

# Mononuclear, trinuclear, and hetero-trinuclear supramolecular complexes containing a new tri-sulfonate ligand and cobalt(II)/copper(II)-(1,10-phenanthroline)<sub>2</sub> building blocks

Yunfang Yu<sup>a</sup>, Yongqin Wei<sup>a</sup>, Ria Broer<sup>b</sup>, Rongjian Sa<sup>a</sup>, Kechen Wu<sup>a,\*</sup>

<sup>a</sup>State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fujian 350002, China

<sup>b</sup>Zenike Institute for Advanced Materials, Rijksuniversiteit Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received 29 September 2007; received in revised form 19 December 2007; accepted 27 December 2007

Available online 1 January 2008

## Abstract

Novel mononuclear, trinuclear, and hetero-trinuclear supermolecular complexes, [Co(phen)<sub>2</sub>(H<sub>2</sub>O)(HTST)]·2H<sub>2</sub>O (**1**), [Co<sub>3</sub>(phen)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>(TST)<sub>2</sub>]·7H<sub>2</sub>O (**2**), and [Co<sub>2</sub>Cu(phen)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>(TST)<sub>2</sub>]·10H<sub>2</sub>O (**3**), have been synthesized by the reactions of a new tri-sulfonate ligand (2,4,6-tris(4-sulfophenylamino)-1,3,5-triazine, H<sub>3</sub>TST) with the M<sup>2+</sup> (M = Co, Cu) and the second ligand 1,10-phenanthroline (phen). Complex **1** contains a *cis*-Co(II)(phen)<sub>2</sub> building block and an HTST as monodentate ligand; complex **2** consists of two TST as bidentate ligands connecting one *trans*- and two *cis*-Co(II)(phen)<sub>2</sub> building blocks; complex **3** is formed by replacing the *trans*-Co(II)(phen)<sub>2</sub> in **2** with a *trans*-Cu(II)(phen)<sub>2</sub>, which is the first reported hetero-trinuclear supramolecular complex containing both the Co(II)(phen)<sub>2</sub> and Cu(II)(phen)<sub>2</sub> as building blocks. The study shows the flexible multifunctional self-assembly capability of the H<sub>3</sub>TST ligands presenting in these supramolecular complexes through coordinative, H-bonding and even π–π stacking interactions. The photoluminescent optical properties of these complexes are also investigated and discussed as well as the second-order nonlinear optical properties of **1**.

© 2007 Elsevier Inc. All rights reserved.

**Keywords:** Supermolecule; Cobalt; Copper; Luminescent; Nonlinear optics; Ab initio

## 1. Introduction

In recent years the design and synthesis of supramolecular coordination framework structures have attracted great attentions in which the coordinative, hydrogen bonding, and π–π stacking interactions are widely employed [1–5]. With the development of self-assembly supramolecular chemistry, the rational design and synthesis of supramolecular architectures based on covalent or supermolecular interactions have been an important content of coordination chemistry and have been found applications in searching novel materials with catalytic, biological, and photophysical properties such as luminescent and nonlinear optical properties [6,7]. However, finding appropriate molecular materials from organic

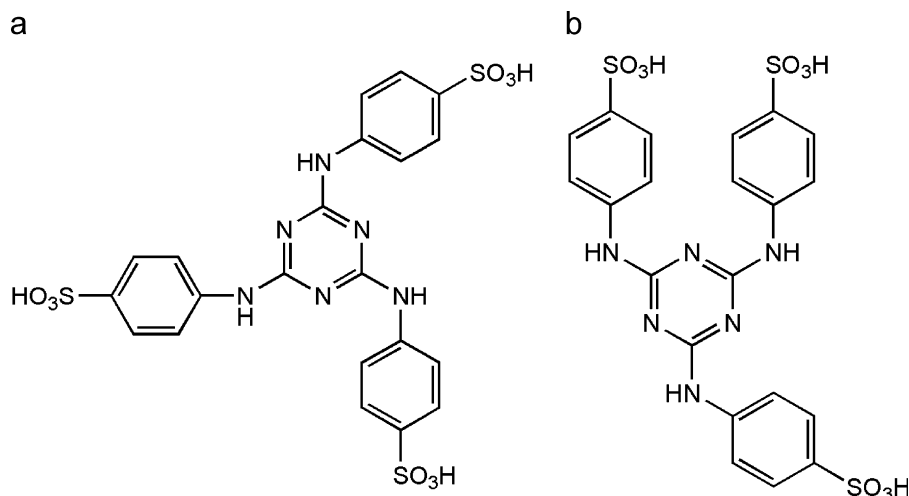
ligands and transition metals building blocks to construct novel supramolecular architectures are still a challenge to chemists [6].

As organic ligands, sulfonate ligands are possible to afford coordinative [8–10] and hydrogen bonding interactions [11]. In the past years some studies have been reported with organic sulfonate ligands towards transition metals in the field of supramolecular chemistry, especially the studies with rigid bi- and tri-sulfonate ligands [12–15]. However, comparing to aromatic polycarboxylate ligands, the coordination chemistry of sulfonate ligands is less explored owing to their relatively weak coordination ability [16]. The supramolecular complex systems containing flexible tri-sulfonate ligands and hetero-metal building blocks are limited reported as well [17].

In order to study the coordination information of flexible tri-sulfonate ligand and its behaviors in the construction of supramolecular architectures, we designed

\*Corresponding author. Fax: +86 591 8379 2932.

E-mail address: wkc@fjirsm.ac.cn (K. Wu).



Scheme 1. Two possible conformations of  $H_3TST$ : (a)  $\Delta$ -conformation and (b)  $\varphi$ -conformation.

and synthesized a new tri-sulfonate ligand, namely  $H_3TST = 2,4,6$ -tris(4-sulfophenylamino)-1,3,5-triazine.

This ligand is a flexible aromatic ligand with three  $SO_3H$  groups which are located at the end of molecule “arms” that can rotate around the C–NH–C bonds. Through this rotation it has two different possible conformations,  $\Delta$  and  $\varphi$ , as shown in Scheme 1. Besides the three sulfonate groups in tri-sulfonate ligand, the three N–H groups and the aromatic rings of triazine and phenyl groups are also helpful to construct supramolecular architectures.

By using  $H_3TST$  and 1,10-phenanthroline (phen) as ligands, we synthesized three new transition metal supermolecular complexes,  $[Co(phen)_2(H_2O)(HTST)] \cdot 2H_2O$  **1**,  $[Co_3(phen)_6(H_2O)_2(TST)_2] \cdot 7H_2O$  **2**, and  $[Co_2Cu(phen)_6(H_2O)_2(TST)_2] \cdot 10H_2O$  **3**, which presented mononuclear, trinuclear, and hetero-trinuclear architectures, respectively. The latter is the first reported hetero-metallic supramolecular complex containing both  $Co(II)(phen)_2$  and  $Cu(II)(phen)_2$  building blocks. These three supermolecular complexes also illustrate the coordination chemistry of tri-sulfonate TST/HTST ligands toward  $Co(II)/Cu(II)(phen)_2$  building blocks in the aqueous solution and their contributions in supramolecular self-assembly techniques.

The special photophysical properties of the supermolecular architectures containing transition metals have attracted great interests due to the various features of the linear and nonlinear optical responses. The rational design of the supermolecular chromophores with large molecular hyperpolarizability mainly organometallic dipolar chromophores encourages the present study. The first hyperpolarizability of one of the three complexes was experimentally determined and theoretically analyzed to understand the structure–property relationship, which may benefit to the further novel optical material developments.

## 2. Experimental section

### 2.1. Materials and measurements

All commercially available solvents and starting materials were used as received without further purification. Elemental analyses (C, H, and N) were performed with a Vario EL III CHNOS Elemental Analyzer. Metal elemental analysis of complex **3** was carried out on an Ultima-2 ICP Emission Spectrometer. The infrared spectrum of KBr pellet was recorded on a Perkin-Elmer Spectrum One FT-IR Spectrometer. The emission spectrum was recorded on an FLS920 fluorescence spectrophotometer. Thermogravimetric analyses (TGA) were carried out under an  $N_2$  atmosphere at a heating rate of  $15^\circ C/min$ . The HRS measurement was performed with a pulsed Nd: YAG laser at  $1.064 \mu m$ . Solution of the sample in DMSO was used with *p*-nitroaniline as a reference. The weak contributions of two-photon induced fluorescence in the HRS measurements were directly subtracted to HRS signal as background noises using a high-resolution monochromator near  $532 nm$ .

### 2.2. Preparation of $H_3TST \cdot 7H_2O$

A solution of 4-aminobenzenesulfonic sodium (14.72 g, 0.075 mol) in 200 ml water was added dropwise into cyanuric chloride (4.61 g, 0.025 mol) in 100 ml acetone at  $0-5^\circ C$  under stirring. After 1 h, the mixture was heated to  $45^\circ C$  and reacted under stirring for 8 h. After cooling, white deposit  $H_3TST \cdot 7H_2O$  was filtered from the mixture, washed with acetone and water, oven-dried at  $60^\circ C$  in 76% yield. Anal. calc. for  $H_3TST \cdot 7H_2O$ : C 34.99, H 4.48, N 11.66; found: C 35.03, H 4.39, N 11.73.  $^1H$  NMR (DMSO): N–H 9.664, phenyl 7.714 7.570,  $H_2O$  3.913. IR (KBr pellet,  $cm^{-1}$ ): 3452(b), 1631(s), 1588(s), 1561(s), 1509(s), 1493(s), 1412(m), 1378(w), 1335(w), 1190(s), 1130(s), 1068(w),

Download English Version:

<https://daneshyari.com/en/article/1333721>

Download Persian Version:

<https://daneshyari.com/article/1333721>

[Daneshyari.com](https://daneshyari.com)