Electronic Supplementary Information

Naphthalene-tagged highly stable and reusable luminescent metal-organic probes for selective and fast detection of 4-nitroaniline in water

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Section S-1: Spectroscopic characterization of **1- 4**

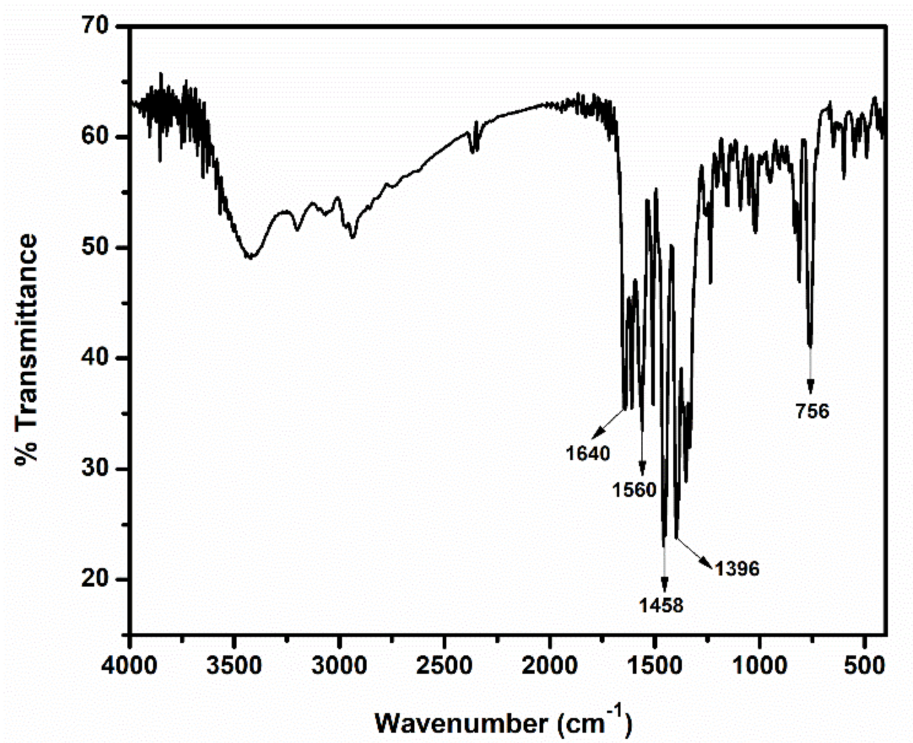


Fig. S1 FTIR spectrum of **1**.

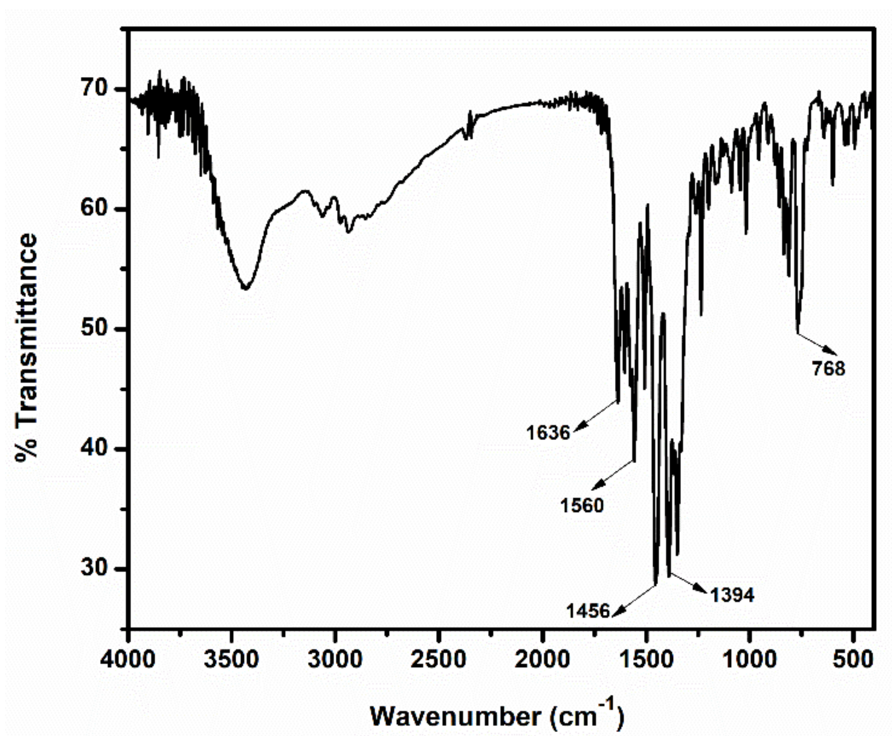


Fig. S2 FTIR spectrum of **2**.

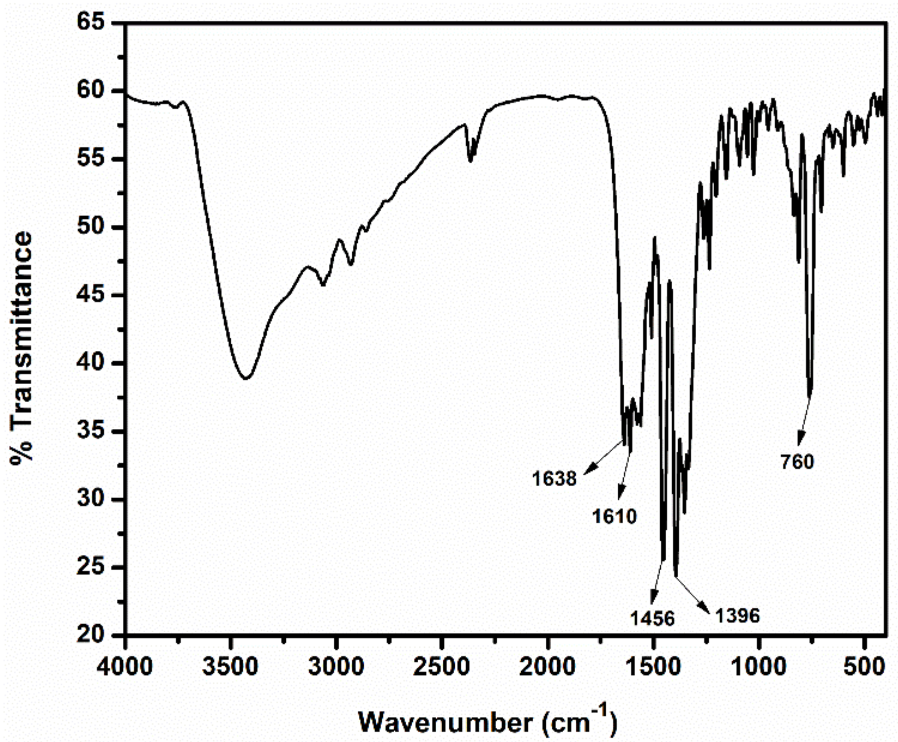


Fig. S3 FTIR spectrum of **3**.

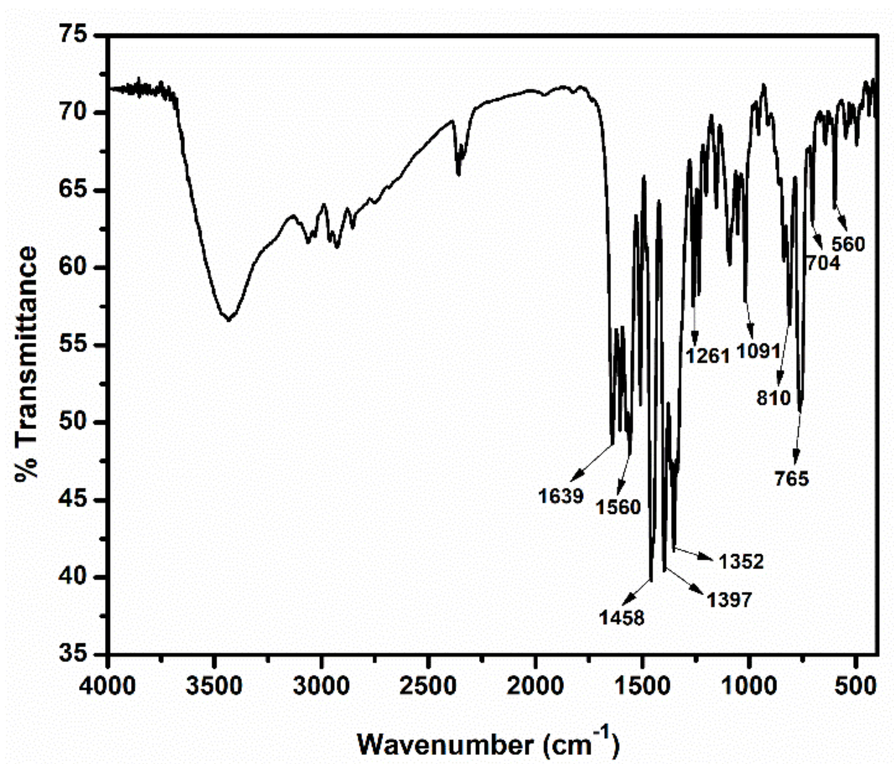
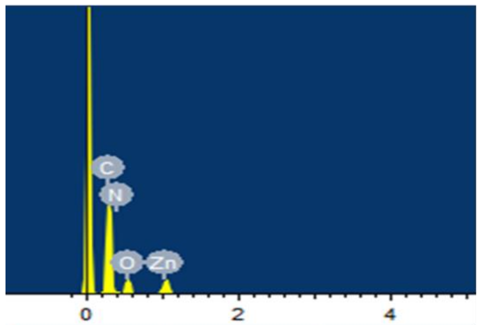


Fig. S4 FTIR spectrum of **4**.

Section S-2: Study of surface morphology of **1-4**



Element	Weight%	Atomic%
C	63.64	73.14
N	6.85	6.75
O	21.31	18.38
Zn	8.20	1.73

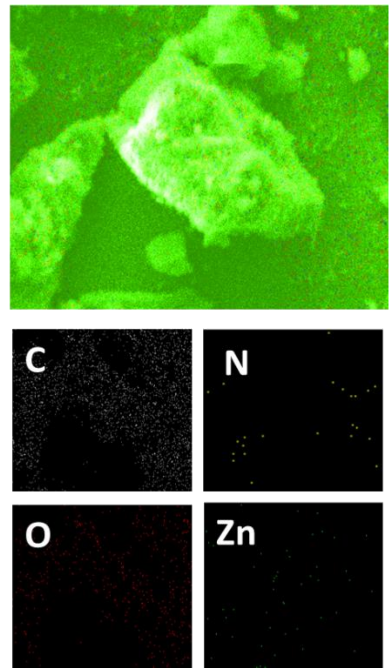
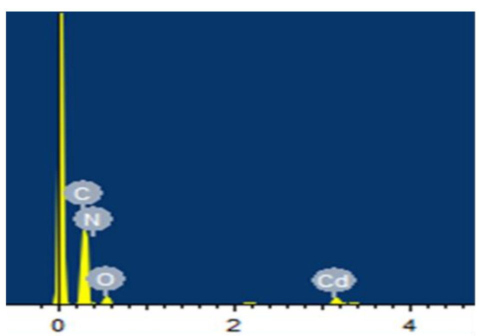


Fig. S5 EDX and elemental mapping of **1**.



Element	Weight%	Atomic%
C	63.88	77.59
N	1.26	1.31
O	21.19	19.32
Cd	13.67	1.77

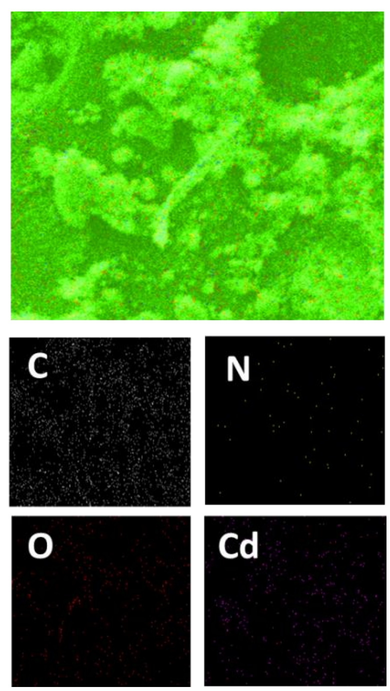
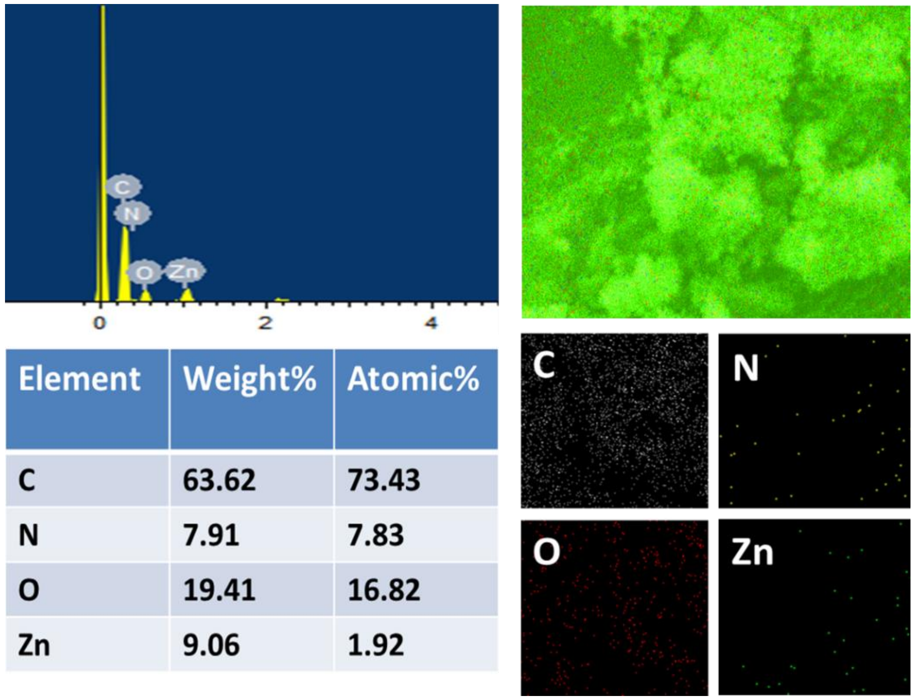
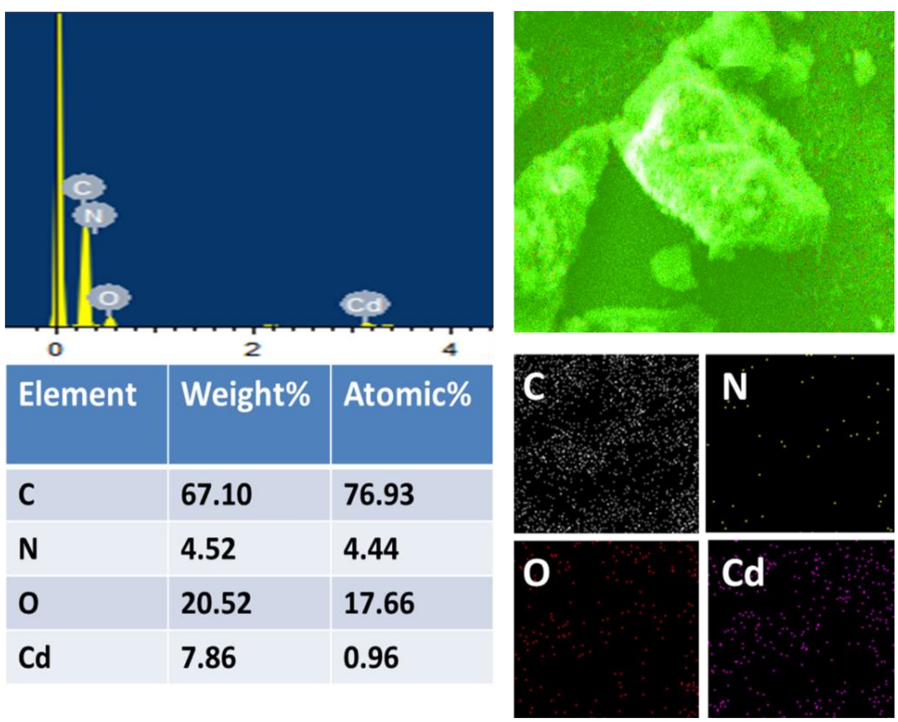


Fig. S6 EDX and elemental mapping of **2**.



Element	Weight%	Atomic%
C	63.62	73.43
N	7.91	7.83
O	19.41	16.82
Zn	9.06	1.92

Fig. S7 EDX and elemental mapping of **3**.



Element	Weight%	Atomic%
C	67.10	76.93
N	4.52	4.44
O	20.52	17.66
Cd	7.86	0.96

Fig. S8 EDX and elemental mapping of **4**.

Section S-3: Spectroscopic details for the sensing of different amines by **1-4**

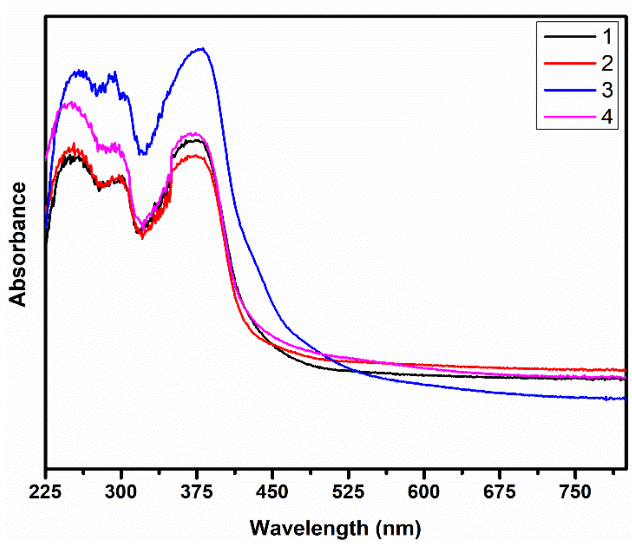


Fig. S9 Solid-state diffuse reflectance spectra of **1-4**.

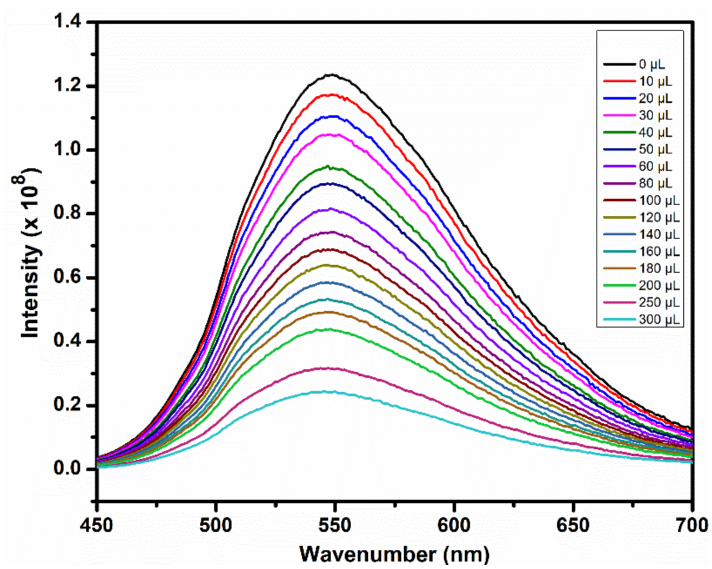


Fig. S10 Emission spectra of **1** dispersed in aqueous solution upon incremental addition of 4-NA solution (1 mM).

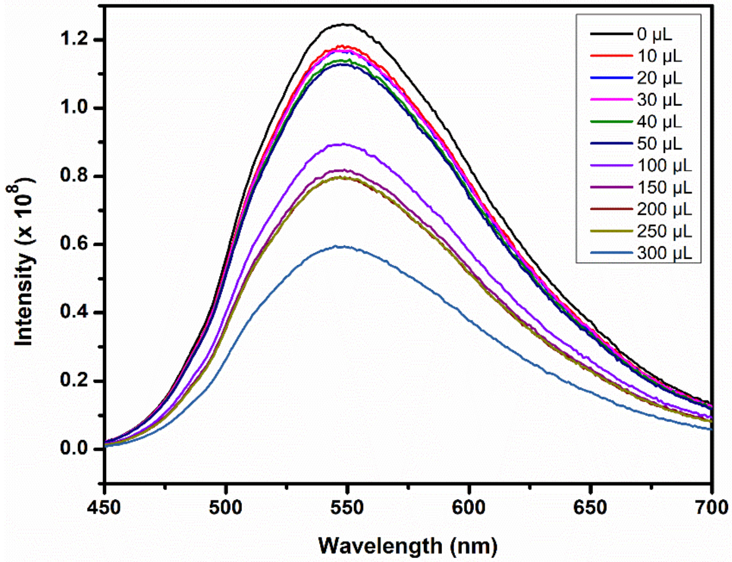


Fig. S11 Emission spectra of **1** dispersed in aqueous solution upon incremental addition of 2,6-DCNA solution (1 mM).

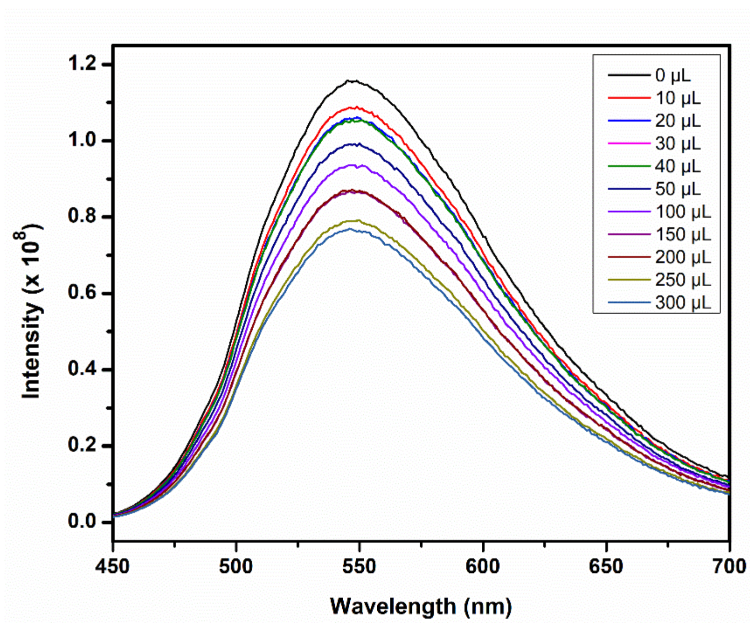


Fig. S12 Emission spectra of **1** dispersed in aqueous solution upon incremental addition of 2,4-DNA solution (1 mM).

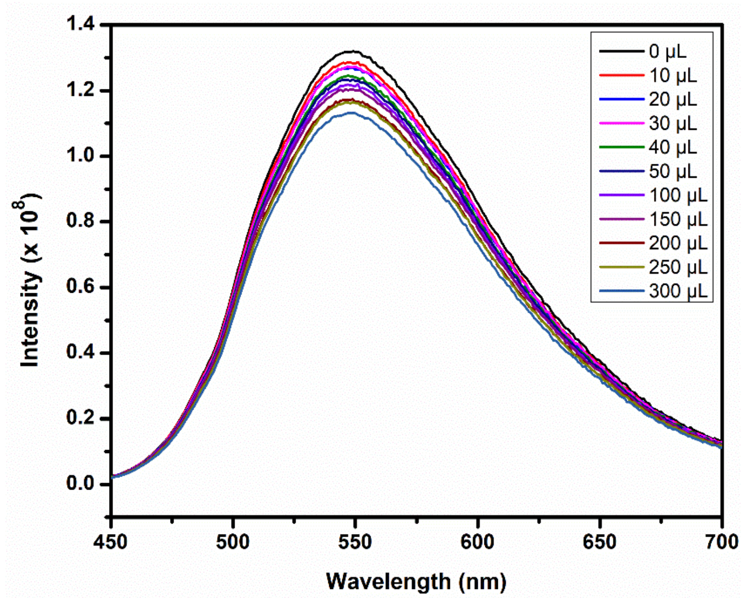


Fig. S13 Emission spectra of **1** dispersed in aqueous solution upon incremental addition of 3-NA solution (1 mM).

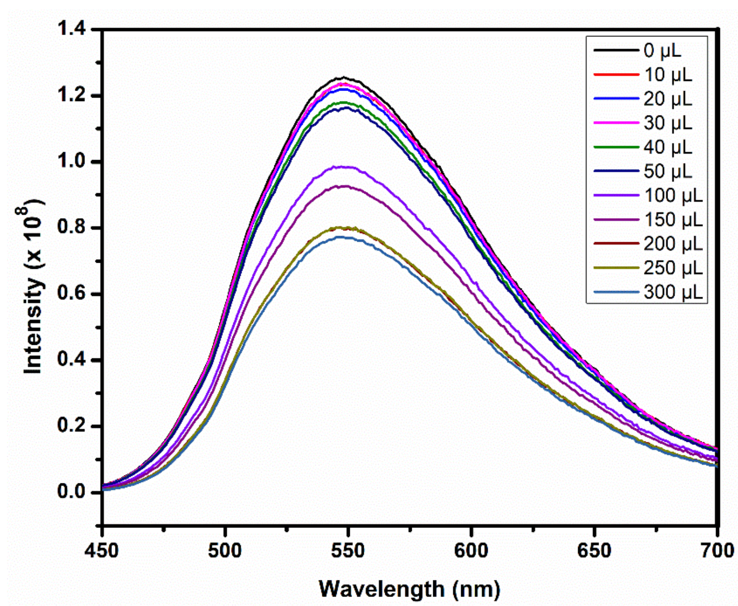


Fig. S14 Emission spectra of **1** dispersed in aqueous solution upon incremental addition of 2-NA solution (1 mM).

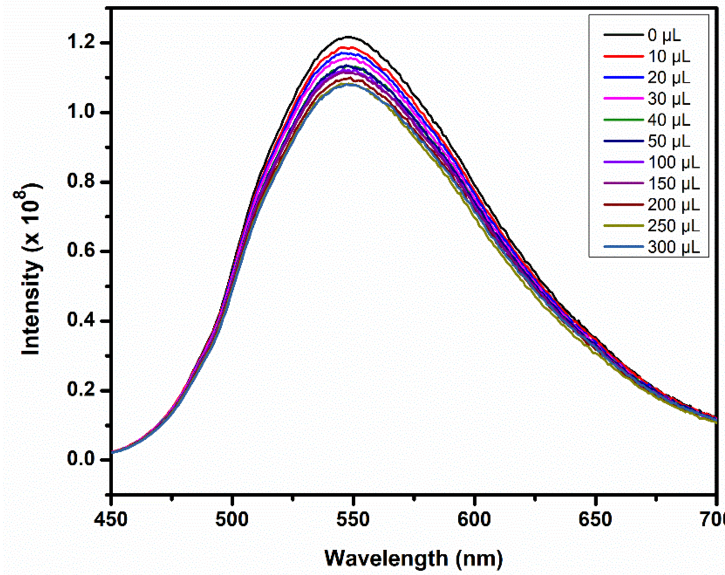


Fig. S15 Emission spectra of **1** dispersed in aqueous solution upon incremental addition of Aniline solution (1 mM).

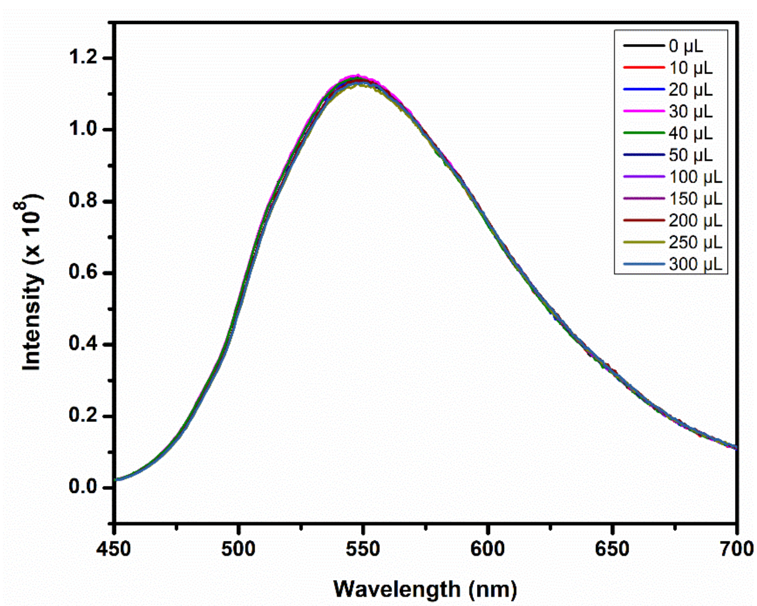


Fig. S16 Emission spectra of **1** dispersed in aqueous solution upon incremental addition of EDA solution (1 mM).

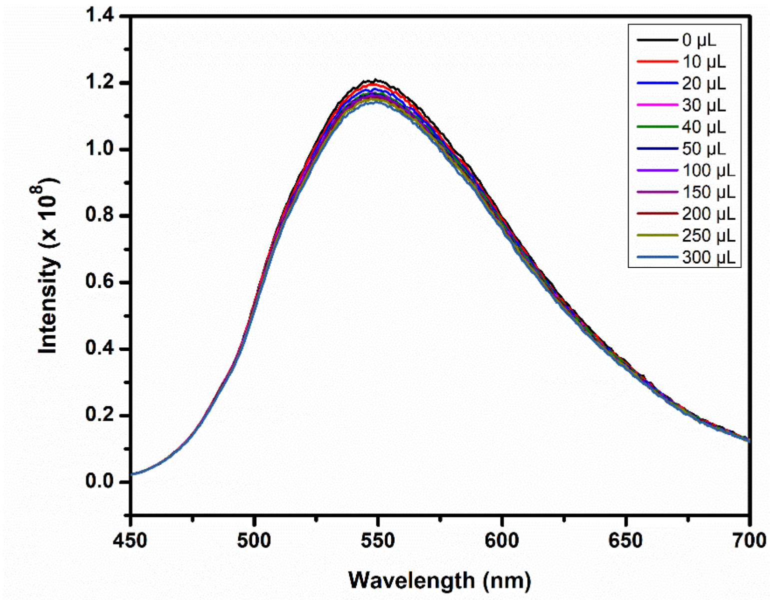


Fig. S17 Emission spectra of **1** dispersed in aqueous solution upon incremental addition of TEA solution (1 mM).

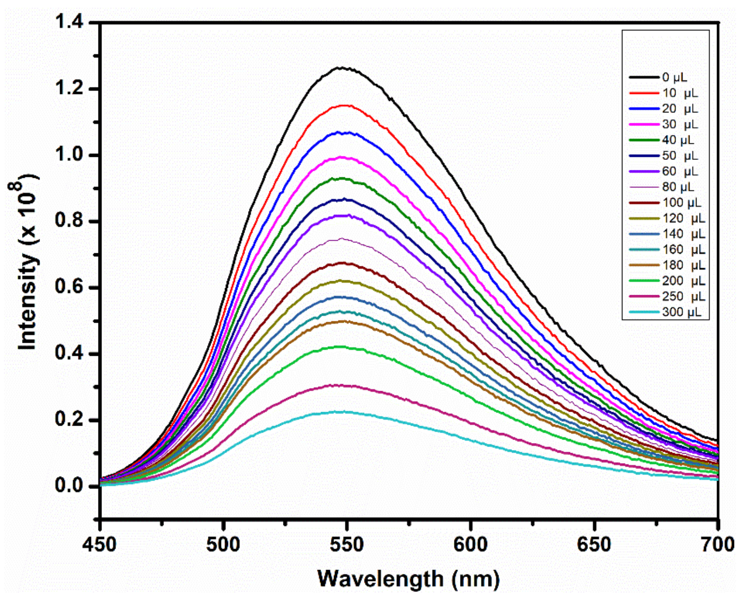


Fig. S18 Emission spectra of **2** dispersed in aqueous solution upon incremental addition of 4-NA solution (1 mM).

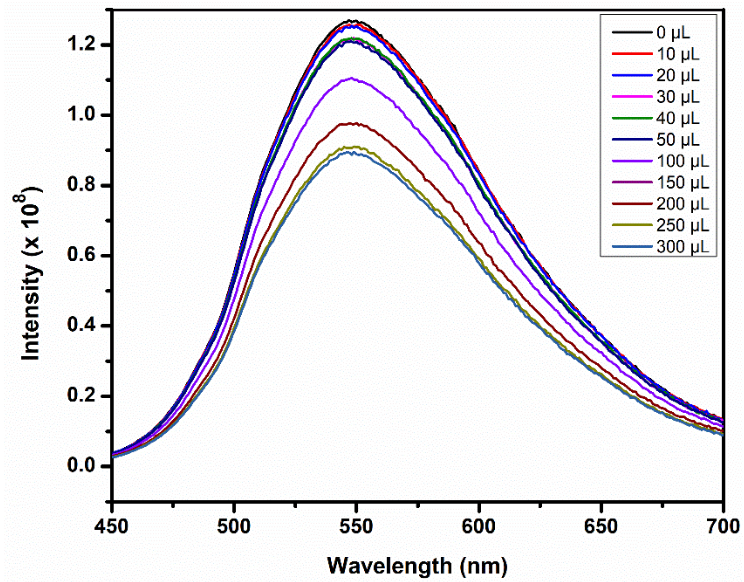


Fig. S19 Emission spectra of **2** dispersed in aqueous solution upon incremental addition of 2,6-DCNA solution (1 mM).

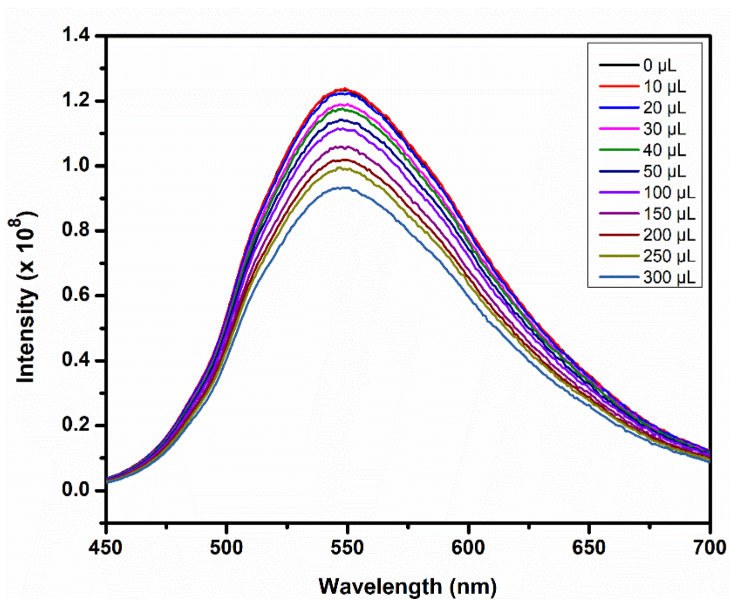


Fig. S20 Emission spectra of **2** dispersed in aqueous solution upon incremental addition of 2,4-DNA solution (1 mM).

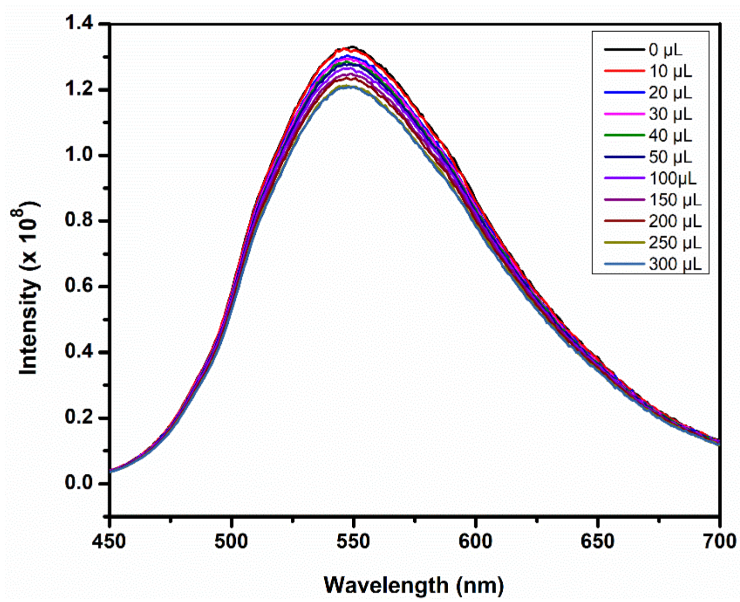


Fig. S21 Emission spectra of **2** dispersed in aqueous solution upon incremental addition of 3-NA solution (1 mM).

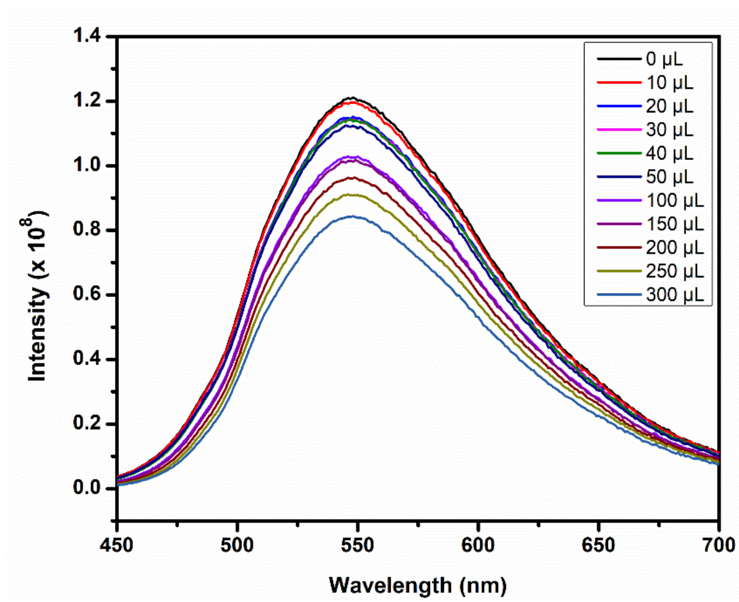


Fig. S22 Emission spectra of **2** dispersed in aqueous solution upon incremental addition of 2-NA solution (1 mM).

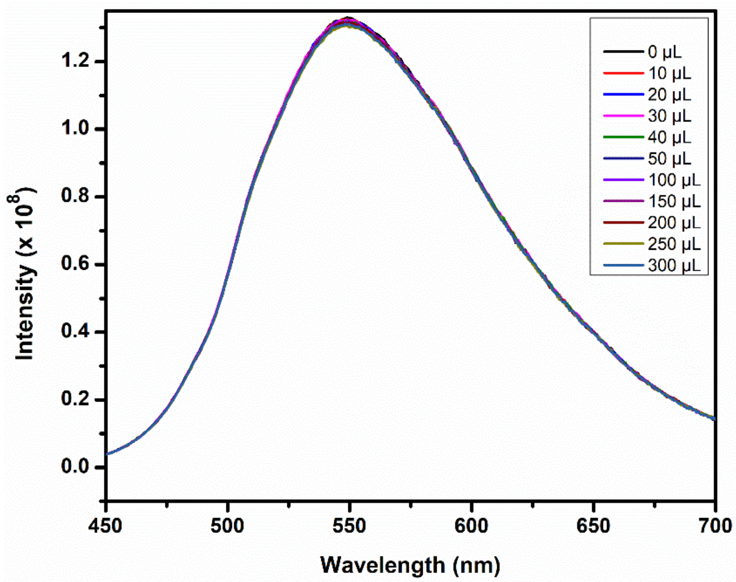


Fig. S23 Emission spectra of **2** dispersed in aqueous solution upon incremental addition of Aniline solution (1 mM).

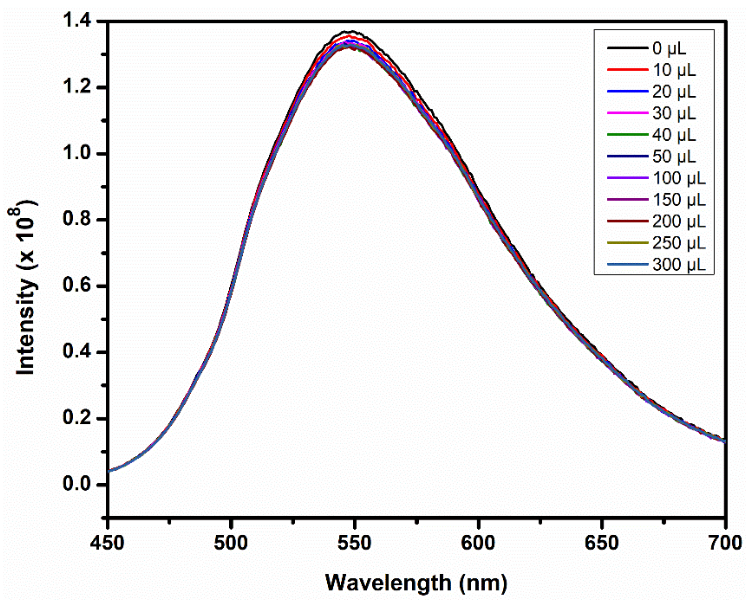


Fig. S24 Emission spectra of **2** dispersed in aqueous solution upon incremental addition of EDA solution (1 mM).

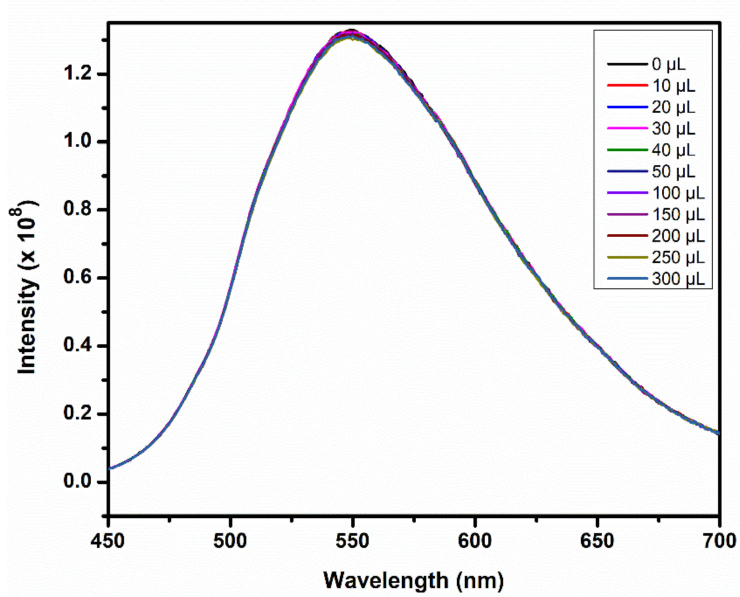


Fig. S25 Emission spectra of **2** dispersed in aqueous solution upon incremental addition of TEA solution (1 mM).

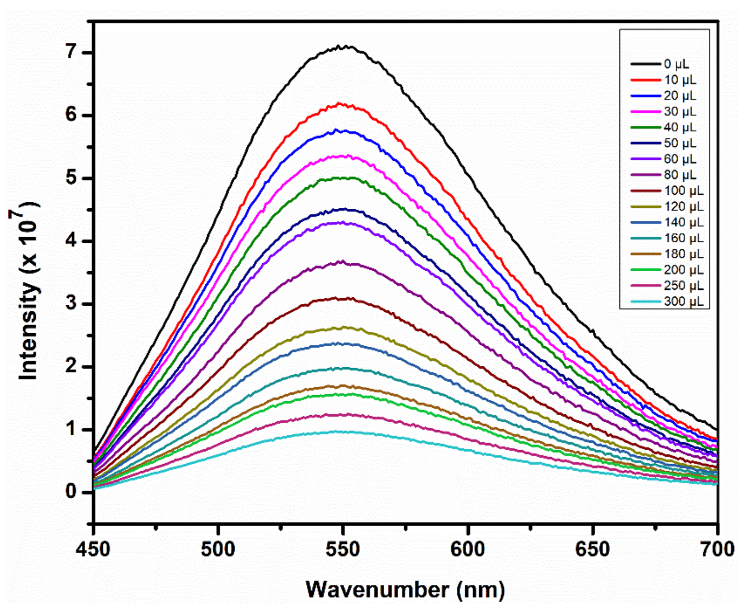


Fig. S26 Emission spectra of **3** dispersed in aqueous solution upon incremental addition of 4-NA solution (1 mM).

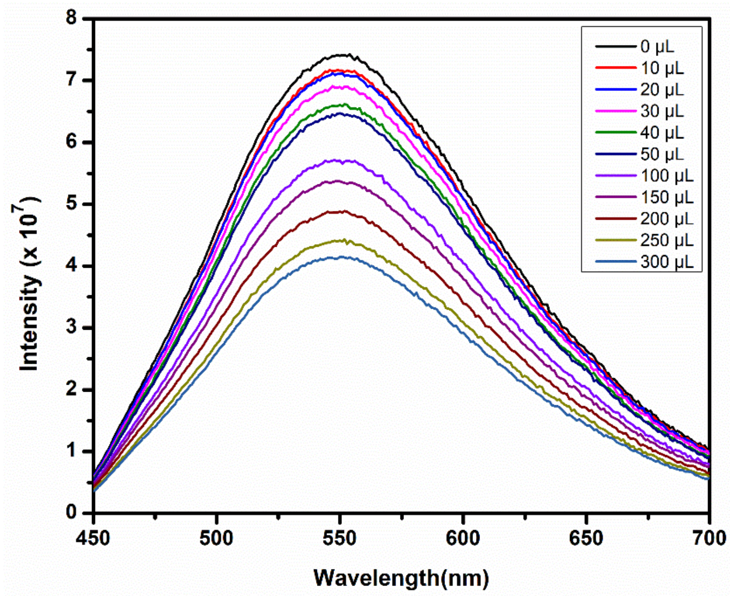


Fig. S27 Emission spectra of **3** dispersed in aqueous solution upon incremental addition of 2,6-DCNA solution (1 mM).

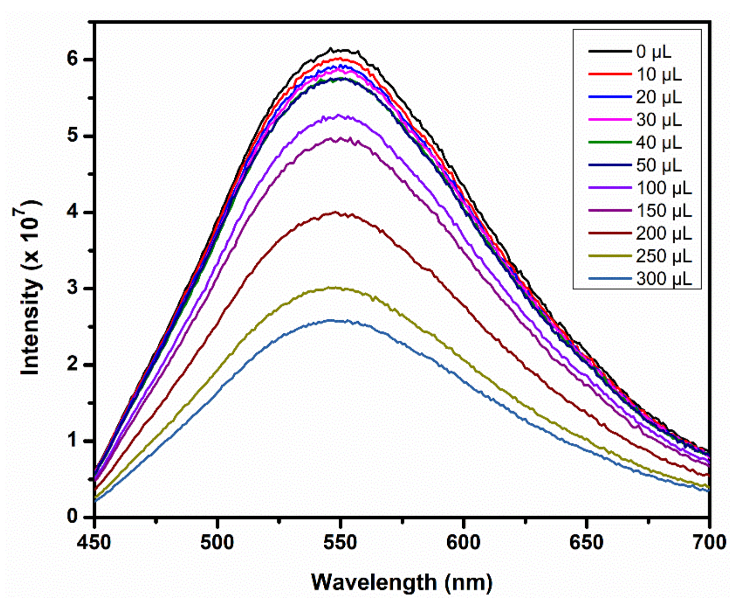


Fig. S28 Emission spectra of **3** dispersed in aqueous solution upon incremental addition of 2,4-DNA solution (1 mM).

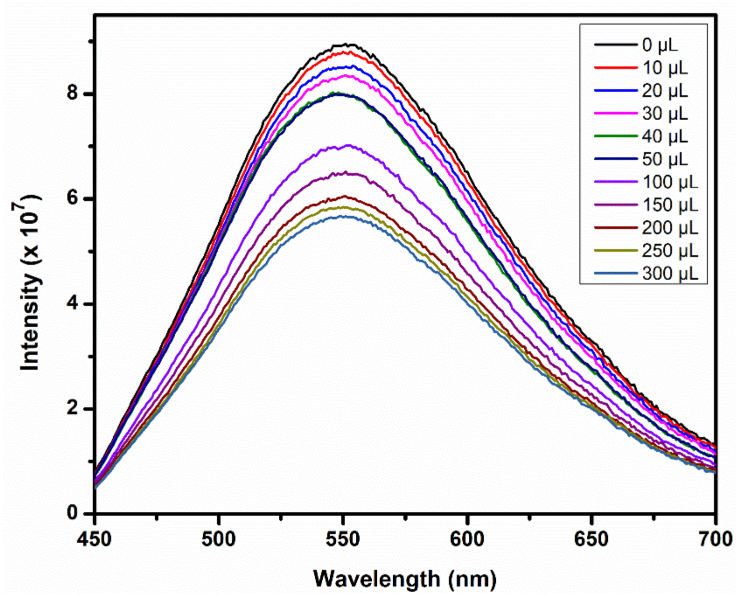


Fig. S29 Emission spectra of **3** dispersed in aqueous solution upon incremental addition of 3-NA solution (1 mM).

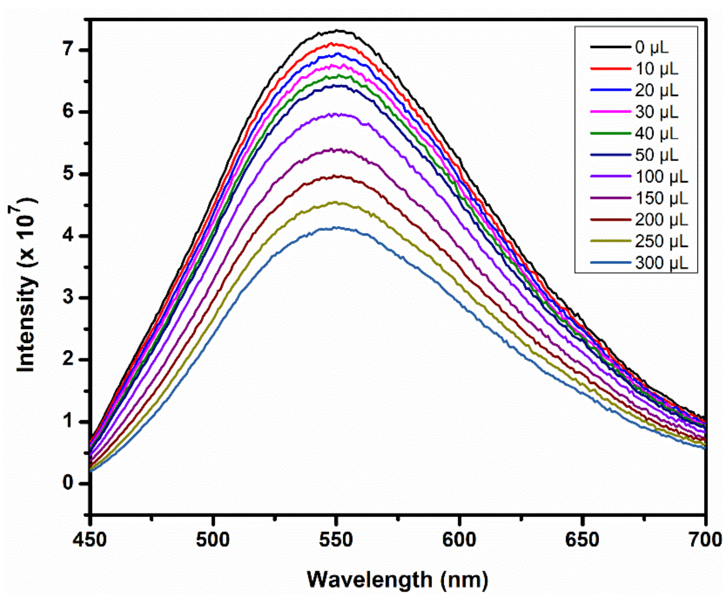


Fig. S30 Emission spectra of **3** dispersed in aqueous solution upon incremental addition of 2-NA solution (1 mM).

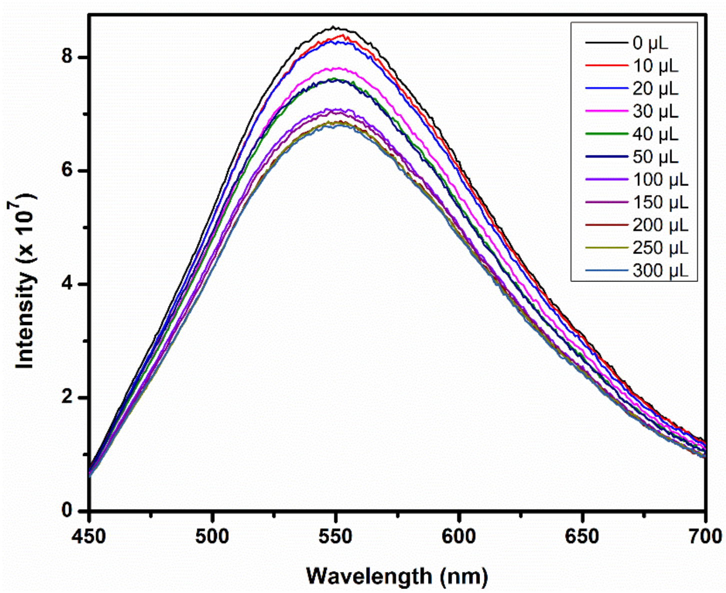


Fig. S31 Emission spectra of **3** dispersed in aqueous solution upon incremental addition of Aniline solution (1 mM).

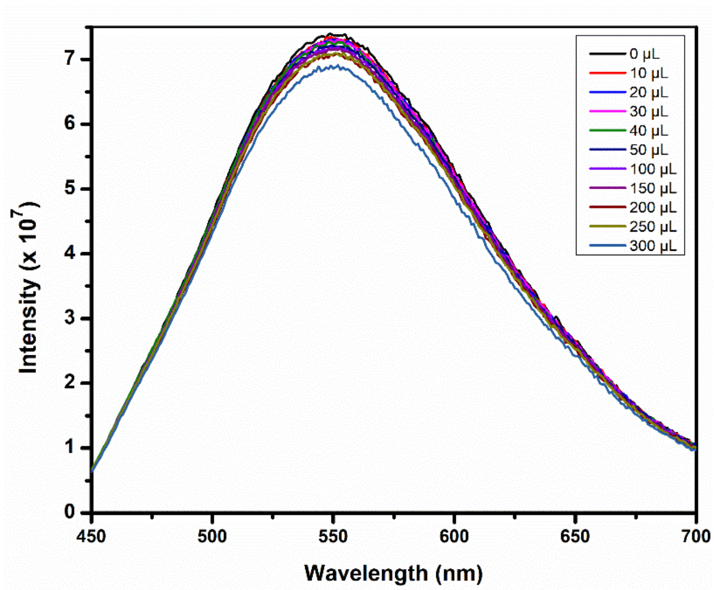


Fig. S32 Emission spectra of **3** dispersed in aqueous solution upon incremental addition of EDA solution (1 mM).

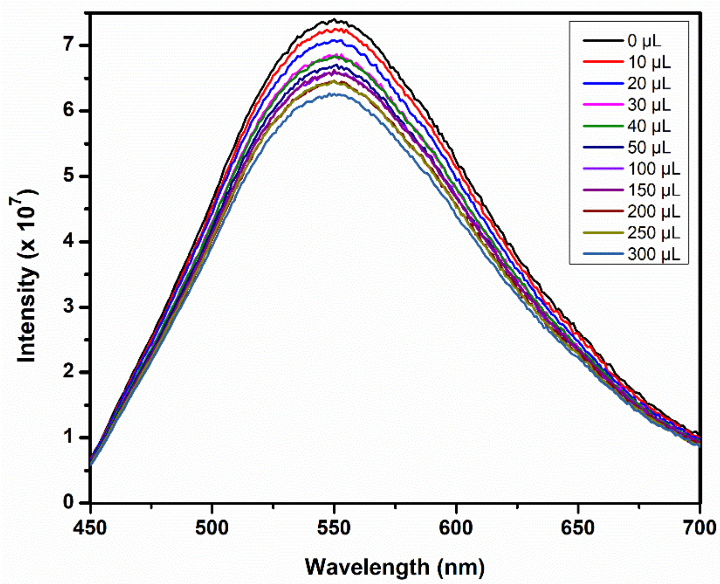


Fig. S33 Emission spectra of **3** dispersed in aqueous solution upon incremental addition of TEA solution (1 mM).

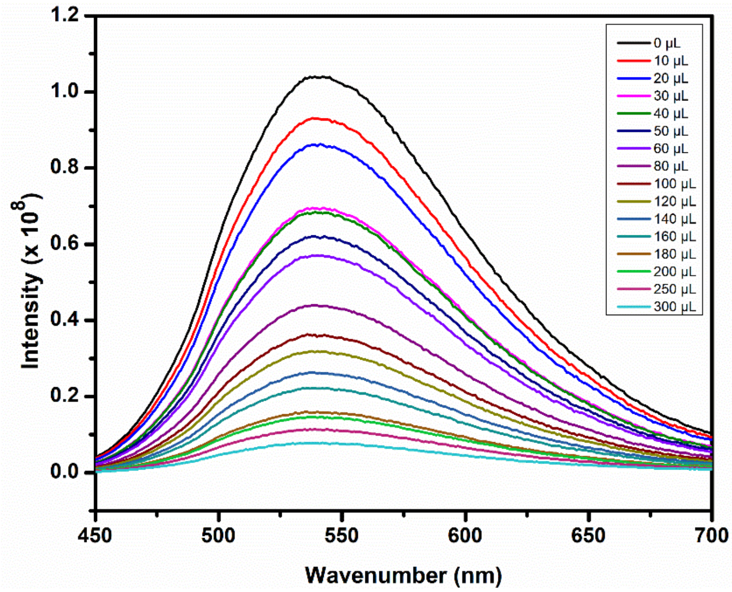


Fig. S34 Emission spectra of **4** dispersed in aqueous solution upon incremental addition of 4-NA solution (1 mM).

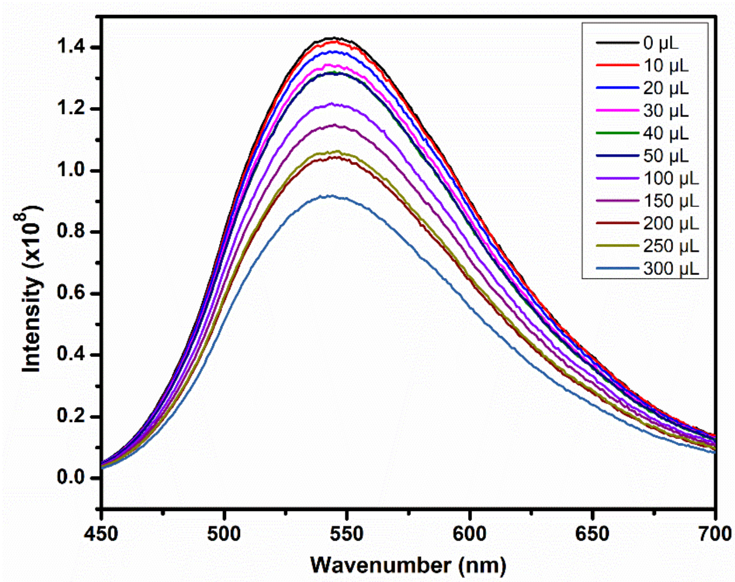


Fig. S35 Emission spectra of **4** dispersed in aqueous solution upon incremental addition of 2,6-DCNA solution (1 mM).

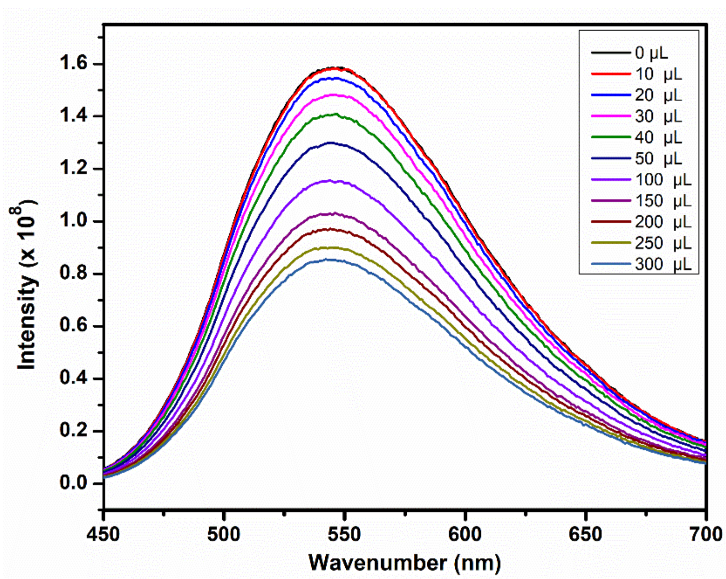


Fig. S36 Emission spectra of **4** dispersed in aqueous solution upon incremental addition of 2,4-DNA solution (1 mM).

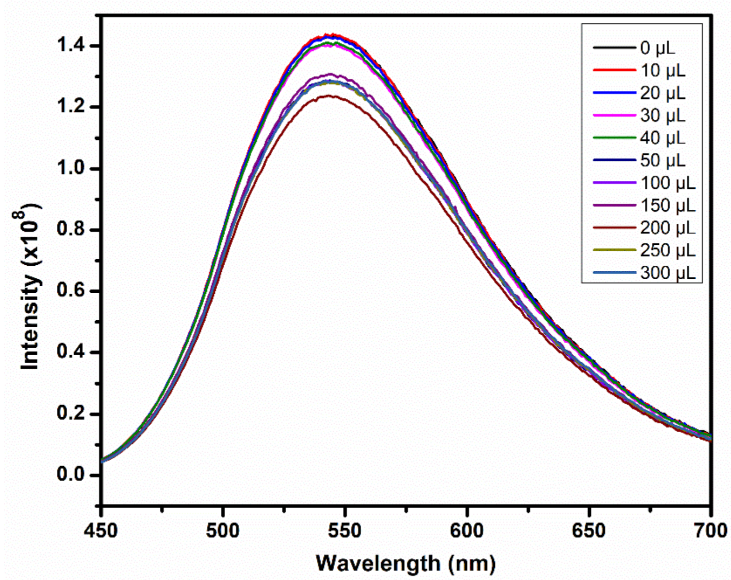


Fig. S37 Emission spectra of **4** dispersed in aqueous solution upon incremental addition of 3-NA solution (1 mM).

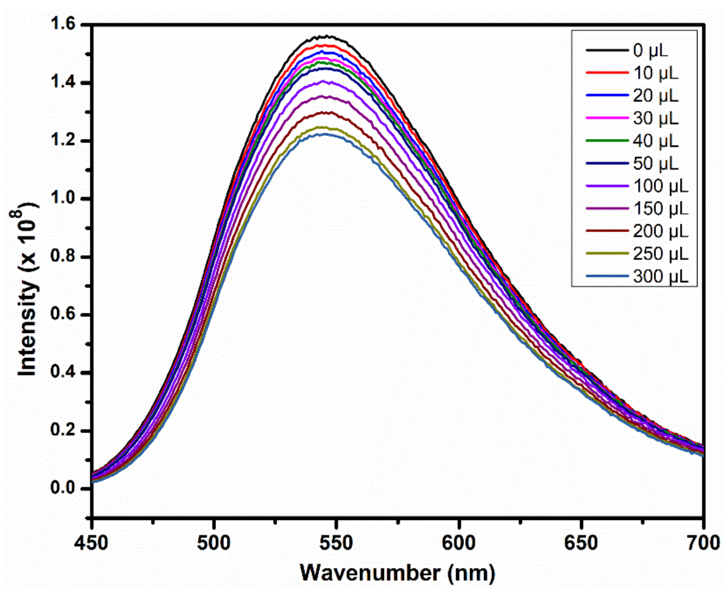


Fig. S38 Emission spectra of **4** dispersed in aqueous solution upon incremental addition of 2-NA solution (1 mM).

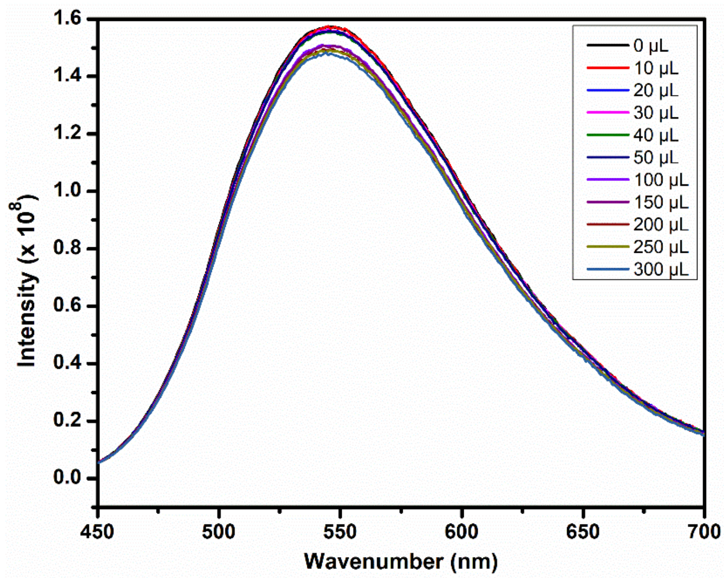


Fig. S39 Emission spectra of **4** dispersed in aqueous solution upon incremental addition of Aniline solution (1 mM).

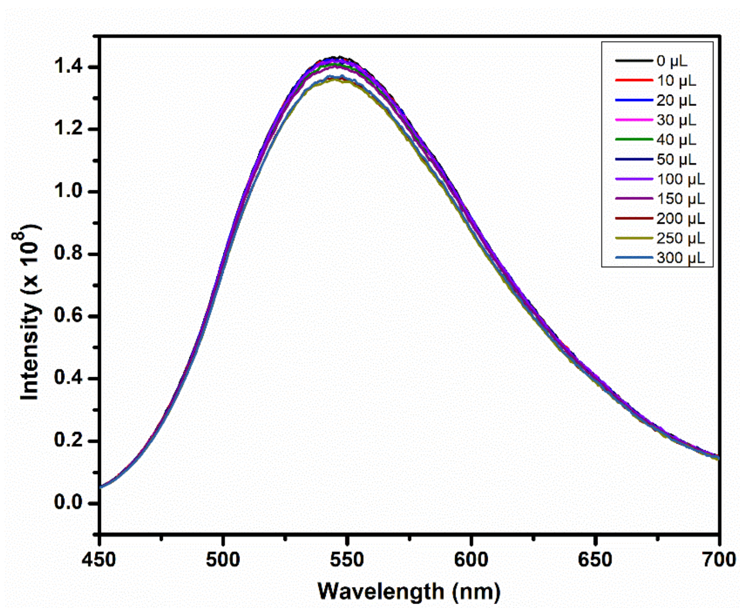


Fig. S40 Emission spectra of **4** dispersed in aqueous solution upon incremental addition of EDA solution (1 mM).

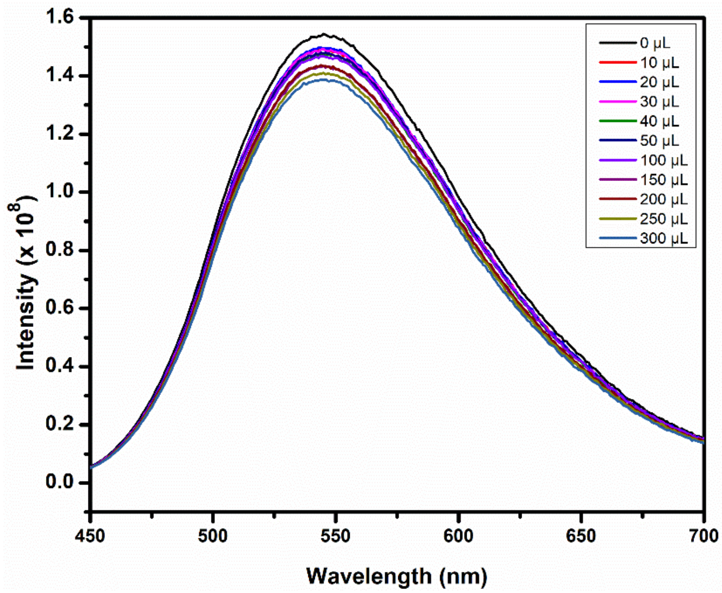


Fig. S41 Emission spectra of **4** dispersed in aqueous solution upon incremental addition of TEA solution (1 mM).

Section S-4: Stern-Volmer plots of 4-NA in presence of **1-4**

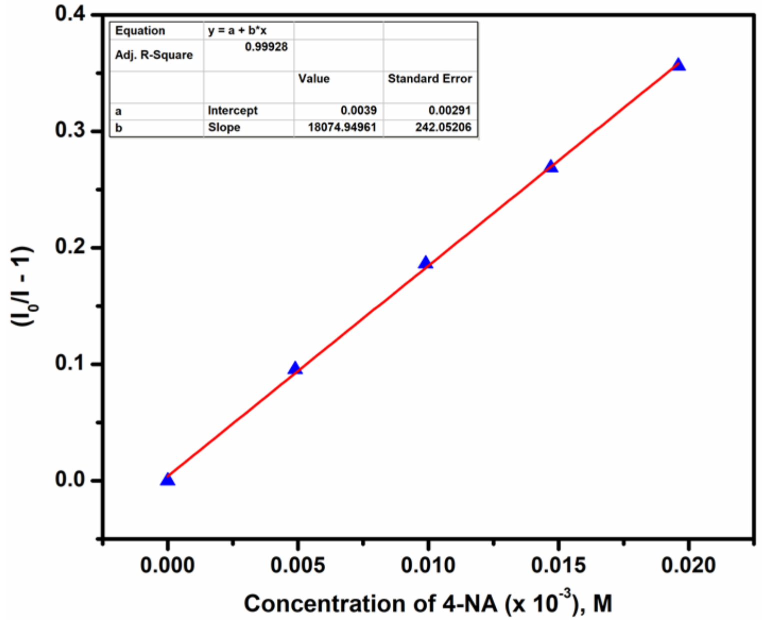


Fig. S42 Stern-Volmer (SV) plot for 4-NA of **1**. The relative fluorescence intensity is linear with 4-NA concentration in the range of 0-20 μM, $I_0/I = 1 + 18074.94961$ ([4-NA]) ($R^2 = 0.999288$).

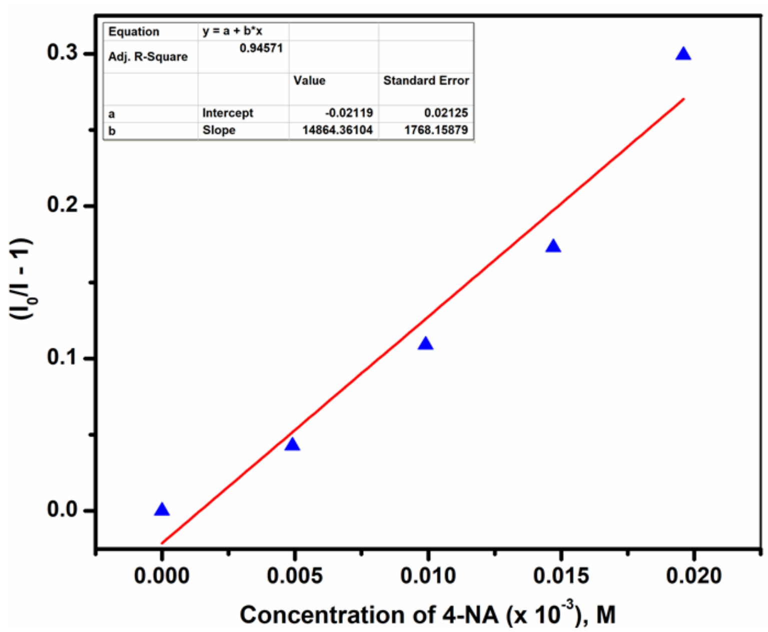


Fig. S43 Stern-Volmer (SV) plot for 4-NA of **2**. The relative fluorescence intensity is linear with 4-NA concentration in the range of 0-20 μM, $I_0/I = 1 + 14864.36104$ ([4-NA]) ($R^2 = 0.94571$).

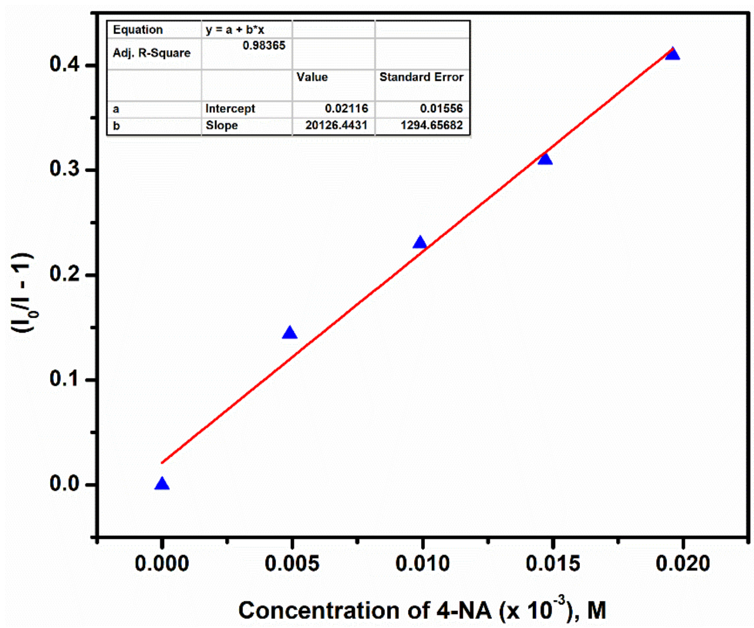


Fig. S44 Stern-Volmer (SV) plot for 4-NA of **3**. The relative fluorescence intensity is linear with 4-NA concentration in the range of 0-20 µM, $I_0/I = 1 + 20126.4431$ ([4-NA]) ($R^2 = 0.98365$).

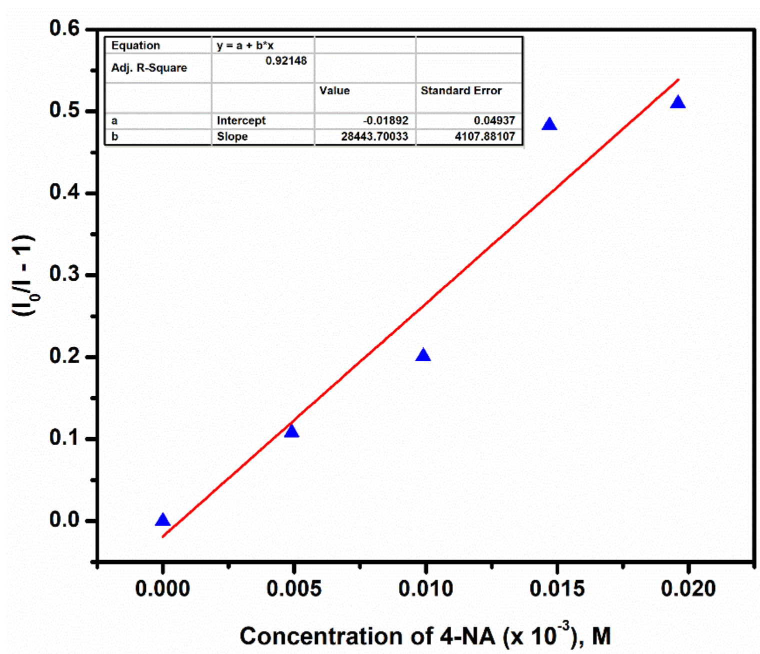


Fig. S45 Stern-Volmer (SV) plot for 4-NA of **4**. The relative fluorescence intensity is linear with 4-NA concentration in the range of 0-20 µM, $I_0/I = 1 + 28443.70033$ ([4-NA]) ($R^2 = 0.92148$).

Section S-5: Detection limit calculations for **1-4**

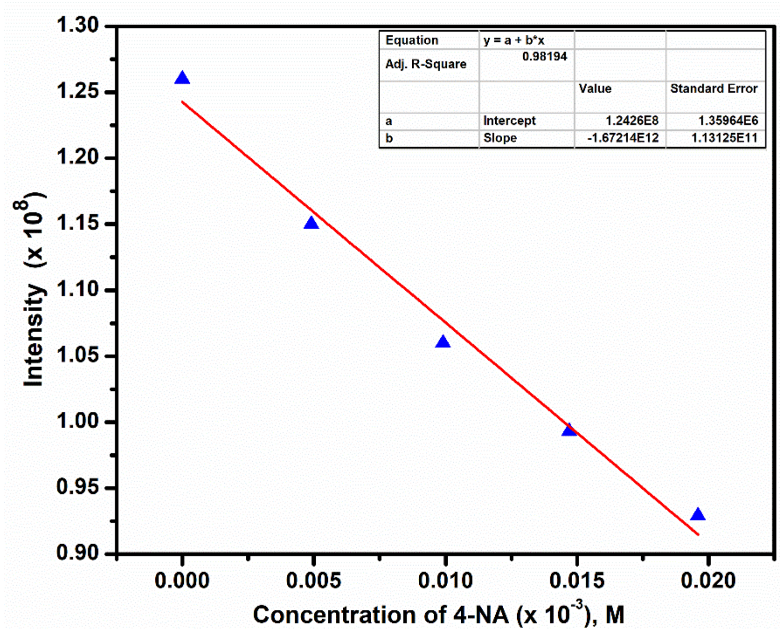


Fig. S46 Linear region of fluorescence intensity of **1** upon incremental addition of 4-NA (1 mM stock solution) at λ_{em}= 548 nm (upon λ_{ex} = 380 nm) (R^2 = 0.98194).

Calculation of Standard Deviation of 1:

Blank Readings(5)	Fl Intensity
Reading 1	1.281×10^8
Reading 2	1.292×10^8
Reading 3	1.284×10^8
Reading 4	1.281×10^8
Reading 5	1.291×10^8
Standard Deviation (σ)	5.612×10^5

Determination of Detection Limit of 1:

Detection limit was calculated using the following equation:

Detection limit = 3σ/m

Where 'σ' is the calculated standard deviation from five blank measurements and 'm' is the slope obtained from the plot of fluorescence emission with increasing concentration of 4-NA.

Slope from Graph	1.67214×10^{12} M^{-1}
Detection Limit (3σ/m)	1.006 µM (**138 ppb**)

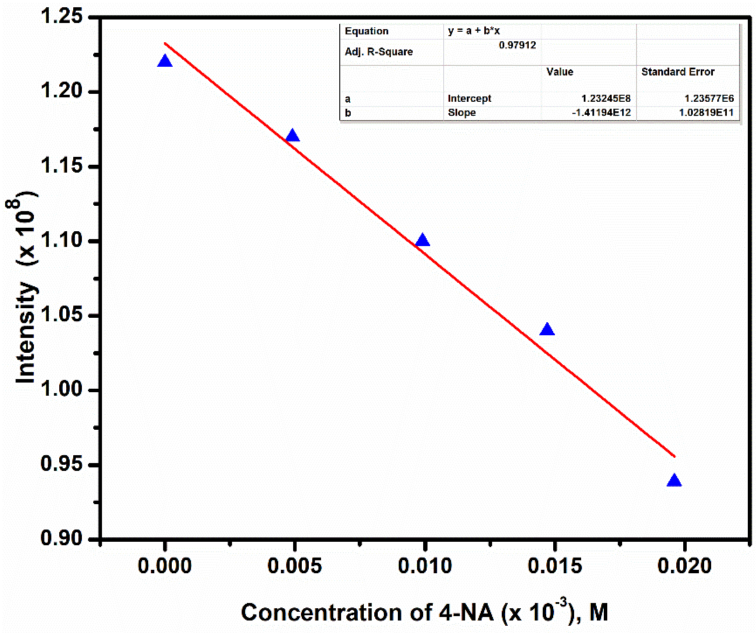


Fig. S47 Linear region of fluorescence intensity of **2** upon incremental addition of 4-NA (1 mM stock solution) at λ_{em}= 548 nm (upon λ_{ex} = 380 nm) (R^2 = 0.97912).

Calculation of Standard Deviation of 2:

Blank Readings(5)	Fl Intensity
Reading 1	1.138×10^8
Reading 2	1.127×10^8
Reading 3	1.15×10^8
Reading 4	1.156×10^8
Reading 5	1.145×10^8
Standard Deviation (σ)	1.121×10^6

Determination of Detection Limit of 2:

Detection limit was calculated using the following equation:

Detection limit = 3σ/m

Where 'σ' is the calculated standard deviation from five blank measurements and 'm' is the slope obtained from the plot of fluorescence emission with increasing concentration of 4-NA.

Slope from Graph	1.41×10^{12} M^{-1}
Detection Limit (3σ/m)	2.38 μM (**329 ppb**)

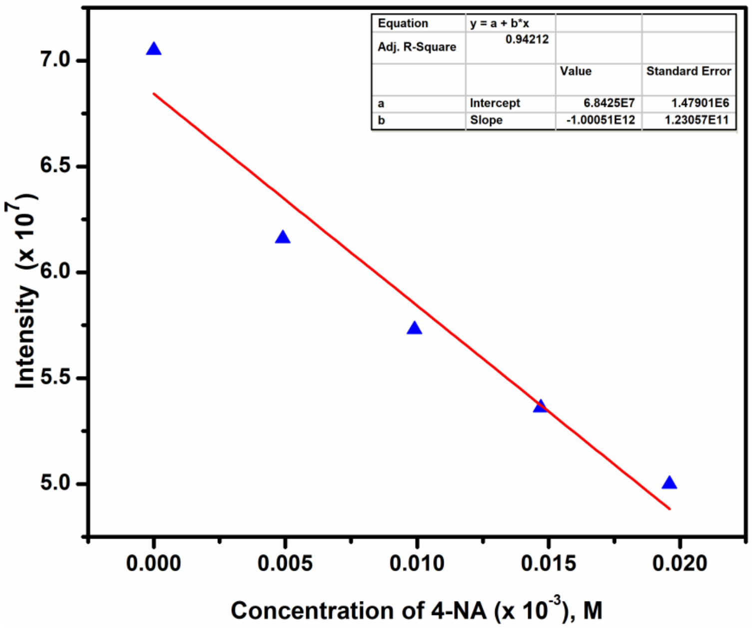


Fig. S48 Linear region of fluorescence intensity of **3** upon incremental addition of 4-NA (1 mM stock solution) at λ_{em}= 551 nm (upon λ_{ex} = 380 nm) (R^2 = 0.94212).

Calculation of Standard Deviation of 3:

Blank Readings(5)	Fl Intensity
Reading 1	5.16×10^7
Reading 2	5.19×10^7
Reading 3	5.13×10^7
Reading 4	5.14×10^7
Reading 5	5.12×10^7
Standard Deviation (σ)	2.77×10^5

Determination of Detection Limit of 3:
Detection limit was calculated using the following equation:
Detection limit = 3σ/m
Where 'σ' is the calculated standard deviation from five blank measurements and 'm' is the slope obtained from the plot of fluorescence emission with increasing concentration of 4-NA.

Slope from Graph	1.0005×10^{12} M^{-1}
Detection Limit (3σ/m)	0.830 μM (**114 ppb**)

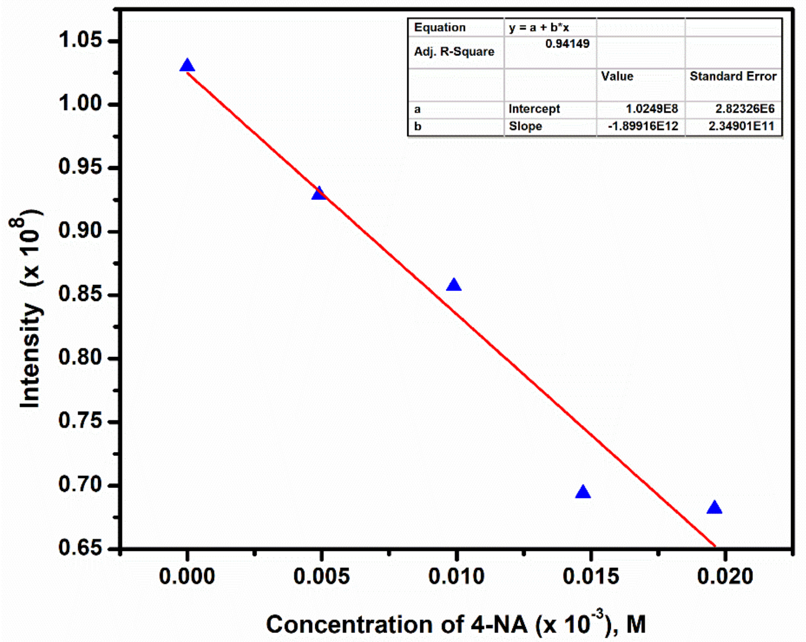


Fig. S49 Linear region of fluorescence intensity of **4** upon incremental addition of 4-NA (1 mM stock solution) at λ_{em}= 547 nm (upon λ_{ex} = 380 nm) (R^2 = 0.94149).

Calculation of Standard Deviation of 4:

Blank Readings(5)	Fl Intensity
Reading 1	1.35×10^8
Reading 2	1.36×10^8
Reading 3	1.34×10^8
Reading 4	1.36×10^8
Reading 5	1.36×10^8
Standard Deviation (σ)	4.47×10^5

Determination of Detection Limit of 4:

Detection limit was calculated using the following equation:

Detection limit = 3σ/m

Where 'σ' is the calculated standard deviation from five blank measurements and 'm' is the slope obtained from the plot of fluorescence emission with increasing concentration of 4-NA.

Slope from Graph	1.89916×10^{12} M^{-1}
Detection Limit (3σ/m)	0.706 µM (**97 ppb**)

Section S-6: Photoluminescence study of H_2(mbhna)

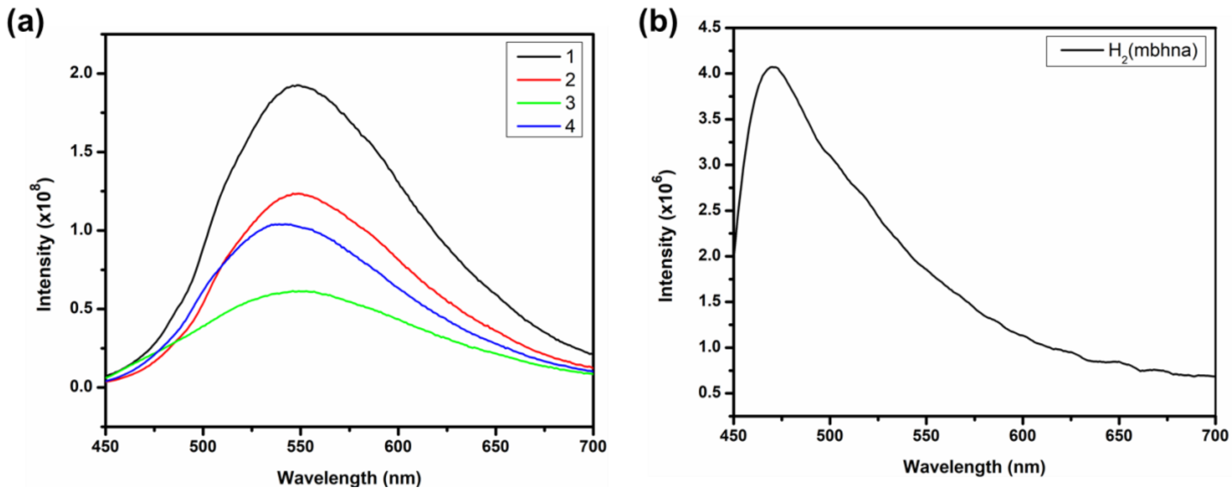


Fig. S50 (a) Emission spectra of **1**-**4**; (b) Emission spectrum of H_2(mbhna) dispersed in aqueous solution (λ_{ex} = 380 nm).

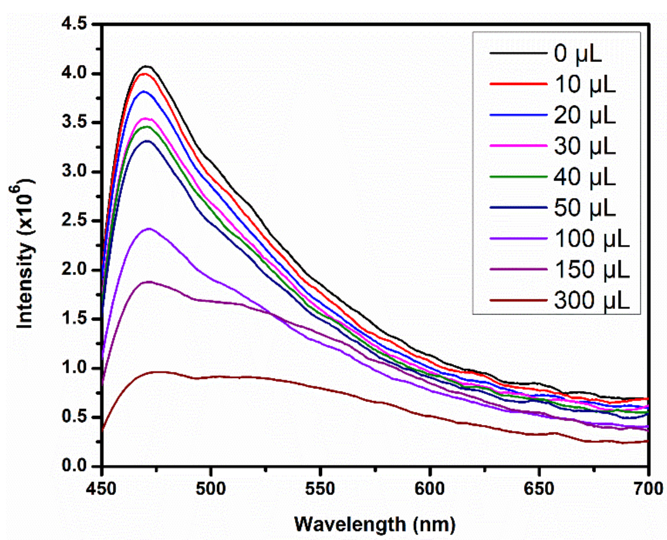


Fig. S51 Emission spectra of H_2(mbhna) dispersed in aqueous solution upon incremental addition of 4-NA solution (1 mM) (λ_{em} = 470 nm and λ_{ex} = 380 nm).

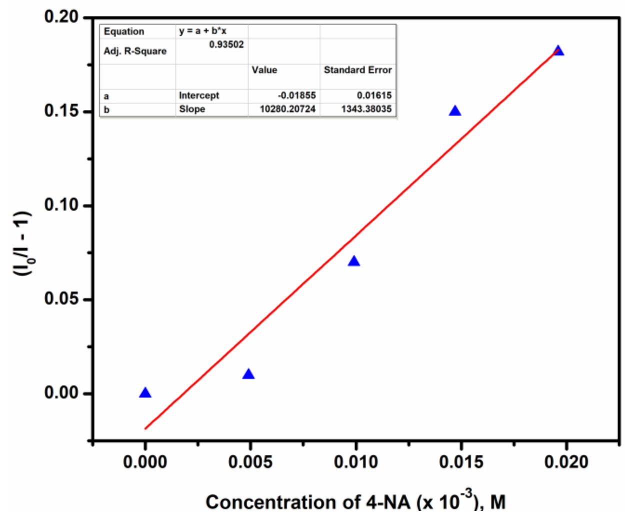


Fig. S52 Stern-Volmer (SV) plot for 4-NA of H_2(mbhna). The relative fluorescence intensity is linear with 4-NA concentration in the range of 0-20 µM, $I_0/I = 1 + 10280.20724$ ([4-NA]) ($R^2 = 0.93502$).

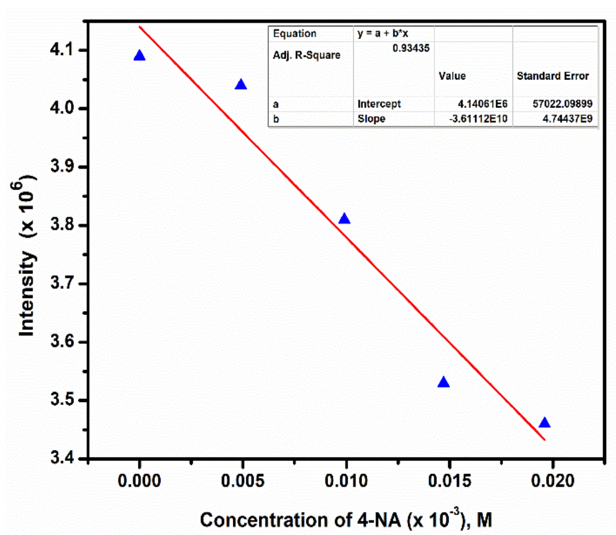


Fig. S53 Linear region of fluorescence intensity of H_2(mbhna) upon incremental addition of 4-NA (1 mM stock solution) at λ_{em}= 470 nm (upon λ_{ex} = 380 nm) (R^2 = 0.93435).

Calculation of Standard Deviation of H_2(mbhna):

Blank Readings(5)	Fl Intensity
Reading 1	4.09×10^6
Reading 2	3.96×10^6
Reading 3	3.68×10^6
Reading 4	3.34×10^6
Reading 5	3.24×10^6
Standard Deviation (σ)	3.72182×10^5

Determination of Detection Limit of H_2(mbhna):
Detection limit was calculated using the following equation:
Detection limit = 3σ/m
Where 'σ' is the calculated standard deviation from five blank measurements and 'm' is the slope obtained from the plot of fluorescence emission with increasing concentration of 4-NA.

Slope from Graph	3.611×10^{10} M^{-1}
Detection Limit (3σ/m)	30.9 µM (**4.2 ppm**)

Section S-7: Spectral overlap and possible interaction sites in **1-4**

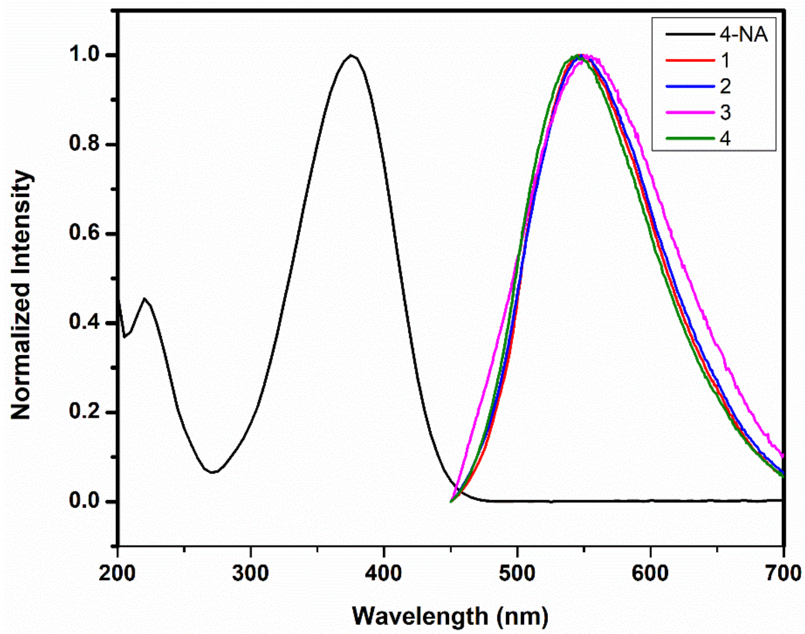


Fig. S54 Spectral overlap of absorption spectrum of 4-NA and emission spectra of **1-4**.

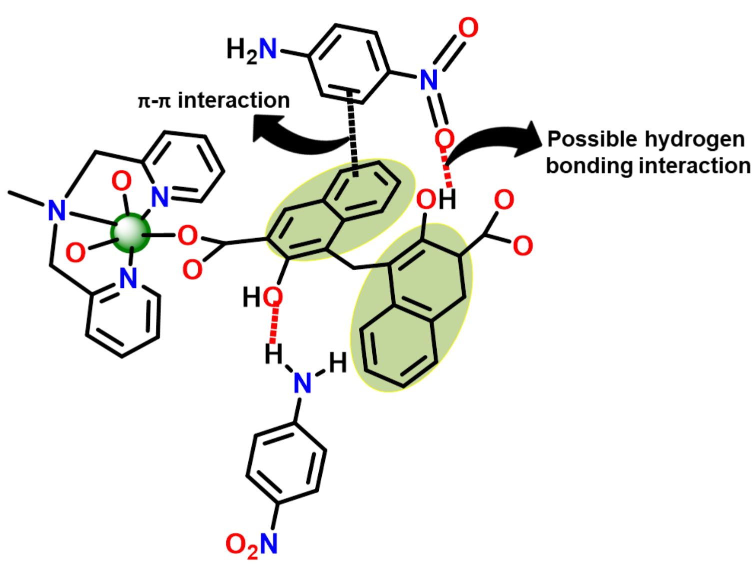


Fig. S55 Possible interaction sites in **1-4** with 4-NA.

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Section S-8: Stability of **1-4** in 4-NA

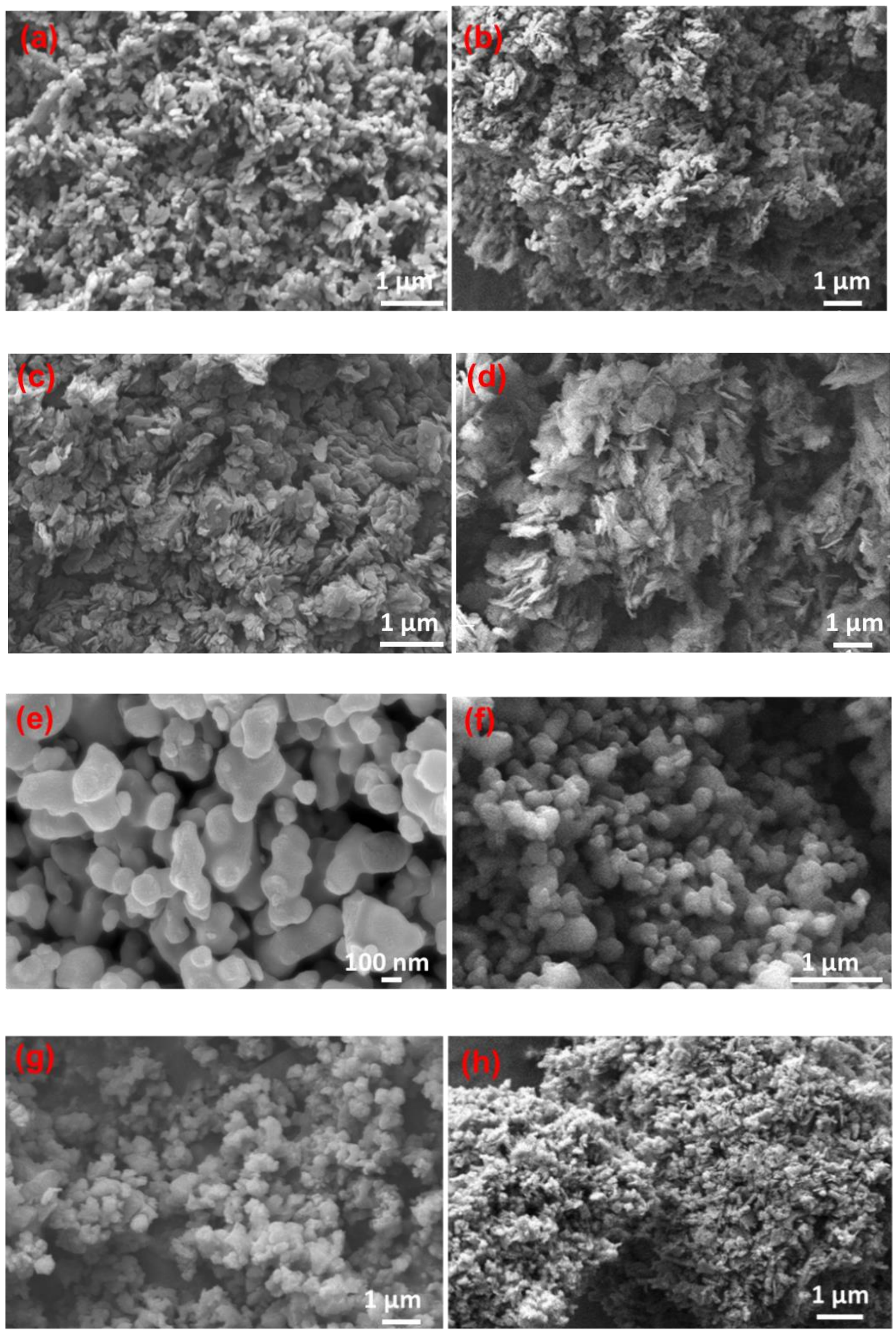

Fig. S56 FESEM images of **1-4** before (a,c,e,g) and after (b,d,f,h) immersing in 4-NA.

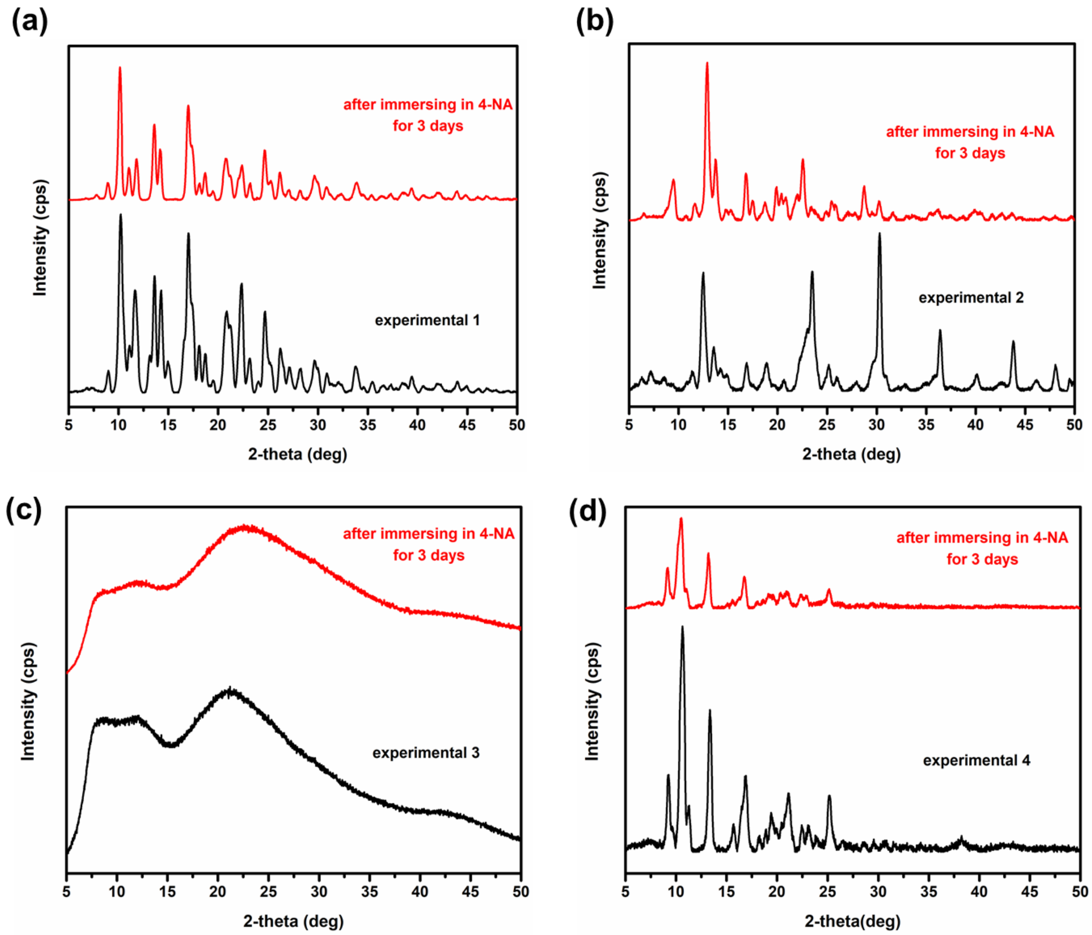

Fig. S57 PXRD patterns of **1**-**4** before and after immersing in 4-NA for 3 days.

Table S1 Literature survey on 4-NA detection

Compound	K_{SV} (M^{-1})	Detection Limit	Solvent	Reference
{[Zn(mbhna)(bpea)]}$_n$ (**1**) {[Cd(mbhna)(bpea)]}$_n$ (**2**) {[Zn(mbhna)(bpba)]·CH_3OH·H_2O}$_n$ (**3**) {[Cd(mbhna)(bpba)]}$_n$ (**4**)	1.80 x 10^4 1.48 x 10^4 2.01 x 10^4 2.84 x 10^4	130 ppb 330 ppb 114 ppb 97 ppb	Water Water Water Water	*This work* *This work* *This work* *This work*
{Zn_4(TPOM)(1,4-NDC)$_4$}$_n$	7.87 x 10^4	88 ppb	Water	*ACS Appl. Mater. Interfaces*, 2018, **10**, 42406–42416.
[Zn_2(tpbn)(mbhna)$_2$]·3.5H_2O·1.5DMF {[Cd_2(tpbn)(mbhna)$_2$]·2DMF}$_n$	2.23 x 10^4 2.87 x 10^4	0.74 ppm 0.46 ppm	Water Water	*Chem. Asian J.*, 2019, **14**, 3712–3720.
[Cd(H_2BDDA)]$_n$ where, H_4BDDA = 4,4-([2, 2'-bipyridine]-6,6'-diylbis(oxy) diphthalic acid	8.79 x 10^4	0.68 ppm	Water	*ChemistrySelect*,2017, **2**, 12046–12050.
{Zn(bpba)(NO_3)}$_n$ Hbpba = 4-(bis(4-(pyridin-4-yl)phenyl)amino)benzoic acid)	2.28 x 10^4	0.1 ppm	DMF	*Dalton Trans.*, 2018, **47**, 7222–7228.
[Zn(mbhna)(bpma)]$_n$ {[Cd(mbhna)(bpma)]·DMF}$_n$ [Zn(mbhna)(bpta)]$_n$ {[Cd(mbhna)(bpta)(CH_3OH)]}$_n$	7.01 x 10^3 2.20 x 10^4 2.11 x 10^4 1.57 x 10^4	7.15 ppm 1.33 ppm 1.94 ppm 4.50 ppm	Water Water Water Water	*Eur. J. Inorg. Chem.*, **2021**, 2595–2605.
{Cd(5-asba)(bimb)}$_n$ where, $H_2$5-asba = 2-amino-5-sulfobenzoic acid and bimb = 1,4-bis(1H-imidazol-1-yl)butane	9.8 x 10^4	0.52 ppm	Water/ MeOH	*J. Mater. Chem. C*, 2016, **4**, 11404–11418.
TPDC-DB	1.7 x 10^4	0.45 ppm	THF	*J. Mater. Chem. C*, 2016, **4**, 4427–4433.
{[Zn_4(μ_3-OH)$_2$(L)(H_2O)$_2$]·2DMF}$_n$ where L = [1,1'; 4',1'']terphenyl-3,5,2',5',3'',5''-hexacarboxylic acid	NA	4 ppm	DMF	*J. Mater. Chem. A*, 2015, **3**, 22369–22376.
{Zn_3L_3(DMF)$_2$}$_n$ {Zn_3L_3(DMA)$_2$(H_2O)$_3$}$_n$ where, L = 4,4′-stillbene dicarboxylic acid	5.99 x 10^4 2.18 x 10^4	NA NA	Acetonitrile	*Journal of Solid State Chemistry*, 2015, **232**, 96–101.
{[Eu_2(TDC)$_3$(CH_3OH)$_2$] ·CH_3OH}$_n$ {[Tb_2(TDC)$_3$(CH_3OH)$_2$] ·CH_3OH}$_n$ where, TDC = 2,5-thiophene dicarboxylic acid	4.32 x 10^4 9.52 x 10^3	NA NA	MeOH	*RSC Adv.*, 2016, **6**, 91741–91747.
{[Zn_2(oba)$_2$(4-bpdb)]·2DMF}$_n$ (TMU-4) where, H_2oba = 4,4'-oxybisbenzoic acid and 4-bpdb = 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene	2.95 x 10^4	5 x 10^{-5} M (6.9 ppm)	Acetonitrile	*Sensors and Actuators B*, 2017, **243**, 353–360.
H_2Tyr-N-Dan	NA	NA	MeOH	*RSC Adv.*, 2014, **4**, 47249–47253.
Cd-PDA where, H_2PDA = 9-phenylcarbazole-3,6-dicarboxylic acid	4.07 x 10^4	3.5 ppb	Water	*J. Mater. Chem. A*, 2016, **4**, 16349–16355.