

Supplementary Information

Mixed matrix membranes containing fluorescent coordination polymers for detecting $\text{Cr}_2\text{O}_7^{2-}$ with high sensitivity, stability and recyclability

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Instruments and Methods

Instruments and Methods: All reagents were used as received from commercial suppliers without further purification. NMR experiments of all compounds were recorded at 400 MHz on a Bruker Avance III HD 400 spectrometer using tetramethylsilane. X-ray single-crystal diffraction data was collected on a Rigaku SCX-mini diffractometer at 298 K with Mo-K α radiation ($I=0.71073$) in ω scan mode. Powder X-ray diffraction data (PXRD) were collected over the 2θ range 3–50° on a Bruker Advance D8 diffractometer using Cu-K α_1 radiation ($\lambda = 1.54056$ Å, 40 kV/40 mA). Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer Diamond TG-DTA analyzer at a heating rate of 5 °C min⁻¹, with an empty Al₂O₃ crucible used as reference. Simulation of the PXRD pattern was performed based on single-crystal data using diffraction-crystal module of the Mercury program. Fluorescence spectra were recorded on a HITACHI F-4600 fluorescence spectrophotometer equipped with a plotter unit. UV–Visible absorption spectra were measured on a UV-1750 Spectrophotometer. The top surfaces of the membranes were characterized by scanning electron microscopy (SEM) on a HITACHI SU-8010.

Experimental Section

All reagents were used as received from commercial suppliers without further purification.

Synthesis of 9,10-di(4-pyridyl)anthracene (*dpa*): *dpa* was synthesized following reported procedures [1-3]. 9,10-Dibromoanthracene (1.01 g, 3 mmol), 4-pyridylboronic acid (0.92 g, 7.5 mmol), K₂CO₃ (4.15 g, 30 mmol), and Pd(PPh₃)₄ (350 mg, 0.3 mmol) were dissolved in a solvent mixture of DMF (120 mL) and water (15 mL). The mixture was heated at 100 °C for 24 hours under Ar, and then was cooled down to room temperature. The solvent was removed under reduced pressure, light yellow product was obtained by column chromatograph (yield: 82%). ¹H NMR (400 MHz, CDCl₃): δ =8.87 (d, J=6.0 Hz, 4H; ArH), 7.61 (m, 4H, ArH), 7.44 (d, J=6.0 Hz, 4H; ArH), 7.40 ppm (m, 4H, ArH).

Synthesis of 1, $[\text{Cd}_2(\text{dpa})_2(\text{cda})\text{Cl}_2]_n$: A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (15.0 mg, 0.05 mmol), *dpa* (16.6 mg, 0.05 mmol), *cda* (8.6 mg, 0.05 mmol), DMF (4.0 mL) and hydrochloric acid (0.05 mL, 1.0 M) was transferred into a 25 mL Teflon lined autoclave and sealed. Reaction took place at 80 °C for 3 days, and afforded pale yellow crystals, which were collected by filtration, washed with fresh DMF and then acetone (yield: 80% based on ligand). Elemental analysis (%) for **1**, $\text{C}_{28}\text{H}_{21}\text{CdClN}_2\text{O}_2$: Calcd: C, 59.49; H, 3.74; N, 4.96. Found: C, 59.56; H, 3.85; N, 4.90.

Synthesis of 2, $[\text{Cd}(\text{dpa})_2(\text{cda})]_n$: A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (15.0 mg, 0.05 mmol), *dpa* (16.6 mg, 0.05 mmol), *cda* (8.6 mg, 0.05 mmol) and DMF (4.0 mL) was transferred into a 25 mL Teflon lined autoclave and sealed. Reaction took place at 80 °C for 3 days, and afforded colorless needle crystals, which were collected by filtration, washed with fresh DMF and then acetone (yield: 81% based on ligand). Elemental analysis (%) for **2**, $\text{C}_{56}\text{H}_{48}\text{CdN}_4\text{O}_7$: Calcd: C, 67.17; H, 4.83; N, 5.59. Found: C, 67.26; H, 4.98; N, 5.65.

Synthesis of 3, $[\text{Cd}(\text{dpa})(\text{cda})(\text{H}_2\text{O})]_n \cdot n\text{DMF}$: A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (15.0 mg, 0.05 mmol), *dpa* (16.6 mg, 0.05 mmol), *cda* (8.6 mg, 0.05 mmol) and DMF (4.0 mL), deionized water (0.5 mL) was transferred into a 25 mL Teflon lined autoclave and sealed. Reaction took place at 80 °C for 3 days, and afforded colorless needle crystals, which were collected by filtration, washed with fresh DMF and then acetone (yield: 81% based on ligand). Elemental analysis (%) for **3**, $\text{C}_{38}\text{H}_{42}\text{CdN}_4\text{O}_7$: Calcd: C, 58.58; H, 5.43; N, 7.19. Found: C, 58.63; H, 5.48; N, 7.23.

Preparation of 1@M and 2@M: Submicrometre-sized CPs particles was prepared according to reference with minor modifications, and the procedures for preparing **1@M** and **2@M** were same. The crystals (50 mg) of **1** were soaked in liquid nitrogen for 20 minutes and grinded with agate mortar. And then dispersed the ground sample in dichloromethane (DCM, 10 ml), in which a small fraction of

micrometre-sized crystals settled, while the majority of submicrometre-sized crystals remain suspended, which were sucked out and dried under vacuum at room temperature.

PMMA (0.3 g) was dissolved in acetone (3.0 mL) and sonicated for 30 minutes resulting in a sticky solution. Submicrometre-sized powder of **1** (0.03 g) was added into the acetone solution of PMMA, and then sonicated for 30 minutes resulting in a homogeneously dispersed solution, which was then cast onto a glass plate by a scraper. **1@M** was dried at room temperature overnight [4-6].

Procedure for detecting $\text{Cr}_2\text{O}_7^{2-}$: **1@M** and **2@M** were cut into the suitable size and were immersed in $\text{Cr}_2\text{O}_7^{2-}$ aqueous solution of different concentrations. The luminescence response spectrum were collected from 375 to 600 nm with the excitation wavelength fixed at 350 nm.

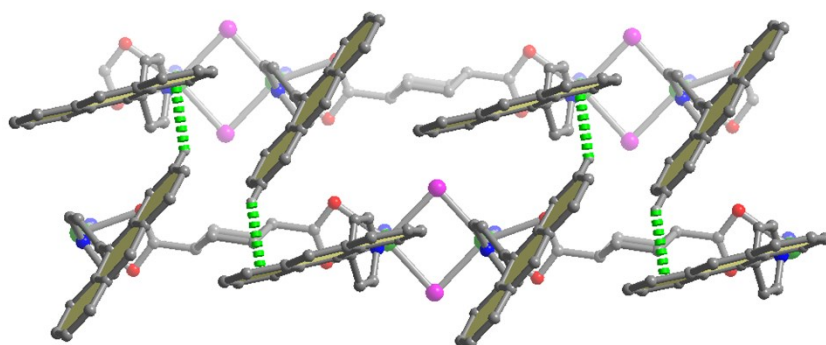


Figure S1. The C-H... π interactions between the anthracene groups of adjacent layers in **1**.

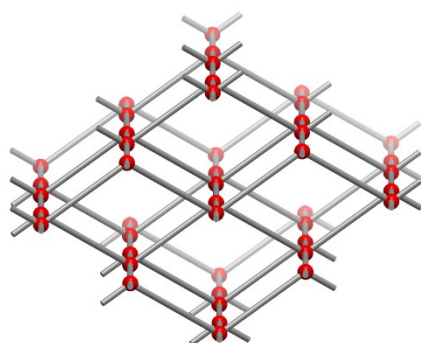


Figure S2. The schematic view showing the diamondoid network in **2**.

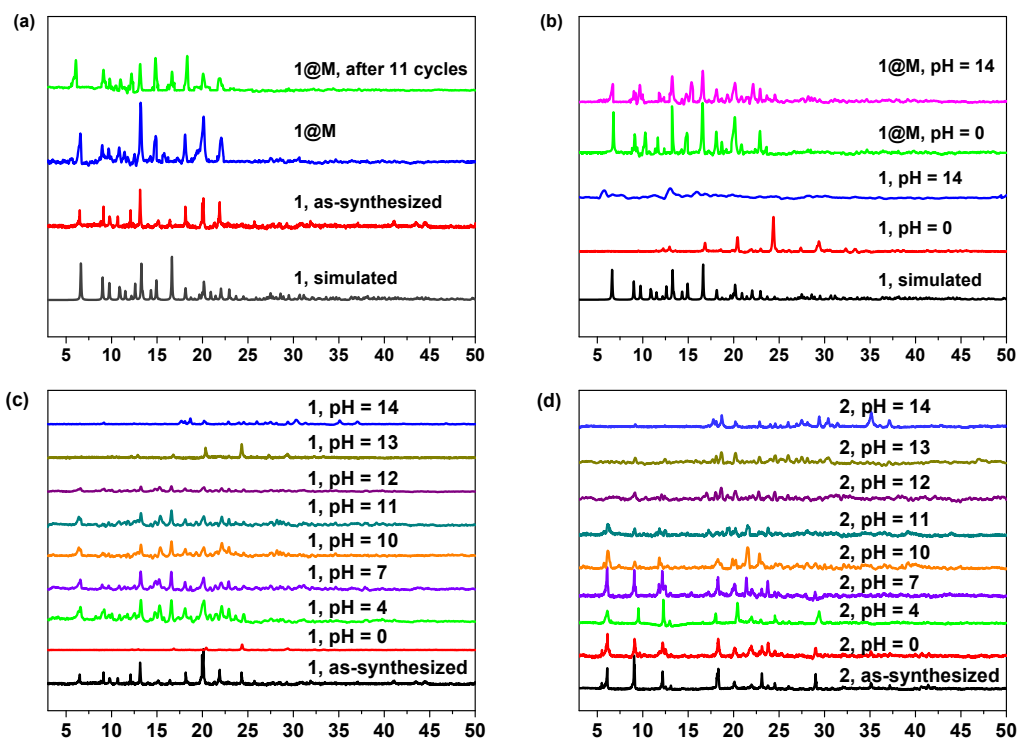


Figure S3. (a) The PXRD patterns of **1**, **1@M** and **1@M** after 11 cycles detecting tests. (b) The PXRD patterns of **1** and **1@M** immersed in aqueous solutions of different pH for 24 hours. (c, d) The PXRD of **1** and **2** immersed in aqueous solutions of different pH for 24 hours.

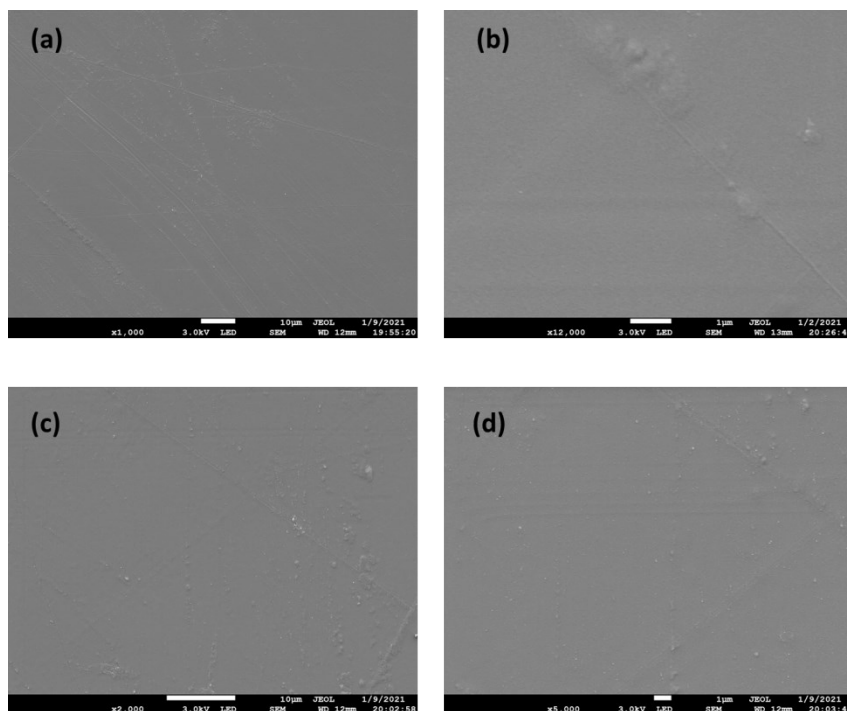


Figure S4. The SEM images at different scales for 10 μm (a, c) and 1 μm (b, d) of **1@M** and **2@M**.

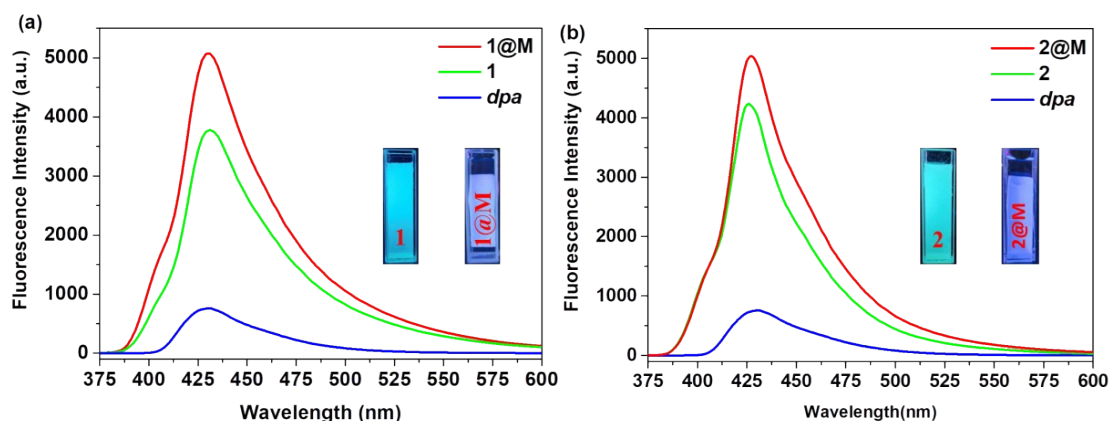


Figure S5. (a) The emission spectra of *dpa*, **1** and **1@M** in the aqueous solution ($\lambda_{\text{ex}}=350$ nm). (b) The emission spectra of *dpa*, **2** and **2@M** in the aqueous solution ($\lambda_{\text{ex}}=350$ nm). Inset: the photographs of **CPs** and **MMMs** in the aqueous solution under 365 nm UV light.

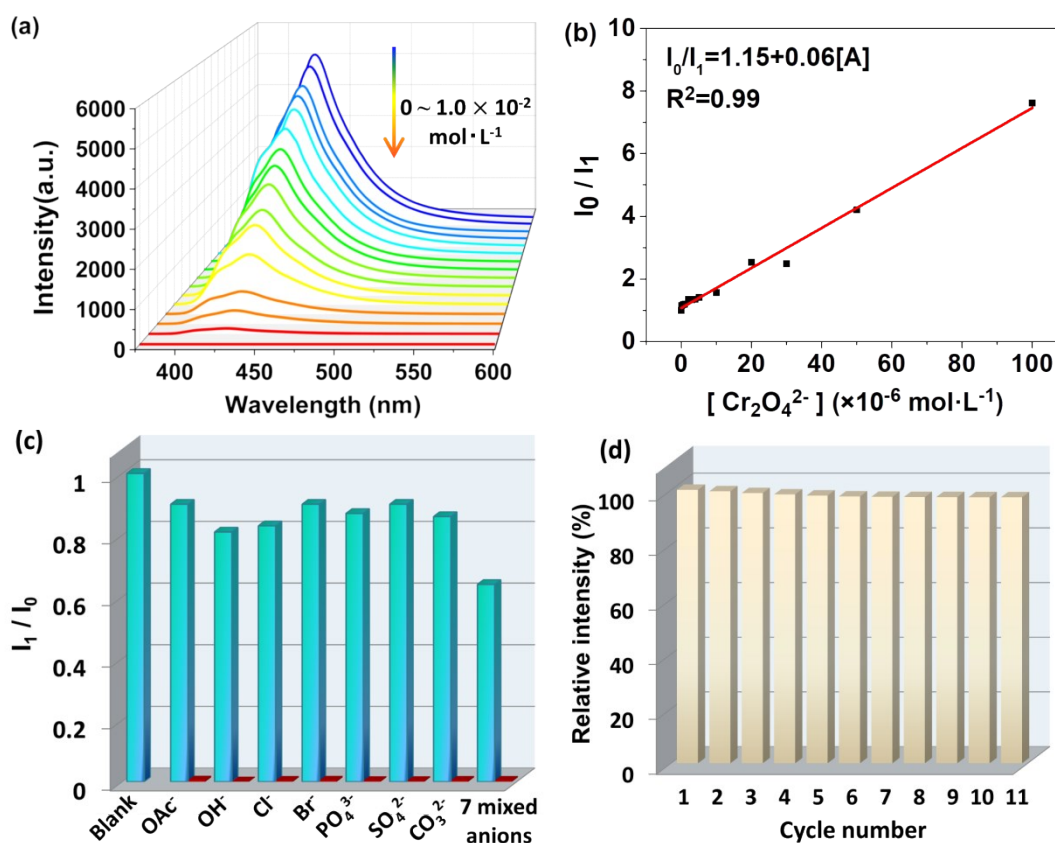


Figure S6. (a) Fluorescence quenching effect of **1@M** towards different concentrations of $\text{Cr}_2\text{O}_7^{2-}$ ($0 \sim 1 \times 10^{-2} \text{ mol L}^{-1}$) in aqueous solution ($\lambda_{\text{ex}}=350$ nm). (b) **1@M** Stern-Volmer plot of I_0/I_1 vs. the concentration of $\text{Cr}_2\text{O}_7^{2-}$ solution. (c) Relative fluorescence intensity of **1@M** dispersed in aqueous solutions upon addition of $1 \times 10^{-2} \text{ mol L}^{-1}$ selected anions (blue) and subsequent addition of $\text{Cr}_2\text{O}_7^{2-}$ (red). (d) The variations of relative fluorescence intensity of **1@M** for probing $\text{Cr}_2\text{O}_7^{2-}$ under 11 cycles.

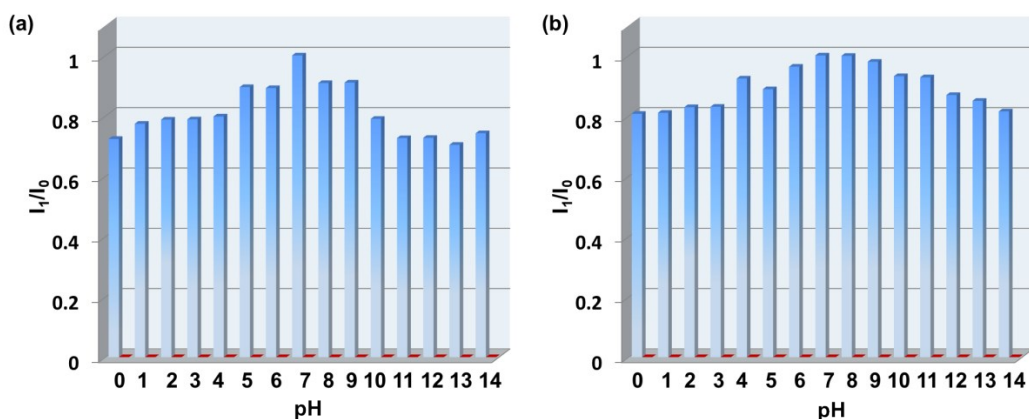


Figure S7. Relative fluorescence intensity of **1@M** (a) and **2@M** (b) in different pH aqueous solutions (blue) and subsequent addition of $\text{Cr}_2\text{O}_7^{2-}$ (red).

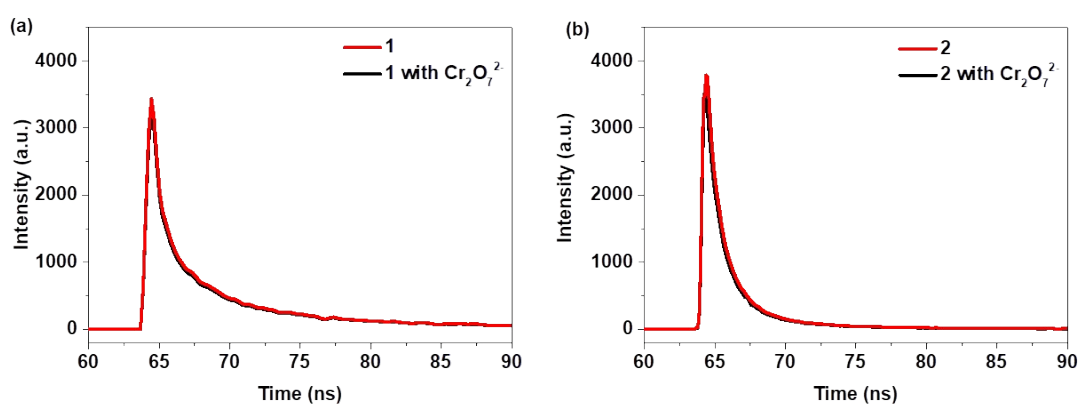


Figure S8. Time-resolved fluorescence decay curves of **1**, (a) and **2**, (b) before and after the addition of $\text{Cr}_2\text{O}_7^{2-}$.

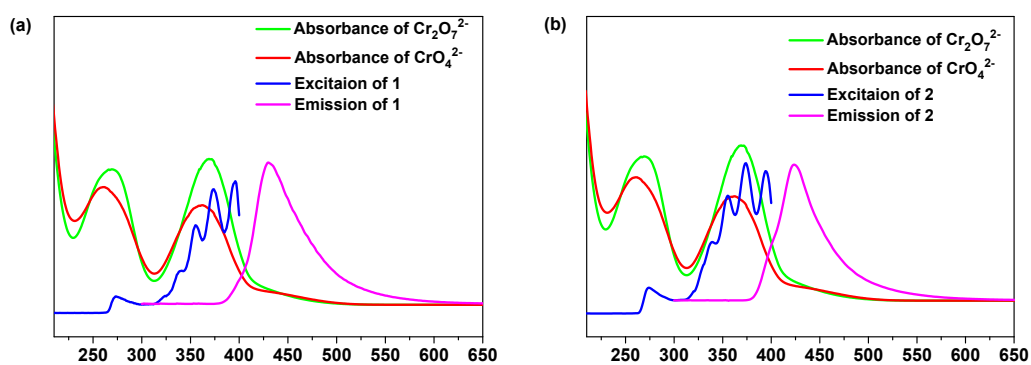


Figure S9. The excitation and emission spectra of **1** and **2** and the UV-Vis absorption spectra of $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} in H_2O .

Table S1. Crystal data and structure refinement details for **1**, **2** and **3**.

	1	2	3
Formula	C ₂₈ H ₂₁ CdClN ₂ O ₂	C ₅₆ H ₄₈ CdN ₄ O ₇	C ₃₈ H ₄₂ CdN ₄ O ₇
Molecular weight	565.32	1001.38	779.15
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>P</i> 2/ <i>c</i>
a (Å)	9.272(1)	58.626(2)	15.209(1)
b(Å)	9.938(1)	20.813(4)	6.052(1)
c(Å)	13.485(1)	8.986(3)	19.056(1)
α (°)	92.121(3)	90	90
β (°)	98.182(4)	91.397(5)	102.175(1)
γ (°)	98.858(3)	90	90
V (Å ³)	1213.0(3)	10962(5)	1714.87(9)
Z	2	8	2
F(000)	568	4128	804
μ (mm ⁻¹)	1.038	0.450	0.694
D _c (g/cm ³)	1.548	1.214	1.509
R(int)	0.0395	0.0320	0.0392
GOF on F ²	1.026	1.025	1.050
R ₁ ^a [I>2σ(I)]	0.0414	0.0724	0.0319
wR ₂ ^b [I>2σ(I)]	0.0757	0.0972	0.0587

$${}^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; {}^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}.$$

Table S2. Performance of fluorescent CPs for Cr₂O₇²⁻ detection.

CPs	LOD(μM)	Linear range (mM)	K _{SV} (M ⁻¹)	Response time	ref
{[Zn ₂ (5N ₃ -IPA) ₂ (4,4'-azp) ₂](H ₂ O) ₈] _n	0.004	-	5.87 × 10 ⁴	-	7
Zn(NIPH) ₂ (HPF) ₂	0.02	-	1.3 × 10 ⁴	-	8
Zn(tpbpc) ₂	0.047	0-250	1.65 × 10 ⁵	10 min	9
SQDs@UiO-66-NH ₂	0.16	0-200	2.9 × 10 ⁴	10 s	10
2@M	0.2	0-100	1.38 × 10⁴	seconds	This work
CDs@Eu-CPs	0.21	2-100	5.56 × 10 ³	5 min	11
1@M	0.4	0-100	1.45 × 10⁴	seconds	This work
[Cd _{1.5} (L) ₂ (bpy)(NO ₃) ₂ ·2DMF·2H ₂ O]	0.422	-	5.42 × 10 ⁴	-	12
[Al(OH)(IPA-CHO)]·0.5H ₂ O·0.4DMF	0.69	-	1.43 × 10 ⁴	seconds	13
Zr(IV)-CPs	1.5	-	1.57 × 10 ⁴	-	14
NU-100	1.8	-	1.34 × 10 ⁴	-	15
[Ag(btX) _{0.5} (DCTP) _{0.5}] _n	2.04	5-50	1.92 × 10 ⁴	-	16
[Zn ₂ (TPOM)(NDC) ₂]·3.5H ₂ O	2.35	0-120	9.31 × 10 ³	seconds	17
[Cd(IPA)(3-PN)] _n	2.52	0-400	2.91 × 10 ³	-	18
{[Zn ₂ (TPOM)(NH ₂ -BDC) ₂]·4H ₂ O} _n	3.9	-	7,59 × 10 ³	-	19
NH ₂ -Zn-CPs	3.9	0-100	7.59 × 10 ³	seconds	19
[Zn(IPA)(3-PN)] _n	12.02	-	1.37 × 10 ³	-	17
{[Cd(4-BMPD)(BPDC)]·2H ₂ O} _n	37.6	-	6.40 × 10 ³	-	20

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