Electronic Supporting Information (ESI) for

Efficient fixation of atmospheric CO_2 as carbonate by lanthanide-based complex via synergistic effect of zinc ion

Bin Zhang, Xiaodu Zheng, Hao Su, Yu Zhu, Chenxia Du* and Maoping Song*

The College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, 450052 (PR China.) E-mail: dcx@zzu.edu.cn, * corresponding author

Synthesis

General. Reagent grade chemicals and solvents obtained from commercial sources were used as received. Elemental analyses were performed with a Perkin–Elmer 240C elemental analyzer. IR spectra were recorded as KBr pellets with a Bruker Vectop22 FT-IR spectrophotometer. Hydrated europium (III) chloride salts were prepared from its oxides using a modified version of previously published procedures.[1]

Synthesis of ZnL(H_2O): 1,2-propanediamine (0.74 g, 10 mmol) was added to a solution of 3-methoxysalicylaldehyde (3.20 g, 21 mmol) in absolute ethanol (30 mL). The resulting mixture was stirred and refluxed for 1 hour. Then, zinc (II) acetate dihydrate (2.20g 10 mmol) in 10 mL ethanol solution was added. After refluxing for another 2 hours, the reaction mixture was cooled and the resulting precipitate was filtered off. The precipitate was recrystallized in ethanol as white needle crystals. The product was dried in vacuum. Yield: 3.22g (76%). Elemental analysis calcd (%) for the complex $C_{19}H_{22}N_2O_5Zn$ (M= 423.77): C, 53.85; H, 5.23; N, 6.61. Found: C, 53.78; H, 5.26; N, 6.56.

Synthesis of [$Zn_4Eu_4L_4(CO_3)_6$]•EtOH: To a stirred suspension of ZnL(H_2O) (0.36 g, 1 mmol) in 30mL ethanol, a solution of $EuCl_3$ (1 mmol) in ethanol (2 mL) was added. The mixture was then neutralized with Et_3N ethanol solution. Prismatic yellow crystals of [$Zn_4Eu_4L_4(CO_3)_6$]•EtOH suitable for X-ray diffraction were obtained in 43% yield by slow evaporation of the solution in air over two weeks. Elemental analysis calcd (%) for the complex $C_{84}H_{86}N_8O_{35}Zn_4Eu_4$ (M= 2636.99): C, 38.26; H, 3.29; N, 4.25; found: C 38.29, H 3.22, N 4.23. IR (KBr, cm−1): 3386(br), 3053(w),

2900(w), 2834(w), 1633(s), 1604(m), 1536(s), 1505(m), 1471(s), 1443(s), 1395(m), 1318(w), 1240(m), 1220(m), 1169(w), 1077(w), 1036(w), 966(w), 849(m), 736(m), 693(w)

X-Ray Crystallographic Analysis

Crystallographic measurements were made on a Bruker SMART APEXII CCD diffractometer by using graphite-monochromated Mo Kα (λ = 0.71073 Å). The data were corrected with the SMART suite of programs and for absorption effects with SADABS.[2] All crystal structures were solved by direct methods and refined by full-matrix least-squares techniques with SHELXTL–97 program.[3] the occupancy factors for disordered C8, C9 and C10 of 1,2-propanediamine were refined to be 0.69/0.31. The oxygen atoms of the carbonate anions are refined to be disordered over two possible sites with site occupancy factors of 0.57: 0.43. Hydrogen atoms were added geometrically and refined using a riding model.

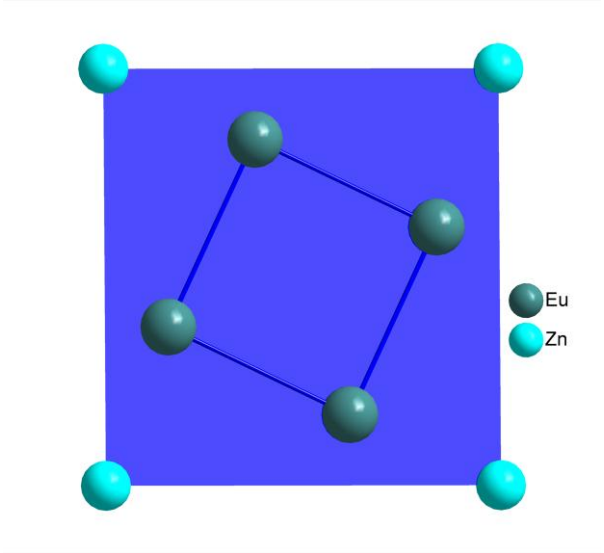

Fig. S1 Parallelogram geometry of Zn_4 and Eu_4

Table. S1 Crystal data and structure refinement for $[Zn_4Eu_4L_4(CO_3)_6]$•EtOH

Chemical formula	$C_{43}H_{46}Eu_2N_4O_{18}Zn_2$
Formula Mass	1341.50
Crystal system	triclinic
a/Å	14.7702(5)
b/Å	14.9866(6)
c/Å	15.7271(8)
α/°	109.520(4)
β/°	93.854(4)
γ/°	115.671(4)
Unit cell volume/Å^3	2863.8(2)
Temperature/K	291(2)
Space group	*P-1*
No. of formula units per unit cell, *Z*	2
Radiation type	MoKα
Absorption coefficient, μ/mm^{-1}	3.052
No. of reflections measured	22603
No. of independent reflections	11620
R_{int}	0.0523
Final R_1 values ($I > 2\sigma(I)$)	0.0524
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1213
Final R_1 values (all data)	0.0951
Final $wR(F^2)$ values (all data)	0.1373
Goodness of fit on F^2	1.030

The crystallographic data for $[Zn_4Eu_4L_4(CO_3)_6]$•EtOH has been deposited in the Cambridge Crystallographic Data Centre with the deposition number CCDC 910926. This data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Table. S2 Selected Bond Distances (Å) and Angles (deg) of $[Zn_4Eu_4L_4(CO_3)_6]$•EtOH

Distances (Å)		Angles (deg)	
Eu(1)-O(1)	2.402(3)	O(9)-Eu(1)-O(10)	53.86(9)
Eu(1)-O(9)	2.404(4)	O(1)-Eu(1)-O(2)	66.34(11)
Eu(1)-O(10)	2.418(3)	O(15)#1-Eu(1)-O(16)	74.58(18)
Eu(1)-O(15)#1	2.429(5)	O(15)#1-Eu(1)-O(19)	69.0(3)
Eu(1)-O(2)	2.437(3)	O(1)-Eu(1)-O(3)	59.01(10)
Eu(1)-O(16)	2.450(5)	O(2)-Eu(1)-O(4)	58.36(10)
Eu(1)-O(12)#1	2.485(4)	O(3)-Eu(1)-O(4)	144.13(12)
Eu(1)-O(3)	2.768(4)	O(13)-Eu(2)-O(12)	53.29(12)
Eu(1)-O(4)	2.776(3)	O(5)-Eu(2)-O(6)	66.70(12)
Eu(2)-O(17)	2.309(7)	O(17)-Eu(2)-O(16)#1	74.3(2)
Eu(2)-O(13)	2.368(3)	O(6)-Eu(2)-O(8)	58.22(11)
Eu(2)-O(5)	2.420(3)	O(5)-Eu(2)-O(7)	58.40(11)
Eu(2)-O(12)	2.426(3)	O(6)-Eu(2)-O(7)	122.77(11)
Eu(2)-O(6)	2.427(3)	O(8)-Eu(2)-O(7)	147.41(9)
Eu(2)-O(10)	2.491(2)	O(14)#1-Zn(1)-O(2)	108.96(16)
Eu(2)-O(16)#1	2.552(7)	O(14)#1-Zn(1)-O(1)	108.20(14)
Eu(2)-O(8)	2.786(4)	O(2)-Zn(1)-O(1)	81.75(14)
Eu(2)-O(7)	2.794(3)	O(14)#1-Zn(1)-N(2)	105.0(2)
Zn(1)-O(14)#1	1.952(4)	O(14)#1-Zn(1)-N(1)	105.89(19)
Zn(1)-O(2)	2.020(4)	N(2)-Zn(1)-N(1)	78.5(2)
Zn(1)-O(1)	2.026(3)	O(11)-Zn(2)-O(5)	106.43(13)
Zn(1)-N(2)	2.028(5)	O(11)-Zn(2)-O(6)	107.13(13)
Zn(1)-N(1)	2.054(5)	O(5)-Zn(2)-O(6)	81.91(13)
Zn(2)-O(11)	1.970(3)	O(11)-Zn(2)-N(4)	102.04(14)
Zn(2)-O(5)	2.028(3)	O(11)-Zn(2)-N(3)	110.17(14)
Zn(2)-O(6)	2.037(3)	N(4)-Zn(2)-N(3)	79.66(19)
Zn(2)-N(4)	2.038(5)	O(11)-Zn(2)-Eu(2)	94.81(10)
Zn(2)-N(3)	2.041(5)		

Reference

1. Yang, C.; Liu, L.; Gao, Y.; Zhang, W.; Zhang, X.; Zhang, L. *Luminescence* **2006**, *21*, 98

2. Sheldrick, G. M. SADABS. Program for empirical absorption correction of area detector data, University of Göttingen, Germany (1996).

3. SHELXS-97 and SHELXL-97. Programs for crystal structure solution and refinement. University of Göttingen, Germany (1997).