Supporting Information for

Covalent Organic Frameworks Encapsulated Europium Clusters for Convenient Detection of Ag+ Released by Nanosilver

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1. EXPERIMENTAL SECTION

1.1 Apparatus.

All reagents of analytical grades were obtained from commercial sources and used without further purification. The UV-vis absorption spectra were collected UV-2450 spectrophotometer (Shimadzu, Japan). JEOL2010 on transmission electron microscope (TEM, Japan) were used to characterize the morphologies of the materials. Fluorescence spectra were performed on an F-97 Pro fluorescence spectrometer (Shanghai Lingguang Technology Co. LTD, Shanghai, China). The slit widths (including excitation and emission) and the photomultiplier tube (PMT) voltage were set at 10 nm and 750 V, respectively. The X-ray photoelectron spectroscopy (XPS) was conducted with a Thermo ESCALAB 250 spectrometer (USA) using an Al Ka monochromator source (hv=1486.6 eV) and a multidetection analyzer. Fourier transform infrared (FTIR) spectra were recorded in the 4000-400 cm⁻¹ region using KBr pellets and a Nicolet/Nexus-670 FTIR spectrometer. Powder X-ray diffraction patterns (PXRD) were determined with a Rigaku Smart Lab diffractometer (Bragg-Brentano geometry, Cu K α 1 radiation, λ = 1.54056 Å).

1.2 Fluorescence quantum yield measurement.

The absolute quantum yields (QY) was calculated as the ratios between the emitted light and the absorbed excitation light by the materials. The measurements were performed using an integrating sphere attached to Edinburgh FLS 1000 with the excitation light at 330 nm from a 450 W Xenon

lamp. The suspension of each material was placed in a UV quarts cuvette with a light path of 10 mm to measure its QY. Meanwhile, the solvent (water) filled in another quart's cuvette was used as a blank sample for reference. The spectral correction curve that related to the sensitivity of the monochromator, detector, sphere coating, and optics to wavelength was deducted.

1.3 XPS test

In this work, the X-ray photoelectron spectroscopy (XPS) was conducted with a Thermo ESCALAB 250 spectrometer (USA) using an Al Ka monochromator source (hv=1486.6 eV) and a multidetection analyzer. The sample was prepared on silicon substrate by aluminum double-tape. The sample based film was loaded into Thermo Fisher Scientific ESCALAB 250 XPS system, where Ar+ bombardment was performed and surface chemical state of the sample was characterized. XPS spectra were recorded using a monochromated Al Kα (1486.6 eV) X-ray source with the take-off angle of 90° after different Ar+ bombardment time. The Ar+ bombardment was operated with EX05 argon ion gun whose angle arrangement given the sample surface normal is 45° at a chamber pressure of 1×10-6 Pa. The ion beam voltage was 3 kV and the emission current was 2 μ A. The spectra were collected and analyzed by Avantage software.

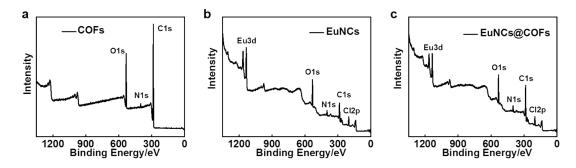


Figure S1. XPS spectra of (a) COFs, (b) EuNCs and (c) EuNCs@COFs, respectively.

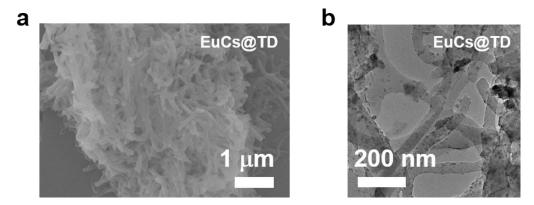


Figure S2. (a) SEM and (b) TEM images of EuNCs@COFs, respectively.

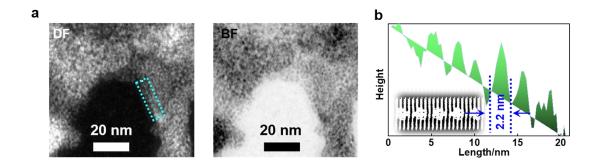


Figure S3. (a) SEM image of EuCs@TD. (b) TEM image of EuCs@TD. (e) HAADF images of EuCs@TD. DF represents dark field. BF represents bright field. (f) EDS mapping of the C, N, O, CI and Eu elements in EuCs@TD.

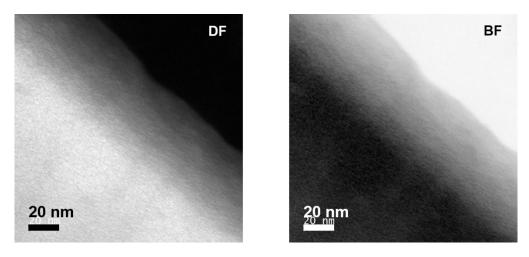


Figure S4. HAADF images of TD COFs. DF represents dark field. BF represents bright field.

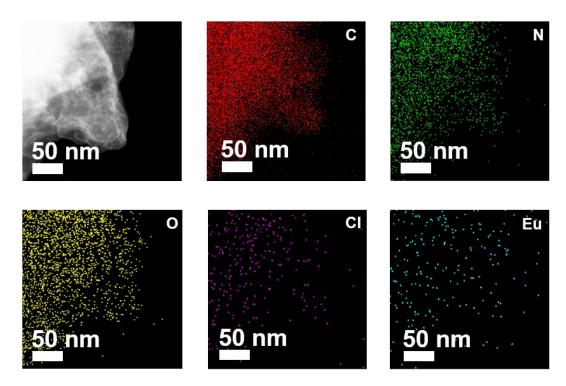


Figure S5. EDS mapping of the C, N, O, Cl and Eu elements in EuNCs@COFs.

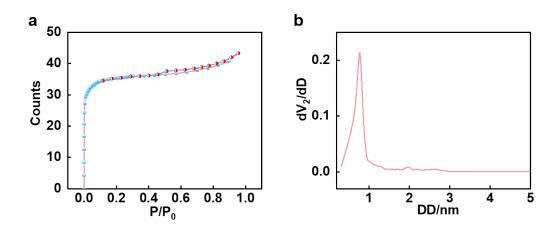


Figure S6. (a) N_2 isothermal adsorption-desorption curves of TD COFs. (b) Corresponding pore size distribution of TD COFs.

Table S1. Comparison with other methods for sensing Ag⁺.

Methods	Materials	Response	Linear Range	LOD	OD References	
		Time	(nM)	(nM)	References	
Colorimetric	TiO ₂ PNZs	300 s	0-200000	920	1	
Colorimetric	AuNCs	600 s	500-10000	204	2	
Colorimetric	TMB-DNA	900 s	1	1.9	3	
Electrochemical	MXene	10 s	500-10000	615	4	
Fluorescence	TPE-4TA	7200 s	40-15000	2.3	5	
Fluorescence	LnMOF-2	/	1	50	6	
Fluorescence	TbC	/	0-800000	14900	7	
Fluorescence	EuCs@TD	Real time	1-10000	0.35	This work	

Table S2 Various fluorescent sensing strategies for detection of UO₂²⁺.

Commercial	EuNCs@	RSD(n=3)	Ag⁺	Consistency	
AgNPs	COFs	K3D(II-3)	electrode	Consistency	
1	52.7 nM	7.8%	58.6	93%	
2	23.5 nM	11.5%	20.1	117%	

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