Supplementary Material

A turn-on fluorescent probe for Cd^{2+} detection in aqueous environment based on imine functionalized nanoscale metal-organic framework

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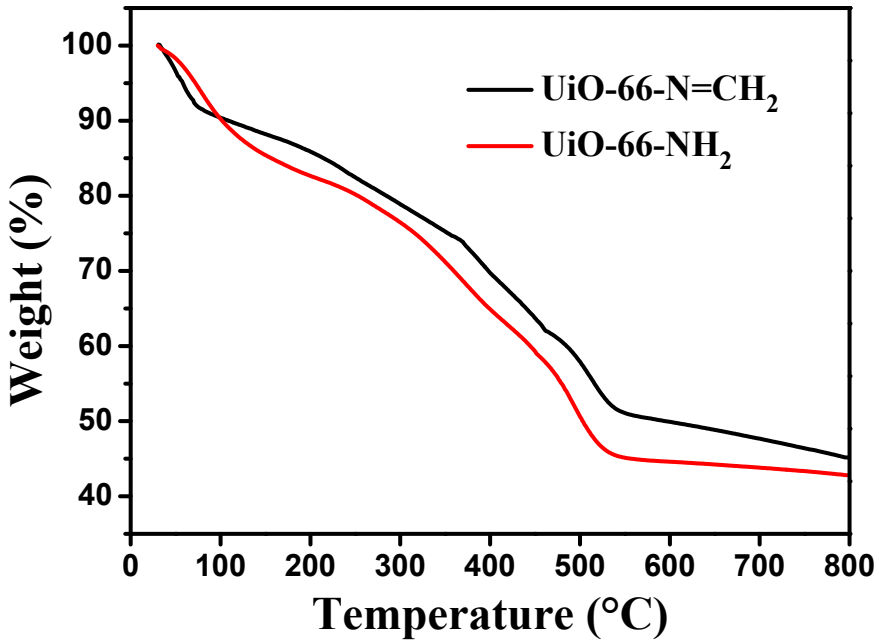

Fig. S1 TGA analysis of UiO-66-NH_2 (red line) and UiO-66-N=CH_2 (black line).

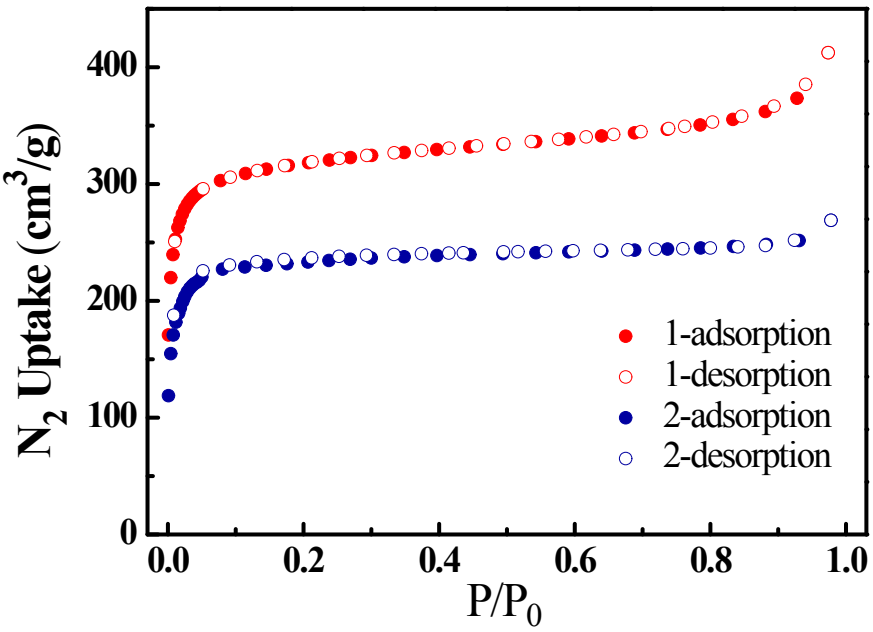

Fig. S2 N_2 sorption isotherms of UiO-66-NH_2(1) andUiO-66-N=CH_2(2) at 77 K. Solid symbols: adsorption, open symbols: desorption.

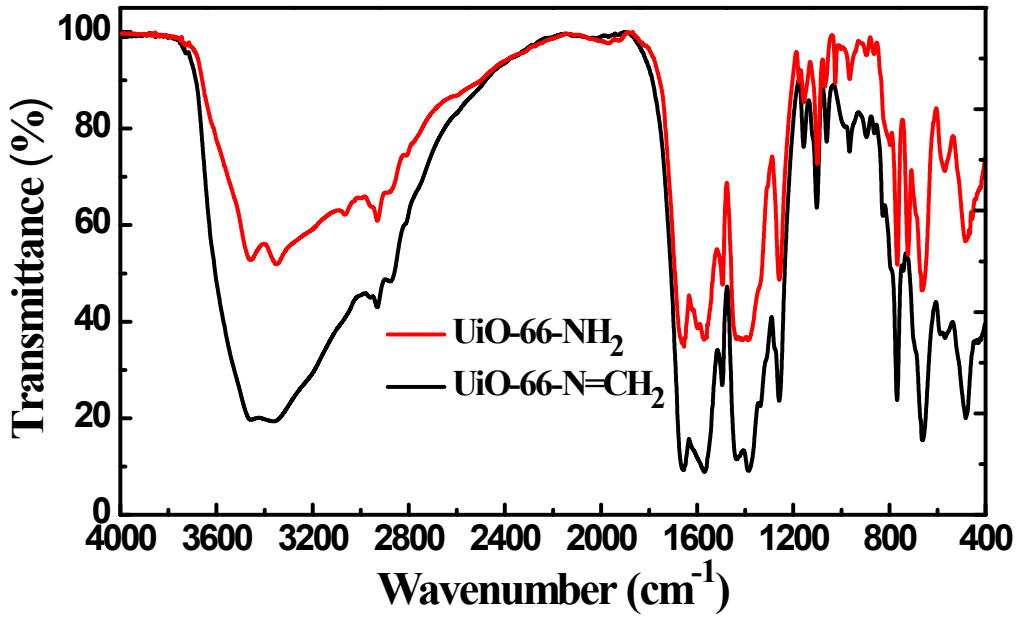

Fig. S3 FT-IR spectra of UiO-66-NH_2(red) and UiO-66-N=CH_2(black).

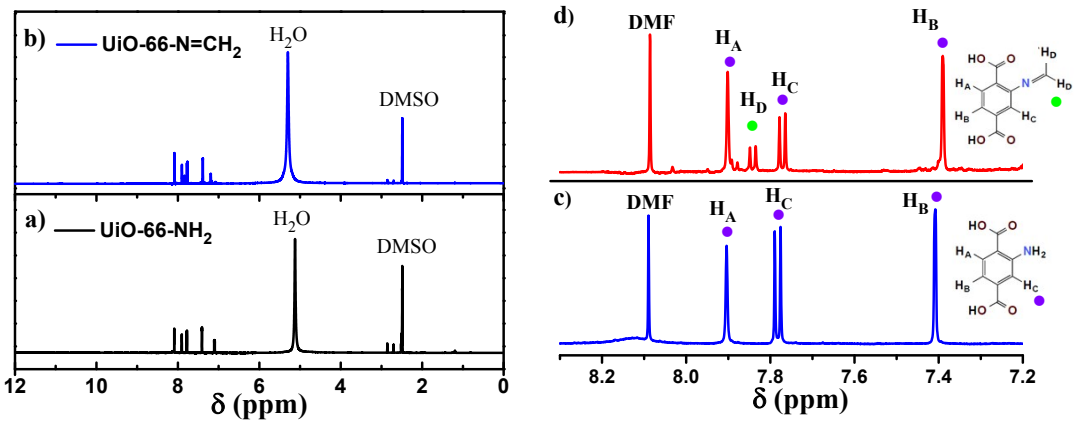

Fig. S4 Full ^{1}H-NMR spectra (500 MHz) of UiO-66-NH_2 (a) and UiO-66-N=CH_2 (b) and partial spectra of UiO-66-NH_2 (c) and UiO-66-N=CH_2 (d) between 7.2-8.3 ppm.

Table S1 Protons and their ^{1}H NMR chemical shifts of UiO-66-N=CH_2 and the calculated percent of imine functionalization.

Proton	Chemical shift, ppm(splitting)	Predicted Integration	Actual Integration	Percent of functionalization
H_A	7.90 (doublet)	1 H	1.00 H	
H_B	7.39 (multiplet)	1 H	0.99 H	
H_C	7.77 (doublet)	1 H	1.02 H	
H_D	7.85 (doublet)	2 H	0.64 H	32 %
DMF	8.09 (singlet)	--	--	
H_2O	5.00 (singlet)	--	--	

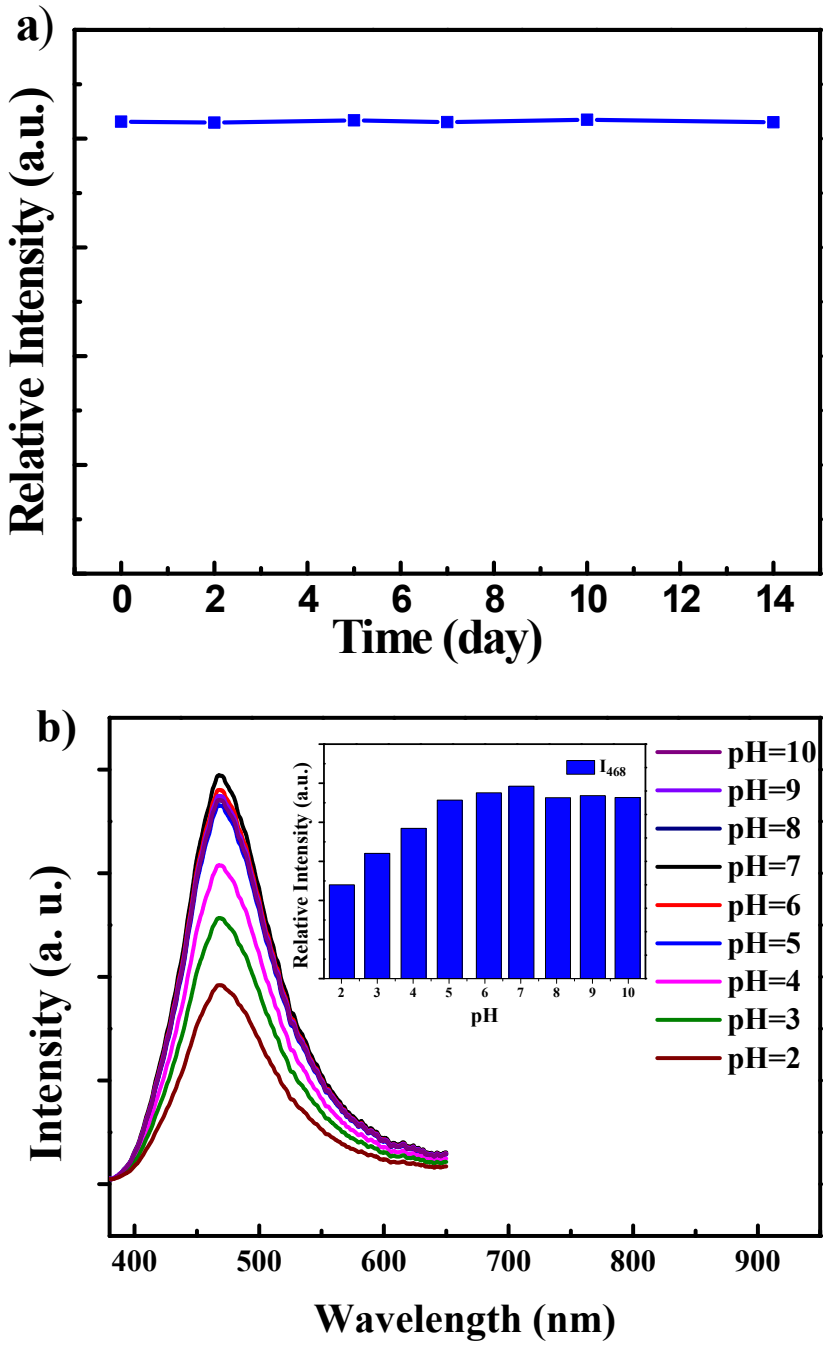

Fig. S5 Day-to-day stability of fluorescent intensity (at 468 nm) of **UiO-66-N=CH$_2$** (1.0 mg/mL) in H_2O (a), and the emission spectra of **UiO-66-N=CH$_2$** in different pH aqueous solution (b), λ_{ex} = 342 nm.

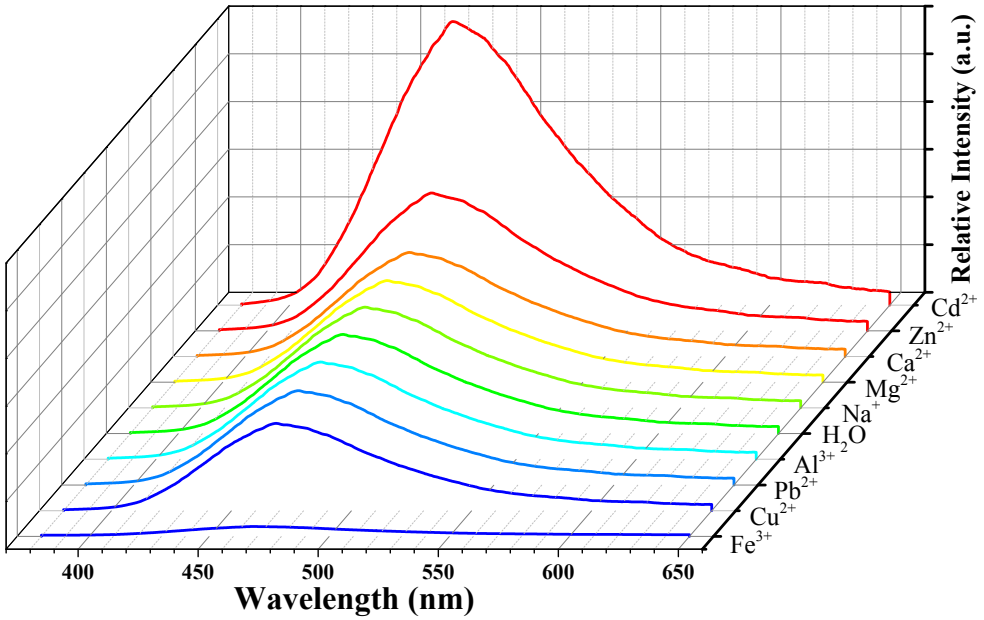

Fig. S6 The luminescent emission spectra of **UiO-66-N=CH$_2$** (1 mg/mL) dispersed in different metal ion solutions (500 μM).

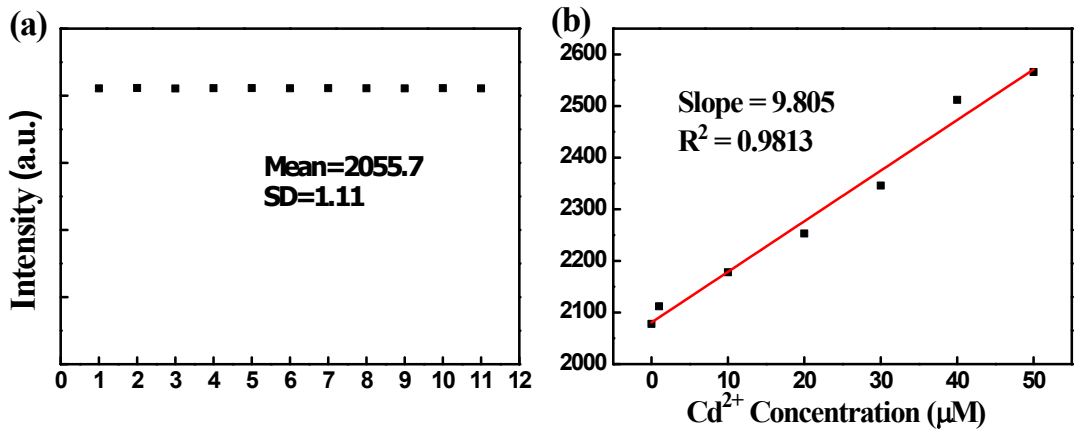

Fig. S7 The replicating experiments of blank solutions (a) and the fitting curve (b) of the emission intensity (468 nm) of **UiO-66-N=CH$_2$** in Cd^{2+} solutions with concentrations from 0 to 50 μM.

Linear Equation: $y = 9.805 \times 10^6 \times x + 2080.6$;

Slope = 9.805 × 10^6 M^{-1};

SD = $\sqrt{\frac{\sum (F - F_0)^2}{N-1}}$ = 1.11 (N=11);

LOD = 3SD/Slope = 0.336 μM

Slope is the slope of the fitting curve in Fig. S7b; SD is the standard deviation for replicating detections of blank solutions (Fig. S7a); F is the fluorescence intensity of **UiO-66-N=CH$_2$** in water and F_0 is the average intensity of 11 times blank experiment.

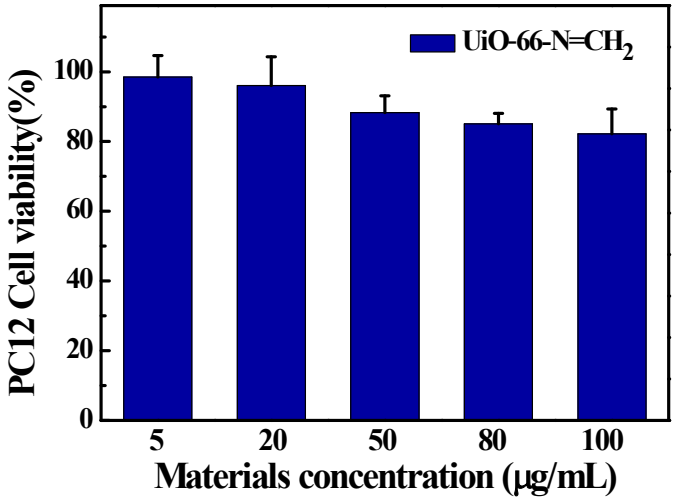

Fig. S8 MTT experiment of **UiO-66-N=CH$_2$.** PC12 cell viability after exposure to different concentrations of **UiO-66-N=CH$_2$** for 24 hours.

Table S2 Quantum yields of UiO-66-N=CH$_2$ and Cd^{2+}@ UiO-66-N=CH$_2$ when excited by 390 nm.

Sample	Quantum yield
UiO-66-N=CH$_2$	2.53 %
Cd^{2+}@ UiO-66-N=CH$_2$	5.38 %

Integration time: 10000 ms.

Integration range of absorption wavelength: 350-410 nm.

Integration range of emission wavelength: 411-600 nm.

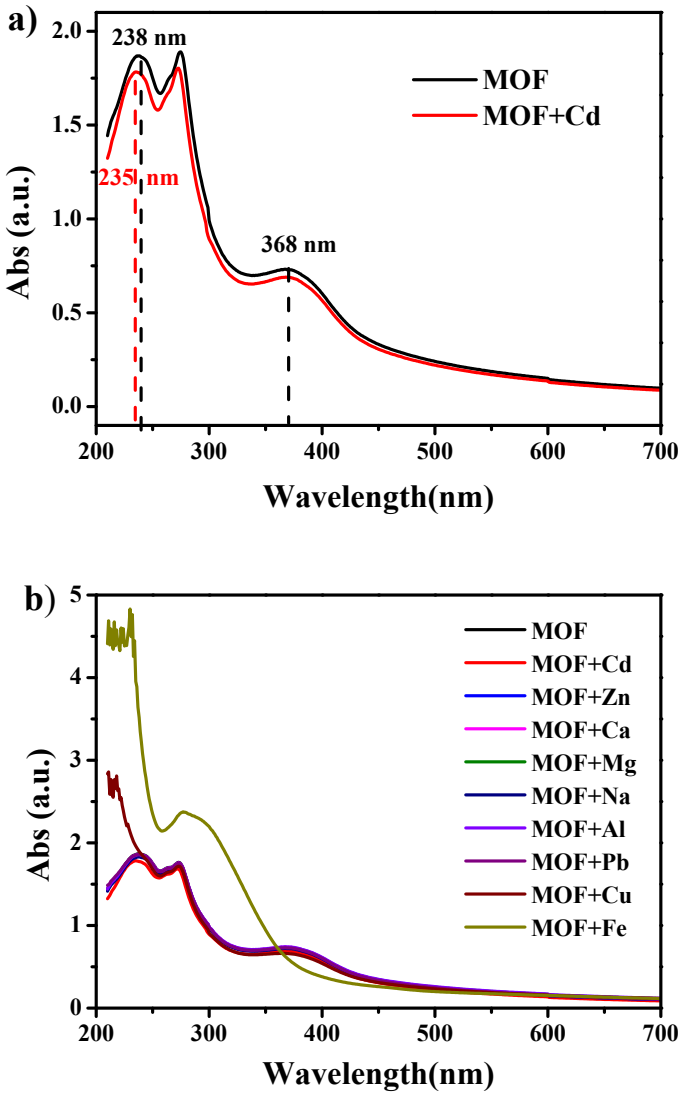

Fig. S9 (a) UV-vis absorption spectra of **UiO-66-N=CH$_2$** solution in the absence and presence of Cd^{2+}; (b) UV-vis spectra of **UiO-66-N=CH$_2$** solution in the absence and presence of different metal ions.

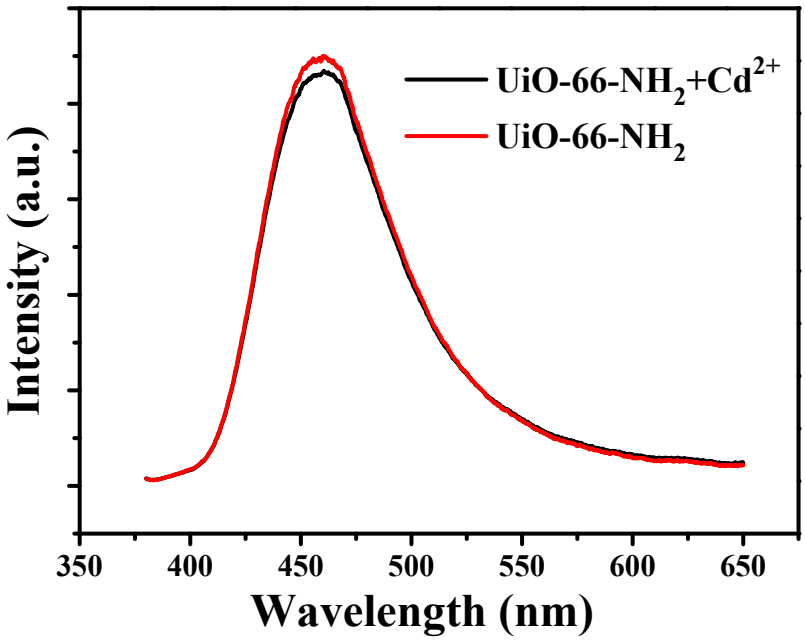

Fig. S10 The luminescent emission spectra of **UiO-66-NH_2** (1 mg/mL) in the absence and presence of Cd^{2+} (500 μM).

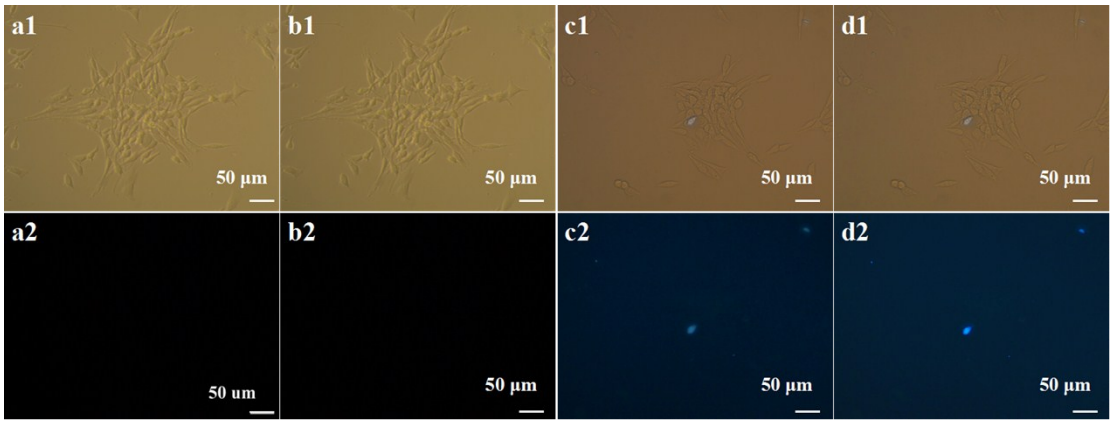

Fig. S11 Optical microscopy images of PC12 cells a) without treatment, b) incubated with 10^{-3} M Cd^{2+}, c) incubated with 50 μg/mL **UiO-66-N=CH$_2$** and d) subsequent addition of 10^{-3} M Cd^{2+}. Optical bright field microscopy image for a1, b1, c1 and d1, optical luminescent field microscopy image illuminated with 365 nm light for a2, b2, c2 and d2.