Journal of Solid State Chemistry 231 (2015) 47–52

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Coordination polymers assembled from semirigid fluorene-based ligand: A couple of enantiomers

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ARTICLE INFO

Article history:
Received 8 May 2015
Received in revised form
25 July 2015
Accepted 3 August 2015
Available online 4 August 2015

Keywords:
Chiral
Fluorene
Fluorescence
Second-order nonlinear optical

ABSTRACT

A couple of Mg(II)-based coordination polymer enantiomers $[MgL(DMF)(H_2O)_3]_n$ (R-**MgL** and S-**MgL**), and a Zn(II)-based coordination polymer $[ZnL(DMF)]_n$ (**ZnL**) have been synthesized by the solvothermal reactions between the achiral ligand 4,4′-(9,9-dimethyl-9H-fluorene-2,7-diyl)dibenzoic acid (**H$_2$L**) and the corresponding metal salts. The **MgL** was obtained as the racemic conglomerate from the one pot reaction. The single crystal X-ray structural analyses reveal that **MgL** crystallize in the chiral space group $P2_1$ and possesses the right- or left-handed homochiral 1D Mg–O–C helical chain. The **ZnL** crystallize in the non-centrosymmetrical space group *Aba*2 and possesses the 2D network comprised of 1D Zn–O–C *meso*-helical chains and ligands. The **MgL** and **ZnL** complexes exhibit strong coordination-perturbed ligand-centered blue emissions when excited at 320 nm. Their second-order nonlinear optical effects and thermal properties have also been studied.

1. Introduction

Fluorene derivatives display significant modificability in both molecular structures and luminescence properties. In the past two decades, a large amount of researches and studies on structure modification and adjustment of luminescent properties of fluorene derivatives have been reported [1–3]. The luminescence property of a fluorene derivative is governed by the electronic property [4], which is closely related with molecular configuration [5–7]. So, various elegant strategies have been developed to design new fluorene derivatives for potential applications, for example, LED [8,9] and sensing [10]. Miteva et al. reported the polyfluorene homopolymers, for which the emission with tunable wavelength has been demonstrated with impressive efficiency via end-capping [11].

Coordination polymers (CPs) which have infinite 1D chains or 2D or 3D networks that composed of metal ions and organic ligands have been an active research area because of their multi-functional properties [12] and potential applications in material science [13,14] such as sensing [15,16], catalysis [17], and nano-materials [18]. Among all of the factors that could impose effects on the construction of CPs, ligands have drawn great attention as they are the most important influencing factor. It is known that ligands usually induce significantly diversities on both structures and properties of CPs by only tiny changes in molecular structure. As continuation of our previous work, we dedicate to prepare functional coordination polymers constructed from new fluorene-based ligands that exhibit strong luminescence. The A–B–A type molecules (A and B connected by single covalent bond, A and B are the different aromatic systems. In this work, B is fluorene.) attracted our attention. Due to the rotation of A relative to B through the covalent bond between A and B, the conformations of the molecules could be devided into two types. When two A rotate along the same direction, the *cis*-conformation is expected to be observed. On the contrary, the *trans*-conformation is to be observed. Thus, unlike 2,7-fluorenedicarboxylic acid [19,20], the longer and semirigid fluorene-based A–B–A ligands should in principle be subject to a large abundance of luminescence properties and accommodate a wide range of network topologies. However, only a few coordination polymers constructed from fluorene-based A–B–A ligands are known so far. Zhang et al. [21] had reported a serial of nano coordination polymers that constructed from fluorene-based A–B–A ligands, for which the single crystals were not obtained. Chen et al. had reported two coordination polymers based on 5,5′-(9H-fluorene-2,7-diyl)diisophthalic acid [22] and 5,5′-(9,9-dimethyl-9H-fluorene-2,7-diyl)

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http://dx.doi.org/10.1016/j.jssc.2015.08.003
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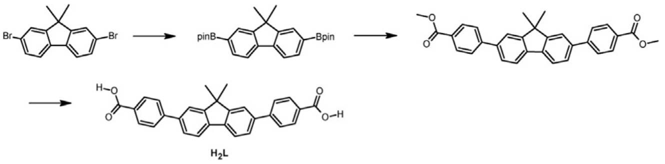

Scheme 1. Synthetic strategy used for the preparation of **H_2L**.

Table 1
Crystallographic data for **MgL** and **ZnL**.

	R-**MgL**	S-**MgL**	**ZnL**
Formula	$C_{32}H_{33}MgO_8N$	$C_{32}H_{33}MgO_8N$	$C_{32}H_{27}ZnO_5N$
Fw	583.90	583.90	570.92
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_1$	*Aba*2
a, Å	9.2754(6)	9.32(2)	15.6909(8)
b, Å	6.9509(4)	7.024(1)	43.795(2)
c, Å	22.048(1)	22.067(4)	7.7177(4)
α, deg	90	90.00	90.00
β, deg	93.329(2)	93.105(4)	90.00
γ, deg	90	90.00	90.00
V, Å^3	1419.1(2)	1442.3(4)	5303.4(5)
Z	2	2	8
D_{calcd}, g cm^{-3}	1.366	1.344	1.430
T/ K	100(2)	293(2)	293(2)
μ, mm^{-1}	0.117	0.116	0.969
F(000)	616	616	2368
Reflections collected	6804	9245	14,824
Unique reflections	4519	4962	5677
Flack parameter	−0.07(18)	0.2(2)	−0.009(11)
GOF (F^2)	1.146	1.103	1.005
R_{int}, R_{sigma}	0.0287, 0.0548	0.0200, 0.0311	0.0437, 0.0553
R_1[a],wR_2[b] ($I > 2\sigma(I)$)	0.0465, 0.1045	0.0340, 0.0824	0.0405, 0.0784
R_1[a],wR_2[b] (all data)	0.0527, 0.1079	0.0383, 0.0855	0.0565, 0.0845

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

diisophthalic acid [23] (in this case, A is isophthalic acid), in which the ligand exhibits *cis*-conformation. Dong et al. [24] had reported a Cu-coordination polymer based on the fluorene-based A–B–A ligand with pyridine as A, in which the ligand exhibits *trans*-conformation. Herein, we report three coordination polymers, R-**MgL**, S-**MgL** and **ZnL**, which constructed from 4,4′-(9,9-dimethyl-9H-fluorene-2,7-diyl)dibenzoic acid (**H_2L**, Scheme 1). These coordination polymers were characterized by single crystal X-ray diffraction, X-ray powder diffraction, TGA and fluorescence.

2. Experimental

2.1. General

The chemicals used in this work are of analytical grade and available commercially and were used without further purification.

The FT-IR spectra were measured with KBr pellets in the range of 4000–400 cm^{-1} on a PerkinElmer FT-IR Spectrometer. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. The thermogravimetric analyses (TGA) were performed in a SHIMADZU DTG-60 simultaneous DTA-TG apparatus instrument, under dynamic N_2 atmosphere (20 mL/min) and heating rate of 10 °C/min from room temperature to 800 °C. The ^{1}H and ^{13}C NMR spectra in $CDCl_3$ or d^6-DMSO were recorded at room temperature on a Bruker 400 M NMR spectrometer with tetramethylsilane (TMS) used as internal standard. Powder X-ray diffraction investigation on polycrystalline MgL and ZnL were carried out with a Bruker D8 advanced diffractometer equipped with a diffracted-beamed monochromator set for Cu Kα ($\lambda = 1.5418$ Å) radiation. The data were collected using a Ni-filtered Cu-target tube at room temperature in the 2θ range from 5° to 50° at an angular rate of 0.1 s/step, with a scan step width of 0.02°. The circular dichroism spectra were recorded on a JASCO J-810 spectropolarimeter with KBr pellets. The second-order nonlinear optical effects were determined on a LAB130 Pulsed Nd:YAG laser. Photoluminescent spectra were measured using a PerkinElmer LS55 Fluorescence Spectrometer.

2.2. Synthesis of H_2L

9,9-dimethyl-9H-2,7-dipinacolborylfluorene: the solution of 9,9-dimethyl-9H-2,7-dibromofluorene (17.6 g, 50 mmol) in anhydrous THF (100 mL) was stirred and cooled to −78 °C, to which the n-Butyllithium (2.5 M, 44 mL) was added over a period of 30 min. Two hours later isopropoxyboronic acid pinacol ester (25.5 mL) was added and the mixture was still stirred at room temperature for two hours. After the addition of NH_4Cl (20%, 20 mL), the solvents were removed and the residue was extracted by dichloromethane. The solvent was removed in a vacuum and the crude product was pure enough for next step directly. Yield: 90%. ^{1}H NMR ($CDCl_3$) δ 1.38(s, 24H), 1.52(s, 6H), 7.76(d, 2H), 7.82(q, 2H), 7.89(s, 2H) (Fig. S2).

Dimethyl 4,4′-(9,9-dimethyl-9H-fluorene-2,7-diyl)dibenzoate: the mixture of 9,9-dimethyl-9H-2,7-dipinacolborylfluorene (8.9 g, 20 mmol), methyl 4-Iodolbenzoate (11.5 g, 44 mmol), K_2CO_3 (13.8 g, 100 mmol), 3% [$Pd(PPh_3)_4$] and 12% PPh_3 were deaerated under nitrogen for 20 min. Then fresh anhydrous THF (200 mL) and methanol (100 mL) were added to the mixture. The mixture was heated at 80 °C for 3 days under N_2. After cooling to room temperature, 50 mL water was added, the solid was separated, washed with water and extracted with dichloromethane. The CH_2Cl_2 solution was evaporated to dryness. White powders (8.5 g) were obtained. Yield: 92%. ^{1}H NMR ($CDCl_3$) δ 1.61(s, 6H), 3.96(s, 6H), 7.64(d, 2H), 7.70(s, 2H), 7.75(d, 4H), 7.84(d, 2H), 8.14(d, 4H) (Fig. S3).

4,4′-(9,9-dimethyl-9H-fluorene-2,7-diyl)dibenzoic acid: the dimethyl 4,4′-(9,9-dimethyl-9H-fluorene-2,7-diyl)dibenzoate (0.46 g, 1 mmol) was suspended in methanol (20 mL), to which 20 mL of 20% NaOH solution was added. The mixture was stirred under 100 °C for 3 days and boiling water (200 mL) was added. Then the solution was acidified using 2 M HCl solution. The precipitate was collected by filtration, washed with water, and dried to give 4,4′-(9,9-dimethyl-9H-fluorene-2,7-diyl)dibenzoic acid (0.41 g). Yield: 95%. ^{1}H NMR (^{6}d DMSO) δ 1.56(s, 6H), 7.74(d, 2H), 7.89(d, 4H), 7.98 (t, 4H), 8.04(d, 4H) (Fig. S4).

2.3. Synthesis of MgL

A mixture of **H_2L** (0.05 mmol, 21.7 mg), $Mg(NO_3)_2 \cdot 6H_2O$ (0.1 mmol), DMF (5 mL), ethanol (2 mL) and H_2O (1 mL) was sealed in a 15 mL Parr Teflon-lined stainless steel vessel and heated at 80 °C for 2 days. Colorless crystals were obtained in 85% yield, which were washed with ethanol, and dried under ambient condition. Elemental analysis calc. for $C_{32}H_{33}MgO_8N$: C, 65.82; H, 5.70; N, 2.40%. Found: C, 65.72; H, 5.53; N, 2.58%. IR (KBr, cm^{-1}) 3430, 2974, 1671, 1593, 1542, 1407, 787, 870, 838, 702 (Fig S5).

2.4. Synthesis of ZnL

ZnL was prepared by a method similar to that of **MgL** by using $Zn(NO_3)_2 \cdot 6H_2O$ instead of $Mg(NO_3)_2 \cdot 6H_2O$. Colorless crystals were obtained in 80% yield. Elemental analysis calc. for $C_{32}H_{27}ZnO_5N$: C, 67.32; H, 4.77; N, 2.45%. Found: C, 67.22; H, 4.89; N, 2.31%. IR (KBr, cm^{-1}) 2975, 1654, 1600, 1541, 1406, 779, 870, 836 (Fig S5).