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Two Chelating-Amino-Functionalized Lanthanide Metal-Organic Frameworks for Adsorption and Catalysis

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Two chelating-amino-functionalized lanthanide metal-organic frameworks, Er-DADQ and Eu-DADQ, were synthesized with a flexible dicarboxylate ligand based on quinoxaline (H₂DADQ = N, N'-dibenzoic acid-2, 3-diaminoquinoxaline). N₂ adsorption indicates they exhibits stable microporous framework with BET surface area of 136.78 m² g⁻¹. CO₂ adsorptions have also been studied at different temperatures. The amino groups in the MOFs enhanced the uptakes of RhB with COOH groups. RhB-MO and RhB-CV separations can also been successfully conducted. The MOFs act as efficient Lewis acid catalyst for the cyanosilylation of aldehydes and ketones in high yields in short reaction time due to the higher Lewis acidity and the open sites of the metal ions after activation.

Introduction

Recently, the design and construction of porous metal organic frameworks (MOFs) bridged by organic ligands with carboxyl groups have been attracted a great deal of interest in material chemistry, owing to their extraordinary molecular topologies and fascinating chemical and physical properties such as gas storage ^[1], heterogeneous catalysis ^[2], photoluminescent ^[3] and magnetism behaviours ^[4]. Though some series of complexes constructed on carboxylate ligands with distinctive architectures and diversity of functions have been explored, the design of MOFs with excellent properties that combine high porosity with multi-properties still poses one of the major challenges in the pursuit of multifunctional materials ^[5]. One challenge is to control the target structures due to the coordination geometry of the central metal ions and connective features of the organic ligands, which have big influences on the resulted structures and functionalities of the porous materials.

Among these MOFs, MOFs with lanthanide ions (LnMOFs), have been much less explored than their transition metal MOFs and attracted increasing attention because of their versatile structures and interesting properties combining light emission, magnetism, catalysis and molecular separation properties arising from 4f electrons ^[6]. LnMOFs with flexible coordination motifs can create coordinative unsaturated metal centers, which have great potential to be excellent heterogeneous catalysts ^[7]. The guest solvents in the holes can be removed after activation to form permanent pores. The water molecules coordinated to the metal centers can also been taken off to give unsaturated metal centers which is essential for the catalytic property. Meanwhile, the flexibility of the coordination geometry of lanthanides is a positive factor for high thermal stability of the materials due to the results in infinite rod-shaped or discrete lanthanide cluster secondary building units (SBUs)^[8].

Multiple carboxylate ligands have been widely used as bridging ligands to build MOFs. Elongated dicarboxylate ligands have been widely used to construct porous MOFs because of their versatile coordination modes as well as their ability to act as H-bond acceptors and donors to assemble supramolecular structures^[9].

A dicarboxylic acid ligand based on quinoxaline with functional amino sites has been designed yet for MOFs with multi applications (H₂DADQ= N, N'-dibenzoic acid-2, 3-diamino-quinoxaline). The size between the terminals carboxyl is about 15 Å and it provides the possibility of large pores even metal-organic nanotubes (MONTs) ^[10]. Moreover, grafting amino groups into the channels of porous materials is another strategy that has been applied for enhancing adsorption of the acidic CO₂ molecule ^[11]. The alkaline group in the ligands will impact on the MOFs' ability of CO₂ absorptions.

Herein we report crystal structures of two 3D porous carboxylic LnMOFs based on H_2DADQ as linkers and trivalent lanthanide (III) ions (Er and Eu) as connectors. The functionalized channels show good separations of RhB-MO and RhB-CV mixtures, as well as CO_2 absorption. The metal ions act as strong Lewis acid sites for catalyzing the cyanosilylation of aldehydes and ketones in very short reaction time with no-solvent reactions.

Experimental

Materials and Physical Measurements

All of the starting materials employed were purchased from commercial sources and used as received without further purification. Elemental analyses for C, H and N were determined with a Perkin-Elmer 240. Fourier transform infrared (FT-IR) spectra were Dalton Transactions Accepted Manuscript

measured as KBr pellets on a Nicolet FT-170SX spectrometer in the range of 400 cm⁻¹-4000 cm⁻¹. Thermogravimetric analysis (TGA) experiments were carried out on an integrated thermal STA 449C analyzer heated from room temperature to 800 °C under N₂ atmosphere. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku D/max2500VB3+/PC diffractometer equipped with Cu-K\alpha radiation ($\lambda = 1.5406$ Å). The UV-Vis spectra were measured on UV-2450 spectrophotometer

Synthesis of H₂DADQ

Dichloroquinoxaline (3 mmol, 0.600 g) and 4-aminobenzoic acid (12 mmol, 1.60 g) were added to a flask with 100 mL ethanol. The clear mixture was refluxed for 24h and a yellow solid was precipitated, filtered and washed with cold ethanol, finally dried in vacuum. Yield: 0.95g (80%). Anal. Calcd. For $C_{22}H_{16}N_4O_4$: C, 66.00, H, 4.02, N, 13.99%. Found: C, 65.74, H, 4.21, N, 13.89 %. IR (cm⁻¹): 3314(w), 3146(w), 2839(m),1672(s), 1634(s), 1609(m), 1556(s), 1515(s), 1475(m), 773(m), 1407(m), 1296(m), 1240(m), 1186(m), 1108(w), 858(w), 761(w), 680(w), 600(w). The product was dissolved in DMF/H₂O (1:1) solution and yellow prism crystals were formed after two weeks.

Synthesis of {[Er(H_{0.5}DADQ)₂(H₂O)₂]·5H₂O}_n (Er-DADQ)

A mixture containing H₂DADQ (0.0300 g, 0.075 mmol) and $Er(NO_3)_3 \cdot 6H_2O$ (0.0700 g, 0.15 mmol) in 3 mL of DMF/H₂O (1:1) and 0.6 mL of 6 M HCl solution was sealed in a Teflon-lined autoclave and heated at 120 °C under autogenous pressure for two days and then allowed to cool to room temperature. The yellow crystals were washed with DMF, water and air-dried. Yield: 54% (based on H₂DADQ). Anal. Calcd for C₄₄H₄₃ErN₈O₁₅ (*M*r: 1091.12): C, 48.43; H, 3.97; N, 10.27%. Found: C, 51.18; H, 3.92; N, 11.46%. IR (cm⁻¹): 3403(w), 3314(w), 3043(w),1655(s), 1596(s), 1531(w), 1396(s), 1304(w), 1240(m), 1180(m), 867(w), 786(w), 750(m), 683(w), 597(w), 570(w).

Synthesis of {[Eu(H_{0.5}DADQ)₂(H₂O)₂]·5H₂O}_n (Eu-DADQ)

The preparation of Eu-DADQ was similar to that of Er-DADQ except that $Eu(NO_3)_3 \cdot 6H_2O$ (0.0670 g, 0.15 mmol) was used instead of $Er(NO_3)_3 \cdot 6H_2O$ (0.0732 g, 0.15 mmol). The yellow crystals were washed with DMF, H₂O and air-dried. Yield: 34% (based on H₂DADQ). Anal. Calcd for C₄₄H₄₃EuN₈O₁₅ (*M*r: 1075.82): C, 49.12; H, 4.03; N, 10.42%. Found: C, 52.11; H, 3.88; N, 11.43%. IR (cm⁻¹): 3406(w), 3312(w), 3048(w),1651(m), 1599(s), 1570(m), 1396(s), 1306(w), 1306(m), 1182(m), 861(w), 786(s), 751(w), 683(m), 596(w), 571(w).

X-Ray crystallographic structure determinations

The X-ray intensity data for the three compounds were collected on a Rigaku Saturn 724+ CCD diffractometer with graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). The crystal structures were solved by direct methods using difference Fourier synthesis with SHELXTS ^[12], and refined by full-matrix leastsquares method using the SHELXL-97 program ^[13]. The nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms except for those of guest molecules were added according to theoretical models. The solvent molecules in Er-DDAQ and Eu-DDAQ were highly disordered and were impossible to been found in the Fourier maps and fixed in the ideal position. To resolve this issue, the contribution of solvent electron density was removed by SQUEEZE routine in PLATON ^[14]. The structures were then refined again by using the data generated. Crystal data and details of the structure determination for the three compounds are listed in Table S1.

Gas Adsorption Experiments

Prior to gas adsorption experiments, the samples were soaked in methanol to exchange solvents, which was then followed by evacuation under a dynamic vacuum at 120 °C for the 8 hours. All the gas adsorption isotherms were measured using a Micromeritics ASAP 3Flex analyzer employing a standard volumetric technique up to saturated pressure. The N₂ adsorption isotherms were monitored at 77 K. while CO_2 adsorption isotherms were obtained at 273 K and 293 K.

Dye Adsorption and Desorption Experiments

Compound (10mg) was added into a 5 mL of 50 mg/L dyecontaining water solution under stirring at room temperature. The solution was centrifuged, and the clear liquid was analyzed by UVvis absorption spectroscopy. For desorption experiments, the dyes loaded powders were placed in 5 mL fresh water in a glass bottle and the dyes releases were also measured by UV-vis absorption spectroscopy. Separation experiments were carried out by adding 5mg compound to 10 mL RhB-MO or RhB-CV mixtures.

Catalytic Test for Aldehyde and Ketone Cyanosylation Reaction

Into a 10 mL screw-cap vial was successively placed aldehyde (1.0 mmol) in trimethylsilyl cyanide (TMSCN, 2 mmol) and desolvated compound (2.5 mol%) was then added to initiate the reaction with ultrasound for an hour in the sealed vial. To less reactive the ketones cyanosylation reaction, the reaction time extended to three hours with the same ratio of the reactants. After the reaction completed, the catalyst was removed by centrifugation and then filtered with THF quickly. The conversion of aldehydes and ketones were determined by gas chromatography (GC, Agilent 7890A) analysis and GC-MS (HP 6890) spectra with those of authentic samples.

Results and discussion

Er-DADQ and Eu-DADQ were characterized by PXRD, TGA analysis, and FT-IR spectroscopy. The experimental PXRD patterns for Er-DADQ and Eu-DADQ 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 their good phase purity. The PXRD pattern of activated Er-DADQ indicates that the framework is stable after removing the solvent in the channels (Fig S2). The chemical stability of Er-DADQ was also examined by suspending samples in methanol, alcohol, acetone and dichloromethane for one week. The PXRD patterns collected for each samples confirmed that Er-DADQ retaining their crystalline after immersing in different solvents (Fig S3). TGA analysis of Er-DADQ and Eu-DADQ revealed that all the MOF materials have good thermal stabilities, since they start to decompose beyond 300 °C (Fig S4).

The characteristic absorption peaks of the main functional groups in FT-IR spectra for all the compounds are listed in Fig S5. The asymmetric stretching vibrations $v_{as}(COO^{-})$ were observed in about 1596 cm⁻¹ and symmetric stretching vibrations $v_s(COO^{-})$ in 1396 cm⁻¹. The above stretching vibrations shifted to lower values by 20

cm⁻¹, compared to the carbonyl frequencies of free H₂DADQ ligand. The difference $\Delta(v_{as}(COO^{-})-v_{s}(COO^{-}))$ was around 198 cm⁻¹, characteristic for coordinated carboxylate groups ^[16].

Structure of H₂DADQ

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The chemical structure of H₂DADQ is illustrated in Fig 1. From the crystal structure, two flexible C-N-C angles are 127.70 and 129.83°, which can be slightly adjusted when constructing the MOFs with metal ions (Fig S6). The two carboxyl points can catch the metal ions and form the MOFs with 1D, 2D and 3D frameworks. The lengths of the arms are about 7.44 Å and 7.53 Å separately, and the distance between the two carboxyl groups is about 15 Å. All these provide the possibility of constructing the complexes with large porosities. There are strong π - π interactions between Cg (C16-C21) and quinoxaline rings with the centroid to centriod distance of 3.5784 Å.



Fig 1. Chemical structure of H₂DADQ

Because of the isostructural Er-DADQ and Eu-DADQ, the structure and properties of Er-DADQ are described in detail here as a representative example. Er-DADQ crystallizes in the orthorhombic space group Pccn. The ORTEP view of Er-DADQ is shown in Fig 2a. The symmetric unit contains half crystallographically independent Er(III) ion, one H_{0.5}DADQ^{1.5-} ligand and one coordinated water molecule. As shown in Fig 2b, each Er ion is eight-coordinated by oxygen atoms from six ligands and two water molecules to finish a distorted square antiprism coordination geometry. The Er-O (carboxylate) bond distances vary from 2.253(4) to 2.447(4) Å, and the Er-O (water) bond distance is 2.403(4) Å (Table S2). The O-Er-O bond angles vary from 69.48(14)° to 148.33(14)°. Obviously, the polyhedron of the Er(III) coordination sphere for Er-DADQ is best described as a distorted dodecahedron (Fig 2c). The two carboxylates of the ligand exhibit two different coordination modes: μ_2 - η^1 : η^1 mode chelating one Er atom as well as the η^1 mode. The chelating carboxylate groups which connect two Er ions to bridge a centro-symmetric one dimensional metal chains with a Er...Er distance of 5.006 (1) Å, which do not indicate any significant direct interactions between the metal atoms but is constrained by the bridging geometry (Fig 4a). The one dimensional metal chains are linked via the bridging ligands to form the infinite three dimensional frameworks with 8.47 Å × 8.47 Å dimensions (atom-to-atom distances) along the c axis, as shown in Fig 3. It is worthy note that there are strong π - π interactions between the adjacent quinoxaline planes of ligands with the centroid-centroid distance of 3.6726 Å. PLATON calculated suggested a solventaccessible volume of 833.9 Å³ (approximately 18.7% of unit cell) by excluding the guest water molecules. For a better insight into the nature of this complicated 3D framework, network topological approach has been regarded as essential tool for the design and analysis of MOFs ^[17]. The Er-O-C rods which can be simplified as a [ErC₄O₂] SBU (Fig 4b) in this structure are constructed from 8-coordinated Er (III) centers, where each is bonded to carboxyl groups of six DADQ linkers (Fig 4c), resulting in parallel packing of **sra** type^[18].



Fig 2. (a) View of the asymmetric unit of Er-DADQ; (b) View of the local coordination environment of Er(III) atom; (c) Polyhedron of coordination center.



Fig 3. Packing diagram of Er-DADQ, showing the 1D channels along c axis.





Fig 4. (a) View of the 1D metal chain; (b) The inorganic polyhedral SBU. (c) View of crystalline framework with inorganic SBUs with a **sra** net.



Fig 5. N₂ adsorption isotherm of Er-DADQ at 77 K.



Fig 6. CO₂ adsorptions of Er-DADQ at 273 K and 293 K.

To investigate the permanent porosity of desolvated Er-DADQ, the adsorption isotherm of N₂ as a probe gas molecule was measured at 77 K. The uptake of N₂ increases when pressurized and reach to about 94.58 cm⁻³ g⁻¹ (STP) indicating a BET surface area of 136.78 m² g⁻¹. The pore size of Er-DDAQ is about 4.68 Å using Horvath-Kawazoe (HK) method (Fig S7). The adsorption experiments of CO₂ were also measured at 273 K and 293 K (Fig. 6). The PXRD pattern of Er-DDAQ shows that there is no apparent change after the N₂ adsorption (Fig S8). Adsorption measurements of CO₂ were carried out up to about 800 torr. CO₂ with higher polarizability can well interact with desolvated Er-DADQ which is mainly due to the chelating-amino groups which can have strong interactions with the CO₂ molecules as well as the open metal sites in the framework. It starts to take up CO₂ from the low-pressure region, and the adsorption amount gradually increases to ca. 26 cm⁻³ g⁻¹ (4.9 wt%) at 273 K. Taking the 18.7% void volume into consideration, the amount of CO₂ adsorption at low pressure is good enough compared to some MOFs reported such as $Zn_2(BPNDC)_2(bpy)$ (52.6% void volume, 4.7 wt%) [^{20]} and $Zn(DHBP)(DMF)_2$ (39.0% void volume, 0.56 wt%) [^{21]}.



Fig 7. UV-vis absorption spectra of desorption of RhB, MO and CV absorbed Er-DADQ in water solutions.



Fig 8. UV-vis absorption spectra of separation of RhB-MO and RhB-CV mixtures with Er-DADQ.

We also employed the dye adsorption/desorption experiments with different harmful dyes suspended in water solution. We screen Er-DADQ for its ability to take up rhodamine B (RhB), methyl orange (MO) and crystal violet (CV) at room temperature in water solution. The adsorption abilities were measured by UV-vis absorption spectroscope. As shown in Fig S9, RhB was well absorbed; however, MO and CV were slightly absorbed. The length of RhB molecule is ca. 17 Å, and the width is ca. 6 Å^[22]. The width of MO is ca. 2.5 Å which indicates good passing ability from the channels. The carboxylic groups of RhB can be fixed in the channels with the association with the chelating N-H groups, while MO which has no acid groups is not the favour guest. Contrasting the infrared spectra between Er-DADQ and RhB absorbed Er-DADQ, a new strong and wide peak was found at 3405 cm⁻¹, which is the result of the association between COOH of RhB and amine groups (Fig S10). As a result, the host-guest interaction will be the essential point for the dye uptakes between RhB and MO. The PXRD pattern of RhB absorbed Er-DADQ is shown in (Fig S12). The length and width of CV are ca.13 and 8.5 Å, respectively^[23]. The adsorbent can uptake CV slightly though the channels are a little small than the width of CV. We attributed it to the breathing transitions after activate of sra

topologies ^[24]. To verify the interaction between the host-guest molecular which enhanced the adsorptions, we participate in the desorption experiment. MO and CV adsorbed Er-DADQ release about 40% and 11% after stirring for 6h. The difference is mainly due to the sizes of the dyes. The CV molecules are too big to escape most from the channels, while the smaller MO molecules can pass though the channel more easily. In addition, the adsorbents with RhB hardly release the RhB, which confirmed our hypothesis of host-guest interactions (Fig 7).

In light of the remarkable difference between these three dyes in the adsorption behaviour, it can be forecast that the Er-DADQ may has the ability to separate the dye mixtures with RhB/MO or RhB/CV. Er-DADQ were used to separate dye mixtures with equal amounts of RhB/MO or RhB/CV. After stirring for 6h, we can see the colour changes in the adsorption process as illustrated in Fig S11. The UV-Vis spectra of the mixtures before and after adsorption have been measured (Fig 8). The results indicate clearly that Er-DADQ is a good material for the separation of the RhB/MO and RhB/CV mixtures.

Scheme 1 The cyanosilylation reaction in the presence of Er-DADQ.



Table 1. Comparison of the catalytic activity for Er-DADQ: aldehydes or ketones cyanosilylation reaction performed with different substrates.

Entry	Substrate	Yield (%) ^a	TOF $(h^{-1})^{b}$
1	СНО	98(0.5)	39.2
2	сіСно	>99	>39.6
3		61(1.2)	8.1
4	cic=0	>99	>39.6
5		>99	>39.6
6	Br-C=0	81(0.6)	10.8

^{*a*} Yield determined by GC-MS, an average value of three runs (the value in the parentheses is standard deviation ^{*b*} TOF = (yield) / ((mol% cat.) *t*).



Fig 9. The conversions of cyanosilylation of benzaldehyde in different solvents catalyzed by desolvated Er-DADQ.



Scheme 2 The possible catalytic mechanism for cyanosilylation reaction with Er-DADQ after activation

The reaction using Er-DADQ as a Lewis acid catalyst was conducted in our work. As we know, cyanosilylation reaction is widely used to test the Lewis acid catalysis of MOFs ^[25]. Carbonyl compounds can be catalyzed by the Lewis acid with cyanide to gain the useful cyanohydrin trimethylsilyl ethers (Scheme 1). First, the materials were tested with benzaldehyde as the standard molecule and varying the different solvents (Fig. 9). The results are summarized in Table 1. Comparatively, we found that the sample without solvent presents the highest catalytic activity with a TOF value of 39.2 h⁻¹. Indeed, TMSCN acted both as reagent and solvent here. Er-DADQ showed more than 99% conversions in the cyanosilylation of benzaldehyde and 4-chlorobenzal-dehyde in only one hour. Meanwhile, 4-chloroacetophenone and 2-chloroacetophenone could be completely conversed when extending reaction times to three hours, while acetophenone and 4-bromoacetophenone afforded lower yields (61(1.2)% and 81(0.6)%). The electronwithdrawing groups which are advantageous to the nucleophilic reactions make the difference indeed. We attribute the high conversions to high Lewis acid and the open metal sites after removing the coordinated H₂O and solvents. The possible catalytic mechanism for cyanosilylation reaction in the case of Er-DADQ has been reasonably predicted in Scheme 2. The observed catalytic activities are already ahead of most of the cyanosilvlation reactions with different MOFs reported under no-solvent condition ^[25]. The heterogeneity of the reaction was confirmed by the filtration test

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(Table S4). To demonstrate their recyclability, successive reactions were carried out for cyanosilylation of benzaldehyde for the same reaction time, showing that the recovered catalyst can be reused without an appreciable loss after five cycles at least (Table S3). The PXRD pattern of the retrieved catalyst was identical with that of the fresh catalyst (Fig S13).

Conclusions

In summary, for the purpose of porous materials for multi applications, we have synthesized a new chelating-aminofunctionalized ligand and constructed two microporous LnMOFs with **sra** net successfully using solvothermal reactions. The chelating-amino groups lie in channels enhancing the CO_2 and RhB adsorptions. RhB-MO and RhB-CV separations can be successfully conducted and the results demonstrate well enough. In comparison with other crystalline porous MOFs, our LnMOFs catalyze the aldehydes and ketones with higher yields and TOFs, which are responsible for the strong Lewis acid of Ln(III) ions after activation.

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Notes and references

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Graphical Abstract



The chelating-amine groups lie in channels enhance CO_2 and dyes adsorptions. The LnMOFs also show good catalytic activities.

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