A New Synthetic Approach to Functionalize Oxomolybdenum Complexes

Baokuan Chen [a,b][+], Zhengguo Lin [a][+], Bo Wang*[a], Xiao Feng [a], Linyuan Fan [a], Song Yang [a], Xianqiang Huang[a] and Changwen Hu[a]*

[a] *Key Laboratory of Cluster Science, Ministry of Education of China, School of Chemistry, Beijing Institute of Technology, Beijing 100081, P. R. China*

[b] *College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, People's Republic of China*

[+]*These authors contributed equally to this work.*

General experimental section and synthesis methods

Materials and physical methods

All reagents and solvents for synthesis were purchased from commercial sources and usedwithout further purification. The elemental analyses were conducted on Perkin-Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on Nicolet 170 SXFT/IR spectrometer. A diffuse reflectance UV-vis spectrum ($BaSO_4$ pellet) was obtained from the solid state with a Varian Cary 500 UV-vis-NIR spectrometer. Mass spectra measurements were made in the negative ion mode on an Agilent 6520 Q-TOF LC/MS mass spectrometer. Sample solutions were made to about 10^{-5} M in water and transferred to the electrospray source by direct injection.

(1) Synthesis and discussion

Synthesis of 1: H_2MoO_4 (0.324 g, 2 mmol) in 1-methylimidazole (5 mL) was allowed to be sealed in a 23 mL Teflon-lined stainless steel container, which was heated to 100 °C under autogenously pressure for 72 hours. Yield: 80% (based on Mo). CHN anal. calcd (found) for C32H52Mo8N16O26: C, 20.84 (21.01); H, 2.84 (2.76); N, 12.15 (11.98). IR spectrum, ν (cm^{-1}): 3113 (m), 1581 (m), 1543 (m), 1454(m), 1406(m), 1371(m), 1313 (m), 1273 (m), 1243 (m), 1097 (s), 933 (s), 897 (s), 848 (s), 769 (s), 710 (s), 641(s), 556 (s), 523 (s), 487(s), 441 (s).

Synthesis of 2: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.247 g, 0.2 mmol) in 1-methylimidazole (10 mL) was allowed to be sealed in a 25 mL bunsen beaker container, which was heated to 70 °C under stirrings. After the color of the reaction solution turned clear, the resultant was filtered to give a light yellow filtrate. Colorless crystals of **2** were formed after 2 days, Yield: 90% (based on Mo). CHN anal. calcd (found) for C40H64Mo8N20O26: C, 23.92 (24.11); H, 3.21 (3.29); N, 13.95

(13.84). IR spectrum, ν (cm^{-1}) : 3113(m), 1636(m), 1581(m), 1544 (m), 1531 (m), 1455(m), 1405(w), 1372(w), 1313(w), 1273(m), 1243(m), 1114(w), 1098(m), 932(s) , 897(s), 848(s), 769 (m),748(w), 709(w), 669(s), 555(s), 522(m), 486(m), 441(m).

Synthesis of 3: The synthetic procedure was the same as for compound **1** except that eIM was used instead of mIM. Yield: 75% (based on Mo). CHN anal. calcd (found) for C30H52Mo8N12O26: C, 20.42 (20.58); H, 2.97 (3.05); N, 9.53 (9.69). IR spectrum, ν (cm^{-1}) : 3125(m), 2981(m), 2939(m), 1574(m), 1540(m), 1446(m), 1405(w), 1284(m), 1240(m), 1098(m), 932(s), 843(s), 766(m), 679(s), 628(w) , 559(m), 525(m), 482(m).

Synthesis of 4: The synthetic procedure was the same as for compound **2** except that eIM was used instead of mIM. Yield: 72% (based on Mo). CHN anal. calcd (found) for C40H56Mo8N16O26: C, 24.68 (24.31); H, 2.88 (2.61); N, 11.52 (11.24). IR spectrum, ν (cm^{-1}): 3212(m), 2982(m), 2939(m), 1653(w), 1507(s), 1464(m), 1404(w), 1378(w), 1319(s), 1237(s), 1113(s), 1082(s), 1038(m), 935(s), 877(s), 846(m), 822(m), 751(s), 660(s).

Synthesis of 5: H_2MoO_4 (0.16 g, 1 mmol) in 1-isopropylimidazole (5 mL) was allowed to be sealed in a 23 mL Teflon-lined stainless steel container, which was heated to 100 °C under autogenously pressure for 72 hours. Yield: 5% (based on Mo). CHN anal. calcd (found) for C36H64Mo8N12O26: C, 23.39 (23.88); H, 3.49 (3.05); N, 9.09 (9.69). IR spectrum, ν (cm^{-1}) : 31219(m), 2947(w), 1635(w), 1572(s), 1539(s), 1508(s), 1458(s), 1420(s), 1374(s), 1298(s), 1241(s), 1191(m), 1136(m), 1104(s), 939(s), 896(s), 758(m), 559(m), 518(m), 437(m).

Synthesis of 6: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.247 g, 0.2 mmol) in 1-isopropylimidazole (10 mL) was allowed to be sealed in a 25 mL bunsen beaker container, which was heated to 70 °C under stirrings. After the color of the react ion solution turned clear, the resultant was filtered off to give a light yellow filtrate. Colorless crystals of **6** were formed after 6 days, Yield: 8% (based on Mo). CHN anal. calcd (found) for C48H88Mo8N16O28: C, 28.14 (28.48); H, 4.33 (4.85); N, 8.20 (8.69). IR spectrum, ν (cm^{-1}): 3122(m), 2977(m), 1568(s), 1538(s), 1508(s), 1457(s), 1421(s), 1374(m), 1300(m), 1241(s), 1170(w), 1105(s), 933(s), 896(s), 849(m), 759(m), 664(m), 634(m), 559(m), 524(m), 484(m), 435(m).

Synthesis of 7: The synthetic procedure was the same as for compound **2** except that mIM was used instead of vIM. Yield: 72% (based on Mo). CHN anal. calcd (found) for

C30H36Mo3N12O9: C, 36.13 (36.71); H, 3.613(3.423); N, 16.86 (16.34). IR spectrum, ν (cm^{-1}) : 3108(s), 2993(m), 1647(s), 1504(s), 1419(m), 1376(m), 1329(m), 1287(s), 1220(s), 1088(s), 1004(m), 965(m), 914(m), 872(s), 830(m), 792(s), 650(m), 592(w), 433(m).

Synthesis of 8: MoO_3 (0.286 g, 2 mmol), $N_2H_4·H_2SO_4$ (0.078, 0.6mmol) in 1-methylimidazole (5 mL) was allowed to be sealed in a 23 mL Teflon-lined stainless steel container, which was heated to 100 °C under autogenously pressure for 72 hours. Yield: 80% (based on Mo). CHN anal. calcd (found) for C64H96Mo9N32O32S3: C, 27.60 (27.01); H, 3.47 (2.96); N, 16.09 (16.88). IR spectrum, ν (cm^{-1}) : 3111(m), 3107(w), 1790(w), 1701(w), 1611(m), 1540(s), 1520(s), 1474(m), 1426(s), 1373(m), 1339(m), 1279(m), 1234(m), 1207(s), 1134(s), 1099(s), 985(m), 931(s), 908(s), 834(m), 801(m), 745(s), 655(s), 611(s), 589(w), 470(m), 433(m).

Synthesis of 9: $(NH_4)_6Mo_7O_{24}·4H_2O$ (0.247 g, 0.2 mmol), $N_2H_4·H_2SO_4$ (0.013 g, 0.1 mmol) in 1-methylimidazole (10 mL) was allowed to be sealed in a 25 mL bunsen beaker container, which was heated to 70 °C under stirrings. After the color of the react ion solution turned clear, the resultant was filtered off to give a light yellow filtrate. Colorless crystals of **9** were formed after 3 days, Yield: 85% (based on Mo). CHN anal. calcd (found) for C12H18MoN6O3: C, 36.90 (36.61); H, 4.61 (4.26); N, 21.52 (21.98). IR spectrum, ν (cm^{-1}): 3109(m), 2926(w), 1919(s), 1580(m), 1541(m), 1515(s), 1455(m), 1413(s), 1371(m), 1277(s), 1244(m), 1233(m), 1096(s), 930(m), 900(m), 845(m), 768(w), 551(w),432(w).

(2) Crystal data and structure refinements for compounds 1–9

Single-crystal X-ray diffraction data for compounds **1**–**9** were conducted on a Bruker-AXS CCD diffractometer equipped with a graphite-monochromated Mo Ka radiation (k = 0.71073 Å) at 296 K. All absorption corrections were applied using multi-scan technique. The structures were solved by the direct method and refined through full-matrix least-squares techniques method on F^2 using the SHELXTL 97 crystallographic software package[1, 2]. The hydrogen atoms of the organic ligands were refined as rigid groups. The high R-factors of 2 may be due to the quality of the crystals and the disordered atoms. Global rigid bond restraints (SIMU) were applied to keep thermal parameters reasonable for compound **2**. The atom C16 in compound **3** is left isotropic, because it is the disordered atom in the main eIM framework and exhibits high Ueq values compared to other atoms. The atoms (N6, N2, C20, C21, C22) in compound **4** are the disordered atoms in the main eIM framework and exhibit high Ueq values compared to other atoms. However, they could not be better modelled as disordered. For compound **6**, the crystal is a little weakly diffracting, and the atoms (N8, C20, C21, C23, C24) in compound **6** are the disordered atoms in the main iIM framework and exhibit high Ueq values compared to other atoms. The disordered part C atoms and N atoms in compound **6** were refined using C or N atoms split over two equivalent sites, with a total occupancy of 1, respectively. In the $[MO_4]^{2-}$ of compound **8,** because of the similar valence state of Mo^{6+} and S^{6+}, some M sites are actually occupied by these two different atoms, but the sum of the occupancies of Mo/S was constrained to be 1 in the structural refinements. Elemental analyses show the mass ratio of Mo/S being 9, so the occupancies of sulfur are 75% and the molybdenum are 25% in the M sites. Crystallographic data for compounds **1-9** are summarized in Table S1 and S2. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as entries 939800-939805, 939887-939888, 940197.

Table S1. Crystallographic data for compounds **1- 5**

Compounds	***1***	***2***	***3***	***4***	***5***
Formula	C32H52Mo8 N16O26	C40H64Mo8 N20O26	C30H52Mo8 N12O26	C40H68Mo8 N16O26	C36H64Mo8 N12 O26
M_r	1844.42	2008.63	1764.36	1956.58	1848.51
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	P 2_1/c	P 2_1/c	P -1	P2_1/c	P 2_1/c
Temperature	296(2) K	296(2) K	296(2) K	296(2) K	296(2) K
a (Å)	12.025(5)	17.379(3)	11.3366(13)	12.1992(4)	10.1921(4)
b (Å)	19.464(8)	10.932(2)	11.3529(13)	23.5887(6)	21.5036(9)
c (Å)	15.323(5)	24.384(4)	11.3639(14)	11.8092(4)	15.3277(5)
α (deg)	90	90	72.391(2)	90	90
β (deg)	126.97(2)	134.332(8)	71.058(2)	109.758(3)	120.334(2)
γ (deg)	90	90	80.060(2)	90	90
V (Å^3)	2865(2)	3313.8(11)	1314.1(3)	3198.20(18)	2899.42(19)
Z	2	2	1	2	2
$D_{calc.}$ (g cm^{-3})	2.138	2.013	2.230	2.015	2.117
$F(000)$	1800.0	1976	860	1896	1816
$R_1[I>2\sigma(I)]$	0.0223	0.1255	0.0234	0.0402	0.0230
$wR_2[I>2\sigma(I)]$	0.0557	0.3294	0.0576	0.1025	0.0767
R_1(all data)	0.0250	0.1302	0.0276	0.0530	0.0282
wR_2(all data)	0.0568	0.3351	0.0604	0.1104	0.1076
GOOF	1.060	1.183	1.027	1.015	1.234
Nref	5161	5970	4733	5655	5221
R_{int}	0.0183	0.0262	0.0147	0.0351	0.0197

Table S2. Crystallographic data for compounds **6-9**

Compounds	***6***	***7***	***8***	***9***
Formula	C48H88Mo8 N16O28	C30H36Mo3 N12O9	C64H96Mo8 N32O32($S_{0.75}Mo_{0.25}$)$_4$	C12H18Mo N6O3
M_r	2104.64	996.53	2785.14	390.26
Crystal system	Monoclinic	Monoclinic	Monoclinic	rhombohedral
Space group	$P2_1/c$	$P\ 2_1$	$P\ 2_1/c$	R-3
Temperature	296(2) K	296(2) K	296(2) K	296(2) K
a (Å)	12.5903(18)	9.6874(7)	15.878(3)	11.6102(9)
b (Å)	11.8542(16)	18.8238(14)	10.1503(19)	11.6102(9)
c (Å)	24.806(3)	10.3652(6)	16.704(3)	19.4306(14)
α (deg)	90	90	90	90
β (deg)	100.449(2)	102.994(7)	115.779(3)	90
γ (deg)	90	90	90	120
V (Å^3)	3640.9(8)	1841.7(2)	2424.1(8)	2268.3(4)
Z	2	2	1	6
$D_{calc.}$ (g cm^{-3})	1.894	1.797	1.908	1.714
F(000)	2040	996	1385.9	1188
$R_1[I>2\sigma(I)]$	0.0850	0.0599	0.0734	0.0380
$wR_2[I>2\sigma(I)]$	0.2152	0.0780	0.1772	0.0663
R_1(all data)	0.1500	0.0973	0.1150	0.0442
wR_2(all data)	0.2680	0.0867	0.2803	0.0706
GOOF	1.015	1.000	1.231	1.119
Nref	8458	5070	4266	912
Rint	0.1035	0.0758	0.0338	0.1244

Table S3. Bond valance sum calculations for compound **1-9.**[3]

1	**Mo site**	Mo1	Mo2	Mo3	Mo4
	BVS	5.69	5.67	5.67	5.57
	assigned O.S.	6	6	6	6
2	**Mo site**	Mo1	Mo2	Mo3	Mo4
	BVS	5.93	5.87	5.6	6.2
	assigned O.S.	6	6	6	6
3	**Mo site**	Mo1	Mo2	Mo3	Mo4
	BVS	6.04	6.08	5.95	6.07
	assigned O.S.	6	6	6	6
4	**Mo site**	Mo1	Mo2	Mo3	Mo4
	BVS	5.93	6.22	5.95	5.91
	assigned O.S.	6	6	6	6
5	**Mo site**	Mo1	Mo2	Mo3	Mo4
	BVS	5.98	5.98	5.92	5.77
	assigned O.S.	6	6	6	6
6	**Mo site**	Mo1	Mo2	Mo3	Mo4
	BVS	6.00	6.05	5.76	5.80
	assigned O.S.	6	6	6	6
7	**Mo site**	Mo1	Mo2	Mo3	
	BVS	5.76	5.73	5.89	
	assigned O.S.	6	6	6	
8	**Mo site**	Mo1	Mo2		
	BVS	5.26	4.93		
	assigned O.S.	5	5		
9	**Mo site**	Mo1			
	BVS	5.74			
	assigned O.S.	6			

(3) Crystal structure of $[\gamma\text{-}Mo_8O_{26}]^{4-}$ and $[Mo_8O_{26}N_2]^{4-}$ in compounds 1-6.

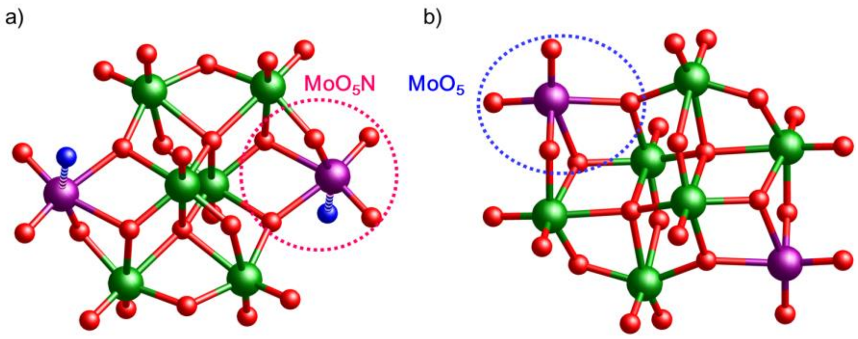

Fig. S1 The structure of (a) organic functionalization of $[Mo_8O_{26}N_2]^{4-}$ in compounds **1-6 and** (b) $[\gamma\text{-}Mo_8O_{26}]^{4-}$. Color code: Mo($MoO_6$), green; Mo ($MoO_5$), purple; O, red; N, blue; C, gray.

(4) IR Spectra of compounds 1-9.

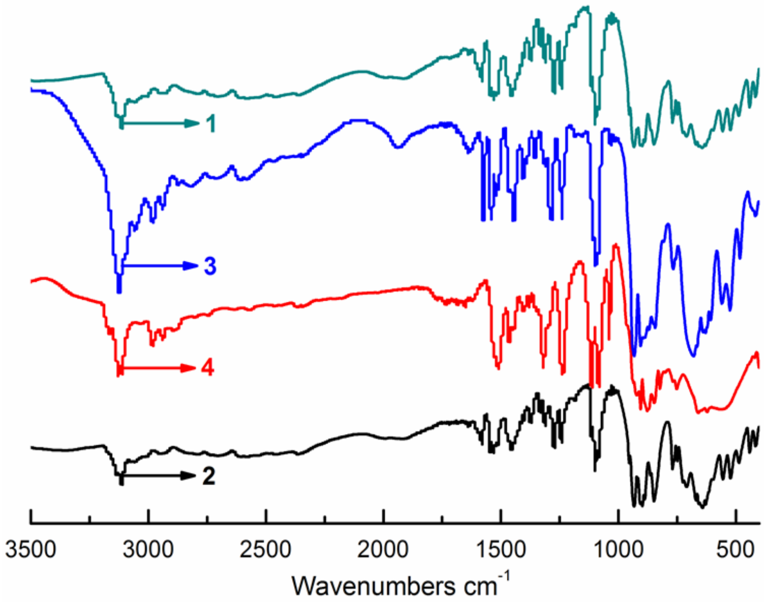

Fig. S2 The FT-IR spectra of compounds **1-4**.

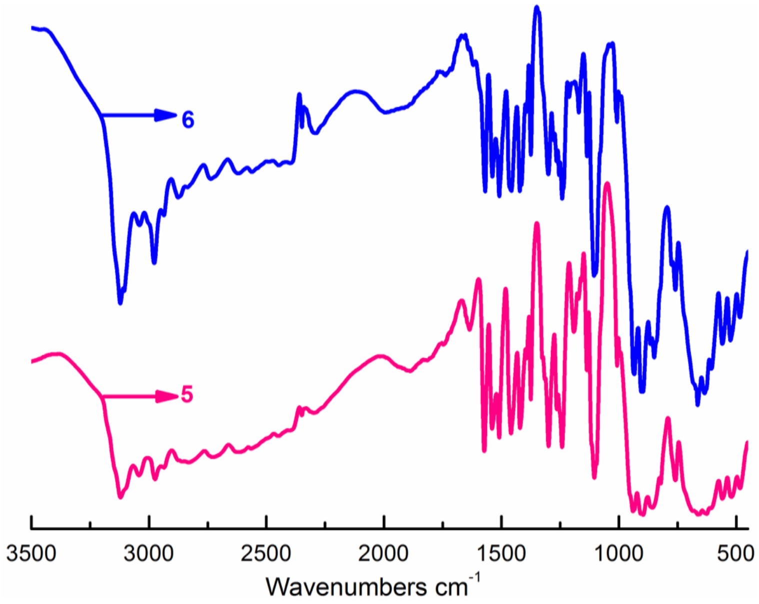

Fig. S3 The FT-IR spectra of compounds **5-6**.

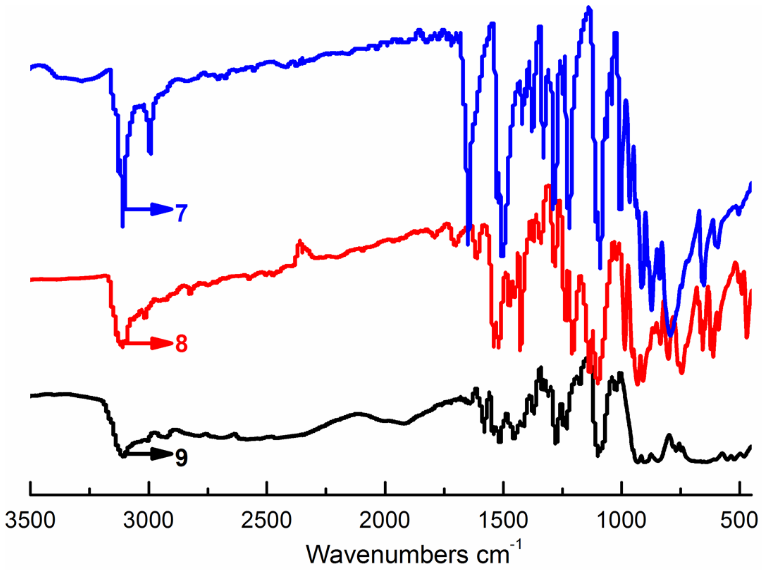

Fig. S4 The FT-IR spectra of compound **7-9**.

(5) The UV-vis absorption spectra of compounds 1-4 and 7-9.

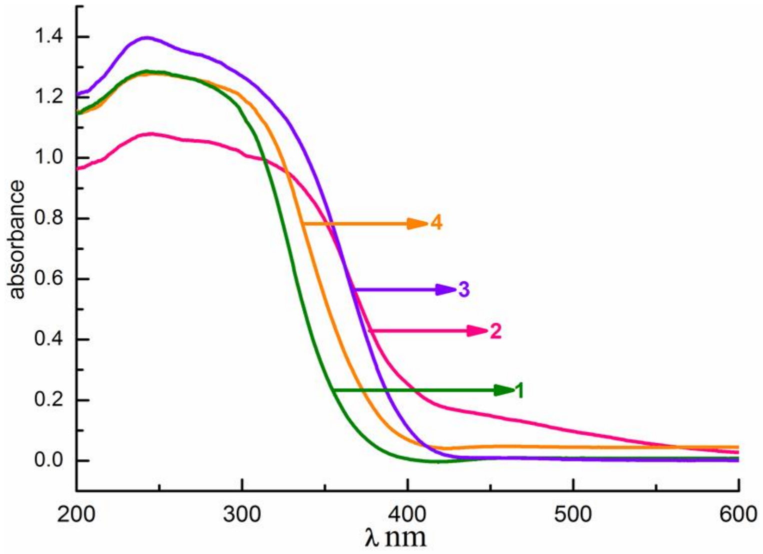

Fig. S5 The UV-vis absorption spectra of **1-4.**

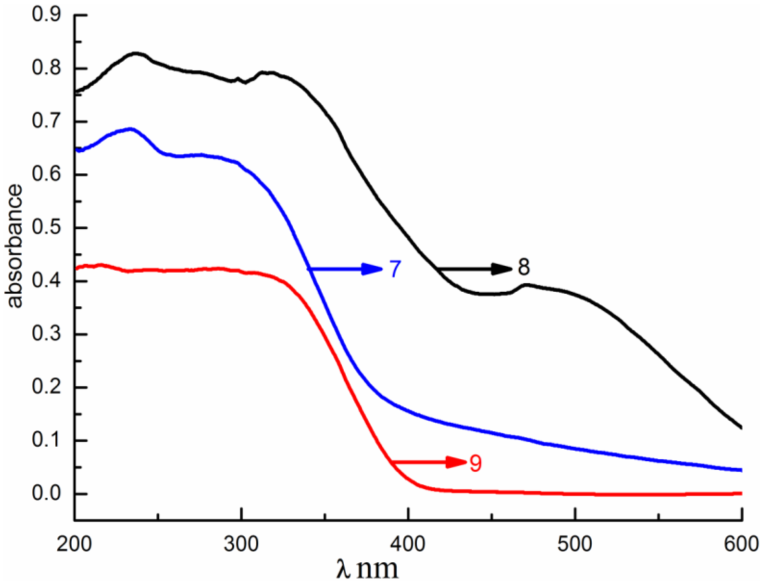

Fig. S6 The UV-vis absorption spectra of **7-9.**

The diffuse reflectance spectra of compounds **1-4** and **7-9**, recorded at room temperature, are presented in Fig. S5-6. The oxygen-to-metal charge transfer absorption maxima occur at 245 nm for **1-4**; 235, 298, 318 nm for **7**; 233, 276 nm for **8**; 285, 308 nm for **9**[4, 5].

(6) The luminescence spectra of compounds 1-4 and 7-9

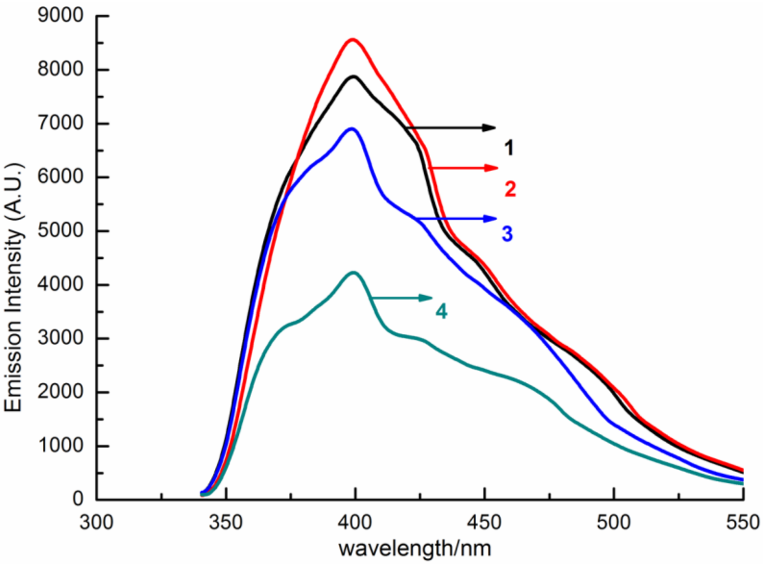

Fig. S7 The luminescence spectra of compounds **1-4.**

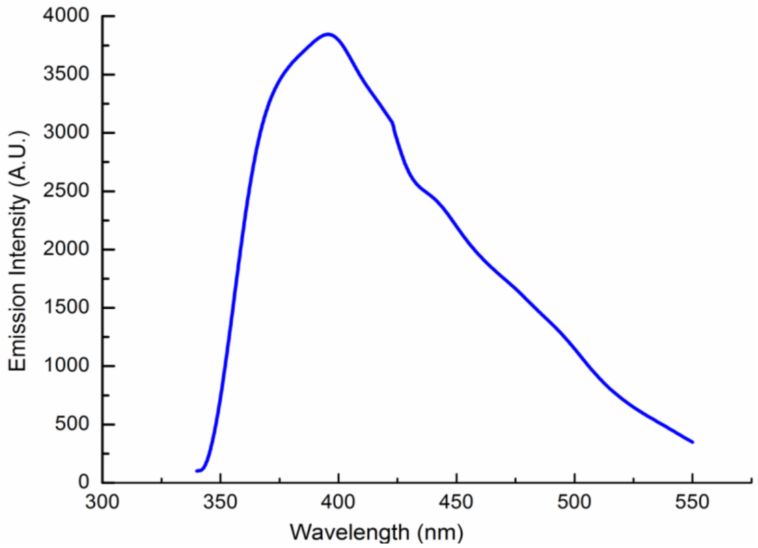

Fig. S8 The luminescence spectrum of compounds **7.**

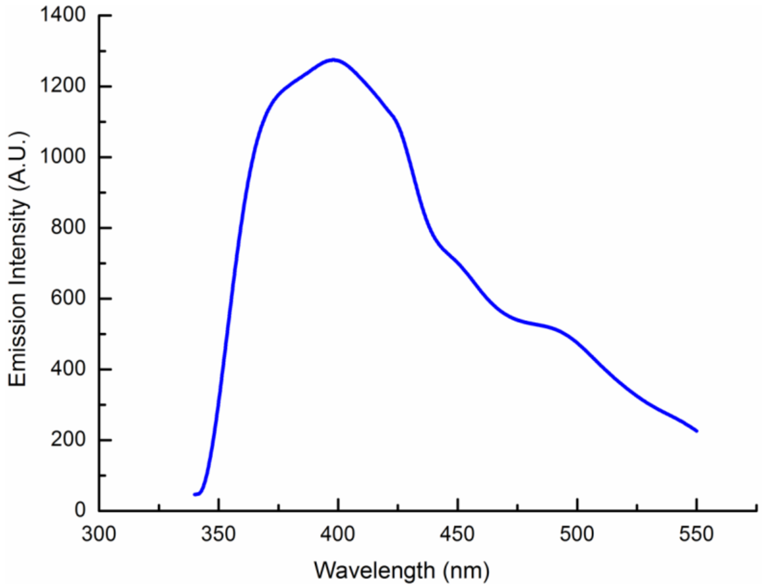

Fig. S9 The luminescence spectrum of compound **8.**

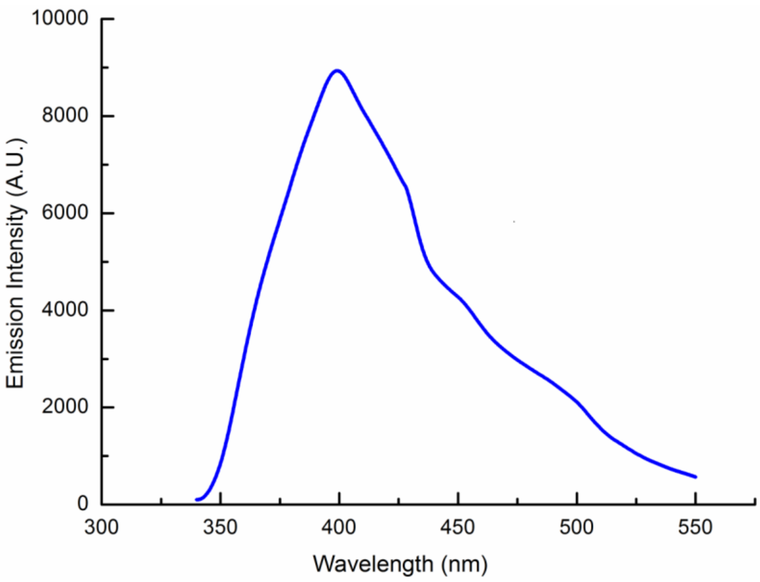

Fig. S10 The luminescence spectrum of compound **9.**

The emission spectra of compounds **1-4** an**d 7-9** in the solid state at room temperature are depicted in Fig.S9-12. It can be observed that intense emissions occur at 399 nm (Fig. S9, λ_{ex} = 320 nm) for **1- 4**, 396 nm (Fig. S10, λ_{ex} = 320 nm) for **7**, 398 nm (Fig. S11, λ_{ex} = 320 nm) for **8**, 399 nm (Fig. S12, λ_{ex} = 320 nm) for **9**, which may be assigned to the intraligand fluorescent emission[6, 7].

(7) ESI-MS spectra of compounds 1-4 dissolved in water.

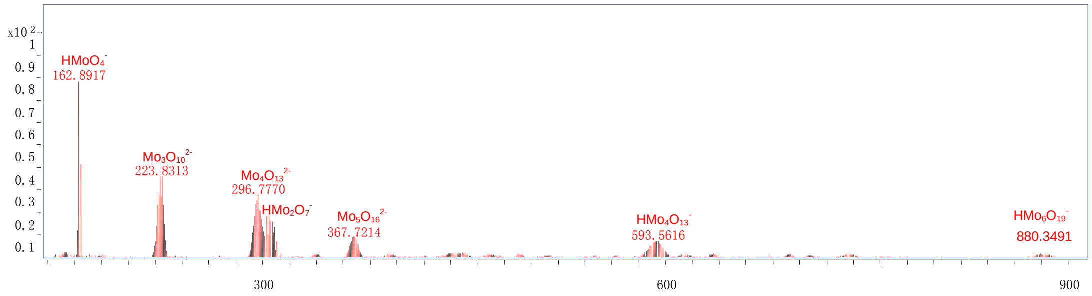

Fig.S11 Negative ion mass spectrum of compound **1** dissolved in H_2O.

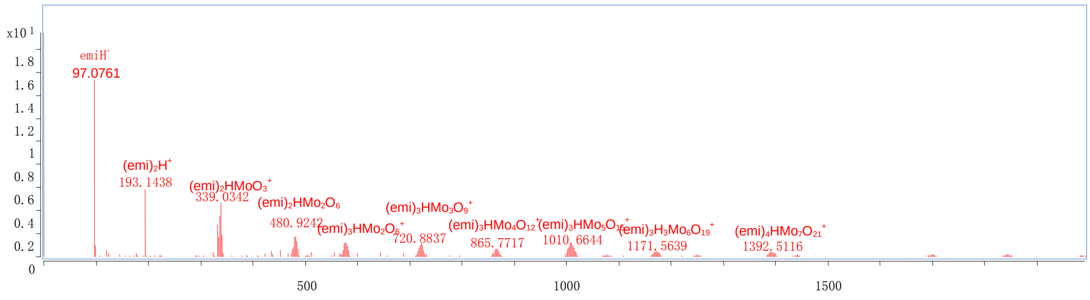

Fig. S12 Positive ion mass spectrum of compound **2** dissolved in H_2O.

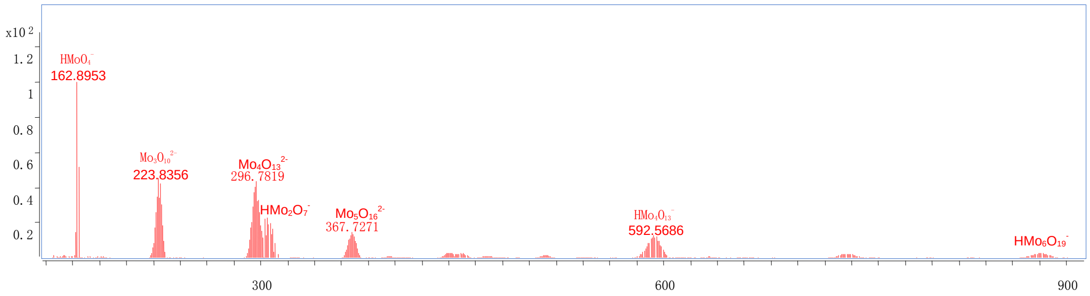

Fig. S13 Negative ion mass spectrum of compound **2** dissolved in H_2O.

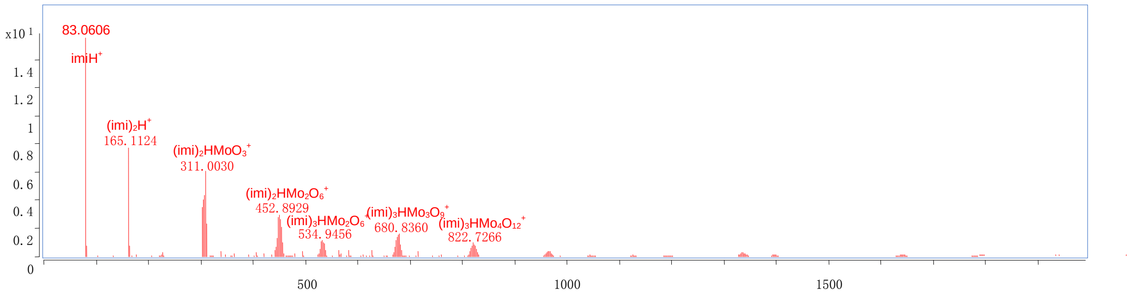

Fig. S14 Positive ion mass spectrum of compound **3** dissolved in H_2O.

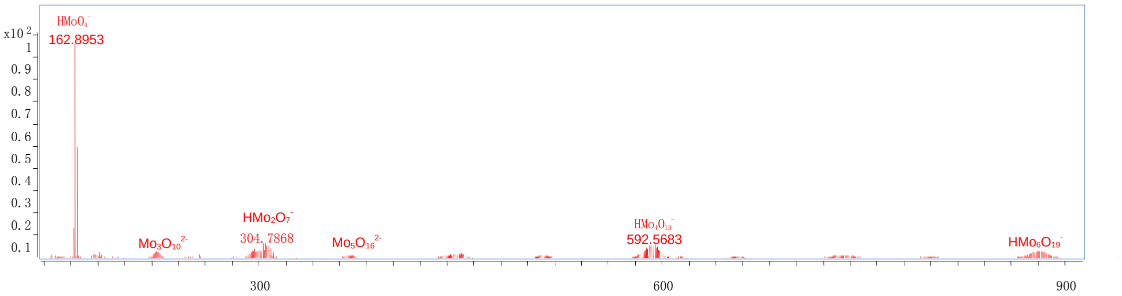

Fig. S15 Negative ion mass spectrum of compound **3** dissolved in H_2O.

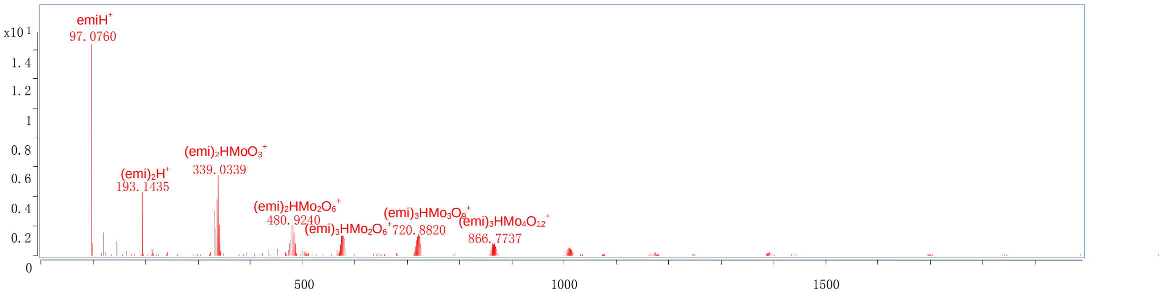

Fig. S16 Positive ion mass spectrum of compound **4** dissolved in H_2O.

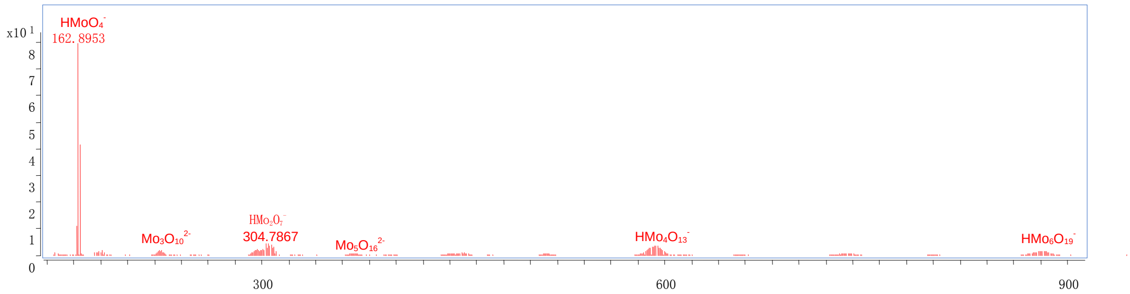

Fig. S17 Negative ion mass spectrum of compound **4** dissolved in H_2O.

(8) The 3D supramolecular framework based on H-bonds of 1-4 and 6-7.

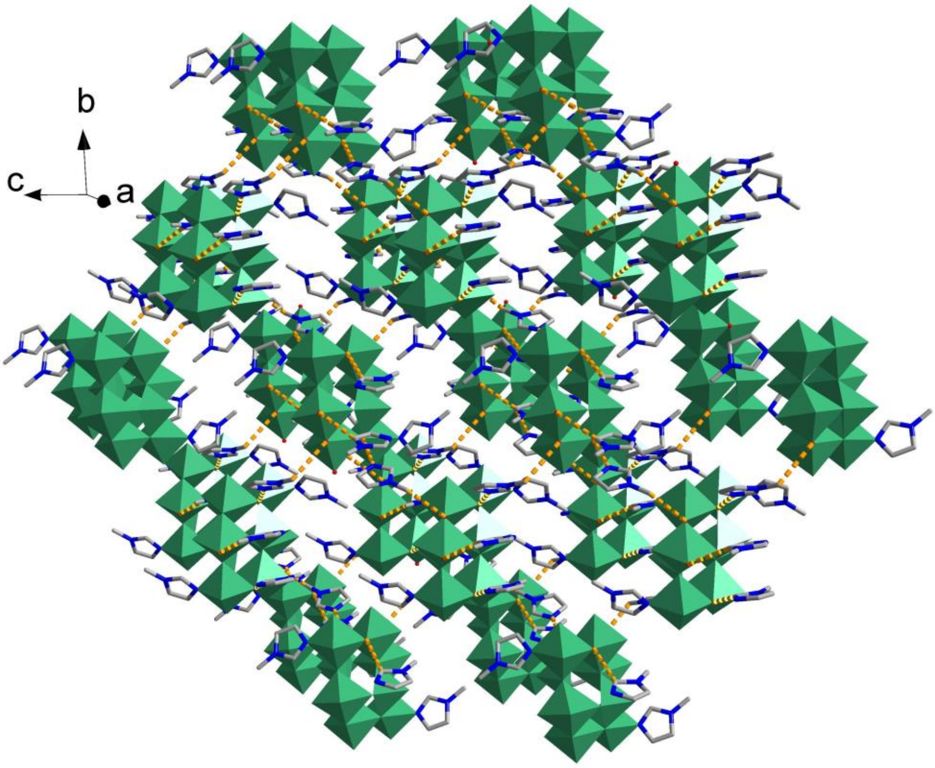

Fig. S18 The 3D supramolecular of compound **1.**

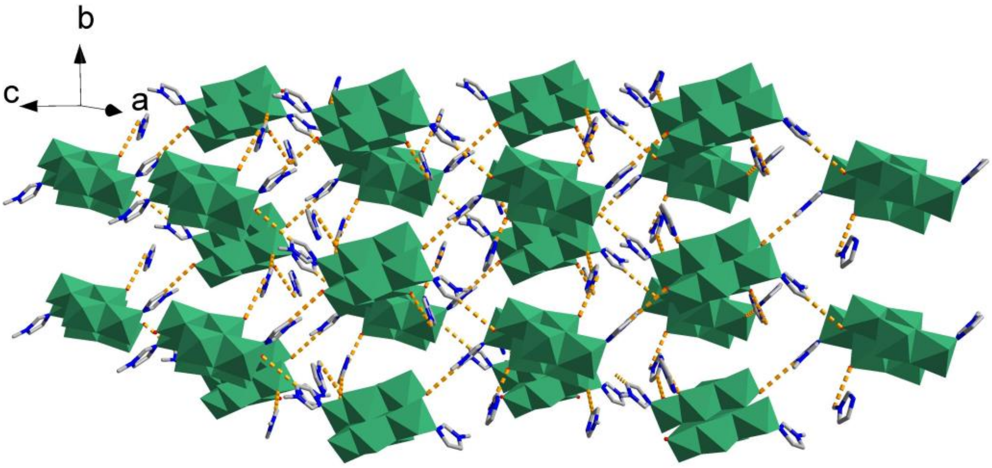

Fig. S19 The 3D supramolecular of compound **2.**

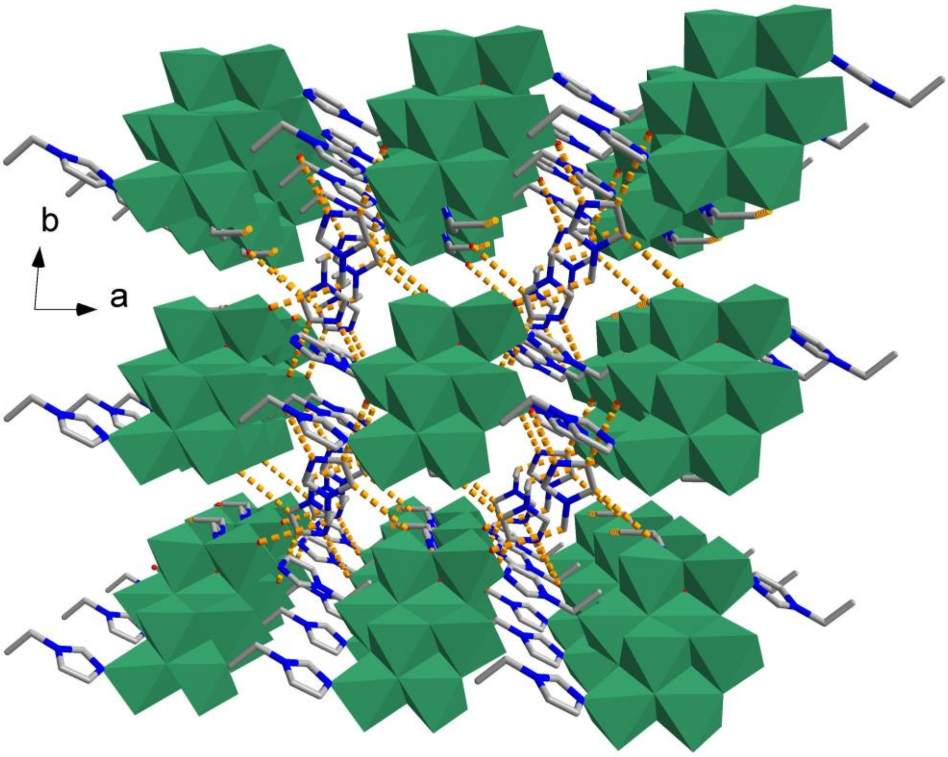

Fig. S20 The 3D supramolecular of compound **3.**

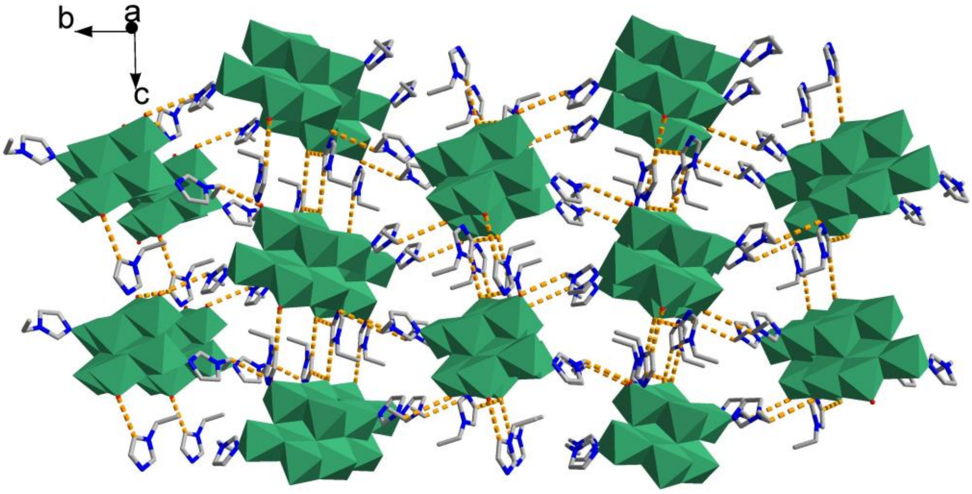

Fig. S21 The 3D supramolecular of compound **4.**

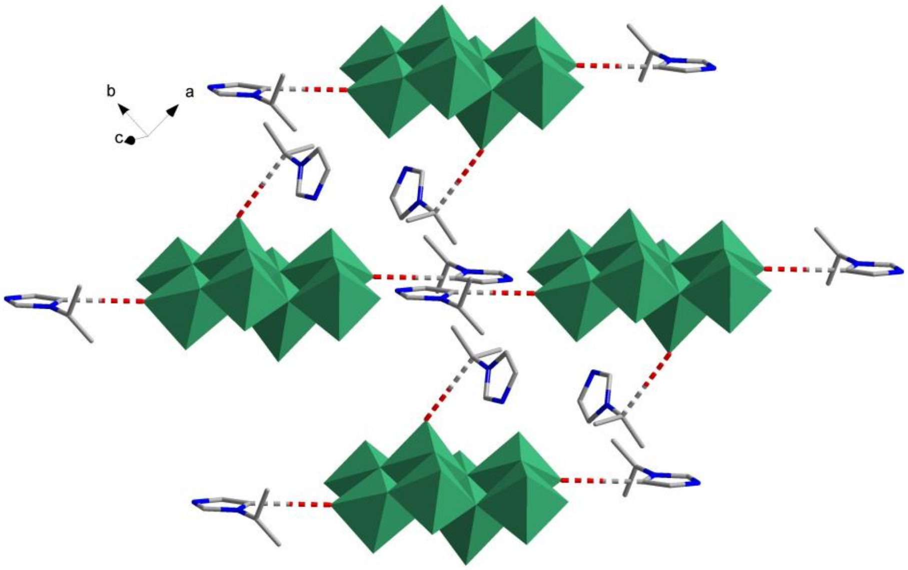

Fig. S22 The 3D supramolecular of compound **6.**

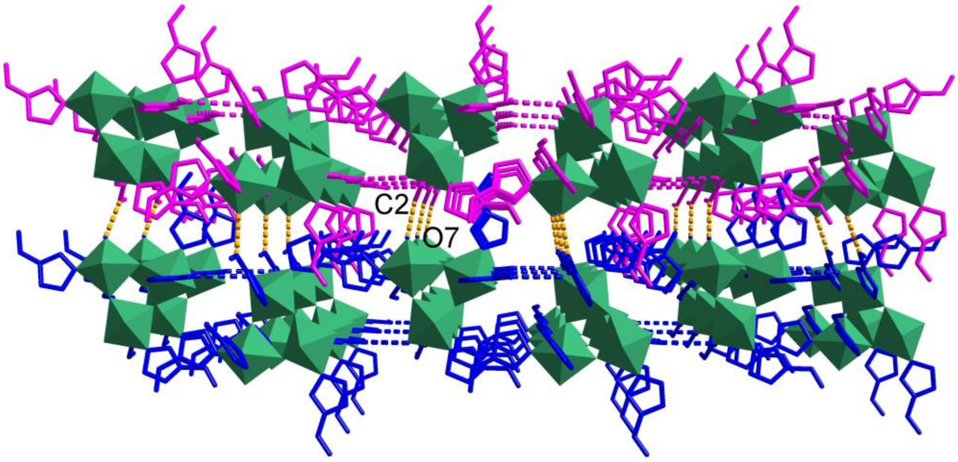

Fig. S23 The 3D supramolecular of compound **7.**

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