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*Cryst. Growth Des.*, **Just Accepted Manuscript** • DOI: 10.1021/acs.cgd.6b00779 • Publication Date (Web): 06 Jul 2016

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# A Polyhedral Metal-Organic Framework Based on the Supramolecular Building Block: Catalysis and Luminescent Sensing of Solvent Molecules

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Supporting Information Placeholder

**ABSTRACT:** A multi-functional polyhedral metal-organic framework with a *pcu* network topology based on supramolecular building blocks (SBBs) can be constructed by the reaction of $Eu(NO_3)_3$ and pyridine-3,5-dicarboxylic acid ($H_2PDC$). The basic $Eu^{III}$ paddlewheel nodes as secondary building units (SBUs) are connected by PDC ligands to generate a nanosized metal-organic cuboctahedra (MOCs), which is further connected by sharing the paddlewheel SBUs to give rise to the 3D primitive cubic network arrangement. The obtained MOF exhibits excellent catalytic activity towards the cyanosilylation of aromatic aldehydes and could be reused without loss of activity. In addition, it can also be considered as fluorescent probes for nitrobenzene sensing based on luminescence quenching effects arising from host-guest interactions. This porous MOF combining catalytic and fluorescent properties could meet further requirement as multi-functional material.

## 1. INTRODUCTION

Over the last two decades, metal-organic frameworks (MOFs) as a flourishing subclass of well-ordered porous crystalline materials with high porosity, large surface area and chemical tenability have attracted tremendous interest owing to their widely potential applications in gas storage and separation,[1] heterogeneous catalysis,[2] drug delivery[3] and luminescence,[4] and so forth. Although remarkable progress has been made in the field of crystal engineering depending on the efficient design strategies, the construction of predictable MOFs is still a challenging problem. In addition to the traditional MOFs with simple metal nodes and organic linker, MOFs based on metal-organic polyhedral (MOPs) using secondary building units (SBUs) might provide a better way for the construction of porous MOFs with specific network topologies.[5] Another efficient strategy for the construction of porous polyhedral MOFs is the use of supramolecular building blocks (SBBs).[6] Utilization of MOPs as the building blocks can guarantee the generation of a porous framework because metal-organic polyhedra themselves have cavities regardless of the network topology. Most prepared polyhedral MOFs based on trigonal bipyramid, hexahedra, hexagonal bipyramid, truncated octahedra, octahedra, cuboctahedra, cubohemioctahedra are achieved by linking transition metal ions with either nitrogen or carboxylate donor units, such as pyridine-based ligands, imidazole-based ligands, 1,3,5-benzenetricarboxylic acid and its derivatives.[7-10] Recently, Zhou and co-workers reported a porous polyhedral MOF containing cuboctahedral cages based on a novel multidentate ligands with two isophthalate and one pyridine groups connected through amide bonds.[10c] However, most of the reported polyhedral MOFs based on supramolecular building blocks are limited to transition metal MOFs, especially the Cu and Zn metals. Reported here is a polyhedral rare earth-based MOF with a primitive cubic network.

In this work, we have used pyridine-3,5-dicarboxylic acid ($H_2PDC$) as a tritopic ligand to obtain a highly porous polyhedral Eu-MOF with *pcu*-type network topology based on SBBs. To the best of our knowledge, this is the first example of lanthanide-based polyhedral Eu-MOF built with SBBs. Moreover, its catalytic performance and luminescent property were also studied.

## 2. EXPERIMENTAL SECTION

**2.1. General Information.** All the reagents and solvents were commercially available and used as received. Infrared spectra were collected from KBr pellets in the range of 4000 - 400 $cm^{-1}$ region on a Nicolet/Nexus-670 FT-IR spectrometer. $^1H$ NMR spectra were recorded with a Varian Mercury Plus 300 MHz spectrometer. The X-ray powder diffraction patterns were measured on a Bruker D8 Advance diffractometer at 40 kV and 40 mA with a Cu target tube and a graphite monochromator. Thermogravimetric analyses (TGA) were performed on a Netzsch Thermo Microbalance TG 209 F3 Tarsus from room temperature to 900 ℃ with a heating rate of 10 ℃/min under flowing nitrogen. The elemental analyses were obtained with a Perkin-Elmer 240 elemental analyzer. The luminescent spectra for the solid state were recorded at room temperature on Hitachi F-2500 and Edinburgh-FLS-920 with a xenon arc lamp as the light source.

**2.2 Synthesis of [$Eu_2(PDC)_3·2H_2O$]$·4H_2O$ (1).** $Eu(NO_3)_3·6H_2O$ (112 mg, 0.25 mmol), $H_2PDC$ (42 mg, 0.25 mmol) and two drops of HOAc were mixed and dissolved in DMF (4 mL) and $H_2O$ (4 mL) . Then the mixture was sealed in a Teflon-lined autoclave and heated under autogenous pressure at 100 ℃ for three days. After cooling to room temperature, colorless block-shaped crystals of **1** were obtained and washed with DMF. Yield: 65% (based on the ligand). IR (KBr, $cm^{-1}$): 3453(br), 2934(m), 2858(w), 1614(w), 1575(w), 1506(m), 1466(m), 1377(m),1317(m), 1264(m), 1185(w), 1108(s), 1080(s), 981(m), 827(m),770(m), 740(w), 621(m), 460(w). Elemental Anal (%), Calcd for $C_{21}H_{21}N_3O_{18}Eu_2$: C, 27.80; H, 2.33; N, 4.63, found: C, 27.85; H, 2.25; N, 4.59.

**2.3. X-Ray Structure Determination.** Single crystal X-ray data for **1** was collected on a Bruker APEX II diffractometer at 298 K using graphite monochromatic Mo-$K_a$ radiation ($\lambda$ = 0.71073 A) by using $\phi$ and $\omega$ scan.[11] The reflections have been corrected by empirical absorption corrections. The structures were solved by the direct method and refined by full-matrix least-squares on $F^2$ using SHELXL programs.[12] All non-hydrogen atoms were refined anisotropically. In **1**, free solvent molecules were disordered, therefore, the diffused electron densities resulting from these residual solvent molecules were removed from the data set using the *SQUEEZE* routing of *PLATON* and refined further using the data generated.[13] A summary of the crystal structure refinement data is shown in Table 1, and selected bond angles and distances are listed in Table S1. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC reference number 1456991.

**Table 1.** Crystallographic data for **1**.

| | |
|---|---|
| Empirical formula | $C_{21}H_{21}N_3O_{18}Eu_2$ |
| Formula weight | 907.33 |
| Crystal system | Rhombohedral |
| Space group | *R*3 |
| *a* (Å) | 19.674(5) |
| *b* (Å) | 19.674(5) |
| *c* (Å) | 21.910(5) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 90 |
| $\gamma$ (°) | 120 |
| $V$ (Å$^3$) | 7345(3) |
| $Z$ | 9 |
| $\rho_{cald}$ (g/cm$^3$) | 1.846 |
| $F$(000) | 3942 |
| $\mu$ (mm$^{-1}$) | 3.884 |
| Reflections collected | 14806 |
| GOF | 1.043 |
| $R_1$, $wR_2$ indices [ I> 2σ (I)] | 0.0286, 0.0751 |
| $R_1$, $wR_2$ indices (all data) | 0.0295, 0.0758 |

$^a$ $R_1=\sum||F_o|-|F_c||/\sum|F_o|$. $^b$ $wR_2=\{\sum[w(F_o^2-F_c^2)^2]/\sum(F_o^2)^2\}^{1/2}$

**2.4. Typical Procedure for Carbonyl Cyanosilylation.** Prior to the catalytic examination, the samples are activated via the following procedure: the as-prepared samples are activated in vacuum at 160 ℃ for 5 h to generate unsaturated europium metal center. Then a mixture of benzaldehyde (53.0 mg, 0.5 mmol) and TMSCN (99.2 mg, 1 mmol) was placed into a Pyrex-glass screw-cap vial (10 mL), and catalyst Eu-PDC (3 mol%) was added and the resulting reaction mixture is stirring with a Teflon-coated magnetic stir bar at room temperature. The conversions of the product were determined by $^1$H NMR analysis. After the reaction was completed, the catalyst was removed by filtration from the reaction mixture.

**2.5. Fluorescence measurements.** The solvent sensing experiment was performed as follows: The solvent-free samples of Eu-PDC (8 mg) were immersed in different organic solvents (3 mL) for 24 h, then they were filtered and dried naturally in air before the solid state fluorescence was measured at room temperature.

## 3. RESULTS AND DISCUSSION

**3.1. Syntheses and Structural Description.** Solvothermal reaction of $H_2PDC$ with $Eu(NO_3)_3·6H_2O$ in a mixed solvent of 4 mL *N,N'*-dimethylformamide (DMF) and 4 mL water containing HOAc afforded a high yield of block-shaped colorless crystals of **1**, which crystallizes in the rhombohedral space group R3. The formula of [$Eu_2(PDC)_3·2H_2O$]$·4H_2O$ was further confirmed by elemental analysis and thermogravimetric analysis (TGA). Single-crystal X-ray diffraction studies reveal it possesses a three-dimensional (3D) polyhedral MOF with the paddlewheel $Eu_2(COO)_4$ as the basic SBU. As shown in Figure S1, the Eu(1) ion is eight-coordinated in a bicapped trigonal prism geometry, binding four oxygen atoms from four PDC ligands with monodentate coordination mode, two oxygen atoms from the fifth PDC ligand with chelating mode, and two nitrogen atoms from other two PDC ligands. The Eu(2) ion is also eight-coordinated, surrounded by five oxygen atoms from five carboxylate groups of 3,5-PDC in monodentate coordination mode, one nitrogen atom from the sixth PDC ligand, and two coordinated $H_2O$ molecules (O1W and O2W). Four carboxylate groups from different PDC ligands connect two Eu(III) ions to generate the paddlewheel secondary building unit (SBU). Twenty-four PDC ligands adopting $\mu_5$-$\eta^1$:$\eta^1$:$\eta^1$:$\eta^1$:$\eta^1$ coordination mode (Scheme S1, mode I) and twelve paddlewheel motifs assemble into an edge-directed corner-linked cuboctahedral building unit, where the PDC units are used for 24 edges and square paddle wheel units for 12 corners of the MOC (Figrure 1a and 1b). The interior cavity of the MOC is ~13 Å in diameter. Similar to the other MOFs consisting of isophthalate moieties, the paddlewheel SBUs are usually constructed by the carboxylate groups of the ligands, however, these SBUs are connected to the MOC by the ligands through its coordinated nitrogen atoms and the carboxylate groups simultaneously. In fact, the SBUs are also constructed by the other PDC ligands with different $\mu_3$-$\eta^1$:$\eta^2$:$\eta^1$ coordination mode (Scheme S1, mode II, and Figure S2), thus reduced the size of the cavity to ~10 Å in diameter. However, such ligands with coordination mode II to some extent only satisfy the coordination number to the central metal ions and don't obviously change the whole framework. The exterior shape of the metal-organic cuboctahedral can be accessed *via* triangular windows or square windows (Figure 1c). The cuboctahedral cages can be considered as the supramolecular building blocks (SBBs) of the whole structure. These SBBs are connected to one another by sharing the paddlewheel SBUs to generate a 3D porous polyhedral MOF (Figure. S3). In this network, each MOC is connected by using 24 ligands, which results in 12 surrounding MOCs to the primitive cubic arrangement (Figure 1d). The prepared MOF using MOCs leads to a high porosity network and the void volume of network is 7344 Å$^3$ per unit cell, which occupies 39 % of the total crystal volume (calculated by Platon).

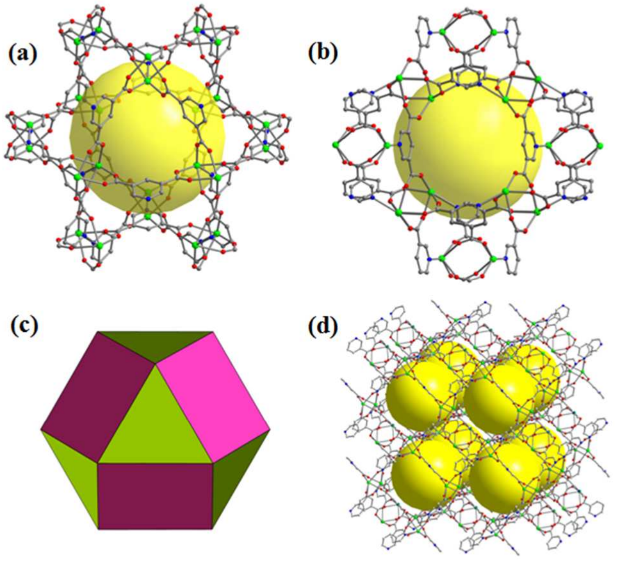
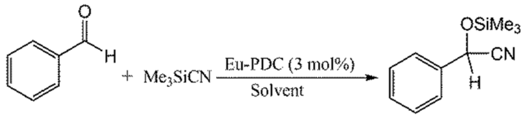


**Figure 1.** MOC assembled from 24 PDC units and 24 Eu$^{3+}$ ions, which has eight triangular windows (a) and six square windows (b). The yellow ball of 13 Å diameters represents the size of the cavity when the PDC ligands with the coordination mode II and the ligated water molecules are ignored. (c) The cuboctahedron in Eu-PDC. (d) The primitive cubic network after considering the cuboctahedron as supramolecular building blocks.

**3.2. Heterogeneous Catalysis.** To explore the catalytic activity of porous Eu-PDC, the Lewis acid-catalyzed cyanosilylation reaction of carbonyl compounds with cyanide in the presence of Eu-PDC was performed. Before the catalytic tests, the fresh as-prepared samples were activated under vacuum at 160 ℃ for 5 h to remove the physically and chemically guest molecules, generating the dehydrated phase Eu-PDC. The TGA curves and XRD pattern of the Eu-PDC show that the guests have been completely removed and the framework remains intact (Figure S4 and S8). Since Eu-PDC is insoluble in most organic solvents, we had used *n*-hexane, dichloromethane, tetrahydrofurane, ethyl acetate, acetonitrile, ethanol and water as solvents. As shown in Table 2, the reaction on *n*-hexane was accelerated in comparison to those in other organic solvents. In general, solvents of low polarity are beneficial for the use of Eu-PDC because of the low solubility in such solvents, and also due to the fact that the donor type solvents don't coordinate the acidic sites and the substrates have more chances to access the Lewis acidic Eu$^{III}$ coordinatively unsaturated sites.

Herein, we employed a molar ratio of 1:2 to select aromatic benzaldehyde and cyanotrimethylsilane in *n*-hexane at room temperature for 3 h with 3 mol% catalyst loading, which generated the corresponding product with the 93 % yield (entry 1, Table 3). The yield is slightly less than the powerful Lewis acid catalyst Nd(btc) ($H_3$btc=1,3,5-benzenetricarboxylic acid) with a 99% conversion in 2 h with 9.0% catalyst loading,[14] but represents a significant improvement compared to the other reported MOFs.[15]

**Table 2.** Reaction of benzaldehyde with cyanotrimethylsilane in the presence of Eu-PDC: Effect of solvents.



| Entry | Solvent | Time (h) | Yield[a] (%) |
|---|---|---|---|
| 1 | n-Hexane | 3 | 93 |
| 2 | Benzene | 3 | 92 |
| 3 | Ethyl acetate | 5 | 3 |
| 4 | Acetonitrile | 7 | 7 |
| 5 | Dichloromethane | 8 | 25 |
| 6 | Tetrahydrofurane | 7 | 2 |
| 7 | Water | 15 | 92 |

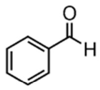
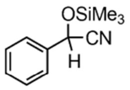
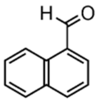
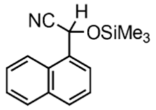
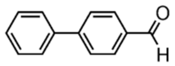
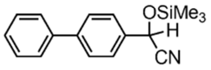
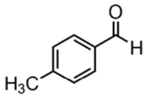
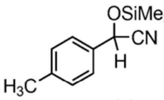
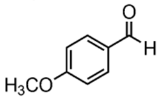
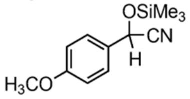
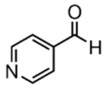
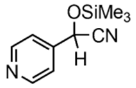
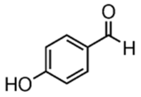
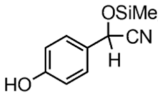
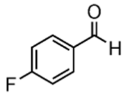
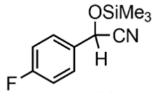
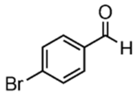
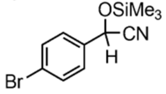
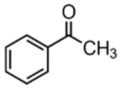
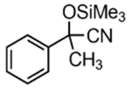
[a] Reaction conditions: catalyst (3 mol %), benzaldehyde (0.5 mmol), $Me_3SiCN$ (1 mmol), solvent (2 mL), room temperature.

In order to understand the scope and limitations of Eu-MOF catalyzed procedure for the cyanosilylation reaction, various aldehydes were treated with $Me_3SiCN$ under the similar conditions. On one hand, the size/shape of the substrates to some extent has influences on the conversion catalyzed by Eu-PDC (entries 1-3). On the other hand, the product yields are very sensitive to the properties of the electronic groups on the aromatic aldehydes (entries 4-10). Aldehydes with electron-donating groups have greater reactivity compared to those having electron-withdrawing groups. As is known, ketones are much less reactive than aldehydes. Thus, the conversion of acetophenone to the cyanosilylated product under the similar condition only reached 4 % yield after 16 h.

For comparison, we used $Eu(NO_3)_3·6H_2O$ as homogeneous catalyst instead of Eu-PDC to conduct the catalytic experiment, which is less efficient to prompt the catalytic transformation (Yield: 4%). When $Eu(NO_3)_3·6H_2O$ was used as catalyst and $H_2$PDC ligand as additive, a negligible conversion of 6% was detected. These results show that the catalytic centers may be partially ligated by the nitrate anions or the ligands, which can't be easily accessed by the substrates, demonstrating the enhanced catalytic activity of solid Eu-MOF under the catalytic conditions. Moreover, the as-made samples of **1** containing solvent molecules were used instead of the activated ones (Table 3, entry 1d). However, the catalytic results are inferior to that of dehydrated Eu-PDC under the similar conditions (Yield: 35%), which indicates that the catalytic Eu$^{3+}$ sites might be easily blocked by the solvent molecule, and the substrates compete with the solvent molecules during the catalytic process.[16]

To check the heterogeneity of Eu-PDC catalyst in the liquid phase, we monitored the process of the catalytic transformations and a filtering experiment was carried out. At the 51% conversion of the benzaldehyde in the presence of Eu-PDC for 30 min, the catalysts were filtered off and the filtrate was allowed to stir for another 100 min (Figure 2). It was found that the conversion rose to 56% with only 5% increase during the reaction. Thus, we ascribe the additional 5% conversion to the leached europium ions during the process and believed that the reaction is basically heterogeneous. Similar behaviors can also be investigated for the cyanosilylation of 1-naphthaldehyde and 4-phenylbenzaldehyde, respectively (Figure 2, Figure S5-S7).

**Table 3.** Comparison of the catalytic activity of Eu-PDC: the aldehydes or ketone cyanosilylation reaction performed with different substrates.

| Entry | Substrate | Product | Yield[a] (%) |
|---|---|---|---|
| 1 |  |  | 93<br>4[b]<br>6[c]<br>35[d] |
| 2 |  |  | 80 |
| 3 |  |  | 53 |
| 4 |  |  | 100 |
| 5 |  |  | 100 |
| 6 |  |  | 100 |
| 7 |  |  | 43 |
| 8 |  |  | 88 |
| 9 |  |  | 78 |
| 10 |  |  | 4[e] |

[a] Reaction conditions: catalyst (3 mol %), benzaldehyde (0.5 mmol), $Me_3SiCN$ (1 mmol), *n*-hexane, room temperature, 3 h. [b] Catalyzed by $Eu(NO_3)_3 \cdot 6H_2O$ (6 mol %) for 5 h. [c] Catalyzed by a mixture of 4 mol % $Eu(NO_3)_3 \cdot 6H_2O$ and 6 mol % $H_2PDC$ ligands. [d] Catalyzed by the as-made samples of Eu-PDC containing solvent molecules (3 mol%) for 3 h. [e] Catalyzed by Eu-PDC ( 3 mol %) for 16 h.

To verify the framework robustness, the powder X-ray diffraction (PXRD) pattern of the recovered Eu-PDC after the reaction was obtained and showed no signs of framework collapse and decomposition compared to that of the original crystal (Figure S8). The maintenance of the crystalline information of the used Eu-PDC during the reaction process suggested that it is possible to be recycled with comparable catalytic activity. One remarkable feature of catalyst is that it can be easily isolated from the reaction suspension by filtration alone and could be reused at least four times with only a slight decrease in the reactivity (Figure 3).

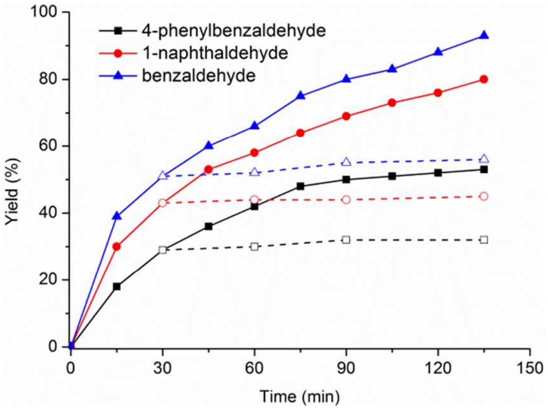


**Figure 2.** Kinetic profiles of cyanosilylation for different aldehydes catalyzed by Eu-PDC (solid line), and the conversion for the same reaction upon removal of Eu-PDC by filtration after 3 h (dot line).

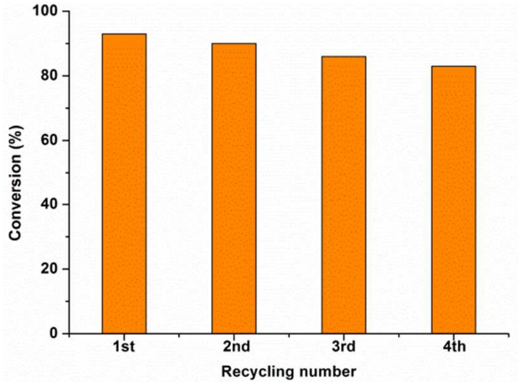


**Figure 3.** Recycling test for cyanosilylation reaction of benzaldehyde with cyanosilylation catalyzed by Eu-PDC.

**3.3. Luminescence and sensing studies.** The solid state luminescence of the solvent-free framework Eu-PDC was measured at excitation wavelength of 312 nm under ambient temperature (Figure 4a). It exhibited the characteristic emission peaks of Eu(III) ion at 567, 592, 618, 654, and 703 nm, corresponding to $^5D_0 \rightarrow ^7F_n$ (n=0-4) transitions, respectively. The strongest emission is due to the $^5D_0 \rightarrow ^7F_2$ transition, which is usually observed in many europium compounds.[17]

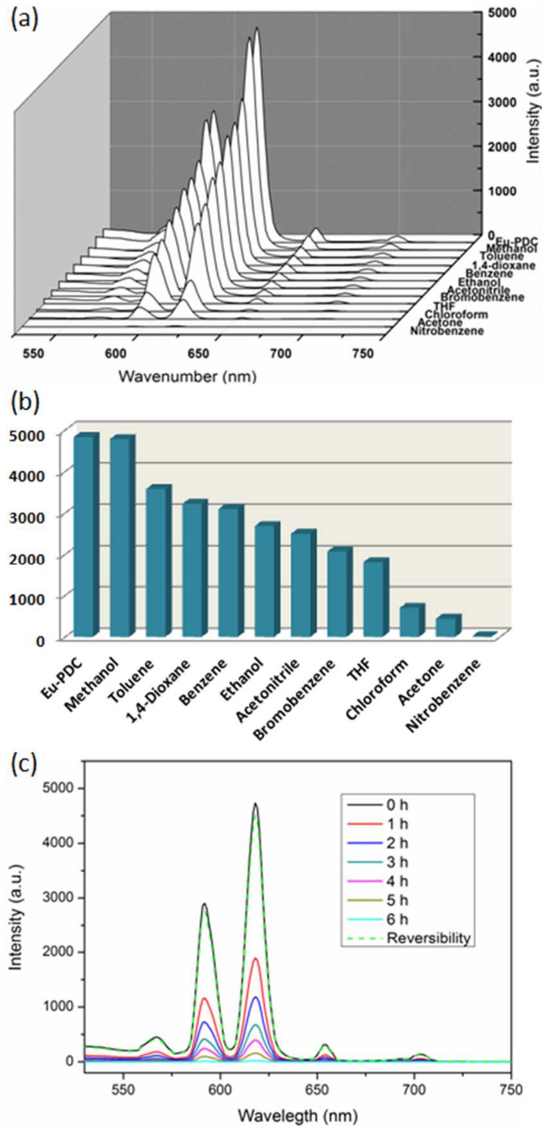


**Figure 4.** (a) Luminescent spectra and (b) the ${}^5D_0 \rightarrow {}^7F_2$ transition intensities of Eu-PDC after immersed in different organic solvents for 24 h (excited at 312 nm); (c) Emission spectra of Eu-PDC after immersed in nitrobenzene for different time (excited at 312 nm).

To examine the potential applications of Eu-PDC for responding to organic solvents, the Eu-PDC samples were immersed in various organic solvents for 24 h, including acetone, chloroform, bromobenzene (BB), 1,4-dioxane, benzene, toluene, nitrobenzene (NB), methanol, ethanol, acetonitrile and THF, then they were filtered and dried naturally in air. The PXRD patterns of the samples were almost identical to that of the simulated one (Figure S9), indicating that the frameworks were stable in these organic solvents. As shown in Figure 4a, the characteristic emission of the Eu ion was observed after immersed in most of the solvents. Evidently, the luminescence intensity of Eu-PDC largely depends on the organic solvent molecules, particularly nitrobenzene, which exerted the most significant quenching effect (Figure 4b). Further detailed experiments were undertaken to examine the detection ability for nitrobenzene. By decreasing the time of sample immersed in nitrobenzene solvent, we found that the luminescence intensity significantly decreased when the time increased, even the samples were immersed in nitrobenzene only for 1 h (Figure 4c). The luminescence was nearly completely quenched when the time reached up to 6 h, implying that Eu-PDC is a highly sensitive sensor for nitrobenzene. The nitrobenzene molecules inside the lattice can be diffused out when immersed in pure methanol solvent for 1 day after sensing tests. Regenerated Eu-PDC exhibited the similar luminescence response with respect to methanol solvent molecules (Figure 4c). Interestingly, the luminescence could be completely quenched once more when the recovered Eu-PDC samples were immersed in nitrobenzene solvent for another 24 h, suggesting that this MOF could be reused and showed excellent reversibility as fluorescent probe for nitrobenzene.

As we know, the luminescence intensity of lanthanide ions depends on the efficiency of the energy transfer from the ligand to the $Ln^{3+}$ center (antenna effect).[18] According to the above discussion, the energy transfer process is less effective with the introduction of solvent molecules. To explain the observed quenching, the electronic structures of four aromatic molecules (NB, BB, benzene and toluene) are described in detailed. The electron-withdrawing abilities of the substituent groups are in a descending order: $-NO_2 > -Br > -CH_3$ (benzene was selected as the standard), which is fully in agreement with the order of the quenching efficiency of the four solid samples (NB > BB > benzene > toluene). Therefore, the photoinduced electron-transfer mechanism appears to provide a good explanation for the quenching effect. The nitrobenzene with electron-deficient group can obtain electron from excited ligand, which has been demonstrated by molecular orbital theory.[19] Therefore, the excited state electrons can transfer from the framework of Eu-PDC (as an electron donor) to nitrobenzene (as an electron acceptor). On the other hand, the quenching behavior might also be ascribed to the interaction between the guest solvents molecules and the framework of Eu-PDC.[20]

## 4. CONCLUSION

In summary, we have firstly presented a multifunctional rare earth-based polyhedral MOF with a primitive cubic network based on the SBBs, where the Eu(III) ions have been combined with PDC ligands to construct metal-organic cuboctahedra. On the other hand, the micro-porosity, open $Eu^{3+}$ site in this MOF enable it to excellently catalyze the cyanosilylation of aromatic aldehydes, which can be easily recovered and reused at least four times without losing activity. Furthermore, it could be employed as a potential luminescent sensor for the detection of nitrobenzene.

## ASSOCIATED CONTENT

### Supporting Information

Crystallographic data in CIF format, table of selected bond lengths and angles and TGA curves for **1**, experimental and simulated PXRD patterns of **1**, and ${}^1$HNMR spectra after the catalytic reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of P. R. China (Grant No. 21471061 and 21401059), Applid Science and Technology Planning Project of Guangdong Province (2015B010135009), Science and Technology Program of Guangzhou (Grant No. 2014J4100051), Open Project of State Key Laboratory of Structural Chemistry (20150013).

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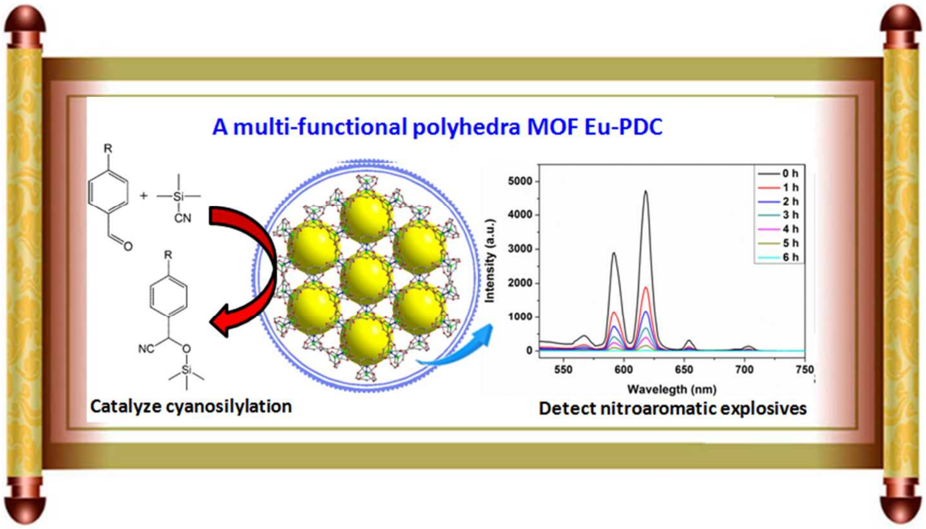
# TOC



A 3D porous polyhedral metal-organic framework Eu-PDC with primitive cubic network is presented. This multi-functional material shows open metal sites and could be acted as Lewis acid catalyst to cyanosilylation reaction. Moreover, luminescent property in various organic solvents indicates that it may be used as a potential reversible sensor for the detection of nitrobenzene.