



Synthesis, structure, photophysical and electrochemical properties of a novel metalloporphyrin with a condensed three-dimensional porous open framework



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ABSTRACT

A novel 4f–3d metalloporphyrin, [EuZn(TPPS)H₂O]_n (**1**) (H₂TPPS = tetra(4-sulfonatophenyl)porphyrin), has been synthesized via a solvothermal reaction and structurally characterized by single-crystal X-ray diffraction. Compound **1** features a three-dimensional (3-D) structure with two kinds of one-dimensional (1D) infinite chains. Based on the condensed 3-D porous open framework, compound **1** has a large void space of 223 Å³, corresponding to 9.4% of the unit-cell volume. Compound **1** shows high thermal and aqueous stability. Magnetic measurements reveal that compound **1** has an antiferromagnetic behavior.

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1. Introduction

Porphyrins with plentiful properties are one of the most widely studied chemical systems. Porphyrins have been found their applications in the areas of optical, medicine, catalysis, adsorption, solar energy conversion, and so forth [1–10]. The modification of a porphyrin through inserting a metal ion into the center of a porphyrinic ring, or decorating the periphery of a porphyrinic ring, can provide various building blocks to prepare new porphyrinic compounds, which may have different chemical, electronic or redox properties. More and more efforts have thus far been devoted to synthesize metalloporphyrinic frameworks (MPFs) with reformative features that may allow them to be put into practical applications [11,12].

Nowadays, MPFs have gained increasing interest because of their useful characteristics in structural robustness, reaction catalysis, energy and electron transfer [13,14]. Tetraarylporphyrins like TPYP (*meso*-tetra(4-pyridyl)porphyrin), TCMOPP (tetrakis(4-(carboxymethyleneoxy)phenyl)porphyrin), TCPP (tetrakis(4-carboxyphenyl)porphyrin), and TDCPP (tetrakis(3,5-dicarboxyphenyl)porphyrin)

are square planar building units and they have been widely adopted to synthesize novel MPFs [15–18]. However, H₂TPPS (tetra(4-sulfonatophenyl)porphyrin) has been rarely used to prepare new MPFs, although it is one of the tetraarylporphyrins. To our knowledge, only two examples of TPPS-containing MPFs have so far been found [19,20]. Actually, the large, rigid and square planar symmetrical H₂TPPS is a useful building unit for the construction of new MPFs because H₂TPPS can provide a lot of coordination sites: one at the center of the macrocyclic porphyrin ring and several at the oxygen atoms of four sulfonic ligands. However, the crystal structures and physicochemical properties of the TPPS compounds have yet to be explored.

Lanthanide compounds have attracted increasing attention because of their abundant properties, such as photoluminescence and magnetism [21,22]. In recent years, a lot of lanthanide compounds with various organic ligands have been prepared [23–25]. The zinc ion (Zn²⁺), as one of the 3d elements, is particularly attractive for the following reasons: the variety of coordination numbers and geometries provided by its d¹⁰ configuration, fluorescence, photoelectric properties, and its essential role in biological systems.

Recently, we focus on the study of the 4f–3d TPPS MPFs that possibly have different frameworks and properties like gas adsorption, photoluminescence and magnetism. We report herein the rational preparation, crystal structure and various properties

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of a 4f–3d TPPS metalloporphyrin, $[\text{EuZn}(\text{TPPS})\text{H}_3\text{O}]_n$ (**1**) (H_2TPPS = tetra(4-sulfonatophenyl)porphyrin), which was obtained via solvothermal reactions and features a condensed 3D porous open framework. It should be pointed out that compound **1** displays not only good thermal stability, but also wonderful aqueous stability; even it has been ultrasonicated for several hours in distilled water. Based on its good bistability and in order to explore its potential applications, we measured its properties as detailed as we can. The title compound was characterized in detail by using single-crystal X-ray diffraction, UV–Vis spectra, FT-IR, fluorescence, quantum yield, luminescence lifetime, CV/DPV, adsorption measurement, TG/DTA and magnetic measurements.

2. Experimental

2.1. Materials and instrumentation

All reactants of A.R. grade were obtained commercially and used without further purification. Elemental analysis was carried out with an Elementar Vario EL III microanalyzer. The infrared spectra were recorded on a Nicolet 5DX FT-IR spectrophotometer over the frequency range 4000–400 cm^{-1} using the KBr pellet technique. The solution UV–Vis spectra were recorded at room temperature on a computer-controlled PE Lambda 900 UV–Vis spectrometer. The diffuse reflectance spectrum was recorded at room temperature on a computer-controlled Lambda 35 UV–Vis spectrometer equipped with an integrating sphere in the wavelength range 190/1100 nm. BaSO_4 powder was used as a reference (100% reflectance), on which the ground powder sample was coated. The absorption spectra were calculated from reflection spectra by the Kubelka–Munk function: $\alpha/S = (1-R)^2/2R$, α is the absorption coefficient, S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm , and R is the reflectance. The band gap energy value was determined by extrapolation from the linear portion of the absorption edge in a (α/S) versus energy plot.

The photoluminescent study was conducted on an Edinburgh FLS920 fluorescence spectroscopy instrument under room temperature. Measurement of an emission quantum yield of solution sample was carried out on a Hamamatsu C9920-0X(PMA-12) U6039-05 fluorescence spectrofluorometer with a integrating sphere adapted to a rightangle configuration at room temperature, involving determination of the diffuse reflectance spectra of the sample. The result was corrected for the detector response as a function of wavelength.

Photoluminescent lifetime measurement was conducted using a Photon Technology International GL-3300 nitrogen laser with a Photon Technology International GL-302 dye laser and a nitrogen laser/pumped dye laser system equipped with a four-channel digital delay/pulse generator (Standard Research System Inc., model DG535) and a motor driver (Photon Technology International, model MD-5020). The excitation wavelength was 421 nm with use of a POPOP chromophore.

Measurements of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed at 298 K using a BAS 100 W electrochemical analyzer in deaerated benzonitrile containing 0.1 M TBAPF₆ (tetra-*n*-butylammonium hexafluorophosphate) as a supporting electrolyte. A conventional three-electrode cell was used with a platinum working electrode and a platinum wire as a counter electrode. The measured potentials were recorded with respect to the Ag/AgNO_3 (1.0×10^{-2} M). All electrochemical measurements were carried out under an atmospheric pressure of argon.

Thermo-gravimetry (TG) and differential thermal analysis (DTA) were performed on an NETZSCH STA 449C analyzer.

The adsorption measurement of CO_2 was conducted on an intelligent gravimetric sorption analyzer (IGA100B). As-synthesized sample was dipped in CH_2Cl_2 solutions for 24 h and evacuated under a dynamic vacuum (10^{-3} Torr) at 423 K for 8 h before the adsorption measurement.

Variable-temperature magnetic susceptibility and field dependence magnetization measurements on polycrystalline samples were performed on a PPMS 9T Quantum Design SQUID magnetometer. All data were corrected for diamagnetism estimated from Pascal's constants.

2.2. Synthesis of $[\text{EuZn}(\text{TPPS})\text{H}_3\text{O}]_n$ (**1**)

The title compound was prepared by mixing $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.1 mmol, 37 mg), ZnBr_2 (0.1 mmol, 22 mg), H_2TPPS (0.1 mmol, 94 mg) and 10 mL distilled water in a 25 mL Teflon-lined stainless steel autoclave and heating the mixture at 473 K for 5 d. After cooling slowly the mixture to room temperature at a rate of 6 K/h, red crystals suitable for X-ray analysis were obtained. The yield was 41% (based on europium). *Anal. Calc.* for $\text{C}_{44}\text{H}_{27}\text{EuN}_4\text{O}_{13}\text{S}_4\text{Zn}$: C, 45.35; H, 2.34; N, 4.81. *Found*: C, 45.27; H, 2.38; N, 4.87%. Fourier transform IR (KBr, cm^{-1}): 3422(s), 3102(w), 2359(m), 1602(m), 1401(w), 1336(w), 1240(s), 1171(s), 1126(vs), 1052(s), 997(vs), 860(w), 809(m), 745(s), 667(w), and 640(s).

2.3. Crystal structure determination

The intensity data set was collected on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption corrections [26]. The structure was solved by the direct method with the Siemens SHELXTL™ Version 5 package of crystallographic software [27]. The difference Fourier maps based on these atomic positions yield the non-hydrogen atoms, while the hydrogen atoms were generated theoretically, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters. The structure was refined using a full-matrix least-squares refinement on F^2 . All atoms except for hydrogen atoms were refined anisotropically. A summary of crystallographic data and structure analysis is listed in Table 1, and selected bond distances and bond angles are given in Table 2.

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

Formula	$\text{C}_{44}\text{H}_{27}\text{EuN}_4\text{O}_{13}\text{S}_4\text{Zn}$
Formula weight	1165.27
Color	red
Crystal size (mm^3)	0.25 0.15 0.14
crystal system	tetragonal
space group	$P4/mcc$
a (\AA)	15.507(5)
c (\AA)	9.930(5)
V (\AA^3)	2387.8(16)
Z	2
$2\theta_{\text{max}}$ ($^\circ$)	50
Reflections collected	11467
Independent, observed reflections (R_{int})	1040, 997 (0.0499)
d_{calc} (g/cm^3)	1.621
μ (mm^{-1})	2.045
T (K)	123.15
$F(000)$	1160
R_1, wR_2	0.0481, 0.1224
S	1.016
Largest and mean Δ/σ	0, 0
$\Delta\rho$ (max, min) ($\text{e}/\text{\AA}^3$)	0.951, -0.584

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