



Research paper

Construction of a series of rare earth metal-organic frameworks supported by thiophenedicarboxylate linker: Synthesis, characterization, crystal structures and near-infrared/visible luminescence



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ABSTRACT

Six novel rare earth metal organic-frameworks with the general formula $\{[RE_2(2,5\text{-tdc})(\text{dmsO})_2]\cdot\text{H}_2\text{O}\}_n$ ($RE = Y^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Er^{III}$ and Tm^{III} ; $2,5\text{-tdc}^{2-} = 2,5\text{-thiophenedicarboxylate anion}$; $\text{dmsO} = \text{dimethylsulfoxide}$) were synthesized and their complete characterization, including single crystal X-ray diffraction, FTIR spectroscopy and thermal analysis (TG/DTA) are reported. Structure analysis reveals that RE^{III} ions show distorted capped trigonal – prismatic geometry. The $2,5\text{-tdc}^{2-}$ ligands connect four RE^{III} centers, adopting $(\kappa^1 - \kappa^1) - (\kappa^1 - \kappa^1) - \mu_4$ coordination mode, generating an interesting 3D network with potential application for gas adsorption. Photophysical properties were studied using excitation/emission spectra and the photoluminescence data show the near infrared (NIR) and visible (Vis) emission with the characteristic transitions: ${}^1D_2 \rightarrow {}^3F_2$ for Pr^{III} , ${}^4F_{3/2} \rightarrow {}^4I_1$ ($J = 9/2, 11/2$ and $13/2$) for Nd^{III} , ${}^4G_{5/2} \rightarrow {}^6H_J$ ($J = 5/2, 7/2, 9/2$ and $11/2$) for Sm^{III} and ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ for Er^{III} . This study indicates that $2,5\text{-tdc}^{2-}$ ligand is able to act as a sensitizer for emission in NIR and Vis region in these ions.

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1. Introduction

Metal-organic frameworks (MOFs) are extended crystalline structures wherein metal cations or clusters of cations are connected by polytopic organic linkers to form one-, two-, or three-dimensional structural arrangement. Such compounds have attracted great attention from both academia and industry because of their potential applications in a wide variety of fields such as: magnetism [1], catalysis [2], gas storage [3] and molecular separation [4]. In this context, the use of rare earth ions in the construction of metal-organic frameworks results in a specific class of compounds called *Rare Earth Metal-Organic Frameworks* (REMOFs) with unique optical and magnetic properties. Different from other metal ions and molecular species, the rare earth ions have a narrow absorbance and emission bands with high quantum yields when excited via antenna effect [5,6]. This process consists in the use of suitable chromophores, employed as antennas (or sensitizers)

with the capability of transferring energy indirectly to rare earth ions as for example the carboxylate ligands. This intramolecular energy transfer is crucial once that some rare earth ions systems with direct absorption in the f excited states is very inefficient because the $4f\text{-}4f$ transitions are parity forbidden, resulting in very low absorption coefficients. Some REMOFs, specially containing lanthanide Eu^{III} and Tb^{III} ions, usually exhibit intense luminescence and are potentially applicable for sensors, lightning and optical devices [7]. Recently, interest towards the compounds containing Er^{III} , Pr^{III} and Nd^{III} ions, which emit in the near infrared (NIR) region, has increased. This is mainly due the potential applications in telecommunication network as optical signal amplifier, and in biological and medical systems as luminescent probes [8]. Taking advantage of the high affinity of rare earth ions for oxygen, a number of REMOFs with various dimensionality and topologies have been synthesized from multicarboxylate ligands [9,10]. In this paper, we chose the rigid ligand 2,5-thiophenedicarboxylic acid ($2,5\text{-H}_2\text{tdc}$) to promote the formation of extended REMOFs structures, which exhibit high connectivity, stabilize bridges among several metal centers [11–13], adopting several coordination

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modes, and producing multidimensional networks, including 2D and 3D structures. Given the important potential applications, we described the synthesis, characterization, structures and luminescence properties of rare earth metal-organic frameworks of general formula $\{[RE_2(2,5\text{-tdc})_3(\text{dmsO})_2]\cdot\text{H}_2\text{O}\}_n$ (RE = Y^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Er^{III} and Tm^{III}; 2,5-tdc²⁻ = 2,5-thiophenedicarboxylate anion; dmsO = dimethylsulfoxide).

2. Experimental

2.1. Materials and physical measurements

Elemental analyses for C and H were carried out using a Perkin-Elmer 2400CHN analyzer. X-ray diffraction patterns (PXRD) of the single crystals were recorded on a Rigaku RINT2000 diffractometer using Cu K α radiation (30 kV and 15 mA) from 5° to 70° and 0.02° of pass time. FTIR spectra were recorded with a Bomem Michelson 102 FTIR spectrophotometer using KBr pellets in the wavenumber range of 4000–400 cm⁻¹ with an average of 128 scans and 4 cm⁻¹ of spectral resolution. Thermal analysis (TGA/DTA) was obtained on a Shimadzu TG-60 equipment with 6–10 mg sample being heated at 10 °C/min from room temperature to 800 °C in a dynamic nitrogen atmosphere (flow rate = 100 mL/min). The images of scanning electron microscopy were obtained using a Shimadzu SS-50 with tungsten filament working at 2.0 kV, work distance 17 and probe 4.0. Diffuse reflection (DR) spectra were acquired with a Cary 500 spectrophotometer from 200 to 1500 nm with spectral resolution of 1 nm. The luminescence excitation and emission spectra were obtained with a Jobin-Yvon Model Fluorolog FL3-22 spectrophotometer equipped with a R928 Hamamatsu photomultiplier and 450 W xenon lamp as excitation source and the spectra were corrected with respect to the Xe lamp intensity and spectrometer response.

2.2. Synthesis of $\{[RE_2(2,5\text{-tdc})_3(\text{dmsO})_2]\cdot\text{H}_2\text{O}\}_n$

2.2.1. Synthesis of $\{[Y_2(2,5\text{-tdc})_3(\text{dmsO})_2]\cdot\text{H}_2\text{O}\}_n$ (**1**)

Compound (**1**) was synthesized using a two layered solution in a tube of 1.5 cm inner diameter and 18 cm height. The bottom layer was 10 mL of N,N'-dimethylformamide and dimethylsulfoxide mixture (1:1) containing 0.24 mmol (42 mg) of 2,5-thiophenedicarboxylic acid. The upper one was 5 mL of an ethanolic solution containing 0.16 mmol (50 mg) of YCl₃·6H₂O. The resulting solution was allowed to stand and after five weeks, colorless block crystals suitable for single crystal X-ray diffraction analysis were obtained. Yield: 57%. Anal. Calc. for Y₂C₂₂H₂₀O₁₅S₅: C, 30.6; H, 2.34%; Found: C, 31.0; H, 2.33%.

2.2.2. Synthesis of compound $\{[Pr_2(2,5\text{-tdc})_3(\text{dmsO})_2]\cdot\text{H}_2\text{O}\}_n$ (**2**)

Compound (**2**) was obtained by applying the same synthetic procedure as described for (**1**), except that PrCl₃·6H₂O (50 mg, 0.14 mmol) was used instead of YCl₃·6H₂O. The resulting solution was allowed to stand and after five weeks, light green block crystals were formed. Yield: 49%. Anal. Calc. for Pr₂C₂₂H₂₀O₁₅S₅: C, 27.3; H, 2.09%; Found: C, 27.1; H, 2.06%.

2.2.3. Synthesis of compound $\{[Nd_2(2,5\text{-tdc})_3(\text{dmsO})_2]\cdot\text{H}_2\text{O}\}_n$ (**3**)

Compound (**3**) was obtained by applying the same synthetic procedure as described for (**1**), except that NdCl₃·6H₂O (50 mg, 0.13 mmol) was used instead of YCl₃·6H₂O. The resulting solution was allowed to stand and after six weeks, lilac block crystals were formed. Yield: 47%. Anal. Calc. for Nd₂C₂₂H₂₀O₁₅S₅: C, 27.1; H, 2.07%; Found: C, 26.8; H, 2.04%.

2.2.4. Synthesis of compound $\{[Sm_2(2,5\text{-tdc})_3(\text{dmsO})_2]\cdot\text{H}_2\text{O}\}_n$ (**4**)

Compound (**4**) was obtained by applying the same synthetic procedure as described for (**1**), except that SmCl₃·6H₂O (50 mg, 0.14 mmol) was used instead of YCl₃·6H₂O. The resulting solution was allowed to stand and after six weeks, colorless block crystals were formed. Yield: 49%. Anal. Calc. for Sm₂C₂₂H₂₀O₁₅S₅: C, 26.8; H, 2.05%; Found: C, 27.1; H, 2.07%.

2.2.5. Synthesis of compound $\{[Er_2(2,5\text{-tdc})_3(\text{dmsO})_2]\cdot\text{H}_2\text{O}\}_n$ (**5**)

Compound (**5**) was obtained by applying the same synthetic procedure as described for (**1**), except that ErCl₃·6H₂O (50 mg, 0.13 mmol) was used instead of YCl₃·6H₂O. The resulting solution was allowed to stand and after six weeks, light pink block crystals were formed. Yield: 53%. Anal. Calc. for Er₂C₂₂H₂₀O₁₅S₅: C, 25.9; H, 1.98%; Found: C, 26.1; H, 2.01%.

2.2.6. Synthesis of compound $\{[Tm_2(2,5\text{-tdc})_3(\text{dmsO})_2]\cdot\text{H}_2\text{O}\}_n$ (**6**)

Compound (**6**) was obtained by applying the same synthetic procedure as described for (**1**), except that TmCl₃·6H₂O (50 mg, 0.13 mmol) was used instead of YCl₃·6H₂O. The resulting solution was allowed to stand and after six weeks, colorless block crystals were formed. Yield: 44%. Anal. Calc. for Tm₂C₂₂H₂₀O₁₅S₅: C, 25.8; H, 1.97%; Found: C, 25.8; H, 1.96%.

All the compounds synthesized are stable in air and insoluble in ethanol, acetonitrile, acetone, tetrahydrofuran (THF), but soluble in the 1:1 mixture of dimethylformamide (dmf) and dimethylsulfoxide (dmsO).

2.3. Single crystal X-ray diffraction

The single crystal X-ray diffraction data of compound X was collected at room temperature on a Bruker D8 Venture diffractometer equipped with Photon 100 CMOS detector and using MoK α radiation (0.71073 Å) from a INCOATEC micro-focus source. Final lattice parameter values and integrated intensities were obtained using SAINT software and a multi-scan absorption correction was applied with SADABS.

X-ray diffraction data collections for compounds (**1**) and (**5**) were collected on a Bruker D8 Venture diffractometer equipped with Photon 100 CMOS detector and using MoK α radiation (0.71073 Å) from a INCOATEC micro-focus source. Final lattice parameter values and integrated intensities were obtained using SAINT software and a multi-scan absorption correction was applied with SADABS. For the compound (**6**), the data collection were performed on an Oxford-Diffraction GEMINI diffractometer using Graphite-Enhance Source Mo-K α radiation (λ = 0.71073 Å). Data integration and scaling of the reflections and absorption corrections were carried out with the programs of the CrysAlis suite [14]. Final unit cell parameters were based on the fitting of all reflection positions. The structures were solved using direct methods using the Sir-92 program [15]. The positions of the carbon, oxygen, sulfur, and metal atoms of the molecules were unambiguously assigned on consecutive difference Fourier maps. Refinements were performed with SHELXL-2013 [16] based on F2 through a full-matrix least-squares routine. All atoms were refined with anisotropic atomic displacement parameters, except for hydrogen. The latter were located in difference maps and included as fixed contributions according to the riding model [17]. The structures were drawn using the programs ORTEP-3 for Windows [18], MERCURY [19] and Topos 4.0 [20]. Through the latter, the Voronoi-Dirichlet polyhedral volumes and the molecular coordination numbers generated and projected.

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