Supporting info

$CsPbBr_3$ perovskite quantum dot integrated ZIF-8 MOF: A selective dual recognition fluorometric visual probe for 4 – nitroaniline and rhodamine blue

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1. Sample preparation and sensing measurement: For nitroaniline sensing 5 mg ml^{-1} $CsPbBr_3$@ZIF-8 composite was dispersed in methanol and sonicated for 10 min to become homogeneous. Then the PL emission was measured using the 3 ml dispersion of composite. Separately, different concentration of nitroanilines (0 - 64 µM) are prepared in methanol by diluting a stock solution of 1mM. Thereafter, for sensing experiment 100 µl of different concentrations of analyte (0–64 µM) were continuously added into $CsPbBr_3$@ZIF-8 standard and incubating at room temperature for 60 sec. Using a $1cm^3$ quartz cuvette, the PL emission spectra of the solutions were measured at an excitation wavelength of 365 nm and an slit width of 10 nm.

For the detection of RhB dye, first a 0.1 mM aqueous stock solution was prepared and then diluted to various concentrations. Once the RhB solution was ready, 100 µl of the solution was added to 3 ml of $CsPbBr_3$@ZIF-8 dispersion and the mixture was homogenized. The PL spectra were obtained at an excitation wavelength of 365 nm following an incubation period of 2 minutes at room temperature.

2. Preparation of paper sensor: To prepare a paper sensor for the purpose of studying the visual detection of analytes by the $CsPbBr_3$@ZIF-8, square size (1.5 cm×1.5cm) cellulose filter papers were used. Thereafter, the paper strips were dripped into 5 ml of 1.5 mg/ml CPB@ZIF-8 dispersion for 30 min. After room temperature drying process, 4-NA of concentration 0-10µM was dropped into the test strips, forming a simple and low cost visual sensing platform. Similar procedure was followed for RhB dye paper sensor preparation.

3. Sample preparation for real sample analysis: For the analysis of 4-NA in soil samples, 13.8 mg of 4-NA were first added to 2.0 g of soil sample and mixed the content using a mortar pestle. Then, 100 mL of methanol was added and ultrasonicate the mixture for 30 min. Following the centrifugation of the mixture for 5 min at 5000 rpm, supernatant was collected which was then diluted to prepare different known concentration of 4-NA. Then 4 ml of $CsPbBr_3$@ZIF-8 dispersion was mixed with the prepared soil samples and fluorescence measurements were performed under the excitation wavelength of 365 nm. Similarly different known concentrations (0, 0.5, 5 and 10 μM) of 4-NA were added to tap water sample and then fluorescence measurements were carried out using 4 ml of $CsPbBr_3$@ZIF-8 dispersion.

Similarly real sample analysis of the sensor for RhB, fruit juice samples were first centrifuged and the supernatants were collected. Then the supernatant solutions were diluted to 100-fold dilution with distilled water and mixed with various concentrations of RhB for fluorescence measurements.

4. Photoluminescence quantum yield determination: The relative PLQY measurement was performed using fluorescein as a reference standard (QY = 0.95 in 0.1 M NaOH) using the formula as follows-

$$QY_S = QY_F \times I_S/I_F \times A_F/A_S \times \eta_s^2/\eta_F^2 \qquad (1)$$

Where, QY = quantum yield of the sample.

A = Absorbance at the excitation wavelength.

I = Integrated emission intensity

η = Refractive index (1.375 for hexane, 1.33 for 0.1 M NaOH)

The subscript 'S' stands for sample and F means Fluorescein (reference standard). We have prepared five different solutions of fluorescein dye and $CsPbBr_3$@MOF composite with sufficient dilution having absorbance below 0.1 and calculated the QY according to the above mentioned equation. [1]

Figure S1

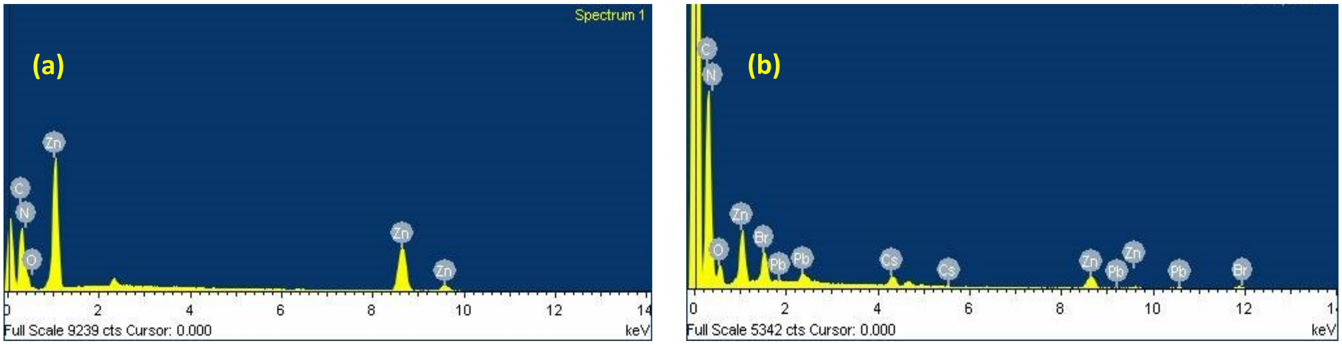
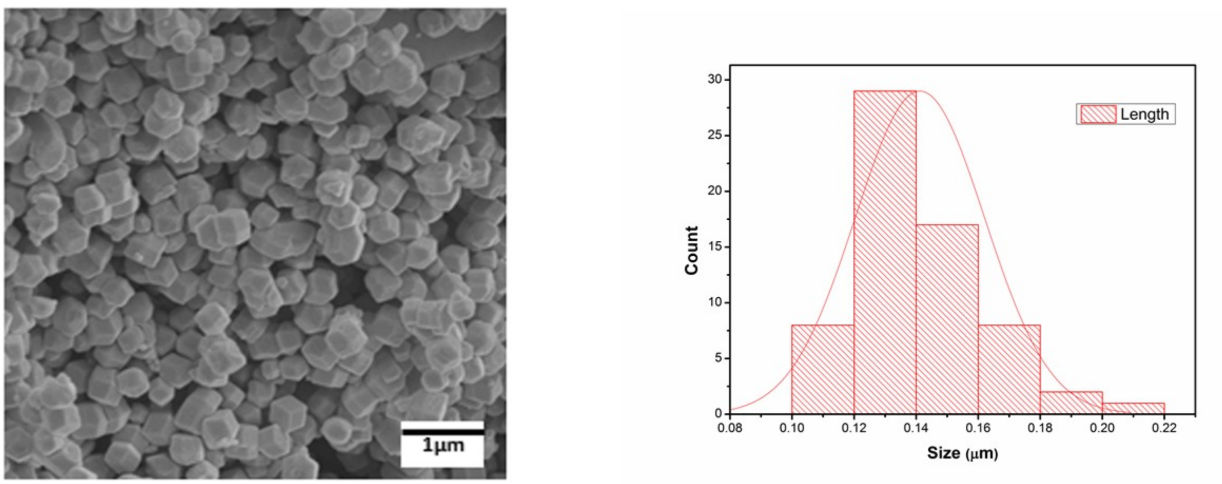


Figure S2



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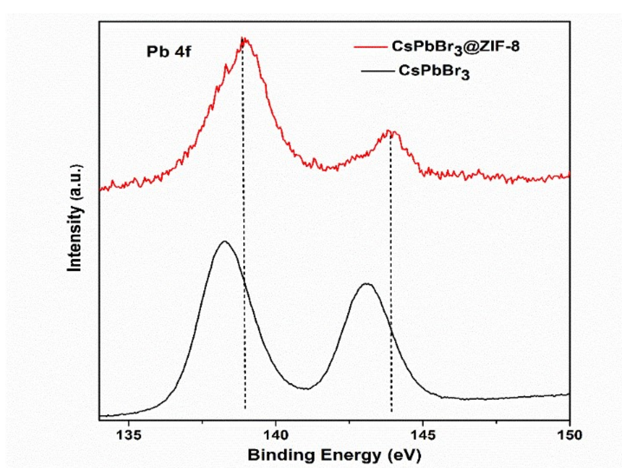

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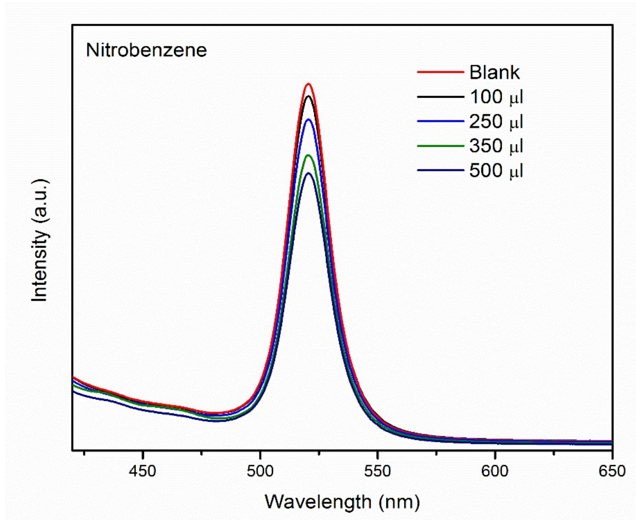
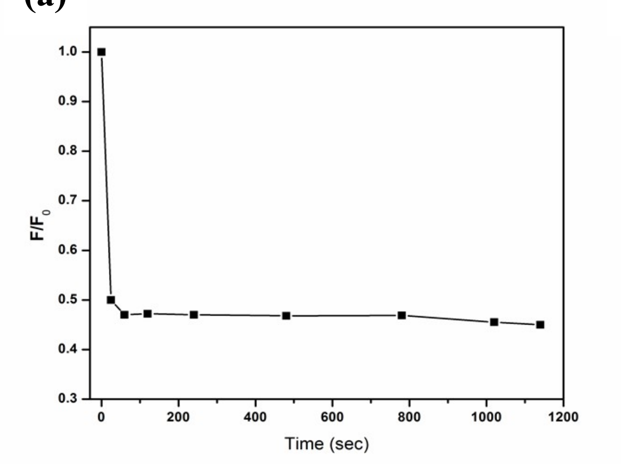


Figure S5

(a)



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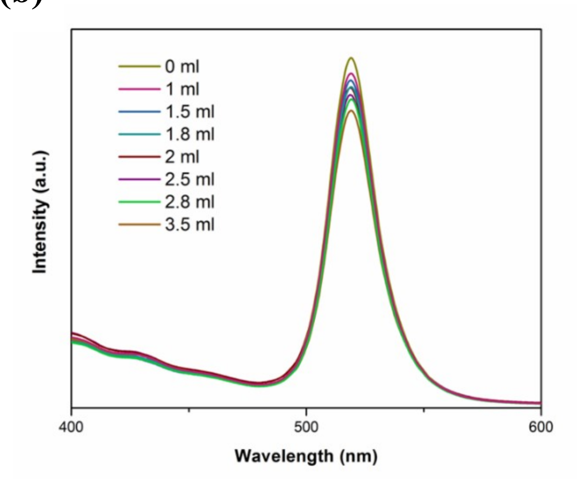

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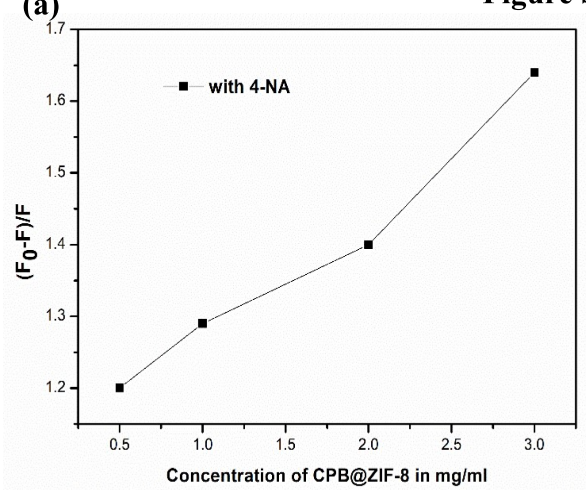
(a)



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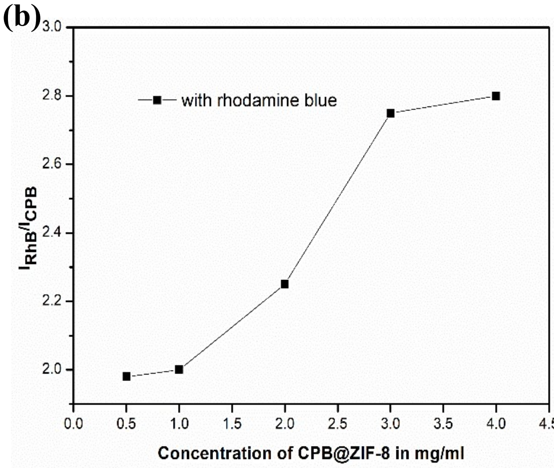

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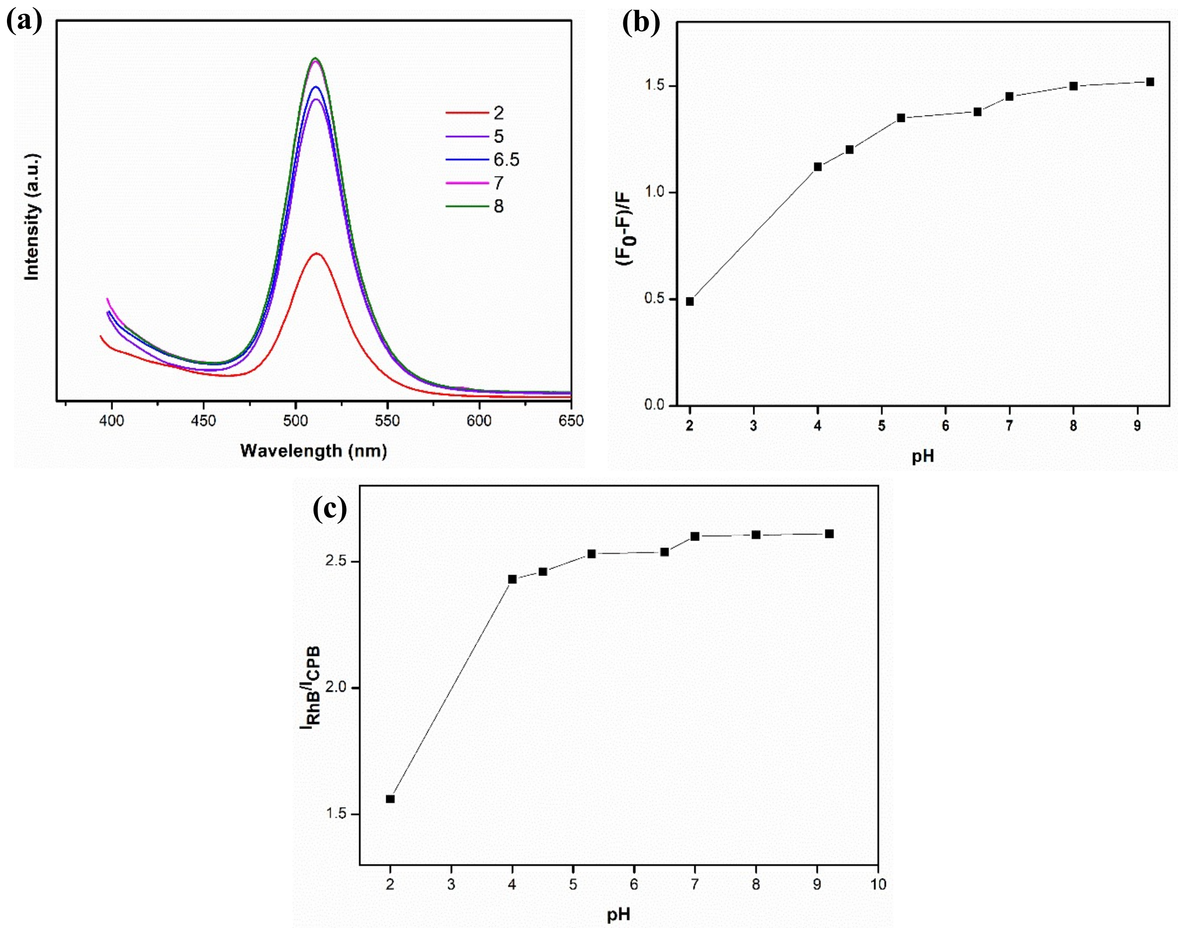

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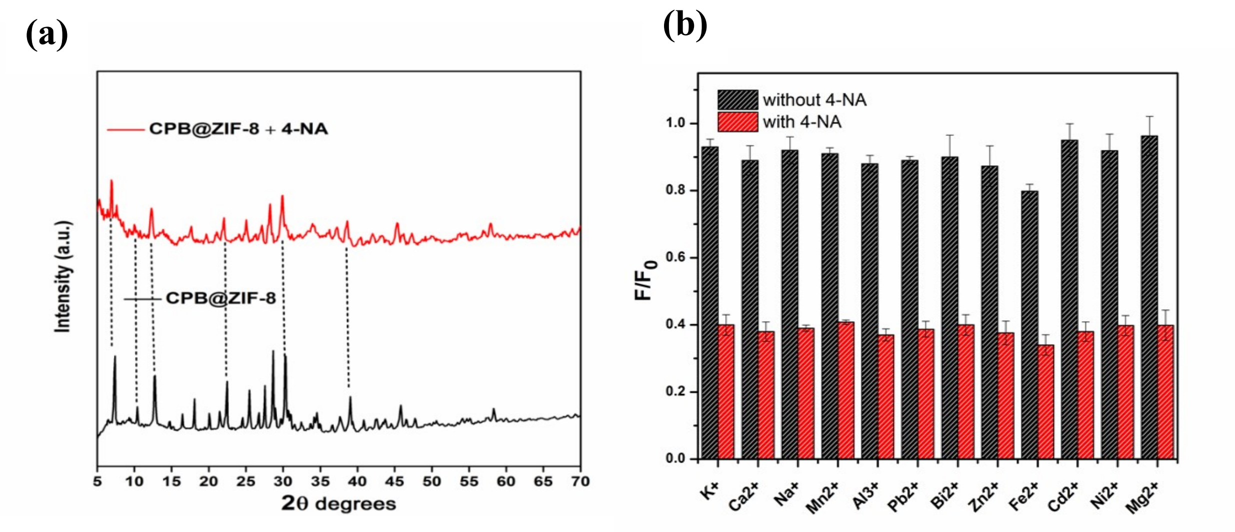

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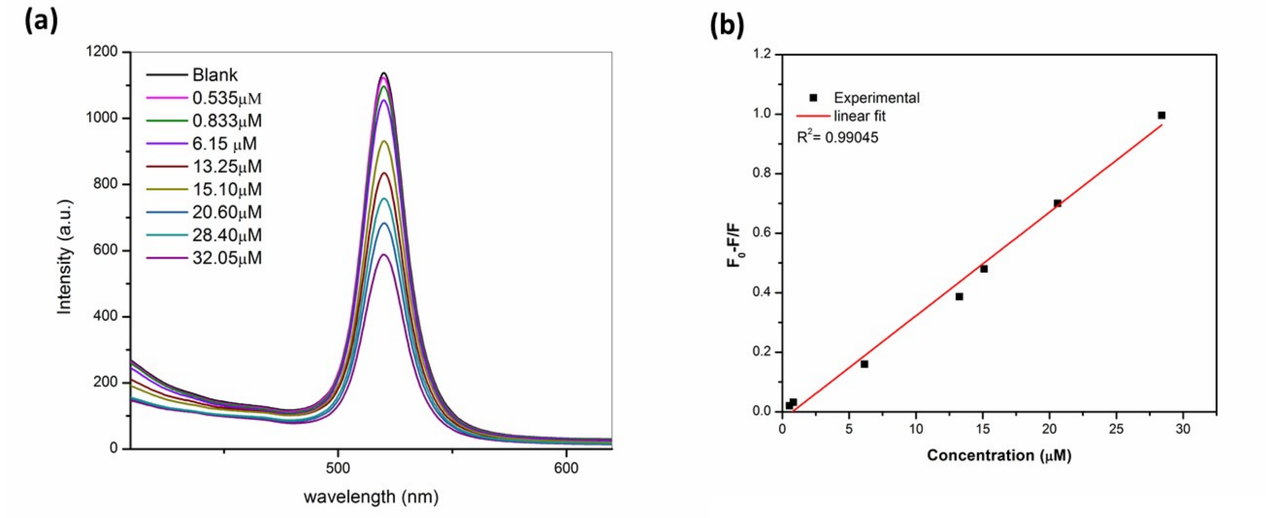

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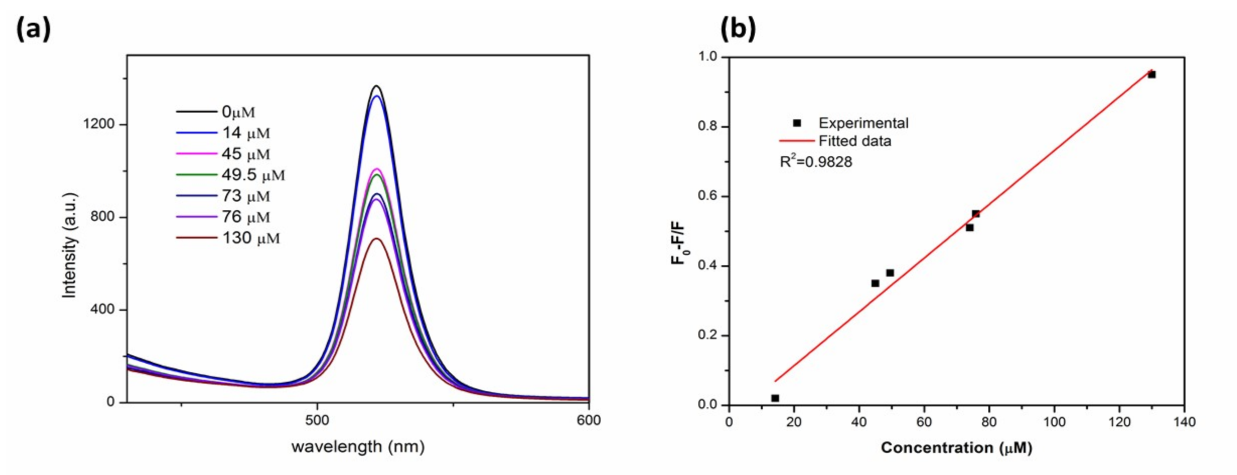

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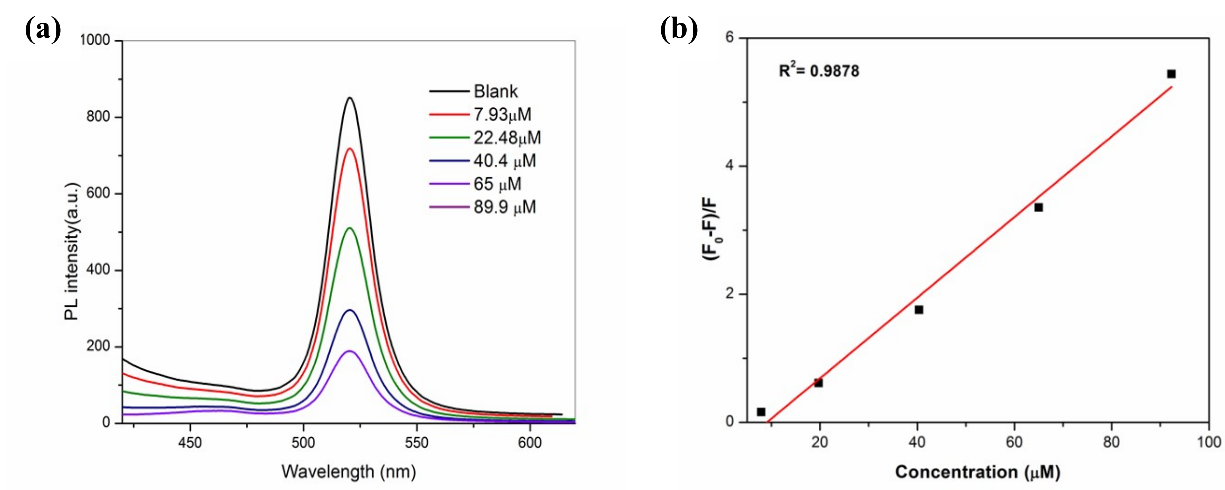

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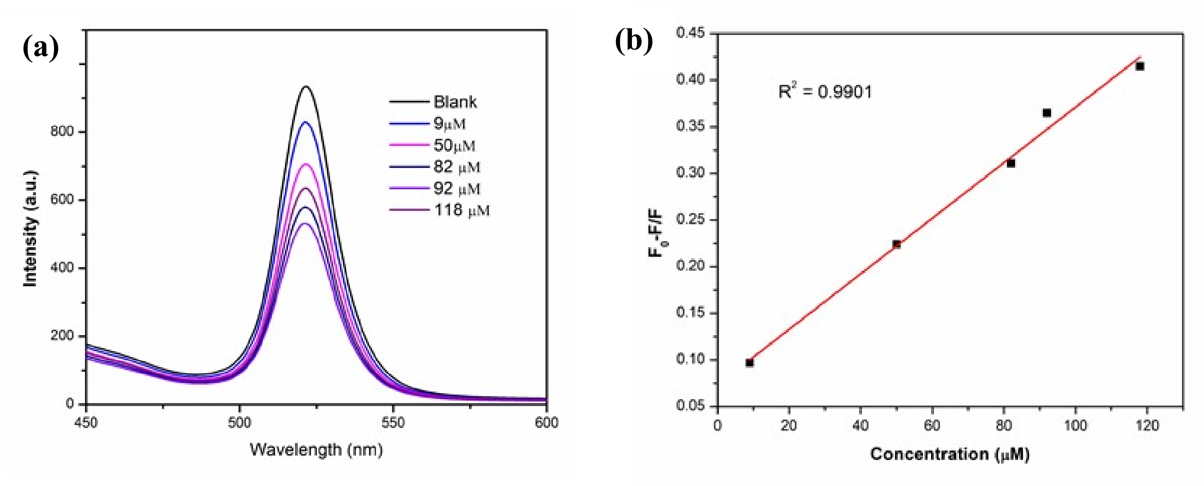

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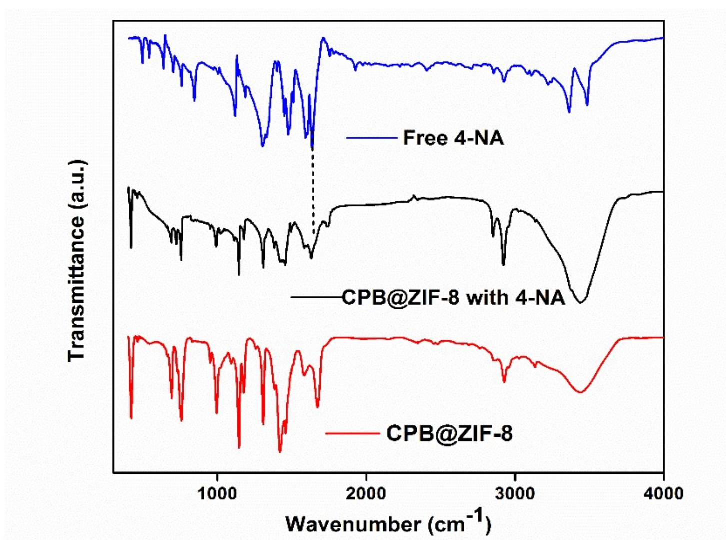

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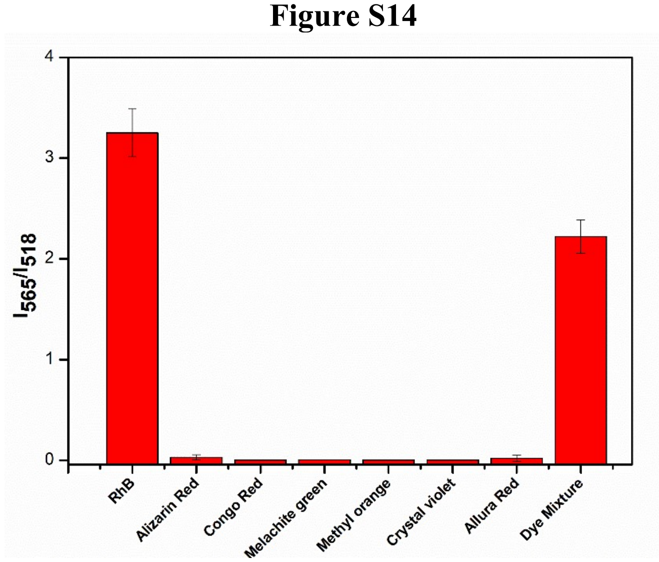

Table S1: Chemical stability study of CPB/ZIF-8 in different solvents.

Percentage of retained emission intensity of CPB@ZIF-8

Solvents	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Methanol	98	95.33	88.85	84.30	81.77	80.52	75.08
Ethanol	98.05	97.55	90.78	88.65	84.49	80.20	77.96
Butanol	95.28	93.49	90.88	89.25	86.77	82.67	80.49
Isopropanol	98.55	96.50	89.40	87.95	84.78	80	79.16
DMF	93.33	88.10	85.40	81.07	78.85	76.22	72.5
DMSO	91.05	87.06	83.47	79.28	76.9	72.3	65.80
Acetonitrile	96.70	91.04	86	82.59	79.20	74.60	70.35
NMP	97.50	92.75	87.60	83.06	75.90	74	73
Water	93.56	81.80	77.72	71.50	68	61.20	52

Table S2: Comparison of performance of CPB/ZIF-8 with previous literatures for 4-nitroaniline detection.

Fluorescent System	LOD (nM)	K_{SV}	Linear range (M)	Response time	Ref
N-doped carbon dots (Blue) Green	111.6 nM 68.9 nM	$1.4 \pm 0.2 \times 10^4$ M^{-1} $2.9 \pm 0.1 \times 10^4$ M^{-1}	0 − 40 μM 0− 50 μM	N/A	2
FJI-H26 MOF	0.025 mM	4.1×10^4 M^{-1}	0.005 − 0.025 mM	N/A	3
Cd– PDA MOF	25 nM	$4.0\ 7\times10^4$ M^{-1}	0−10 μM	N/A	4
Porous organic polymer (TPDC-DB)	455 ppb	1.7×10^4 M^{-1}	N/A	N/A	5
Cd MOF	0.52 ppm	9.8×10^4 M^{-1}	0 – 0.0001 M	3 min	6
Triphenylamine functionalized sensor	724 nM (0.10 ppm)	2.28 × 104 M^{-1}	0 – 40 μM	30 sec	7
1,2,3-triazolyl based conjugated microporous polymer	4.2 μM	7.08×10^4 M^{-1}	0.5–4 μM	N/ A	8
W-N-CDs and E-N-CDs	1 and 0.1 μM	8.82×10^3 M^{-1} 1.25×10^4 M^{-1}	(0–1) 10^{-4} M (0–0.8) 10^{-4} M	N/ A	9
$CsPbBr_3$@ZIF-8	60.58 nM (8.36 ppb)	5.942×10^5 M^{-1}	0.368 – 51.5 μM	25 sec	This work

Table S3: Comparison of quenching constant (Ksv), LOD and, correlation values of different NACs analytes.

Analytes	**K_{sv}**	**LOD**	**Correlation coefficient (R^2)**
4-nitroaniline	5.942×10^5	60.58 nM	0.99058
2-nitroaniline	7.73×10^3	0.176 μM	0.98280
3-nitroaniline	3.18×10^3	0.186 μM	0.9901
2,4-dinitroaniline	3.48×10^4	0.120 μM	0.99045
Picric acid	6.52×10^4	0.137 μM	0.9878

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