Electronic Supporting Information

A quantitative transmetalation with a metal organic framework compound in a solid-liquid interface reaction: synthesis, structure, kinetics, spectroscopy and electrochemistry

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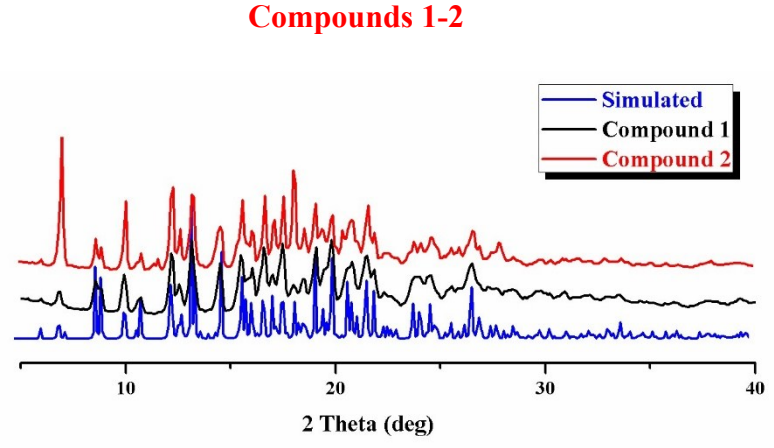
Table of contents

SECTION-1

Powder X-ray diffraction (PXRD) patterns of the compounds 1–3

(a)



(c)

Compound 1 **Compound 2**

(b)

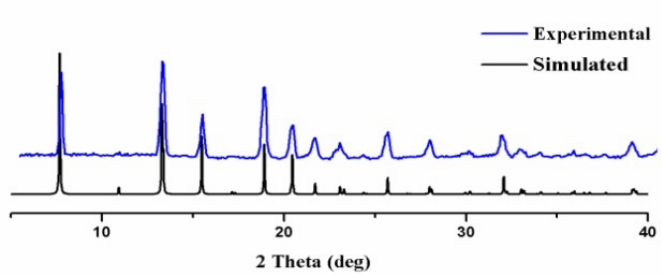


Fig. S1. (a) Experimental powder X-ray diffraction (PXRD) patterns of the compounds **1** (black**)** and **2** (red), including the simulated pattern (blue), obtained from SCXRD data of compound **1** (since both the compounds are isomorphous to each other, the simulated pattern of compound **1** is chosen for comparison). (b) PXRD patterns of the compound **3**, (blue plot-experimental; black plot-simulated). (c) Optical images of powdered samples of compounds **1** (right) and **2** (left), before and after transmetalation, respectively, clearly showing colour change from light yellow to green.

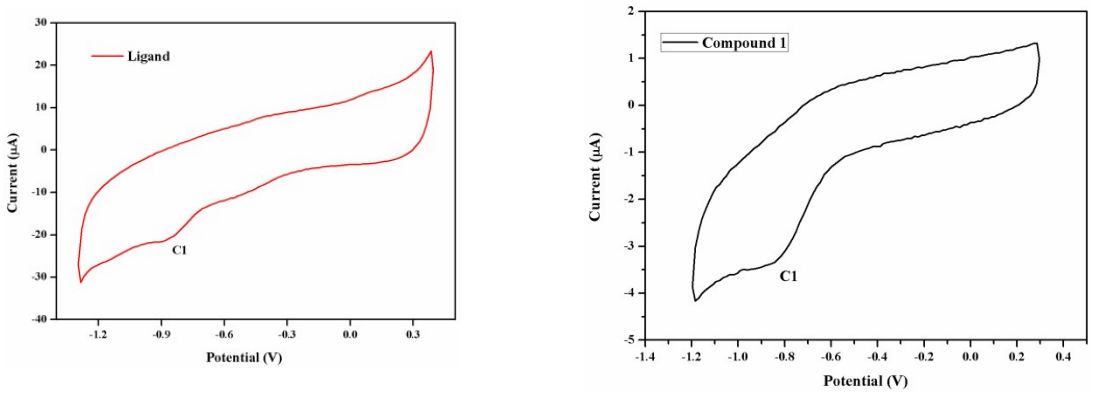
SECTION-2

Sample Preparation.

4 mg of the compound/ligand and 1 mg of carbon black were weighed into a sample vial, to which 1 mL of ethanol and Milli-Q water mixture (3:2) and 10 µL of Nafion was added, the resulting suspension was sonicated for 30-40 min. From this mixture, 10 µL of sample was drop casted on Glassy Carbon (GC) electrode, which then used as working electrode against the Ag/AgCl reference electrode.

Electrochemical properties of 1,4-bpeb ligand and compounds 1 and 2.

(a) (b)



(c)

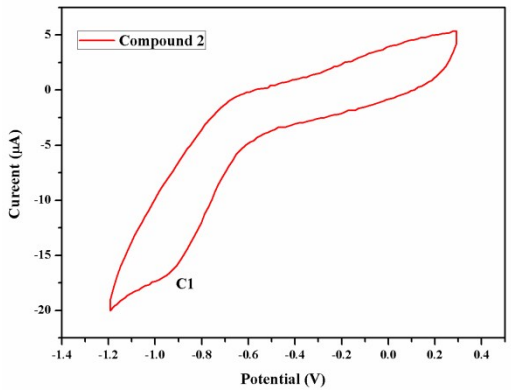
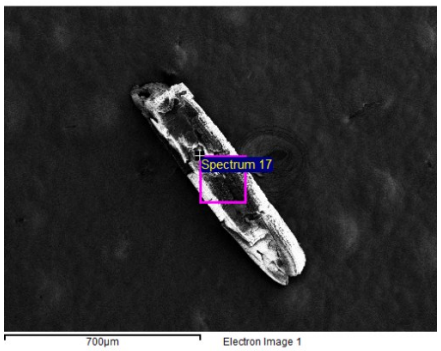


Fig. S2. Cyclic voltamograms (CVs) of (a) 1,4-bpeb ligand in 0.1 M Na_2SO_4 aqueous solution; (b–c) compounds **1** and **2** in acetonitrile (MeCN) solvent using tetra butyl ammonium tetra fluoroborate ($TBABF_4$) as supporting electrolyte. In all the cases, Ag/AgCl electrode was used as reference electrode at a scan rate of 100 mV/s.

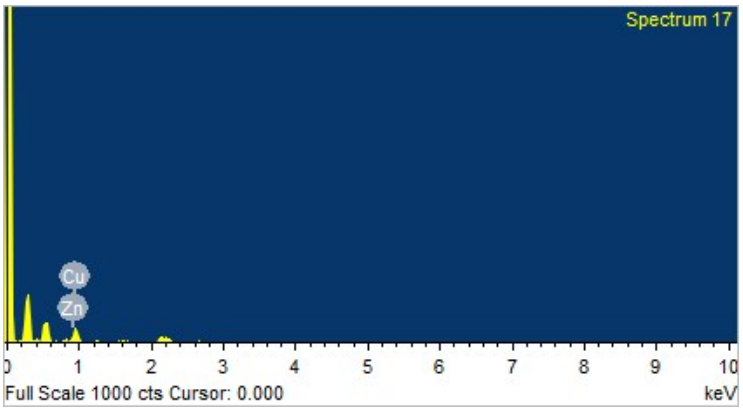
SECTION-3

A. FESEM experiments of compound 2 in 0.05 M Cu(II) solution

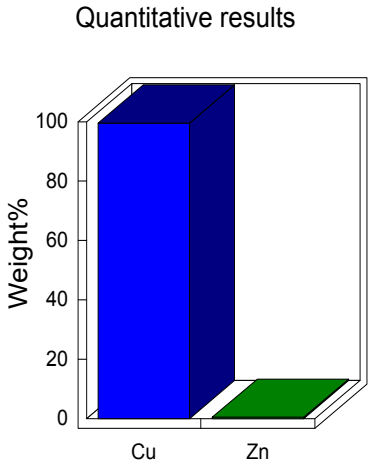
(a)



(b)



(c)



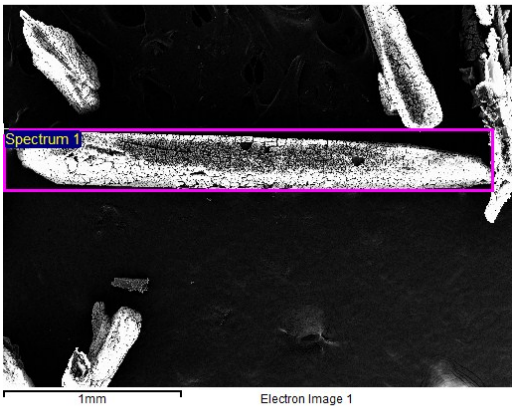
(d)

Element	Weight%	Atomic%
Cu L	99.52	99.53
Zn L	0.48	0.47
Totals	100.00	

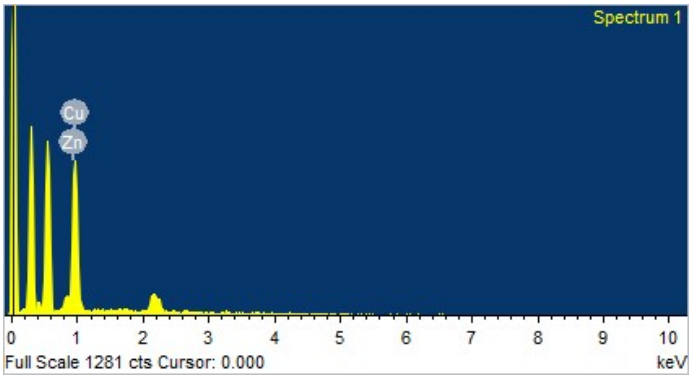
Fig. S3. (a) SEM image of single crystal of compound **2** in **0.05 M** Cu(II) solution. (b) The corresponding EDX plot. (c) Graphical representation (in weight percentages) of the metal content in compound **2**. (d) EDX results showing metal composition (as %) in **2**, after completion of transmetalation reaction.

B. FESEM experiments of compound 2 in 0.1 M Cu(II) solution

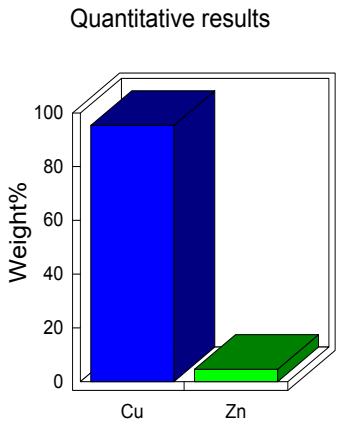
(a)



(b)



(c)



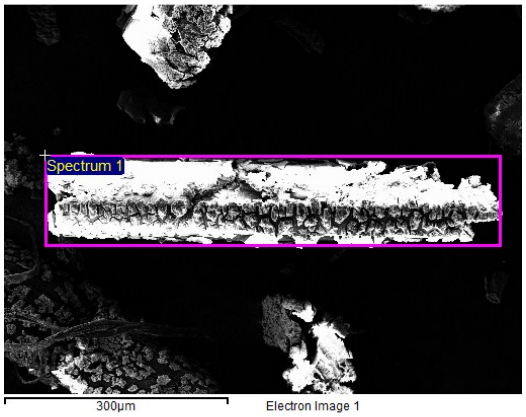
(d)

Element	Weight%	Atomic%
Cu L	95.37	95.50
Zn L	4.63	4.50
Totals	100.00	

Fig. S4. (a) SEM image of single crystal of compound **2** in **0.1 M** Cu(II) solution. (b) The corresponding EDX plot. (c) Graphical representation (in weight percentages) of the metal content in compound **2**. (d) EDX results showing metal composition (as %) in **2**, after 2 days of soaking.

C. FESEM experiments of compound 2 in 0.01 M Cu(II) solution

(a)



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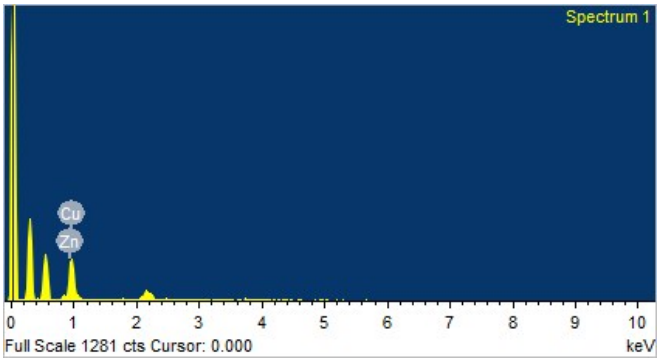
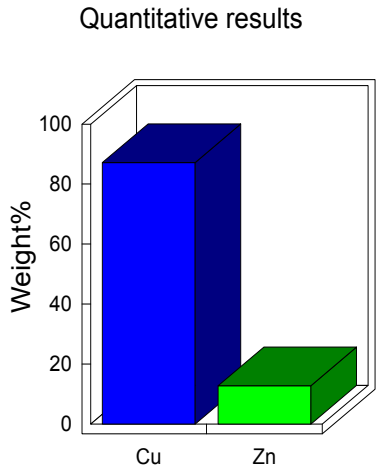


(c)



(d)

Element	Weight%	Atomic%
Cu L	87.20	87.52
Zn L	12.80	12.48
Totals	100.00	

Fig. S5. (a) SEM image of single crystal of compound **2** in **0.01 M** Cu(II) solution. (b) The corresponding EDX plot. (c) Graphical representation (in weight percentages) of the metal content in compound **2**. (d) EDX results showing metal composition (as %) in **2**, after 5 days of soaking.

SECTION-4

Inductively Coupled Plasma (ICP) analysis of compound 2

PBMDJFKBOEKFIC
NFIDPHJF
PNCJCCCAEDCJPE
IBGPLGDF
PDBCNFCJGEKFII
DBNJEGBF

Issued to:

Prof Samar K.Das
School Of Chemistry
University of Hyderabad, Gachibowli,
Hyderabad-500046

Report No. : LLPL/D/16-17/001590
Issue Date : 26/09/2016
Customer Ref.: TRF

Ref.Date : 22/09/2016

Sample Particulars : SKD7-1

Qty. Received : 1no Vial

Test Parameters : Zinc as Zn

Date of Receipt of Sample : 22/09/2016
Date of Starting of Analysis : 26/09/2016
Date of completion of analysis : 26/09/2016

SAMPLE TESTED AS RECEIVED

TEST RESULTS

S.No.	Parameters	UOM	Results
1	Zinc as Zn	% by mass	0.81

Instrument Used: ICP-OES Varian 720-ES
NOTE : This report and results relate only to the sample / items tested.

Fig. S6. Inductively Coupled Plasma **(**ICP) analysis report of compound **2** (in weight percentage).

SECTION-5

Crystal structure images of compounds 1–3, showing N–N separation within 1,4-bpeb ligand

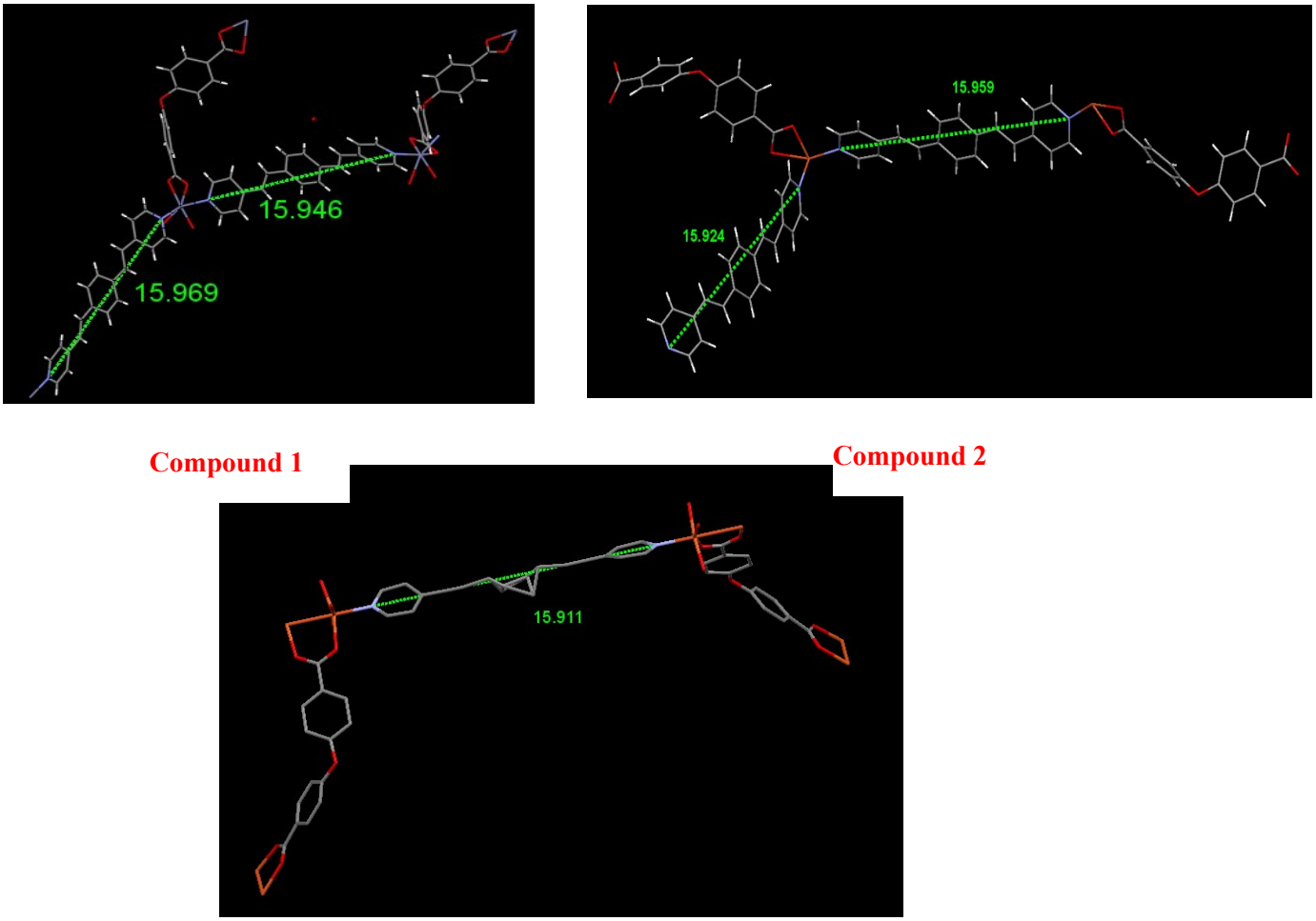


Fig. S7. Crystal structure features of compounds **1-3**; N–N separation between two pyridyl moieties within the 1,4-bpeb ligand in compound **3** is compared with that in the compounds **1** and **2**.

SECTION-6

Optical images of compounds 1 and 2

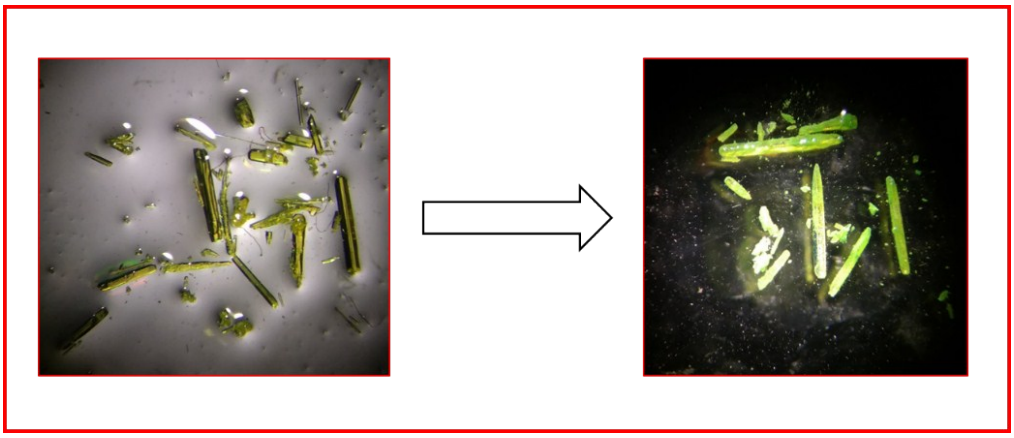


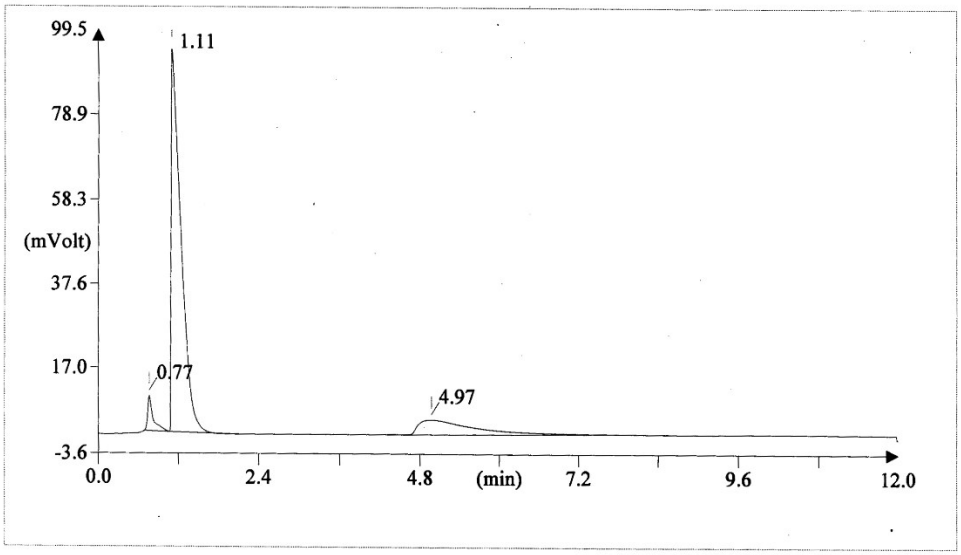
Fig. S8. Bulk crystal images of compound **1**, left [Zn(II)-yellow] and compound **2**, right [Cu(II)-green].

SECTION-7

CHNS analysis of compound 1

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	SKD-7 (# 23)
Analysis type:	UnkNown
Chromatogram filename:	UNK-12012016-3.dat
Sample weight:	2.365



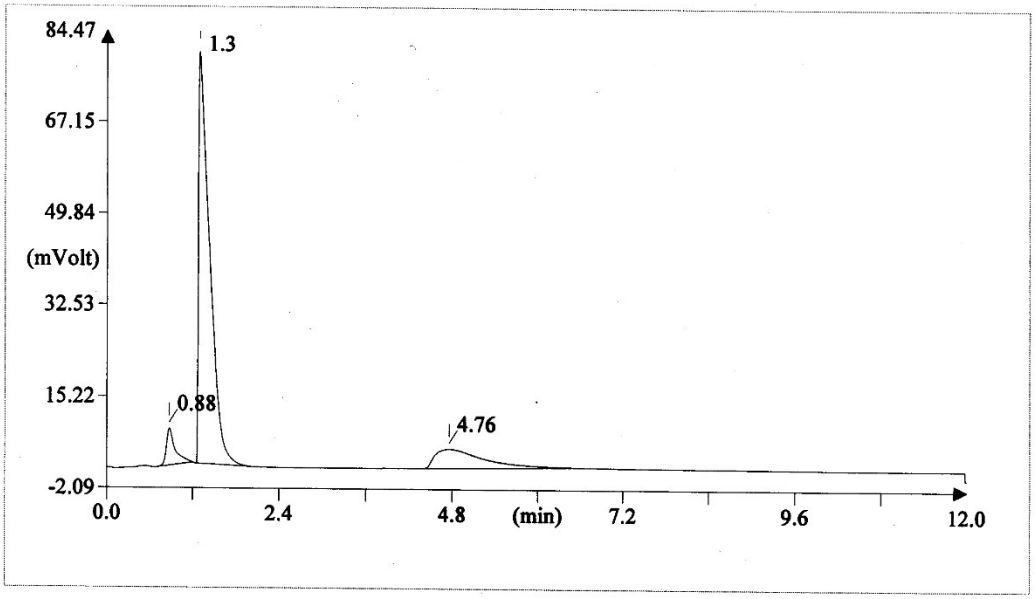
Element Name	Element %	Ret. Time
Nitrogen	4. 51	0. 77
Carbon	66. 39	1. 11
Hydrogen	3. 98	4. 97

Fig. S9. CHNS analysis report of compound **1**.

CHNS analysis of compound 2.

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	SKD-32 (# 21)
Analysis type:	UnkNown
Chromatogram filename:	UNK-18122018-1.dat
Sample weight:	2.115



Element Name	Element %	Ret. Time
Nitrogen	4. 54	0. 88
Carbon	66. 52	1. 30
Hydrogen	4. 16	4. 76

Fig. S10. CHNS analysis report of compound **2**.

CHNS analysis of compound 3.

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
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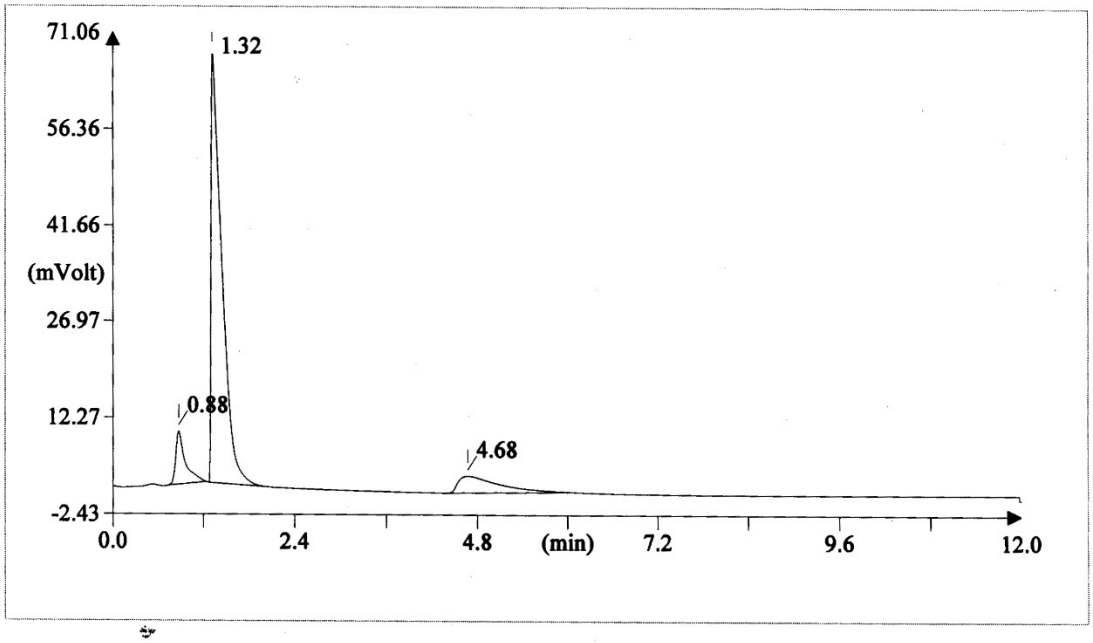
Sample weight:	1.732



Element Name	Element %	Ret. Time
Nitrogen	3. 08	0. 88
Carbon	62. 51	1. 32
Hydrogen	3. 45	4. 67

Fig. S11. CHNS analysis report of compound **3**.

SECTION 8

Infrared (IR) spectrum of compound 1.

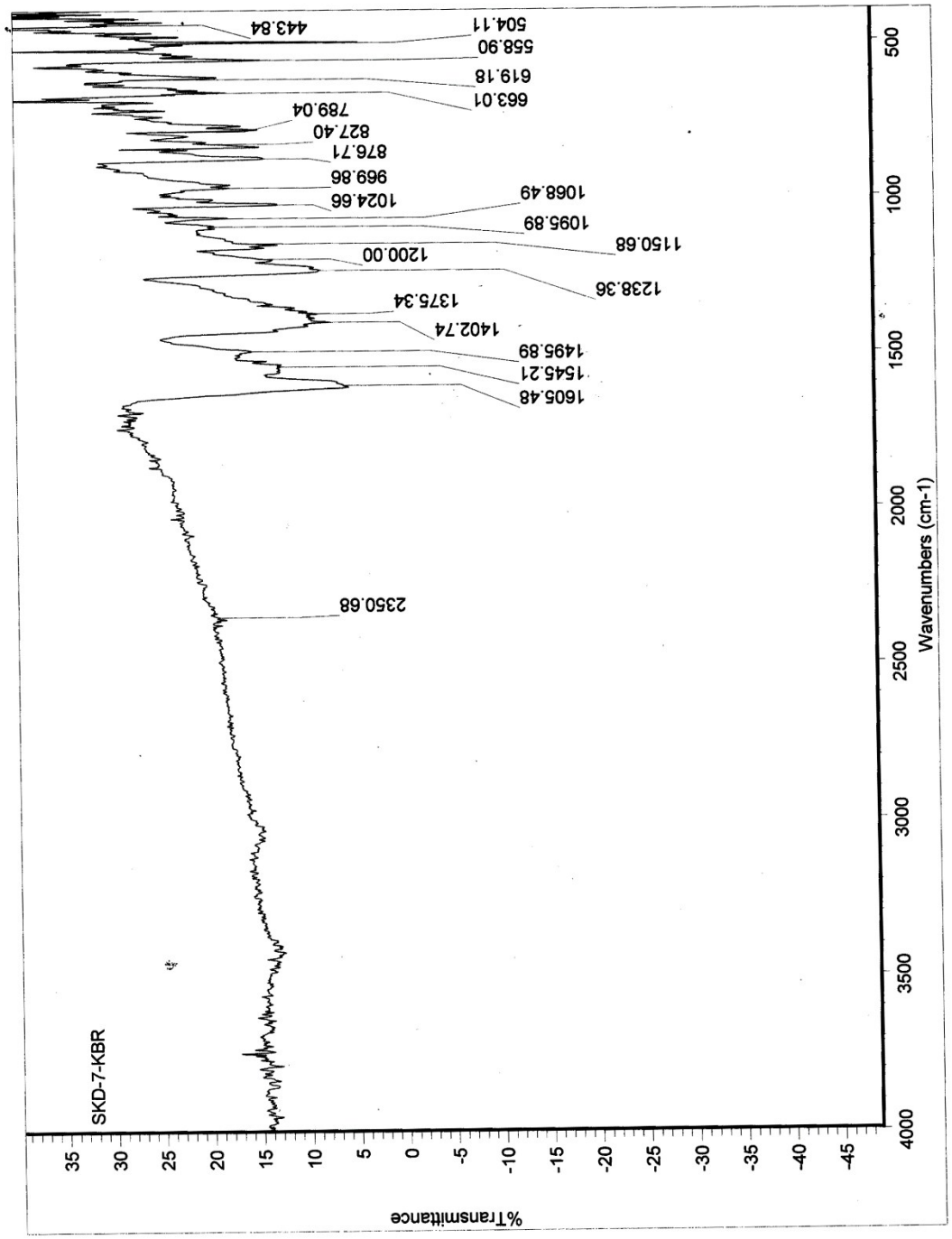


Fig. S12. Infrared (IR) spectrum of compound **1**.

Infrared (IR) spectrum of compound 2.

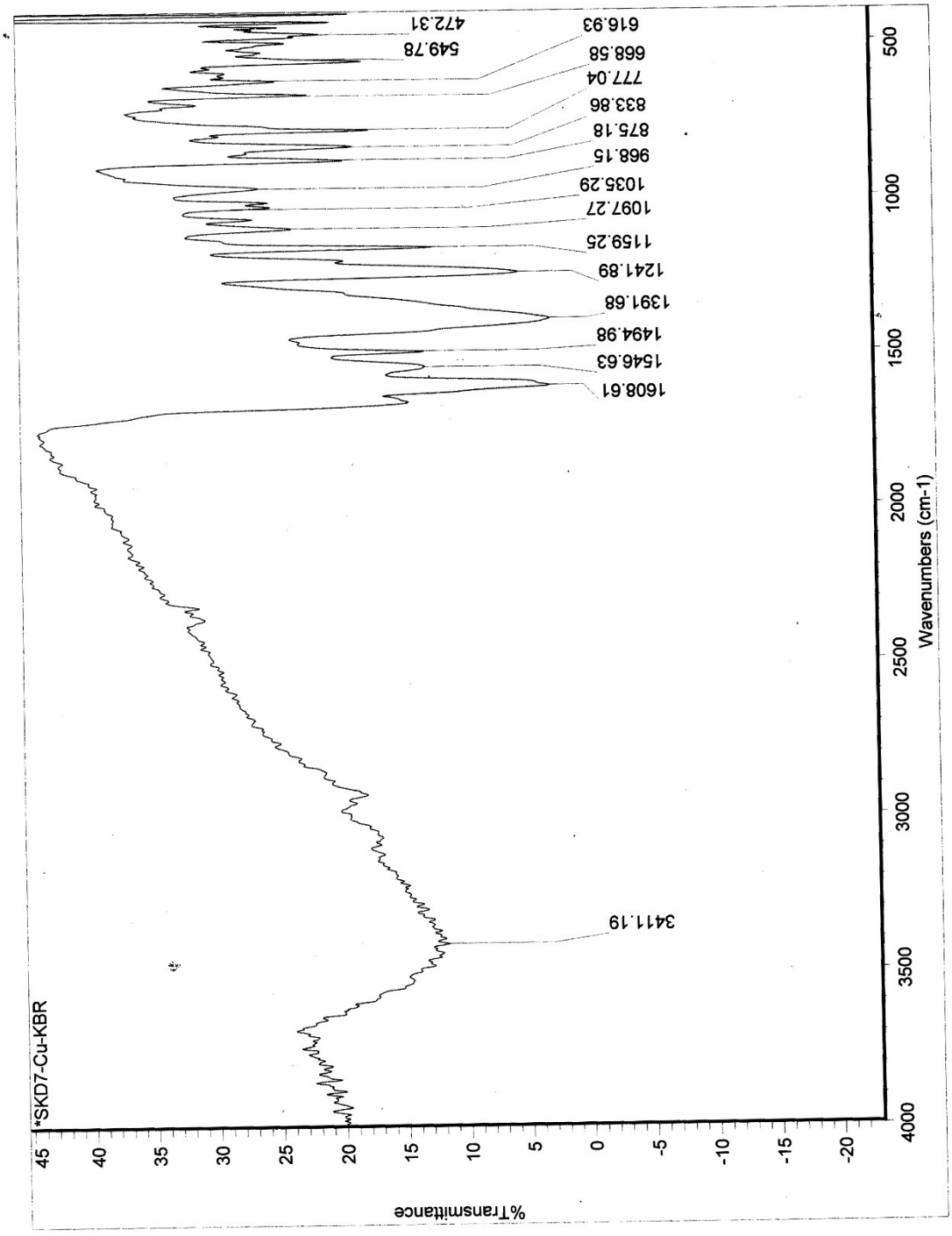


Fig. S13. Infrared (IR) spectrum of compound **2**.

Infrared (IR) spectrum of compound 3.

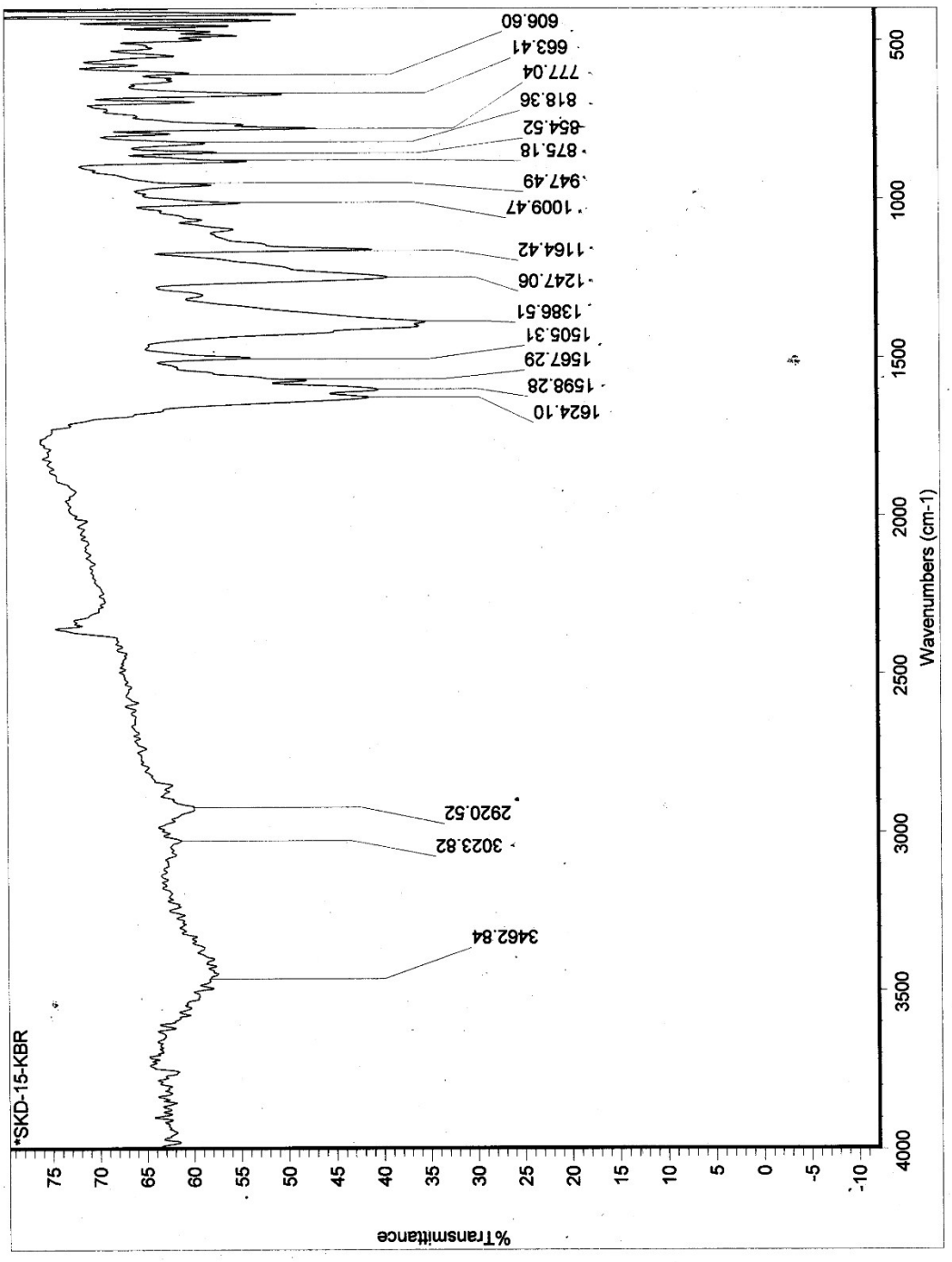


Fig. S14. Infrared (IR) spectrum of compound **3**.

SECTION 9

Table S1: Selected bond lengths and bond angles found in the crystal structures of compounds 1-3.

Compound 1

Zn(01)-O(10)#1	2.039(3)	O(10)#1-Zn(01)-O(6)	154.13(13)
Zn(01)-O(6)	2.061(3)	O(10)#1-Zn(01)-N(2)	100.70(13)
Zn(01)-N(2)	2.066(3)	O(6)-Zn(01)-N(2)	98.85(14)
Zn(01)-N(4)#2	2.091(3)	O(10)#1-Zn(01)-N(4)#2	95.61(12)
Zn(01)-O(9)#1	2.339(3)	O(6)-Zn(01)-N(4)#2	98.56(13)
Zn(01)-O(7I)	2.357(4)	N(2)-Zn(01)-N(4)#2	97.26(12)
Zn(01)-C(68T)#1	2.498(4)	O(10)#1-Zn(01)-O(9)#1	59.75(11)
Zn(02)-O(1B)	2.002(4)	O(6)-Zn(01)-O(9)#1	104.84(12)
Zn(02)-O(4)#3	2.035(3)	N(2)-Zn(01)-O(9)#1	86.91(12)
Zn(02)-N(3)	2.057(3)	N(4)#2-Zn(01)-O(9)#1	155.32(12)
Zn(02)-N(1A)	2.084(3)	O(10)#1-Zn(01)-O(7I)	98.54(12)
Zn(02)-O(5C)#3	2.442(3)	O(6)-Zn(01)-O(7I)	58.17(13)
Zn(02)-C(14W)#3	2.558(5)	N(2)-Zn(01)-O(7I)	154.12(15)
O(10)-C(68T)	1.265(5)	N(4)#2-Zn(01)-O(7I)	97.91(13)
O(10)-Zn(01)#4	2.039(3)	O(9)#1-Zn(01)-O(7I)	87.99(12)
O(9)-C(68T)	1.243(5)	O(10)#1-Zn(01)-C(68T)#1	30.28(13)
O(9)-Zn(01)#4	2.339(3)	O(6)-Zn(01)-C(68T)#1	132.30(15)
N(4)-Zn(01)#5	2.091(3)	N(2)-Zn(01)-C(68T)#1	92.65(13)
N(3)-C(35)	1.348(5)	N(4)#2-Zn(01)-C(68T)#1	125.76(15)
O(6)-C(55M)	1.239(5)	O(9)#1-Zn(01)-C(68T)#1	29.56(12)
O(4)-C(14W)	1.242(5)	O(7I)-Zn(01)-C(68T)#1	95.33(13)
O(4)-Zn(02)#6	2.035(3)	O(1B)-Zn(02)-O(4)#3	149.87(18)
N(1A)-C(19Z)	1.327(5)	O(1B)-Zn(02)-N(3)	102.01(16)
O(1B)-C(1)	1.194(7)	O(4)#3-Zn(02)-N(3)	101.65(13)
O(5C)-Zn(02)#6	2.442(3)	O(1B)-Zn(02)-N(1A)	98.74(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x-1,y+1/2,-z+3/2 #2 x,y-1,z+1 #3 -x+2,y+1/2,-z+1/2

#4 -x-1,y-1/2,-z+3/2 #5 x,y+1,z-1 #6 -x+2,y-1/2,-z+1/2

Compound 2

Cu(01)-O(1)	2.040(3)	O(1)-Cu(01)-N(3)	100.45(15)
Cu(01)-N(3)	2.072(4)	O(1)-Cu(01)-O(5)#1	155.78(15)
Cu(01)-O(5)#1	2.086(4)	N(3)-Cu(01)-O(5)#1	97.94(17)
Cu(01)-N(1)	2.100(4)	O(1)-Cu(01)-N(1)	95.39(14)
Cu(01)-O(4F)#1	2.317(4)	N(3)-Cu(01)-N(1)	97.35(15)
Cu(01)-O(2)	2.336(3)	O(5)#1-Cu(01)-N(1)	97.75(14)
Cu(01)-C(1M)	2.513(5)	O(1)-Cu(01)-O(4F)#1	99.22(15)
Cu(01)-C(14V)#1	2.526(5)	N(3)-Cu(01)-O(4F)#1	153.85(17)
Cu(02)-O(6)	1.980(4)	O(5)#1-Cu(01)-O(4F)#1	58.91(15)
Cu(02)-O(10B)#2	2.053(4)	N(1)-Cu(01)-O(4F)#1	97.77(15)
Cu(02)-N(2)	2.069(4)	O(1)-Cu(01)-O(2)	59.69(12)
Cu(02)-N(4A)#3	2.094(4)	N(3)-Cu(01)-O(2)	86.48(14)
Cu(02)-O(9C)#2	2.370(4)	O(5)#1-Cu(01)-O(2)	106.19(14)
Cu(02)-C(48)#2	2.534(7)	N(1)-Cu(01)-O(2)	155.02(14)
O(1)-C(1M)	1.270(5)	O(4F)#1-Cu(01)-O(2)	88.74(14)
O(2)-C(1M)	1.249(6)	O(1)-Cu(01)-C(1M)	30.19(14)
N(1)-C(15I)	1.334(5)	N(3)-Cu(01)-C(1M)	92.50(16)
N(1)-C(19V)	1.342(5)	O(5)#1-Cu(01)-C(1M)	133.75(18)
O(5)-C(14V)	1.264(6)	N(1)-Cu(01)-C(1M)	125.46(17)
O(5)-Cu(01)#4	2.086(4)	O(4F)#1-Cu(01)-C(1M)	95.92(15)
N(3)-C(53)	1.334(6)	O(2)-Cu(01)-C(1M)	29.57(13)
O(6)-C(35)	1.215(7)	O(1)-Cu(01)-C(14V)#1	127.3(2)
O(10B)-C(48)	1.235(7)	N(3)-Cu(01)-C(14V)#1	126.7(2)
O(10B)-Cu(02)#6	2.053(4)	O(5)#1-Cu(01)-C(14V)#1	29.92(17)
O(9C)-C(48)	1.246(7)	N(1)-Cu(01)-C(14V)#1	99.78(15)
O(9C)-Cu(02)#6	2.370(4)	O(4F)#1-Cu(01)-C(14V)#1	29.01(16)
O(3D)-C(5X)	1.390(5)	O(2)-Cu(01)-C(14V)#1	97.52(15)
O(3D)-C(8Z)	1.400(6)	C(1M)-Cu(01)-C(14V)#1	116.20(19)

Symmetry transformations used to generate equivalent atoms:

#1 -x-1,y+1/2,-z+1/2 #2 -x+2,y-1/2,-z+3/2 #3 x,y+1,z+1

#4 -x-1,y-1/2,-z+1/2 #5 x,y-1,z-1 #6 -x+2,y+1/2,-z+3/2

Compound 3

Cu(1)-O(5)	1.927(4)	C(19)-N(1)-C(15)	114.7(6)
Cu(1)-O(4)	1.929(4)	C(19)-N(1)-Cu(1)	122.7(5)
Cu(1)-O(2)	2.004(4)	C(15)-N(1)-Cu(1)	122.6(5)
Cu(1)-O(1)	2.008(4)	C(1)-O(2)-Cu(1)	124.0(4)
Cu(1)-N(1)	2.159(4)	C(8)-O(1)-Cu(1)	123.9(4)
Cu(1)-Cu(1)#1	2.6473(11)	C(1)#1-O(5)-Cu(1)	122.2(4)
N(1)-C(19)	1.275(10)	C(8)#1-O(4)-Cu(1)	122.1(4)
N(1)-C(15)	1.277(10)		
O(2)-C(1)	1.255(7)		
O(1)-C(8)	1.276(7)		
O(5)-C(1)#1	1.247(7)		
O(4)-C(8)#1	1.262(7)		

O(5)-Cu(1)-O(4)	173.07(19)
O(5)-Cu(1)-O(2)	87.61(19)
O(4)-Cu(1)-O(2)	91.08(16)
O(5)-Cu(1)-O(1)	91.20(16)
O(4)-Cu(1)-O(1)	88.07(19)
O(2)-Cu(1)-O(1)	163.14(16)
O(5)-Cu(1)-N(1)	93.6(2)
O(4)-Cu(1)-N(1)	93.3(2)
O(2)-Cu(1)-N(1)	98.7(2)
O(1)-Cu(1)-N(1)	98.2(2)
O(5)-Cu(1)-Cu(1)#1	86.33(13)
O(4)-Cu(1)-Cu(1)#1	86.74(12)
O(2)-Cu(1)-Cu(1)#1	81.40(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,z+0 #2 y+0,-x+3/2,z-3/4 #3 -y+3/2,x+0,z+3/4

#4 -x+0,-y+0,z+0

***************End of Supporting Information****************