Supporting Information

Multifunctional Lanthanide-Organic Frameworks for Fluorescent Sensing, Gas Separation and Catalysis

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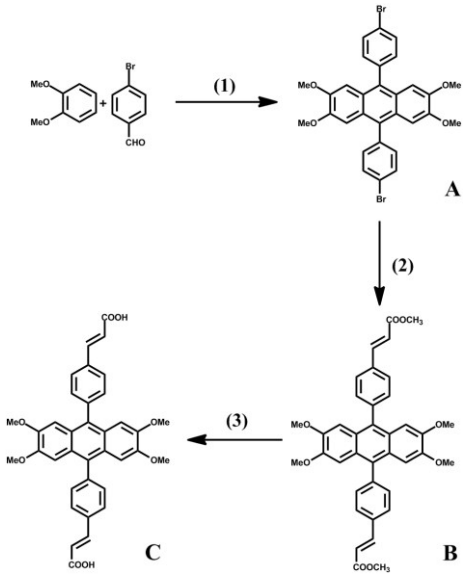
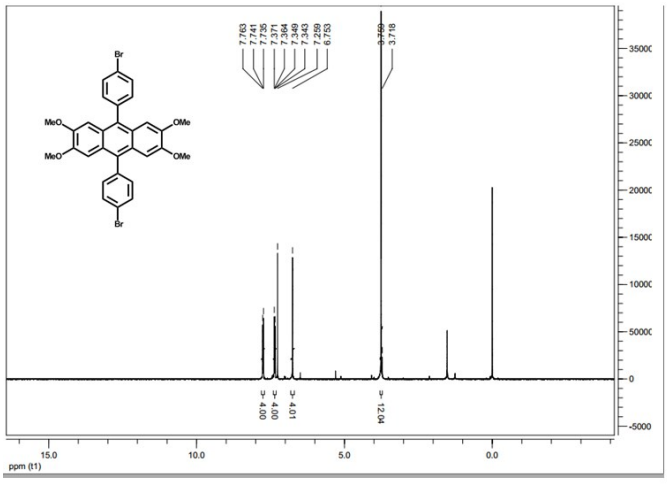
Contents

1. Synthesis of ligand H_2L^{OMe}

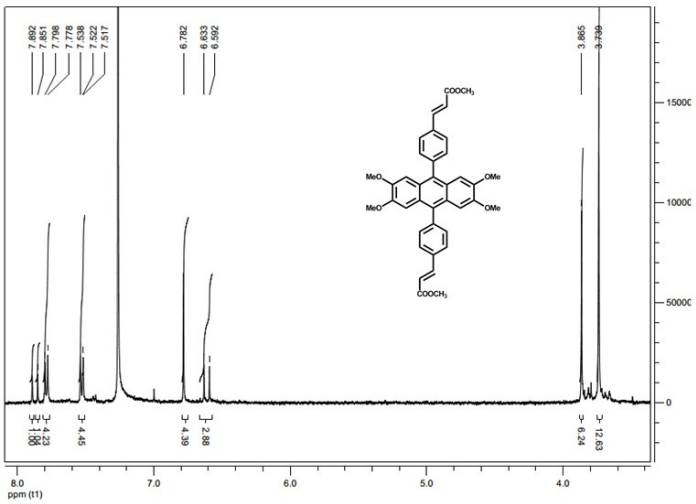


Synthesis of A: The mixture of 1,2-dimethoxybenzene (3.3 g, 24 mmol), 4-bromobenzaldehyde (8.3 g, 45 mmol) and PWA (4.0 g, 1.4 mmol) were added in a 50ml three-necked flask with magneton. The mixture was heated to 75 °C for 30 minutes. Then the 4-bromobenzaldehyde (7.4 g, 40 mmol), Ac_2O (8.17 g, 80mmol) and PWA (1.15 g, 0.4 mmol) were dissolved in glacial AcOH (40 mL), which were added into the flask and heated to 75 °C for another 90 minutes. After the solutions cooled to room temperature, the mixture was neutralized with $NaHCO_3$. Then it was extracted several times with CH_2Cl_2. The organic layer was then dried with MgSO4, and the solvent was removed with rotary evaporator. The resulting crude product was purified by column chromatography (CH_2Cl_2 as the eluent). The product 9,10-bis(4-bromophenyl)-2,3,6,7-tetramethoxyanthracene was obtained after removal of the solvents (3.1 g, 42.6% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, 4H); 7.37 (d, 4H); 6.75 (s, 4H); 3.80 (s, 12H).

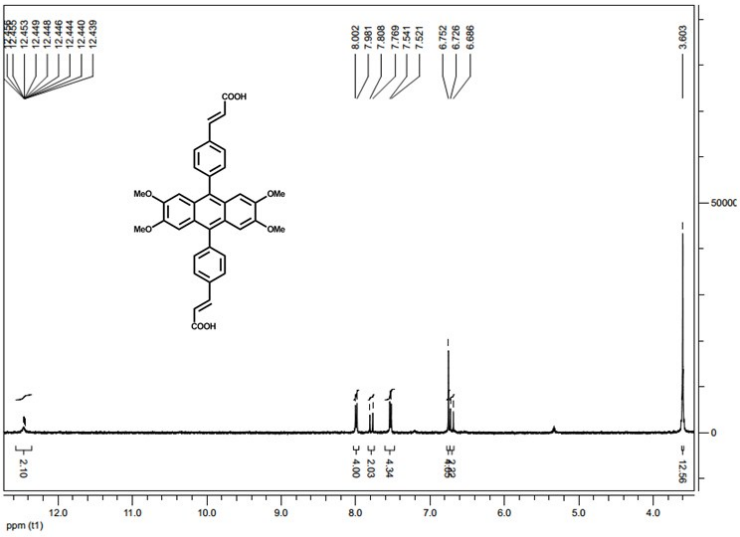


Synthesis of B: A 250 mL three-necked flask with magneton was charged with a mixture of

9,10-bis(4-bromophenyl)-2,3,6,7-tetramethoxyanthracene (2.4 g, 4 mmol), $Pd(OAc)_2$ (90 mg, 0.4 mmol) and tris(*o*-tolyl)phosphine (580 mg, 1.9 mmol). The flask was degassed and filled with nitrogen, which was repeated for three times. Waterless DMF (80 mL) was added with a syring under nitrogen. After this, methyl acrylate (0.8 mL, 8 mmol) was added to the solution. The pressure vessel was sealed, and the reaction mixture was heated to 140 ℃ in an oil bath for 3 days under N_2 atmosphere. After the mixture was cooled to room temperature, it was extracted with CH_2Cl_2 and washed three times with H_2O. The organic layer was then dried with MgSO4, and the solvent was removed with rotary evaporator. The resulting crude product was purified by column chromatography ($CHCl_3$:CH_3OH = 70:1 as the eluent). The product 3,3'-((2,3,6,7-tetramethoxyanthracene-9,10-diyl)bis(4,1-phenylene))diacrylate was obtained after removal of the solvents (1.1 g, 45.1% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, 2H); 7.78 (d, 4H); 7.54 (d, 4H); 6.78 (s, 4H); 6.63 (d, 2H); 3.87(s, 6H); 3.74 (s, 12H).



Synthesis of C: To a suspension of 3,3'-((2,3,6,7-tetramethoxyanthracene-9,10-diyl)bis(4,1-phenylene))diacrylate in 30 mL THF was added to 30 mL MeOH and 40 mL 3M aqueous KOH solution. The mixture was heated at 60 ℃ overnight. After this, the mixture was cooled to room temperature, poured into an ice/HCl mixture, then followed by filtration, and washed several times with H_2O. The product 3,3'-((2,3,6,7-tetramethoxyanthracene-9,10-diyl)bis(4,1-phenylene))diacrylic acid was obtained after the organic layer was collected and the solvent was removed via rotary evaporator. ^{1}H NMR (400 MHz, DMSO-d^6): δ 12.45 (s, 2H); 8.00 (d, 4H); 7.81 (d, 2H); 7.54 (d, 4H); 6.75 (s, 4H); 6.69 (d, 2H); 3.60 (s, 12H).



2. Crystal Data for Complexes 1-2

Table S1. Crystallographic data for complexes 1 and 2.

	1	2
empirical formula	$C_{68}H_{81.5}O_{19.5}N_{3.5}Eu$	$C_{46}H_{64.5}O_{17.5}N_{2.5}Pr$
formula weight	1411.85	1073.41
temperature (K)	295	200
crystal system	triclinic	monoclinic
space group	*P*-1	*P*2/c
a (Å)	8.7719(3)	43.7247(5)
b (Å)	20.0756(5)	12.93615(17)
c (Å)	20.1325(5)	8.49651(12)
α (deg)	72.939(2)	90.00
β (deg)	85.154(2)	94.3334(12)
γ (deg)	80.362(2)	90.00
volume (Å^3)	3339.14(16)	4792.13(11)
Z	2	4
ρcalc (g/cm^3)	1.065	1.111
μ (mm^{-1})	0.989	1.062
F (000)	1090.0	1628.0
data/restraints/params	11856/0/630	8580/7/466
GOF on F^2	1.076	1.054
final *R* indices [$I > 2s(I)$]	$R_1 = 0.0650$ $wR_2 = 0.1949$	$R_1 = 0.0694$ $wR_2 = 0.1845$

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

3. Selected Bond Lengths and Angles

Table S2: The selected bond distances (Å) and angles (deg) for complex **1**.

Eu1—O3	2.389 (4)	Eu1—O1W	2.452 (4)
Eu1—O12^{i}	2.574 (5)	Eu1—O1	2.475 (5)
Eu1—O12	2.394 (5)	Eu1—O2W	2.367 (8)
Eu1—O2	2.482 (5)	Eu1—O4	2.600 (5)
Eu1—O5	2.498 (5)	O12—Eu1^{i}	2.574 (5)
O3—Eu1—O12	88.16 (18)	O1W—Eu1—O1	145.62 (16)
O3—Eu1—O12^{i}	145.47 (18)	O1W—Eu1—O4	73.01 (15)
O3—Eu1—O2	73.98 (19)	O1—Eu1—O12^{i}	74.88 (15)
O3—Eu1—O5	146.42 (19)	O1—Eu1—O2	52.53 (17)
O3—Eu1—O1W	124.24 (17)	O1—Eu1—O5	88.65 (18)
O3—Eu1—O1	76.27 (17)	O1—Eu1—O4	124.88 (16)
O3—Eu1—O4	51.89 (16)	O2W—Eu1—O3	88.8 (2)
O3—Eu1—C36	71.93 (19)	O2W—Eu1—O12^{i}	124.16 (19)
O3—Eu1—C1	156.80 (19)	O2W—Eu1—O12	155.30 (19)
O3—Eu1—C54	26.00 (19)	O2W—Eu1—O2	75.6 (2)
O12—Eu1—O12^{i}	66.21 (16)	O2W—Eu1—O5	77.1 (2)
O12—Eu1—O2	126.68 (17)	O2W—Eu1—O1W	82.98 (19)
O12—Eu1—O5	116.90 (16)	O2W—Eu1—O1	128.12 (19)
O12—Eu1—O1W	78.55 (16)	O2W—Eu1—O4	73.8 (2)
O12—Eu1—O1	74.68 (16)	O5—Eu1—O4	144.90 (19)
O12^{i}—Eu1—O4	140.39 (15)	O5—Eu1—C36	81.3 (2)
O12—Eu1—O4	85.18 (17)	O5—Eu1—C1	24.91 (19)
O2—Eu1—O12^{i}	102.30 (17)	O5—Eu1—C54	153.9 (2)
O2—Eu1—O5	73.05 (18)	O1W—Eu1—O12^{i}	74.80 (15)
O2—Eu1—O4	116.95 (17)	O1W—Eu1—O2	151.83 (18)
O5—Eu1—O12^{i}	50.70 (16)	O1W—Eu1—O5	84.55 (17)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+2; (ii) −*x*+2, −*y*+1, −*z*+1; (iii) *x*+2, *y*−1, *z*; (iv) *x*−2, *y*+1, *z*.

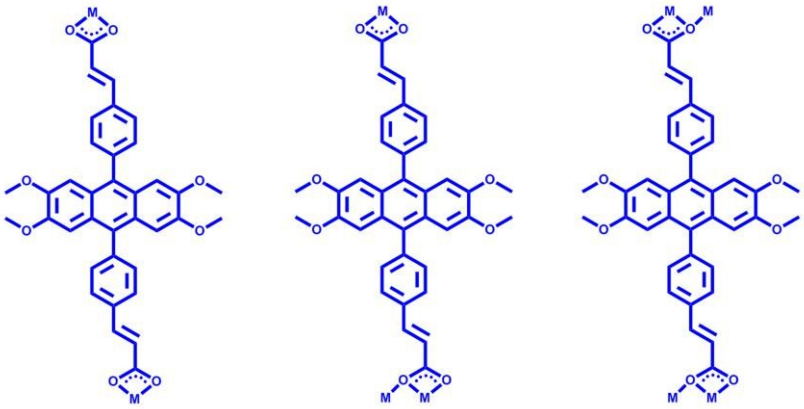
Table S3: The selected bond distances (Å) and angles (deg) for complex **2**.

Pr1—O2^{i}	2.437 (3)	Pr2—O4	2.635 (6)
Pr1—O2^{ii}	2.589 (4)	Pr2—O4^{v}	2.476 (6)
Pr1—O2	2.437 (3)	Pr2—O4^{vi}	2.476 (6)
Pr1—O2^{iii}	2.589 (4)	Pr2—O4^{iv}	2.635 (6)
Pr1—O1^{i}	2.543 (4)	Pr2—O3W	2.491 (8)
Pr1—O1	2.543 (4)	Pr2—O3W^{iv}	2.491 (8)
Pr1—O1W^{i}	2.489 (5)	Pr2—O4WA	2.12 (2)
Pr1—O1W	2.489 (5)	Pr2—O4WB^{iv}	2.494 (9)
Pr1—O2W	2.440 (9)	Pr2—O4WB	2.494 (9)
Pr2—O3	2.510 (5)	O2—Pr1^{iii}	2.589 (4)
Pr2—O3^{iv}	2.510 (5)	O4—Pr2^{vi}	2.476 (6)
O2^{i}—Pr1—O2	156.6 (2)	O4WA—Pr2—O4^{iv}	86.59 (15)
O2—Pr1—O2^{iii}	64.55 (13)	O4WA—Pr2—O4^{v}	74.14 (16)
O2^{i}—Pr1—O2^{iii}	121.90 (14)	O4WA—Pr2—O4	86.59 (15)
O2^{i}—Pr1—O2^{ii}	64.54 (13)	O4WA—Pr2—O4^{vi}	74.14 (16)
O2—Pr1—O2^{ii}	121.89 (14)	O3W^{iv}—Pr2—O4WB^{iv}	143.2 (5)
O2^{ii}—Pr1—O2^{iii}	151.8 (2)	O4WA—Pr2—O3W^{iv}	148.8 (3)
O2—Pr1—O1^{i}	114.41 (12)	O4WA—Pr2—O3W	148.8 (3)
O2^{i}—Pr1—O1^{i}	73.34 (13)	O4WB—Pr2—O3	137.0 (5)
O2^{i}—Pr1—O1	114.41 (12)	O4WB—Pr2—O3^{iv}	76.3 (5)
O2—Pr1—O1	73.34 (13)	O4WB^{iv}—Pr2—O3^{iv}	137.0 (5)
O2—Pr1—O1W^{i}	79.82 (16)	O4WB^{iv}—Pr2—O3	76.3 (5)
O2^{i}—Pr1—O1W^{i}	81.09 (16)	O4WB—Pr2—O4^{iv}	60.7 (4)
O2^{i}—Pr1—O1W	79.82 (16)	O4WB^{iv}—Pr2—O4	60.7 (4)
O2—Pr1—O1W	81.09 (16)	O4WB—Pr2—O4	112.8 (4)
O2^{i}—Pr1—O2W	101.68 (11)	O4WA—Pr2—O3^{iv}	106.86 (16)
O2—Pr1—O2W	101.68 (11)	O4WA—Pr2—O3	106.86 (16)
O1^{i}—Pr1—O2^{iii}	50.33 (12)	O4^{vi}—Pr2—O3^{iv}	75.96 (19)

O1—Pr1—O2^{ii}	50.33 (12)	O4^{v}—Pr2—O4^{vi}	148.3 (3)
O1—Pr1—O2^{iii}	119.09 (13)	O4^{v}—Pr2—O4^{iv}	64.26 (17)
O1^{i}—Pr1—O2^{ii}	119.09 (13)	O4^{iv}—Pr2—O4	173.2 (3)
O1^{i}—Pr1—O1	143.6 (2)	O4^{v}—Pr2—O4	113.69 (18)
O1W—Pr1—O2^{iii}	133.23 (16)	O4^{vi}—Pr2—O4^{iv}	113.69 (18)
O1W—Pr1—O2^{ii}	73.39 (16)	O4^{vi}—Pr2—O4	64.26 (17)
O1W^{i}—Pr1—O2^{ii}	133.23 (16)	O4^{v}—Pr2—O3W	134.2 (3)
O1W^{i}—Pr1—O2^{iii}	73.39 (16)	O4^{vi}—Pr2—O3W^{iv}	134.2 (3)
O1W—Pr1—O1	75.86 (16)	O4^{v}—Pr2—O3W^{iv}	76.7 (4)
O1W^{i}—Pr1—O1	139.15 (17)	O4^{vi}—Pr2—O3W	76.7 (4)
O1W—Pr1—O1^{i}	139.15 (16)	O4^{v}—Pr2—O4WB^{iv}	73.1 (4)
O1W^{i}—Pr1—O1^{i}	75.86 (16)	O4^{v}—Pr2—O4WB	79.9 (4)
O1W—Pr1—O1W^{i}	69.9 (2)	O4^{vi}—Pr2—O4WB	73.1 (4)
O2W—Pr1—O2^{iii}	75.91 (10)	O4^{vi}—Pr2—O4WB^{iv}	79.9 (4)
O2W—Pr1—O2^{ii}	75.91 (10)	O3W^{iv}—Pr2—O3	76.2 (2)
O2W—Pr1—O1^{i}	71.79 (11)	O3W^{iv}—Pr2—O3^{iv}	75.1 (3)
O2W—Pr1—O1	71.79 (11)	O3W—Pr2—O3^{iv}	76.2 (2)
O2W—Pr1—O1W^{i}	145.03 (12)	O3W—Pr2—O3	75.1 (3)
O2W—Pr1—O1W	145.03 (12)	O3W—Pr2—O4^{iv}	115.5 (3)
O3^{iv}—Pr2—O3	146.3 (3)	O3W^{iv}—Pr2—O4^{iv}	70.8 (3)
O3^{iv}—Pr2—O4^{iv}	49.98 (17)	O3W^{iv}—Pr2—O4	115.5 (3)
O3—Pr2—O4^{iv}	132.65 (18)	O3W—Pr2—O4	70.8 (3)
O3^{iv}—Pr2—O4	132.65 (18)	O3W—Pr2—O3W^{iv}	62.4 (6)
O3—Pr2—O4	49.98 (17)	O3W—Pr2—O4WB^{iv}	131.3 (5)
O4^{v}—Pr2—O3^{iv}	113.65 (17)	O3W—Pr2—O4WB	143.2 (5)
O4^{vi}—Pr2—O3	113.65 (17)	O3W^{iv}—Pr2—O4WB	131.4 (5)
O4^{v}—Pr2—O3	75.95 (19)		

Symmetry codes: (i) −*x*, *y*, −*z*+3/2; (ii) *x*, −*y*+2, *z*−1/2; (iii) −*x*, −*y*+2, −*z*+2; (iv) −*x*+1, *y*, −*z*−1/2; (v) *x*, −*y*+1, *z*−1/2; (vi) −*x*+1, −*y*+1, −*z*; (vii) *x*, −*y*+2, *z*+1/2.

4. Coordination modes



Scheme S1. Coordination modes of H_2L^{OMe} in complexes **1** and **2**.

5. Powder X-Ray Diffraction

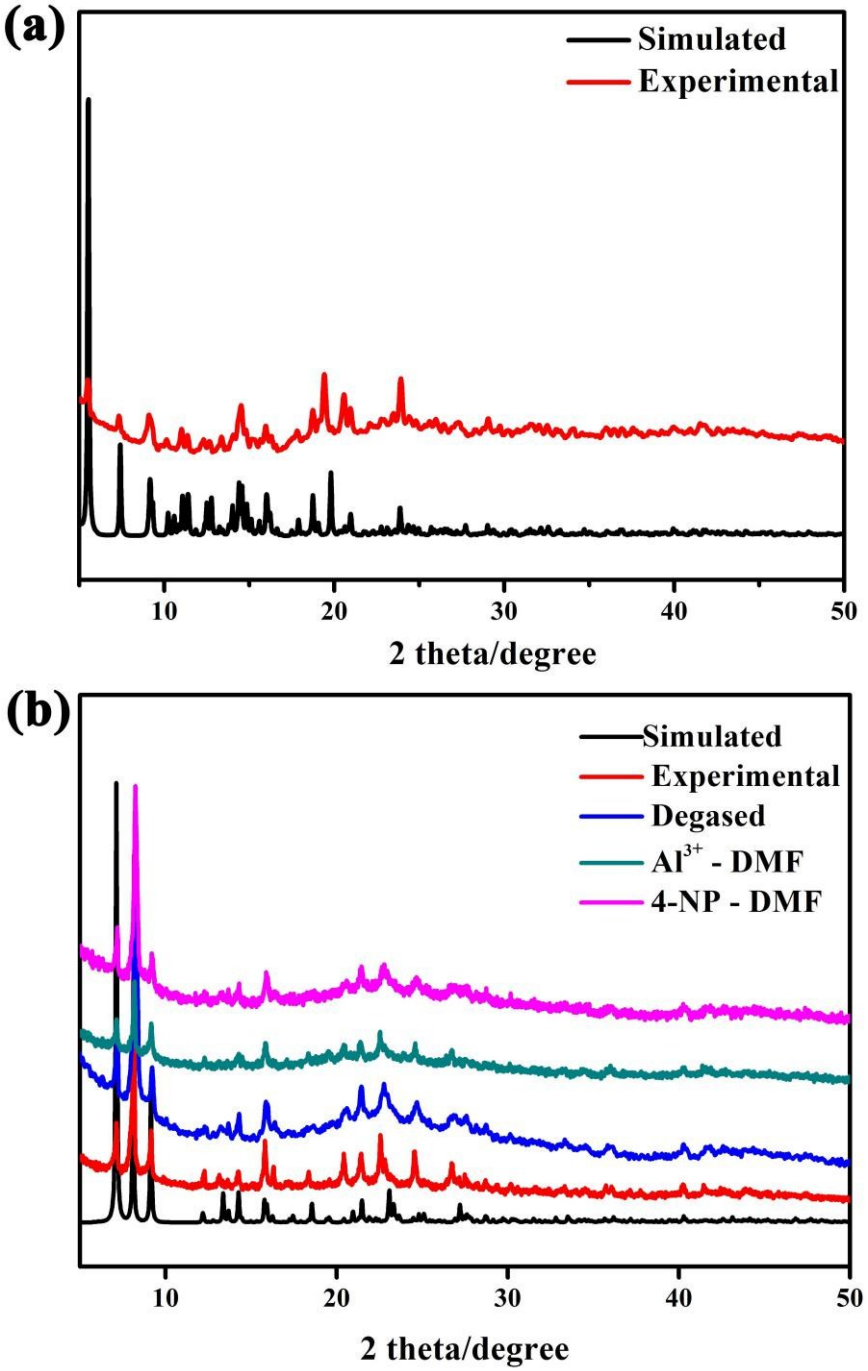


Figure S1. PXRD patterns of **1** (a) and **2** (b).

6. Infrared spectra

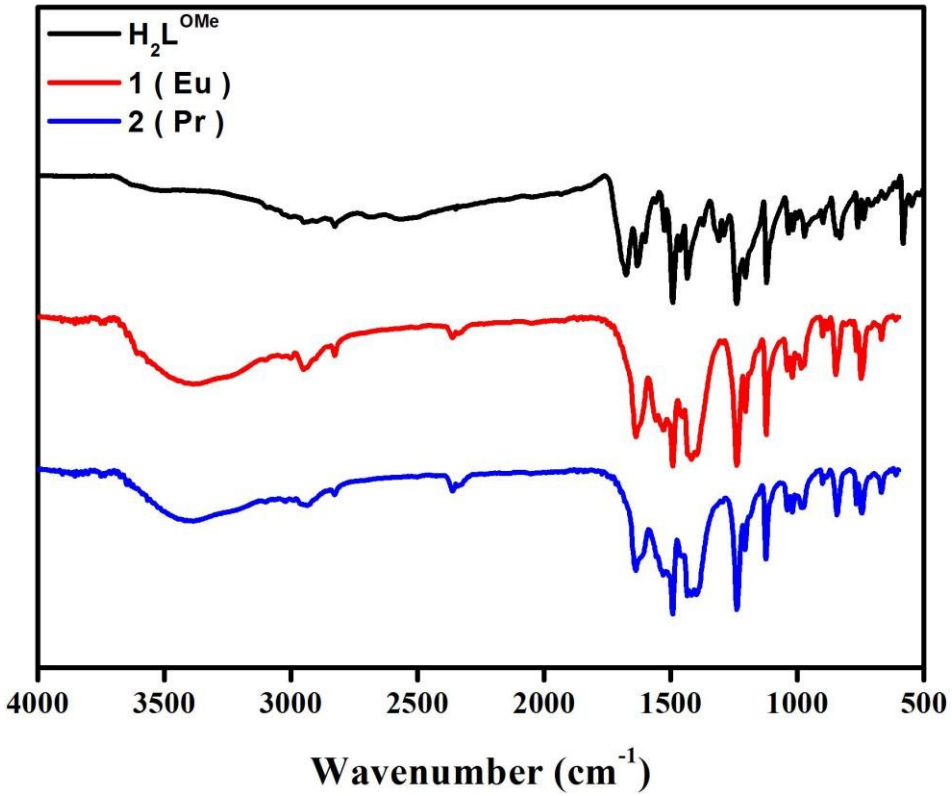


Figure S2. IR spectra for complexes **1** and **2**.

7. Thermogravimetric Analysis.

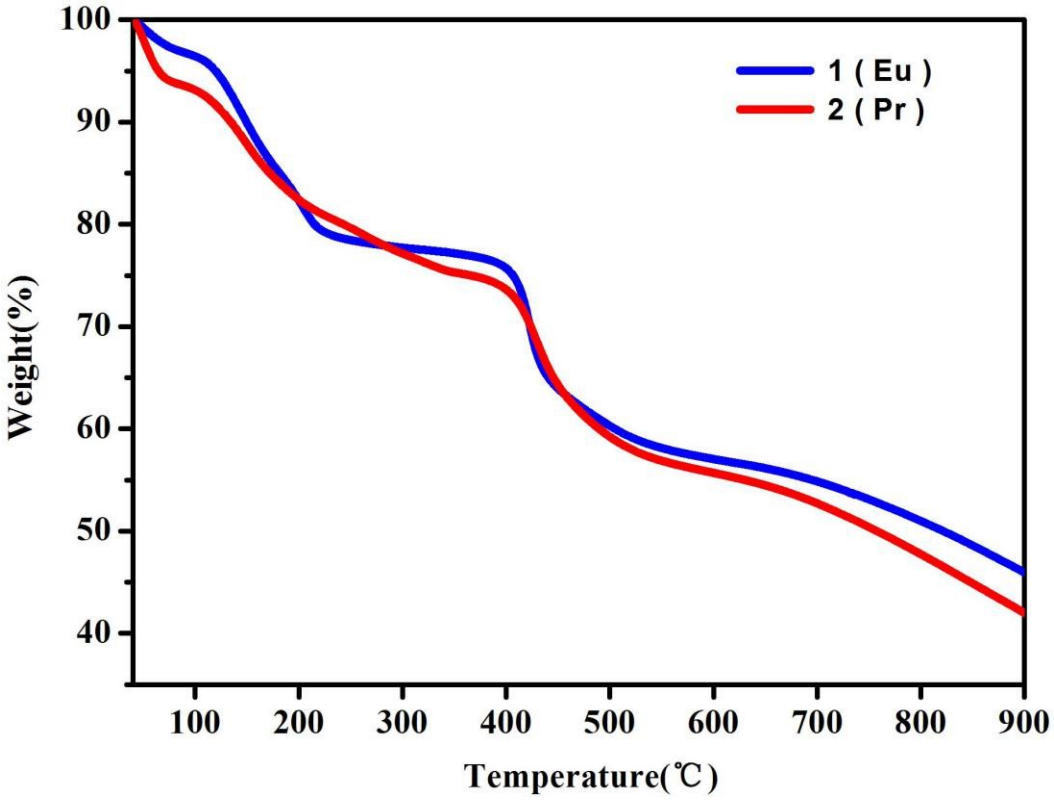


Figure S3. TGA plots of complexes **1** and **2**

8. Luminescence Properties

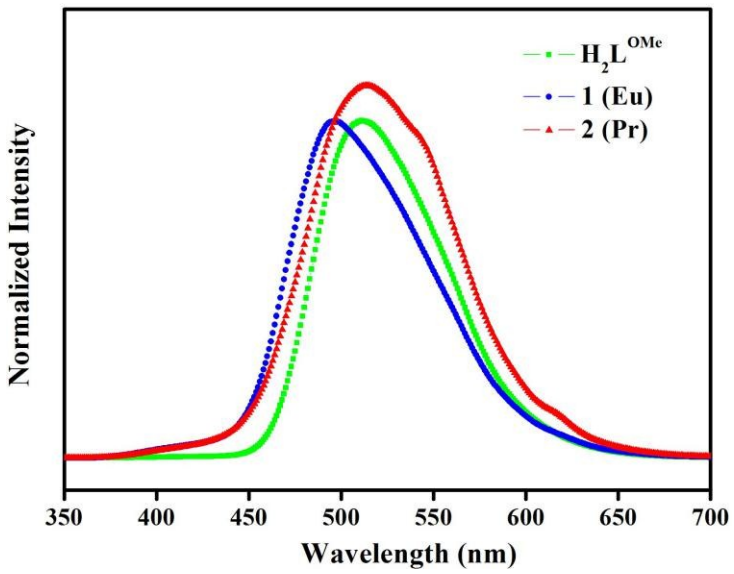


Figure S4. Photoluminescences of H_2L^{OMe} ligand, **1** and **2**.

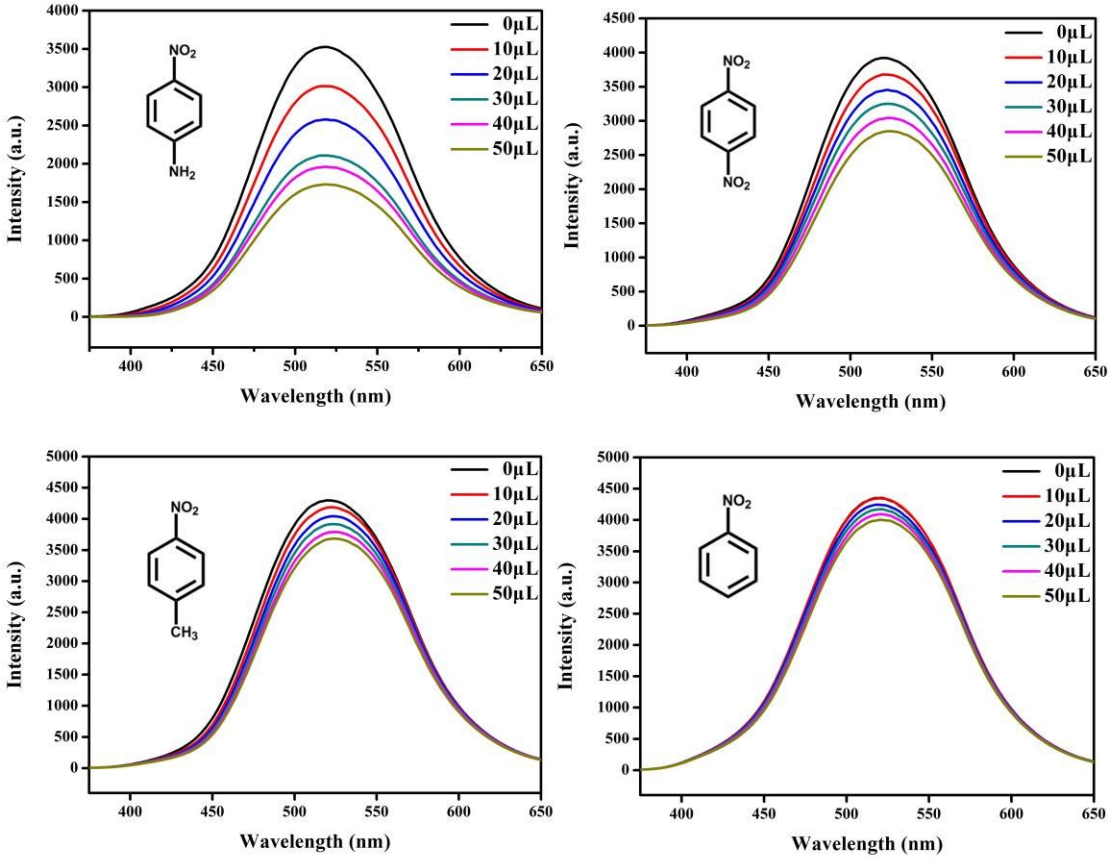


Figure S5. Emission intensity of complex **2** dispersed in DMF upon incremental addition of aromatic compounds (4-NA, 1,4-DNB, 1-M-4-NB and NB) solution (10 mM) in DMF.

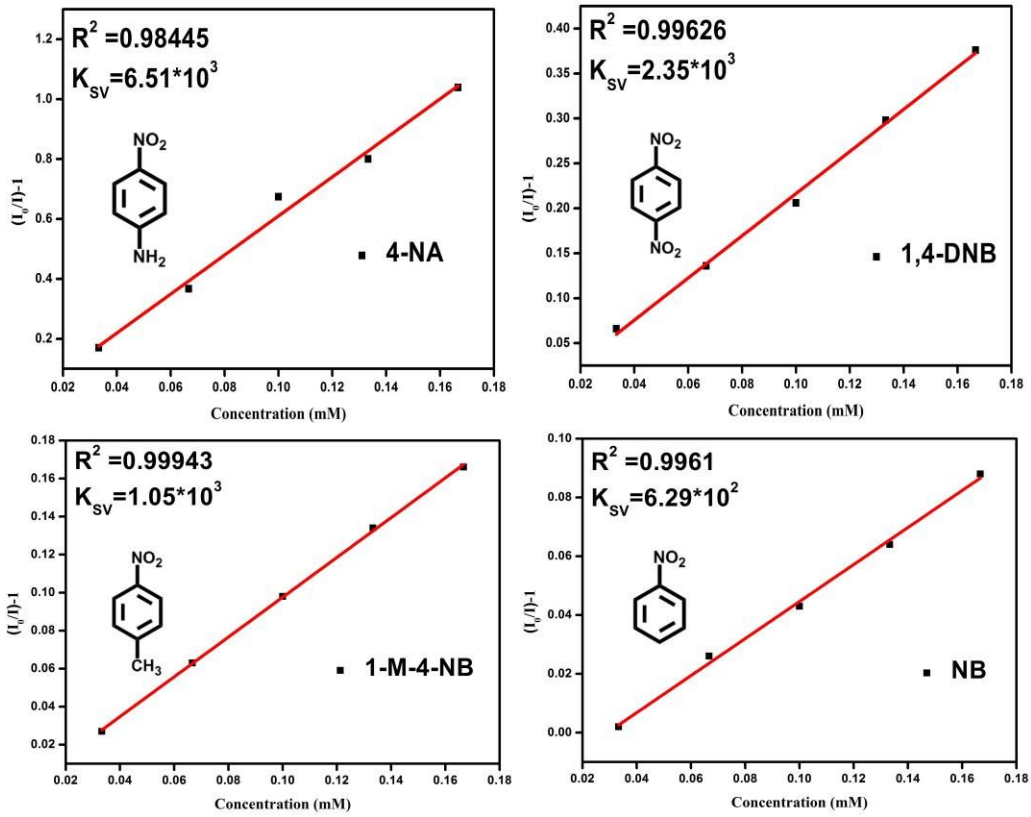


Figure S6. The Stern-Volmer plots for complex **2** with 4-NA, 1,4-DNB, 1-M-4-NB and NB in the relatively high concentration region. The solid lines fit to the concentration-resolved data using the Stern-Volmer equation.

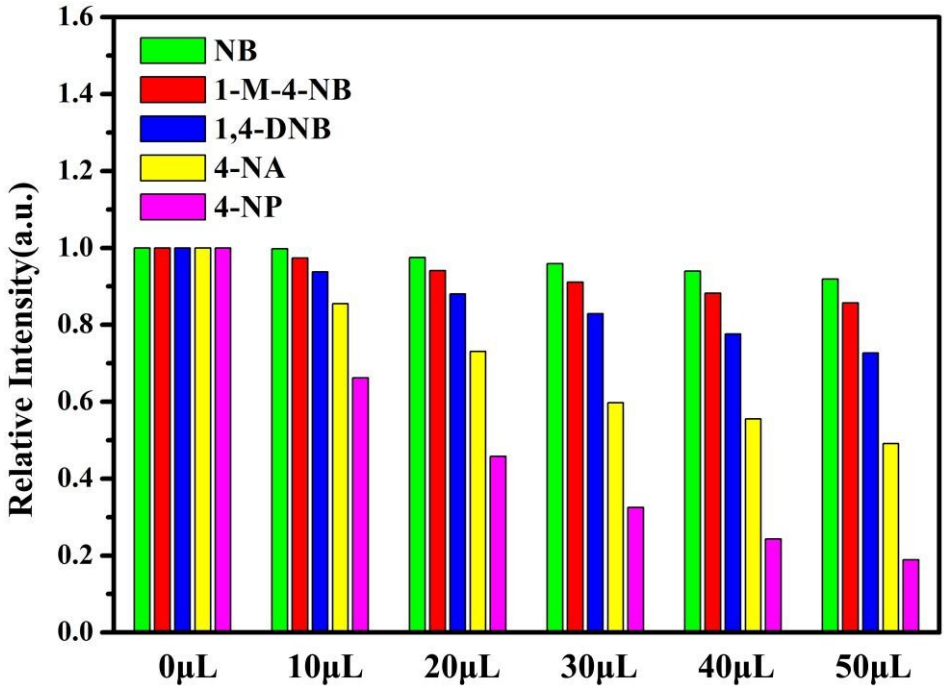


Figure S7. Percentage of fluorescence quenching obtained by introducing different nitrobenzene derivatives into the DMF-emulsion of complex **2**.

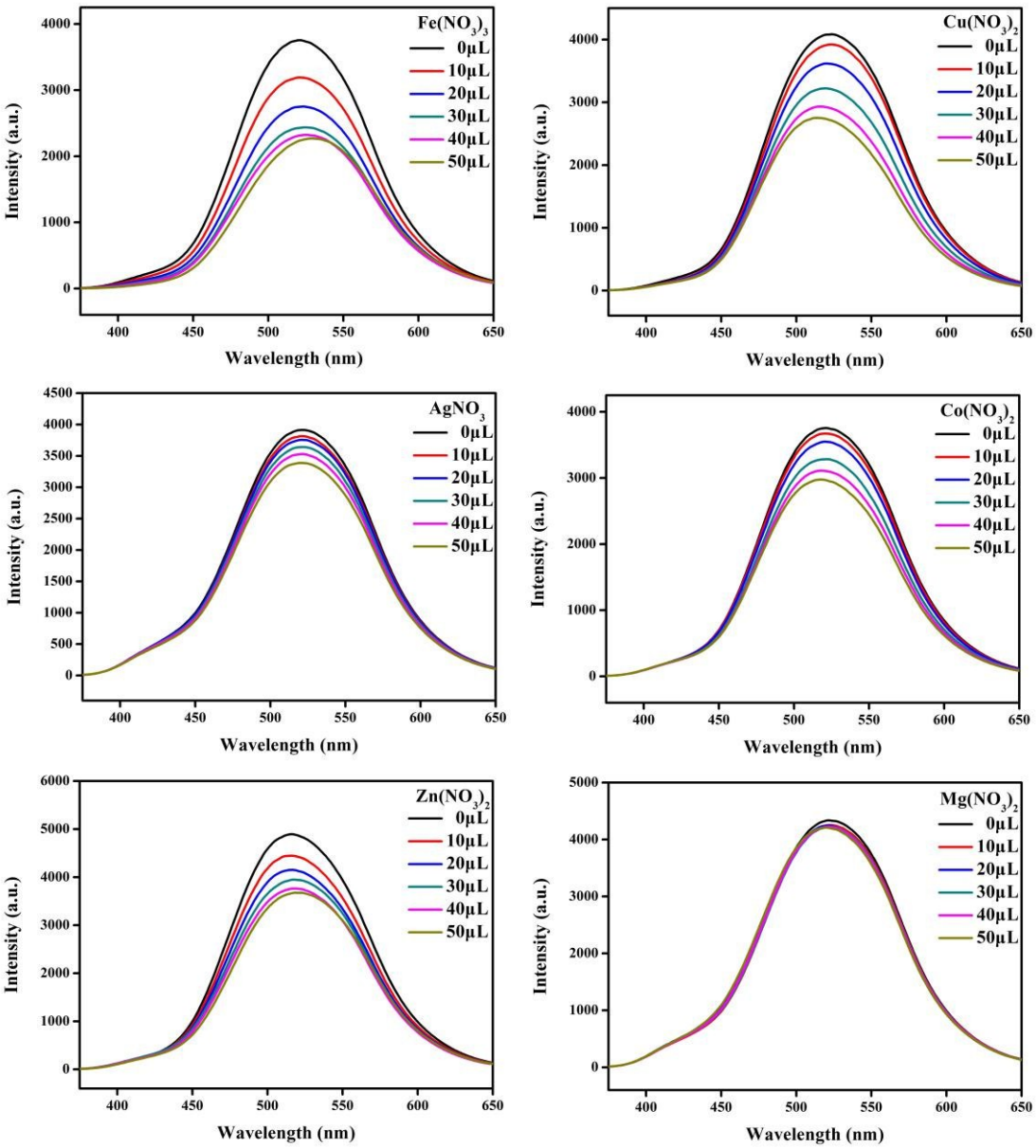


Figure S8. Emission intensity of complex **2** dispersed in DMF upon incremental addition of a $M(NO_3)_x$ (M= Fe^{3+}, Cu^{2+}, Ag^{+}, Co^{2+}, Zn^{2+}, Mg^{2+}) solution (10 mM) in DMF.

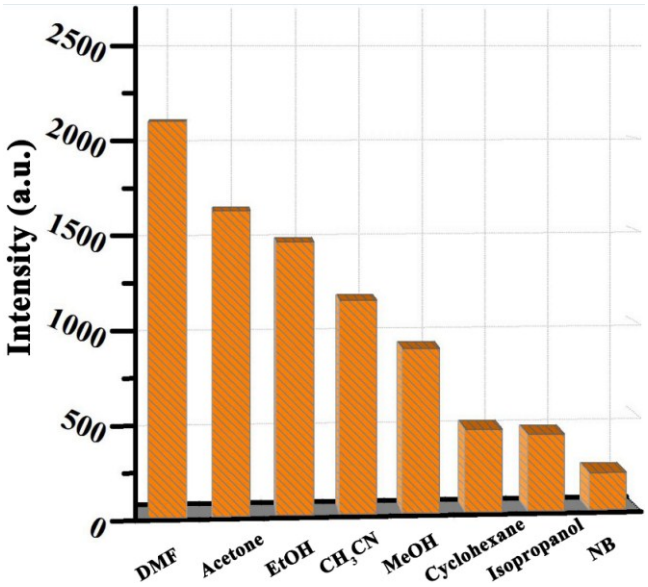


Figure S9. Percentage of fluorescence quenching by introducing different organic solvent molecules into the DMF-emulsion of **1**.

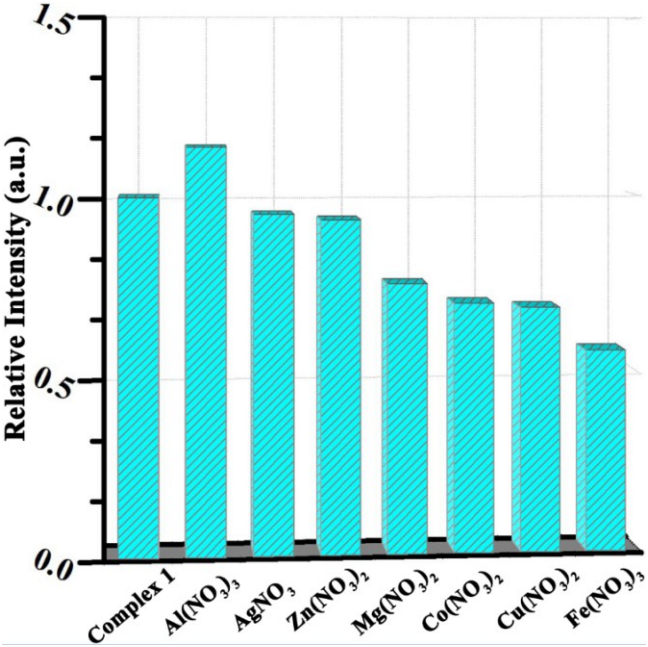


Figure S10. Relative intensity by introducing different metal ions into the DMF-emulsion of **1**.

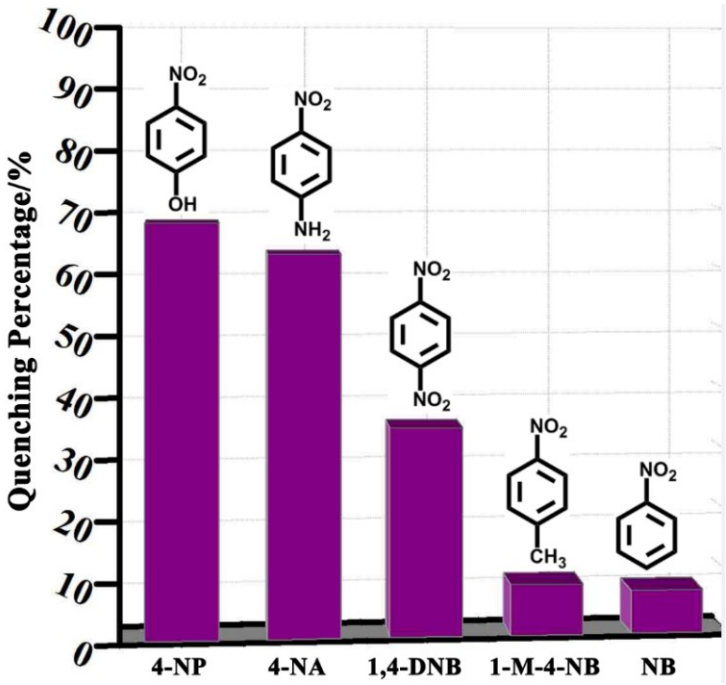


Figure S11. Percentage of fluorescence quenching by introducing different aromatic compounds into the DMF-emulsion of **1**.

9. Gas Sorption

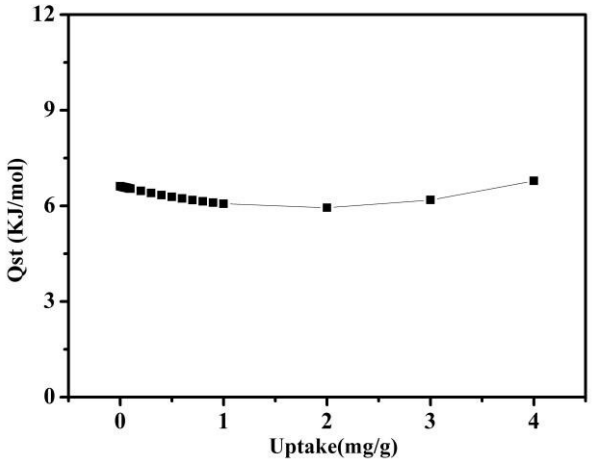


Figure S12. The isosteric heat of adsorption for H_2 in complex **2**.

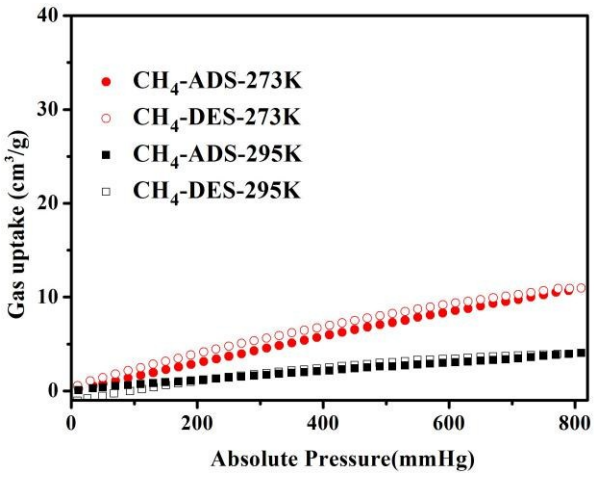


Figure S12. The CH_4 sorption isotherms of complex **2** at 273 K and 295K under 1 atm.

10. Catalytic Properties

Under the N_2 atmosphere, a solution of aldehyde (0.5 mmol) and cyanotrimethylsilane (1 mmol) was added to activated samples (10 mg) at room temperature. After the solution was stirred for 14 hours, the mixtures were separated by centrifugal machine. The liquid part was utilized to analyze the conversions by Gas Chromatograph-Mass Spectrometry. The recycled experiment was carried out for the cyanosilylation of p-methoxy benzaldehyde with complex **2**. The reaction was carried out under the standard conditions. After the reaction was completed, the catalyst was recovered by filtration, washed with DMA, and reactivated prior to being used for the recycled experiment.

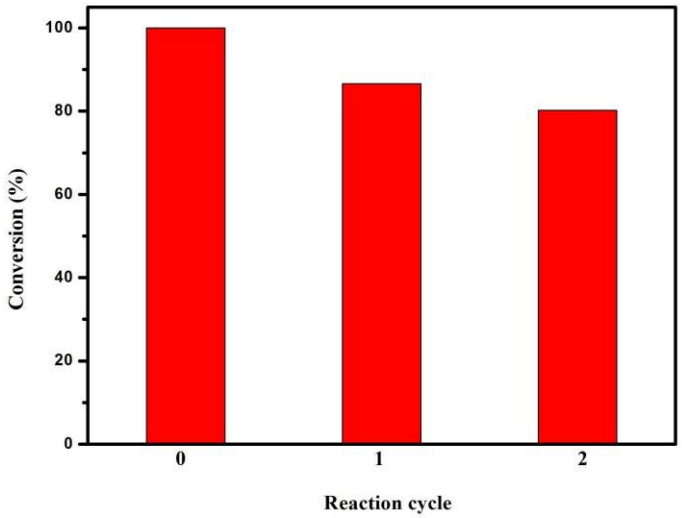


Figure S13. The recycled experiments of complex **2** for p-methoxy benzaldehyde.