Electronic Supplementary Information

Re-understanding photoinduced charge transfer process of ammonium polyoxomolybdate

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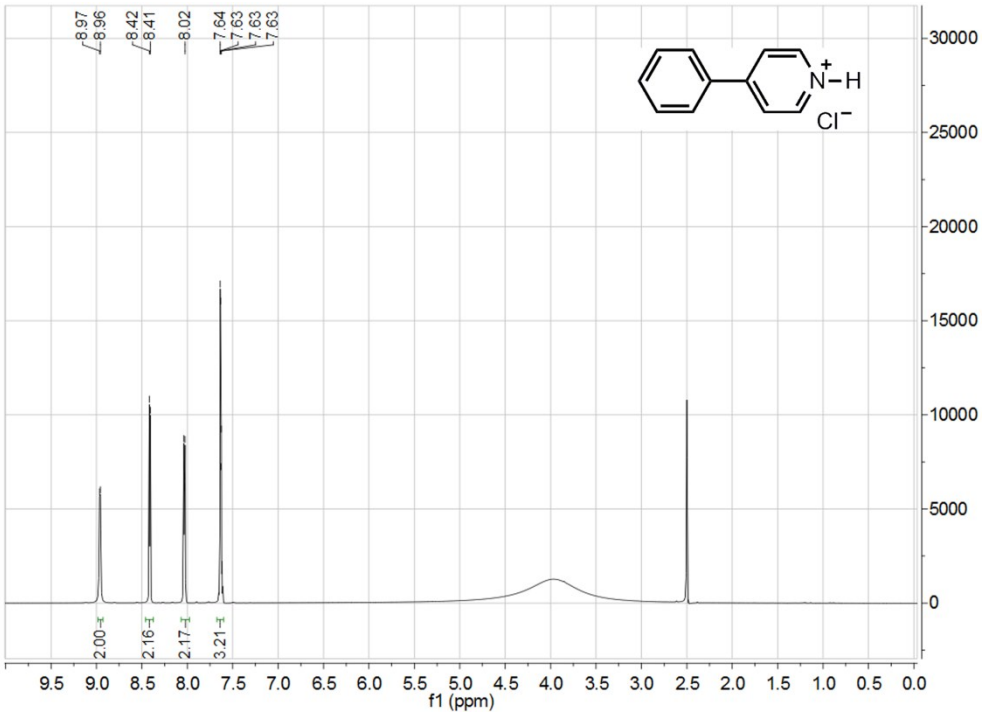


Fig. S1 ^{1}H NMR of 4-phenylpyridine hydrochloride (4PPHCl) in DMSO.

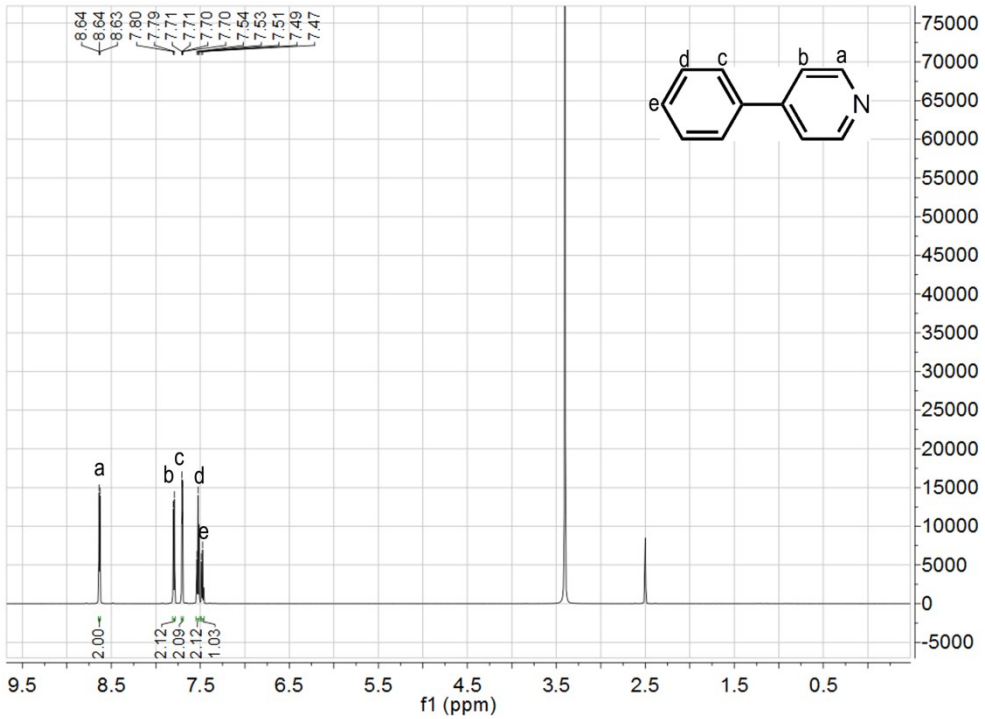


Fig. S2 ^{1}H NMR of 4-phenylpyridine (4PP) in DMSO.

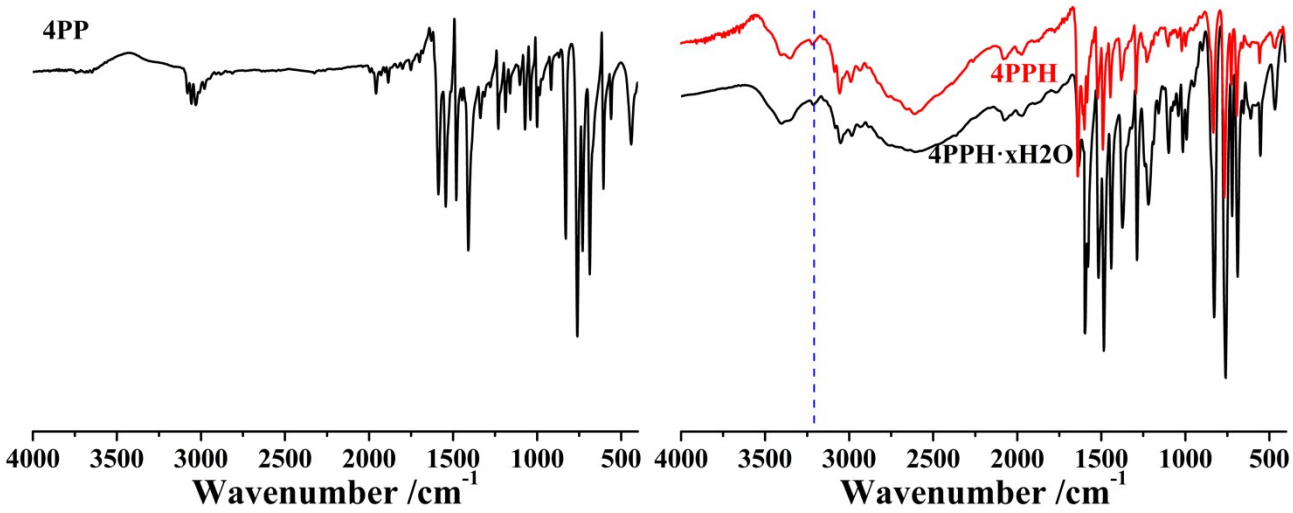


Fig. S3 FT-IR spectra of 4-phenylpyridine (left) and 4-phenylpyridine hydrochloride (right). Labels: **4PP**: 4-phenylpyridine; **4PPH·xH2O**: aqueous 4-phenylpyridine hydrochloride; **4PPH**: anhydrous 4-phenylpyridine hydrochloride.

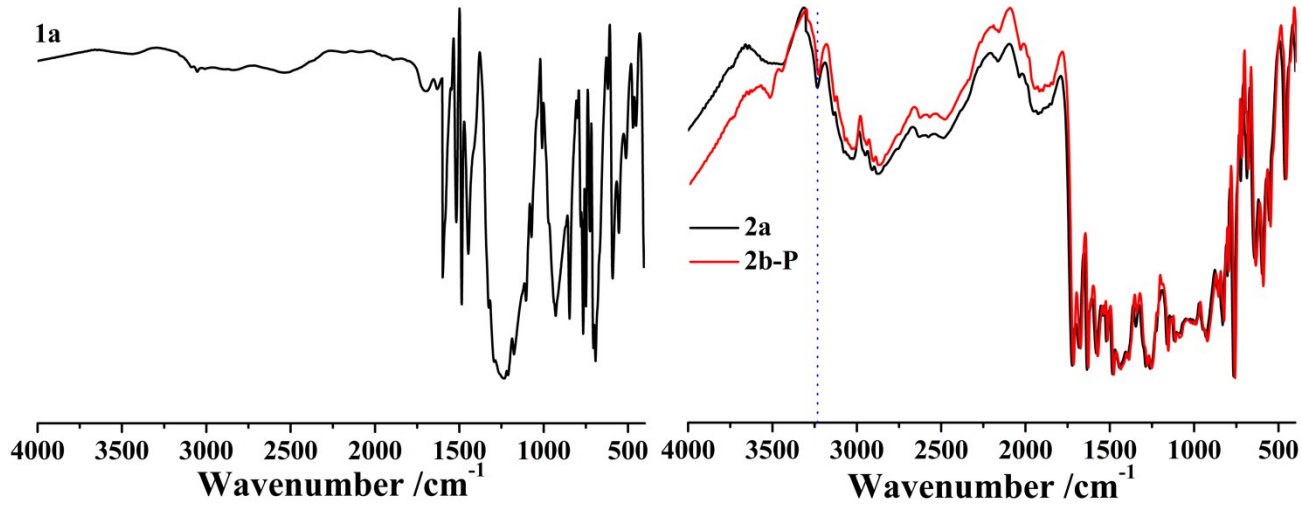


Fig. S4 IR patterns of **1** (left) and **2** (right). Labels: **1a** and **2a**: before irradiation, **2b-P**: after irradiation.

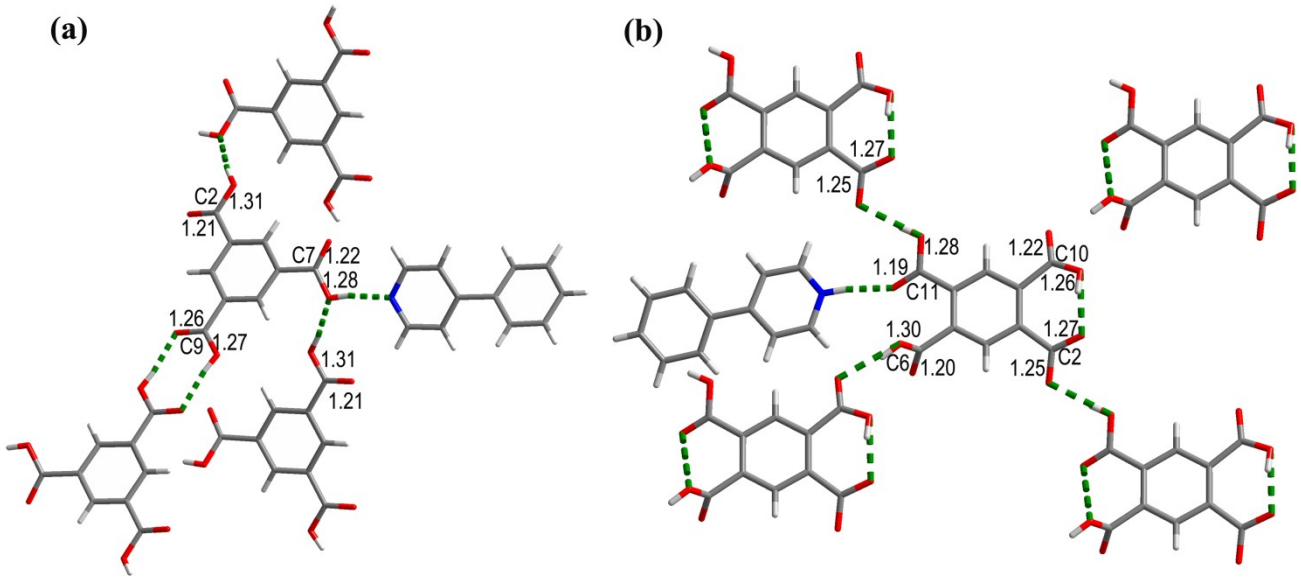


Fig. S5 H-bonds around the trimesic acid and pyromellitic acid in compounds **1** (a) and **2** (b), respectively. All distances for H bonds are labelled in angstrom.

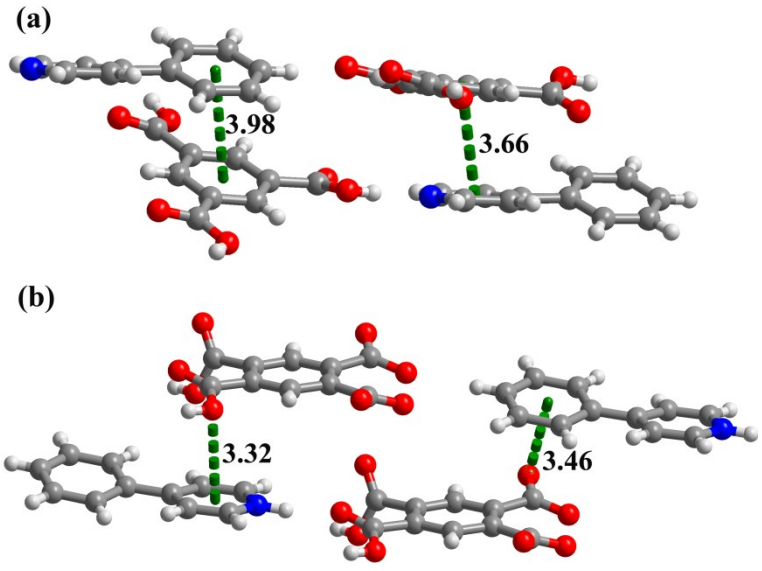


Fig. S6 (a) π···π stacking interactions in compound **1**; (2) p···π stacking interactions around benzene, pyridine rings and O atoms from pyromellitic acid in compound **2**. All distances for H bonds are labelled in angstrom. Color scheme: carbon, grey-50%; nitrogen, blue; oxygen, red; hydrogen, grey-25%.

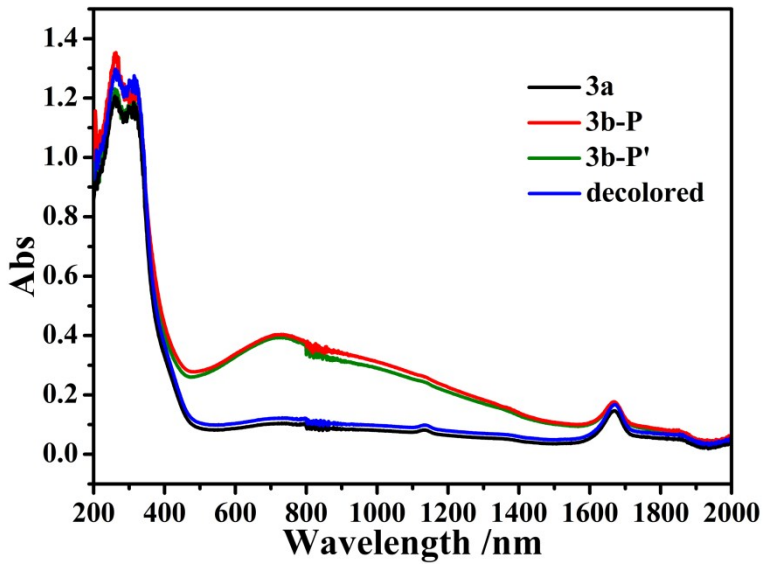


Fig. S7 UV–Vis absorption spectra of **3** in the photochromic process. Labels: **3a**: before photo irradiation; **3b-P**: after exposure in a 300 W Xe lamp; **decolored**: heating in 120 °C for 2 h; **3b-P′**: the decolored samples exposed to the same Xe lamp again.

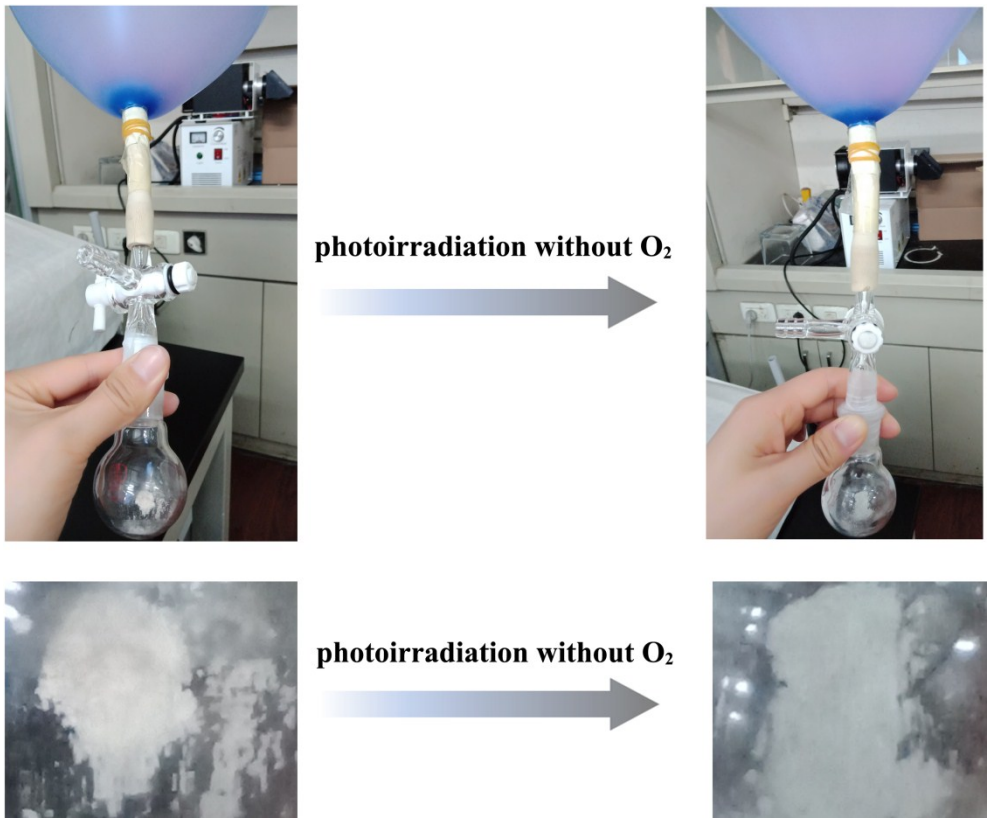


Fig. S8 Photochromism of compound **3** at room temperature in N_2. The balloon is filled with nitrogen.

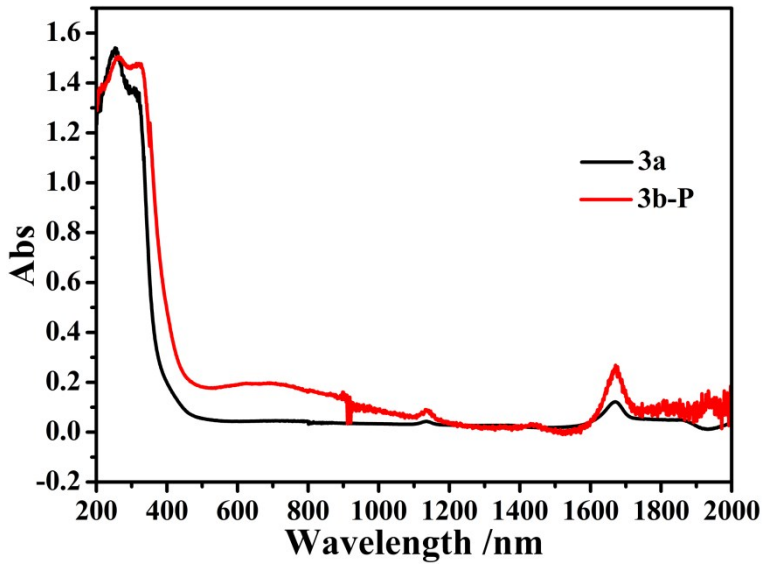


Fig. S9 UV–Vis absorption spectra of **3**. Labels: **3a**: before photo irradiation; **3b-P**: Photochromism of compound **3** at room temperature in N_2.

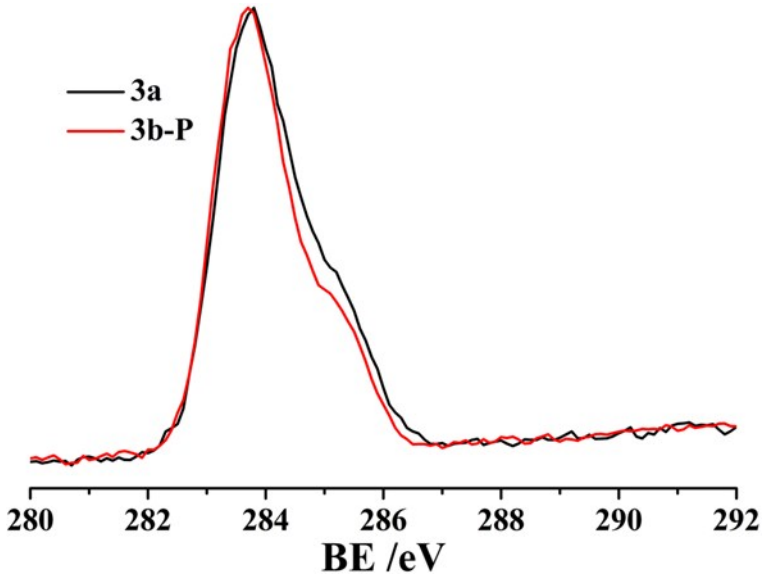


Fig. S10 C 1s XPS (Al-*Kα*) core-level spectra of compound **3** before and after photo irradiation in a vacuum. Labels: **3a**, before irradiation; **3b-P**, after photo irradiation; BE: Binding Energy.

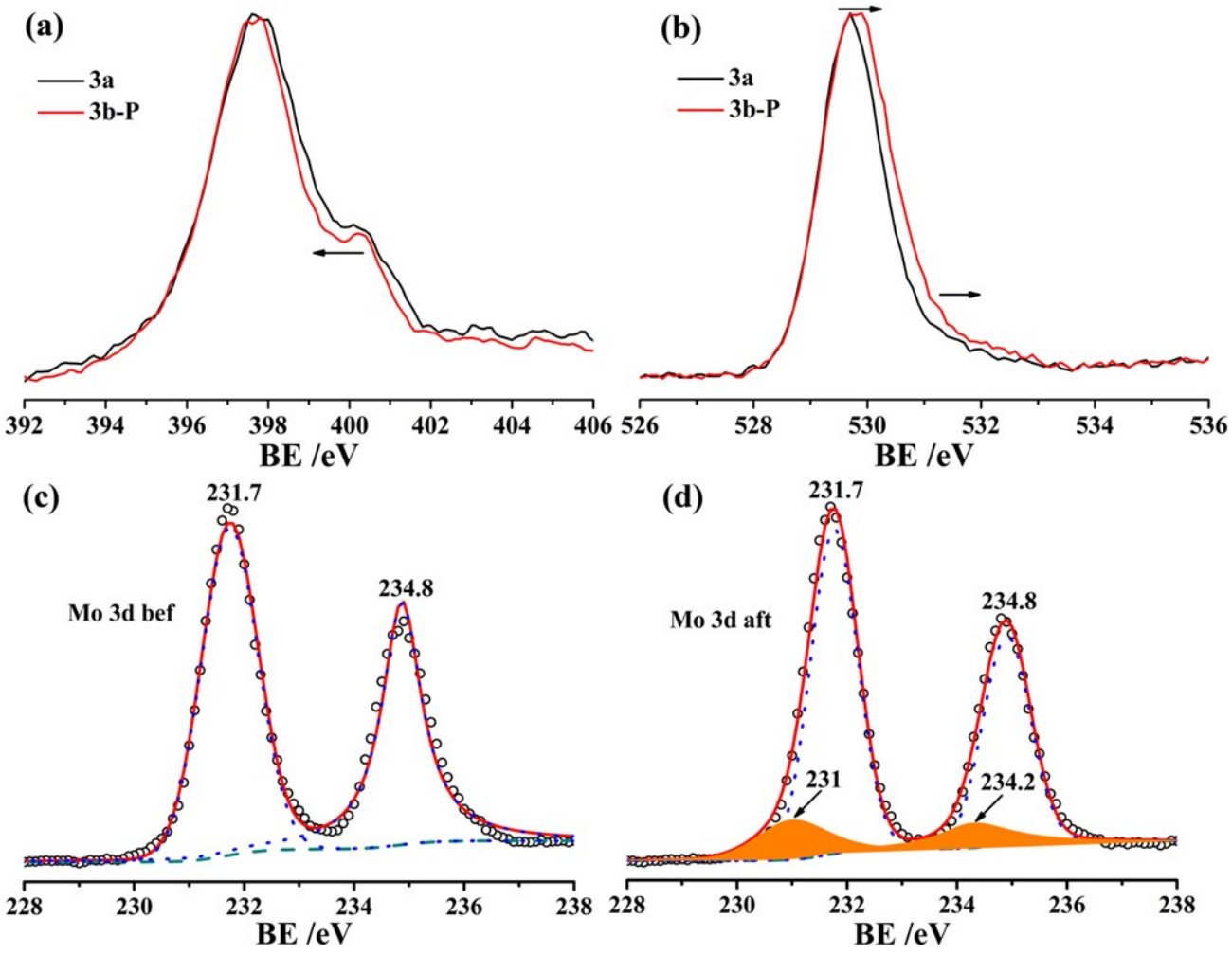


Fig. S11 The core-level spectra of N 1s XPS (Al-*Kα*) (a), O 1s XPS (Al-*Kα*) (b), Mo 3d XPS (Al-*Kα*) before photo irradiation (c), Mo 3d XPS (Al-*Kα*) after photo irradiation (d) for compound **3** in a vacuum. Labels: **3a** before irradiation; **3b-P** after photo irradiation; BE: Binding Energy.

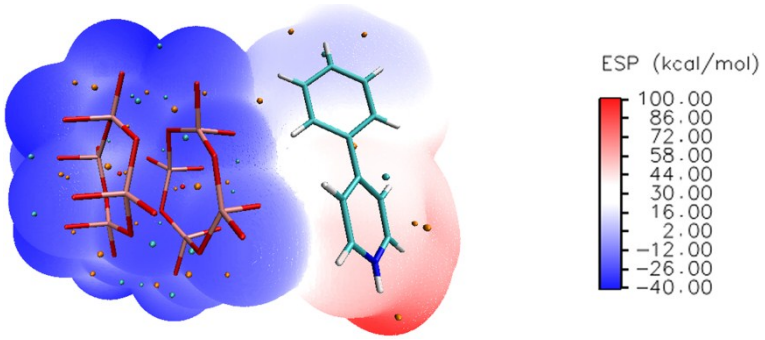


Fig. S12 Electrostatic potential (ESP) surfaces of the neutral coordination molecule in **3** before irradiation. Significant surface local minima and maxima are represented as orange and cyan spheres, respectively.

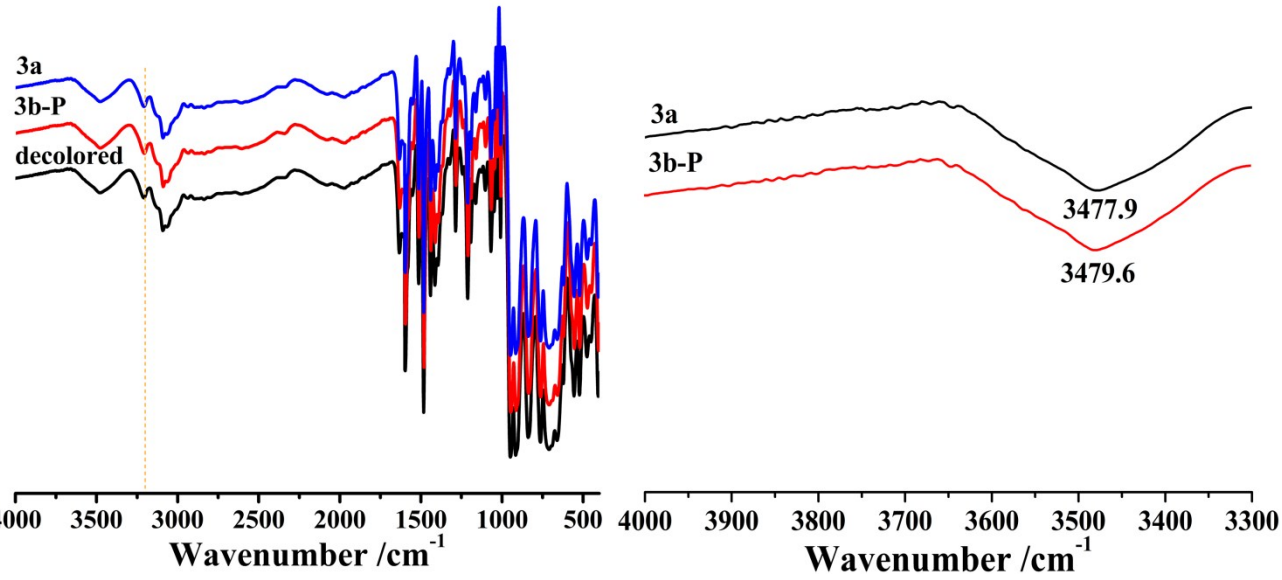


Fig. S13 FT-IR spectra of **3**. Labels: **3a**, before irradiation; **3b-P**, after photo irradiation; **decolored**, heating in 120 °C for 2 h.

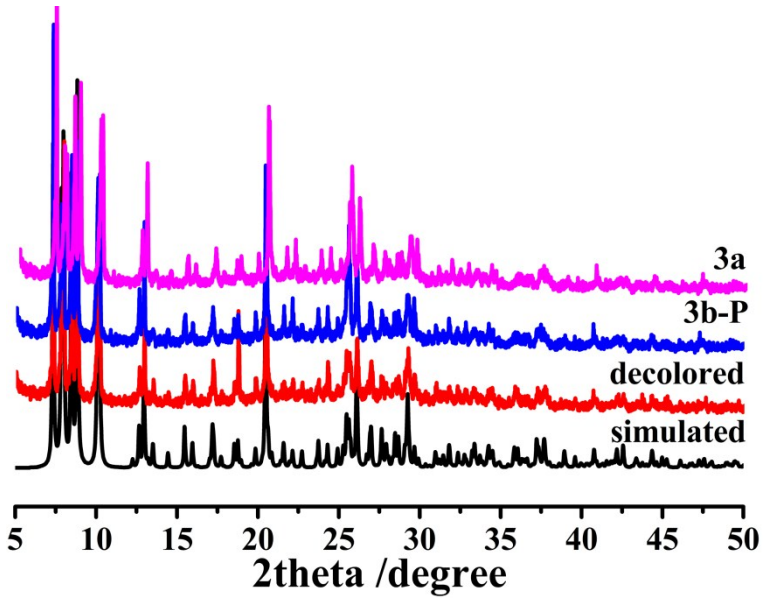


Fig. S14 PXRD patterns of **3**. Labels: **3a**: before irradiation; **3b-P**: after photo irradiation; **decolored**: heating in 120 °C for 2 h; **simulated**: simulated patterns from single-crystal X-ray structure data.

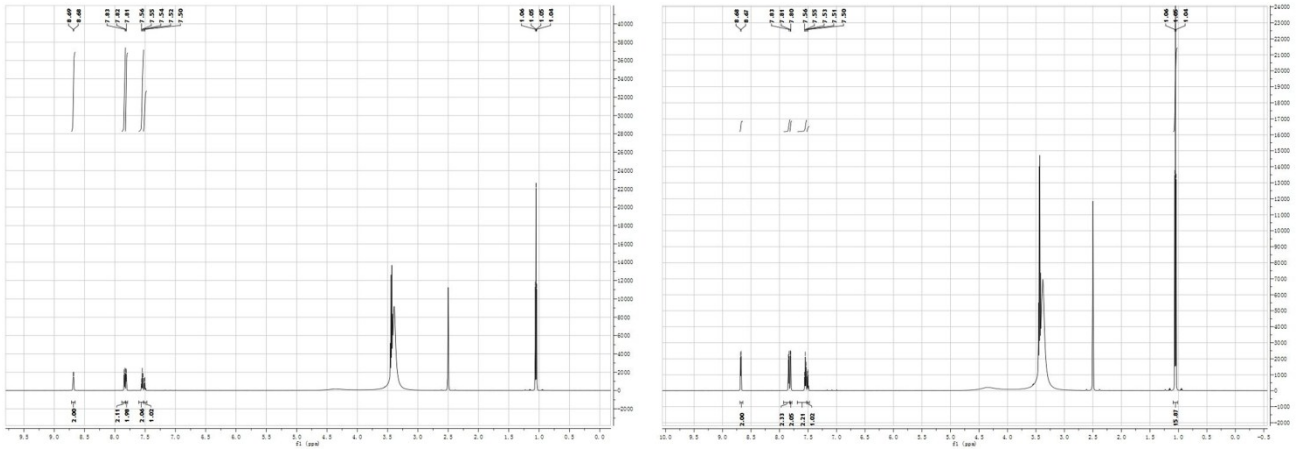


Fig. S15 ^{1}H NMR of compound **3** before and after photo irradiation in DMSO.

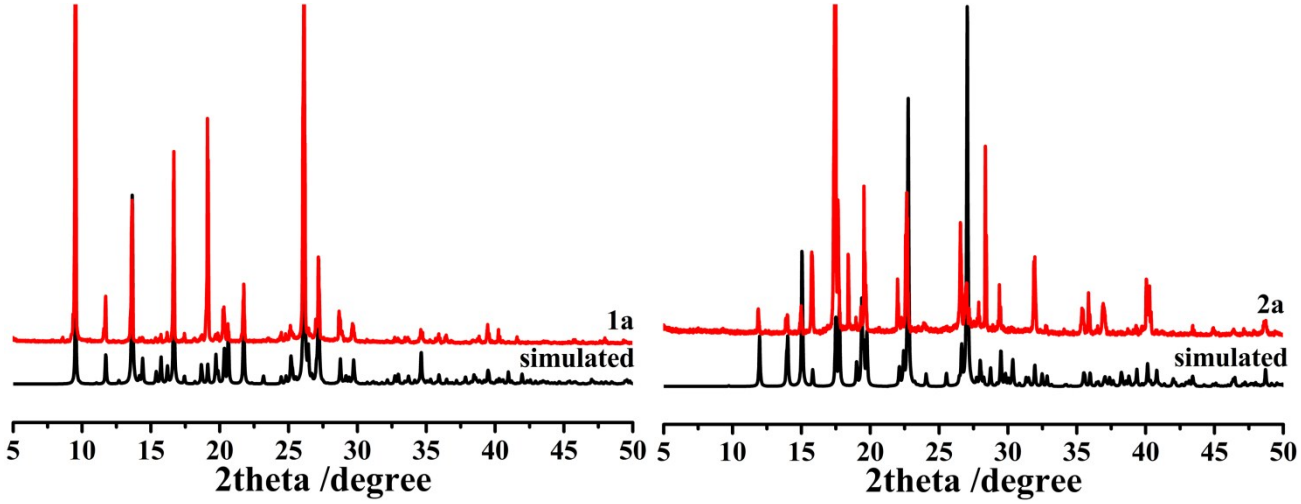
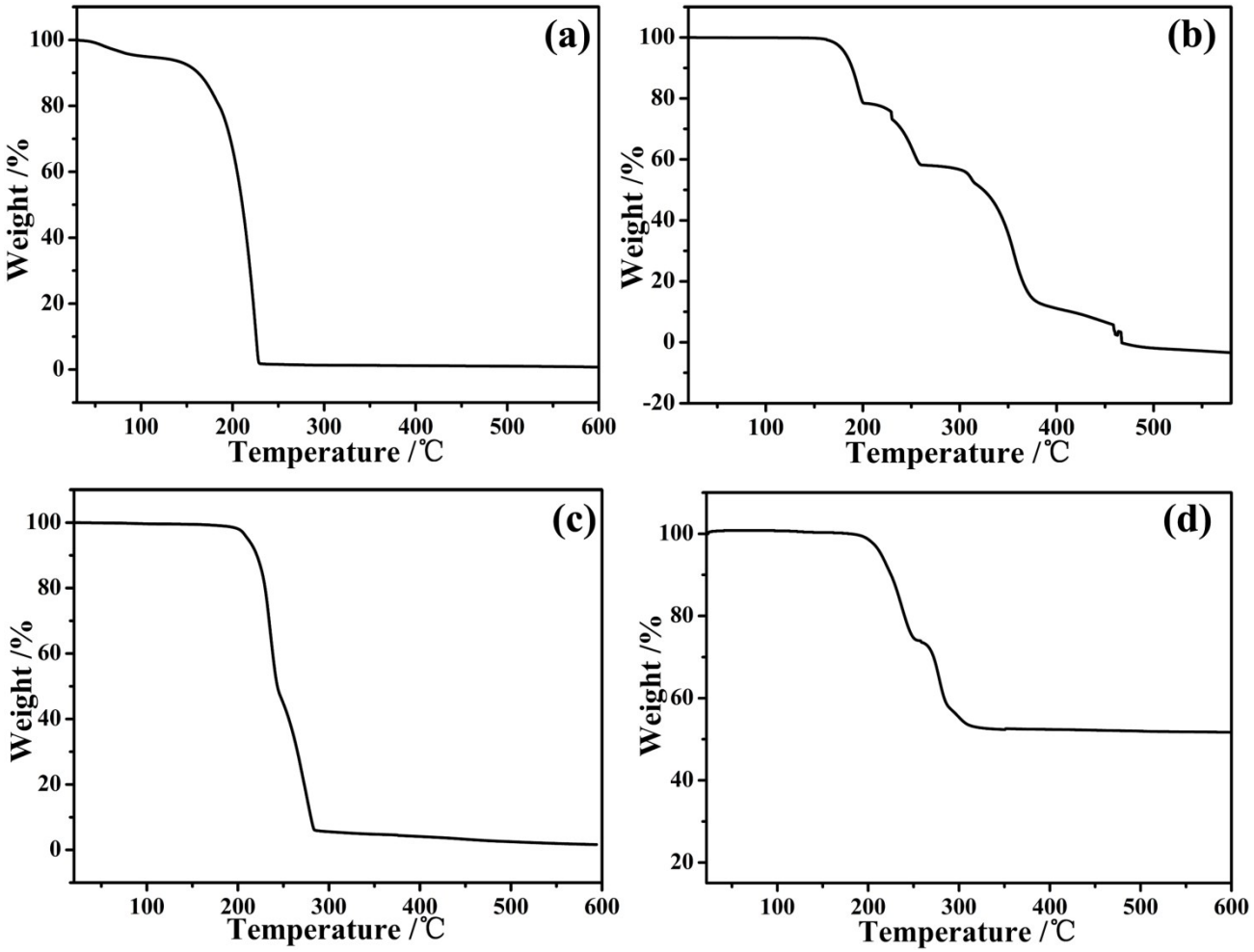


Fig. S16 PXRD patterns of **1** and **2**. Labels: **1a, 2a**: before irradiation; **simulated**: simulated patterns from single-crystal X-ray structure data.



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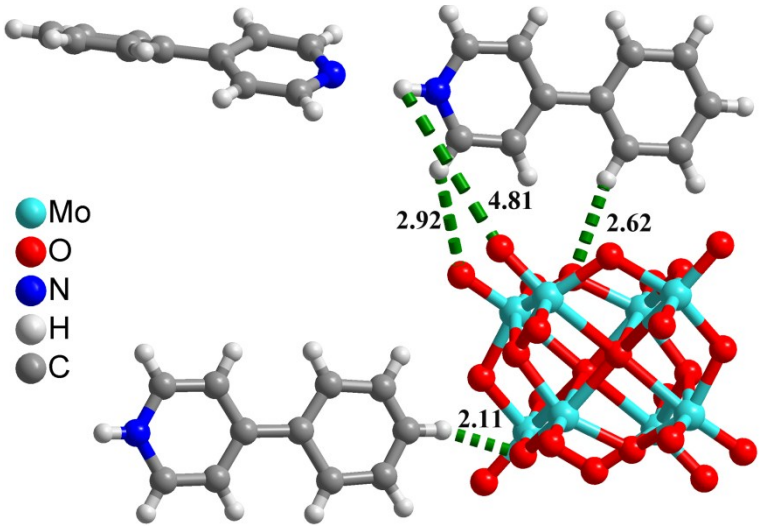

Fig. S18 Molecular structures of compound **3**. All distances for H bonds are labelled in angstrom.

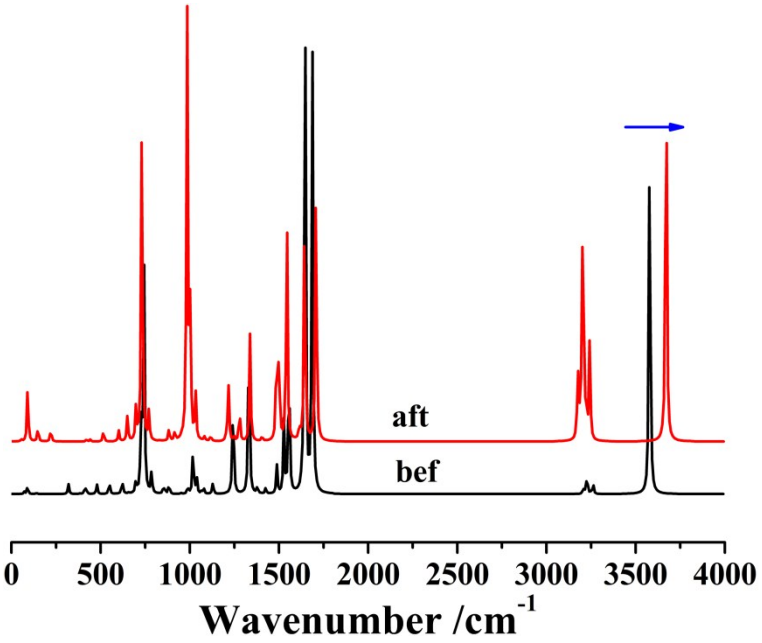

Fig. S19 The infrared theoretical calculation of protonated 4- phenylpyridine (4PPH) before and after accept one electron using the Gaussian 09 package was carried out at the B3LYP/6-31+G(d,p) level.

3. Tables.

Table S1. Crystal Data and Structure Refinements for **1**, **2** and **3**.

Empirical formula	$C_{20}H_{15}NO_6$ **(1)**	$C_{21}H_{15}NO_8$ **(2)**	$C_{66}H_{58}Mo_8N_6O_{26}$ **(3)**
Formula weight	365.33	409.34	2118.70
Temperature /K	273	294	293
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	P_1	$P\bar{1}$

a /Å	10.5965(14)	6.7875(6)	11.4623(5)
b /Å	12.9681(17)	7.4323(7)	13.4719(6)
c /Å	13.0204(17)	9.6959(8)	13.5825(6)
α /deg	90	85.473(5)	114.442(2)
β /deg	106.415(2)	69.797(4)	112.183(2)
γ /deg	90	84.779(5)	90.361(2)
Volume /Å^3	1716.3(4)	456.54(7)	1734.92(13)
Z	4	1	1
D_c /g·cm^{-3}	1.414	1.489	2.208
Absorption coefficient /mm^{-1}	0.106	0.116	1.485
Goodness-of-fit on F^2	1.073	1.024	1.073
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0442, wR_2 = 0.1209	R_1 = 0.0435, wR_2 = 0.1050	R_1 = 0.0434, wR_2 = 0.1104
R indices (all data)	R_1 = 0.0545, wR_2 = 0.1307	R_1 = 0.0604, wR_2 = 0.1162	R_1 = 0.0792, wR_2 = 0.1453

[a]$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, [b]$wR_2 = \{\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(F_o)_2]^2\}^{1/2}$.

Table S2. Selected bond lengths (Å) for **1**, **2** and **3**.

1		**2**		**3**	
O(1)-C(9)	1.2694(19)	O(1)-C(2)	1.244(3)	Mo(1)-O(7)	1.683(5)
O(4)-C(2)	1.3103(18)	O(2)-C(2)	1.270(3)	Mo(2)-O(6)	1.900(4)
N(1)-C(15)	1.326(2)	O(3)-C(11)	1.286(3)	Mo(2)-O(3)	2.341(4)
C(1)-C(2)	1.491(2)	O(8)-C(11)	1.195(3)	Mo(3)-O(12)	1.707(5)
C(4)-C(6)	1.384(2)	O(4)-C(6)	1.300(3)	Mo(4)-O(10)	1.694(5)
O(3)-C(2)	1.2104(18)	O(7)-C(6)	1.202(4)	N(2)-C(11)	1.335(10)
O(6)-C(7)	1.2205(18)	N(1)-C(19)	1.316(5)	N(1)-C(6)	1.319(10)
C(12)-C(16)	1.387(3)	C(8)-C(9)	1.389(3)	C(1)-C(7)	1.398(10)

Table S3. Selected angles (deg) for **1**, **2** and **3**.

1		**2**		**3**	
C(7)-O(2)-H(2)	109.5	O(8)-C(11)-O(3)	124.1(2)	O(7)-Mo(1)-O(5)	103.7(2)
O(6)-C(7)-O(2)	124.39(13)	C(11)-O(3)-H(3)	109.5	O(9)-Mo(2)-O(6)	100.7(2)
C(5)-C(3)-C(7)	121.14(12)	O(1)-C(2)-O(2)	121.6(2)	O(2)-Mo(2)-O(3)	73.07(15)
O(5)-C(9)-C(4)	118.88(13)	O(7)-C(6)-C(3)	123.2(3)	O(13)-Mo(3)-O(3)	94.4(2)

C(14)-C(10)-C(12)	121.20(15)	C(4)-C(9)-C(8)	123.1(2)	O(10)-Mo(4)-O(4)	100.9(2)
N(1)-C(15)-H(10)	119.6	C(3)-C(12)-H(12)	118.4	Mo(4)-O(4)-Mo(3)	115.5(2)
C(19)-C(20)-C(17)	120.5(2)	N(1)-C(14)-H(14)	119.8	C(8)-C(1)-C(7)	116.7(6)
O(3)-C(2)-O(4)	124.03(14)	C(21)-C(22)-H(22)	119.3	N(1)-C(12)-H(9)	119.2