Supporting Information

A 42-metal Yb(III) nanowheel with NIR luminescent response to anions

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Contents

1. General Procedures

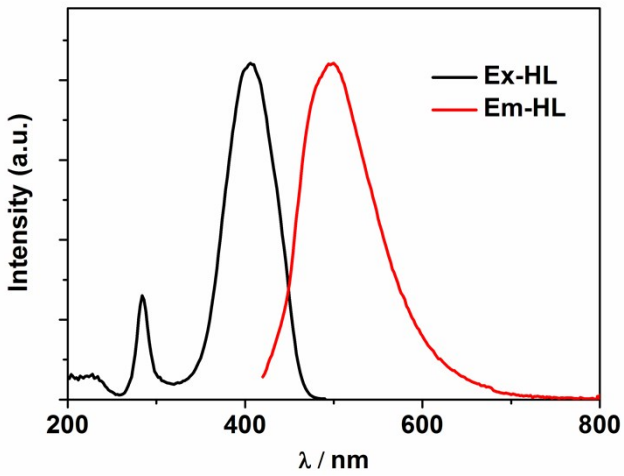
Metal salts and solvents were purchased from Meryer and used directly without further purification. All reactions were performed under dry oxygen-free dinitrogen atmospheres using standard Schlenk techniques. Physical measurements: NMR: AVANCE III AV500. 500 spectrometer (^{1}H, 500 MHz) at 298 K; Powder XRD: D8ADVANCE; HRMS(ESI) analysis: MicroOTOF-QII; IR: Nicolet IS10 spectrometer. Melting points were obtained in sealed glass capillaries under dinitrogen and are uncorrected. The thermogravimetric analyses were carried out on a TA Instruments Q600. Elemental analyses (C, H, N) were carried out on a EURO EA3000 elemental analysis. Field emission scanning electron microscopy (FESEM) images were recorded on a Nova NanoSEM 200 scanning electron microscope. Absorption spectra were obtained on a UV-3600 spectrophotometer, and excitation and emission spectra on a FLS 980 fluorimeter.

Photophysical Studies Visible and NIR luminescence spectra were recorded on a FLS 980 fluorimeter. The light source for the spectra was a 450 W xenon arc lamp with continuous spectral distribution from 190 to 2600 nm. Liquid nitrogen cooled Ge PIN diode detector was used to detect the NIR emissions from 800 nm to 1700 nm. The temporal decay curves of the fluorescence signals were stored by using the attached storage digital oscilloscope. The quantum yields (Φ_{em}) were obtained by using an integrating sphere, according to eqn $\Phi_{em} = N_{em} / N_{abs}$, where N_{em} and N_{abs} are the numbers of emitted and absorbed photons, respectively. Systematic errors have been deducted through the standard instrument corrections. All the measurements were carried out at room temperature.

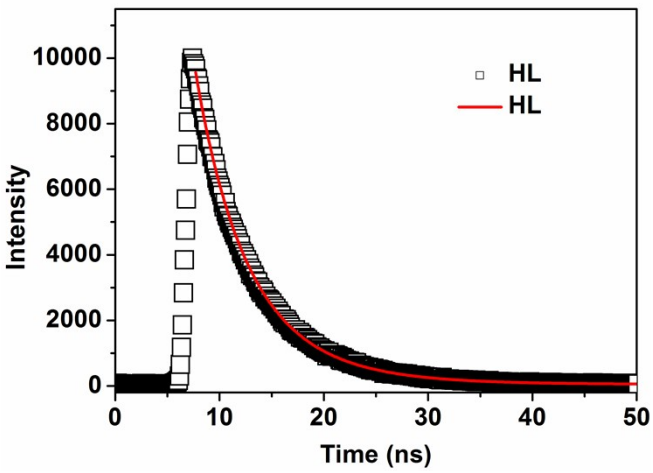
2. Synthesis of 1

$[Yb_{42}(L)_{14}(OH)_{28}(OAc)_{84}]$ (1) $Yb(OAc)_3$ (0.40 mmol, 0.1401 g) and HL (2-Hydroxy-3-methoxybenzaldehyde)(0.30 mmol, 0.0456 g) were dissolved in 30 mL EtOH at room temperature, and a solution of Triethylamine in EtOH (1.0 mol/L, 1 ml) was then added. The resulting solution was stirred and heated under reflux for 30 mins. It was allowed to cool and was then filtered. Diethyl ether was allowed to diffuse slowly into the filtrate at room temperature and pale yellow crystals were obtained after one week. The crystals were filtered off, washed with EtOH (3×5 ml) and dried in the air for one week. Yield (based on $Yb(OAc)_3$): 0.0549 g (40 %). m. p. > 199 ^oC (dec.). Elemental analysis: Found: C, 20.03; H, 2.64 %. Calc. for $C_{280}H_{378}Yb_{42}O_{238}$: C, 19.97; H, 2.66 %. IR (CH_3CN, cm^{-1}): 1620 (s), 1475 (s),1385 (w), 1355 (w), 1265 (s), 1200 (s), 1136 (m), 1106 (w), 1070 (m), 1043 (w), 967 (vs), 873 (m), 843 (m), 823 (m), 781 (s), 735 (vs), 694 (w), 626 (w).

3. Photophysical properties of the free ligand HL



(a)



(b)

Figure S1. (a) The excitation and visible emission spectra of the free ligand HL in CH_3CN.

(b) The lifetime of the emission of the free ligand HL.

4. Photophysical properties of 1

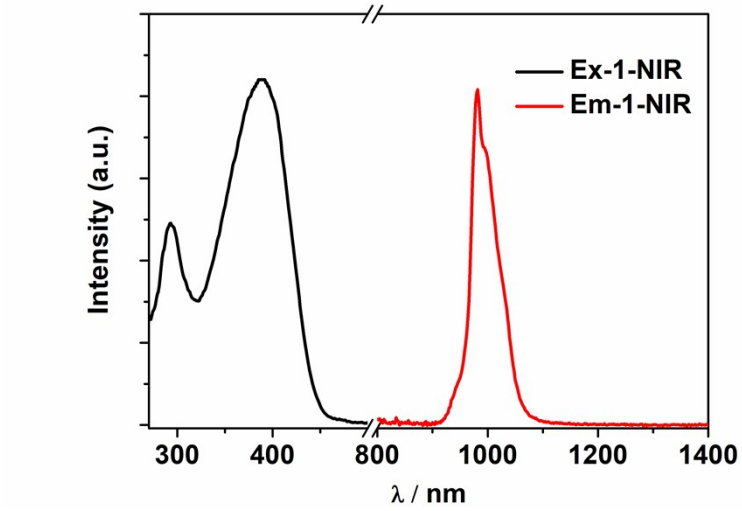


Figure S2. The excitation and NIR emission spectra of **1** in CH_3CN.

5. Visible emission spectra of 1 with the addition of F^- anion

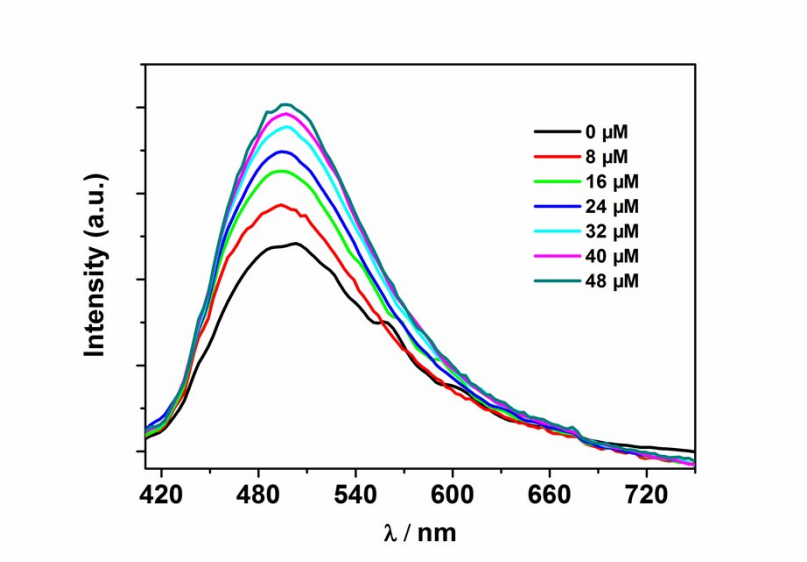
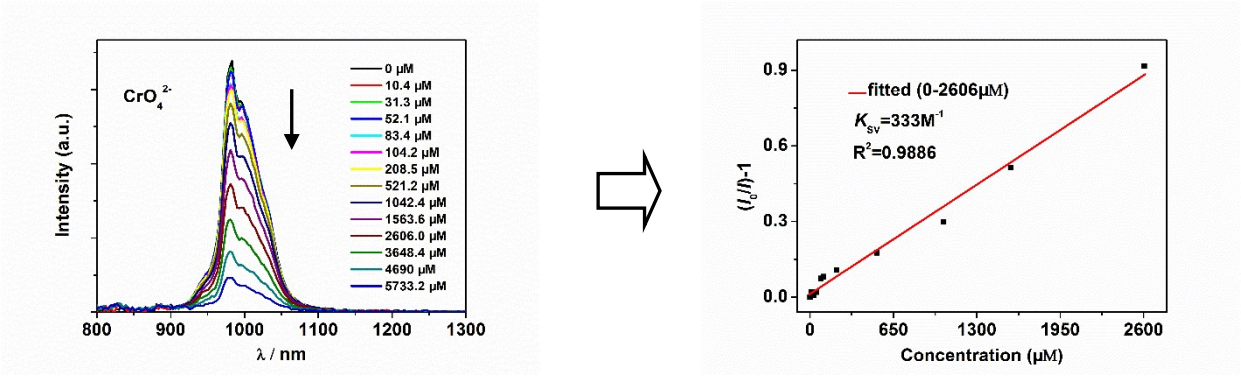
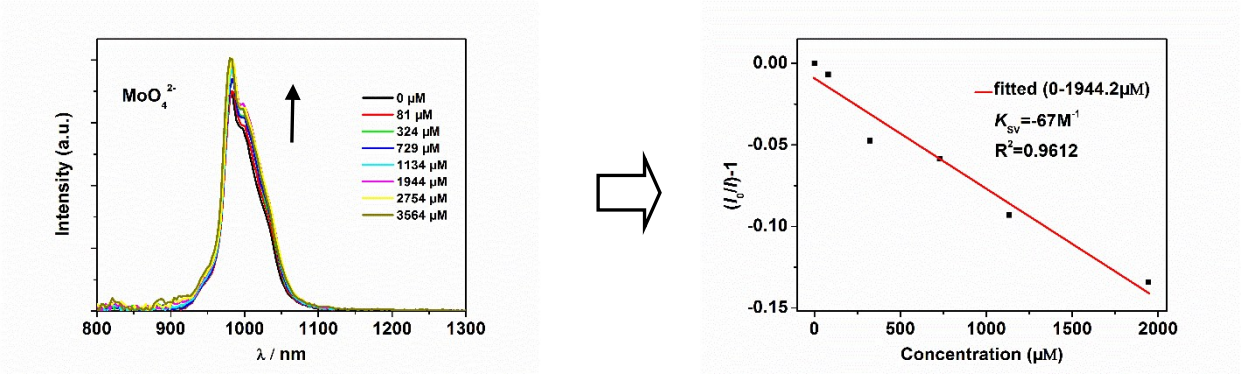
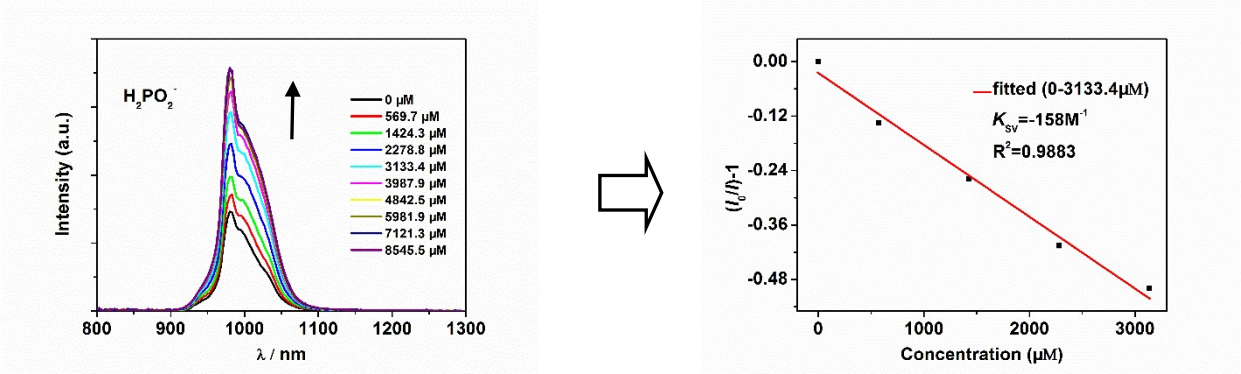


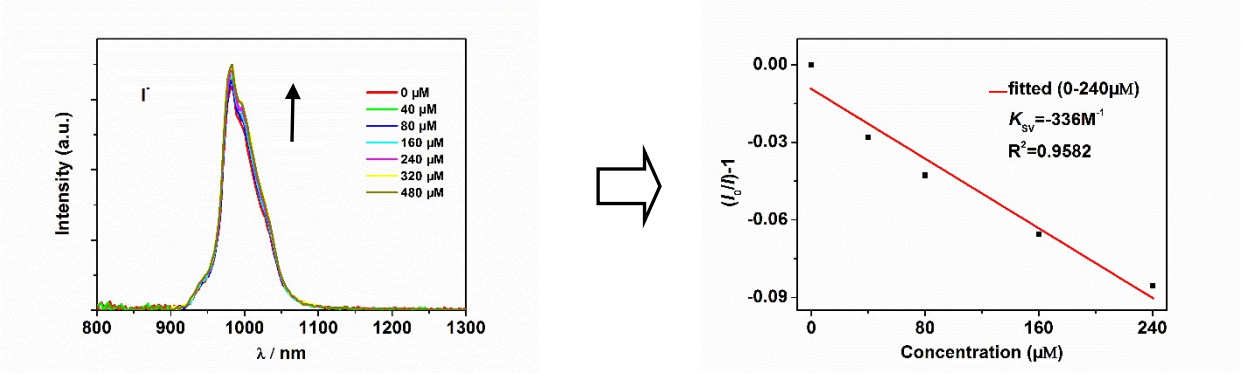
Figure S3. Visible emission spectra of **1** with the addition of different concentrations of F^- anion in CH_3CN.

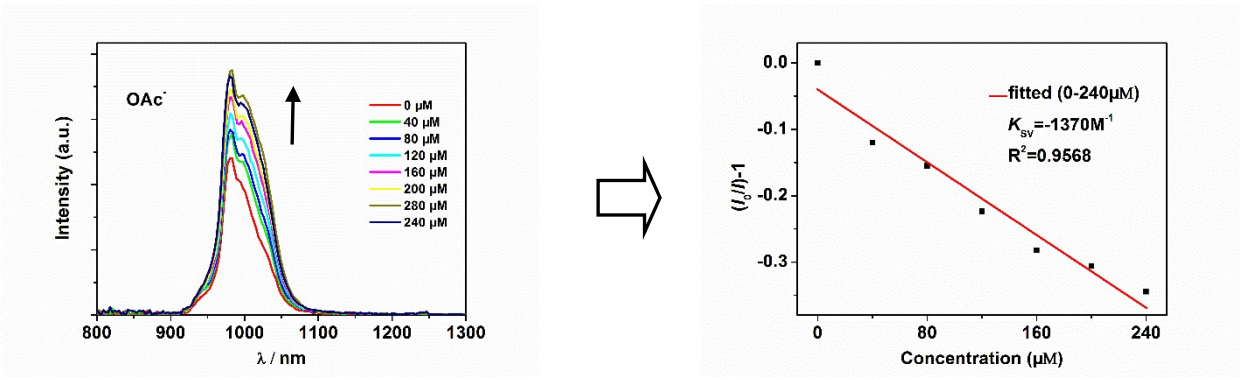
6. NIR luminescent sensing of 1 to anions

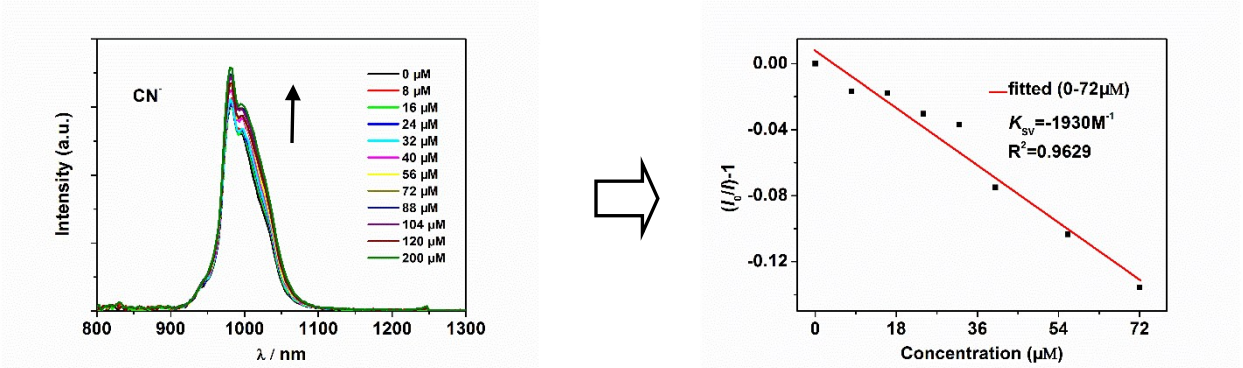


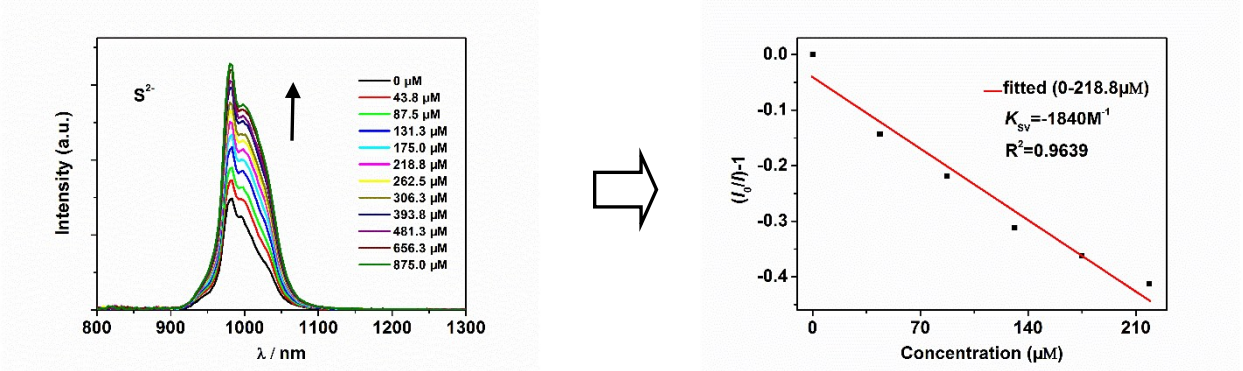


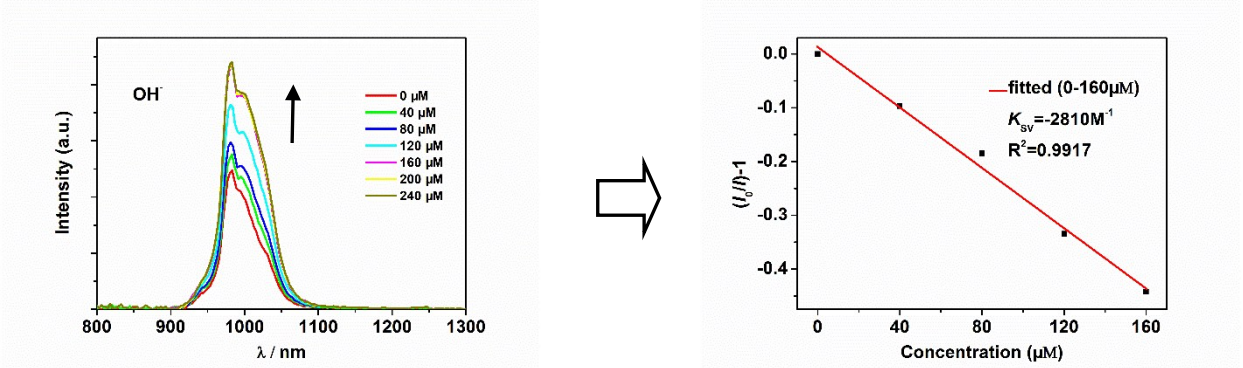


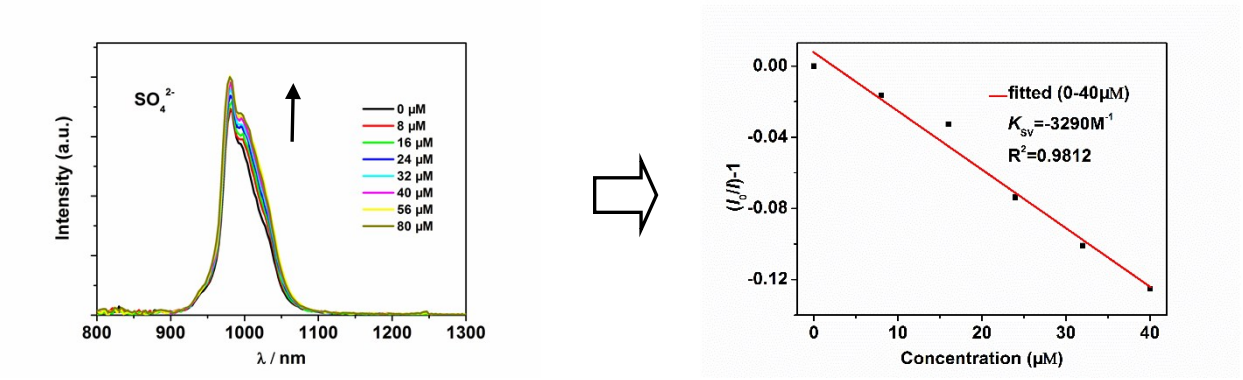


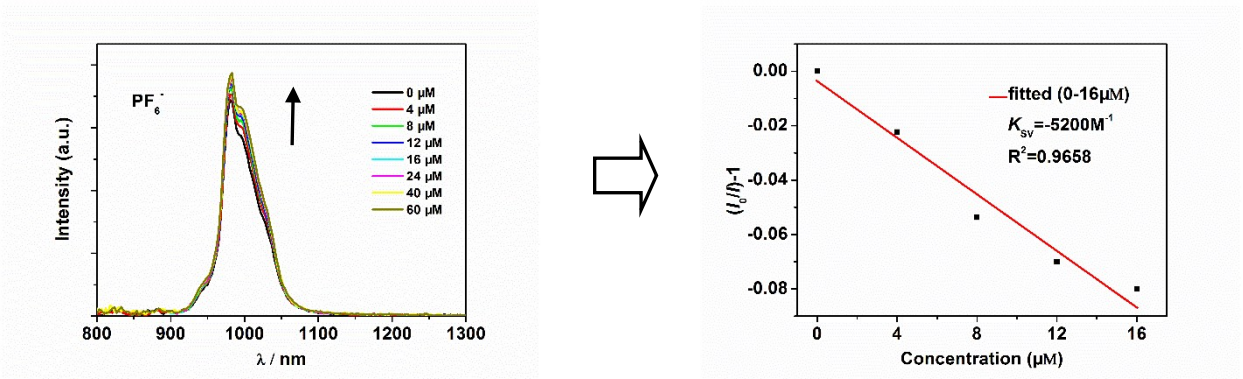

OAc-
0 μM
40 μM
80 μM
120 μM
160 μM
200 μM
280 μM
240 μM
Intensity (a.u.)
λ / nm
fitted (0-240μM)
K_{SV}=-1370M^{-1}
R^2=0.9568
(I_0/I)-1
Concentration (μM)

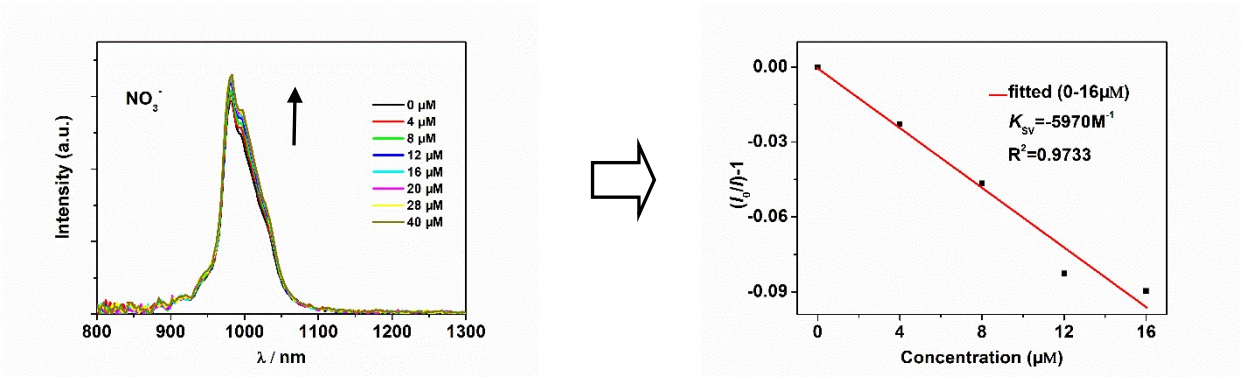

CN-
0 μM
8 μM
16 μM
24 μM
32 μM
40 μM
56 μM
72 μM
88 μM
104 μM
120 μM
200 μM
Intensity (a.u.)
λ / nm
fitted (0-72μM)
K_{SV}=-1930M^{-1}
R^2=0.9629
(I_0/I)-1
Concentration (μM)

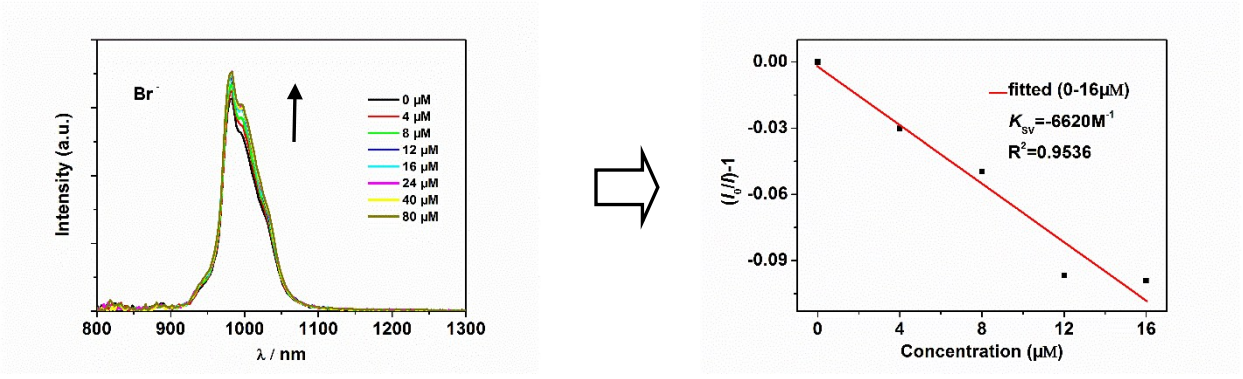

S2-
0 μM
43.8 μM
87.5 μM
131.3 μM
175.0 μM
218.8 μM
262.5 μM
306.3 μM
393.8 μM
481.3 μM
656.3 μM
875.0 μM
Intensity (a.u.)
λ / nm
fitted (0-218.8μM)
K_{SV}=-1840M^{-1}
R^2=0.9639
(I_0/I)-1
Concentration (μM)


OH-
0 μM
40 μM
80 μM
120 μM
160 μM
200 μM
240 μM
Intensity (a.u.)
λ / nm
fitted (0-160μM)
K_{SV}=-2810M^{-1}
R^2=0.9917
(I_0/I)-1
Concentration (μM)


SO4 2-
0 μM
8 μM
16 μM
24 μM
32 μM
40 μM
56 μM
80 μM
Intensity (a.u.)
λ / nm
fitted (0-40μM)
KSV=-3290M-1
R2=0.9812
(I0/I)-1
Concentration (μM)


PF6 -
0 μM
4 μM
8 μM
12 μM
16 μM
24 μM
40 μM
60 μM
Intensity (a.u.)
λ / nm
fitted (0-16μM)
KSV=-5200M-1
R2=0.9658
(I0/I)-1
Concentration (μM)


NO3 -
0 μM
4 μM
8 μM
12 μM
16 μM
20 μM
28 μM
40 μM
Intensity (a.u.)
λ / nm
fitted (0-16μM)
KSV=-5970M-1
R2=0.9733
(I0/I)-1
Concentration (μM)


Br -
0 μM
4 μM
8 μM
12 μM
16 μM
24 μM
40 μM
80 μM
Intensity (a.u.)
λ / nm
fitted (0-16μM)
KSV=-6620M-1
R2=0.9536
(I0/I)-1
Concentration (μM)

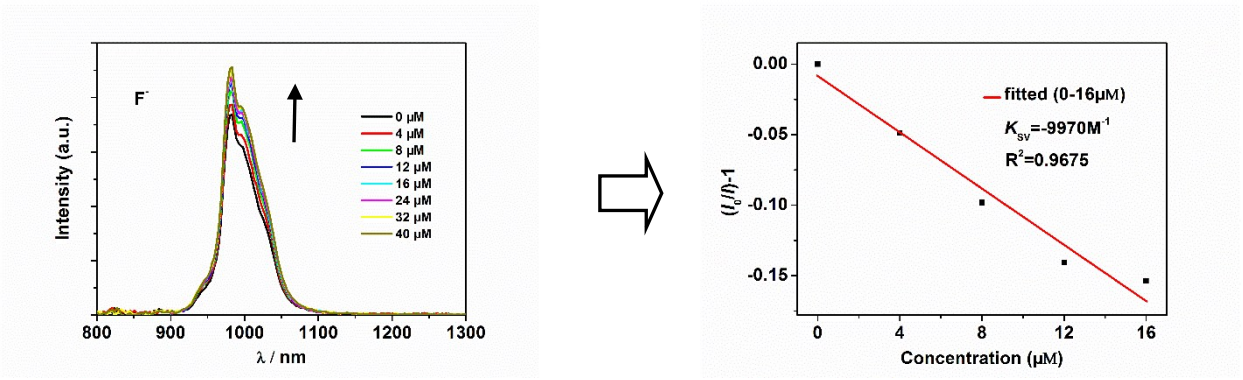


Figure S4. NIR luminescent sensing of **1** (15 μM) to anions in CH_3CN (λ_{ex} = 390 nm).

7. The NIR emission lifetimes of 1 before and after the addition of SO_4^{2-} anion

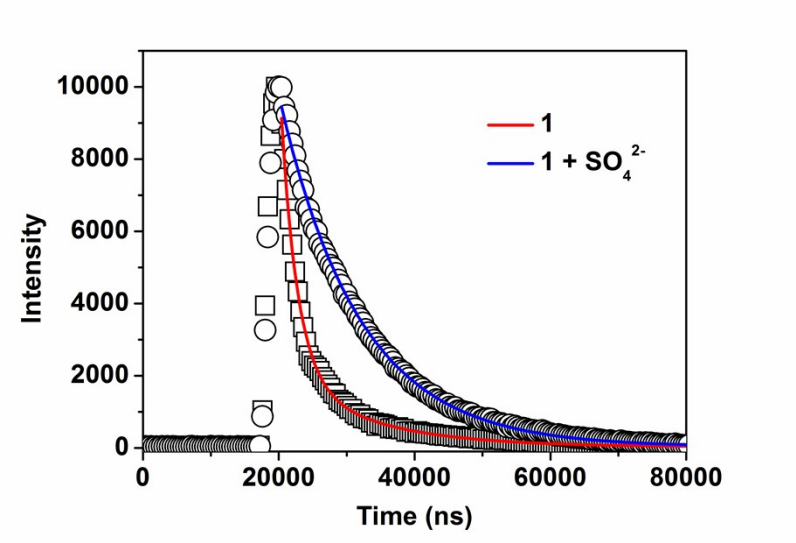


Figure S5. The NIR emission lifetimes of **1** (15 μM) before and after the addition of SO_4^{2-} anion in CH_3CN. (Red line: before the addition of anion; Blue line: after the addition of 120 μM SO_4^{2-} anion)

8. X-Ray Crystallography

Data were collected on a Smart APEX CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 190 K. The data set was corrected for absorption based on multiple scans and reduced using standard methods. Data reduction was performed using DENZO-SMN.[1] The structures were solved by direct methods and refined anisotropically using full-matrix least-squares methods with the SHELX 97 program package.[2] Coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[3]

For the crystal structure of **1**, some uncoordinated solvent molecules such as C_2H_5OH, $C_2H_5OC_2H_5$ and H_2O molecules were found to be badly disordered. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to these solvent molecules were removed by use of the utility SQUEEZE (Sluis and Spek, 1990) in PLATON98 (Spek, 1998). PLATON98 was used as incorporated in WinGX (Farrugia, 1999). Crystallographic data for **1** are presented in Table S1. See http://www.rsc.org/suppdata/cc/ for crystallographic data in CIF format (CCDC reference number 1947262).

Ref. (1) DENZO-SMN. (**1997**). Z. Otwinowski, W. Minor, *Methods in Enzymology*, 276: *Macromolecular Crystallography, Part A*, 307 – 326, C. W. J. Carter, M. I. Simon, R. M. Sweet, Editors, Academic Press.

(2) G. H. Sheldrick, SHELX 97, *A software package for the solution and refinement of X-ray data*; University of Göttingen: Göttingen, Germany, **1997**.

(3) D. T. Cromer, J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, vol. 4, **1974**, Table 2.2A.

Table S1. Crystal data and structure refinement for **1**.

	1
Formula	$C_{280}H_{378}O_{238}Yb_{42}$
Fw	14819.50
Crystal system	Triclinic
Space group	P-1
a [Å]	16.5526(7)
b [Å]	32.2692(11)
c [Å]	32.7633(11)
α [deg]	103.703(2)
β [deg]	102.725(2)
γ [deg]	100.939(2)
V / [Å^3]	16034.9(10)
d / [g/cm^3]	1.535
Z	1
T [K]	190(1)
F(000)	6902
μ, mm^{-1}	6.120
θ rang, deg	3.03-25.00
reflns meads	55673
reflns used	55673
params	2516
R1[a], wR2[a] [$I > 2\sigma(I)$]	0.0824, 0.1869
R1, wR2 (all data)	0.1649, 0.2143
Quality of fit	0.823

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma|[w(F_o^2)^2]]^{1/2}$. $w=1/[\sigma^2(F_o^2)+(0.075P)^2]$, where $P = [\max(F_o^2,0)+2F_c^2]/3$.