

Supporting Information

Two Series of Ln(III)-Ag(I) Heterometallic-Organic Frameworks Constructed from Isonicotinate and 2, 2'-Biphenyldicarboxylate: Synthesis, Structure and Photoluminescent Property

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Table S1. Selected bond lengths (Å) and bond angles (°) for **1-6**.

Compound 1			
Nd(1)-O(4)#1	2.529(9)	O(4)#1-Nd(1)-O(6)#2	146.7(3)
Nd(1)-O(1W)	2.556(9)	O(1W)-Nd(1)-O(6)#2	77.8(4)
Nd(1)-O(2W)	2.559(9)	O(2W)-Nd(1)-O(6)#2	69.4(3)
Nd(1)-O(5)#1	2.582(9)	O(5)#1-Nd(1)-O(6)#2	108.1(3)
Nd(1)-O(2)	2.598(9)	O(2)-Nd(1)-O(6)#2	135.6(3)
Nd(1)-O(6)#2	2.613(10)	O(4)#1-Nd(1)-O(3)	107.9(3)
Nd(1)-O(3)	2.649(9)	O(1W)-Nd(1)-O(3)	143.5(3)
Nd(1)-O(1)	2.667(8)	O(2W)-Nd(1)-O(3)	79.7(3)
Nd(1)-O(4)	2.789(9)	O(5)#1-Nd(1)-O(3)	143.6(3)
Nd(1)-O(5)#2	2.793(8)	O(2)-Nd(1)-O(3)	72.2(3)
Ag(1)-N(1)#3	2.165(12)	O(6)#2-Nd(1)-O(3)	76.3(3)
Ag(1)-N(1)	2.165(12)	O(4)#1-Nd(1)-O(1)	122.3(3)
O(4)#1-Nd(1)-O(1W)	81.3(3)	O(1W)-Nd(1)-O(1)	136.7(3)
O(4)#1-Nd(1)-O(2W)	78.8(3)	O(2W)-Nd(1)-O(1)	145.9(3)
O(1W)-Nd(1)-O(2W)	67.4(3)	O(5)#1-Nd(1)-O(1)	75.1(3)
O(4)#1-Nd(1)-O(5)#1	88.1(3)	O(2)-Nd(1)-O(1)	49.2(3)
O(1W)-Nd(1)-O(5)#1	69.6(3)	O(6)#2-Nd(1)-O(1)	90.4(3)
O(2W)-Nd(1)-O(5)#1	136.4(3)	O(1)-Nd(1)-O(4)	100.0(3)
O(4)#1-Nd(1)-O(2)	74.2(3)	O(2W)-Nd(1)-O(5)#2	109.4(3)
O(1W)-Nd(1)-O(2)	142.6(4)	O(3)-Nd(1)-O(5)#2	108.1(3)
O(2W)-Nd(1)-O(2)	132.0(3)	O(4)-Nd(1)-O(5)#2	154.9(3)
O(5)#1-Nd(1)-O(2)	81.7(3)	N(1)#3-Ag(1)-N(1)	176.1(8)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,-y+1/2,-z+1; #2 x,y-1,z; #3 -x+1,y,-z+1/2;

#4 x,y+1,z; #5 -x+1,-y+1,-z+1.

Compound 2			
Eu(1)-O(4)#1	2.480(5)	O(4)#1-Eu(1)-O(2)	74.57(17)
Eu(1)-O(1W)	2.502(5)	O(1W)-Eu(1)-O(2)	142.3(2)
Eu(1)-O(2W)	2.517(5)	O(2W)-Eu(1)-O(2)	131.25(18)
Eu(1)-O(5)#1	2.531(5)	O(5)#1-Eu(1)-O(2)	81.13(18)
Eu(1)-O(6)#2	2.545(6)	O(6)#2-Eu(1)-O(2)	135.31(19)
Eu(1)-O(2)	2.556(5)	O(4)#1-Eu(1)-O(3)	108.19(17)
Eu(1)-O(3)	2.579(5)	O(1W)-Eu(1)-O(3)	143.51(19)
Eu(1)-O(1)	2.607(5)	O(2W)-Eu(1)-O(3)	78.39(19)
Eu(1)-O(5)#2	2.791(5)	O(5)#1-Eu(1)-O(3)	143.87(17)
Eu(1)-O(4)	2.796(5)	O(6)#2-Eu(1)-O(3)	76.54(19)
Ag(1)-N(1)#3	2.158(8)	O(2)-Eu(1)-O(3)	72.38(19)
Ag(1)-N(1)	2.158(8)	O(4)#1-Eu(1)-O(1)	123.60(17)
O(4)#1-Eu(1)-O(1W)	80.39(18)	O(1W)-Eu(1)-O(1)	136.35(18)
O(4)#1-Eu(1)-O(2W)	78.80(18)	O(2W)-Eu(1)-O(1)	144.65(19)
O(1W)-Eu(1)-O(2W)	68.42(19)	O(5)#1-Eu(1)-O(1)	75.26(17)
O(4)#1-Eu(1)-O(5)#1	87.24(17)	O(6)#2-Eu(1)-O(1)	88.96(19)

O(1W)-Eu(1)-O(5)#1	69.80(18)	O(2)-Eu(1)-O(1)	50.20(17)
O(2W)-Eu(1)-O(5)#1	137.53(18)	O(3)-Eu(1)-O(1)	68.97(18)
O(4)#1-Eu(1)-O(6)#2	147.02(18)	O(4)#1-Eu(1)-O(5)#2	142.50(16)
O(1W)-Eu(1)-O(6)#2	78.2(2)	O(1W)-Eu(1)-O(5)#2	70.43(17)
O(2W)-Eu(1)-O(6)#2	70.11(19)	O(2W)-Eu(1)-O(5)#2	110.13(17)
O(5)#1-Eu(1)-O(6)#2	108.26(17)	N(1)#3-Ag(1)-N(1)	176.0(5)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,-y+1/2,-z+1; #2 x,y+1,z; #3 -x+1,y,-z+1/2; #4 x,y-1,z; #5 -x,-y-1,-z+1.

Compound 3

Tb(1)-O(3)#1	2.462(5)	O(3)#1-Tb(1)-O(1)	74.64(16)
Tb(1)-O(1W)	2.477(5)	O(1W)-Tb(1)-O(1)	142.33(18)
Tb(1)-O(6)#1	2.504(5)	O(6)#1-Tb(1)-O(1)	80.68(17)
Tb(1)-O(2W)	2.518(5)	O(2W)-Tb(1)-O(1)	131.51(18)
Tb(1)-O(5)#2	2.532(6)	O(5)#2-Tb(1)-O(1)	135.09(18)
Tb(1)-O(1)	2.546(5)	O(3)#1-Tb(1)-O(4)	108.55(17)
Tb(1)-O(4)	2.556(5)	O(1W)-Tb(1)-O(4)	143.54(18)
Tb(1)-O(2)	2.586(5)	O(6)#1-Tb(1)-O(4)	143.44(16)
Tb(1)-O(3)	2.793(5)	O(2W)-Tb(1)-O(4)	78.38(18)
Tb(1)-O(6)#2	2.801(5)	O(5)#2-Tb(1)-O(4)	76.58(18)
Ag(1)-N(1)#3	2.149(7)	O(1)-Tb(1)-O(4)	72.24(18)
Ag(1)-N(1)	2.149(7)	O(3)#1-Tb(1)-O(2)	124.18(17)
O(3)#1-Tb(1)-O(1W)	80.04(17)	O(1W)-Tb(1)-O(2)	136.63(18)
O(3)#1-Tb(1)-O(6)#1	86.70(17)	O(6)#1-Tb(1)-O(2)	75.53(16)
O(1W)-Tb(1)-O(6)#1	70.34(17)	O(2W)-Tb(1)-O(2)	143.72(18)
O(3)#1-Tb(1)-O(2W)	79.44(17)	O(5)#2-Tb(1)-O(2)	88.10(18)
O(1W)-Tb(1)-O(2W)	68.28(18)	O(1)-Tb(1)-O(2)	50.68(17)
O(6)#1-Tb(1)-O(2W)	137.98(17)	O(4)-Tb(1)-O(2)	68.40(17)
O(3)#1-Tb(1)-O(5)#2	147.33(17)	O(3)#1-Tb(1)-O(3)	61.25(18)
O(1W)-Tb(1)-O(5)#2	78.43(18)	O(1W)-Tb(1)-O(3)	122.94(16)
O(6)#1-Tb(1)-O(5)#2	108.52(17)	O(6)#1-Tb(1)-O(3)	138.69(15)
O(2W)-Tb(1)-O(5)#2	69.89(18)	N(1)#3-Ag(1)-N(1)	176.4(5)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,-y+3/2,-z; #2 x,y-1,z; #3 -x,y,-z+1/2; #4 x,y+1,z;

#5 -x+1,-y+1,-z.

Compound 4

Dy(1)-O(3)#1	2.406(6)	O(3)#1-Dy(1)-O(1)	74.41(19)
Dy(1)-O(2W)	2.437(6)	O(2W)-Dy(1)-O(1)	143.0(2)
Dy(1)-O(6)#1	2.467(6)	O(6)#1-Dy(1)-O(1)	81.2(2)
Dy(1)-O(1W)	2.469(6)	O(1W)-Dy(1)-O(1)	130.7(2)
Dy(1)-O(5)#2	2.494(6)	O(5)#2-Dy(1)-O(1)	134.0(2)
Dy(1)-O(1)	2.512(6)	O(3)#1-Dy(1)-O(4)	107.58(19)
Dy(1)-O(4)	2.532(6)	O(2W)-Dy(1)-O(4)	143.4(2)
Dy(1)-O(2)	2.555(6)	O(6)#1-Dy(1)-O(4)	144.14(19)
Dy(1)-O(6)#2	2.801(6)	O(1W)-Dy(1)-O(4)	77.3(2)

Dy(1)-O(3)	2.850(6)	O(5)#2-Dy(1)-O(4)	76.8(2)
Ag(3)-N(1)#3	2.161(8)	O(1)-Dy(1)-O(4)	71.7(2)
Ag(3)-N(1)	2.162(8)	O(3)#1-Dy(1)-O(2)	124.3(2)
O(3)#1-Dy(1)-O(2W)	80.9(2)	O(2W)-Dy(1)-O(2)	136.3(2)
O(3)#1-Dy(1)-O(6)#1	86.5(2)	O(6)#1-Dy(1)-O(2)	76.21(19)
O(2W)-Dy(1)-O(6)#1	70.05(19)	O(1W)-Dy(1)-O(2)	142.6(2)
O(3)#1-Dy(1)-O(1W)	79.8(2)	O(5)#2-Dy(1)-O(2)	86.7(2)
O(2W)-Dy(1)-O(1W)	69.1(2)	O(1)-Dy(1)-O(2)	51.0(2)
O(6)#1-Dy(1)-O(1W)	138.46(19)	O(4)-Dy(1)-O(2)	68.6(2)
O(3)#1-Dy(1)-O(5)#2	148.6(2)	O(3)#1-Dy(1)-O(6)#2	141.67(18)
O(2W)-Dy(1)-O(5)#2	78.7(2)	O(2W)-Dy(1)-O(6)#2	70.17(19)
O(6)#1-Dy(1)-O(5)#2	108.3(2)	O(6)#1-Dy(1)-O(6)#2	60.6(2)
O(1W)-Dy(1)-O(5)#2	70.7(2)	N(1)#3-Ag(3)-N(1)	176.0(6)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,-y+1/2,-z; #2 x,y-1,z; #3 -x,y,-z+1/2; #4 x,y+1,z.

Compound 5

Ho(1)-O(1)	2.280(4)	O(6)#1-Ho(1)-O(3)	147.86(15)
Ho(1)-O(5)	2.296(4)	O(2)#2-Ho(1)-O(3)	71.75(15)
Ho(1)-O(6)#1	2.341(4)	O(1W)-Ho(1)-O(3)	125.17(16)
Ho(1)-O(2)#2	2.344(4)	O(1)-Ho(1)-O(4)#2	104.45(17)
Ho(1)-O(1W)	2.356(4)	O(5)-Ho(1)-O(4)#2	151.49(15)
Ho(1)-O(3)	2.390(4)	O(6)#1-Ho(1)-O(4)#2	75.87(15)
Ho(1)-O(4)#2	2.445(4)	O(2)#2-Ho(1)-O(4)#2	77.14(16)
Ho(1)-O(3)#2	2.480(4)	O(1W)-Ho(1)-O(4)#2	85.31(17)
Ag(1)-N(1)	2.149(6)	O(3)-Ho(1)-O(4)#2	124.05(14)
Ag(1)-N(1)#3	2.149(5)	O(1)-Ho(1)-O(3)#2	73.20(14)
O(1)-Ho(1)-O(5)	81.08(15)	O(5)-Ho(1)-O(3)#2	150.77(14)
O(1)-Ho(1)-O(6)#1	76.33(16)	O(6)#1-Ho(1)-O(3)#2	107.92(14)
O(5)-Ho(1)-O(6)#1	78.47(15)	O(2)#2-Ho(1)-O(3)#2	76.56(14)
O(1)-Ho(1)-O(2)#2	138.95(15)	O(1W)-Ho(1)-O(3)#2	132.01(15)
O(5)-Ho(1)-O(2)#2	117.24(15)	O(3)-Ho(1)-O(3)#2	75.50(15)
O(6)#1-Ho(1)-O(2)#2	140.38(15)	O(4)#2-Ho(1)-O(3)#2	52.42(14)
O(1)-Ho(1)-O(1W)	148.44(16)	O(6)#1-Ho(1)-O(1W)	77.20(16)
O(5)-Ho(1)-O(1W)	77.05(16)	N(1)-Ag(1)-N(1)#3	180.0(4)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1; #2 -x+1,-y+1,-z+1; #3 -x+1,-y,-z+2; #4 -x+2,-y+1,-z.

Compound 6

Yb(1)-O(2)#1	2.280(4)	O(5)#2-Yb(1)-O(4)#1	147.81(14)
Yb(1)-O(6)#1	2.296(4)	O(1)-Yb(1)-O(4)#1	71.86(14)
Yb(1)-O(5)#2	2.340(4)	O(1W)-Yb(1)-O(4)#1	125.40(15)
Yb(1)-O(1)	2.340(4)	O(2)#1-Yb(1)-O(3)	104.48(15)
Yb(1)-O(1W)	2.361(4)	O(6)#1-Yb(1)-O(3)	151.63(14)
Yb(1)-O(4)#1	2.388(4)	O(5)#2-Yb(1)-O(3)	75.94(14)
Yb(1)-O(3)	2.444(4)	O(1)-Yb(1)-O(3)	77.08(15)

Yb(1)-O(4)	2.480(4)	O(1W)-Yb(1)-O(3)	84.90(15)
Ag(1)-N(1)	2.152(5)	O(4)#1-Yb(1)-O(3)	124.02(13)
Ag(1)-N(1)#3	2.152(5)	O(2)#1-Yb(1)-O(4)	73.26(13)
O(2)#1-Yb(1)-O(6)#1	80.89(14)	O(6)#1-Yb(1)-O(4)	150.64(13)
O(2)#1-Yb(1)-O(5)#2	76.39(15)	O(5)#2-Yb(1)-O(4)	107.98(13)
O(6)#1-Yb(1)-O(5)#2	78.46(14)	O(1)-Yb(1)-O(4)	76.55(13)
O(2)#1-Yb(1)-O(1)	138.98(14)	O(1W)-Yb(1)-O(4)	131.53(14)
O(6)#1-Yb(1)-O(1)	117.34(14)	O(4)#1-Yb(1)-O(4)	75.50(14)
O(5)#2-Yb(1)-O(1)	140.32(14)	O(3)-Yb(1)-O(4)	52.35(13)
O(2)#1-Yb(1)-O(1W)	148.70(14)	O(2)#1-Yb(1)-O(4)#1	74.15(14)
O(6)#1-Yb(1)-O(1W)	77.67(15)	O(6)#1-Yb(1)-O(4)#1	84.34(13)
O(5)#2-Yb(1)-O(1W)	77.17(14)	N(1)-Ag(1)-N(1)#3	179.999(1)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1; #2 x-1,y,z; #3 -x+1,-y+2,-z; #4 x+1,y,z;

#5 -x+2,-y+1,-z.

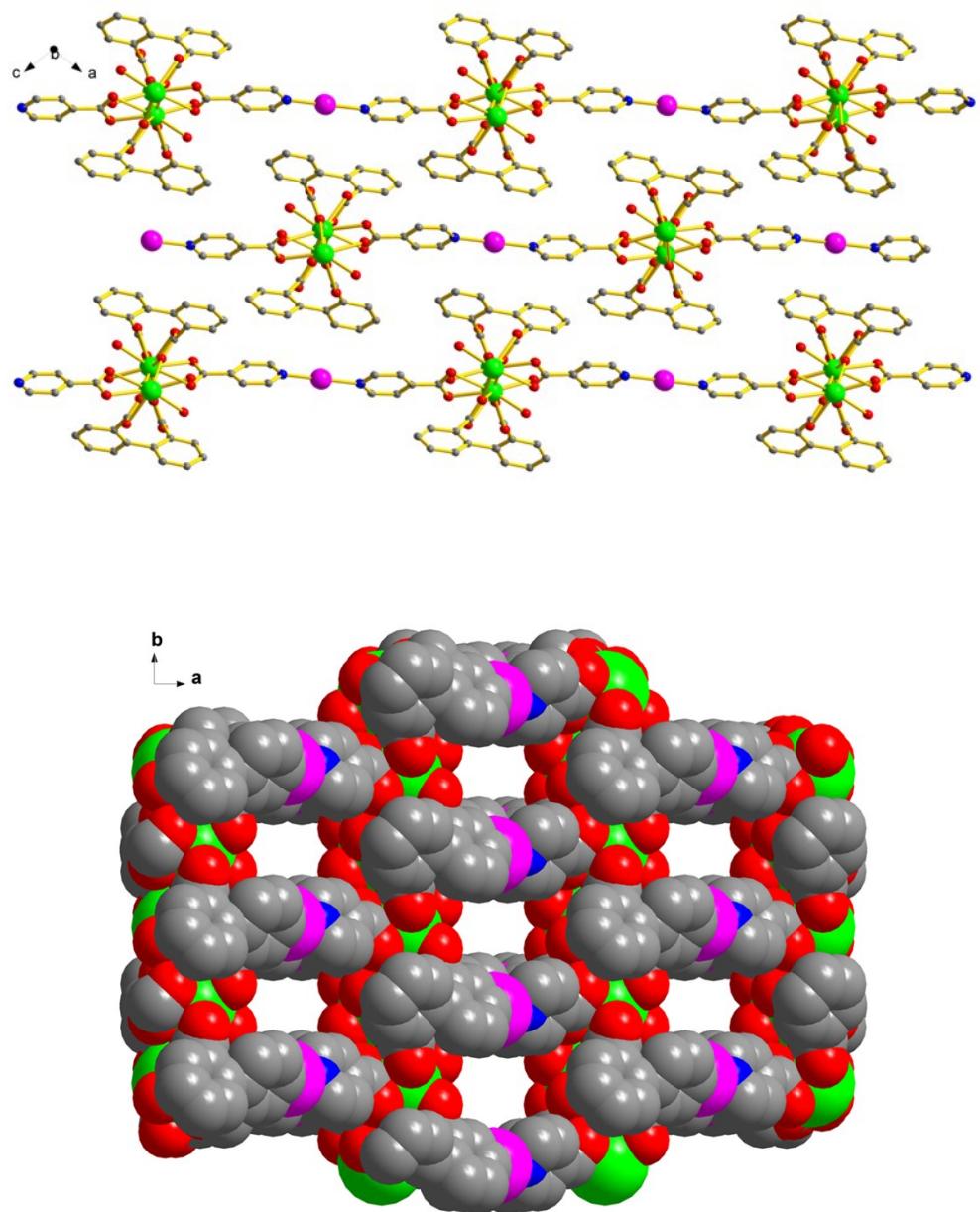


Figure S1. (a) View of the 2-D network stacked in an offset fashion along the *ac* plane; (b) A space-filling view of the porous network showing 1D channels along the crystallographic *c*-axis in **1** (guest molecules and nitrate anions are omitted for clarity).

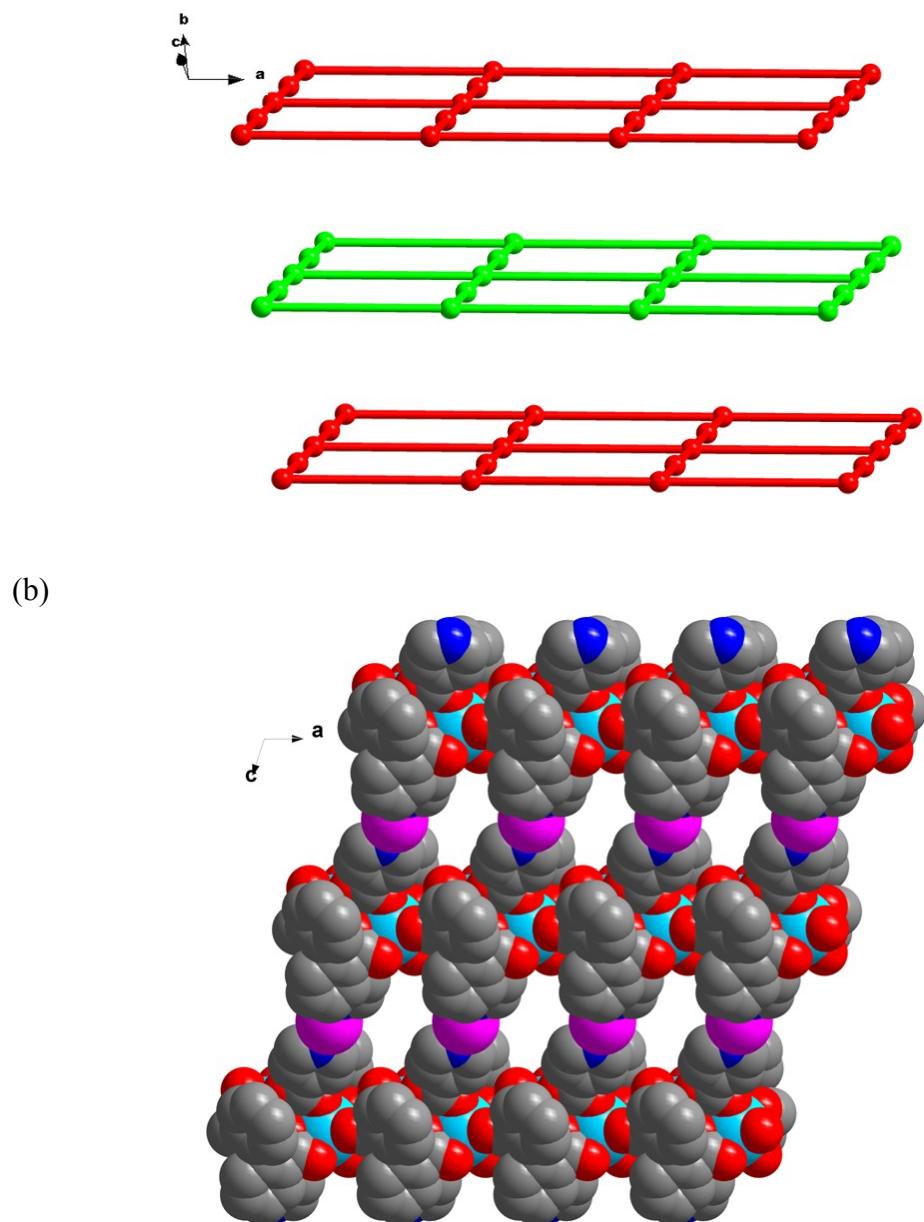


Figure S2. (a) Parallel stacking of 2D layers; (b) A space-filling view of the porous network showing 1D channels along the crystallographic *b*-axis in **5** (guest molecules and nitrate anions are omitted for clarity).

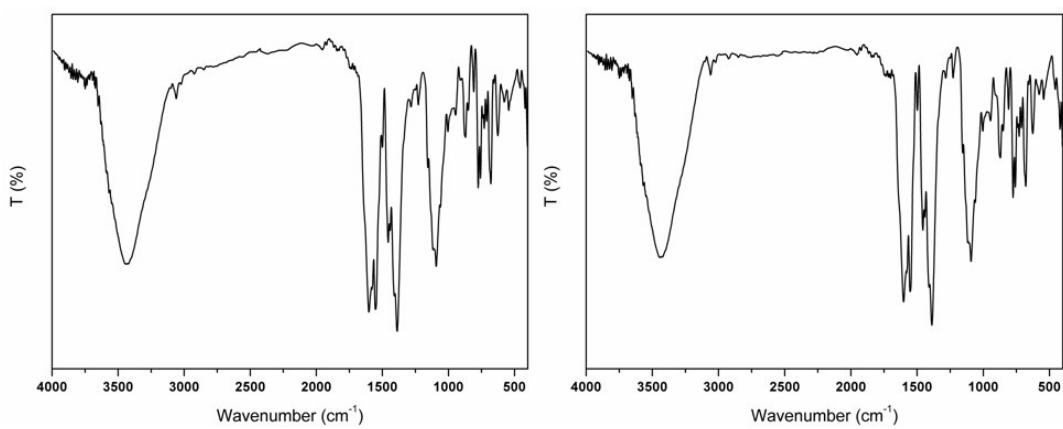


Figure S3. The IR spectra of **1** (left) and **2** (right).

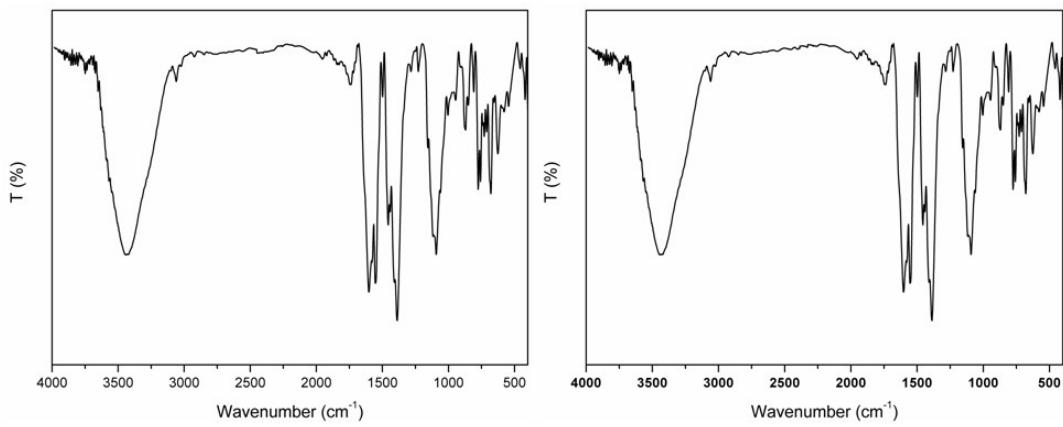


Figure S4. The IR spectra of **3** (left) and **4** (right).

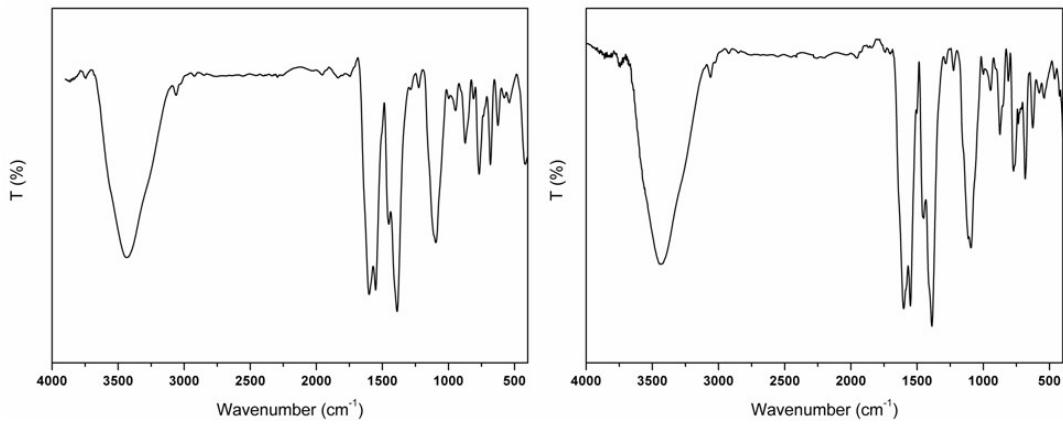


Figure S5. The IR spectra of **5** (left) and **6** (right).

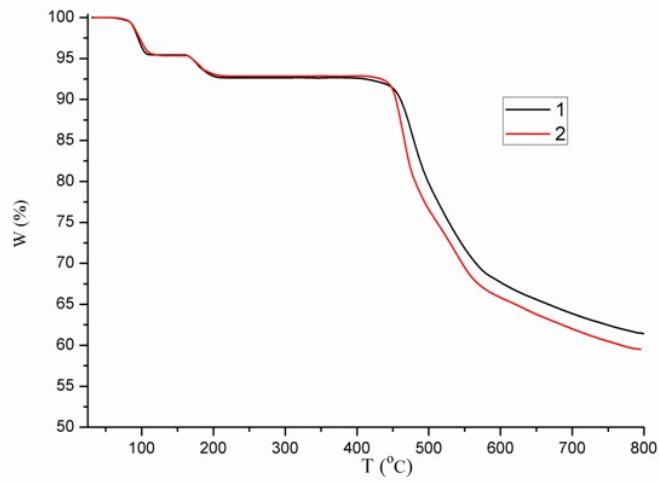


Figure S6.TGA curves of compounds **1** and **2**.

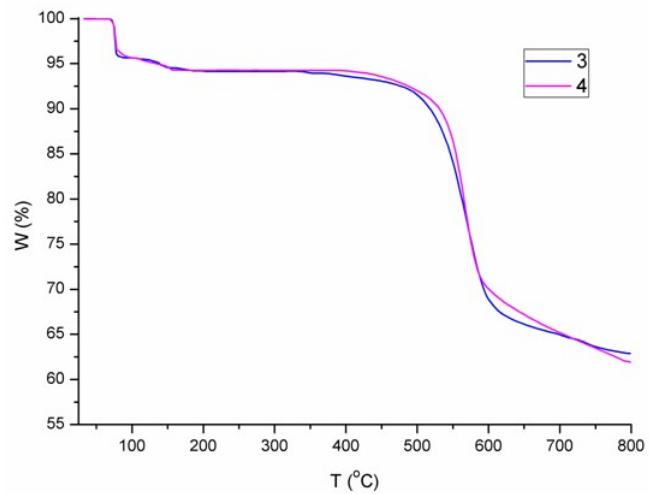


Figure S7. TGA curves of compounds **5** and **6**.

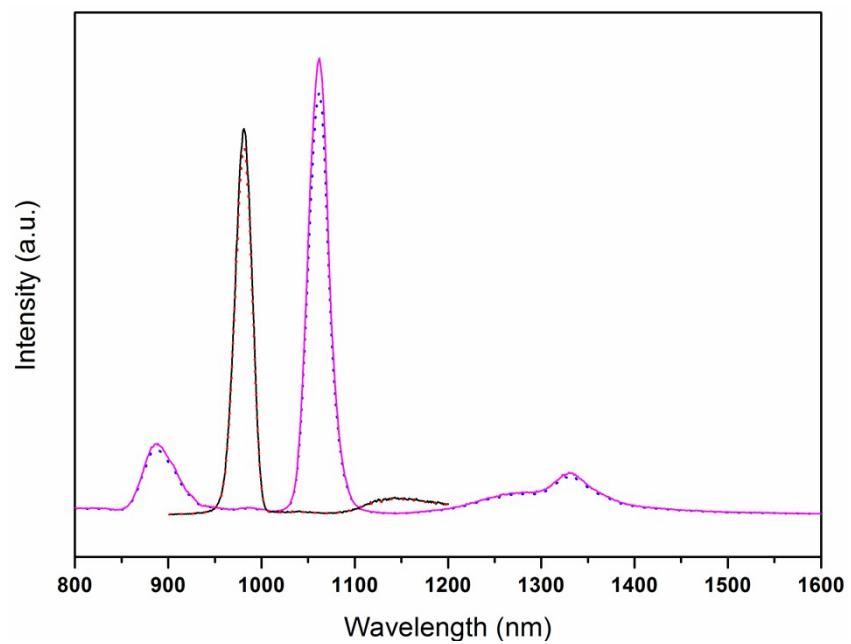
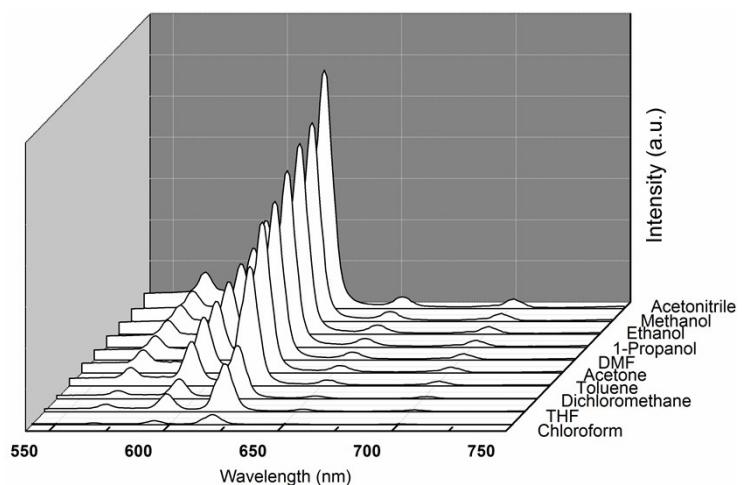


Figure S8. Solid-state emission spectra of **1** ($\lambda_{\text{ex}} = 329$ nm) and **6** ($\lambda_{\text{ex}} = 330$ nm) at room temperature, photoluminescent emission of **1** (dot blue curve) and **6** (dot red curve) recovers by immersed into acetonitrile at room temperature.

(a)



(b)

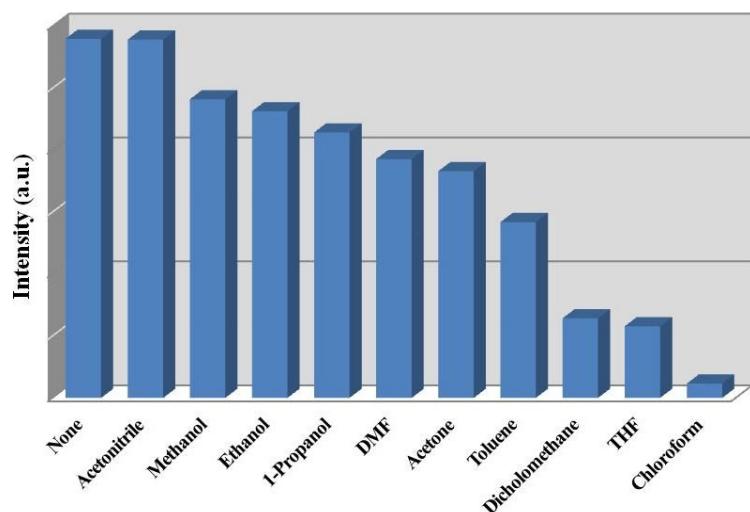
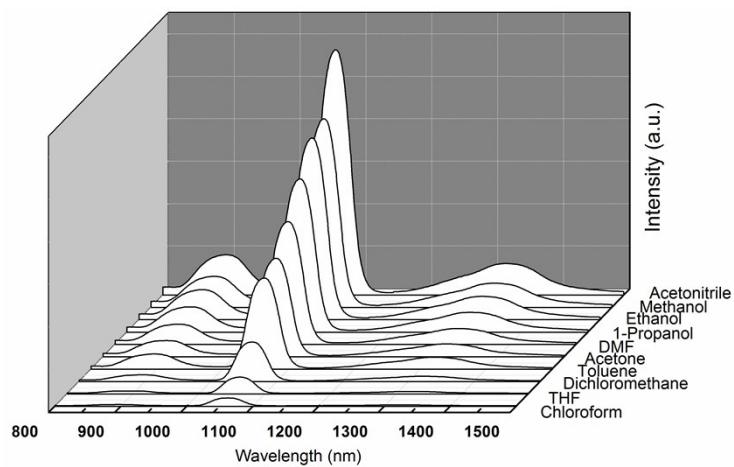


Figure S9. (a) Spectra and (b) the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (619 nm) intensities of **2** in various pure solvent when excited at 325 nm.



(b)

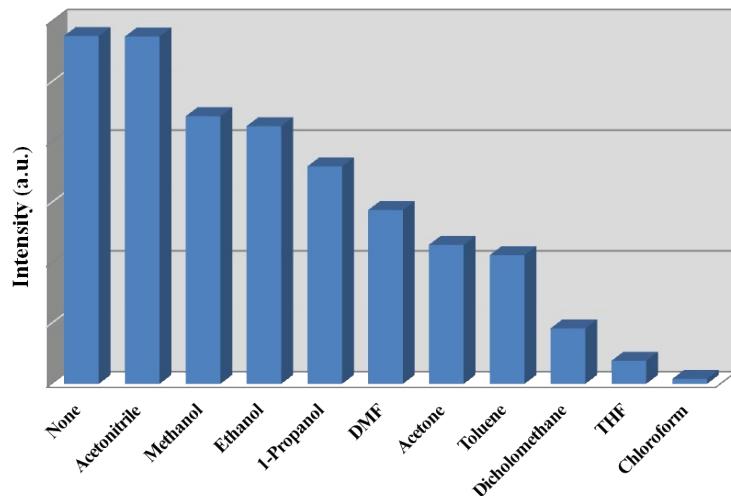


Figure 10. The ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition (1063 nm) intensities of **1** in various pure solvent when excited at 329 nm.

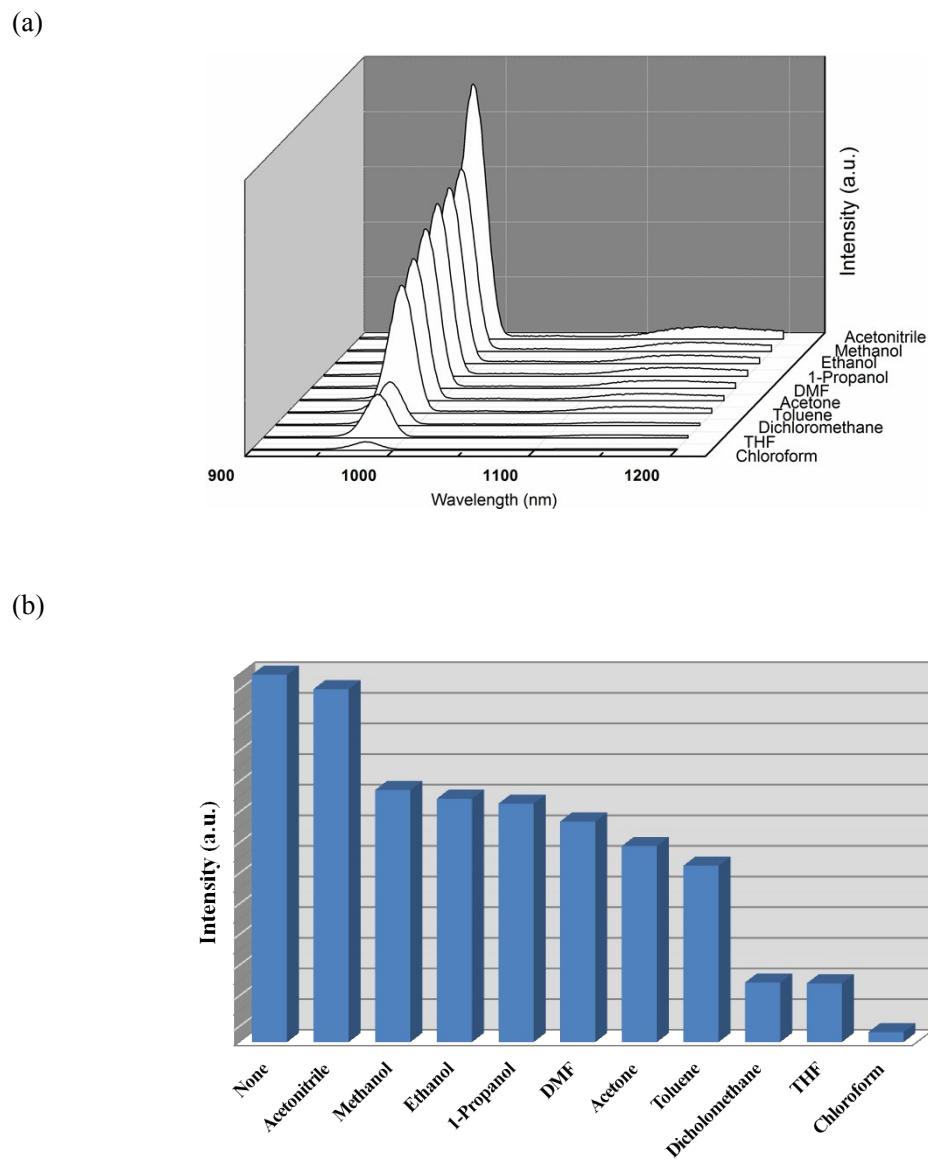


Figure S11. The $^2\text{F}_{5/2} \rightarrow ^7\text{I}_{7/2}$ transition (981 nm) intensities of **6** in various pure solvent when excited at 330 nm.

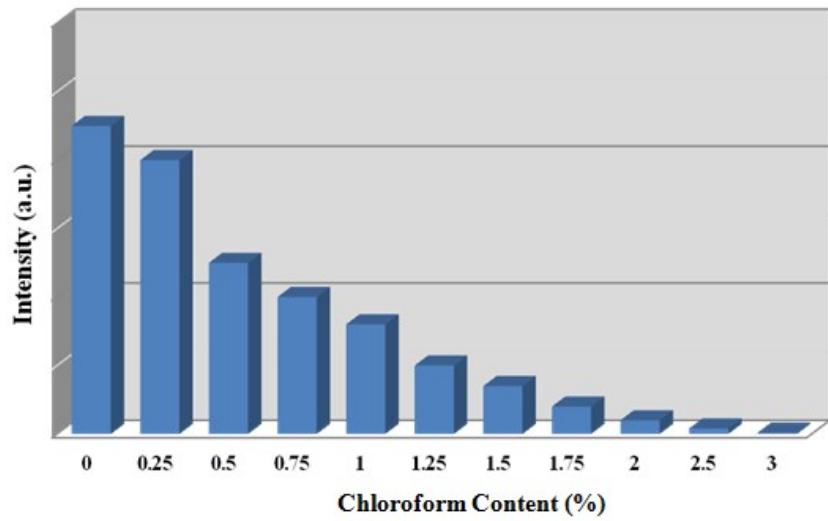


Figure S12. The ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ transition (1063 nm) intensities of **1** after immersing in different amounts of chloroform, $\lambda_{\text{ex}}=329$ nm.

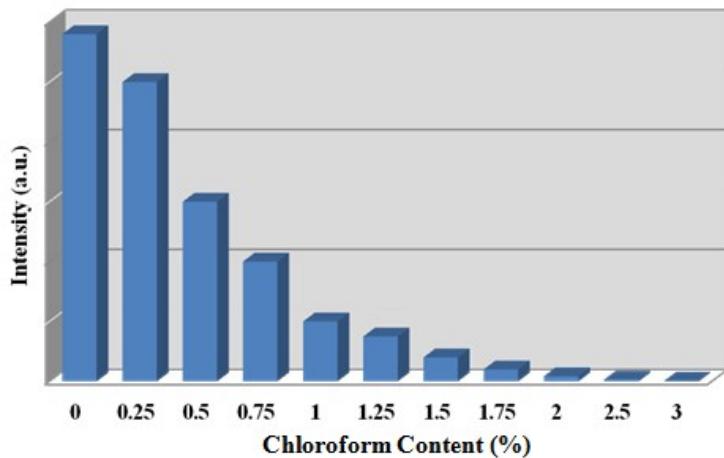


Figure S13. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition (619 nm) intensities of **2** after immersing in different amounts of chloroform, $\lambda_{\text{ex}}=325$ nm.

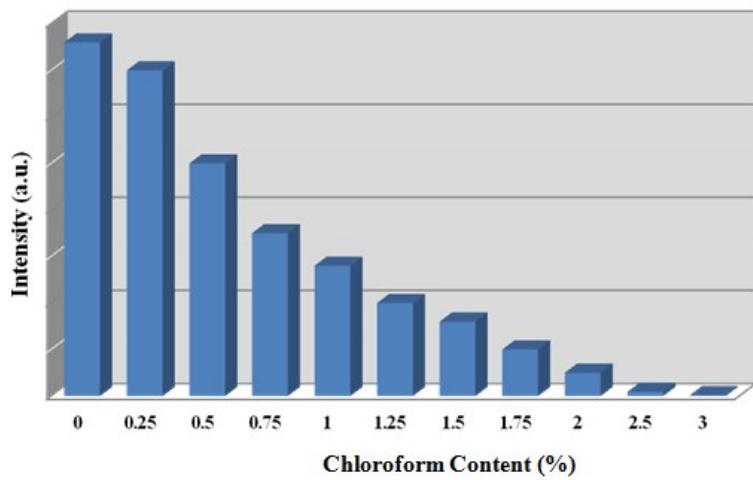


Figure S14. The ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transition (544 nm) intensities of **3** after immersing in different amounts of chloroform, $\lambda_{\text{ex}}=319$ nm.

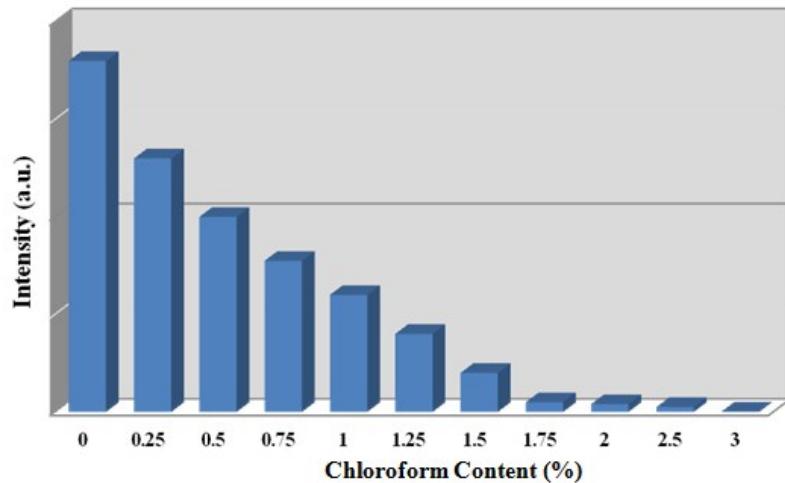


Figure S15. The ${}^2\text{F}_{5/2} \rightarrow {}^7\text{I}_{7/2}$ transition (981 nm) intensities of **6** after immersing in different amounts of chloroform, $\lambda_{\text{ex}}=330$ nm.

Table S2. Structural pore size and solvent molecular sizes^a.

Substance	Structural pore size and molecular size
1-Ln	$8.9 \times 6.7 \text{ \AA}^2$
2-Ln	$7.6 \times 5.3 \text{ \AA}^2$
CH ₃ CN	$5.5 \times 3.8 \times 3.7 \text{ \AA}^3$
CH ₃ OH	$4.9 \times 3.9 \times 4.0 \text{ \AA}^3$
C ₂ H ₅ OH	$5.1 \times 4.2 \times 4.8 \text{ \AA}^3$
CH ₃ CH ₂ CH ₂ OH	$7.5 \times 5.1 \times 5.0 \text{ \AA}^3$
DMF	$6.1 \times 6.0 \times 4.6 \text{ \AA}^3$
(CH ₃) ₂ CO	$5.5 \times 6.0 \times 4.7 \text{ \AA}^3$
Toluene	$7.3 \times 7.2 \times 5.5 \text{ \AA}^3$
Dichloromethane	$4.9 \times 6.0 \times 5.2 \text{ \AA}^3$
THF	$5.5 \times 5.6 \times 6.2 \text{ \AA}^3$
Chloroform	$5.1 \times 5.2 \times 6.4 \text{ \AA}^3$

^a These molecular sizes are calculated based on the MM2 energy minimization mode via Chem 3D program followed by measuring the longest atom-to-atom separations in two dimensions.