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Support information

Selective recognition of aluminum ions using an esculetin@Q[8] host-guest supramolecular fluorescence probe

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Experimental

Main reagents and instruments

Esculetin (analytical purity≥98%) was purchased from Shanghai Yuanye Biochemical Technology Co., Ltd; The water is the secondary resteaming water; Ethyl alcohol was analytical pure; Hydrochloric acid (analytical purity≥99.5%) was purchased from Tianjin Kaixin Chemical Industry Co., Ltd; Deuterated heavy water (analytical purity≥99.9%) was purchased from SAAN Chemical Technology (Shanghai) Co., Ltd.

Perchlorate salts: Na⁺, K⁺, Al³⁺, Ca²⁺, Ba²⁺, Fe²⁺, Fe³⁺, Cu²⁺, Cr³⁺, Mn²⁺, Cd²⁺, Ni²⁺, Zn²⁺, Mg²⁺, CO²⁺, Pb²⁺, Hg²⁺, Ag⁺ and so on are purchased from Aladdin Co., Ltd.

Instruments

UV-2700 dual-beam ultraviolet-visible (UV-Vis) spectrophotometer; VARIANCARYE-CLIPSE Fluorescence Spectrophotometer (Varian, USA); PHS-25 digital pH meter; AKHL-III-08 Eco laboratory ultrapure water machine ; FA2204N Electronic Balance; JNM-ECZ400s MHz Nuclear Magnetic Resonance System (NMR, JEOL); SHA-IIIS constant temperature oscillator; 101-1AB electric heating blast drying oven; Bruker D8 VENTURE diffractometer.

Methods

1. Host-guest interactions between ESC and Q[8]

1.1 Host-guest interaction between ESC and Q[8] was investigated using fluorescence spectroscopy

A 1×10^{-3} mol/L stock solution of ESC was prepared in ethanol and a 1×10^{-4} mol/L stock solution of Q[8] was prepared in water, and the mole ratio method and Job's method were used to determine the host–guest binding ratio.

A volume of 400 µl of ESC stock solution was added to 11 10 ml volumetric flasks, and then Q[8] solution was added with the corresponding mole ratios (0, 0.2, 0.4, ..., 2.0). Then prepare a series of solutions of n(Q[8]):n(ESC + Q[8]) = 0.1, 0.2,0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and finally fix the volume with the solution of pH = 5.0 and vH₂O:vCH₃CH₂OH = 97:3. Fluorescence spectra of the solutions were measured at $\lambda ex = 380$ nm, the slit width was 5 nm/5 nm, the voltage was 580 V, and the scanning range was 200–800 nm.¹



Fig S1. The Job's plot date of ESC with Q[8]

The host–guest binding constant *K* is calculated as follows:

$$\Delta A = \frac{\Delta \alpha ([H]_0 + [G]_0 + 1/K) \pm \sqrt{\Delta \alpha^2 ([H]_0 + [G]_0 + 1/K)^2 - 4\Delta \alpha^2 [H]_0 [G]_0}}{2}$$

where ΔA is the change in the fluorescence intensity of the host after gradually adding ESC, and $\Delta \alpha$ is the constant of the inclusion compound after the host and guest interaction. The total concentrations of the host and guest are represented by [H]₀ and [G]₀.²

1.2 ¹H NMR

Q[8], ESC, ESC₂@Q[8] = 2:1 and ESC₂@Q[8]@Al = 2:1:1 were prepared with 1×10^{-3} mol/L concentration of D₂O (pH = 5.0), and their ¹H NMR spectra were recorded using a JEOL JNM-ECZ400 spectrometer at 25 °C.³

2. Recognition of Al³⁺ by ESC₂@Q[8]

2.1 The selectivity of fluorescent probes to metal ions

A solution of 3×10^{-5} mol/L ESC (pH = 5.0, v/v, H₂O:CH₃CH₂OH = 97:3) was prepared. And 0.2 mol/L secondary water metal ion stock solution. Added 3ml of 30µmol/L probe to the quartz fluorescent cuvette, and then add 10 equivalents of different metal ion solutions (For example, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Al³⁺, Hg²⁺, Fe²⁺, Fe³⁺, Cr³⁺, Co²⁺, Pb²⁺, Zn²⁺, Cd²⁺, Ni²⁺, Cu²⁺, Mn²⁺, etc.) with equimolar concentrations of ESC₂@Q[8]. Finally, the fluorescence intensity was measured under the conditions of (λ ex=380nm), slit width 5nm/5nm, voltage 580v, and scanning range 200-800nm.⁴



Fig S2. The selectivity of fluorescent probes to metal ions



Fig S3. The fluorescence intensity of the probe ESC₂@Q[8]-Al³⁺ system (30 μmol/L after adding different metal ions(pH=5.0, v/v, H₂O:CH₃CH₂OH=97:3, λex= 380 nm)

2.3 Impact of the solution's pH and solvent

A series of probes with a concentration of 3×10^{-5} mol/L (pH = 5.0 and vH₂O:vCH₃CH₂OH = 97:3) at different pH values and solvent were prepared, and Al³⁺ ions (3×10^{-4} mol/L) were added. After mixing, detected at $\lambda ex = 380$ nm, the width of the slit was 5 nm/5 nm, the voltage was 580 V, and the scanning range was 200–800 nm.¹



Fig S4. Effects of different pH values on ESC2@Q[8] and ESC2@Q[8] -A13+ system



Fig S5. Effects of different solvents on Fluorescence spectra of $ESC_2@Q[8]$ and $ESC_2@Q[8]\text{-}Al^{3+}$

2.4. Measurement of the fluorescence quantum yield

Fluorescence quantum yield (Y) is also called fluorescence quantum efficiency, It refers to the fraction of molecules in the excited state that return to the ground state by emitting fluorescence to account for the fraction of all excited state molecules.the fluorescence quantum yield of the tested substance was calculated according to the formula: Yu=Ys•Fu/Fs•As/Au. Among them, Yu and Ys respectively represent the fluorescence quantum yield of the test substance and the reference standard substance. Fu and Fs respectively represent the comprehensive fluorescence intensity of the test product and the reference product;; Au and As respectively represent the absorbance of incident light at the excitation wavelength of the test substance and the reference substance. $(A = \varepsilon bc)^5$:



Fig S6. Fluorescence spectra of quinine sulfate and ESC₂@Q[8]-Al³⁺ (A) and (B) UV-vis absorption spectra 2.5 The interaction between ESC₂@Q[8] and Al³⁺ was investigated using UV absorption spectroscopy

Add 3 ml 30 μ mol/L (pH = 5.0, vH₂O:vCH₃CH₂OH = 97:3) probe solution to a UV cuvette with a width of 1 cm, and then add $n[A1^{3+}]:n[ESC_2@Q[8]] = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0)$ Al³⁺ ion solutions, after mixing uniformly, use the UV spectrometer to determine their absorbance.

2.6 Crystal preparation and measurements

Weigh 0.01 g Q[8], 0.01 g ESC, 0.01 g Al(ClO₄)₃, add 3.00 ml HCl aqueous solution to dissolve, and obtain transparent crystals after standing for a period of time. Then, use the Bruker D8 VENTURE diffractometer to collect and test the crystals, and analyze the crystals. In addition, the crystallographic data for the reported structures have been deposited at the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-2097128, which contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Compound	ESC ₂ @Q[8]@Al ³⁺
Empirical formula	$C_{114}H_{108}AlCl_4N_{64}O_{53}$
Formula weight	3391.42
Crystal system	monoclinic
Space group	I 1 2/c 1
a[Å]	28.162(9)
b[Å]	22.226(7)
c[Å]	28.390(8)
α [°]	90
β [°]	90.21(3)
γ [°]	90
<i>V</i> [Å ³]	17770(9)
Ζ	4
$D_{\text{calcd}}.[\text{g cm}^{-3}]$	1.268

Table S1 X-ray crystal data obtained for ESC₂@Q[8]@Al³⁺

<i>T</i> [K]	273.15
$\mu [mm^{-1}]$	0.164
Parameters	1066
R _{int}	0.1563
$R [I > 2\sigma(I)]^{a}$	0.1225
$wR [I > 2\sigma(I)]^{b}$	0.3810
R (all data)	0.1835
wR (all data)	0.4208
GOF on F^2	1.414

^aConventional *R* on F_{hkl} : $\sum ||F_0| - |F_c|| / \sum |F_0|$.

^bWeighted *R* on $|F_{hkl}|^2$: $\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]^{1/2}$.

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