Electronic Supplementary Information

Dinitrogen Supported Coordination Polymers

Wayne Hsu, Kedar Bahadur Thapa, Han-Yun Chang
and Jhy-Der Chen*

Department of Chemistry, Chung-Yuan Christian University,
Chung-Li, Taiwan, R.O.C.

Experimental Section

General Procedures

Elemental analyses were obtained from a HERAEUS VaruoEL analyzer. IR spectra (KBr disk) were recorded on a Jasco FT/IR-460 plus spectrometer. Thermal gravimetric analyses (TGA) measurements were carried on a TG/DTA 6200 analyzer and the samples were heated up in N_2 with a heating rate of 10 ^oC min^{-1}. Emission spectra were obtained from a Hitachi F-4500 spectrometer. Powder X-ray diffraction measurements were carried out on a PANalytical PW3040/60 X'Pert Pro diffractometer or on a Bruker D2 PHASER X-ray Diffractometer.

Materials

The reagents 2-(aminomethyl)pyridine, 3-(aminomethyl)pyridine and 4-(aminomethyl)aminopyridine were purchased from Alfa Aesar and copper(II) acetate from SHOWA. Triethyl orthoformate and $^{15}N_2$ were obtained from Sigma-Aldrich Co.

Preparation of tppz

A mixture of $Cu(O_2CCH_3)_2$ (0.18 g, 1.0 mmol), 2-(aminomethyl)pyridine (0.5 mL, 4.9 mmol) and triethylorthoformate (3.0 mL, 18 mmol) in 5 mL MeOH was placed in a 23 mL Teflon lined stainless container, which was then bubbled with the nitrogen gas for 1 min. The contained was sealed and heated at 100 ^oC for 48 h under autogenous pressure and then cooled slowly to room temperature. Light yellow plate crystals were collected, washed by diethyl ether, and dried under vacuum. Yield: 0.34 g (71 %). Anal. Calcd. for $C_{24}H_{16}N_6$ (MW = 388.43): C, 74.21; H, 4.15; N, 21.64. Found: C, 73.99; H, 4.27; N, 21.50.

Preparation of $[Cu_{2.5}(3\text{-mpyf})(N_2)_{1.5}]_n$, 1

A mixture of $Cu(O_2CCH_3)_2$ (0.18 g, 1.0 mmol), 3-(aminomethyl)pyridine (0.5 mL, 4.9 mmol) and triethylorthoformate (3.0 mL, 18 mmol) in 5 mL MeOH was placed in a 23 mL Teflon lined stainless container, which was then bubbled with nitrogen gas for 1 min. The contained was sealed and heated at 100 ^oC for 48 h under autogenous pressure and then cooled slowly to room temperature. Light yellow plate crystals were collected, washed with diethyl ether, and dried under vacuum. Yield: 0.073 g (43 %). Anal. Calcd. for $C_{13}H_{13}Cu_{2.5}N_7$ (MW = 426.15): C, 36.64; H, 3.07; N, 23.01. Found: C, 36.60; H, 3.14; N, 22.68. IR (KBr disk, cm^{-1}): 1669(m), 1574(s), 1477(w), 1426(s), 1384(s), 1348(m), 1305(s), 1246(w), 1227(w), 1186(w), 1126(w), 1104(w) 1048(m), 1030(m), 993(m), 832(m), 799(m), 646(m), 528(w), 479(w).

Preparations of $\{[Cu_3(4\text{-}Hmpyf)(N_2)_3]\cdot(CH_3OH)\}_n$, 2

A mixture of $Cu(O_2CCH_3)_2$ (0.18 g, 1.0 mmol), 4-(aminomethyl)pyridine (0.5 mL, 5.0 mmol) and triethylorthoformate (3.0 mL, 18 mmol) in 5 mL MeOH was placed in a 23 mL Teflon lined stainless container, which was the bubbled with nitrogen gas for 1 min. The contained was sealed and heated at 100 ^oC for 48 h under autogenous pressure and then cooled slowly to room temperature. Light yellow plate crystals were collected, washed with diethyl ether, and dried under vacuum. Yield: 0.083 g (47 %). Anal. Calcd. for $C_{14}H_{16}Cu_3N_{10}O$ (MW = 530.99): C, 31.67; H, 3.04; N, 26.38. Found: C, 32.02; H, 2.86; N, 26.45. IR (KBr disk, cm^{-1}): 2105(w), 1655(m), 1640(m), 1603(s), 1582(s), 1551(s), 1496(w), 1450(w), 1418(m), 1382(m), 1353(w), 1307(m), 1266(w), 1217(m), 1146(w), 1087(w), 1064(m), 1010(w), 1003(m), 986(m), 974(m), 934(w), 919(w), 826(m), 787(s), 705(s), 675(w), 644(m), 621(w), 590(m), 495(w), 469(w), 454(w), 423(m), 406(w).

It is noted that excess amount of triethylorthoformate was used to give better yields. The molar ratio of $Cu(O_2CCH_3)_2$: 3-(aminomethyl)pyridine or 4-(aminomethyl)pyridine: triethylorthoformate that gave the highest yield is 1 : 8 : 18 for complexes **1** and **2**.

Preparations of 1-^{15}N, 1', and 2-^{15}N, 2'

A mixture of $Cu(O_2CCH_3)_2$ (0.18 g, 1.0 mmol), triethylorthoformate (3.0 mL, 18 mmol), 5 mL of MeOH, and 3-(aminomethyl)pyridine (0.5 mL, 4.9 mmol) or 4-(aminomethyl)pyridine (0.5 mL, 5.0 mmol), were placed in a 23 mL Teflon lined stainless container. The container was bubbled with $^{15}N_2$ for 20, 40 and 60 sec, respectively, and sealed and heated at 100 ^{o}C for 48 h under autogenous pressure, which was then and allowed to cool slowly to room temperature. The light yellow plate crystals were collected, washed with diethyl ether, and dried under vacuum. The yields for the preparation of **1'** and **2'** are shown as followed. Resonance Raman Spectroscopy has shown they are mixtures of **1** and **1'** or **2** and **2'.**

Complex **1'**	Round 1		Round 2	
bubbled with $^{15}N_2$ (sec)	weight (g)	yield (%)	weight (g)	yield (%)
20	0.034	19.74	0.029	16.85
40	0.030	17.65	0.033	19.44
60	0.039	23.11	0.035	20.39
Complex **2'**	Round 1		Round 2	
bubbled with $^{15}N_2$ (sec)	weight (g)	yield (%)	weight (g)	yield (%)
20	0.056	31.80	0.044	24.71
40	0.034	19.15	0.029	16.66
60	0.036	20.07	0.032	17.83

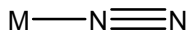
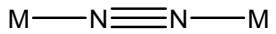
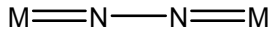
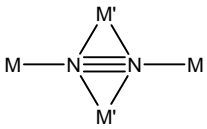
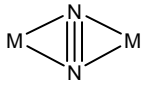
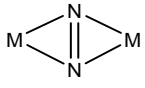
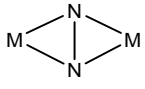
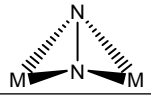
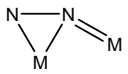
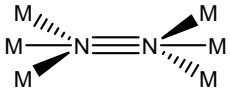
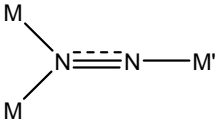
Resonance Raman Spectroscopy

A confocal Raman microscopy module (Jobin Yvon) with a He-Ne laser (514 nm, 20 mW, Melles Griot) was used to characterize the deposition products on small Si chips ($5 \times 5\ mm^2$). The CCD exposure time was varied from 10 to 120 s, depending on the amount of deposition and the degree of interference from background luminescence.

X-ray Crystallography

The diffraction data were collected on a Bruker AXS SMART APEX II diffractometer equipped with a graphite-monochromated MoK_α (λ_α = 0.71073 Å) radiation. Data reduction was performed through standard methods with the use of well-established computational procedures. The structure factors were obtained after Lorentz and polarization correction. An empirical absorption correction based on "multi-scan" was applied to the data. The positions of numerous copper atoms were located by the direct method. The remaining atoms were observed in a series of various alternating Fourier maps and least-square refinements.[1] All hydrogen atoms were added using the HADD command in SHELXTL 5.10 and refined as riding atoms.[2] Basic information pertaining to crystal parameters and structure refinement for **tppz**, **1** and **2** are summarized in Table S1. Selected bond distances and angles are listed in Tables 3 and 4. To confirm the formation of N_2^-, we have checked all the possible atoms for these anions. For complex **1**, the R_1 factors in the final R indices [I / 2sigma(I)] were 0.0364, 0.0396, 0.0381, 0.0406 and 0.0427, and wR_2 factors were 0.0761, 0.0860, 0.0807, 0.0867 and 0.0958 for N_2^-, C_2^-, CN^-, CO^- and O_2^-, respectively. Similarly, the R_1 factors were 0.0536, 0.0572, 0.0571, 0.0610 and 0.0609, and wR_2 factors were 0.1247, 0.1341, 0.1312, 0.1408 and 0.1472 for N_2^-, C_2^-, CN^-, CO^- and O_2^-, respectively, for complex **2**. The refinement results show that N_2^- is best fitted.

Table S1. General bonding modes of N_2 in metal complexes

Coordination mode	Complex	Ref.
End-on Mononuclear 	$[Ru(NH_3)_5N_2]^{2+}$	s3b,
	$[Cu_3(N_2)(L^3)]$	s3p
	$[\{Na_2(thf)_3\}_2\{(PNP)Co(N_2)\}_2]$	s3o
End-on Dinuclear		
(a) 	$(\mu\text{-}N_2)[Mo(N[t\text{-}Bu]Ar)_3]_2$	2g
	$(\mu\text{-}N_2)[Mo(N[t\text{-}Bu]Ar)_3]_2[B(Ar^F)_4]_2(2[B(Ar^F)_4]_2)$	
(b) 	$(\mu\text{-}N_2)[Mo(N[t\text{-}Bu]Ar)_3]_2[B(Ar^F)_4](2[B(Ar^F)_4])$	
	$[\{(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)\}_2(\mu_2,\eta^1\eta^1\text{-}N_2)]$	s3c
	trans,trans-$[(Me_3SiCC)(dmpe)_2Cr]_2(\mu\text{-}N_2)\cdot$Hexane	s3d
	{Cp*M[N(i-Pr)-C(X)N(i-Pr)]}$_2$(μ, η^1:η^1-N_2) (M = Ti, Mo and W; X = Me or NMe_2)	s3e
	$[\{(PNP)Co\}_2(\mu_2\text{-}N_2)]$	s3o
	complex **1** and complex **2**	This work
End-on and Side-on Tetranuclear 	$Na_2[L^1FeNNFeL^1]$.	2f
	$K_2[L^1FeNNFeL^1]$	
	$Na_2[L^1CoNNCoL^1]$	s3r
	$K_2[L^1CoNNCoL^1]$	
	$K_2[L^1NiNNNiL^1]$	s3s
Side-on Dinuclear		
(a) 	$[\{(\eta^5\text{-}C_5Me_4H)_2Zr\}_2(\mu_2,\eta^2\eta^2\text{-}N_2)]$	s3c
	$([Cp^*L^2M]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (M = Nb, Ta, Mo, and W)	s3f
	$((Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)M)_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ (M = Zr, Hf)	s3g
	$[(\eta^5\text{-}C_5Me_4H)_2Hf(X)](\eta^5\text{-}C_5Me_4H)_2HfMe)(\mu_2,\eta^1,\eta^1\text{-}N_2)$	s3h
(b) 	$[(\eta^5\text{-}C_5Me_4H)_2Hf(X)](\eta^5\text{-}C_5Me_4H)_2HfEt)(\mu_2,\eta^1,\eta^1\text{-}N_2)$	
	$[(\eta^5\text{-}C_5Me_4H)_2Hf(X)](\eta^5\text{-}C_5Me_4H)_2Hf(CH_2CH(CH_2)_4)(\mu_2,\eta^1,\eta^1\text{-}N_2)$ (X = Cl, Br, I)	
(c) 	$[(\eta^5\text{-}C_5Me_4H)_2Hf(Cl)](\eta^5\text{-}C_5Me_4H)_2Hf(CH_2CH_2CH{=}CH_2)(\mu_2,\eta^1,\eta^1\text{-}N_2)$	
	$([P_2N_2]Zr)_2(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$	s3i
	$\{[Me_2NN]Co\}_2(\mu\text{-}NAr)_2$	s3q
(d) 		
Side-on End-on Dinuclear 	$([NPN]Ta(\mu\text{-}H))_2(\mu_2\text{-}\eta^1\text{:}\eta^2\text{-}N_2)$	s3j
	$(C_5H_5)_3(C_5H_4)Ti_2(N_2)$	s3k-m
	$[(PNP)_2TaH]_2(N_2)$	s3n
End-on Hexanuclear 	$[(PPh_2MeAu)_6(N_2)]^{2+}$	2a
End-on trinuclear 	$[Cu_3(N_2)(L^3)]$	s3p
	complex **2**	This work

L^1 = N^3-(2,5-diisopropylphenyl)-N^5-(2,6-diisopropylphenyl)-2,2,6,6-tetramethylheptane-3,5-diamide; L^2 = $HC(NCH_3)_2$; L^3 = tris(*β*-diketimine) cyclophane; Ar = 3,5-$C_6H_3Me_2$; Ar^F = 3,5-$C_6H_3(CF_3)_2$; Tol = 4-Me-C_6H_4; dmpe = 1,2-bis(dimethylphosphino)ethane; Cp* = η^5-C_5Me_5; P_2N_2 = $PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$; NPN = $PhP(CH_2SiMe_2NPh)_2$; thf = tetrahydrofuran.

Table S2. Crystallographic data for **tppz, 1** and **2.**

	tppz	**1**	**2**
formula	$C_{24}H_{16}N_6$	$C_{13}H_{13}Cu_{2.5}N_7$	$C_{14}H_{18}Cu_3N_{10}O$
fw	388.43	426.15	533.00
temperature/K	296(2)	296(2)	296(2)
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	9.9194(2)	14.4313(5)	7.3329(3)
b, Å	10.2108(3)	13.2244(6)	18.6223(7)
c, Å	11.9500(4)	7.5812(3)	14.8934(6)
β, deg	126.9340(10)	93.883(3)	101.642(2)
V, Å3	967.47(5)	1443.51(10)	1991.94(14)
Z, Dc/ g cm-3	2, 1.333	4, 1.961	4, 1.777
μ, mm^{-1}	0.083	3.670	3.201
$2\theta_{max}$, deg	52	56.60	56.56
no. of reflns meased	4325	14125	19095
no. of reflns used (R_{int})	1851, 0.0151	3588, 0.0633	4943, 0.0693
data completeness (%)	97.0	100.0	100.0
no. of params	136	205	262
R_1[a]	0.0367	0.0364	0.0536
wR_2[b], final R [$I>2\sigma(I)$]	0.0879	0.0761	0.1247
R_1[a]	0.0539	0.0814	0.1072
wR_2[b] (all data)	0.0974	0.0915	0.1476
GOF on F^2	1.051	0.993	1.005

[a]$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [b]$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$. $w = 1 / [\sigma^2(F_o^2) + (ap)^2 + (bp)]$, $p = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)] / 3$. A = 0.0526, b = 0.0344, **tppz**; a = 0.0328, b = 0.8996, **1**; a =0.0661, b = 1.9283, **2**.

Table S3. Selected bond lengths (Å) and angle (°) for **1**.

1			
Cu(1)---Cu(1A)	2.5605(8)	Cu(2)-N(5)	1.949(3)
Cu(1)-N(2)	1.877(3)	Cu(2)-N(7)	1.911(3)
Cu(1)-N(3A)	1.884(3)	Cu(3)-N(6)	1.849(4)
Cu(2)-N(1)	2.160(3)	N(5)-N(6)	1.168(4)
Cu(2)-N(4B)	2.128(3)	N(7)-N(7C)	1.178(6)
N(2)-Cu(1)-N(3A)	171.93(13)	N(5)-Cu(2)-N(4B)	98.44(12)
N(1)-Cu(2)-N(5)	94.72(12)	N(7)-Cu(2)-N(4B)	106.01(13)
N(1)-Cu(2)-N(7)	104.59(13)	N(5)-Cu(2)-N(7)	144.45(14)
N(1)-Cu(2)-N(4B)	102.30(11)	N(6)-Cu(3)-N(6D)	180.0

A: -x + 2, -y + 2, -z + 1; B: -x + 2, -y -0.5, -z + 0.5; C: -x + 1, -y + 1, -z + 1; D: -x + 2, -y + 1, -z + 1.

Table S4. Selected bond lengths (Å) and angle (°) for **2**.

2			
Cu(1)---Cu(1A)	2.4460(13)	Cu(2)-N(1B)	2.063(4)
Cu(1)-N(7)	1.942(4)	Cu(3)-N(6)	1.931(5)
Cu(1)-N(2)	2.048(5)	Cu(3)-N(9)	1.856(5)
Cu(1)-N(5)	2.011(5)	Cu(3)-N(4D)	2.037(4)
Cu(1)-N(5A)	2.174(5)	N(5)-N(6)	1.161(6)
Cu(2)-N(8)	1.881(5)	N(7)-N(8)	1.152(6)
Cu(2)-N(10C)	1.896(5)	N(9)-N(10)	1.168(6)
Cu(1)-N(5)-Cu(1A)	71.41(16)	N(7)-Cu(1)-N(5A)	111.01(19)
N(2)-Cu(1)-N(7)	109.21(19)	N(8)-Cu(2)-N(1B)	112.90(19)
N(2)-Cu(1)-N(5)	109.38(19)	N(8)-Cu(2)-N(10C)	140.3(2)
N(2)-Cu(1)-N(5A)	100.49(18)	N(1B)-Cu(2)-N(10C)	106.54(18)
N(5)-Cu(1)-N(7)	116.9(2)	N(6)-Cu(3)-N(9)	131.8(2)
N(5)-Cu(1)-N(5A)	108.59(16)	N(6)-Cu(3)-N(4D)	101.92(17)
		N(9)-Cu(3)-N(4D)	126.2(2)

A: -x + 1, -y, -z + 1; B: x + 0.5, -y + 0.5, -z + 0.5; C: -x + 1.5, y + 0.5, -z + 0.5; D: x + 0.5, -y + 0.5, z – 0.5.

Table S5. Summary of natural population analysis for [$Cu_6(NH_3)(\mu_2$-

$N_2)_2(\mu_3\text{-}N_2)_2]^{2+}$

Atom	No	Natural Population				
		Natural Charge	Core	Valence	Rydberg	Total
Cu	1	0.89215	17.99450	10.07528	0.03807	28.10785
Cu	2	0.76843	17.99779	10.17508	0.05870	28.23157
Cu	3	0.89215	17.99450	10.07528	0.03807	28.10785
Cu	4	0.76843	17.99779	10.17508	0.05870	28.23157
Cu	5	0.93531	17.99709	10.01663	0.05097	28.06469
Cu	6	0.93531	17.99709	10.01663	0.05097	28.06469
N	7	-0.38739	1.99972	5.29068	0.09698	7.38739
N	8	-0.43062	1.99965	5.34605	0.08492	7.43062
N	9	-0.29123	1.99981	5.20936	0.08206	7.29123
N	10	-0.38739	1.99972	5.29068	0.09698	7.38739
N	11	-0.43062	1.99965	5.34605	0.08492	7.43062
N	12	-0.29123	1.99981	5.20936	0.08206	7.29123
N	13	-0.53187	1.99975	5.45606	0.07607	7.53187
N	14	-0.53187	1.99975	5.45606	0.07607	7.53187
H	15	0.39956	0.00000	0.59901	0.00142	0.60044
H	16	0.40180	0.00000	0.59663	0.00157	0.59820
H	17	0.39588	0.00000	0.60276	0.00136	0.60412
H	18	0.40180	0.00000	0.59663	0.00157	0.59820
H	19	0.39956	0.00000	0.59901	0.00142	0.60044
H	20	0.39588	0.00000	0.60276	0.00136	0.60412
N	21	-1.15202	1.99974	6.13144	0.02084	8.15202
N	22	-1.15202	1.99974	6.13144	0.02084	8.15202
Total		2.00001	127.97610	118.99795	1.02594	247.99999

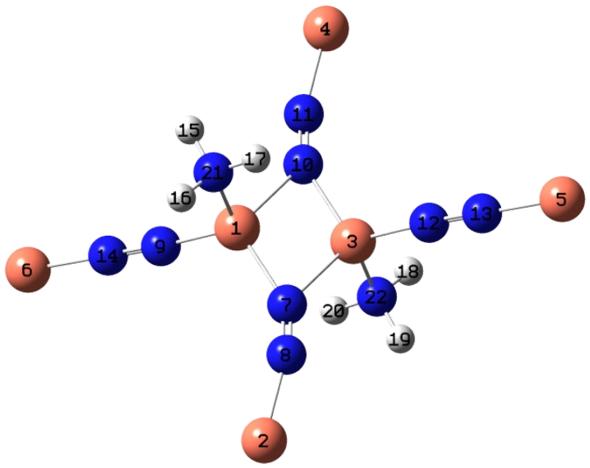


Table S6. Atom-atom net linear NLMO/NPA bond orders.

Atom	No	1	2	3	4	5	6	7	8	9
Cu	1	0	0.052	0.0467	-0.005	-0.0072	-0.0373	0.1269	-0.0707	0.1106
Cu	2	0.052	0	-0.0195	0.0062	-0.0021	0.0577	-0.2076	0.2637	-0.2018
Cu	3	0.0467	-0.0195	0	0.0243	-0.0039	-0.0122	0.0551	0.0033	0.0048
Cu	4	-0.005	0.0062	0.0243	0	0.0544	-0.0063	0.0841	-0.0396	0.0394
Cu	5	-0.0072	-0.0021	-0.0039	0.0544	0	0.001	0.0194	0.0039	0.0082
Cu	6	-0.0373	0.0577	-0.0122	-0.0063	0.001	0	-0.0568	0.0559	-0.0606
N	7	0.1269	-0.2076	0.0551	0.0841	0.0194	-0.0568	0	2.5157	0.4237
N	8	-0.0707	0.2637	0.0033	-0.0396	0.0039	0.0559	2.5157	0	-0.3879
N	9	0.1106	-0.2018	0.0048	0.0394	0.0082	-0.0606	0.4237	-0.3879	0
N	10	0.009	0.1226	0.0828	-0.0738	-0.0489	0.0373	-0.1519	0.1335	0.0188
N	11	-0.0481	0.1206	-0.0343	0.1993	0.0538	0.0444	-0.081	0.0958	0.0852
N	12	-0.0408	-0.1136	0.053	-0.2108	-0.0163	0.0388	-0.0128	0.03	0.031
N	13	0.0031	-0.0335	0.0185	0.0859	0.0964	-0.0313	-0.0393	0.036	-0.027
N	14	-0.0449	0.2058	-0.0081	-0.0309	-0.0188	0.1065	-0.3866	0.3736	2.4504
H	15	0.0006	0	-0.0014	0.0006	0.0005	-0.0001	-0.001	0.0013	-0.0002
H	16	0.0001	0.0006	-0.0006	-0.0012	-0.0006	0.0008	-0.0021	0.001	-0.0017
H	17	0.0008	-0.0003	-0.0002	0.0006	0.0004	-0.0006	-0.0013	-0.0003	-0.002
H	18	-0.0003	-0.0011	0.0002	0.0006	0.0007	-0.0005	-0.0005	0.0017	0.0008
H	19	-0.0014	0.0004	0.0006	-0.0007	-0.0005	0.0003	-0.0017	-0.0001	-0.0003
H	20	-0.0002	0.0004	0.0007	-0.0002	-0.0008	0.0003	-0.0008	0	-0.0007
N	21	0.0311	-0.0002	-0.0025	-0.0004	0.0006	-0.0012	-0.0012	-0.0019	0.0085
N	22	-0.0022	-0.0008	0.0296	-0.0003	0.0001	0.0007	0.0006	0.0016	-0.0025

Atom		10	11	12	13	14	15	16	17	18
Cu	1	0.009	-0.0481	-0.0408	0.0031	-0.0449	0.0006	0.0001	0.0008	-0.0003
Cu	2	0.1226	0.1206	-0.1136	-0.0335	0.2058	0	0.0006	-0.0003	-0.0011
Cu	3	0.0828	-0.0343	0.053	0.0185	-0.0081	-0.0014	-0.0006	-0.0002	0.0002
Cu	4	-0.0738	0.1993	-0.2108	0.0859	-0.0309	0.0006	-0.0012	0.0006	0.0006
Cu	5	-0.0489	0.0538	-0.0163	0.0964	-0.0188	0.0005	-0.0006	0.0004	0.0007
Cu	6	0.0373	0.0444	0.0388	-0.0313	0.1065	-0.0001	0.0008	-0.0006	-0.0005
N	7	-0.1519	-0.081	-0.0128	-0.0393	-0.3866	-0.001	-0.0021	-0.0013	-0.0005
N	8	0.1335	0.0958	0.03	0.036	0.3736	0.0013	0.001	-0.0003	0.0017
N	9	0.0188	0.0852	0.031	-0.027	2.4504	-0.0002	-0.0017	-0.002	0.0008
N	10	0	2.1763	0.408	-0.1346	-0.1293	-0.0012	-0.0006	-0.0005	-0.0017
N	11	2.1763	0	-0.251	0.1292	-0.0977	-0.0001	0.0018	-0.0001	0.0011
N	12	0.408	-0.251	0	2.1759	-0.0401	-0.0005	0.001	-0.0006	-0.0015
N	13	-0.1346	0.1292	2.1759	0	0.0273	0.001	-0.0007	0.0005	0.001

N	14	-0.1293	-0.0977	-0.0401	0.0273	0	-0.0008	0.001	0.0012	-0.0004
H	15	-0.0012	-0.0001	-0.0005	0.001	-0.0008	0	-0.0005	-0.0002	0.0001
H	16	-0.0006	0.0018	0.001	-0.0007	0.001	-0.0005	0	-0.0005	0
H	17	-0.0005	-0.0001	-0.0006	0.0005	0.0012	-0.0002	-0.0005	0	0.0001
H	18	-0.0017	0.0011	-0.0015	0.001	-0.0004	0.0001	0	0.0001	0
H	19	-0.0014	0.0006	0.0001	-0.001	0.0004	-0.0004	0	-0.0003	-0.0006
H	20	-0.0018	-0.0003	-0.002	0.0011	0.0005	-0.0003	0.0003	-0.0002	-0.0003
N	21	0.0009	0.0003	-0.0025	0.0008	0.0012	0.595	0.5926	0.599	0.0005
N	22	-0.0019	-0.0002	0.0095	0.0016	0.0005	-0.0003	0.0006	-0.0001	0.5924

Atom		19	20	21	22
Cu	1	-0.0014	-0.0002	0.0311	-0.0022
Cu	2	0.0004	0.0004	-0.0002	-0.0008
Cu	3	0.0006	0.0007	-0.0025	0.0296
Cu	4	-0.0007	-0.0002	-0.0004	-0.0003
Cu	5	-0.0005	-0.0008	0.0006	0.0001
Cu	6	0.0003	0.0003	-0.0012	0.0007
N	7	-0.0017	-0.0008	-0.0012	0.0006
N	8	-0.0001	0	-0.0019	0.0016
N	9	-0.0003	-0.0007	0.0085	-0.0025
N	10	-0.0014	-0.0018	0.0009	-0.0019
N	11	0.0006	-0.0003	0.0003	-0.0002
N	12	0.0001	-0.002	-0.0025	0.0095
N	13	-0.001	0.0011	0.0008	0.0016
N	14	0.0004	0.0005	0.0012	0.0005
H	15	-0.0004	-0.0003	0.595	-0.0003
H	16	0	0.0003	0.5926	0.0006
H	17	-0.0003	-0.0002	0.599	-0.0001
H	18	-0.0006	-0.0003	0.0005	0.5924
H	19	0	-0.0003	-0.0003	0.5949
H	20	-0.0003	0	-0.0002	0.5986
N	21	-0.0003	-0.0002	0	-0.002
N	22	0.5949	0.5986	-0.002	0

Table S7. Thermal properties of **1** and **2**.

Complex	Weight loss of MeOH, T, °C (found/calc), %	Weight loss of N_2, T, °C (found/calc), %	Weight loss of ligands, T, °C (found/calc), %
1		140 - 200 (9.17 / 9.86)	255 – 450 (53.60 / 52.86)
2	30 – 200 (5.86 / 6.01)	200 – 270 (14.58 / 15.77)	315 – 500 (43.17 / 42.45)

Table S8. Solid-state emission and excitation data for complexes **1**, **1'**, **2** and **2'**.

Complex	Emission λ_{em}, nm	Excitation λ_{ex}, nm
1	418, 466	369, 278
1'	411, 465	377, 282
2	425, 464	370, 319
2'	417, 470	365, 328

Fig. S1. An ORTEP diagram showing the structure **tppz**.

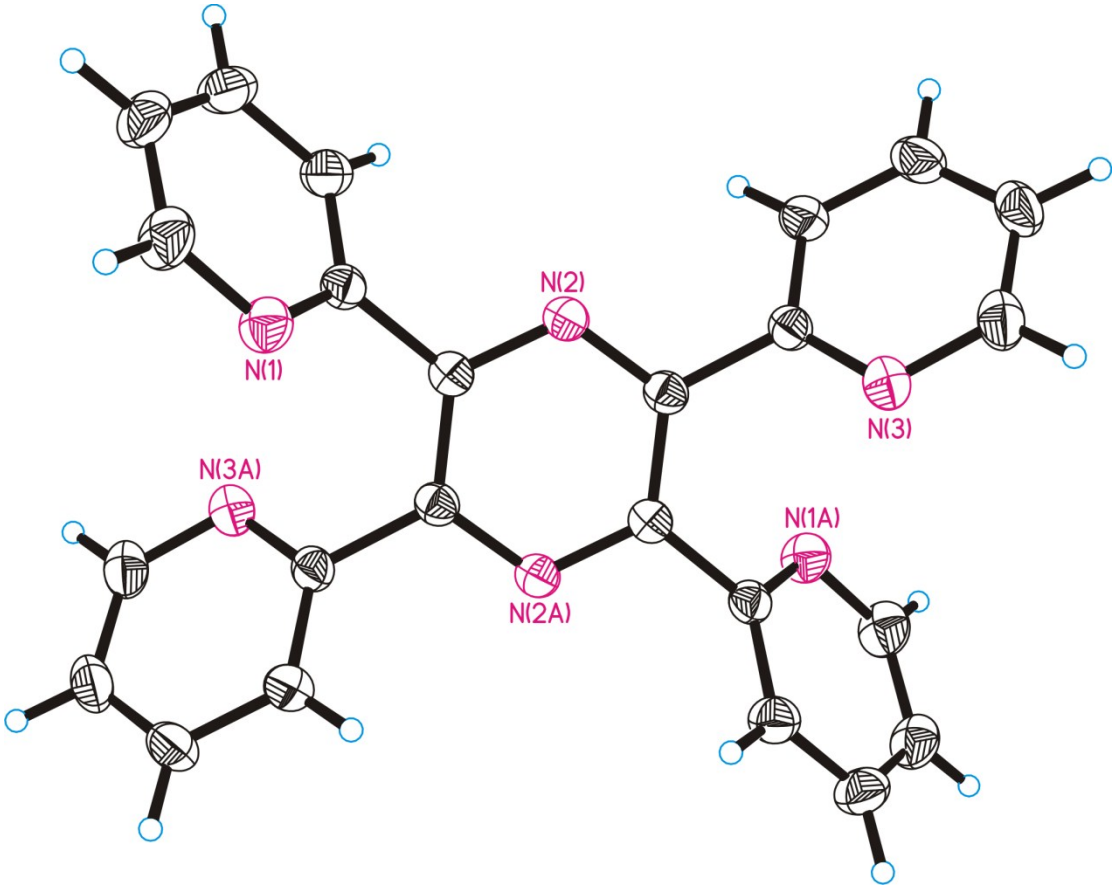
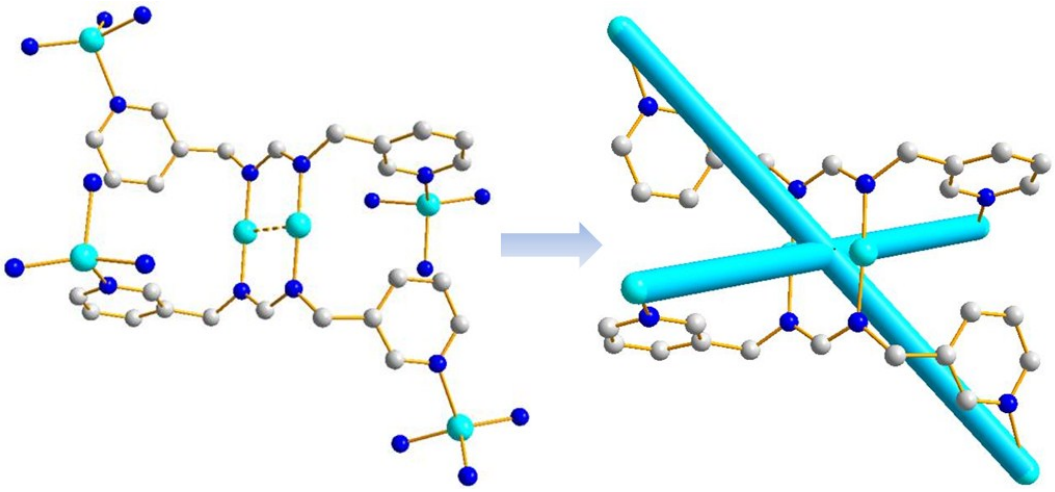
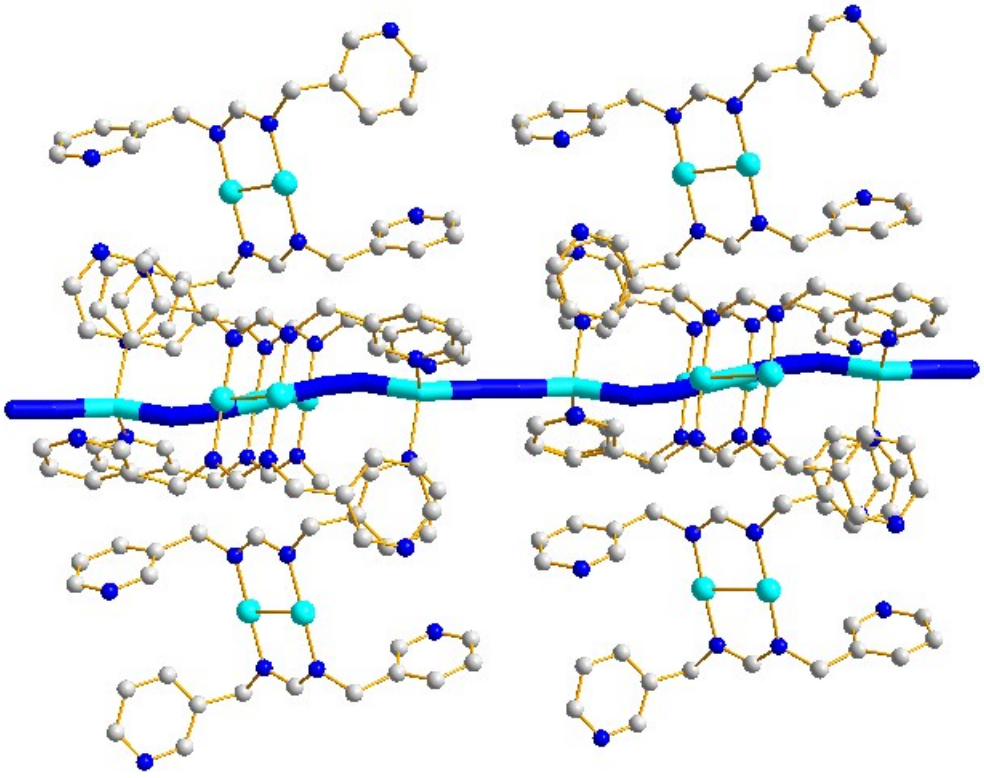


Fig. S2. (a) The 4-connected nodes showing in Cu(1)---Cu(1A). (b) The packing diagram showing -Cu-N_2- 1D linear chain.

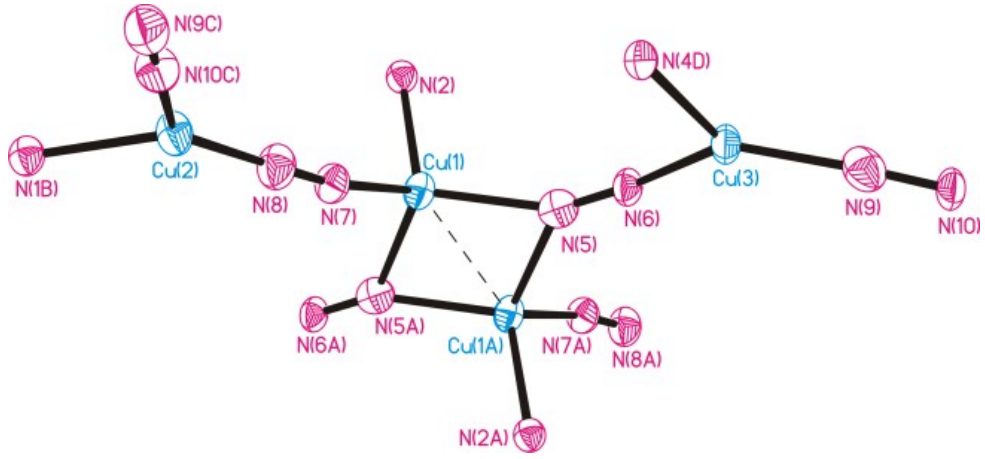


(a)

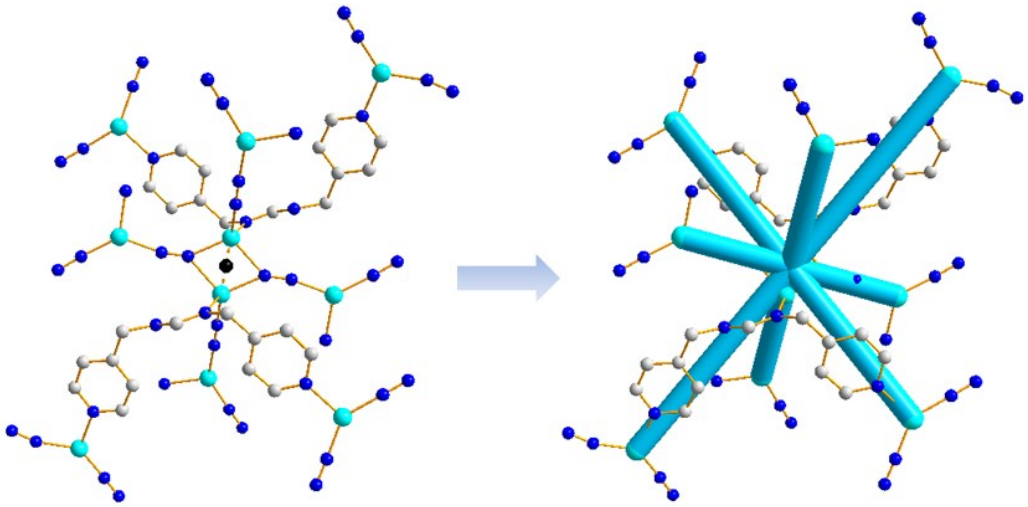


(b)

Fig. S3. (a) An ORTEP diagram showing the coordination environment with Cu(I) ions and nitrogen atoms. (b) The 8-connected nodes showing in Cu(1)---Cu(1A).



(a)



(b)

Fig. S4. TGA curves for **1** and **2**.

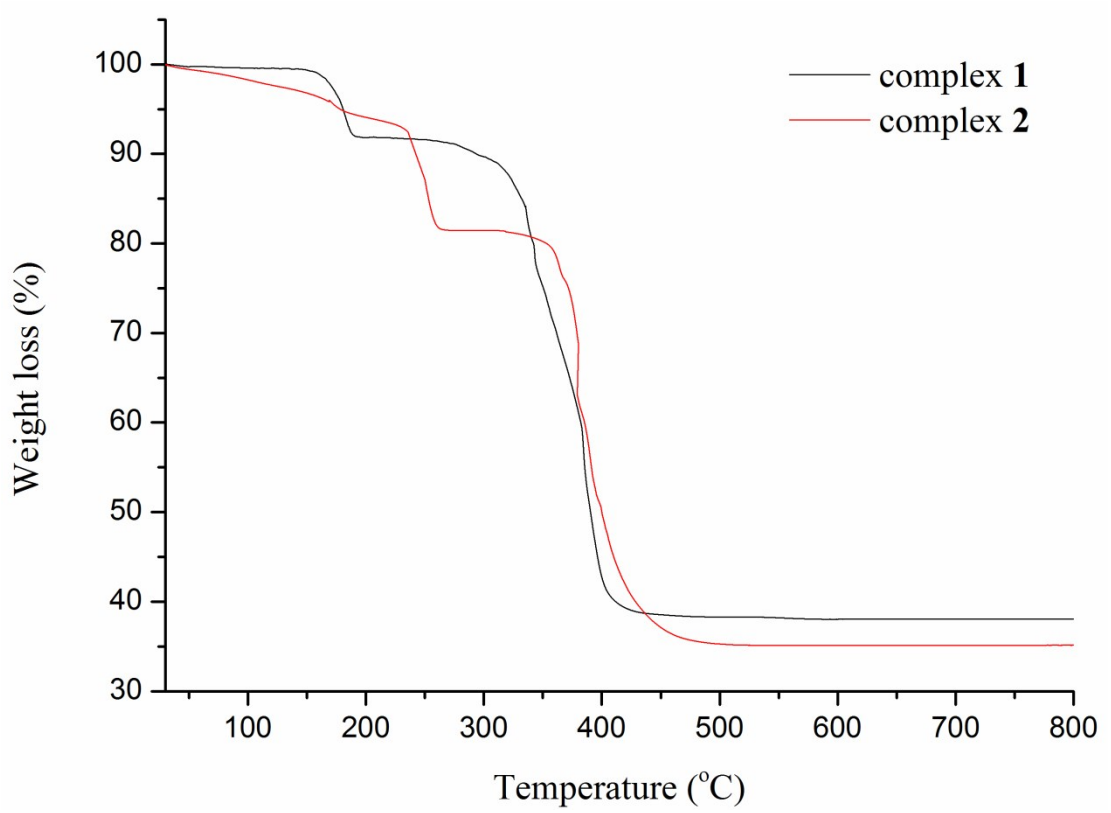


Fig. S5. Simulated (black) and as synthesized (red) PXRD patterns of complex **1**, the pattern (blue) of the complex after heated at 200 ^{o}C for 3hr, and the pattern (green) of de-solvated sample exposed to CH_3OH vapor and N_2 atmosphere.

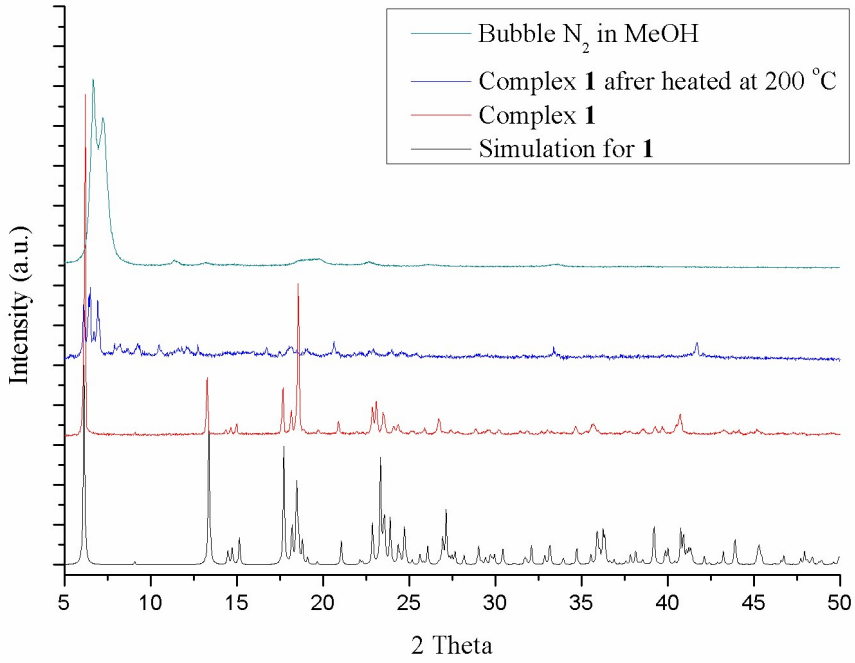


Fig. S6. Simulated (black) and as synthesized (red) PXRD patterns of complex **2**, the pattern (blue) of the complex after heated at 200 °C for 3hr, and the pattern (green) of de-solvated sample exposed to CH_3OH vapor and N_2 atmosphere.

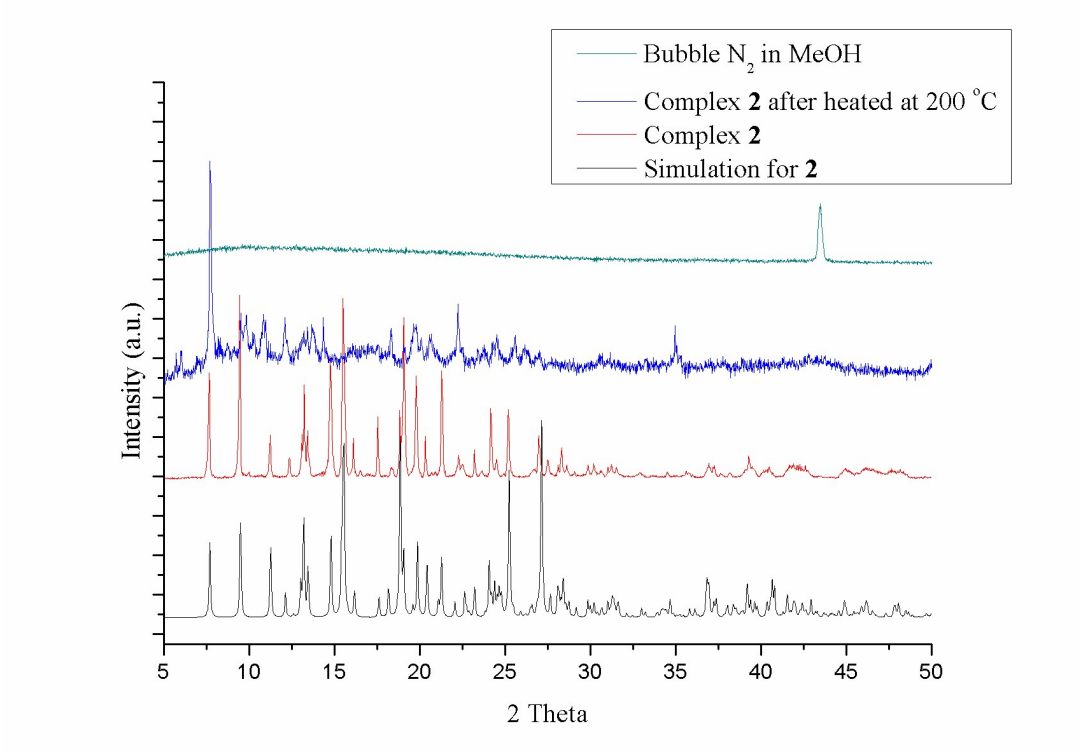
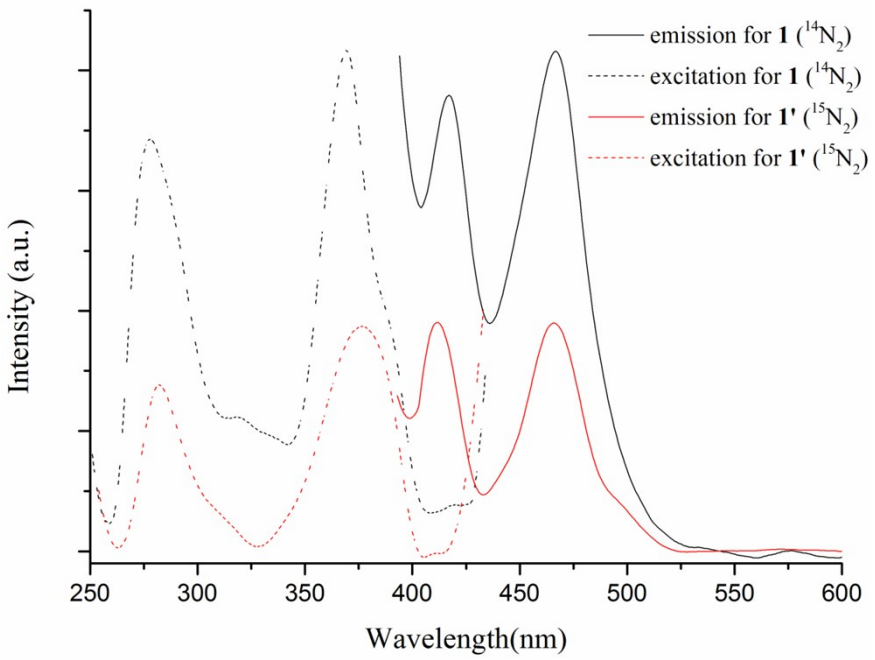
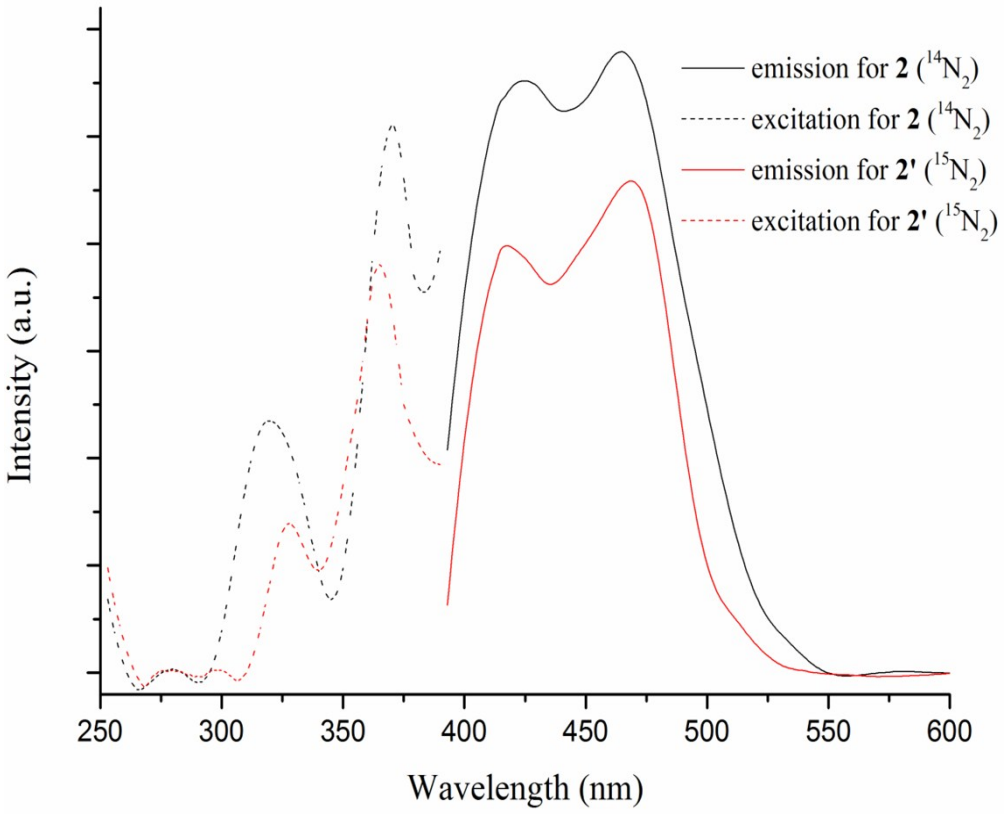


Fig. S7. Emission and excitation spectra for complexes (a) **1**, **1'**, (b) **2** and **2'** in solid-state at RT.



(a)



(b)

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