Electronic Supplementary Information

Exploring the Coordination Chemistry of Bifunctional Organoarsonate Ligands: Syntheses and Characterisation of Coordination Polymers that Contain 4-(1, 2, 4-triazol-4-yl)phenylarsonic Acid

Jian-Di Lin,[a] Rodolphe Clérac,[b,c] Mathieu Rouzières,[b,c] Munuswamy Venkatesan,[d] Theresa O. Chimamkpam,[a] Wolfgang Schmitt [*, a]

[a] School of Chemistry & CRANN, University of Dublin, Trinity College, Dublin 2, Ireland. E-mail: schmittw@tcd.ie; Fax: +353 1 671 2826; Tel: +353 1 896 3495.

[b] CNRS, CRPP, UPR 8641, F-33600 Pessac, France.

[c] Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France.

[d] School of Physics & CRANN, University of Dublin, Trinity College, Dublin 2, Ireland.

Table S1.1 Selected bond lengths (Å) and angles (°) of **1**.

Co1—O11	2.074 (19)	As1B—O11	1.572 (3)
Co1—O21	2.0989 (19)	As1B—O12'	1.687 (14)
Co1—O31^{i}	2.1152 (18)	As1B—O13'	1.701 (14)
Co1—N11^{ii}	2.152 (2)	As21—O21	1.6543 (19)
Co1—N21^{iii}	2.181 (2)	As21—O22	1.684 (2)
Co1—N31	2.137 (2)	As21—O23	1.699 (2)
As1A—O11	1.6729 (19)	As31—O31	1.6642 (18)
As1A—O12	1.662 (2)	As31—O32	1.6664 (19)
As1A—O13	1.729 (2)	As31—O33	1.726 (2)
O11—Co1—O21	175.58 (7)	N31—Co1—N21^{iii}	88.74 (8)
O11—Co1—O31^{i}	90.89 (7)	O11—As1A—O13	109.57 (11)
O11—Co1—N11^{ii}	89.70 (8)	O12—As1A—O11	112.48 (12)

O11—Co1—N21^{iii}	86.66 (8)	O12—As1A—O13	103.30 (12)
O11—Co1—N31	91.19 (8)	O11—As1B—O12'	112.0 (6)
O21—Co1—O31^{i}	87.88 (7)	O11—As1B—O13'	107.9 (5)
O21—Co1—N11^{ii}	94.58 (8)	O12'—As1B—O13'	105.1 (7)
O21—Co1—N21^{iii}	89.04 (8)	O21—As21—O22	106.30 (11)
O21—Co1—N31	89.72 (8)	O21—As21—O23	113.40 (10)
O31^{i}—Co1—N11^{ii}	92.07 (8)	O22—As21—O23	109.83 (12)
O31^{i}—Co1—N21^{iii}	87.00 (8)	O31—As31—O32	115.28 (10)
O31^{i}—Co1—N31	175.15 (8)	O31—As31—O33	109.21 (10)
N11^{ii}—Co1—N21^{iii}	176.22 (9)	O32—As31—O33	106.53 (11)
N31—Co1—N11^{ii}	92.33 (8)		

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) *x*+1, *y*, *z*; (iii) *x*−1, *y*, *z*; (iv) *x*, *y*+1, *z*.

Table S1.2 Hydrogen-bond geometry (Å, º) of **1**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O13—H13···O31^{i}	0.84	1.92	2.659 (3)	146
O23—H23···O32^{v}	0.84	1.69	2.473 (3)	154
O33—H33···O21^{iv}	0.84	1.96	2.771 (3)	161

Symmetry codes: (i) *x*, *y*−1, *z*; (iv) *x*, *y*+1, *z*; (v) −*x*+3/2, *y*−1/2, −*z*+1/2.

Table S2.1 Selected bond lengths (Å) and angles (°) of **2**.

Cu1—Cl1	2.6801 (18)	As1—O1	1.669 (6)
Cu1—O1	1.991 (5)	As1—O2	1.691 (7)
Cu1—N1^{iii}	2.055 (6)	O1^{ii}—Cu1—O1	180
O1—As1—O1^{i}	115.0 (4)	O1—Cu1—N1^{iii}	93.6 (2)
O1^{i}—As1—O2	107.7 (2)	O1^{ii}—Cu1—N1^{iii}	86.4 (2)

Cl1—Cu1—Cl1^{ii}	180	N1^{iii}—Cu1—Cl1	89.51 (19)
O1—Cu1—Cl1^{ii}	88.91 (17)	N1^{iii}—Cu1—Cl1^{ii}	90.49 (19)
O1—Cu1—Cl1	91.09 (17)	N1^{iii}—Cu1—N1^{iv}	180

Symmetry codes: (i) x, $-y$, z; (ii) $-x+3/2$, $-y+1/2$, $-z+1$; (iii) $-x+1$, y, $-z+1$; (iv) $x+1/2$, $-y+1/2$, z.

Table S2.2 Hydrogen-bond geometry (Å, º) of **2**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O4*W*	0.84	1.83	2.661 (11)	172

Table S3.1 Selected bond lengths (Å) and angles (°) of **3**.

As1—O1	1.668 (3)	Co1—Cl1	2.4730 (9)
As1—O2	1.715 (4)	Co1—O1	2.055 (3)
O1—As1—O1^{i}	115.17 (18)	Co1—N1^{iii}	2.128 (3)
O1—As1—O2	108.78 (11)	O1^{ii}—Co1—O1	180
Cl1—Co1—Cl1^{ii}	180	O1^{ii}—Co1—N1^{iii}	93.13 (11)
O1^{ii}—Co1—Cl1	88.86 (8)	O1—Co1—N1^{iii}	86.87 (11)
O1—Co1—Cl1	91.14 (8)	N1^{iii}—Co1—Cl1^{ii}	89.78 (9)
N1^{iv}—Co1—N1^{iii}	180	N1^{iii}—Co1—Cl1	90.22 (9)

Symmetry codes: (i) x, $-y$, z; (ii) $-x+1/2$, $-y+1/2$, $-z$; (iii) $x-1/2$, $y+1/2$, z; (iv) $-x+1$, $-y$, $-z$.

Table S3.2 Hydrogen-bond geometry (Å, º) of **3**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3*W*	0.84	1.81	2.645 (6)	174

Table S4.1 Selected bond lengths (Å) and angles (°) of **4**.

Mn1—O11^{i}	2.090 (2)	As11—O11	1.639 (2)

Mn1—O12^{ii}	2.148 (2)	As11—O12	1.681 (2)
Mn1—O21^{iii}	2.255 (2)	As11—O13	1.7217 (19)
Mn1—O21^{iv}	2.189 (2)	As21—O21	1.6821 (19)
Mn1—N11	2.335 (2)	As21—O22	1.6584 (19)
Mn1—N21	2.279 (2)	As21—O23	1.7306 (19)
O11^{i}—Mn1—O12^{ii}	107.01 (8)	O21^{iii}—Mn1—N11	104.00 (8)
O11^{i}—Mn1—O21^{iii}	160.70 (8)	O21^{iv}—Mn1—N21	98.43 (8)
O11^{i}—Mn1—O21^{iv}	90.87 (8)	O21^{iii}—Mn1—N21	85.28 (8)
O11^{i}—Mn1—N11	89.47 (8)	N21—Mn1—N11	167.82 (9)
O11^{i}—Mn1—N21	83.59 (8)	O11—As11—O12	113.97 (10)
O12^{ii}—Mn1—O21^{iv}	162.12 (8)	O11—As11—O13	110.68 (10)
O12^{ii}—Mn1—O21^{iii}	87.46 (7)	O12—As11—O13	103.59 (9)
O12^{ii}—Mn1—N11	88.20 (8)	O21—As21—O23	106.27 (9)
O12^{ii}—Mn1—N21	84.29 (8)	O22—As21—O21	117.20 (10)
O21^{iv}—Mn1—O21^{iii}	75.22 (8)	O22—As21—O23	104.01 (9)
O21^{iv}—Mn1—N11	91.65 (8)		

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+3/2; (ii) *x*, −*y*+1/2, *z*+1/2; (iii) −*x*, *y*−1/2, −*z*+5/2; (iv) *x*, −*y*+3/2, *z*−1/2; (v) −*x*+1, *y*−1/2, −*z*+3/2; (vi) *x*, −*y*+1/2, *z*−1/2; (vii) −*x*, *y*+1/2, −*z*+5/2; (viii) *x*, −*y*+3/2, *z*+1/2.

Table S4.2 Hydrogen-bond geometry (Å, º) of **4**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O13—H13···O22^{ix}	0.84	1.67	2.508 (3)	178
O23—H23···O12^{x}	0.84	1.70	2.536 (3)	174

Symmetry codes: (ix) −*x*+1, −*y*+1, −*z*+2; (x) −*x*, −*y*+1, −*z*+2.

Table S5.1 Selected bond lengths (Å) and angles (°) of **5**.

Cd1—O11^{i}	2.2156 (17)	As11—O11	1.6360 (17)
Cd1—O12^{ii}	2.2770 (16)	As11—O12	1.6756 (16)
Cd1—O21^{iii}	2.3520 (16)	As11—O13	1.7191 (17)
Cd1—O21^{iv}	2.3053 (16)	As21—O21	1.6759 (16)

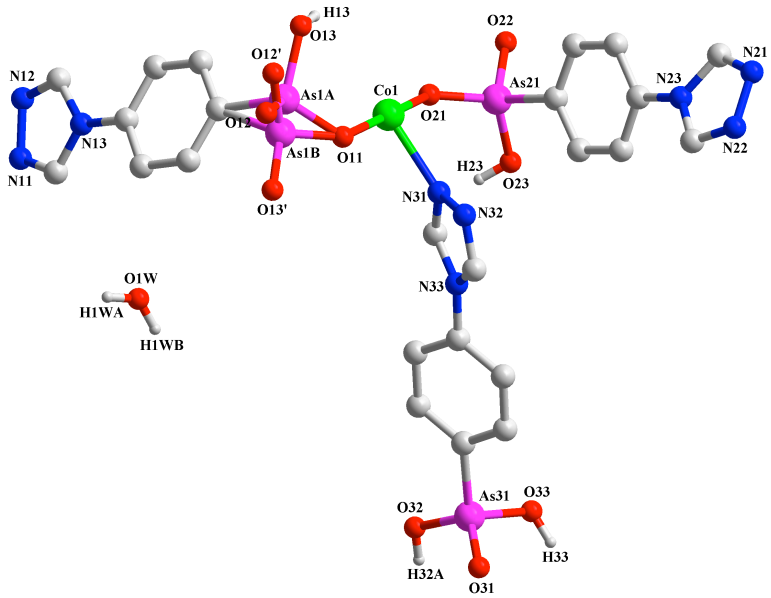
Cd1—N11	2.357 (2)	As21—O22	1.6563 (16)
Cd1—N21	2.339 (2)	As21—O23	1.7317 (16)
O11^{i}—Cd1—O12^{ii}	109.91 (7)	O21^{iii}—Cd1—N11	104.47 (7)
O11^{i}—Cd1—O21^{iii}	158.37 (7)	O21^{iv}—Cd1—N21	96.91 (7)
O11^{i}—Cd1—O21^{iv}	89.06 (6)	N21—Cd1—O21^{iii}	84.41 (7)
O11^{i}—Cd1—N11	90.88 (7)	N21—Cd1—N11	169.05 (7)
O11^{i}—Cd1—N21	82.39 (7)	O11—As11—O12	114.50 (9)
O12^{ii}—Cd1—O21^{iii}	85.44 (6)	O11—As11—O13	111.22 (9)
O12^{ii}—Cd1—O21^{iv}	160.85 (6)	O12—As11—O13	103.71 (8)
O12^{ii}—Cd1—N11	90.70 (7)	O21—As21—O23	106.61 (8)
O12^{ii}—Cd1—N21	83.55 (7)	O22—As21—O21	116.93 (8)
O21^{iv}—Cd1—O21^{iii}	75.59 (6)	O22—As21—O23	104.02 (8)
O21^{iv}—Cd1—N11	91.58 (7)		

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1/2; (ii) *x*, −*y*+3/2, *z*+1/2; (iii) −*x*, *y*+1/2, −*z*+3/2; (iv) *x*, −*y*+1/2, *z*−1/2; (v) −*x*+1, *y*+1/2, −*z*+1/2; (vi) *x*, −*y*+3/2, *z*−1/2; (vii) −*x*, *y*−1/2, −*z*+3/2; (viii) *x*, −*y*+1/2, *z*+1/2.

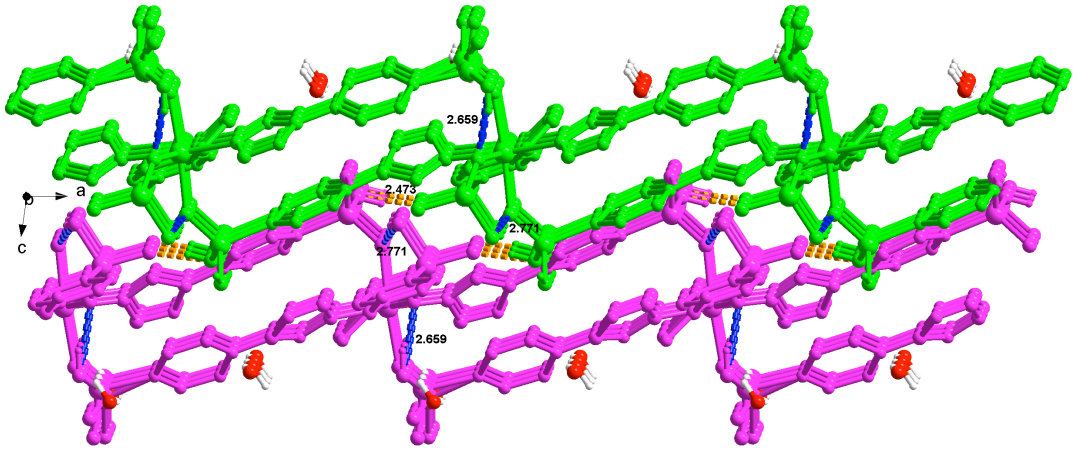
Table S5.2 Hydrogen-bond geometry (Å, º) of **5**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O13—H13···O22^{ix}	0.84	1.67	2.510 (2)	176
O23—H23···O12^{x}	0.84	1.69	2.532 (2)	177

Symmetry codes: (ix) −*x*+1, −*y*+1, −*z*+1; (x) −*x*, −*y*+1, −*z*+1.

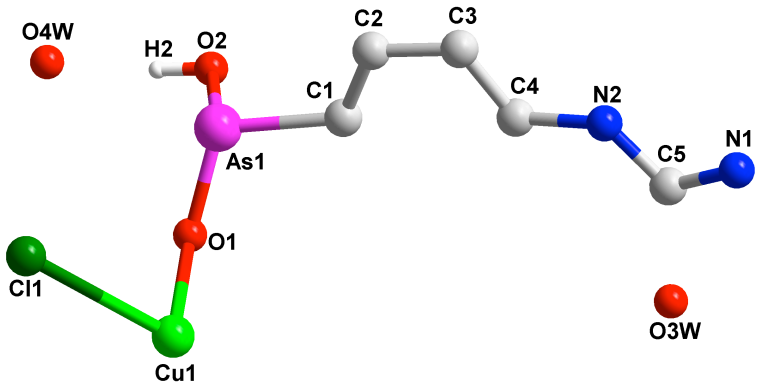


(a)



(b)

Fig. S1 (a) The asymmetric unit of **1**. (b) Intramolecular and intermolecular hydrogen bonds in **1**. The blue dashed lines (2.659 and 2.771 Å) stand for intramolecular hydrogen bonds, the orange dashed lines (2.473 Å) stand for intermolecular hydrogen bonds.



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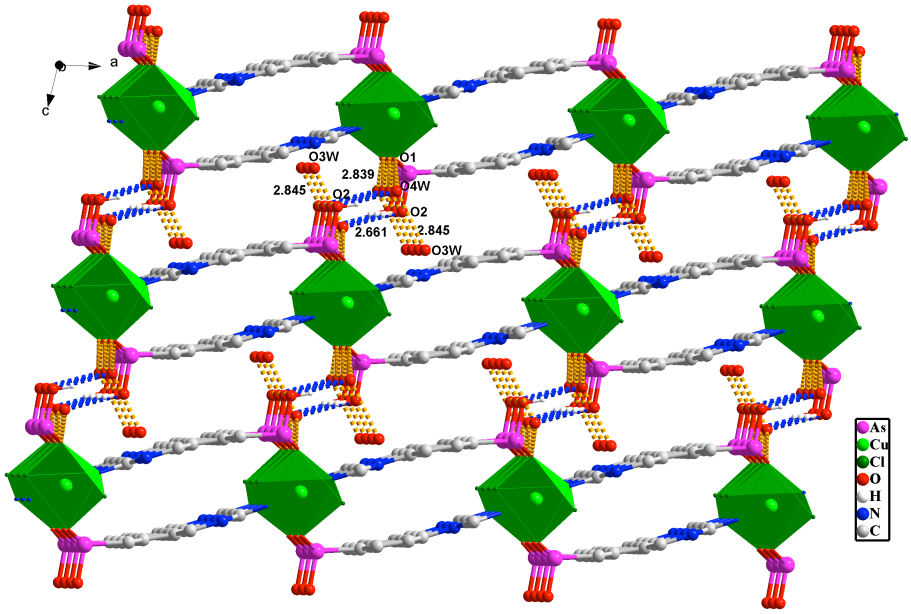
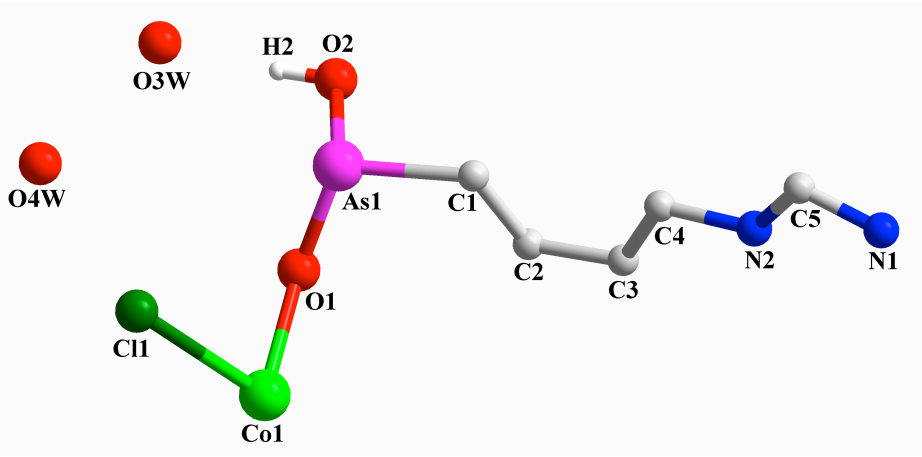
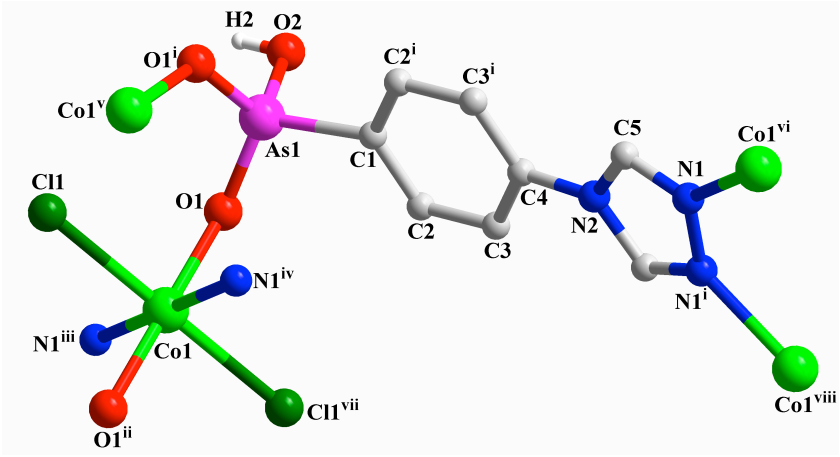


(b)

Fig. S2 (a) The asymmetric unit of **2**. (b) Polyhedral resprentation of intramolecular and intermolecular hydrogen bonds in **2**. The blue dashed lines (2.661 Å) stand for intramolecular hydrogen bonds, the orange dashed lines (2.839 and 2.845 Å) stand for intermolecular hydrogen bonds.


O3W
H2
O2
O4W
As1
C1
C2
C3
C4
C5
N2
N1
O1
Cl1
Co1

(a)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O2
O1i
C2i
C3i
Co1v
As1
C1
C5
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N1
Cl1
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C3
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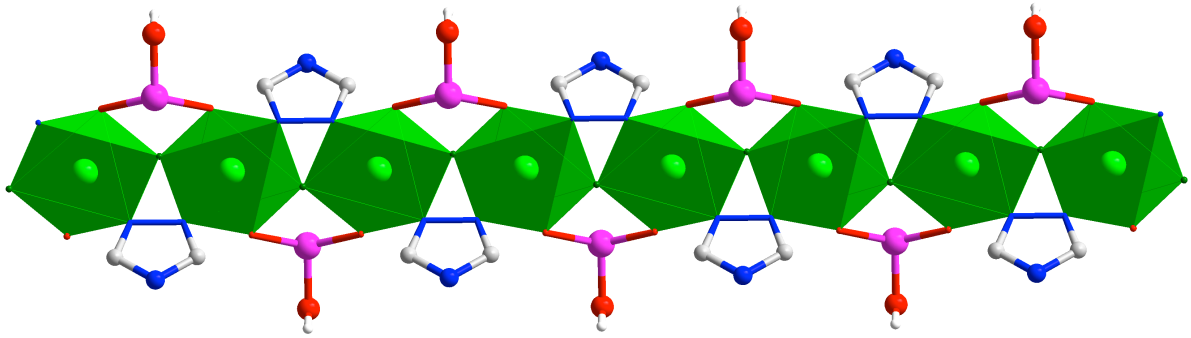
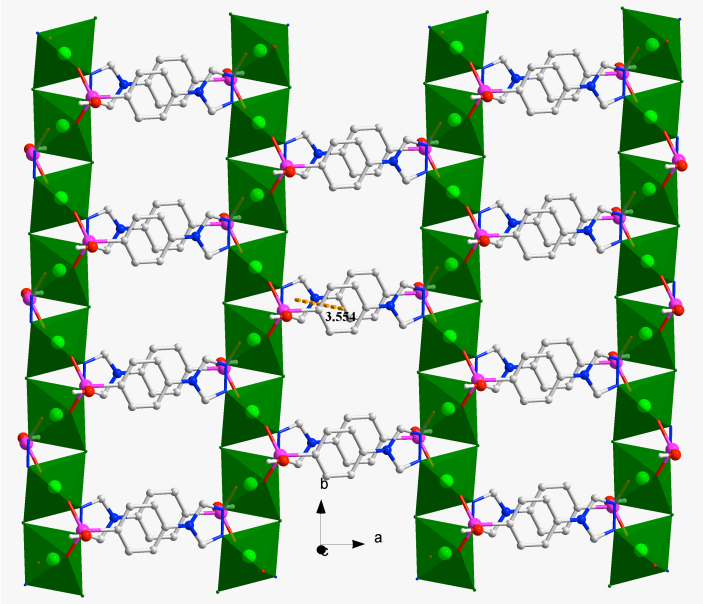
Co1viii

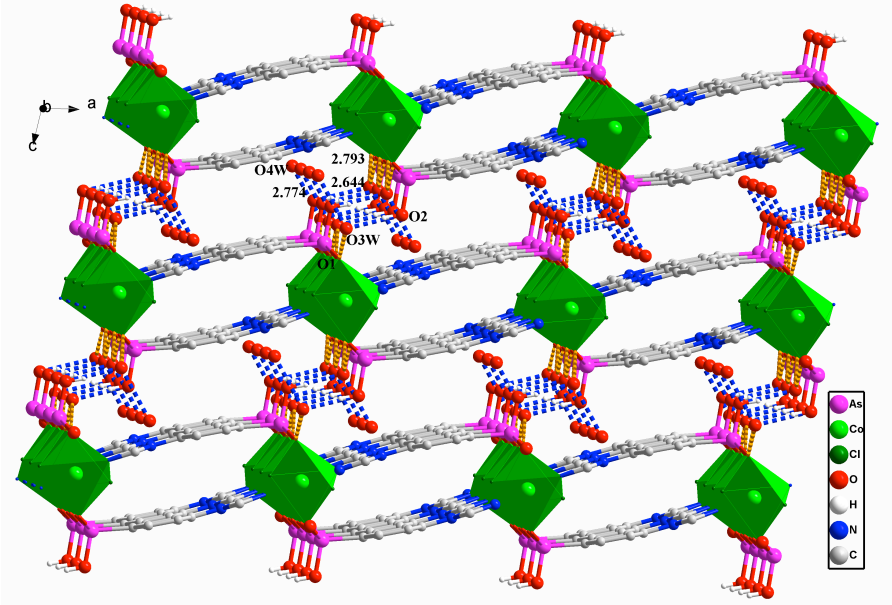
(b)



(c)



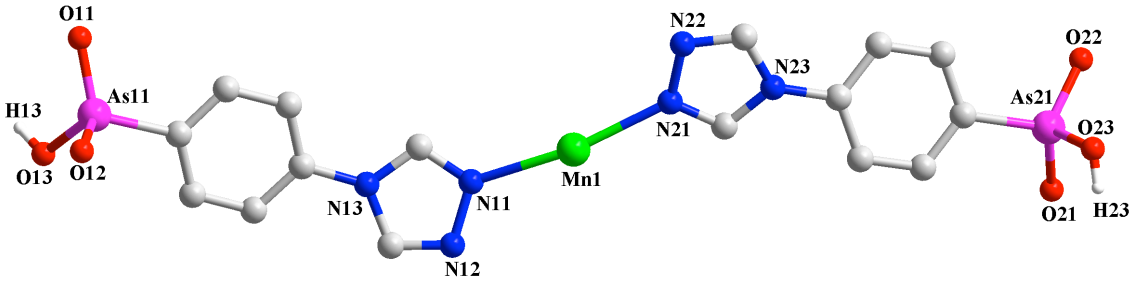
(d)



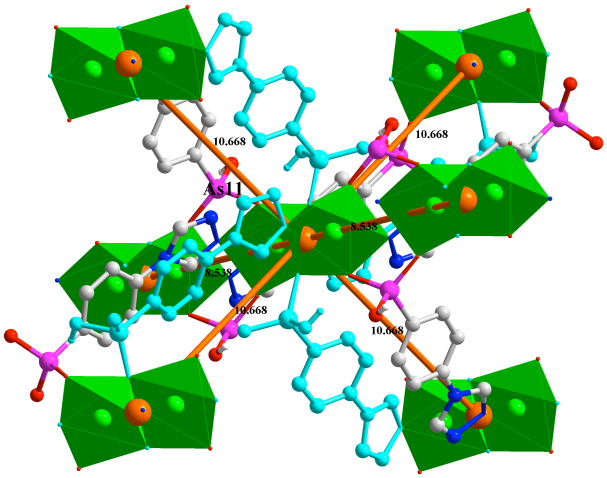
(e)

Fig. S3 (a) The asymmetric unit of **3**. (b) The coordination environment of Co(II) ion and the coordination modes of the ligands in **3**. Symmetry codes: (i) *x*, −*y*, *z*; (ii) −*x*+1/2, −*y*+1/2, −*z*; (iii) *x*−1/2, *y*+1/2, *z*; (iv) −*x*+1, −*y*, −*z*; (v) −*x*+1/2, *y*−1/2, −*z*; (vi) *x*+1/2, *y*−1/2, *z*; (vii) −*x*+1/2, *y*+1/2, −*z*; (viii) −*x*+1, *y*, −*z*. (c) Polyhedral representation of the 1-D substructure along the *b*-axis in **3** involving Co(II) and, Cl^- and the $As1O_3$ moiety. (d) Polyhedral resprentation of the two-dimensional layer structure of **3**. (e) Polyhedral resprentation of intramolecular and intermolecular hydrogen bonds in **3**. The blue dashed

lines (2.644 and 2.774 Å) stand for intramolecular hydrogen bonds, the orange dashed lines (2.793 Å) stand for intermolecular hydrogen bonds.

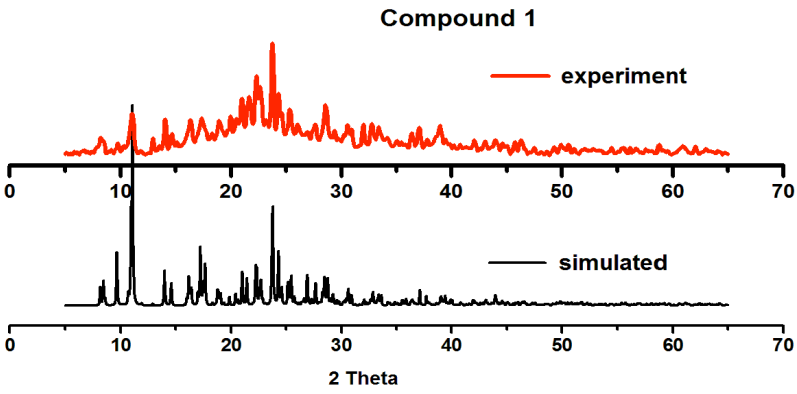


(a)



(b)

Fig. S4 (a) The asymmetric unit of **4**. (b) Polyhedral representation of the topological simplification fashion in **4**.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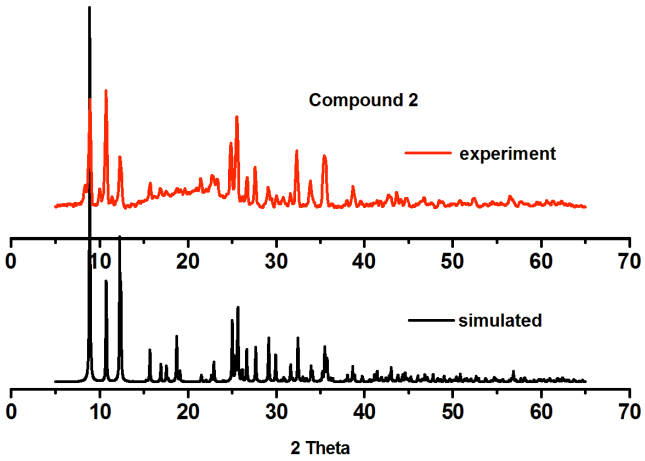
simulated
0
10
20
30
40
50
60
70
2 Theta

(a)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experiment
simulated
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10
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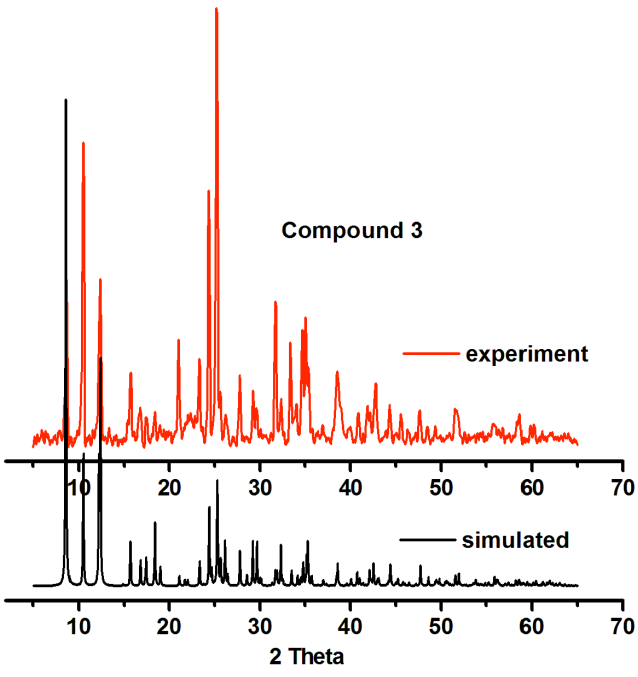
70
2 Theta

(b)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experiment
simulated
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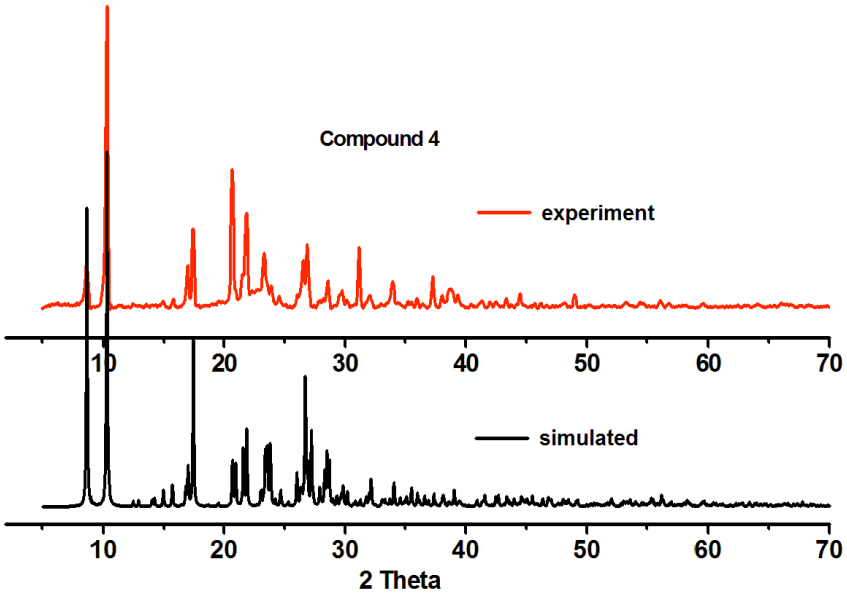
20
30
40
50
60
70
2 Theta

(c)



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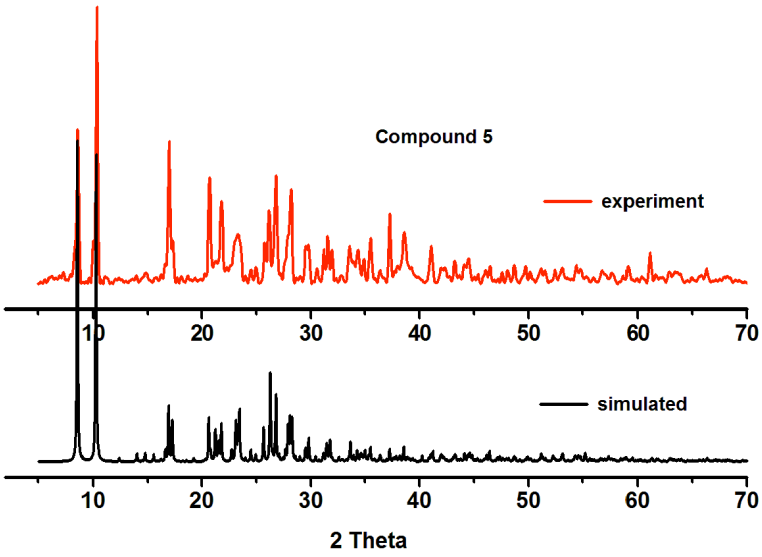
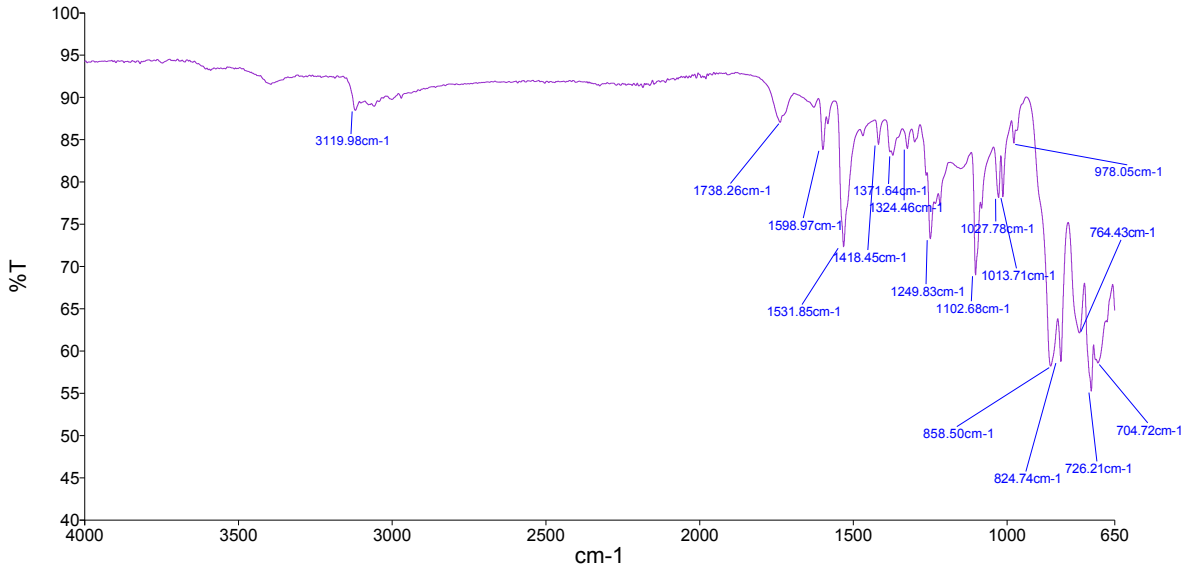
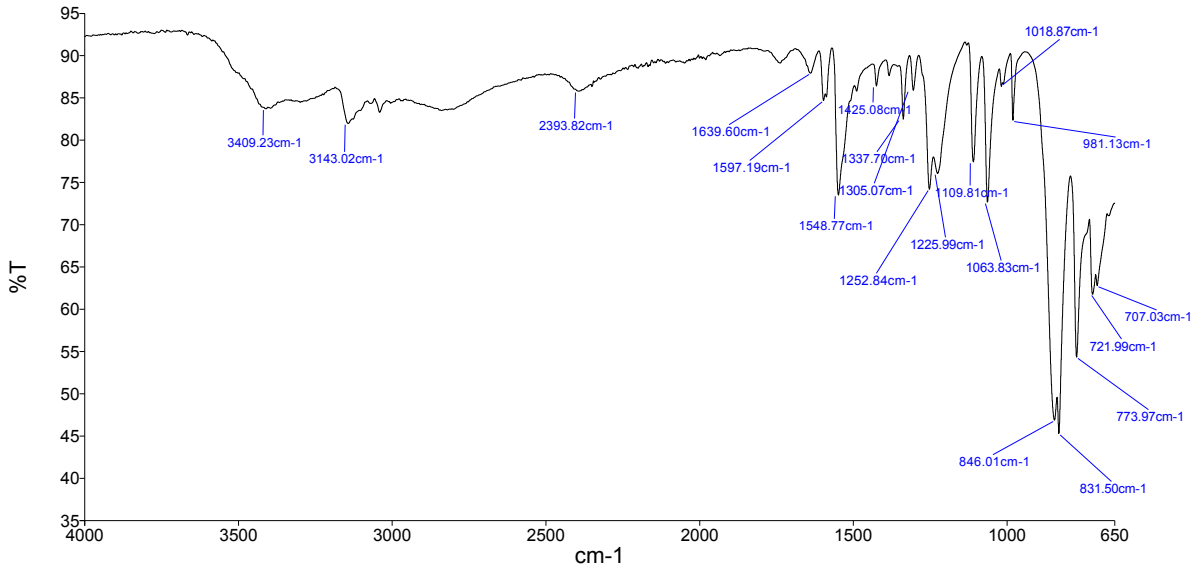


(e)

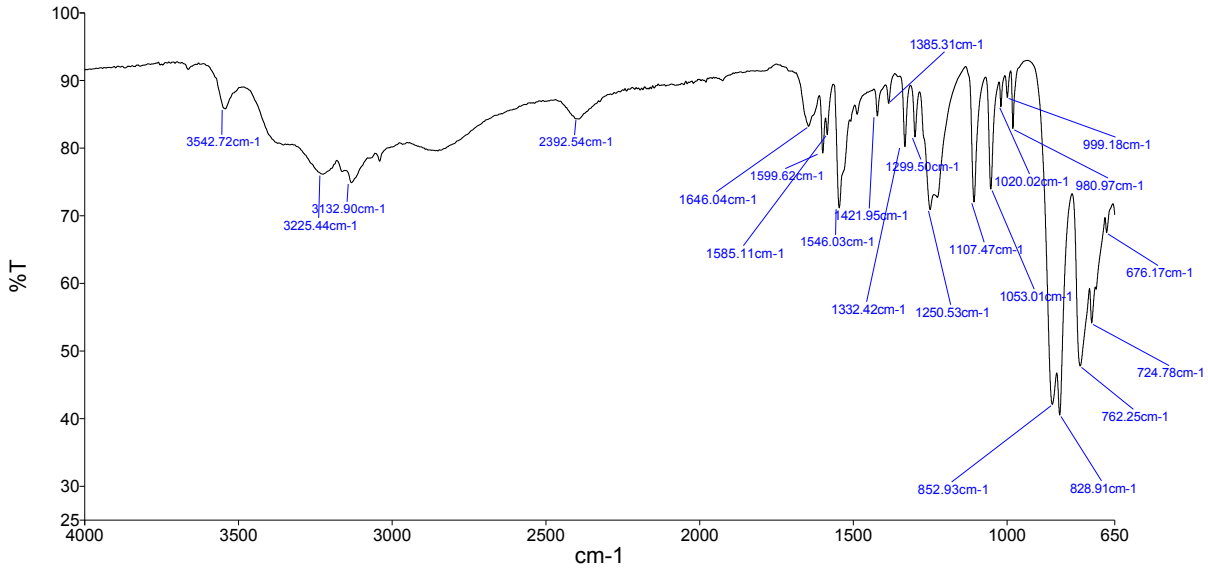
Fig. S5 The power X-ray diffraction patterns for compounds **1**–**5**.



(a) Compound **1**



(b) Compound **2**



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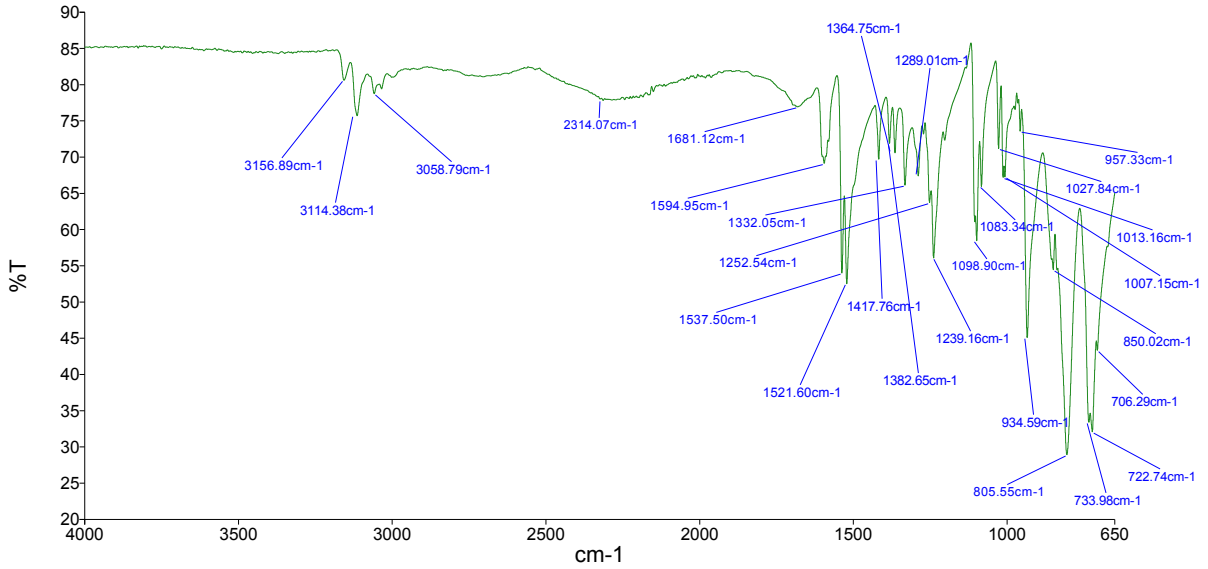
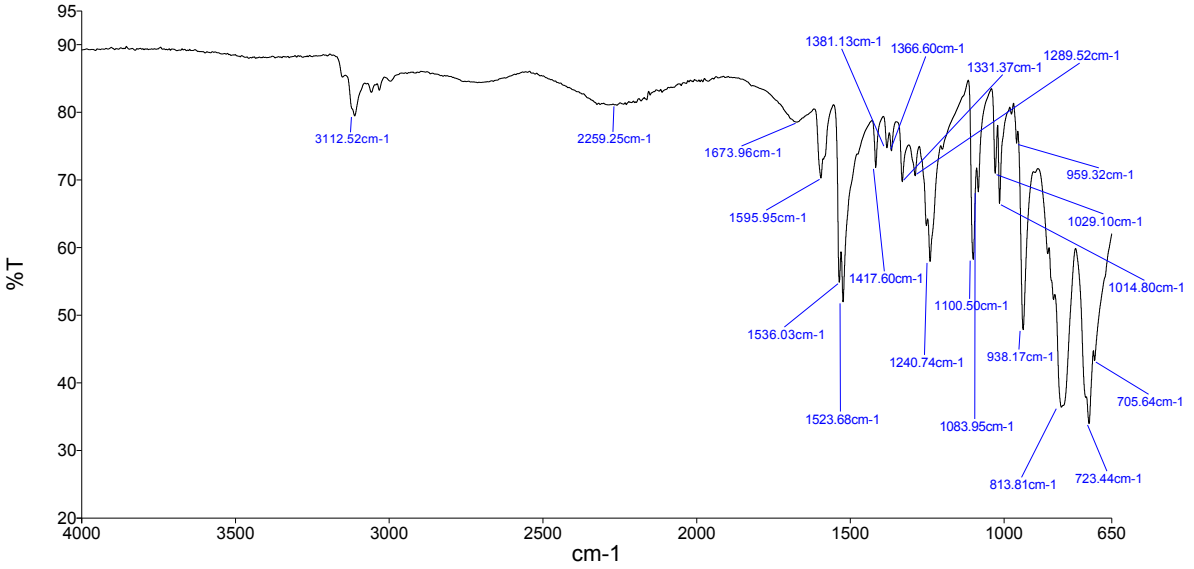
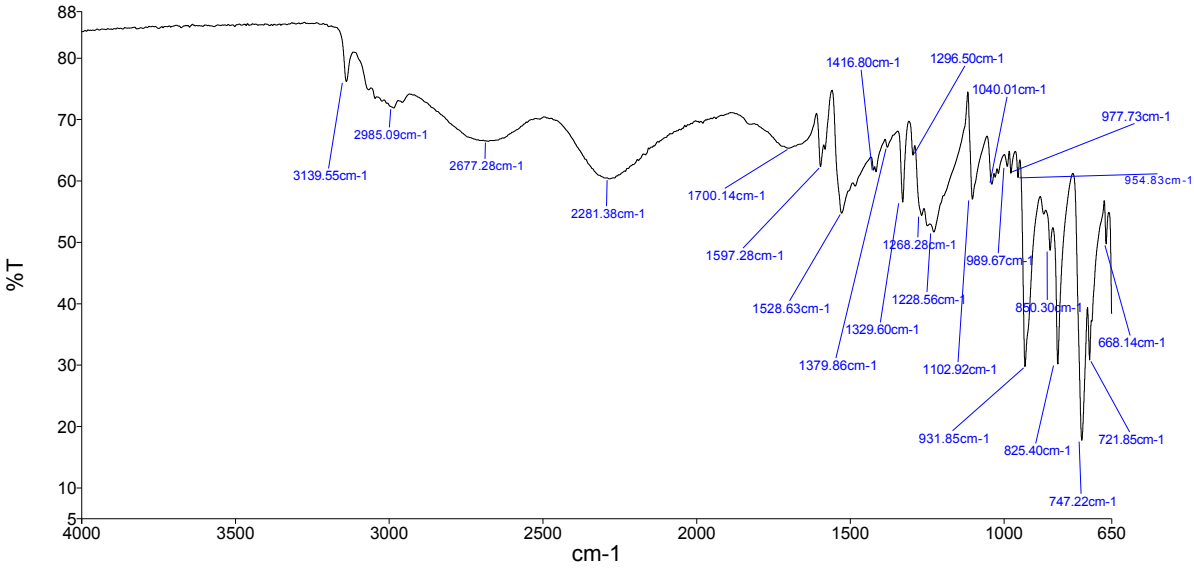


(d) Compound **4**



(e) Compound **5**



(f) H_2TPAA

Fig. S6 IR spectra of compounds **1**–**5** (a-e) and H_2TPAA (f).

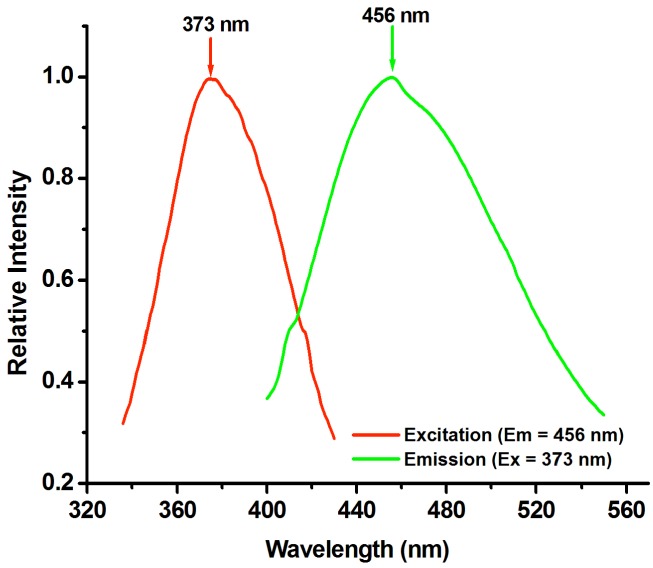


Fig. S7 Photoluminescent spectra of ligand H_2TPAA in the solid state at room temperature.

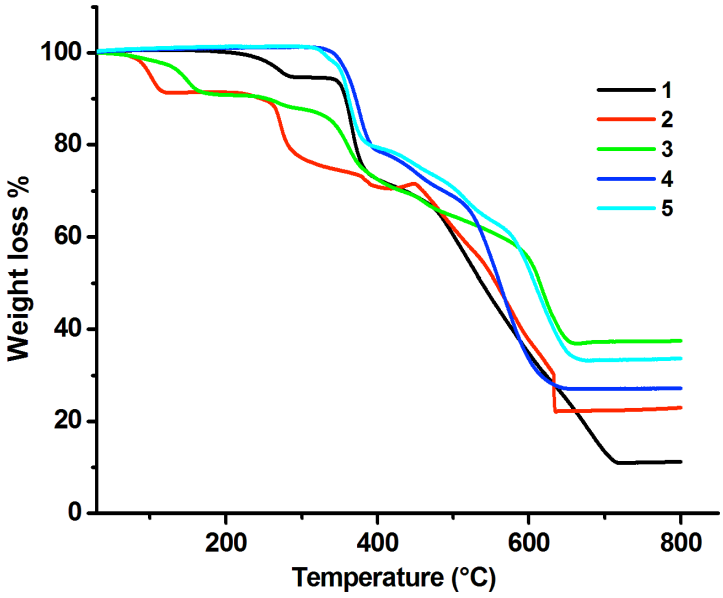


Fig. S8 TGA curves for compounds **1**–**5**.

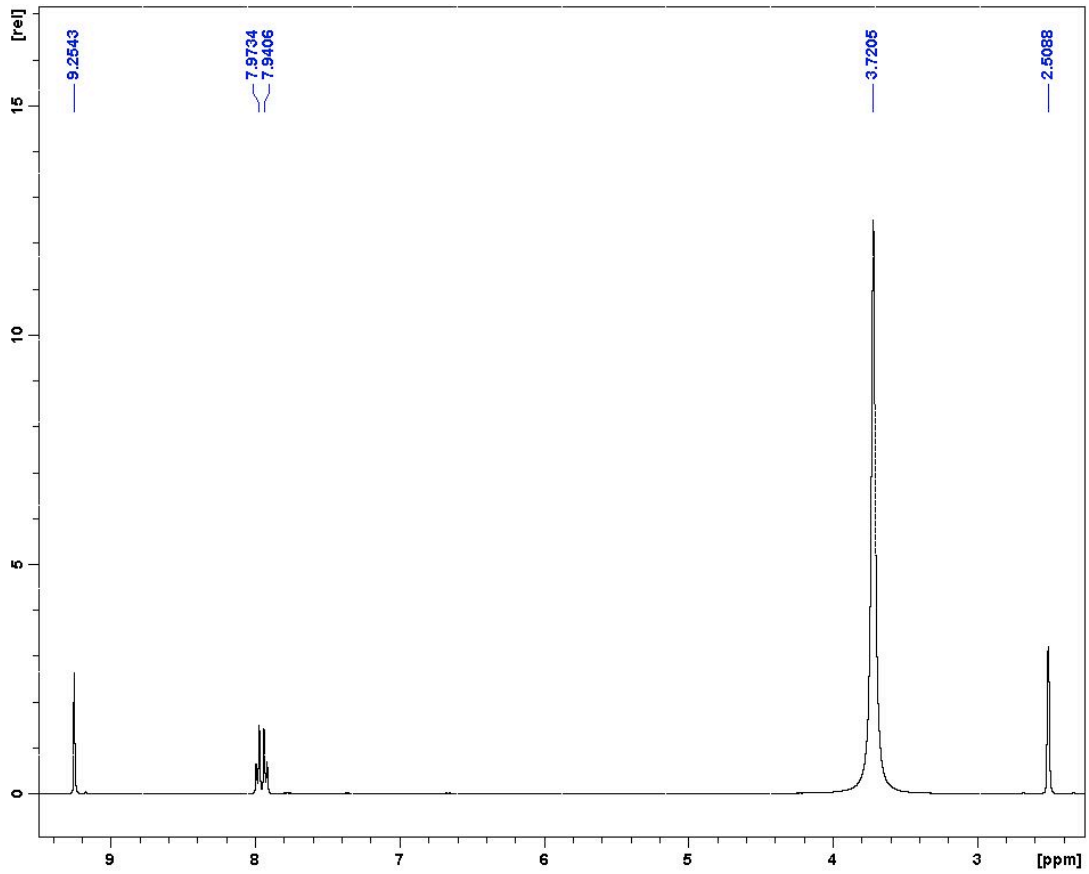


Fig. S9 ^{1}H NMR of H_2TPAA in DMSO-d_6. The strong peak at 3.7205 ppm should be ^{1}H peak of water which could be caused by the recrystallizaion of H_2TPAA from water. 2.5088 ppm is the ^{1}H peak of DMSO-d_6.

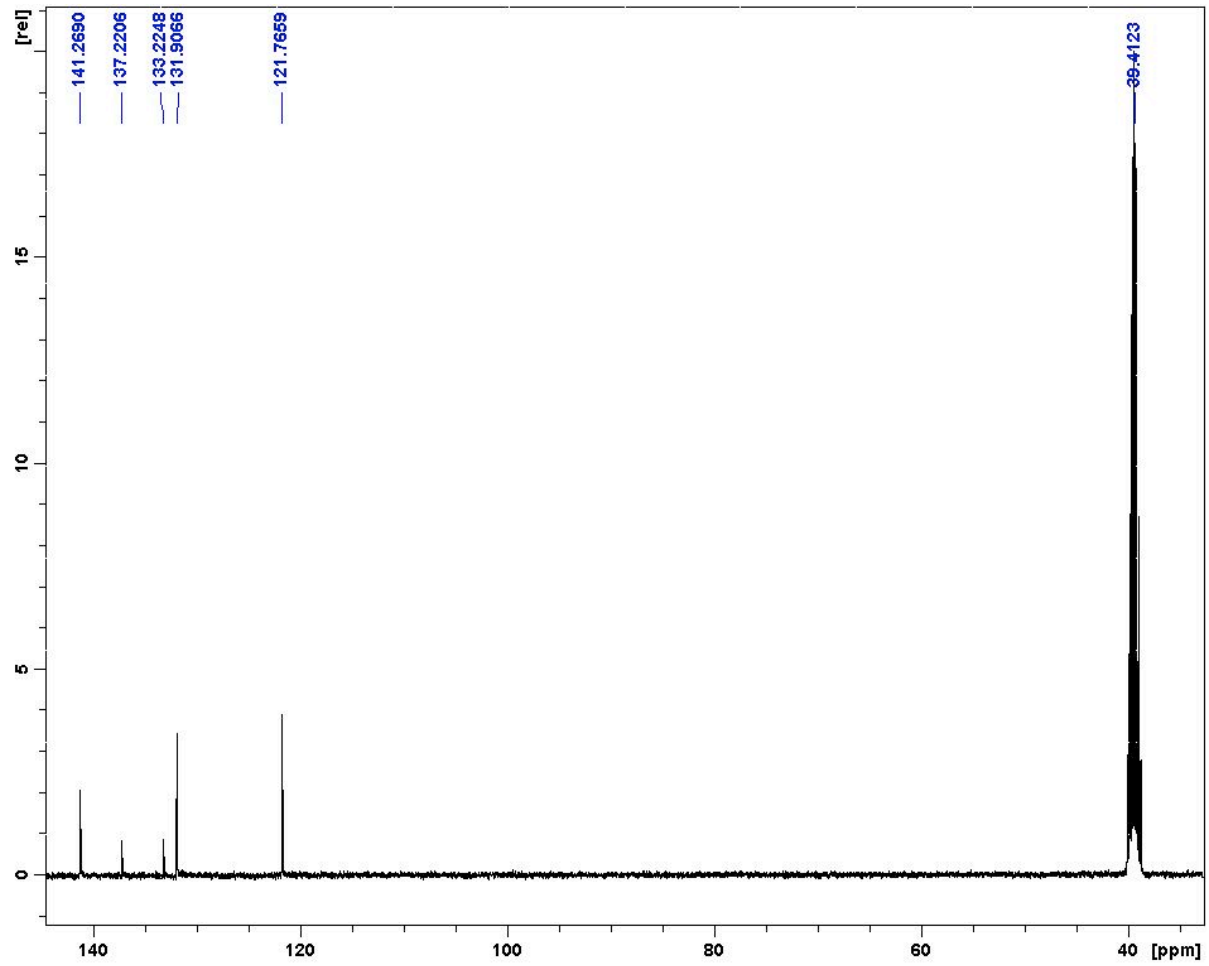


Fig. S10 ^{13}C NMR of H_2TPAA in DMSO-d_6. The strong peak at 39.4123 ppm is the ^{13}C NMR peak of DMSO-d_6.

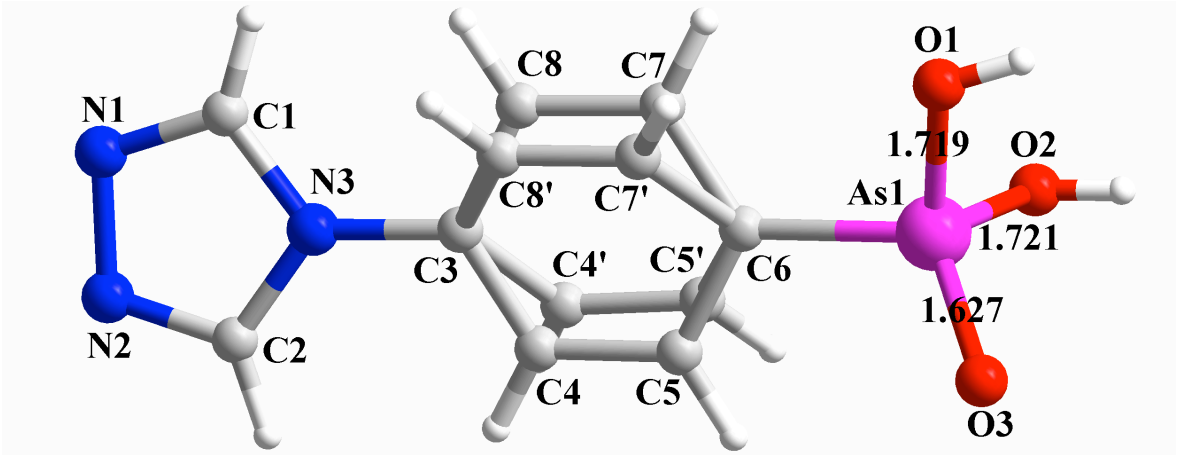


Fig. S11 The structure of H_2TPAA.

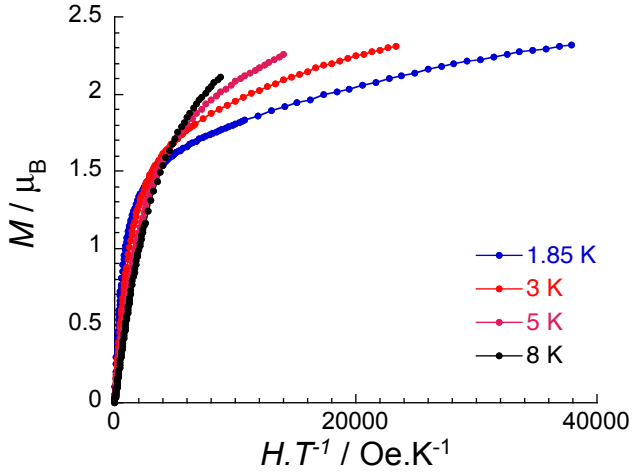


Fig. S12 Field dependence of reduced magnetization at the temperatures indicated for **3**.

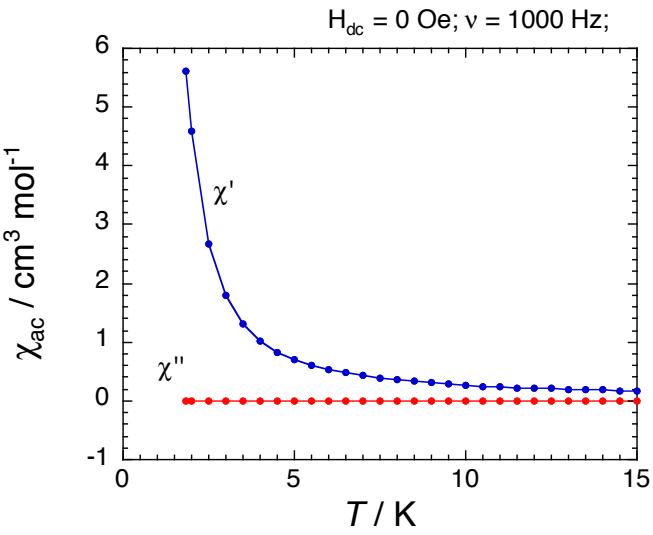


Fig. S13 Temperature dependence below 15 K of the in- and out-of-phase components of ac susceptibility for **3** at 1000 Hz with an amplitude of the ac field of 3 Oe.