Journal of Solid State Chemistry 219 (2014) 259–264

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Syntheses, structures, molecular and cationic recognitions and catalytic properties of two lanthanide coordination polymers based on a flexible tricarboxylate

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ARTICLE INFO

Article history:
Received 12 May 2014
Received in revised form
17 July 2014
Accepted 20 July 2014
Available online 30 July 2014

Keywords:
Crystal structure
Molecular recognition
Ionic recognition
Cyanosilylation

ABSTRACT

Two lanthanide coordination polymers, namely, $\{[La(TTTA)(H_2O)_2]\cdot 2H_2O\}_n$ (La-TTTA) and $[Nd(TTTA)(H_2O)_2]\cdot 2H_2O\}_n$ (Nd-TTTA) have been hydrothermally synthesized through the reaction of lanthanide ions (La^{3+} and Nd^{3+}) with the flexible tripodal ligand 2,2′,2″-[1,3,5-triazine-2,4,6-triyltris(thio)]tris-acetic acid (H_3TTTA). La-TTTA and Nd-TTTA are isostructural and both show three dimensional structures. La-TTTA and Nd-TTTA show good recognition of amine molecules via quenching the luminescent intensities in amines emulsions. They can also recognize Fe^{3+}, Cu^{2+}, Mg^{2+}, Cr^{3+} and Co^{2+} ions with the quenching the peak around 361 nm when the compounds immersed in ionic solutions. The two compounds act as efficient Lewis acid catalysts for the cyanosilylation of benzaldehyde and derivatives in high yields shortly due to the strong Lewis acidity and the possible open sites of the lanthanide ions.

1. Introduction

Studies on the synthesis and design of coordination polymers (CPs) have been extensively developed in recent years, owing to their dynamic structures and promising applications in gas storage and separation, luminescence, catalysis, magnetism, and drug delivery [1]. The design of organic linkers and the coordination tendencies of metal ions besides crystallization conditions have led to a large number of open framework structures quite often endowed with novel topological structures as well as unique functionalities [2]. Especially, exploring highly symmetrical multi-topic ligands and suitable metal salts to construct supramolecular architectures is of higher interest [3]. Flexible ligands, which have been less studied than the rigid ligands, can adopt additional different conformations according to the geometric requirements of different metal ions and may afford unpredictable and interesting supramolecular networks [4]. The self-assembly between metal ions and flexible ligands is also proven to be a most effective synthetic design to achieve chiral, helical frameworks and high-nuclear complexes [5], single-helices [6] with potential applications in selective catalysis, separation and so on [7]. Indeed, the structural frameworks are frequently influenced by external factors, such as solvent systems, pH values, temperature, geometric requirements of metal atoms, metal–ligand ratio, structure of connecting ligands, and nature of counter anions [8]. Moreover, self-assembly of inorganic and organic luminescent moieties into porous coordination polymers can used as luminescent materials for chemical sensing, light-emitting and environmental monitoring [9].

Recently, we have focused on the flexible tripodal ligand 2,2′,2″-[1,3,5-triazine-2,4,6-triyltris(thio)]tris-acetic acid (H_3TTTA) which can be constructed with different metal ions to novel complexes with abundant topologies and interesting applications. Due to its flexibility, the three arms could show significant deviation from the central triazine ring. Besides, the different degrees of protonation will cause numbers of coordination sites which will achieve affluent, unpredictable topologies and interesting properties. Though some complexes based on H_3TTTA with fluorescence and magnetic properties were reported previously [10], the applications on cyanosilylation reaction have never been explored yet. As we know, cyanosilylation reaction is widely used to test the Lewis acid catalysis of complexes. Moreover, The Lewis acid used for the addition of trimethylsilyl cyanide (TMSCN) in aldehydes and ketones primarily includes compounds based on lanthanides metal compounds [11]. Therefore, lanthanide coordination polymers exhibit great potential as Lewis acids in heterogeneous catalysis.

In present work, we have produced two lanthanide coordination polymers assembled with H_3TTTA. We report their syntheses, crystal structures, molecular and cationic recognitions

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http://dx.doi.org/10.1016/j.jssc.2014.07.029
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and catalytic properties. To date, research on the properties of complexes with H_3TTTA and the similar ligands are mainly focused on the luminescence and magnetism and so on. There are few reports about molecular and cationic recognition as well as catalytic properties of these compounds.

2. Experimental

2.1. Materials and physical methods

The ligand was prepared according to the previous procedure [12]. All other reagents were commercially available and used as purchased. The elemental analyses were carried out with a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 400–4000 cm^{-1} on a Nicolet spectrometer. Thermal analyses were performed on integrated thermal STA 449C analyzers from room temperature to 800 °C with a heating rate of 10 °C/min under flowing nitrogen. The fluorescence spectra of compounds in different solvents and solutions were performed on a QuantaMaster TM 40 & Time-Master spectrophotometer. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku D/max2500VB3+/PC diffractometer equipped with Cu-*Kα* radiation (λ=1.5406 Å).

2.2. Synthesis of La-TTTA

A mixture containing H_3TTTA (0.035 g, 0.1 mmol) and La $(NO_3)_3 \cdot 6H_2O$ (0.086 g, 0.2 mmol) in 3 mL water was sealed in a Teflon-lined autoclave and heated to 80 °C under autogenous pressure for two days and then allowed to cool to room temperature. After filtration, the white block crystals were washed with water and dried in air. Anal. Calcd for $C_{18}H_{20}La_2N_6O_{20}S_6$ (*Mr*: 1110.58): C, 19.47; H, 1.82; N, 7.57%. Found: C, 19.08; H, 1.89; N, 7.51%. IR (cm^{-1}): 3426(m), 1582(s), 1479(s), 1419(s), 1385(s), 1269 (w), 1226(m), 848(w).

2.3. Synthesis of Nd-TTTA

Nd-TTTA was obtained in a similar manner to La-TTTA using Nd $(NO_3)_3 \cdot 6H_2O$ (0.086 g, 0.2 mmol). After filtration, the crystals were washed with water and dried in air. Anal. Calcd for $C_9H_{10}NdN_3O_{10}S_3$ (*Mr*: 560.62): C, 19.28; H, 1.80; N, 7.50%. Found: C, 19.13; H, 1.92; N, 7.43%. IR (cm^{-1}): 3424(m), 1580(s), 1474(s), 1418(s), 1384(s), 1270(w), 1224(m), 848(w).

2.4. Crystal structure determination and refinement

The X-ray intensity data for the two compounds were collected on a Rigaku Saturn 724+CCD diffractometer with graphite monochromatized Mo *Kα* radiation (λ=0.71073 Å). The crystal structures were solved by direct methods using difference Fourier synthesis with SHELXTS [13], and refined by full-matrix least-squares method using the SHELXL-97 program [14]. The non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms except for those of guest molecules were added according to theoretical models. Crystal data and details of the structure determination for La-TTTA and Nd-TTTA are listed in Table 1. Selected bond lengths and angles for La-TTTA and Nd-TTTA are listed in Table S1.

2.5. Catalytic test for cyanosylation reaction

Aldehyde (1.0 mmol) in trimethylsilyl cyanide (TMSCN, 2 mmol) was successively placed into a 10 mL screw-cap vial and compound (2.5 mol%) was then added to initiate the reaction with ultrasound for 2 h in the sealed vial. After the reaction completed, the catalyst was removed by centrifugation and then filtered with ethyl acetate quickly. The conversion of aldehydes was determined by gas chromatography (GC, Agilent 7890 A) analysis and GC–MS (HP 6890) spectra with those of authentic samples.

Table 1
Crystal data and structure refinements for La-TTTA and Nd-TTTA.

Compound	**La-TTTA**	**Nd-TTTA**
Empirical formula	$C_{18}H_{20}La_2N_6O_{20}S_6$	$C_9H_{10}N_3NdO_{10}S_3$
Formula weight	1110.58	560.62
Temperature (K)	193	193
Crystal system	Triclinic	Monoclinic
Space group	$P\overline{1}$	*P*21/c
a (Å)	8.9930(18)	8.7281(17)
b (Å)	13.214(3)	14.495(3)
c (Å)	14.518(3)	15.445(5)
α (°)	86.89(3)	90.00
β (°)	87.01(3)	121.07(2)
γ (°)	86.08(3)	90.00
D_c (g/cm^3)	2.149	2.225
Z	2	4
F (0 0 0)	1,080	1,092
Reflections collected	14,845	6,903
Unique reflections	4560	2578
μ (mm^{-1})	2.910	3.535
Goodness-of-fit on F^2	0.931	1.086
R_1 [$I > 2\sigma(I)$]	0.0714	0.1414
wR_2 [$I > 2\sigma(I)$]	0.1890	0.3259
R_1 (all data)	0.0887	0.1459
wR_2 (all data)	0.2057	0.3278

3. Results and discussion

3.1. Synthetic and spectral aspects

The two compounds were characterized by powder XRD, TG analysis, and FT-IR spectroscopy. The experimental powder XRD patterns were measured at room temperature as shown in Fig. S1. The peak positions of the simulated and experimental PXRD patterns are in agreement with each other, suggesting the good phase purity of the two compounds. TG analysis revealed that all these materials have good thermal stabilities, since they start to decompose beyond 300 °C (Figs. S2 and S3).

The characteristic absorption peaks of the main functional groups in FT-IR spectra for all the compounds are shown in Fig. S4. The asymmetric stretching vibrations $\upsilon_{as}(COO^-)$ of the two compounds were observed in about 1582, 1580, 1597 cm^{-1} and symmetric stretching vibrations $\upsilon_s(COO^-)$ in 1385, 1384, 1403 cm^{-1}. The difference $\Delta(\upsilon_{as}(COO^-)-\upsilon_s(COO^-))$ was about 200 cm^{-1}, characteristic for coordinated carboxylate groups [15].

3.2. Crystal structural description of La-TTTA and Nd-TTTA

Single-crystal X-ray analyses indicate that the only small difference between La-TTTA and Nd-TTTA is the coordination mode of La1 metal center. The bond length of La1–O3 is 2.896 (7) Å, which is a little longer than the common La–O bond lengths. However, regarding La1–O3 as a weak coordination bond, La-TTTA and Nd-TTTA are isostructural. Herein, the structures and properties of La-TTTA are described in detail as a representative example. La-TTTA crystallizes in the triclinic space group $P\overline{1}$. The ORTEP view of La-TTTA is shown in Fig. 1. La ion is ten-coordinated by five $TTTA^{3-}$ ligands and two water molecules to finish distorted monocapped square anti-prism coordination geometry. The La–O (carboxylate) bond distances vary from 2.473(7) to 2.896(7) Å, and the average La–O (water) bond distance is 2.566(7) Å. The O–La–O bond angles vary from 50.2(2)° to 157.4(2)°. The three carboxylates of TTTA^{3-} exhibit two different coordination modes: one is chelating with one metal center, while the other two acting as a bridge link two metal ions with μ_2–η^1:η^1 mode (Fig. 2). The chelating carboxylate groups bridge two neighbouring La ions to form a one dimensional metal chain with the La···La distance from 4.3984(12) to 4.6074 (12) Å, which do not indicate any significant direct interactions between the metal atoms but is constrained by the bridging geometry (Fig. 3). As shown in Fig. 4, the tridentate TTTA^{3-} ligands hold three metal chains from *a* axis and further construct a infinite three dimensional structure. The presence of ligands and lattice water molecules leads to the formation of extensive H bonding interactions (C(4)···H(4A)···O(21)), which increases the stability of the whole framework (Fig. 5).

3.3. Molecular recognition properties

The free H_3TTTA ligand displays no fluorescent emission with the excitation at 265 nm, while the two compounds exhibit the same emission at 361, 426 and 487 nm when dispersed into water (Fig. S5). The fluorescent emissions mainly attribute to the ligand-to-metal charge transfer (LMCT) [16].

Considering that the ligand-to-metal charge transfer fluorescent emissions, we explored its sensing capability for various solvents (methanol, ethanol, *n*-hexane, acetonitrile, ethyl acetate, acetone, water, DMF, ethidene diamine, isopropamide, tert-butylamine and benzylamine) at room temperature, changing the environment of the metal centers. Due to the similar luminescent properties in different solvents of two compounds, herein, the luminescent properties of La-TTTA in different solvent emulsions are shown in Fig. 6. The emulsions were prepared by introducing 5 mg of La-TTTA powder into 5 mL of the selected solvents at room temperature. These amines molecules are easily distinguished by monitoring the ratios of emission intensities with the quenching half of the previous intensities. These results

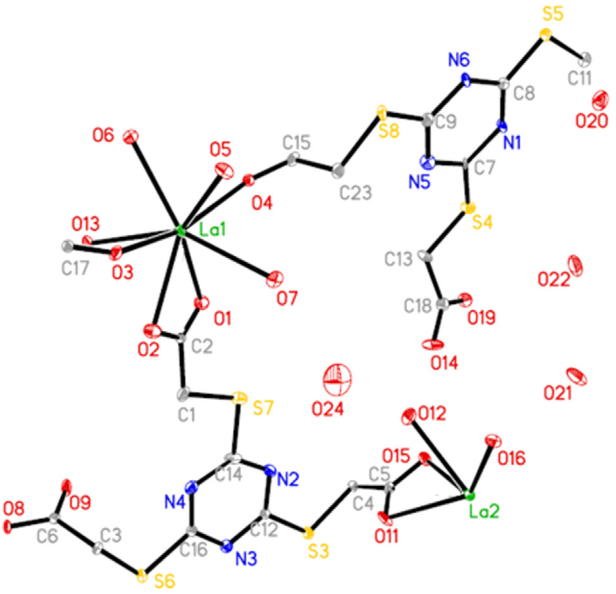


Fig. 1. ORTEP representation of the symmetry expanded local structure of La-TTTA. Displacement ellipsoids are drawn at 30% probability level.

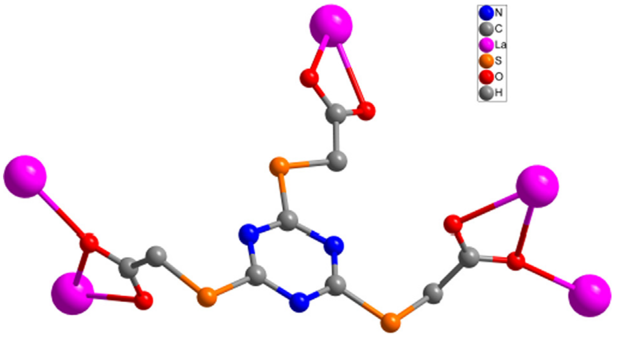


Fig. 2. Coordination modes of the two carboxylates in TTTA^{3-}.

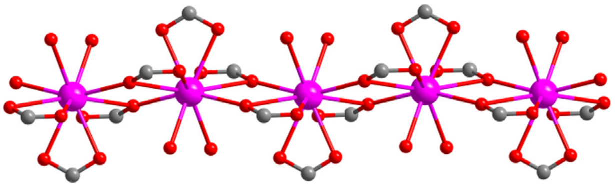


Fig. 3. One dimensional metal chain connected by the chelating carboxylate groups.

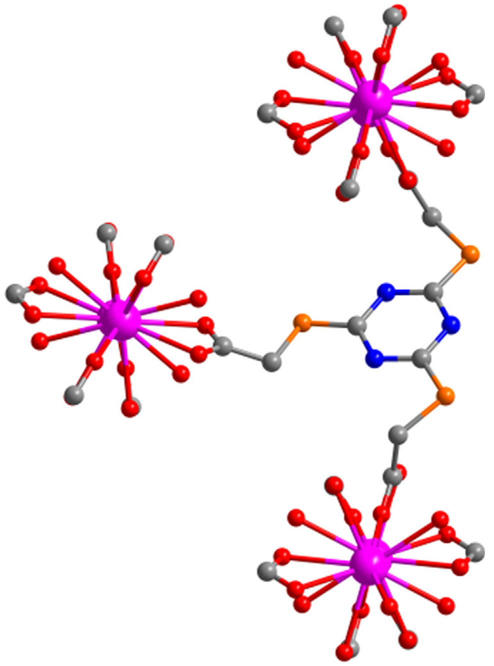


Fig. 4. Metal chains hold by the tridentate TTTA^{3-} ligand.

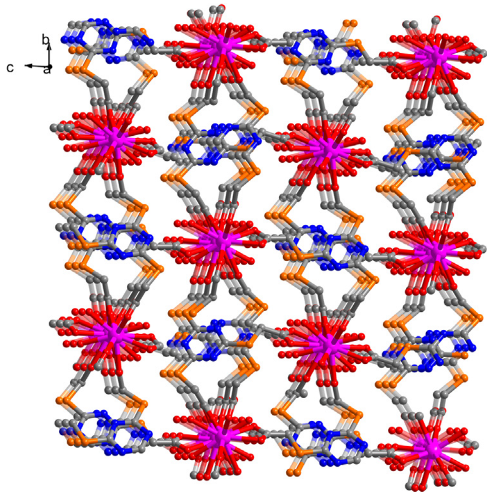


Fig. 5. D3 supramolecular network of La-TTTA as viewed down the *a* axis.

clearly indicate that the two compounds are an excellent sensor for probing amines molecules.

3.4. Cationic recognition properties

The cationic recognition properties were measured by the luminescent method as well. We added La-TTTA (5 mg) into the water solutions (10 mL) with different ions (2 mg/mL) at room temperature for one day. Then we filtered the compounds, washed with water and got the powder after dried in vacuum. The emulsions for testing luminescent properties were prepared by introducing 5 mg of prepared powder above into 5 mL of water. First, we compared the luminescent properties of the powder immersed in anionic solutions (F^-, Cl^-, Br^- and I^-). Visible differences cannot been seen from Fig. S6. However, interesting phenomenon were presented when we turned to the powder immersed in cationic solutions (Zn^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, Mg^{2+}, Fe^{3+}, Co^{2+} and Ni^{2+}) (Fig. 7). The peak around 361 nm was quenched about half of the intensities after immersed in Cr^{3+}, Mg^{2+} and Co^{2+} solutions, while nearly quenched Fe^{3+} and Cu^{2+} solutions. Such a luminescent sensor for probing a range of cations is remarkable with quenching different levels of specified emission intensities. This finding will be useful and practical in environmental protection by monitoring the heavy metal ions (HMI).

3.5. Catalytic tests

As we know, cyanosilylation reaction for cyanalcohol is widely used to test the Lewis acid catalysis of coordination polymers [17]. The two compounds have been tested as heterogeneous Lewis acid catalysts for the cyanosilylation of benzaldehyde and its derivatives (Scheme 1). We selected the non-solvent catalytic reactions because it has been proved to have higher catalytic activity according to the work report [18]. Indeed, TMSCN here acted both as a reagent and a solvent. The results are summarized in Table 2. Without La-TTTA as the catalyst, the conversion in cyanosilylation of benzaldehyde was about 29.2%. However, with La-TTTA in the reaction, excellent catalytic activities were shown with more than 99% conversion in 2 h in the cyanosilylation of benzaldehyde and its derivatives. The observed catalytic activities are already ahead of most of the cyanosilylation reactions with different complexes reported [17]. The high catalytic activities suggest the strong Lewis acidity of the two compounds. Moreover, Ln^{3+} ions have the coordination numbers of eight to twelve, and they have more possibilities to have the open sites which can enhance the catalytic activities. The possible catalytic mechanism for cyanosilylation reaction in the case of La-TTTA has been reasonably predicted in Scheme 2. The heterogeneity of the reaction was confirmed by the filtration test (Table S2). To demonstrate their recyclability, successive reactions in La-TTTA were carried out for cyanosilylation of benzaldehyde, showing that the recovered catalyst can be reused without an appreciable loss after five cycles at least (Fig. 8).

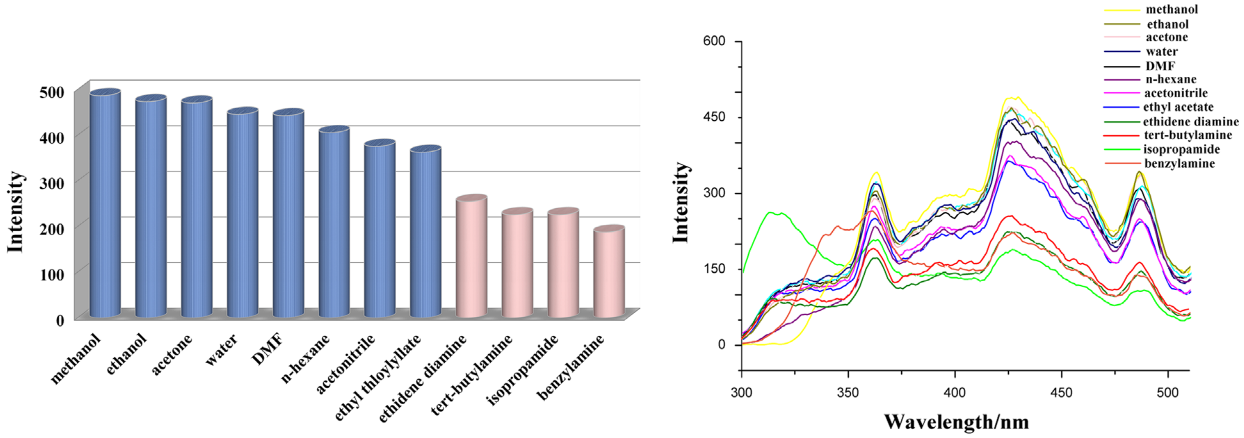


Fig. 6. The different intensities of La-TTTA emulsions in different solvents at 426 nm (left); the luminescent spectra (right).

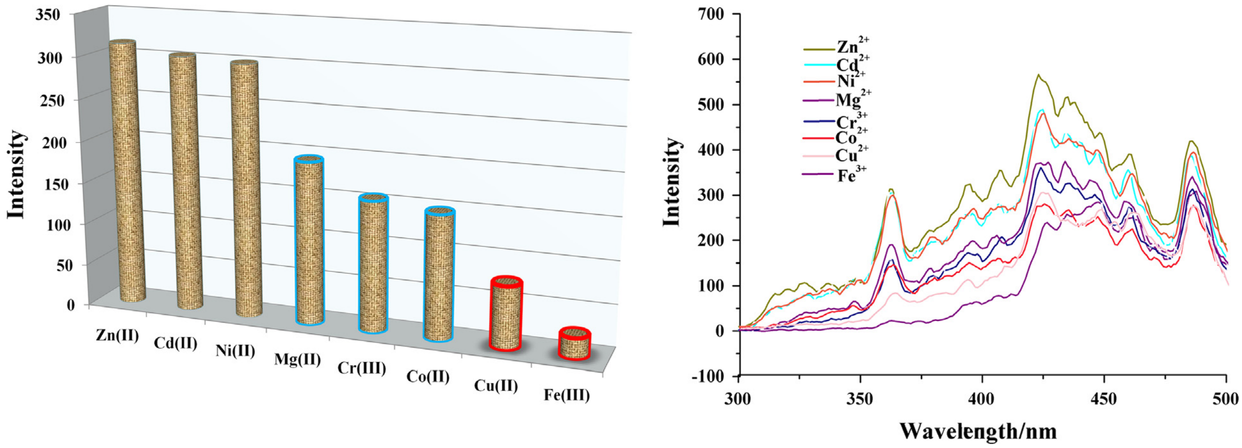
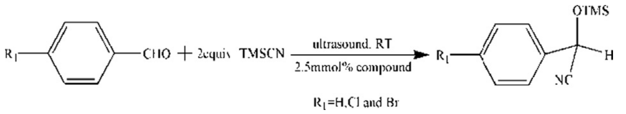
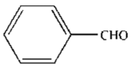
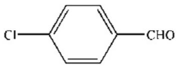
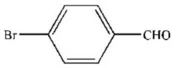


Fig. 7. The different intensities of La-TTTA emulsions in different cationic solutions at 361 nm (left); the luminescent spectra (right).

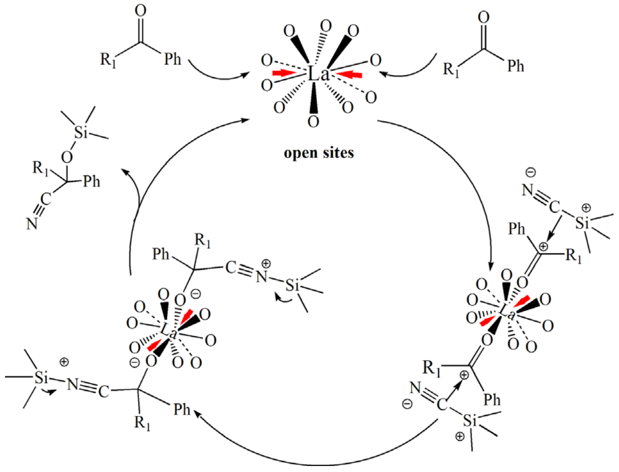


Scheme 1. The cyanosilylation reaction in the presence of selected compound.

Table 2
The catalytic activities for the two compounds (yield [a] and TOF [b]).

	La-TTTA Yield (TOF)	Nd-TTTA Yield (TOF)
	99.70% (39.88)	98.32% (39.33)
	99.67% (39.87)	99.67% (39.87)
	98.72% (39.49)	99.10% (39.64)

[a] Yield determined by GC–MS.
[b] TOF=(yield)/(mol% cat)/(t).



Scheme 2. the possible catalytic mechanism for cyanosilylation reaction in the case of La-TTTA.

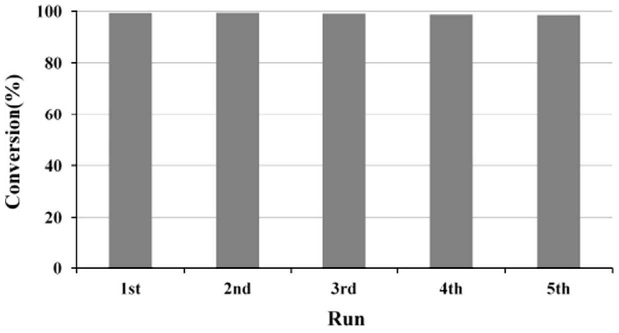


Fig. 8. Recycling tests for cyanosilylation of benzaldehyde catalyzed by desolvated La-TTTA.

The PXRD pattern of retrieved catalyst was identical with that of the fresh catalysts (Fig. S8).

3.6. Conclusions

For the purpose of lanthanide coordination polymers for chemical sensing as well as catalytic applications, we have synthesized two compounds based on H_3TTTA using solvothermal reactions. Isostructural La-TTTA and Nd-TTTA show the three dimensional structures. With quenching of the luminescent intensities in amines emulsions, La-TTTA and Nd-TTTA show good recognition of amine solvents. La-TTTA also has recognition ability for different cations which is important for environmental protection. The two compounds were further applied to catalyze cyanosilylation reactions of benzaldehyde and its derivatives, an important reaction for gaining the useful cyanohydrin trimethylsilyl ethers. The two compounds catalyze the aldehydes and ketones with higher yields and TOF, which are responsible not only for strong Lewis acidity but also for its open sites of the central lanthanide ions.

Acknowledgments

This work was partly supported by National Natural Science Foundation of China (21171075/B010303, 21103073/B030201). Innovation project for graduate student research of Jiangsu Province (1011310003)

Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2014.07.029.

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