

## Supporting Information

### Four structural diversity MOF-photocatalysts readily prepared for the degradation of methyl violet dye under UV-visible light

#### Materials and Method

All the reagents to perform synthesis were obtained from commercial sources and were used without further purification. Powder X-ray diffraction (PXRD) data were collected using Bruker ADVANCE X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda=1.5418$  Å) at 50 kV, 20 mA with a scanning rate of 6°/min and a step size of 0.02°. Fourier transform infrared (FT-IR) spectra for both the MOFs as KBr discs were recorded on Nicolet Impact 750 FTIR in the range of 400-4000 cm<sup>-1</sup>. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere from room temperature to 900 °C at a heating rate of 10 °C min<sup>-1</sup>. The photocatalytic investigations were carried out using Shimadzu UV-Vis 2501PC recording spectrophotometer.

#### X-ray Crystallography

The single crystal X-ray diffraction data for both the MOFs were collected on a Bruker SMART APEX diffractometer which was equipped with graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) by using an  $\omega$ -scan technique. The structures were solved by direct method (SHLEXS-2014) and refined using the full-matrix least-square procedure based on  $F^2$  (Shelxl-2014) [1]. All the hydrogen atoms were generated geometrically and refined isotropically using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic details and selected bond dimensions for 1-4 are listed in Tables S1 and S2, respectively. CCDC numbers: 2022272-2022275.

#### Synthesis of [Mn<sub>2</sub>( $\mu_2$ -H<sub>2</sub>O)<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (1)

A mixture of H<sub>4</sub>L (0.02 mmol, 0.009 g), MnCl<sub>2</sub>·4H<sub>2</sub>O (0.04 mmol, 0.008 g) and 6 mL of acetonitrile/H<sub>2</sub>O (v/v=1:2) was stirred for 30 min and then transferred and

sealed in a 25-mL Teflon-lined reactor and heated to 120 °C for 72 h, and then cooled to room temperature at a rate of 5 °C/h. Yellow block crystals of **1** were obtained in 52 % yield based on H<sub>4</sub>L. Calcd (%) for **1**, C, 56.38; H, 3.49; N, 1.73; Found C, 56.51; H, 3.45; N, 1.70. IR: 3426(v); 3094(m); 2540(m); 1701(v); 1607(m); 1546(v); 1458(v); 1411(m); 1269(m); 1039(m); 754(v).

[Mn(L)<sub>0.5</sub>(phen)·0.5H<sub>2</sub>O] (**2**)

A mixture of H<sub>4</sub>L (0.02 mmol, 0.009 g), phen (0.02 mmol, 0.004 g), MnCl<sub>2</sub>·4H<sub>2</sub>O (0.04 mmol, 0.008 g) and 6 mL of acetonitrile/H<sub>2</sub>O (v/v=1:2) was stirred for 30 min and then transferred and sealed in a 25-mL Teflon-lined reactor and heated to 120 °C for 72 h, and then cooled to room temperature at a rate of 5 °C/h. Yellow block crystals of **2** were obtained in 49% yield based on H<sub>4</sub>L. Calcd (%) for **2**, C, 60.64; H, 3.39; N, 5.89; Found C, 60.48; H, 3.48; N, 5.94. IR: 3398(vs); 2912(m); 1681(vs); 1593(m); 1546(v); 1431(m); 1293(m); 1059(v); 856(m); 727(v).

[Co(H<sub>2</sub>O)<sub>2</sub>(L)<sub>0.5</sub>(bip)·H<sub>2</sub>O] (**3**)

The synthesis procedure of **3** was analogous to that of **2**, except that phen (0.02 mmol, 0.004 g) was replaced by bip (0.02 mmol, 0.005 g), MnCl<sub>2</sub>·4H<sub>2</sub>O (0.04 mmol, 0.008 g) was replaced by Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.15 mmol, 0.012 g). Pink block crystals of **3** were obtained in 66 % yield based on H<sub>4</sub>L. Calcd (%) for **3**, C, 49.74; H, 3.99; N, 12.61; Found C, 49.89; H, 4.04; N, 12.66. IR: 3365(v); 3155(m); 1620(v); 1566(m); 1404(m); 1364(m); 1248(m); 1113(v); 1032(m); 855(m); 775(v).

[Co<sub>2</sub>(L)(bb)<sub>2</sub>·HbbBr] (**4**)

The synthesis procedure of **4** was analogous to that of **3**, except that bip (0.02 mmol, 0.005 g) was replaced by bb (0.04 mmol) and HbbBr (0.02 mmol). Pink block crystals of **4** were obtained in 61 % yield based on H<sub>4</sub>L. Calcd (%) for **4**, C, 62.04; H, 3.69; N, 9.65; Found C, 62.12; H, 3.64; N, 9.50. IR: 3122(m); 2317(m); 1580(v); 1512(m); 1438(v); 1383(m); 1255(v); 1133(m); 1072(v); 836(m); 773(v).

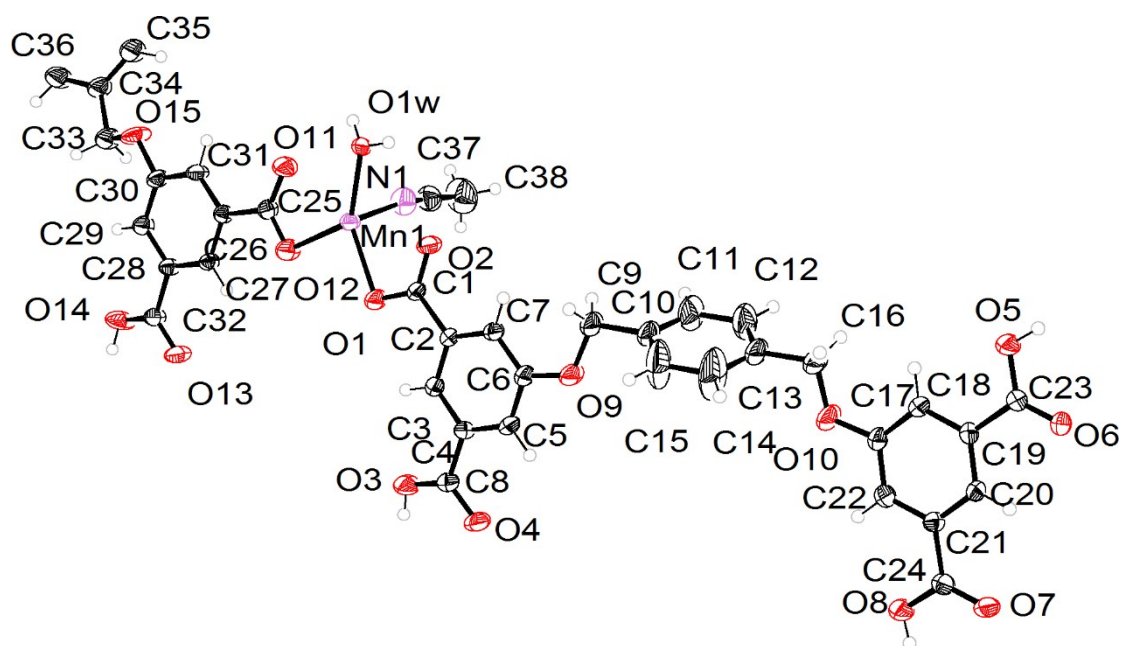


Fig. S1 Coordination environments of the Mn(II) ions in **1** (30% probability displacement ellipsoids).

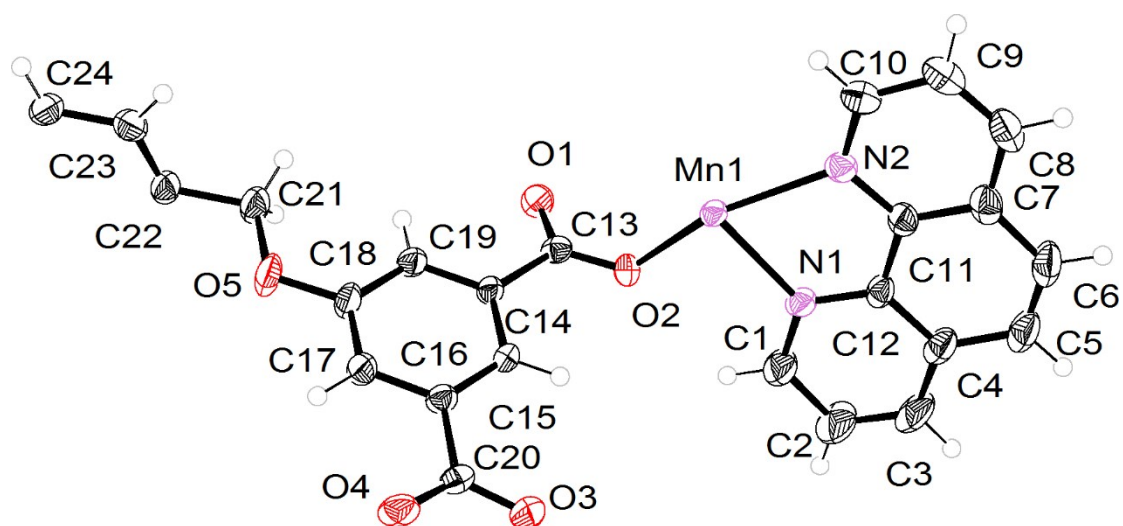


Fig. S2 Coordination environments of the Mn(II) ions in **2** (30% probability displacement ellipsoids).

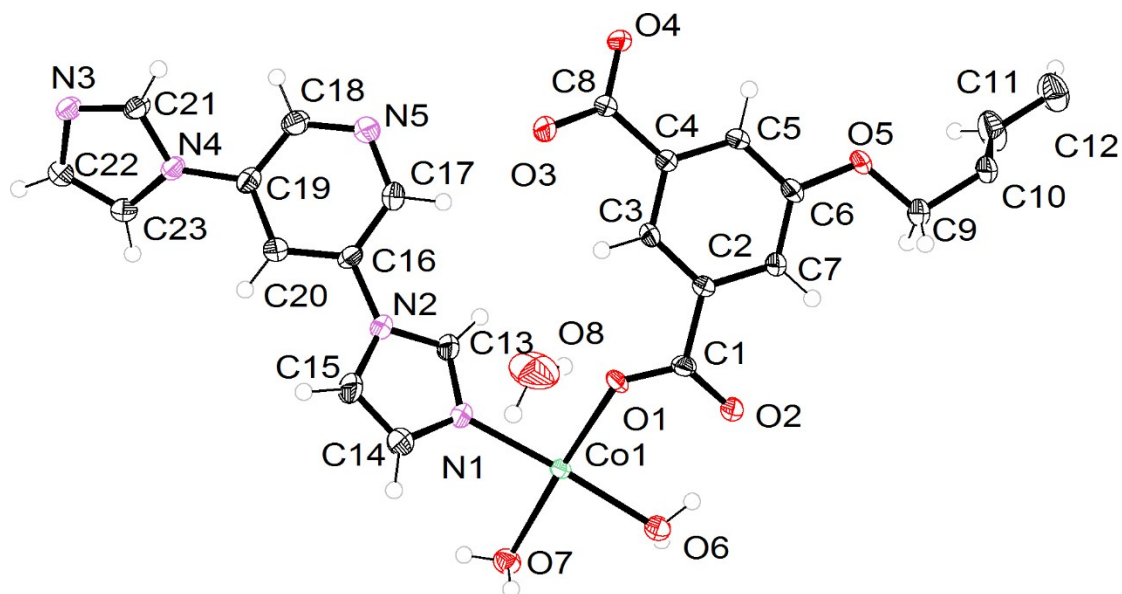


Fig. S3 Coordination environments of the Co(II) ions in **3** (30% probability displacement ellipsoids).

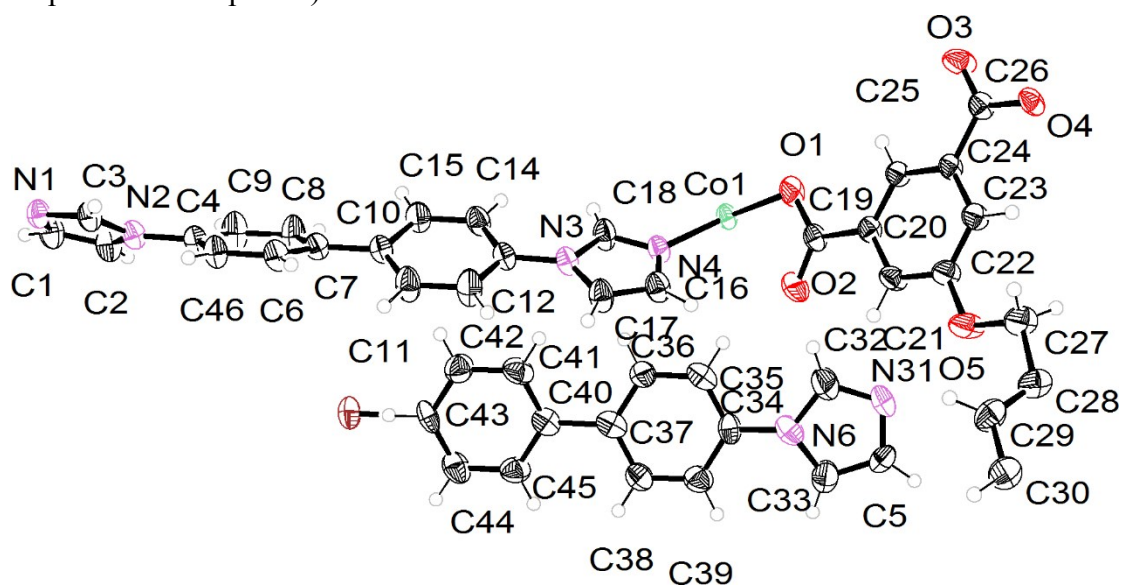


Fig. S4 Coordination environments of the Co(II) ions in **4** (30% probability displacement ellipsoids).

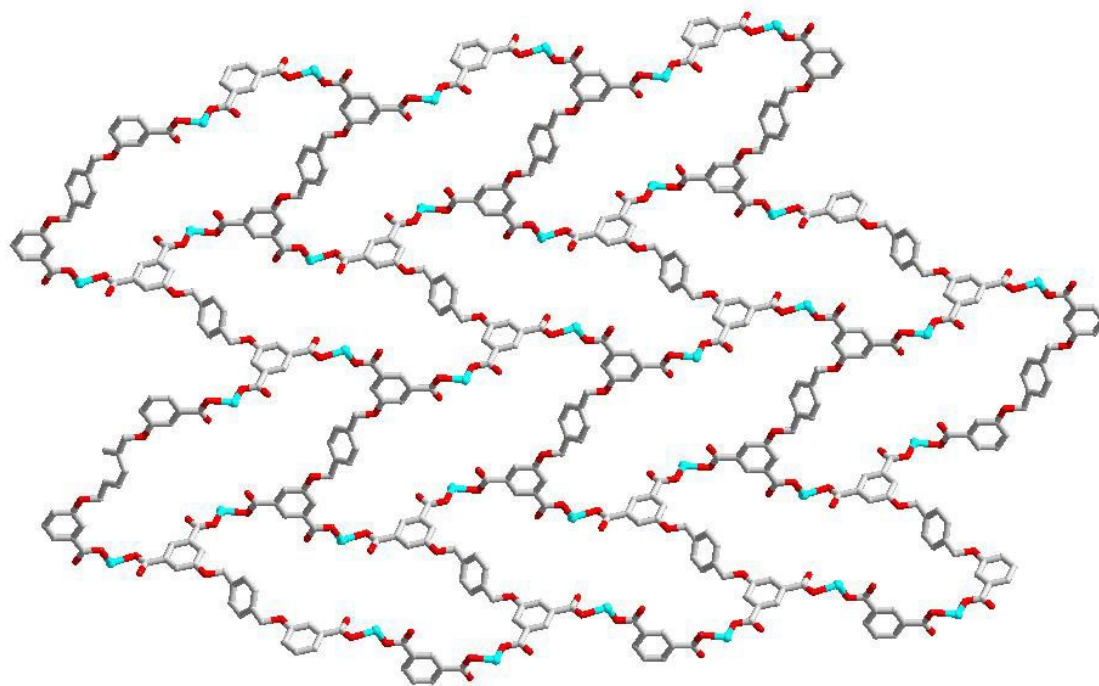


Fig. S5 view of the 2D  $[\text{Zn-L}]_n$  layer in **4**.

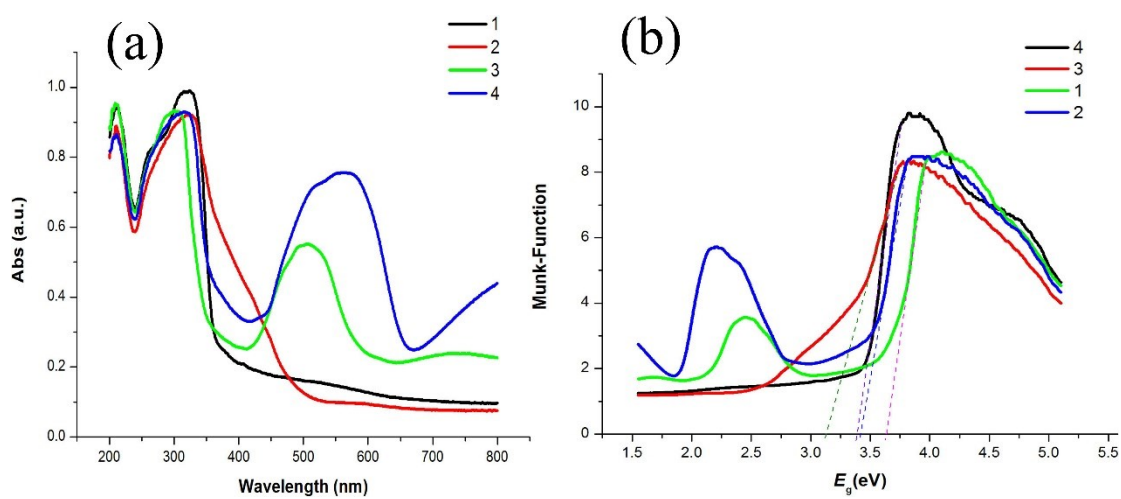


Fig. S6 (a) UV-vis diffuse-reflectance spectra of compounds. (b) Solid-state optical diffuse-reflection spectra of **1–4** derived from diffuse reflectance data at ambient temperature. The intercept of the extrapolated absorption edge on the energy scale (x axis) gives the band gap of the samples.

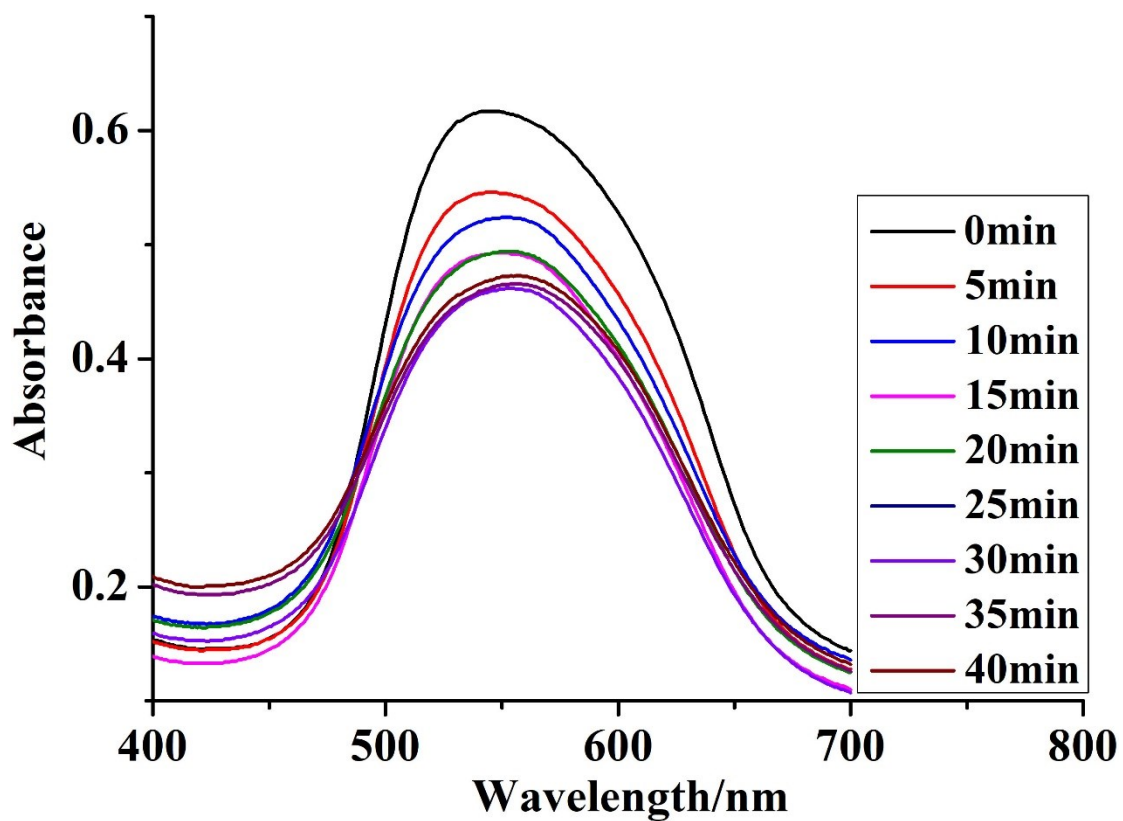


Fig.7 Electronic absorption spectra of the MV solution during the decomposition reaction on UV irradiation in presence of H<sub>4</sub>L

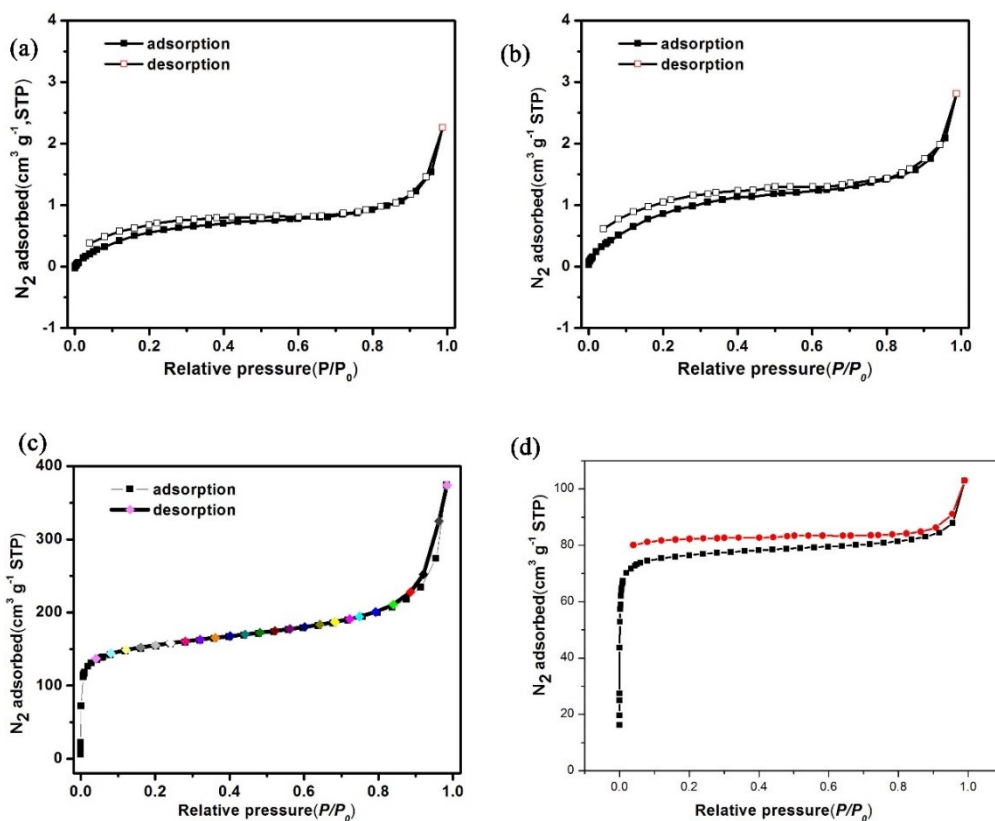


Fig. S8 Nitrogen adsorption-desorption isotherms of these four materials.

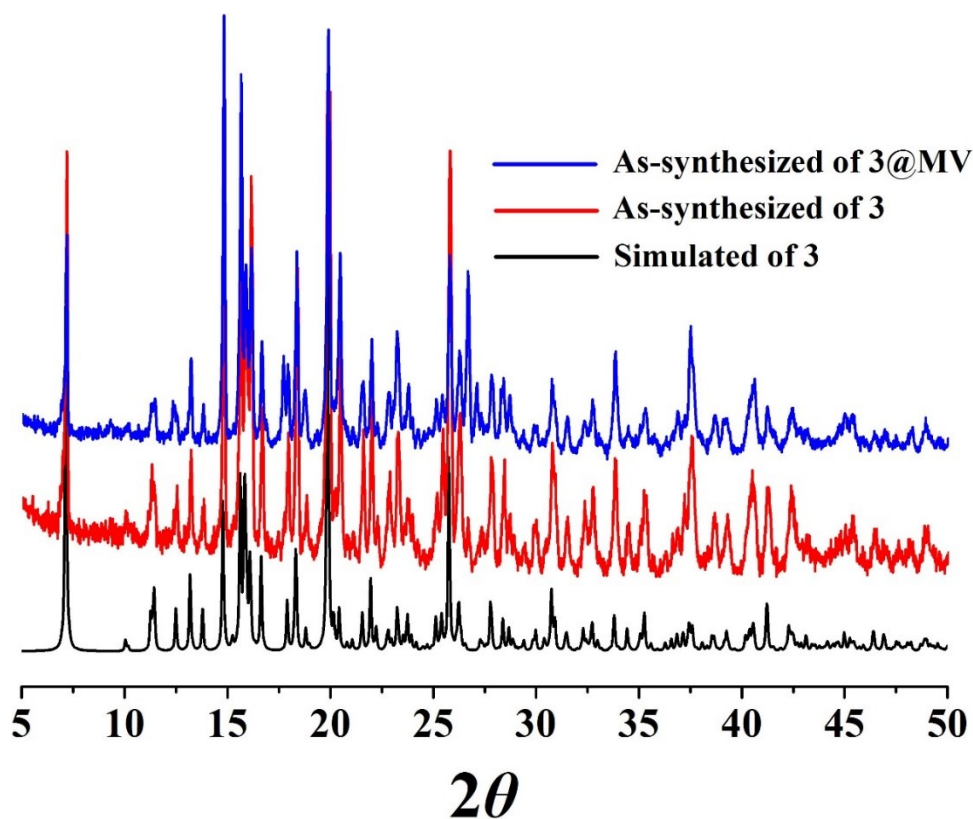


Fig. S9 (a) Powder XRD patterns of the simulated diagram from single crystal data of (black), synthesized samples (red), after photodegradation MV for **3**, respectively.

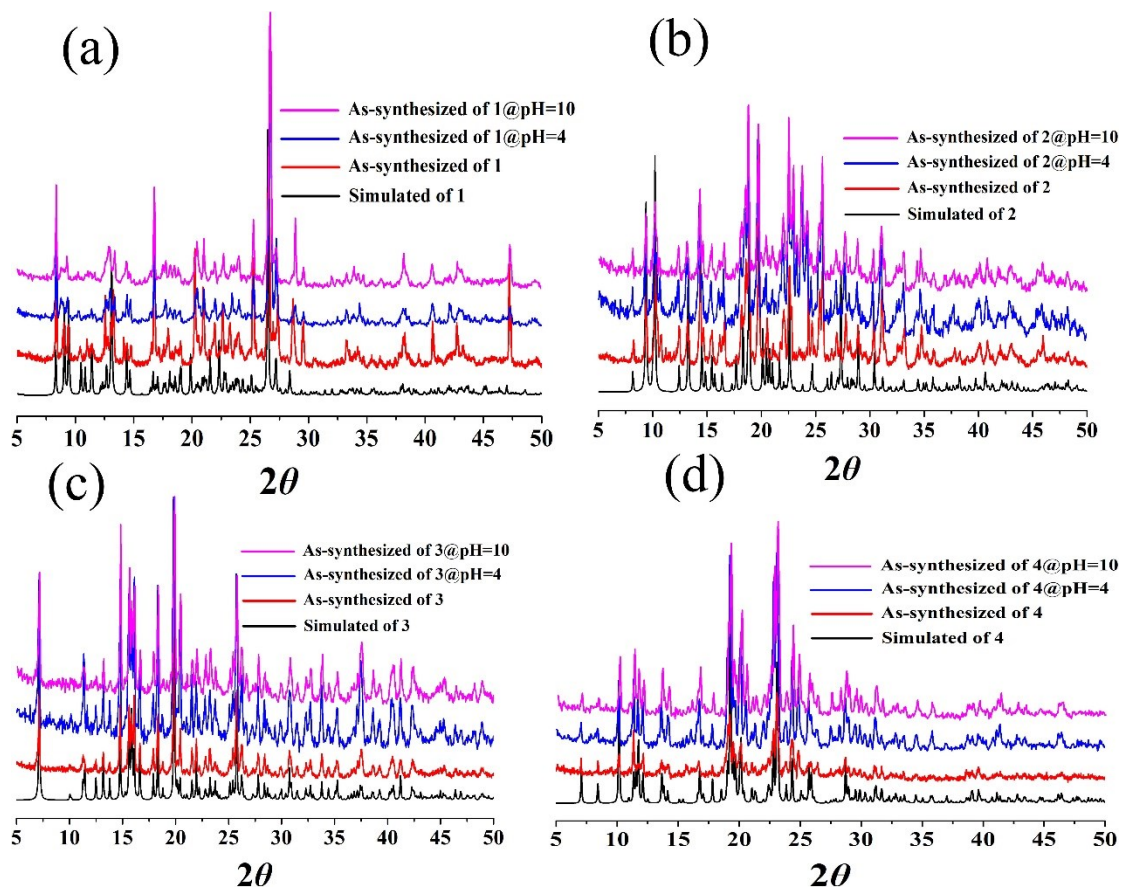
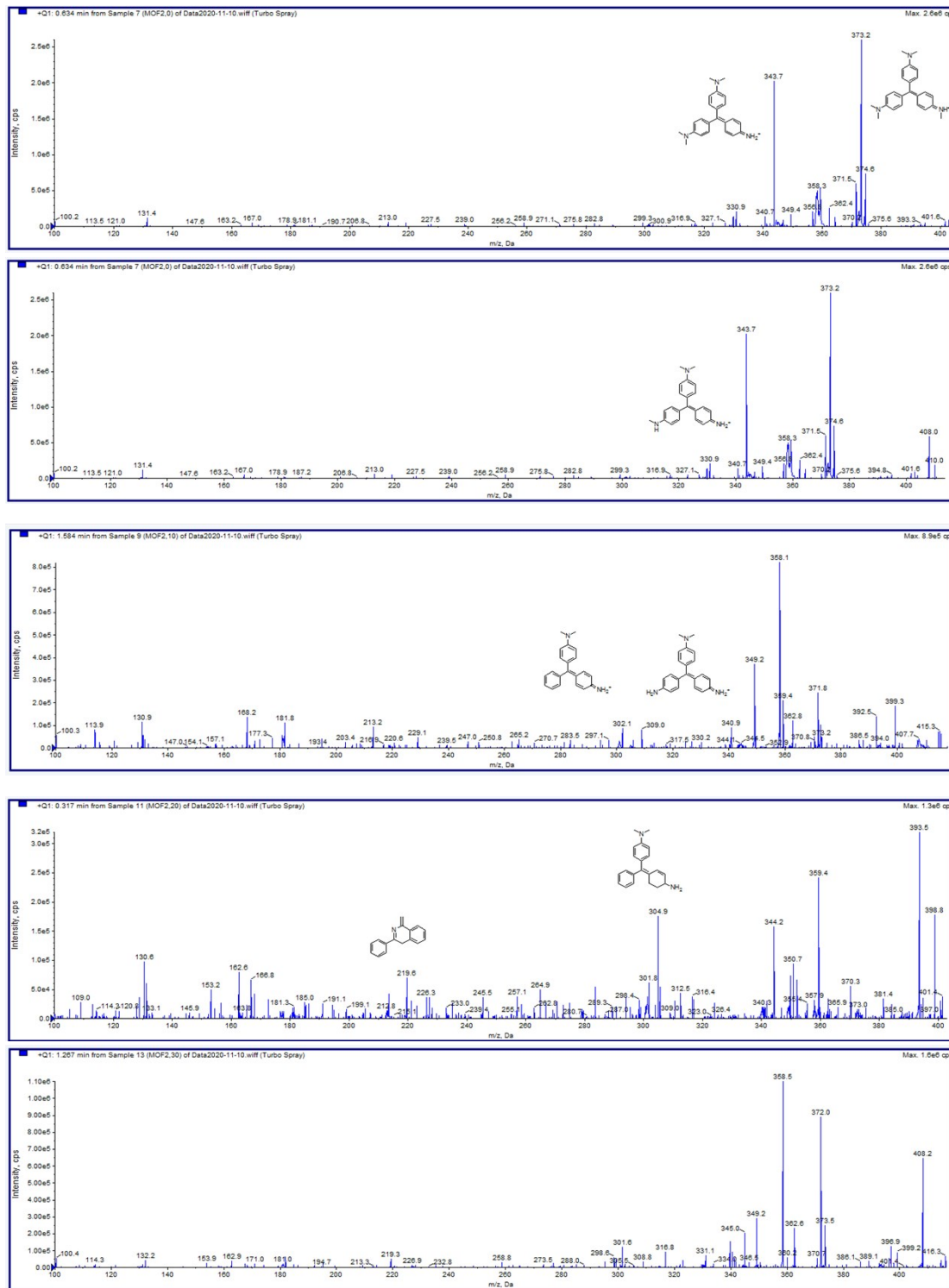


Fig. S10 (a) Powder XRD patterns of the simulated diagram from single crystal data of (black), synthesized samples (red), soaking in pH =4 (blue) and soaking in pH =10 (pink) for 1-4, respectively.





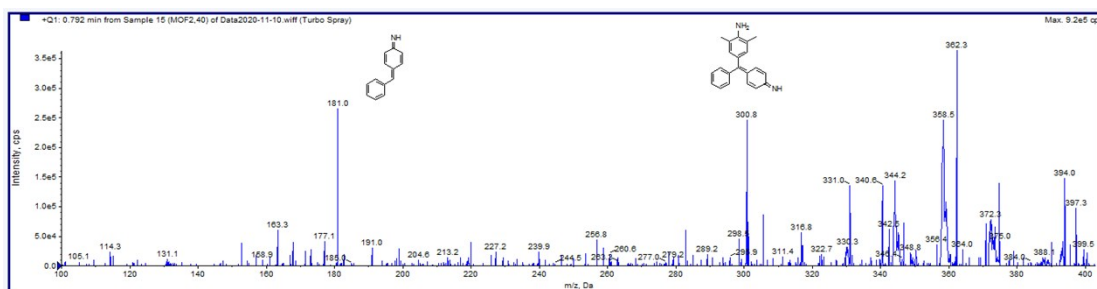


Fig. S11 MS fragmentation pattern of MV dye degraded under irradiation

### FTIR spectroscopy

In the FTIR spectra both the CPs displayed strong and broad stretching vibrations at ca. 3390-3440  $\text{cm}^{-1}$ , which can be assigned to the vibrations arising from the water molecules in **1-4** (Fig. S12). The band around 1700  $\text{cm}^{-1}$  in **1** indicates that the  $\text{H}_4\text{L}$  ligands are not completely deprotonated. The intense bands observed at ca. 1630 and 1438  $\text{cm}^{-1}$  arises because of the asymmetric stretching and symmetric vibration of the carboxylate group of  $\text{H}_4\text{L}$  ligands, respectively. The value differences of  $\nu_{\text{as}(\text{COO})^-}$  vs  $\nu_{\text{sym}(\text{COO})}$  suggest that the  $\text{H}_4\text{L}$  ligands adopts bidentate and monodentate coordination modes, respectively. Additionally, the band observed at ca. 1505  $\text{cm}^{-1}$  can be ascribed to the C=N stretching vibrations of N-donor ligands.

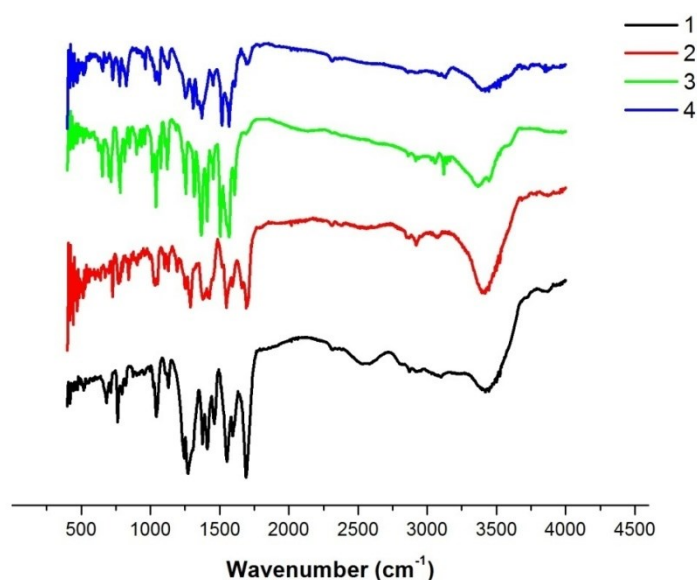


Fig. S12 view of the IR.

### Thermal analyses

To evaluate the thermal stability of the complexes **1-4**, thermogravimetric (TG)

analysis of complexes was performed under N<sub>2</sub> conditions from room temperature to 800 °C with a heating rate of 5 °C min<sup>-1</sup> (Fig. S13). Complex **1** displayed two weight loss stages. The first weight loss stage from 30 to 206 °C results from the complete decomposition of the coordinated CH<sub>3</sub>CN and coordinated H<sub>2</sub>O molecules (obsd: 7.4%, calcd: 7.2%). The second weight loss stage from 246 to 590 °C results from the decomposition of the organic ligands. For complex **2**, the first weight loss stage from 30 to 125 °C results from the complete decomposition of the free H<sub>2</sub>O (obsd: 1.75%, calcd: 1.89%). For complex **3**, the first weight loss stage from 30 to 120 °C results from the complete decomposition of two coordinated H<sub>2</sub>O and one free H<sub>2</sub>O molecule (obsd: 9.5%, calcd: 9.7%). Complex **4** can be stabilized until 360 °C.

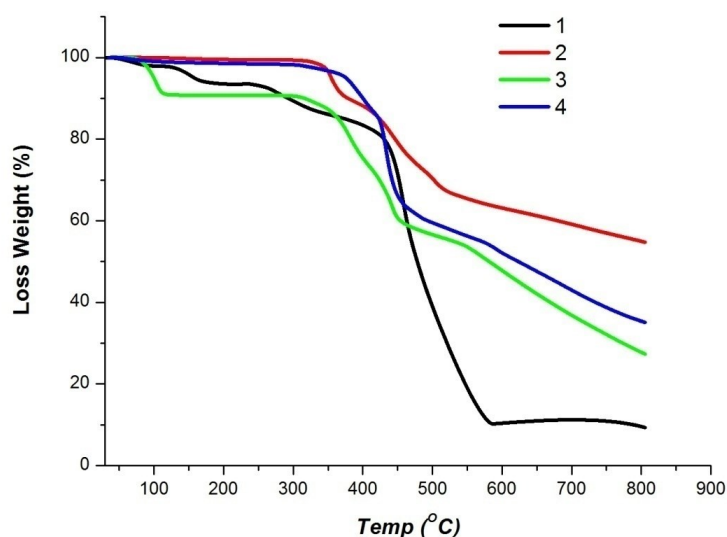


Fig. S13 view of the TGA.

**Table S1 Crystallographic data and structure refinement details for Complexes 1-4**

Parameter	<b>1</b>	<b>2</b>
Formula weight	1623.14	932.64
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2/ <i>n</i>
Crystal Color	Yellow	Yellow

$a$ , Å	8.9317(11)	10.0573(5)
$b$ , Å	10.6571(14)	9.4584(5)
$c$ , Å	21.888(3)	21.6974(11)
$\alpha$ , °	92.819(2)	90
$\beta$ , °	101.376(2)	94.791(4)
$\gamma$ , °	112.551(2)	90
$V$ , Å <sup>3</sup>	1868.3(4)	2056.52(18)
$Z$	1	2
$\rho_{\text{calcd}}$ , g/cm <sup>3</sup>	1.443	1.506
$\mu$ , mm <sup>-1</sup>	0.430	5.569
$F(000)$	836	952
$\theta$ Range, deg	1.9-27.6	4.1-66.0
Reflection Collected	11336	6464
Independent reflections ( $R_{\text{int}}$ )	0.018	0.044
Reflections with $I > 2\sigma(I)$	8160	3573
Number of parameters	518	289
$R_1$ , $wR_2$ ( $I > 2\sigma(I)$ )*	0.0478, 0.1220	0.0445, 0.1053
$R_1$ , $wR_2$ (all data)**	0.0723, 0.1406	0.0541, 0.1121

Parameter	<b>3</b>	<b>4</b>
Formula weight	555.38	1439.42
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Crystal Color	Pink	Pink
$a$ , Å	7.7545(7)	9.5701(2)
$b$ , Å	17.5971(16)	21.0055(5)
$c$ , Å	17.4176(15)	15.5936(4)
$\alpha$ , °	90	90
$\beta$ , °	94.010(2)	91.286(2)

$\gamma, ^\circ$	90	90
$V, \text{\AA}^3$	2370.9(4)	3133.91(13)
$Z$	4	2
$\rho_{\text{calcd}}, \text{g/cm}^3$	1.556	1.525
$\mu, \text{mm}^{-1}$	0.784	5.377
$F(000)$	1144	1474
$\theta$ Range, deg	2.3-27.7	3.5-66.0
Reflection Collected	14206	10050
Independent reflections ( $R_{\text{int}}$ )	0.040	0.036
Reflections with $I > 2\sigma(I)$	5408	5433
Number of parameters	337	480
$R_1, wR_2 (I > 2\sigma(I))^*$	0.0428, 0.0850	0.0519, 0.1259
$R_1, wR_2$ (all data)**	0.0668, 0.0926	0.0632, 0.1327

\*  $R = \sum(F_o - F_c) / \sum(F_o)$ , \*\*  $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum(F_o^2)^2\}^{1/2}$ .

**Table S2** Selected bond distances (Å) and angles (deg) for **1-4**

<b>1</b>			
Mn(1)-O(1)	2.1448(19)	Mn(1)-O(1W)	2.207(2)
Mn(1)-O(2)	2.4713(18)	Mn(1)-O(11)	2.5346(18)
Mn(1)-O(12)	2.127(2)	Mn(1)-N(1)	2.209(3)
Mn(1)-O(1W)#1	2.368(2)		
<b>2</b>			
Mn(1)-O(2)	2.132(2)	Mn(1)-N(1)	2.244(3)
Mn(1)-N(2)	2.260(3)	Mn(1)-O(1)#1	2.182(2)
Mn(1)-O(2)#1	2.843(2)	Mn(1)-O(3)#1	2.408(2)
Mn(1)-O(4)#2	2.218(2)		
<b>3</b>			
Co(1)-O(1)	2.0824(16)	Co(1)-O(6)	2.1329(16)
Co(1)-O(7)	2.1955(16)	Co(1)-N(1)	2.111(2)
Co(1)-N(3)#1	2.130(2)	Co(1)-O(4)#2	2.0937(16)
<b>4</b>			
Co(1)-N(4)	1.980(3)	Co(1)-O(1)	2.019(3)
Co(1)-O(4)#1	1.987(2)	Co(1)-N(1)#2	2.041(3)

<b>1</b>			
O(1)-Mn(1)-O(1W)	134.02(7)	O(1)-Mn(1)-O(2)	55.86(7)
O(1)-Mn(1)-O(11)	144.18(8)	O(1)-Mn(1)-O(12)	89.48(8)
O(1)-Mn(1)-N(1)	98.44(9)	O(1)-Mn(1)-O(1W)#1	87.90(7)
O(1W)-Mn(1)-O(2)	81.28(7)	O(1W)-Mn(1)-O(11)	80.41(8)
O(1W)-Mn(1)-O(12)	131.67(8)	O(1W)-Mn(1)-N(1)	93.70(9)
O(2)-Mn(1)-O(11)	159.66(7)	O(2)-Mn(1)-O(12)	145.33(8)
O(2)-Mn(1)-N(1)	85.80(8)	O(11)-Mn(1)-O(12)	54.81(8)
O(11)-Mn(1)-N(1)	86.60(9)	O(12)-Mn(1)-N(1)	100.12(10)
<b>2</b>			
O(2)-Mn(1)-N(1)	86.05(9)	O(2)-Mn(1)-N(2)	154.94(9)
O(1)#1-Mn(1)-O(2)	100.64(8)	O(2)-Mn(1)-O(2)#1	75.59(7)
O(2)-Mn(1)-O(3)#2	89.10(8)	O(2)-Mn(1)-O(4)#2	108.04(9)
N(1)-Mn(1)-N(2)	73.14(10)	O(1)#1-Mn(1)-N(1)	135.26(8)
O(2)#1-Mn(1)-N(1)	90.63(7)	O(3)#2-Mn(1)-N(1)	83.12(7)
O(4)#2-Mn(1)-N(1)	135.51(8)	O(1)#1-Mn(1)-N(2)	85.31(9)
O(2)#1-Mn(1)-N(2)	90.52(7)	O(3)#2-Mn(1)-N(2)	101.79(8)
O(4)#2-Mn(1)-N(2)	96.70(9)	O(1)#1-Mn(1)-O(2)#1	50.03(7)
O(1)#1-Mn(1)-O(3)#2	140.51(7)	O(1)#1-Mn(1)-O(4)#2	84.66(7)
O(2)#1-Mn(1)-O(3)#2	163.86(7)	O(3)#2-Mn(1)-O(4)#2	56.06(7)
<b>3</b>			
O(1)-Co(1)-O(6)	91.31(6)	O(1)-Co(1)-O(7)	177.40(6)
O(1)-Co(1)-N(1)	90.92(7)	O(1)-Co(1)-N(3)#1	90.94(7)
O(6)-Co(1)-O(7)	86.09(6)	O(6)-Co(1)-N(1)	176.40(7)
O(6)-Co(1)-N(3)#1	88.40(7)	O(4)#2-Co(1)-O(6)	87.54(6)
O(7)-Co(1)-N(1)	91.68(7)	O(7)-Co(1)-N(3)#1	88.94(7)
N(1)-Co(1)-N(3)#1	94.40(8)	O(4)#2-Co(1)-O(7)	90.43(6)
O(4)#2-Co(1)-N(1)	89.65(7)	O(4)#2-Co(1)-N(3)#1	175.92(7)
<b>4</b>			
O(1)-Co(1)-N(4)	112.58(12)	O(1)-Co(1)-N(1)#2	94.68(12)
O(1)-Co(1)-O(4)#1	110.38(10)	N(1)#2-Co(1)-N(4)	103.61(12)
O(4)#1-Co(1)-N(4)	124.95(11)	O(4)#1-Co(1)-N(1)#2	105.87(9)

Symmetry Codes: **For 1:** #1= -x, 1-y, -z. **For 2:** #1= 1/2-x, y, 1/2-z; #2 = 3/2-x, y, 1/2-z. **For 3:** #1= 2-x, -1/2+y, 3/2-z; #2 = x, 1/2-y, -1/2+z. **For 4:** #1= -1/2+x, 3/2-y, -1/2+z; #2 = -1/2-x, 1/2+y, 1/2-z.