Supplementary Information for

A dual-functional fluorescent nanaoprobe based on UIO-66-NH_2 for continuous detection of o-phenylenediamine and Ag^+

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Chemicals

o-Phenylenediamine (OPD), m-phenylenediamine (MPD), p-phenylenediamine (PPD), 2,3-Diaminophenazine (DAP), Zirconium chloride ($ZrCl_4$), 2-amino-terephthalic acid (ATA), N, N-dimethylformamide (DMF), $AgNO_3$, were obtained from Aladdin reagent company (Shanghai, China). All reagents and solvents were commercially available and used as received, without undergoing purification procedure.

Synthesis of UIO-66-NH_2

UIO-66-NH_2 was synthesized using a solvothermal method based on a previously reported approach.[1] In summary, $ZrCl_4$ (1 mmol) and ATA (1 mmol/L) were dissolved in DMF (50 mL) at room temperature, and the resulting mixture under constant stirring to form a clear solution. The resulting mixture was then transferred to a 100 mL Teflon reactor and maintained at 120 °C for 48 h. After cooling to room temperature, the faint yellow powder obtained was centrifuged, washed with DMF and methanol (each wash repeated at least three times) to remove any remaining unreacted ligands and metals, and finally dried under vacuum at 80 °C for 12 h.

Density-functional theory (DFT) calculations

DFT calculations were carried out using the CP2K code. A mixed Gaussian and planewave basis sets were employed to the calculations. Core electrons were represented with norm-conserving Goedecker-Teter-Hutter pseudopotentials, and the valence electron wavefunction was expanded in a double-zeta basis set with polarization functions along with an auxiliary plane wave basis set with an energy cutoff of 400 Ry. The generalized gradient approximation exchange-correlation functional of Perdew, Burke, and Enzerhof (PBE) was used. Each configuration was optimized with the Broyden-Fletcher-Goldfarb-Shanno (BGFS) algorithm with SCF convergence criteria of 3×10^{-6} au. To compensate the long-range van der Waals dispersion interaction between the adsorbate and the zeolite, the DFT-D3 scheme with an empirical damped potential term was added into the energies obtained from exchange-correlation functional in all calculations.

Table S1. Energy spectrum quantitative analysis report of UIO-66-NH_2

UIO-66-NH_2	C	O	Zr	N	Total
wt%	40.72	19.27	36.02	3.99	100.00

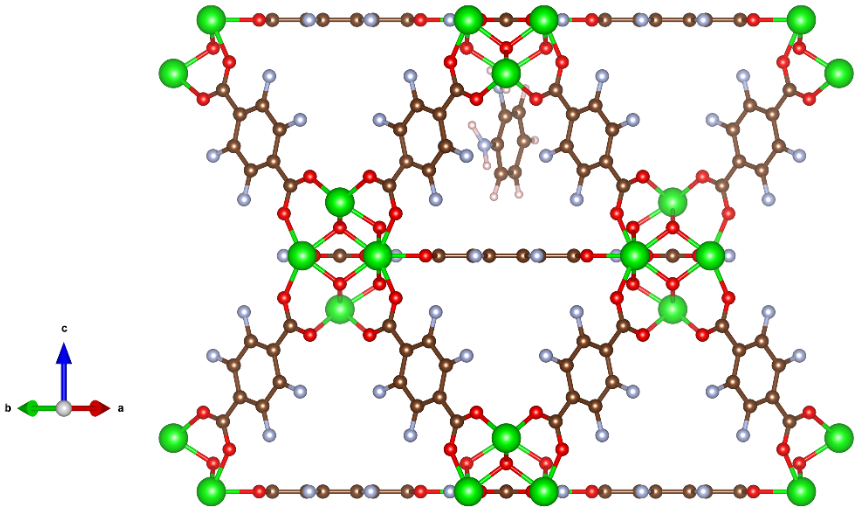

Fig. S1 Diagram of H-bond between o-phenylenediamine and MOFs

Table S2. Comparison of detection performances among different assays for Ag^+ detection.

Detection methods	Linear ranges (μM)	Detection limits (μM)	Ref.
Fluorescence analysis	0-90	0.32	[2]
Fluorescence analysis	0-16	0.87	[3]
Colorimetric analysis	1.07-375	0.41	[4]
Colorimetric analysis	0.50-1000	0.50	[5]
Fluorescence analysis	0.31-225	0.28	This work

Table S3. Determination of Ag^+ in water samples.

Sample	Ag^+ spiked (μM)	Measured concentration (μM)	Recovery (%)	RSD (%, n=3)
Mineral water	0	0.40	-	-
	0.875	1.38	108	8.9
	1	1.39	94	8.6

Reference

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