Syntheses, Structures and Luminescence of Several Coordination Complexes Based on β-octamolybdate and Ag/Cu Phosphine Units

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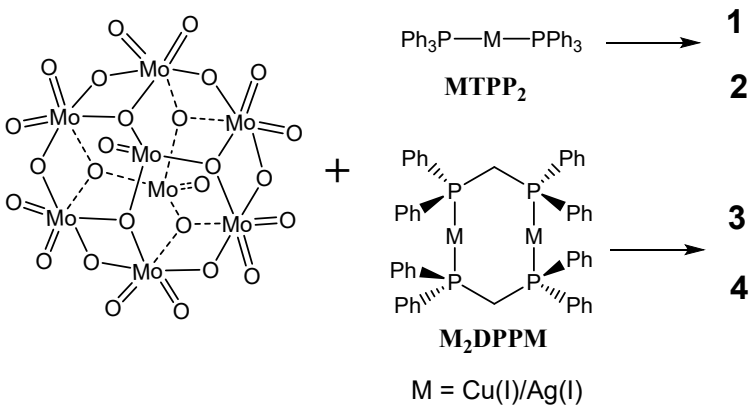

1 $[Cu(TPP)_2(CH_3CN)_2]_2\{[Cu(TPP)_2]_2(\beta\text{-}Mo_8O_{26})\}\bullet 2CH_3CN$

2 $\{[Ag(TPP)]_2\bullet[Ag(TPP)_2]_2\bullet(\beta\text{-}Mo_8O_{26})\}\bullet 6DMF$

3 $\{[Cu_2(DPPM)_2(CH_3CN)]_2(\beta\text{-}Mo_8O_{26})\}\bullet 2CH_3CN\bullet 2DCM$

4 $\{[Ag_2(DPPM)_2(CH_3CN)]_2(\beta\text{-}Mo_8O_{26})\}\bullet 2CH_3CN\bullet 2DCM$

Scheme S1 Synthetic formula of compounds **1** – **4**.

Table S1. Crystal data collection and structure refinement parameters for compounds **1-4**

	1	**2**	**3**	**4**
Empirical formula	$C_{156}H_{138}N_6O_{26}P_8Cu_4Mo_8$	$C_{126}H_{132}N_6O_{32}P_6Ag_4Mo_8$	$C_{110}H_{104}N_4O_{26}Cu_4Mo_8P_8Cl_4$	$C_{110}H_{104}N_4O_{26}Ag_4Mo_8P_8Cl_4$
Formula weight	3782.16	3627.19	3309.21	3486.53
Crystal description	red, Block	yellow, Block	Yellow, Block	white, Block
Temperature(K)	200.00	200.00	150(2) K	200.00
Crystal system.	Triclinic	Triclinic	Monoclinic	orthorhombic
Space group	P-1	P-1	P2(1)/c	$Pna2_1$
a(Å)	15.9275(6)	13.0333(5)	13.265(3)	23.7515(8)
b(Å)	16.1794(6)	15.0730(6)	21.934(4)	17.9116(6)
c(Å)	19.0604(8)	18.2889(7)	23.266(5)	33.5518(11)
α(˚)	81.001(2)	106.8400(10)	90	90
β(˚)	78.9540(10)	92.6010(10)	91.29(3)	90
γ(˚)	88.4190(10)	97.4600(10)	90	90
V(Å^3)	4761.5(3)	3396.6(2)	6768(2)	14273.9(8)
Z	1	1	2	4
ρ_{calc}/g·cm^{-3}	1.319	1.773	1.624	1.622
2θ range /deg	3.64 – 52.742	4.094 – 60.734	3.714 –50.098	6.476 – 114.65
μ(mm^{-1})	1.068	1.419	1.565	7.975
F(000)	1896.0	1800.0	3280	6848
Reflections collected.	106468	48101	37944	136260
Data/restranints/Parameters	19329/81/941	16250/282/917	11941 / 297/ 751	26085/500/1290
*R*1, wR_2 ($I \geq 2\sigma(I)$)*	R_1 = 0.0483, wR_2 = 0.1467	R_1 = 0.0425, wR_2 = 0.1161	R1 = 0.0789, wR2 = 0.1871	R1 = 0.0539, wR2 = 0.1373
*R*1, wR_2 (*all data*)**	R_1 = 0.0665, wR_2 = 0.1563	R_1 = 0.0494, wR_2 = 0.1200	R1 = 0.0960, wR2 = 0.1954	R1 = 0.0574, wR2 = 0.1396
GOF (F^2)	1.122	1.048	1.115	1.054
Largest diff. peak/hole / e Å^{-3}.	0.76/-1.11	1.73/-1.29	1.61/-1.54	1.60/-0.96
CCDC NO.	2355794	2355793	2355795	2355796

*$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R$w^b = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/}$

Table S2 Selected bond lengths of compounds **1** – **4**.

	1	**2**	**3**	**4**	**β-Mo_8O_{26}**
Mo-O_t	1.693(3)	1.6844(15)	1.686(7)	1.664(7)	1.690(2)
	1.695(3)	1.7019(13)	1.692(7)	1.676(9)	1.695(2)
	1.702(3)	1.7030(14)	1.698(7)	1.688(10)	1.698(2)
	1.704(4)	1.7090(11)	1.701(7)	1.692(8)	1.700(2)
	1.709(3)	1.7108(12)	1.709(8)	1.694(8)	1.706(2)
	1.728(3)	1.7167(13)	1.724(7)	1.696(8)	1.709(2)
	1.730(3)	1.7199(13)	1.739(6)	1.707(8)	1.713(2)
				1.717(8)	
				1.720(8)	
				1.728(8)	
				1.730(9)	
				1.738(7)	
				1.741(8)	
				1.743(10)	
Mo-O_b	1.737(3)	1.7461(13)	1.745(7)	1.746(9)	1.745(2)
	1.880(3)	1.8746(12)	1.854(6)	1.811(8)	1.881(2)
	1.880(3)	1.8949(13)	1.875(6)	1.889(8)	1.893(2)
	1.916(3)	1.9175(12)	1.945(6)	1.889(8)	1.931(2)
	1.921(3)	1.9355(10)	1.966(6)	1.905(8)	1.933(2)
	2.267(3)	2.2771(13)	2.262(6)	1.909(8)	2.296(2)
				1.915(8)	
				1.916(8)	
				1.920(7)	
				1.940(7)	
				2.265(9)	
				2.267(8)	
Mo-μ_3-O	1.932(3)	1.9350(10)	1.937(6)	1.935(7)	1.944(2)
	1.935(3)	1.9482(10)	1.939(6)	1.945(7)	1.951(2)
	1.985(3)	2.0116(12)	2.009(6)	1.953(7)	1.982(2)
	1.992(3)	2.0145(12)	2.010(6)	1.960(7)	1.998(2)
	2.357(3)	2.2736(12)	2.323(6)	1.961(7)	2.331(2)
	2.373(3)	2.3003(12)	2.352(6)	1.974(7)	2.343(2)
				2.006(8)	
				2.024(7)	
				2.322(7)	
				2.346(7)	
				2.362(7)	
				2.375(7)	

Mo-μ_5-O	2.146(3)	2.1720(11)	2.183(6)	2.150(7)	2.150(1)
	2.256(3)	2.2683(9)	2.256(6)	2.158(8)	2.309(2)
	2.262(3)	2.3045(10)	2.306(6)	2.255(7)	2.325(1)
	2.457(3)	2.3387(12)	2.401(6)	2.278(7)	2.382(2)
	2.560	2.5059(11)	2.474(6)	2.310(8)	2.463(2)
				2.322(8)	
				2.397(8)	
				2.425(7)	
				2.492(8)	
				2.536	
Cu-O	2.078(3)		2.094(6)		
	2.081(3)		2.137(7)		
Cu-P	2.2415(14)		2.232(3)		
	2.2447(13)		2.241(3)		
	2.2735(14)		2.254(3)		
	2.2782(14)		2.245(3)		
Cu-N	2.032(5)		1.98(1)		
	2.048(4)				
Ag-O		2.3713(11)		2.366(8)	
		2.3806(13)		2.439(8)	
		2.3884(13)		2.491(7)	
		2.5002(12)		2.506(8)	
Ag-N				2.437(12)	
				2.459(12)	
Ag-P		2.3613(5)		2.417(3)	
		2.4164(5)		2.423(3)	
		2.4365(5)		2.434(3)	
				2.433(3)	
				2.442(3)	
				2.442(3)	
				2.464(3)	
				2.467(3)	

The bond lengths of **β-Mo_8O_{26}** were obtained from the Ref "Polyhedron 18 (1999) 3371–3375"

Table S3 Summary of hydrogen bonding in compounds **1**-**4**.

Compound **1**				
D-H...A	d(D-H) Å	d(H...A) Å	d(D...A) Å	<(DHA) º
C116-H116...O12	0.95	2.54	3.2110(1)	128
C124-H124...O9$^{\#1}$	0.95	2.55	3.1452(1)	122
C132-H132...O6	0.95	2.51	3.4025(1)	157
C232-H232...O10	0.95	2.36	3.2195(1)	150
C335-H335...O8	0.95	2.38	3.1792(1)	141
C232-H232...O10$^{\#1}$	0.95	2.36	3.2801(1)	162
Symmetry code: $^{\#1}$: 1-x, -y, 1-z;				
Compound **2**				
C115-H115...O8$^{\#1}$	0.95	2.50	3.3353(1)	146
C124-H124...O12$^{\#2}$	0.95	2.41	3.4568(1)	160
C222-H222...O8	0.95	2.57	3.3618(1)	141
Symmetry code: $^{\#1}$: 1-x, 1-y, 1-z; $^{\#2}$: -1+x, y, z				
Compound **3**				
C4-H4A...O8	0.98	2.52	3.4685(8)	163
C32-H32...O9	0.95	2.41	3.2831(7)	144
C32-H32...O6$^{\#1}$	0.95	2.58	3.3889(8)	143
C35-H35...O3$^{\#2}$	0.95	2.55	3.3351(8)	140
C76-H76...O10$^{\#1}$	0.95	2.29	3.1299(7)	147
C82-H82...O7$^{\#3}$	0.95	2.58	3.2449(7)	127
C76-H76...O10$^{\#3}$	0.95	2.52	3.2698(7)	136
Symmetry code: $^{\#1}$: -x, -y, 2-z; $^{\#2}$: 1-x, -y, 2-z; $^{\#3}$: -x, 1/2+y, 3/2-z;				
Compound **4**				
C3-H3B...O3$^{\#1}$	0.99	2.40	3.3203(1)	155
C116-H116...O19$^{\#2}$	0.95	2.48	3.0974(1)	123
C213-H213...O2$^{\#2}$	0.95	2.38	3.2471(1)	151
C512-H512...O3$^{\#3}$	0.95	2.44	3.3634(1)	163
C513-H513...O15$^{\#3}$	0.95	2.44	3.1964(1)	136
Symmetry code: $^{\#1}$: 1/2-x, -1/2+y, -1/2+z; $^{\#2}$: 1/2+x, 3/2-y, z; $^{\#3}$: -1/2+x, 1/2-y, z;				

Table S4 BVS results of compound **1**.

Compound **1**	$[Cu(TPP)_2(CH_3CN)_2]_2\{[Cu(TPP)_2]_2(\beta\text{-}Mo_8O_{26})\}\cdot 2CH_3CN$						
	Mo1	Mo2	Mo3	Mo4		Cu1	Cu2
O(1)	1.61				**P(1)**	0.48	
O(2)	1.80				**P(2)**	0.48	
O(3)		1.73			**P(3)**		0.44
O(4)		1.71			**P(4)**		0.43
O(5)			1.74		**N(1)**		0.32
O(6)			1.62		**N(2)**		0.31
O(7)				1.77	**O(1)**	0.27	
O(8)		0.38		1.58	**O(6)**	0.27	
O(9)	1.08	0.96					
O(10)	0.79		0.30	0.93			
O(11)		0.98	1.08				
O(12)	0.28		0.81	0.93			
O(13)	0.39	0.17	0.38	0.52			
O(13)[1]				0.23			
∑s	5.95	5.93	5.75	5.96		1.50	1.50

Table S5 BVS results of compound **2**

Compound **2**	{[Ag(TPP)]$_2$·[Ag(TPP)$_2$]$_2$·(β-Mo$_8$O$_{26}$)}·6DMF						
	Mo1	Mo2	Mo3	Mo4		Ag1	Ag2
O(1)	1.67				**P(1)**	0.68	
O(2)	1.83				**P(2)**		0.56
O(3)		1.66			**P(3)**		0.59
O(4)		1.71			**O(1)**	0.21	
O(5)			1.74	0.31	**O(3)**	0.22	
O(6)	0.37		1.54		**O(4)**		0.15
O(7)				1.74	**O(5)**	0.08	
O(8)				1.70	**O(7)**	0.11	
O(9)	0.93	1.09			**O(8)**		0.21
O(10)		0.75	0.93				
O(11)		0.37	0.89	0.75			
O(12)	0.97			1.03			
O(13)	0.20	0.34	0.49	0.38			
O(13)^1			0.31				
∑s	5.97	5.92	5.90	5.91		1.30	1.51

Table S6 BVS results of compound **3**

Compound **3**	{[$Cu_2(DPPM)_2(CH_3CN)]_2$[β-Mo_8O_{26}]}·2CH_3CN·2DCM						
	Mo1	Mo2	Mo3	Mo4		Cu1	Cu2
O(1)	1.59				**P(1)**	0.48	
O(2)	1.83				**P(2)**		0.47
O(3)		1.80			**P(3)**	0.49	
O(4)		1.55			**P(4)**		0.48
O(5)			1.75	0.38	**O(1)**		0.26
O(6)			1.65		**O(6)**		0.23
O(7)				1.74	**N(1)**	0.37	
O(8)				1.72			
O(9)	0.74	0.92	0.30				
O(10)	0.41	0.92	0.76				
O(11)	1.16		1.09	0.91			
O(12)		0.26		0.84			
O(13)	0.35	0.46	0.38	0.22			
∑s	6.01	5.92	5.93	5.81		1.34	1.44

Table S7 BVS results of compound **4**

Compound **4**	{[Ag_2(DPPM)$_2$·(CH_3CN)]$_2$(β-Mo_8O_{26})}·2CH_3CN·2DCM							
	Mo1	Mo2	Mo3	Mo4	Mo5	Mo6	Mo7	Mo8
O(1)	1.63							
O(2)	1.78							
O(3)		1.74						
O(4)		1.77						
O(5)			1.86					
O(6)			1.79					
O(7)			0.38	1.56				
O(8)				1.92				
O(9)					1.28	0.38		
O(10)					1.66			
O(11)						1.61		
O(12)						1.56		
O(13)							1.57	
O(14)							1.77	
O(15)								1.67
O(16)								1.57
O(17)	1.05		1.00					
O(18)		0.97				0.99		
O(19)			0.96				1.05	
O(20)						0.91		1.01
O(21)	0.30	0.85		0.89				
O(22)	0.77	0.29			0.93			
O(23)				0.88			0.29	0.86
O(24)					0.86		0.73	0.33
O(25)	0.39		0.18	0.25	0.52		0.37	
O(26)		0.34		0.51	0.26	0.21		0.36
∑s	5.92	5.96	6.17	6.01	5.51	5.66	5.78	5.80
	Ag1	Ag2	Ag3	Ag4				
P(1)	0.55							

P(2)		0.55		
p(3)	0.57			
P(4)		0.57		
P(5)			0.56	
P(6)				0.58
P(7)			0.52	
P(8)				0.51
O(1)	0.18			
O(4)		0.22		
O(13)			0.22	
O(16)				0.16
N(1)	0.20			
N(2)				0.18
∑s	1.50	1.34	1.30	1.43

Table S8 NBO Calculation Results of compounds **1-4**.

	Mo	Cu1	Cu2	Ag1	Ag2	Ag3	Ag4
1	1.26~1.42	0.45		-	-	-	-
2	1.39~1.49	-	-	0.58	0.52	-	-
3	1.17~1.44	0.33	0.55	-	-	-	-
4	1.31~1.36	-	-	0.39	0.49	0.48	0.41

Computational Details

To perform natural population analysis for the obtained compounds, quantum chemical calculations were carried out using density functional theory with the hybrid functional B3LYP-D3 as implemented in the Gaussian 16 program. Here, the empirical formula DFT-D3 was used for dispersion corrections. All geometry optimizations were carried out with the 6–31G(d,p) basis sets for the H, C, N, O and P elements, and the LanL2DZ pseudopotential and its corresponding basis sets for all metal atoms, including Mo, Cu and Ag.

Table S9 Solubility of compounds **1-4** in common solvents.

	1	**2**	**3**	**4**
DCM	＜0.01mg/ml	＜0.01mg/ml	＜0.01mg/ml	＜0.01mg/ml
CH_3CN	＜0.01mg/ml	＜0.01mg/ml	＜0.01mg/ml	＜0.01mg/ml
CH_3OH	＜0.01mg/ml	＜0.01mg/ml	＜0.01mg/ml	＜0.01mg/ml
H_2O	＜0.01mg/ml	＜0.01mg/ml	＜0.01mg/ml	＜0.01mg/ml
DMF	0.28mg/ml	0.43mg/ml	＜0.01mg/ml	＜0.01mg/ml

The gravimetric method was used to measure solubility (Table **S9)**. Firstly, the excess compound and solvent were mixed in a round-bottomed flask and stirred for more than 5h using a magnetic stirrer at room temperature. After stopping stirring for a period of time, about 10mL of the upper clarified solution was filtered with a filter with 0.22μm pores and transferred into a preweighed vial to obtain a saturated solution. The total weight was then immediately measured by the balance and then put it in the vacuum oven to evaporate the solvent. The round-bottomed flask was reweighed after complete drying. Each experiment was performed three times, and the arithmetic mean was used as the final result.

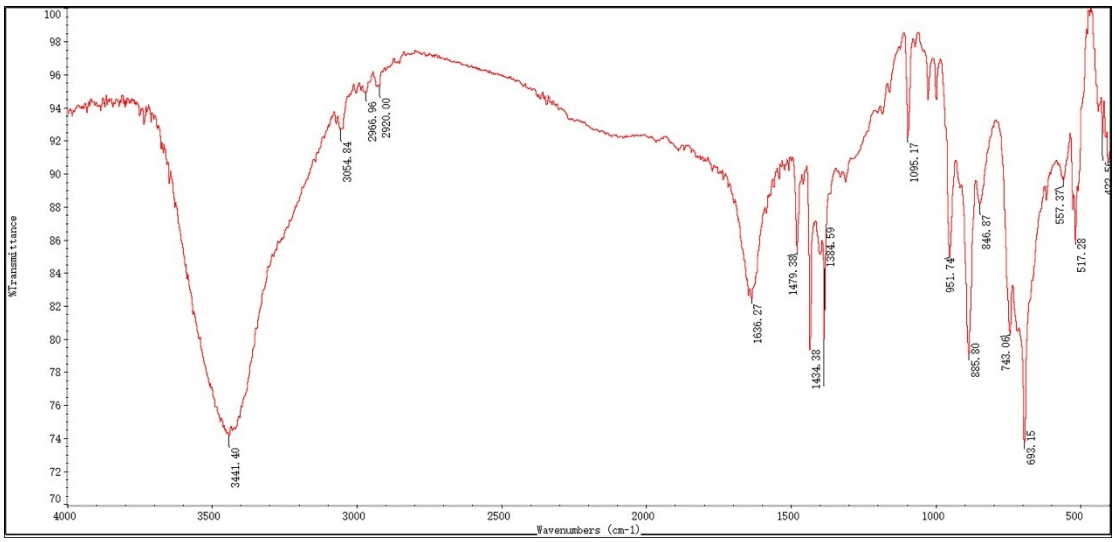

Figure S1**.** FT-IR spectrum of compound **1**

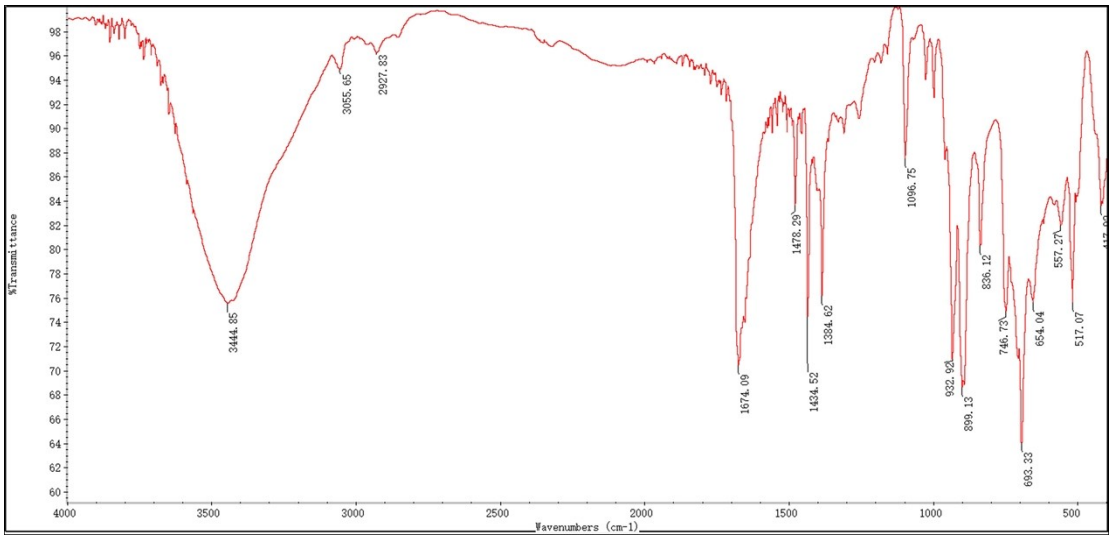

Figure S2**.** FT-IR spectrum of compound **2**

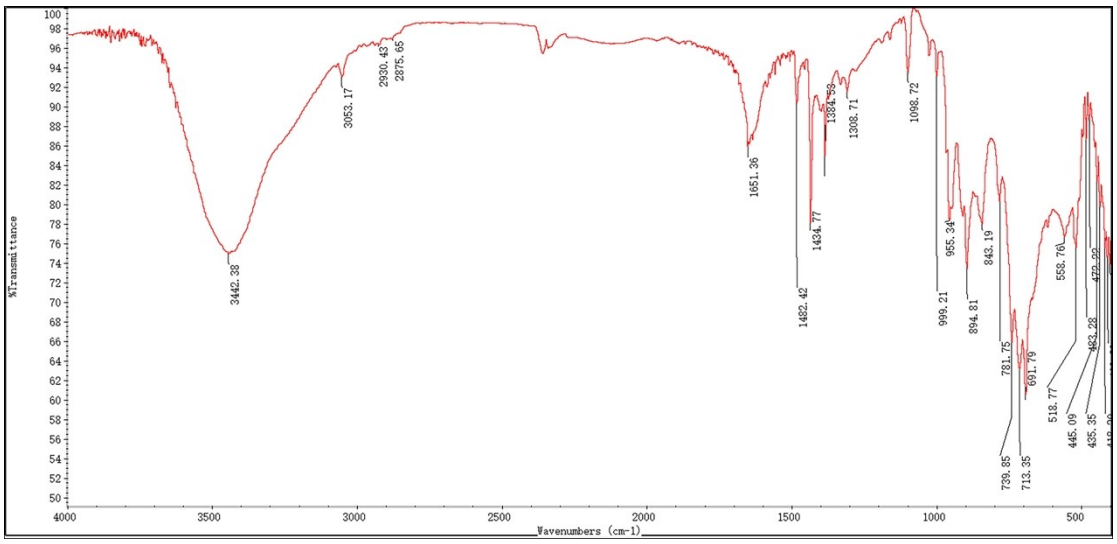

Figure S3. FT-IR spectrum of compound **3**

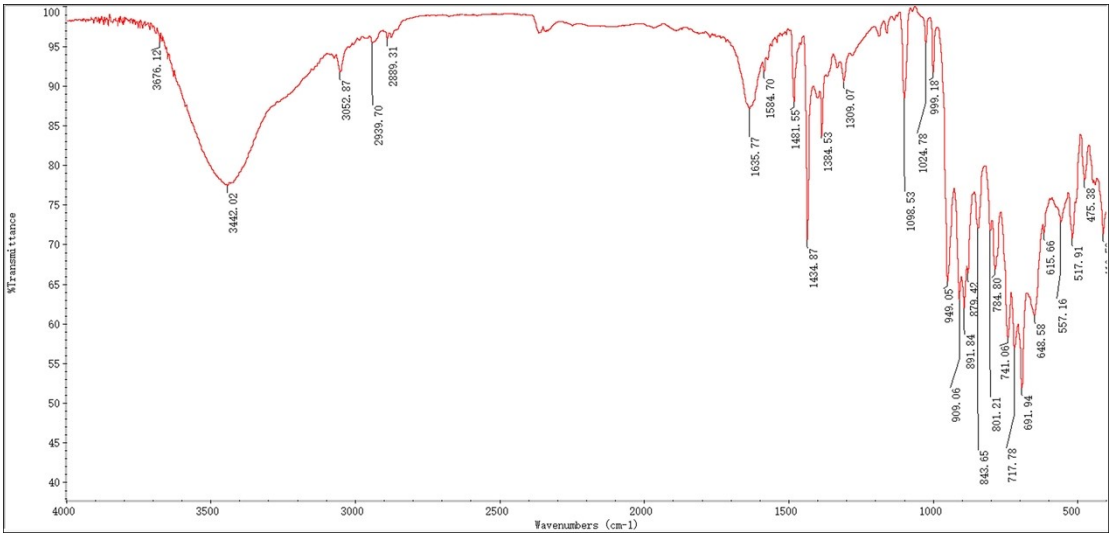

Figure S4**.** FT-IR spectrum of compound **4**

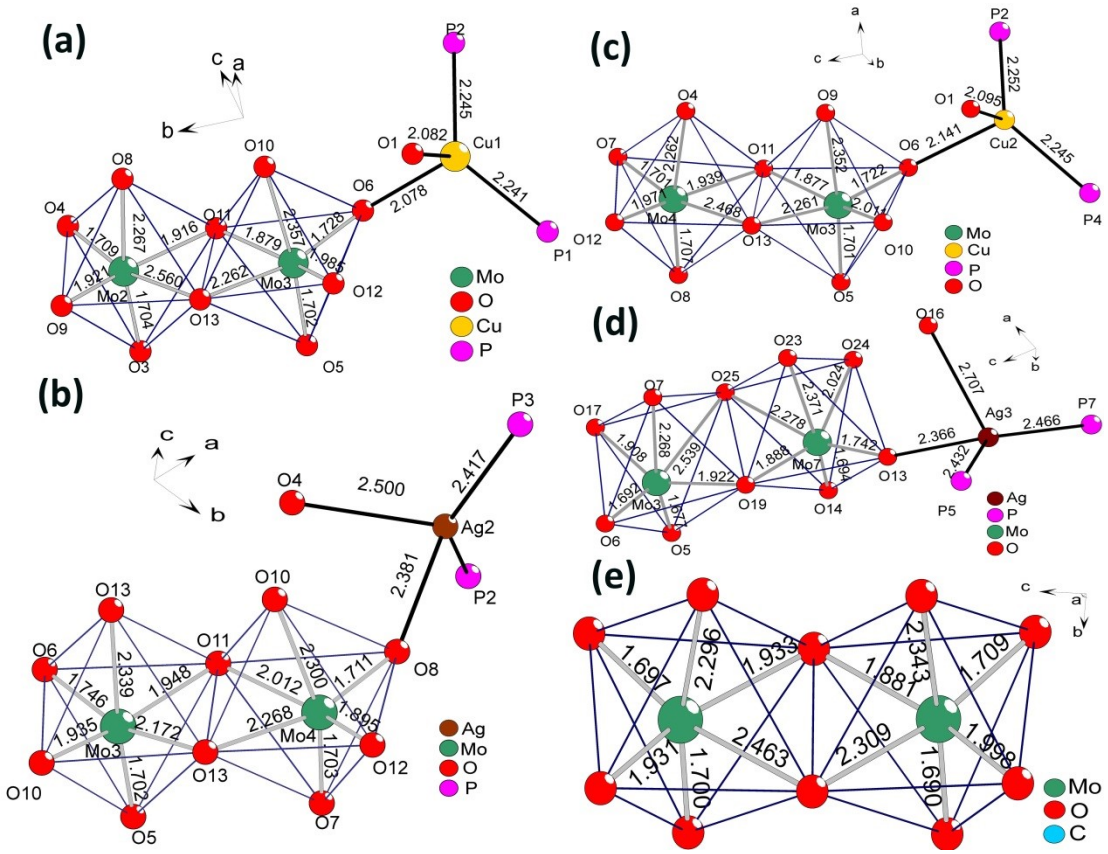

Figure S5**.** Diagrams of coordination sphere in compounds **1** (a), **2** (b), **3** (c), **4** (d) and *β*-octamolybdates (e).

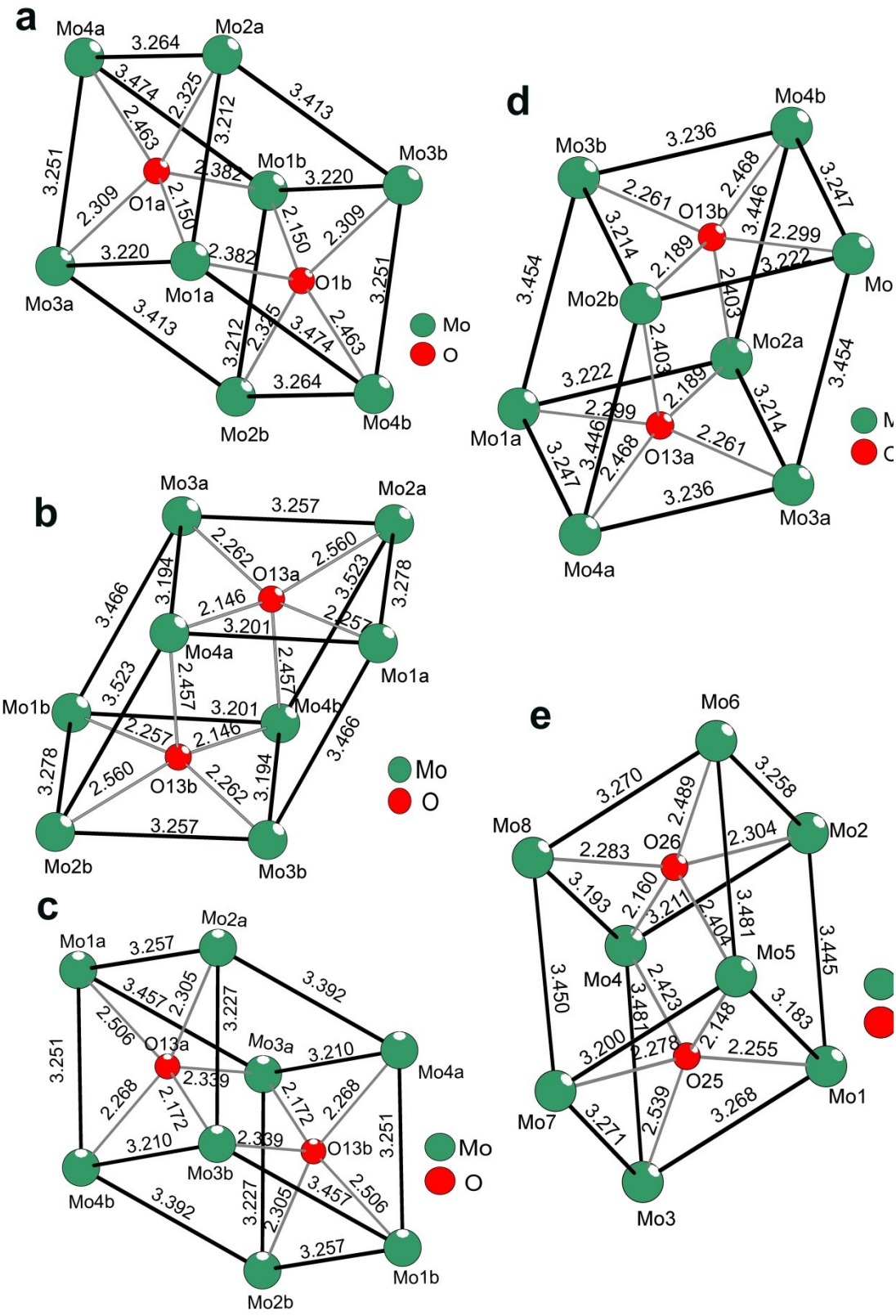

Figure S6**.** Diagrams of cluster skeleton of *β*-octamolybdates (a), compounds **1** (b), **2** (c), **3** (d) and **4** (e).

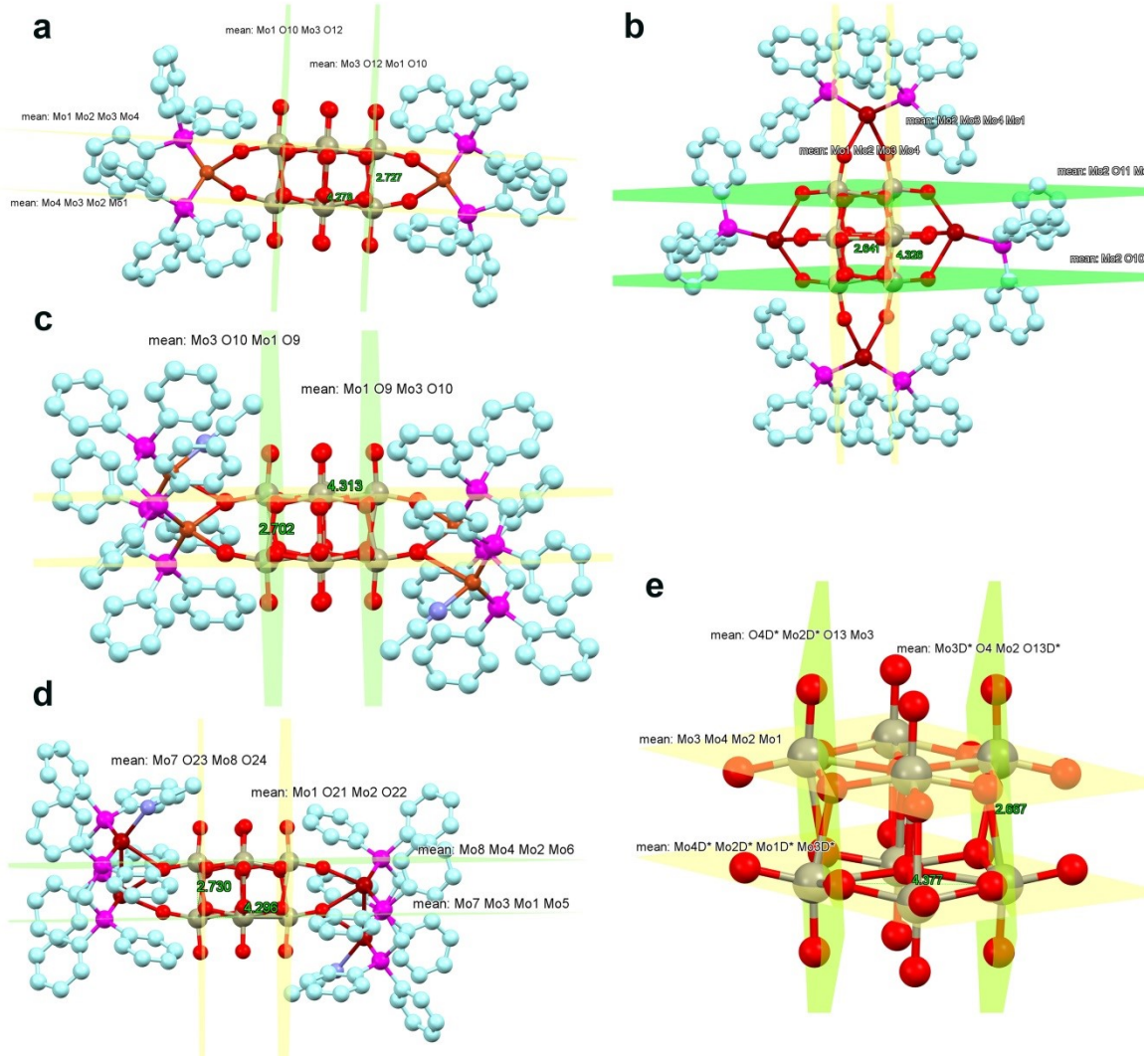

Figure S7**.** The distances between the planes of two adjacent Mo_4 rings (light yellow) and the planes of two adjacent Mo_2O_2 rings (light green) in compounds **1** (a), **2** (b), **3** (c) and **4** (d) and β-octamolybdates (e).

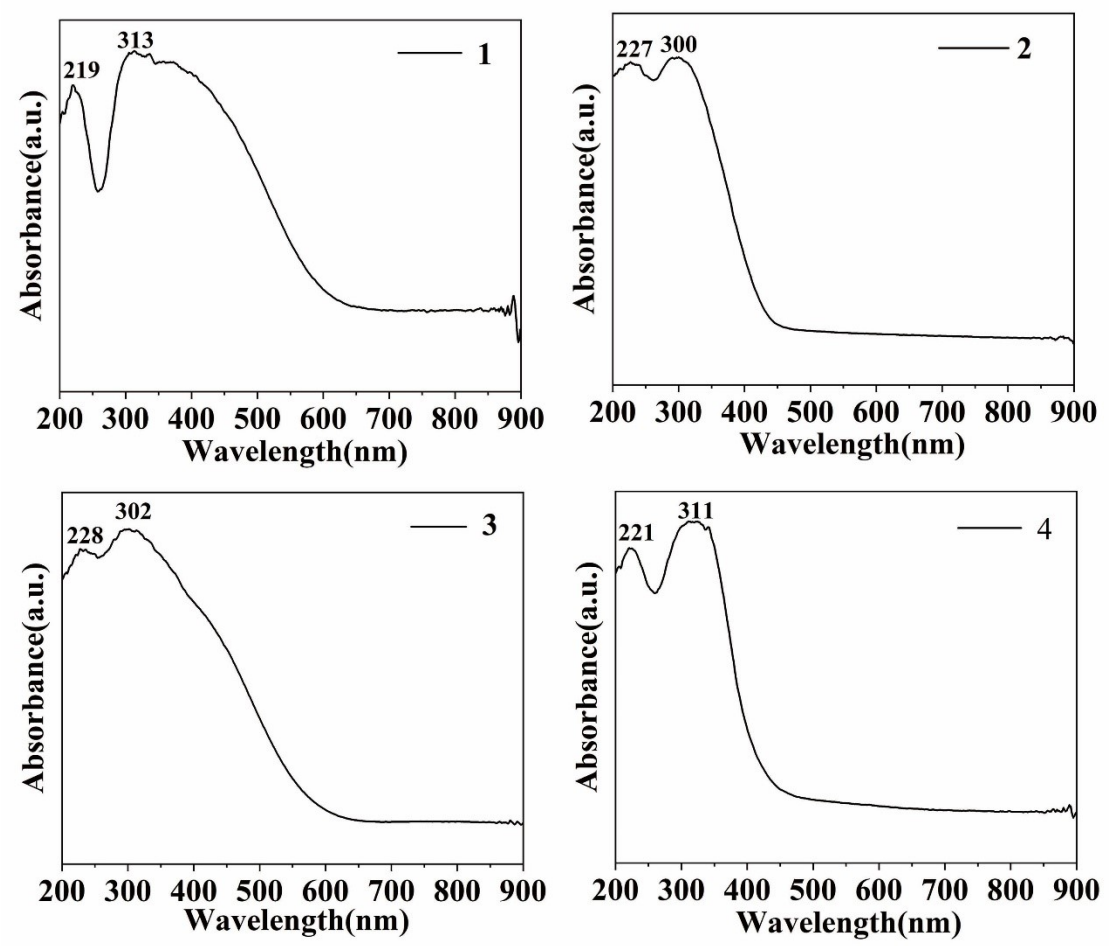

Figure S8. Solid UV/Vis absorption spectra of compounds **1-4**.

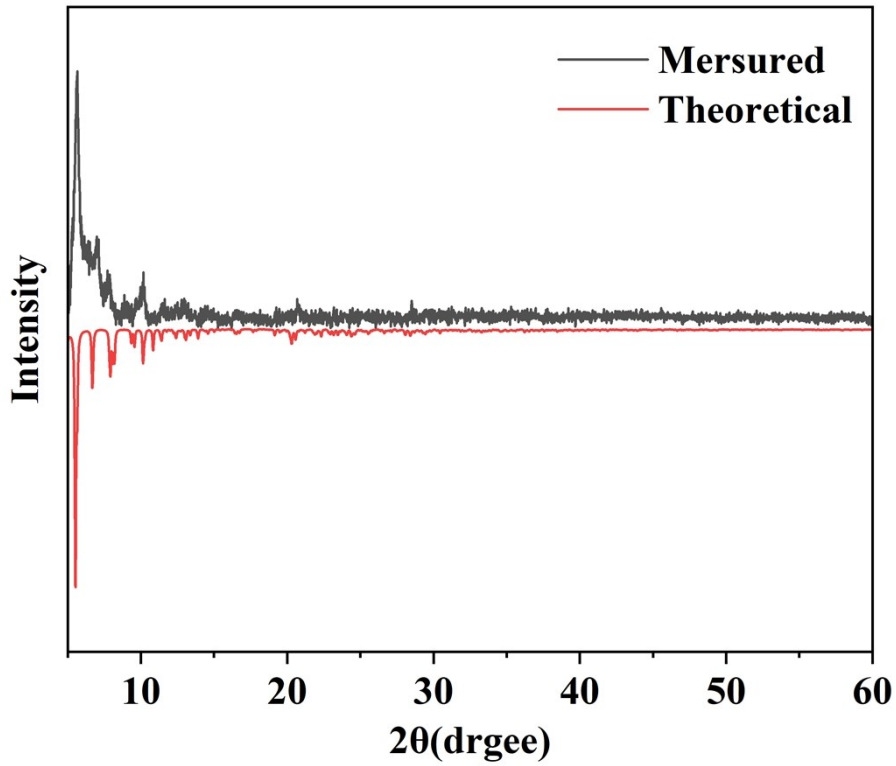

Figure S9. XRD spectrum of compound **1**.

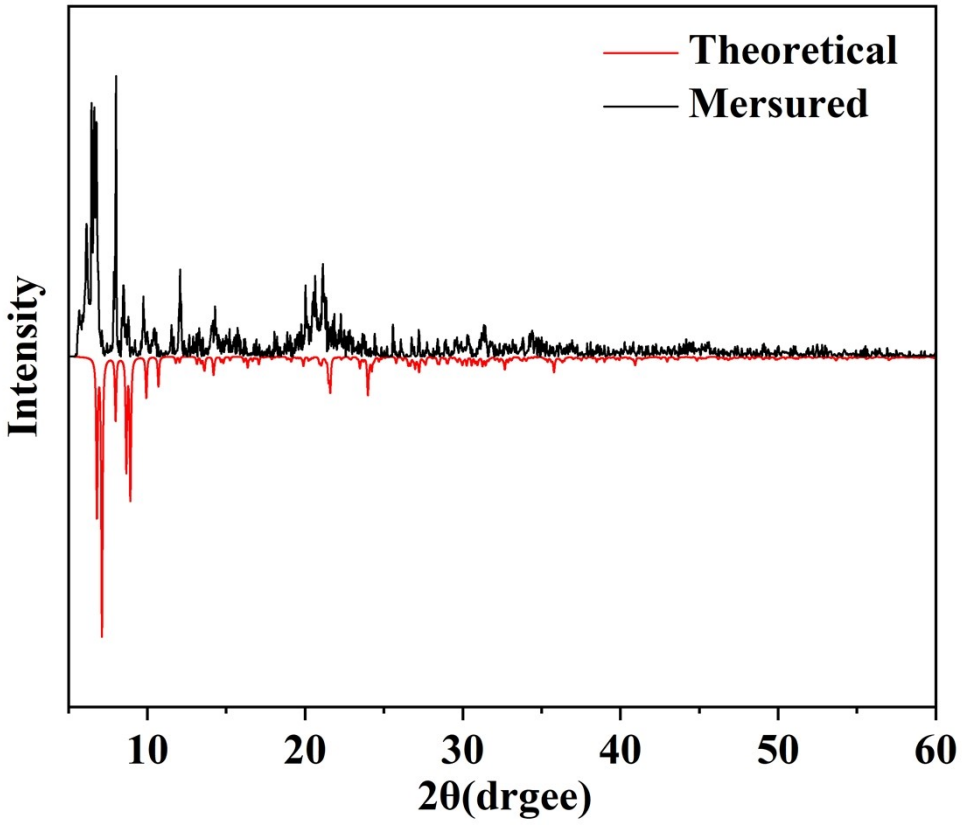

Figure S10. XRD spectrum of compound **2**.

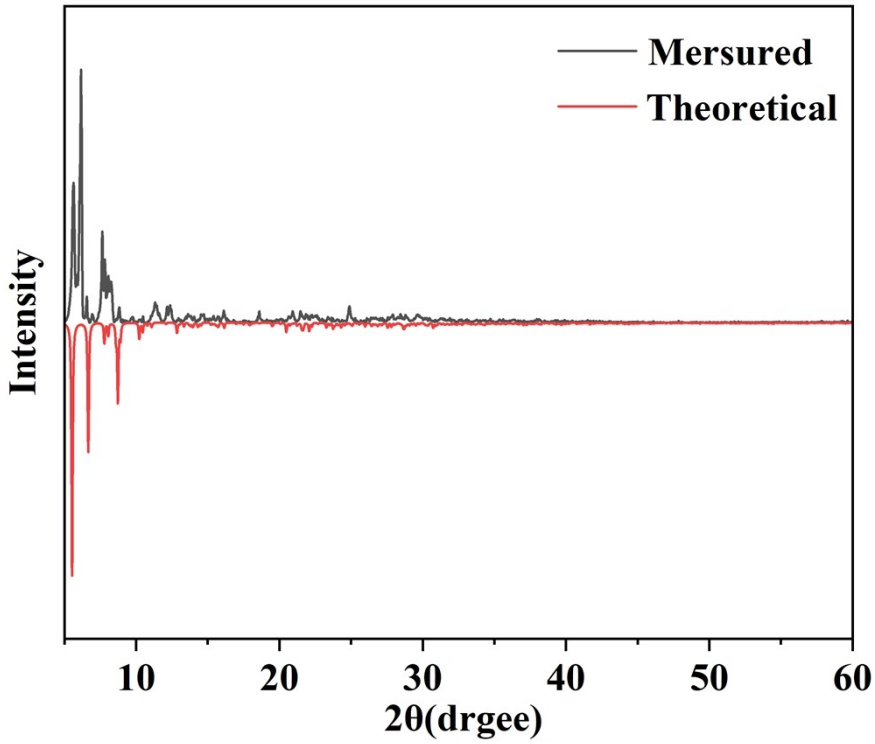

Figure S11. XRD spectrum of compound **3**

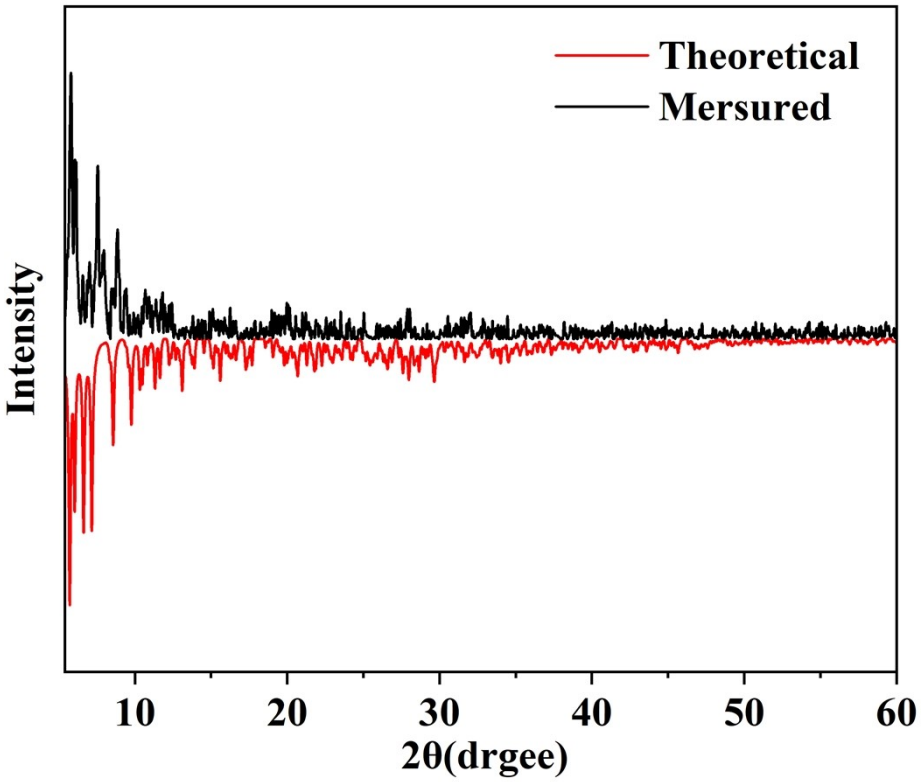

Figure S12. XRD spectrum of compound **4**

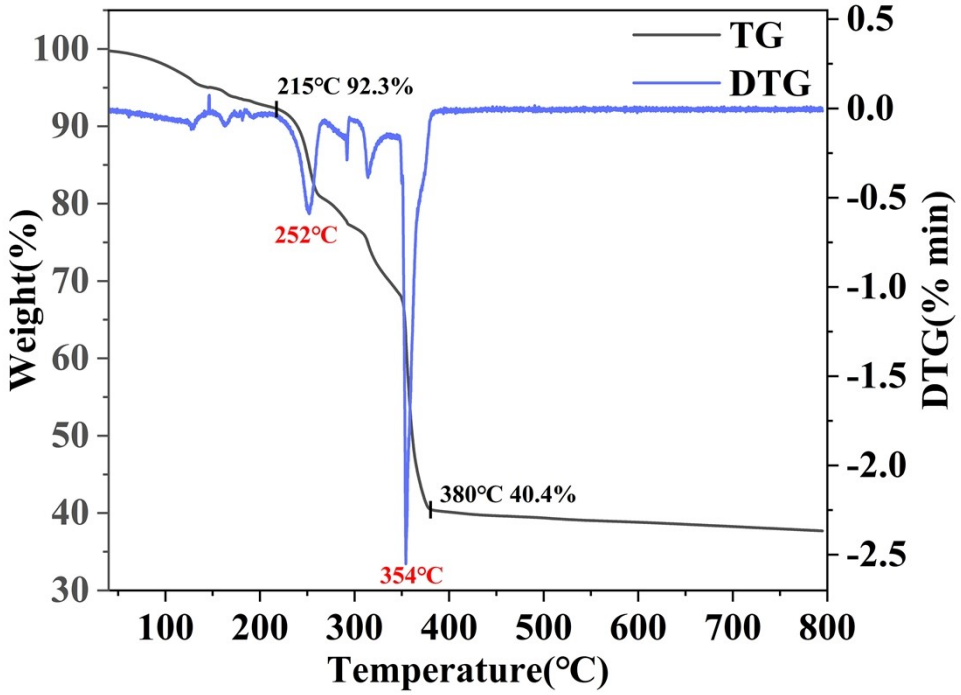

Figure S13. TGA and DTG of compound **1**.

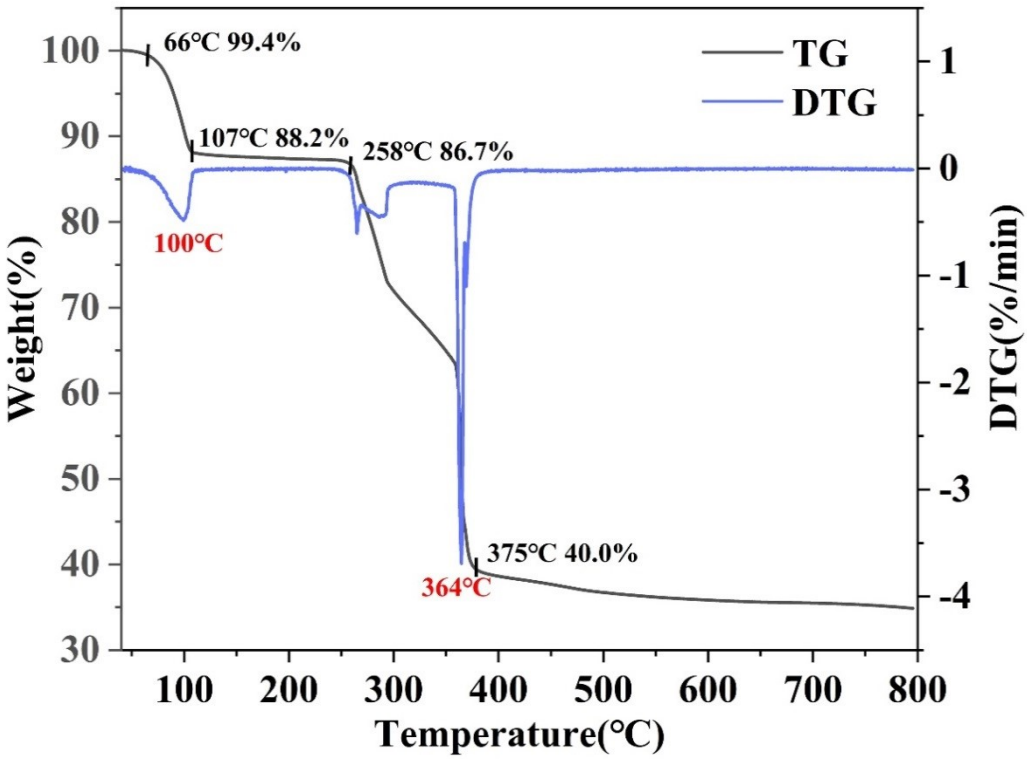

Figure S14. TGA and DTG of compound **2**.

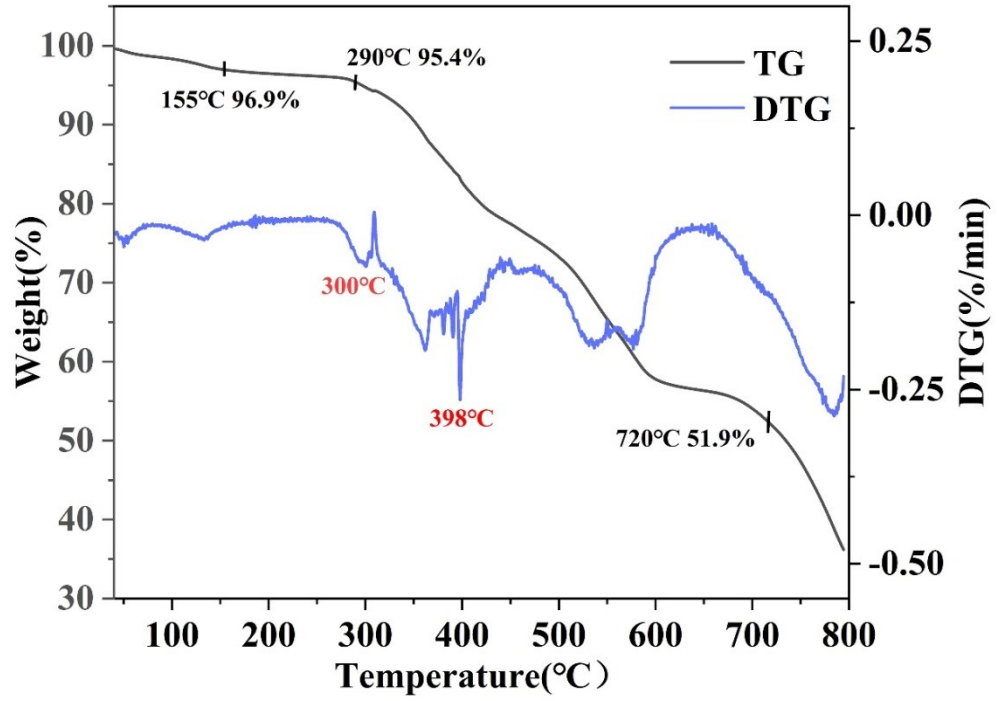

Figure S15. TGA and DTG of compound **3**.

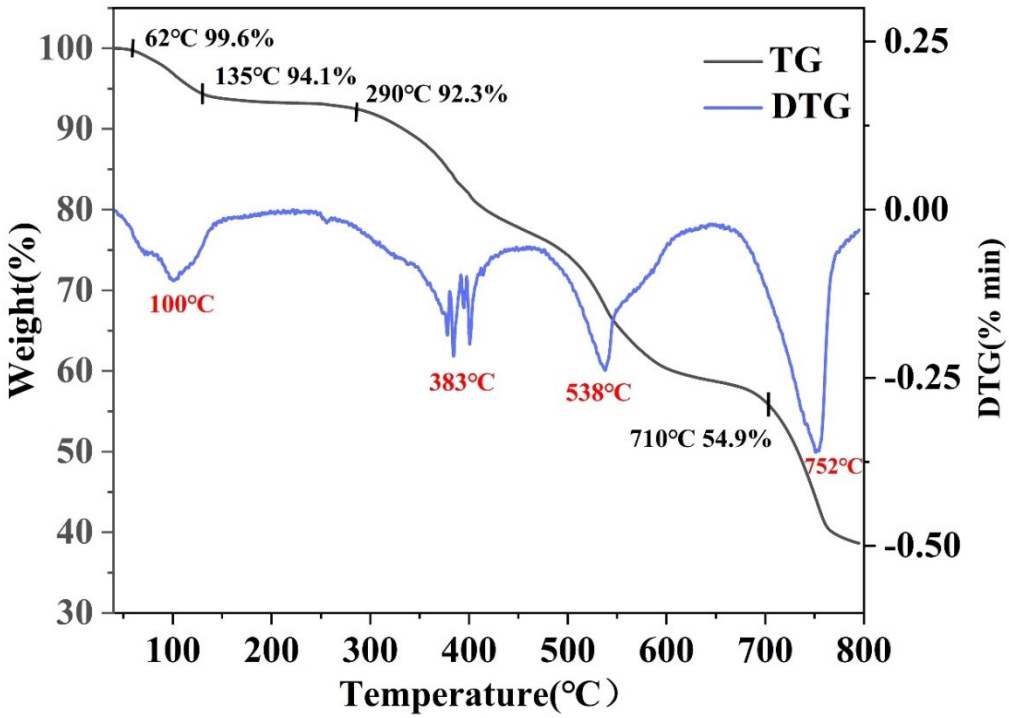

Figure S16. TGA and DTG of compound **4**.

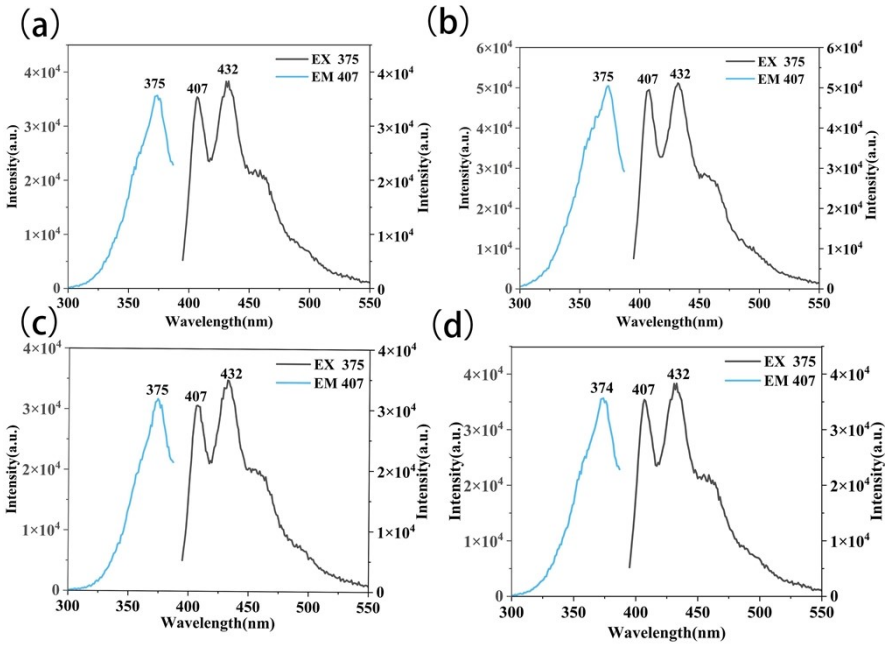

Figure S17. Luminescent spectra of compounds **1 (a),2 (b),3 (c),4 (d)** in their DMF solutions**.**

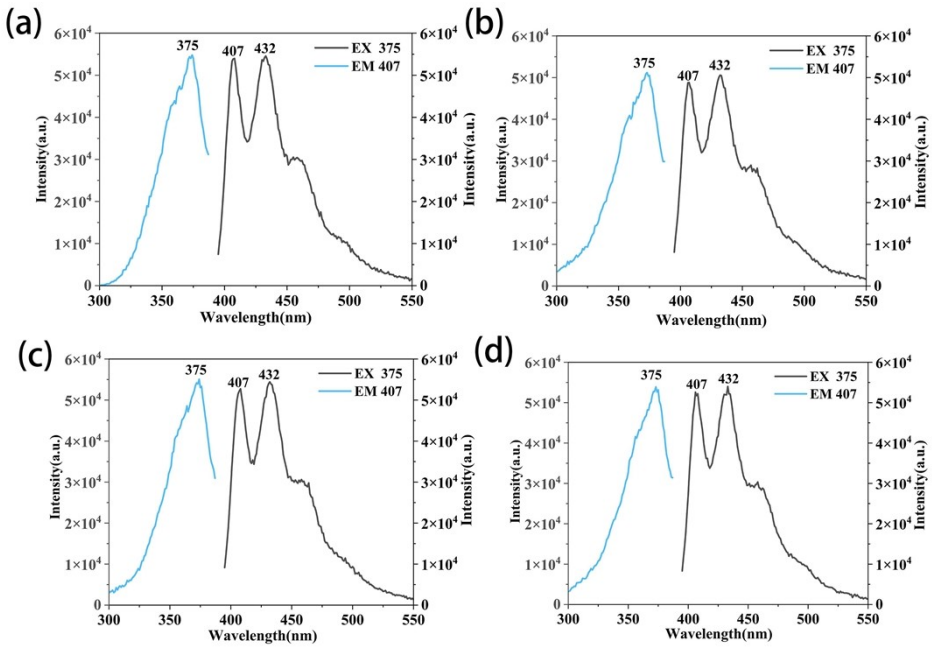

Figure S18. Luminescent spectra of **$CuTPP_2$ (a)**, **$AgTPP_2$ (b)**, **Cu_2DPPM_2 (c)**, **Ag_2DPPM_2 (d)** in their DMF solutions**.**

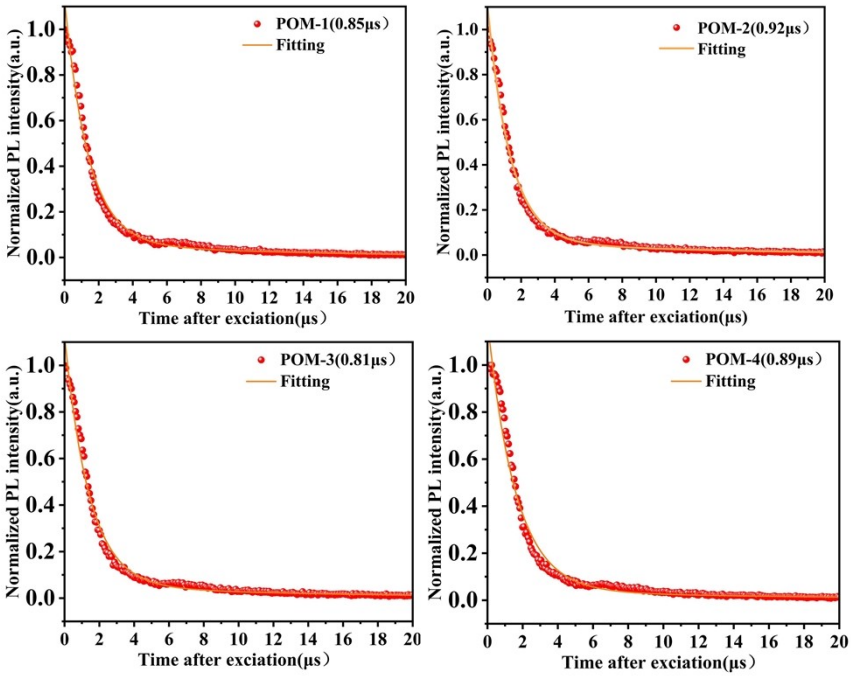

Figure S19. Luminescence lifetime of compounds **1(a), 2(b), 3(c), 4(d).**

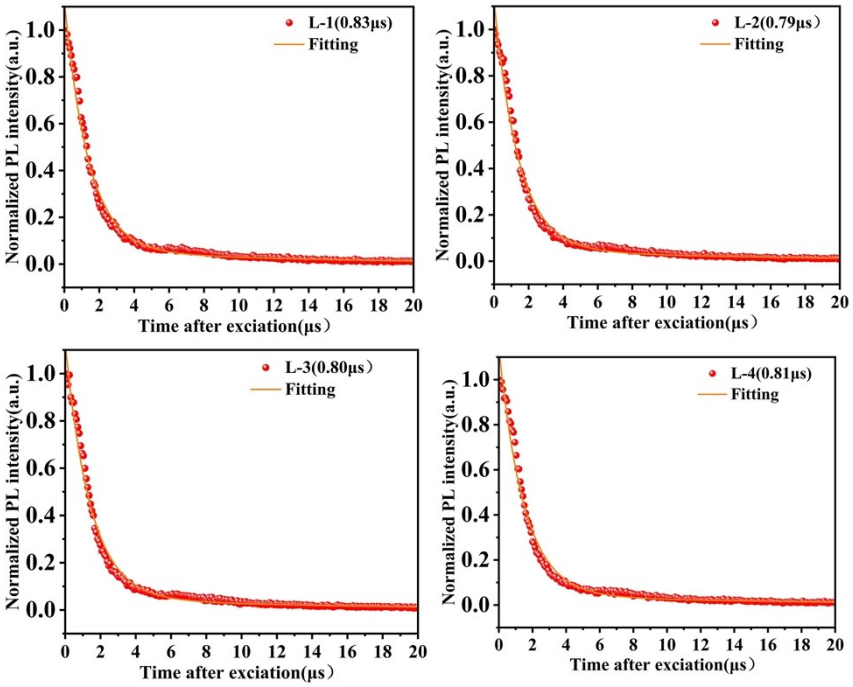

Figure S20. Luminescence lifetime of **$CuTPP_2$ (a)**, **$AgTPP_2$ (b)**, **Cu_2DPPM_2 (c)**, **Ag_2DPPM_2 (d).**