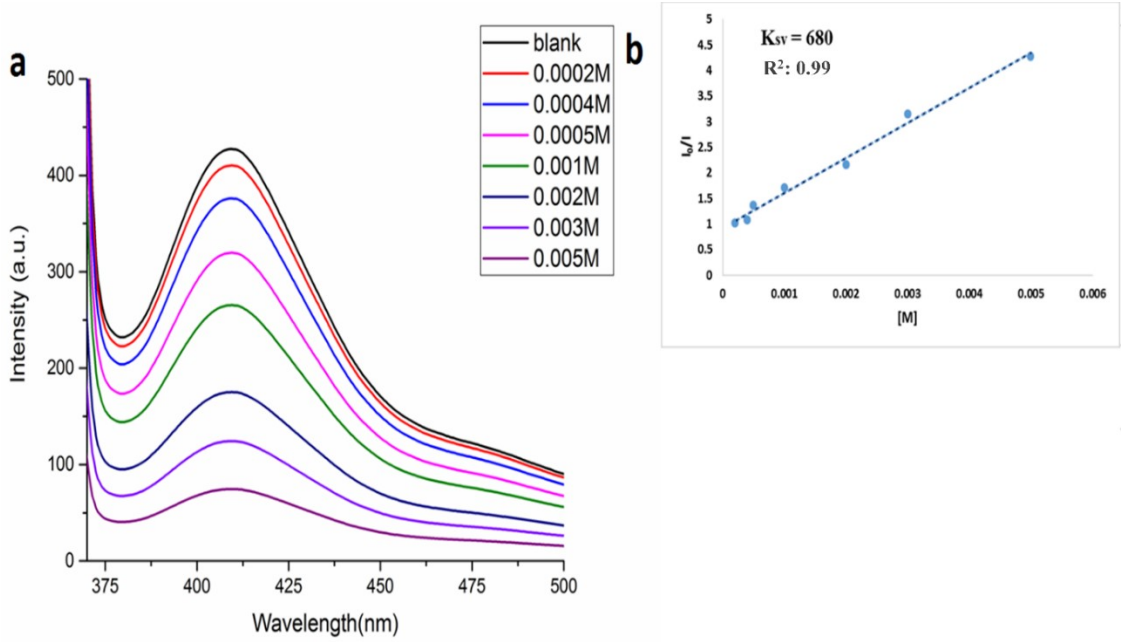


Figure S9: Fluorescence emission spectra of TMU-84 dispersed in EtOH solution of anthraquinone at different concentrations, (a). Stern–Volmer (SV) plots in the presence of 3 mg of TMU-84 in different 1,4-Benzoquinone (b)

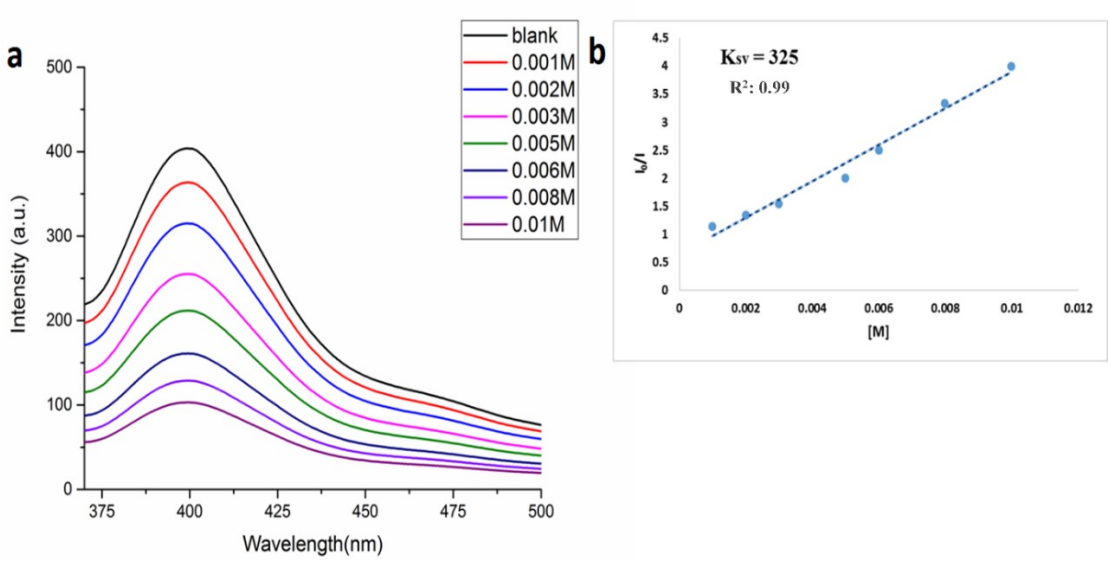


Figure S10: Fluorescence emission spectra of TMU-85 dispersed in EtOH solution of anthraquinone at different concentrations, (a). Stern–Volmer (SV) plots in the presence of 3 mg of TMU-85 in different 1,4-Benzoquinone (b)

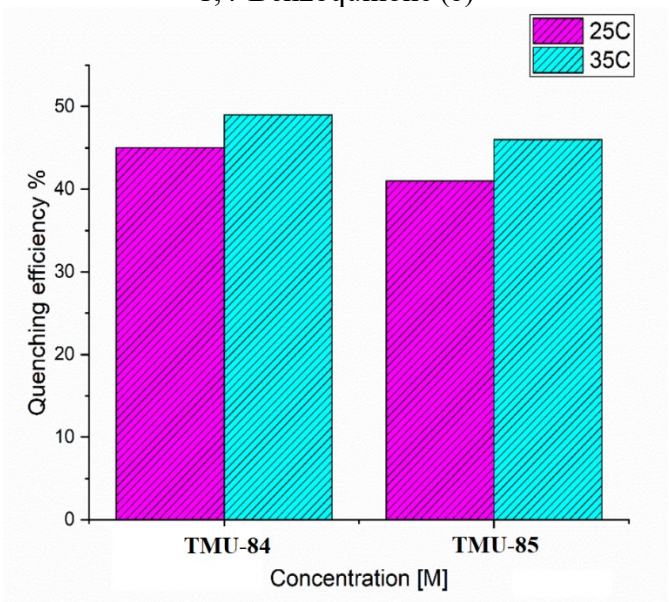


Figure S11: The quenching efficiency at temperatures 25 °C and 35 °C for Danthron detection in 0.0005M

References

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4. R3 G. M. Sheldrick, Acta Cryst. 2015, C71, 3-8.