Supporting Information

Fluorescence of europium from absence to emergence in cadmium-induced heterobimetallic organic frameworks for

ratiometric sensing

Meiling Li, Weiting Yang,* Shuixing Wu, Zhongmin Su and Qinhe Pan*

1. Experimental and methods

1.1 Materials and methods

All materials are purchased and used directly without subsequent treatment. H₄TCPE (1,1,2,2-tetra(4-carboxyphenyl)ethylene) was purchased from Yanshen Science and Technology Co., Ltd., Chinese Academy of Sciences of Jilin Province. Eu(NO₃)₃ and Cd(NO₃)₂ were purchased from Aladdin's Reagent. Seawater was taken in Haikou. Infrared (IR) data of KBr discs were collected in the range of 4000 to 400 cm⁻¹ using Bruker TENSOR-27 IR spectrometer. Elemental analysis was measured by Perkin-Elmer 2400 element analyzer. Thermogravimetric analyses (TGA) were measured by Perkin Elmer TGA7 micro-analyzer under air atmosphere with 10 °C/min⁻¹ heating rate. Powder X-ray diffraction (PXRD) were measured on Rigaku Miniflex 600 X-ray diffractometer at room temperature. The fluorescence data were collected with GangDong RF-6000 fluorescence spectrophotometer at 25 °C.

1.2 X-ray crystallography

Single crystal X-ray diffraction data of HNU-72 were carried out on ROD, Synergy Custom system, Bruker P4 diffraction at 273 K with CuK\a radiation ($\lambda = 1.54187$ Å) by / ω -scan technique. The structure was analyzed by direct method (OLEXS) and refined by full-matrix least-squares procedure based on F^2 (SHELXL). Nonhydrogen atoms were refined with anisotropiwc displacement parameters. The final formula of HNU-72 was determined by single-crystal structure together with elemental analysis and TGA results. The disordered solvents were removed with the SQUEEZE option of PLATON. The crystallographic data of HNU-72 are shown in Table S1 and CCDC

number is 2246317.

1.3 Computational Details

The frequency analysis of free ligands was performed using density functional theory (DFT) at the B3LYP/6-31+G (d, p) level. Based on the optimized results, the energies of the triplet excited states of the ligands were calculated by the time-dependent DFT approach. All calculations were performed using Gaussian 16 software. During the geometry optimizations, only hydrogen atoms were relaxed to fit the lowest-energy situations. Model1 in which the three sequential Europium atoms are coated with the ligands and the other metal atoms surrounding the four TCPE⁴⁻ were truncated with hydrogen atoms to saturate the terminal carboxyl groups. Model2 in which the terminal carboxyl groups to saturate the terminal carboxyl groups to saturate the terminal carboxyl groups.

1.4 PXRD and Thermal Stabilities of HNU-72

The PXRD pattern of synthesized HNU-72 is completely consistent with the simulated one, proving the pure phase of prepared sample (Figure S2). The result of TGA is shown in Figure S3. HNU-72 has a weight loss of about 12.1% in the range of 30~340 °C, which corresponds to the guest molecules in the channel (calced 11.7%). As the temperature goes up to 520 °C, the weight of HNU-72 continues to decrease with the organic ligands disintegrating about 37.1% (calced 36.5%), which illustrates the structure collapse.

Complex	HNU-72
Formula	$C_{66}H_{46}O_{18}N_2CdEu_2$
Mr	1571
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	11.9444(6)
<i>b</i> (Å)	11.9638(7)
<i>c</i> (Å)	14.4885(8)
<i>α</i> (°)	67.002
β(°)	79.817
γ(°)	65.944
$V(Å^3)$	1739.95
Z	2
$D_{\rm calc}(\rm g cm^{-3})$	1.539
<i>F</i> (000)	792.8
$R_{\rm int}$	0.068
GOF on F ²	1.037
$R_1^a[I>2\delta(I)]$	0.0751(5179)
wR_2^{b} (all data)	00.1984(5906)

 Table S1. Crystallographic data of HNU-72.

 ${}^{a}R1 = \Sigma(|F_{o}| - |F_{c}|) / \Sigma|F_{o}|. \ {}^{b}wR_{2} = [\Sigma w(|F_{o}|^{2} - |F_{c}|^{2}) / \Sigma w(F_{o})^{2}]^{1/2}.$

 Table S2. Calculated excited state of H₄TCPE.

Basis set	6-31+G(<i>d</i> , <i>p</i>)			
Name	Triplet (eV)			Singlet (eV)
	T ₁	T_2	T ₃	S ₁
H₄TCPE	2.2661 18240 (cm ⁻¹)	3.0883	3.0946	3.2429 (26102 cm ⁻¹)

	Excitation energy (wave length)	Oscillator strength	MO contributions
S ₁	3.542 eV (350 nm)	0.0026	HOMO \rightarrow LUMO 99.4%
S ₂	3.646 eV (340 nm)	0.7274	HOMO-1 \rightarrow LUMO 84.4% HOMO \rightarrow LUMO+3 13.9%
S ₃	3.697 eV (335 nm)	0.1704	$\begin{array}{ll} \text{HOMO} \rightarrow \text{LUMO+3} & 83.1\% \\ \text{HOMO-1} \rightarrow \text{LUMO} & 14.1\% \end{array}$
S ₄	3.759 eV (330 nm)	0.0001	HOMO \rightarrow LUMO+1 99.7%
T ₁	2.713 eV (457 nm)	0.0000	HOMO-1 \rightarrow LUMO 81.2%
T ₂	2.723 eV (455 nm)	0.0000	HOMO \rightarrow LUMO+3 79.9%
T ₃	3.059 eV (405 nm)	0.0000	HOMO-2 \rightarrow LUMO+2 49.2% HOMO-2 \rightarrow LUMO+7 10.9%
T ₄	3.062 eV (405 nm)	0.0000	HOMO-3 \rightarrow LUMO+1 47.1% HOMO-3 \rightarrow LUMO+5 18.6%

Table S3. Excitation enegies (wave lengths), oscillator strengths and molecular orbital contributions for low-lying singlet and triplet excited states of Model 1 obtained by TDDFT (B3LYP).

Table S4. Excitation enegies (wave lengths), oscillator strengths and molecular orbitalcontributions for low-lying singlet excited states of Model 2 obtained by TDDFT(B3LYP).

	Excitation energy (wave length)	Oscillator strength	MO contributions
			HOMO-2 \rightarrow LUMO 33.1%
S_1	3.565 eV (348 nm)	0.0850	HOMO-3 \rightarrow LUMO+1 25.5%
			HOMO \rightarrow LUMO+2 11.6%
S ₂	3.595 eV (345 nm)	0.0012	HOMO-3 \rightarrow LUMO 30.0%
			HOMO-2 \rightarrow LUMO+1 25.1%
			HOMO-1 \rightarrow LUMO+2 12.7%
			HOMO \rightarrow LUMO+3 12.7%

S.		1 00/2	HOMO \rightarrow LUMO+2	37.5%
	3.621 eV (342 nm)		HOMO-1 \rightarrow LUMO+3	26.0%
33		1.0040	$HOMO-2 \rightarrow LUMO$	18.5%
			HOMO-3 \rightarrow LUMO+1	13.0%
			HOMO-1 \rightarrow LUMO+2	32.5%
S.	3 665 oV (338 nm)	0 00/1	HOMO \rightarrow LUMO+3	26.8%
54	5.005 ev (556 mm)	0.0041	$HOMO-3 \rightarrow LUMO$	18.7%
			HOMO-2 \rightarrow LUMO+1	16.7%
T ₁	2.663 eV (466 nm)	0 0000	HOMO-2 \rightarrow LUMO	36.7%
		0.0000	HOMO-3 \rightarrow LUMO+1	34.3%
т.	2.663 eV (466 nm)	0 0000	HOMO-3 → LUMO	36.5%
12		0.0000	$HOMO-2 \rightarrow LUMO+1$	34.3%
т.	2.673 eV (464 nm)	0.0000	HOMO \rightarrow LUMO+2	36.9%
13		0.0000	HOMO-1 \rightarrow LUMO+3	34.4%
Т	2 673 oV (161 nm)	0 0000	HOMO-1 \rightarrow LUMO+2	36.7%
∎4	2.0/J CV (404 IIII)	0.0000	HOMO \rightarrow LUMO+3	34.5%

 Table S5. Results of HNU-72 for DMS sensing in seawater samples.

HNU-72	Adding (ppm)	Found (ppm)	Recovery (%)	RSD (%)
	0.000	0.001	100.0	1.25
	0.085	0.084	98.8	4.71
Seawater	1.058	1.061	100.3	4.11
	4.230	4.234	100.1	2.62
	8.460	8.462	100.0	2.94

Detection methods	Response probe	Detection limit	Response mode	
Electrochemical		1 15 ppt	mass spectrometry	1
sensor	-	4.15 ppt	mass spectrometry	
Electrochemical	$[CH_{1}SCH_{1} + \Lambda \alpha]$	0.3 npt	mass spectrometry	2
sensor	[CII3SCII3 + Ag]	0.3 ppt	mass spectrometry	
Electrochemical		0.373 pph	BADI DIMS	3
sensor	-	0.375 pp0	DAI I-I IMS	
Electrochemical	Carbonack X	0.323 nnh	GC-FID	4
sensor	Carbopack X	0.525 pp0	00-110	
Electrochemical	electrodes	0.692 nnh	impedance	5
sensor	electiones	0.092 pp0	impedance	
Gas sensor	ZnO	2 ppm	gas sensitive	6
SVG-CL	-	0.184 ppb	chemiluminescence	7
MSSF-CL	-	0.069 ppb	chemiluminescence	8
Colorimetry	sodium nitroprusside	222 ppm	colorimetry	9
Fluorescence	$\mathbf{R}_{\mathbf{e}}(\mathbf{I})_{\mathbf{N}}$	25.5×10^3 nmm	Fluorescence	10
sensor		23.5x10° ppin	Tuorescence	
Fluorescence		14 ppb	Fluorescence	This
sensor	1110-72		Tuorescence	work

 Table S6 Comparison of different methods for DMS detection.



Figure S1. PXRD patterns, and TGA spectrum of HNU-72.



Figure S2. (a) Structural truncation model of HNU-48; (b) Structural truncation model of HNU-72.



Figure S3. Frontier molecular orbitals of Model 1.



Figure S4. Frontier molecular orbitals of Model 1.



Figure S5. Fluorescence spectra of HNU-72 in different solvents.



Figure S6. (a) The fluorescence intensity ratio of HNU-72 to DMS (C_{DMS} =16.9 ppm, λ_{ex} =380 nm) in the presence of other interferers; (b) Five cycles of HNU-72 sensing for DMS.

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