



Solvent-directed lanthanide 7,7,8,8-tetracyano-*p*-quinodimethane complexes: Syntheses, structures, magnetic and electrochemical properties



Ju-Wen Zhang^{a,b}, Yan Wang^a, Peng-Fei Yan^a, Guang-Feng Hou^a, Guang-Ming Li^{a,*}

^a Key Laboratory of Functional Inorganic Material Chemistry (MOE), School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, PR China

^b College of Chemistry, Chemical Engineering and Food Safety, Bohai University, Jinzhou 121000, PR China

ARTICLE INFO

Article history:

Received 7 December 2013

Received in revised form 27 February 2014

Accepted 11 March 2014

Available online 25 March 2014

Keywords:

TCNQ

Lanthanide

Magnetic property

Electrochemical property

ABSTRACT

Reactions between trivalent lanthanide ions and the radical anion of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) produce four mononuclear complexes [Ln(TCNQ)₂(H₂O)₇](TCNQ)·5H₂O·EtOH [Ln = Nd (**1**), Sm (**2**), Eu (**3**) and Gd (**4**)] and three dinuclear complexes [Ln₂(TCNQ)₂(H₂O)₁₅](TCNQ)₄·*x*(*p*-dioxane)·7H₂O [Ln = Ce (**5**, *x* = 2.5), Pr (**6**, *x* = 2.5) and Nd (**7**, *x* = 2)]. One of the coordinated TCNQ^{•−} radical anions is involved in π - π stacking interactions with the uncoordinated TCNQ^{•−} radical anions, and the other coordinated TCNQ^{•−} radical anion is not involved in such π - π interactions in **1–4**. All the TCNQ^{•−} radical anions are involved in π - π interactions in **5–7**. The effect of reaction solvent on the structures of **1–7** was revealed. The magnetic properties of **4** and the electrochemical properties of **1–7** were investigated.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The metal–organic complexes based on TCNQ and its derivatives have attracted considerable attention over the last two decades due to their fascinating structures and potential applications as functional materials in magnetism [1–4], conductivity [5–8], porosity [9–11], and so on. For example, Dunbar and Miller as well as their co-workers carried out a lot of work in this domain [12–19]. Miyasaka and co-workers contributed a series of TCNQ-based ruthenium complexes by introducing diversiform substituents [20–23]. Although transition metal complexes based on TCNQ and its derivatives are quite common, analogous complexes including rare earth elements are still relatively scarce. In 2002, Roesky et al. reported the first TCNQ lanthanide complex {[CuL]₂Gd(TCNQ)₂·TCNQ·CH₃OH·2CH₃CN [L^{2−} = *N,N'*-propylenebis(3-methoxysalicylideneiminato)]} containing three different types of spin carriers (Gd³⁺, Cu²⁺ and TCNQ^{•−}) [24]. As a ferrimagnetic material, the second TCNQ lanthanide complex {[Gd₂(TCNQ)₅(H₂O)₉][Gd(TCNQ)₄(H₂O)₃]}·4H₂O with alternating anionic and cationic layers was obtained by Dunbar and co-workers in 2003 [25]. Recently, Dunbar and co-workers afforded a series of TCNQF₄ lanthanide complexes and investigated their magnetic properties [26,27].

On the other hand, it is noticeable that the reaction solvent has a significant effect on the assembly of TCNQ-based metal complexes. Kitagawa and co-workers synthesized two TCNQ-based zinc complexes with the same components but distinct structures in different solvents [28,29]. Our group harvested a series of lanthanide TCNQ complexes by tuning solvent on the basis of Dunbar's work [25,30,31]. As part of our ongoing interest in this domain, herein, we synthesized four mononuclear complexes [Ln(TCNQ)₂(H₂O)₇](TCNQ)·5H₂O·EtOH [Ln = Nd (**1**), Sm (**2**), Eu (**3**) and Gd (**4**)] and three dinuclear complexes [Ln₂(TCNQ)₂(H₂O)₁₅](TCNQ)₄·*x*(*p*-dioxane)·7H₂O [Ln = Ce (**5**, *x* = 2.5), Pr (**6**, *x* = 2.5) and Nd (**7**, *x* = 2)] in different solvents. Furthermore, the magnetic properties of **4** and the electrochemical properties of **1–7** were investigated.

2. Experimental

2.1. Materials and measurements

Starting materials and solvents were of reagent grade and used without further purification. Ln(NO₃)₃·*n*H₂O were prepared by reactions between Ln₂O₃ and nitric acid. TCNQ and Li(TCNQ) were synthesized by literature procedures [32]. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. Infrared (IR) data were collected on a Perkin-Elmer 100 spectrometer using KBr plates. Ultraviolet (UV) data were recorded on a Perkin-Elmer 35 spectrometer (in methanol). Thermal analyses

* Corresponding author. Tel.: +86 451 86608458.
E-mail address: gmlj_2000@163.com (G.-M. Li).

were carried out on a STA-6000 instrument with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in the range of $30\text{--}800\text{ }^{\circ}\text{C}$ under nitrogen. Magnetic measurements were performed on crushed polycrystalline samples with a Quantum Design SQUID magnetometer MPMSXL7. The data were corrected for diamagnetic contributions calculated from the Pascal constants.

2.2. Electrochemistry

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were carried out on a Metrohm Autolab 101 electrochemical workstation at room temperature using a standard three-electrode system (a working electrode/glassy carbon, an auxiliary electrode/platinum mesh and a reference electrode/Ag/AgCl). The working electrode was polished with $30\text{--}50\text{ nm}$ alumina slurry on the polishing cloth, and rinsed copiously with water and ethanol in an ultrasonic bath prior to use. Nitrogen gas was used to sparge the acetonitrile solutions of **1–7** and $n\text{-Bu}_4\text{NPF}_6$ as supporting electrolyte, in which the three electrodes were placed. CV data were recorded at a scan rate of 100 mV s^{-1} from -600 to 600 mV . DPV data were collected at a scan rate of 20 mV s^{-1} with pulse width of 50 ms and sample width of 16.7 ms from -600 to 600 mV .

2.3. Syntheses of $[\text{Ln}(\text{TCNQ})_2(\text{H}_2\text{O})_7](\text{TCNQ})\cdot 5\text{H}_2\text{O}\cdot\text{EtOH}$ [$\text{Ln} = \text{Nd}$ (**1**), Sm (**2**), Eu (**3**) and Gd (**4**)]

All reactions were performed under an atmosphere of N_2 by Schlenk procedures. A degassed ethanol (20 mL) solution of $\text{Ln}(\text{NO}_3)_3\cdot n\text{H}_2\text{O}$ (0.1 mmol) was slowly diffused into a degassed water (20 mL) solution of $\text{Li}(\text{TCNQ})$ (0.3 mmol). Purple block-shaped crystals of **1–4** were obtained after 7 days. For **1**, yield: 42%. *Anal. Calc.* for $\text{C}_{38}\text{H}_{42}\text{N}_{12}\text{NdO}_{13}$ (1019.08 , wt.%): C, 44.79; H, 4.15; N, 16.49. *Found:* C, 44.57; H, 4.21; N, 16.65%. IR (KBr, cm^{-1}): 3380 (s), 2181 (s), 1577 (m), 1508 (m), 1384 (m), 1334 (m), 1181 (m), 823 (w), 719 (w), 480 (w). UV (MeOH, nm): $\lambda_{\text{max}} = 419$. For **2**, yield: 40%. *Anal. Calc.* for $\text{C}_{38}\text{H}_{42}\text{N}_{12}\text{SmO}_{13}$ (1025.17 , wt.%): C, 44.52; H, 4.13; N, 16.40. *Found:* C, 44.72; H, 4.17; N, 16.28%. IR (KBr, cm^{-1}): 3400 (s), 2181 (s), 1578 (m), 1508 (m), 1384 (m), 1334 (m), 1181 (m), 824 (w), 720 (w), 480 (w). UV (MeOH, nm): $\lambda_{\text{max}} = 419$. For **3**, yield: 42%. *Anal. Calc.* for $\text{C}_{76}\text{H}_{84}\text{N}_{24}\text{Eu}_2\text{O}_{26}$ (2053.59 , wt.%): C, 44.45; H, 4.12; N, 16.37. *Found:* C, 44.35; H, 4.20; N, 16.41%. IR (KBr, cm^{-1}): 3412 (s), 2182 (s), 1578 (m), 1508 (m), 1384 (m), 1337 (m), 1182 (m), 824 (w), 720 (w), 480 (w). UV (MeOH, nm): $\lambda_{\text{max}} = 421$. For **4**, yield: 45%. *Anal. Calc.* for $\text{C}_{38}\text{H}_{42}\text{N}_{12}\text{GdO}_{13}$ (1032.09 , wt.%): C, 44.22; H, 4.10; N, 16.29. *Found:* C, 44.01; H, 4.19; N, 16.05%. IR (KBr, cm^{-1}): 2925 (s), 2197 (s), 1579 (m), 1509 (m), 1369 (s), 1334 (m), 1182 (m), 822 (w), 721 (w), 480 (w). UV (MeOH, nm): $\lambda_{\text{max}} = 419$.

2.4. Syntheses of $[\text{Ln}_2(\text{TCNQ})_2(\text{H}_2\text{O})_{15}](\text{TCNQ})_4\cdot x(p\text{-dioxane})\cdot 7\text{H}_2\text{O}$ [$\text{Ln} = \text{Ce}$ (**5**, $x = 2.5$), Pr (**6**, $x = 2.5$) and Nd (**7**, $x = 2$)]

All reactions were performed under an atmosphere of N_2 by Schlenk procedures. A degassed ethanol (20 mL) solution of $\text{Ln}(\text{NO}_3)_3\cdot n\text{H}_2\text{O}$ (0.1 mmol) was slowly diffused into a degassed water (20 mL) and p -dioxane (0.5 mL) solution of $\text{Li}(\text{TCNQ})$ (0.3 mmol). Purple block-shaped crystals of **5–7** were obtained after 7 days. For **5**, yield: 53%. *Anal. Calc.* for $\text{C}_{82}\text{H}_{88}\text{N}_{24}\text{Ce}_2\text{O}_{27}$ (2122.00 , wt.%): C, 46.41; H, 4.18; N, 15.84. *Found:* C, 46.29; H, 4.13; N, 15.74%. IR (KBr, cm^{-1}): 3349 (m), 2181 (s), 1577 (m), 1508 (m), 1334 (m), 1181 (m), 824 (m), 720 (w), 480 (m). UV (MeOH, nm): $\lambda_{\text{max}} = 394$. For **6**, yield: 52%. *Anal. Calc.* for $\text{C}_{82}\text{H}_{88}\text{N}_{24}\text{Pr}_2\text{O}_{27}$ (2123.58 , wt.%): C, 46.38; H, 4.18; N, 15.83. *Found:* C, 46.55; H, 4.23; N, 15.69%. IR (KBr, cm^{-1}): 3400 (m), 2196 (s), 1579 (m),

1508 (m), 1336 (m), 1181 (m), 824 (w), 720 (w), 480 (w). UV (MeOH, nm): $\lambda_{\text{max}} = 393$. For **7**, yield: 53%. *Anal. Calc.* for $\text{C}_{160}\text{H}_{170}\text{N}_{48}\text{Nd}_4\text{O}_{53}$ (4190.40 , wt.%): C, 45.86; H, 4.09; N, 16.04. *Found:* C, 45.75; H, 4.02; N, 16.12%. IR (KBr, cm^{-1}): 3196 (m), 2181 (s), 1577 (m), 1507 (m), 1334 (m), 1181 (m), 823 (w), 719 (w), 480 (w). UV (MeOH, nm): $\lambda_{\text{max}} = 393$.

2.5. X-ray crystallographic study

X-ray diffraction data for **1–7** were collected on a Rigaku R-AXIS RAPID imaging plate diffractometer with graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073\text{ \AA}$) at 293 K . The structures were solved by direct methods using the program SHELXS-97, and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package [33]. All hydrogen atoms of organic ligands were placed in geometrically idealized positions as a riding mode. The hydrogen atoms of water in **5** and **6** were located from difference Fourier maps. Pertinent crystal data and structure refinements for **1–7** are listed in Table 1. Selected bond lengths (\AA) for **1–7** are given in Tables S1.

3. Results and discussion

3.1. Syntheses

It is known that the reaction solvent has an important effect on the syntheses and structures of lanthanide TCNQ complexes. Dunbar and co-workers synthesized a two-dimensional (2D) gadolinium TCNQ complex $\{[\text{Gd}_2(\text{TCNQ})_5(\text{H}_2\text{O})_9][\text{Gd}(\text{TCNQ})_4(\text{H}_2\text{O})_3]\cdot 4\text{H}_2\text{O}\}$ by slow diffusion of water solutions of $\text{GdCl}_3\cdot 6\text{H}_2\text{O}$ and $\text{Li}(\text{TCNQ})$ [25]. On the basis of Dunbar's work, our group obtained a dinuclear gadolinium TCNQ complex $[\text{Gd}_2(\text{TCNQ})_4(\text{H}_2\text{O})_{10}][2\text{TCNQ}]\cdot 6\text{H}_2\text{O}$ by slowly diffusing a methanol solution of $\text{GdCl}_3\cdot 6\text{H}_2\text{O}$ into a water solution of $\text{Li}(\text{TCNQ})$ [30]. The structural difference of these two gadolinium TCNQ complexes should be attributed to the different reaction solvents. Herein, we synthesized four mononuclear lanthanide TCNQ complexes **1–4** by diffusing an ethanol solution of $\text{Ln}(\text{NO}_3)_3\cdot n\text{H}_2\text{O}$ into a water solution of $\text{Li}(\text{TCNQ})$. When a single solvent of water was replaced by a mixed solvent of p -dioxane and water, three dinuclear lanthanide TCNQ complexes **5–7** were obtained (Scheme 1). The different structures of **1–4** and **5–7** further suggest that the reaction solvent plays an important role in constructing lanthanide TCNQ complexes **1–7**.

3.2. Structural descriptions of **1–7**

X-ray diffraction analysis reveals that **1–4** and **5–7** are isomorphic, respectively, crystallizing in the triclinic space group $P\bar{1}$, so the structural descriptions of **4** and **5** are given as representative examples. The asymmetric unit of **4** consists of one Gd^{3+} ion, three TCNQ^- radical anions, seven coordinated water molecules, five interstitial water molecules and one interstitial ethanol molecule (Fig. 1). The Gd^{3+} ion is nine-coordinated by two nitrogen atoms from two TCNQ^- radical anions and seven oxygen atoms from seven water molecules, adopting a tricapped trigonal prism geometry (Fig. S1). The $\text{Gd}\text{--}\text{O}$ distances are in the range of $2.406(3)\text{--}2.498(3)\text{ \AA}$, and the $\text{Gd}\text{--}\text{N}$ distances are $2.547(4)$ and $2.549(4)\text{ \AA}$ (Table S1), which are similar to the reported TCNQ gadolinium complexes [30,34].

In **4**, one TCNQ^- radical anion of $[\text{Ln}(\text{TCNQ})_2(\text{H}_2\text{O})_7]^+$ cation is involved in $\pi\text{--}\pi$ stacking interactions with the uncoordinated TCNQ^- radical anions, and the other TCNQ^- radical anion is not involved in such $\pi\text{--}\pi$ interactions (Fig. 2a). The interplanar π distances are $3.73\text{ (C}\cdots\text{C)}$, $3.73\text{ (C}\cdots\text{U)}$, $4.16\text{ (U}\cdots\text{U)}$ and 3.94 \AA

Download English Version:

<https://daneshyari.com/en/article/1309948>

Download Persian Version:

<https://daneshyari.com/article/1309948>

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