Supporting Information

Paradoxical Design of A Serendipitous Pyrazolate Bridging Mode: A Pragmatic Strategy for Inducing Ineluctable Ferromagnetic Coupling.

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Contents:

Experimental Procedures:

Material and general method

All reagents and chemicals except ligand were purchased from available commercial sources and were used without further purification. FT-IR spectra were obtained on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. C, H and N microanalyses were carried out with a 2400 Series-II CHN Analyzer, Perkin-Elmer, USA. Magnetic measurements were performed using a Quantum Design VSM SQUID magnetometer. The measured values were corrected for the experimentally measured contribution of the sample holder, while the derived susceptibilities were corrected for the diamagnetism of the samples, estimated from Pascal's tables.

Synthesis ofethyl 4-(3-cyanophenyl)-2-hydroxy-4-oxobutanoate: Potassium tert-butoxide (4.5 g, 40.10mmol) was taken in dry diethyl ether (200ml)at room temperature under N_2 atmosphere at stirring condition. Diethyl oxalate (4.4 ml, 30.10mmol) was added to that solution. After 15 min of stirring, 3-acetylbenzonitrile (4.35 g, 29.96 mmol) was added to the resulting mixtureand the stirring was continuing for overnight.A light yellow precipitate was obtained and the whole resulting mixture is taken in a separating funnel. This solution was washed three times with 20 ml of water. The entire aqueous layer was collected in a beaker, cooled for some time and then dilute HCl (2 ml) was added to it dropwise until the whole solution became just acidic. A yellow precipitate was obtained which was filtered and product ethyl 4-(3-cyanophenyl)-2,4-dioxobutanoatewas isolated as a yellow solid (3.3 g, 76.74 yield).

Synthesis ofethyl 3-(3-cyanophenyl)-1H-pyrazole-5-carboxylate: To a stirred ethanolic (40ml) solution of ethyl 4-(3-cyanophenyl)-2,4-dioxobutanoate, hydrazine monohydrate (0.65 ml) was added drop wise.The resulting solution was stirred and refluxed for 24h. The reaction mixture was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. The residue was washed with water and recrystallized from methanol. 4-(3-cyanophenyl)-2,4-dioxobutanoatewas obtained as a light yellow crystalline powder (3.44gm)

Synthesis of 3-(3-carboxyphenyl)-1H-pyrazole-5-carboxylic acid:

Dried 4-(3-cyanophenyl)-2,4-dioxobutanoate(3.44 g, 14.27mmol) was added portion wise in a water solution of NaOH (880 mg,22 mmol) under stirring condition and refluxed for overnight. A clear golden yellow solution was obtained; then the solution was filtered in a whatmanfilter paper and cooled to room temperature. To this solution 6(N) HCl was added drop wise until the pH of the solution become just acidic. The off white precipitate was filtered and dried. The product thus obtained was recrystallized in methanol and the yield was 47.5% (with respect to 3-acetylbenzonitrile).

^{1}H NMR (DMSO-d^6, 500 MHz): δ 13.7(3H brS); 8.09(3 H, d); 8.35(3H, t); 7.82(3H, d); 7.53(3H, t); 6.5(2H, d)

IR (400-4000 cm^{-1}):3604(m); 3197(br); 2917(m); 1696(s); 1515(s); 1424(s); 1289(s)

HRMS: Calcd: 232.05, Found (M+Na): 255.07.

Elemental Analysis: **Calcd; C:** 56.90; **N:** 3.47**; H:** 12.06**; Observed; C:** 52.70**; N:** 3.70; **H:**11.27.

Table S1: Crystallographic data and Refinement Parameters for Complex 1-5

Complex	Complex 1	Complex 2	Complex 3	Complex 4	Complex 5
Empirical formula	$C_{52}H_{34}Cu_2N_{10}O_{10}$	$C_{78}H_{56}Cu_2N_{10}O_{14}$	$C_{46}H_{34}Cl_2Cu_2N_8O_{12}$	$C_{48}H_{30}Cu_2N_8O_{16}$	$C_{106}H_{104}Cu_5N_{18}O_{30}$
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Formula weight	1085.97	1484.41	1088.79	1101.88	2427.77
Space group	*P ī*	*P ī*	*P21/c*	*P -1*	*P ī*
a/Å	7.662(3)	7.728(3)	7.4682(15)	7.6549(6)	9.968(8)
b/Å	11.728(4)	15.278(5)	12.244(2)	11.8774(10)	11.307(9)
c/Å	13.861(5)	15.982(6)	23.789(5)	14.2863(12)	24.796(19)
α/°	66.772(5)	67.547(5)	90.00	66.863(2)	96.56(3)
β/°	88.819(5)	88.845(5)	92.242(6)	85.137(2)	90.82(3)
γ/°	83.752(5)	85.603(5)	90.00	82.646(2)	103.37(3)
V/Å3	1137.4(6)	1738.9(10)	2173.7(7)	1183.77(17)	2699(4)
Reflections collected	8912	18521	31581	8131	34099
unique reflections	4391	5315	5569	5315	10471
observed reflections	2352	2621	2915	2621	4251
R1	0.0741	0.0837	0.0610	0.0573	0.1264
wR2	0.1948	0.2203	0.1332	0.1528	0.3007
CCDC no.	1811296	1937570	1937572	1937573	1937571

Table S2. Selected hydrogen bonding distances (Å) and angles (deg) for the Complex**2**

D-H….A	Symmetry operation	D-H (Å)	A…H (Å)	D….A (Å)	<D-H-A(deg)
C_3-H_{3A} ... O_3	x, y, z	0.930	2.437	2.764	100.58
C_5-H_{5A} ... N_2	x, y, z	0.930	2.659	2.937	98.05
C_7-H_{7A} ... O_4	x, y, z	0.930	2.464	2.783	100.13
C_1-H_{1AA} ...O_1	x, y, z	0.930	2.546	3.050	114.35
C_{10A}-H_{10}...N_1	x, y, z	0.930	2.880	3.320	110.34
C_{10A}-H_{10A}...N_2	x, y, z	0.930	2.439	3.195	138.42
C_{10A}-H_{10A}...O_1	-x,-y+2,-z+1	0.930	2.971	3.488	116.63
C_{10A} -H_{10A} ...N_1	-x,-y+2,-z+1	0.930	2.929	3.087	90.92
C_{14A}-H_{14A}...O_3	-x,-y+2,-z+1	0.930	2.627	3.133	114.78
C_1 -H_{16A}...O_2	-x,-y+1,-z+1	0.930	2.911	3.684	141.50
C_{18} -H_{18A}...O_3	-x+1,-y+2,-z+1	0.930	2.768	3.648	158.24
C_{20A} -H_{20A}...O_4	-x+1,-y+2,-z+1	0.930	2.533	3.344	145.90
$C2_{1A}$ -H_{21A} ...O_4	x,+y-1,+z+1	0.930	2.557	3.311	138.50

Table S3. Selected hydrogen bonding distances (Å) and angles (deg) for the **Complex 3**

D-H….A	Symmetry operation	D-H (Å)	A…H (Å)	D….A (Å)	<D-H-A(deg)
C_3 -H_{3A} ...O_1	x, y, z	0.930	2.524	2.802	97.54
C_5 -H_{5A} ...N_2	x, y, z	0.930	2.522	2.845	100.66
C_7 -H_{7A} ...O_2	x, y, z	0.930	2.493	2.800	99.40
C_{1A}-H_{1AA} ...O_4	x, y, z	0.930	2.472	2.987	115.03
C_{10A}-H_{10A} ...N_1	x, y, z	0.930	2.809	3.290	113.30
C_{10A} -H_{10A}...N_2	x, y, z	0.930	2.418	3.199	141.57
C_{12A} -H_{12C} ...$O_{1'}$	x, y, z	0.960	2.628	3.396	137.24
$C_{3'}$ -$H_{3'A}$ ...$O_{1'}$	x, y, z	0.930	2.530	2.802	97.17
$C_{5'}$ -$H_{5'A}$ ...$N_{2'}$	x, y, z	0.930	2.541	2.855	100.13
$C_{7'}$ -$H_{7'A}$ ...$O_{2'}$	x, y, z	0.930	2.463	2.776	99.77
$C_{1A'}$-H_{1AB}...$O_{4'}$	x, y, z	0.930	2.522	3.045	115.90
$C_{10''}$-H_{10}B ...$N_{1'}$	x, y, z	0.930	2.803	3.278	112.89
$C_{10''}$-H_{10B} ...$N_{2'}$	x, y, z	0.930	2.356	3.133	140.94
$C_{12''}$-H_{12F} ...O_2	x, y, z	0.960	2.597	3.515	160.09
C_9-H_{9A} ...$O_{2'}$	x-1/2,-y+1/2,+z+1/2	0.930	2.720	3.396	130.27
C_{11A}-H_{11B}...$O_{3'}$	x+1,+y,+z	0.960	2.636	3.593	174.51
C_{11A} -H_{11B} ...$O_{4'}$	x+1,+y,+z	0.960	2.842	3.519	128.35
C_{12A}-H_{12B} ...O_1	-x+1,-y+1,-z+2	0.960	2.589	3.533	167.49
C_{12A}-H_{12C} ...O_3	x+1/2,-y+1/2,+z-1/2	0.960	2.904	3.749	147.49
$C_{9'}$-$H_{9'A}$ ...O_2	x+1/2,-y+1/2,+z-1/2	0.930	2.851	3.525	130.29
$C_{4'}$ -$H_{4'A}$ ...O_1	-x,-y+1,-z+2	0.930	2.552	3.304	138.23
$C_{4'}$ -$H_{4'A}$ ...$O_{3'}$	-x+1/2,+y+1/2,z+1/2+1	0.930	2.885	3.523	126.89
$C_{2A'}$ -H_{2AB} ...$O_{1'}$	-x+1/2,+y-1/2,-z+1/2+1	0.930	2.534	3.055	115.72
$C_{1A'}$ -H_{1AB} ...$O_{1'}$	-x+1/2,+y-1/2,-z+1/2+1	0.930	2.428	3.011	120.72
$C_{11''}$-H_{11D} ...O_4	-x,-y,-z+2	0.960	2.869	3.789	160.80
$C_{11''}$-H_{11F} ...O3'	-x,-y,-z+2	0.960	2.656	3.395	134.14
$C_{2A'}$-H_{2AB} ...O3	-x,-y,-z+2	0.930	2.665	3.569	164.39
$C_{12''}$ -H_{12E} ...N_2	x-1,+y,+z	0.960	2.657	3.429	137.75

Table S4. Selected hydrogen bonding distances (Å) and angles (deg) for the **Complex 4**

D-H….A	Symmetry operation	D-H (Å)	A…H (Å)	D….A (Å)	<D-H-A(deg)
C_3-H_{3A} ...O_1	x, y, z	0.930	2.616	2.876	96.63
C_5-H_{5A} ...N_2	x, y, z	0.930	2.725	2.960	95.33
C_7-H_{7A} ...O_2	x, y, z	0.930	2.369	2.704	100.90
C_{1A}-H_{1AA}...O_{2W}	x, y, z	0.930	2.850	3.762	167.10
C_{2A}-H_{2AA}...O_{1W}	x, y, z	0.930	2.850	3.723	156.76
C_{3A}-H_{3AA}...Cl_1	x, y, z	0.930	2.717	3.089	104.86
C_3 -H_{3A} ...O_{2W}	-x+1,+y-1/2,-z+1/2	0.930	2.644	3.499	153.21
O_2-H_2...O_{1W}	-x+1,+y-1/2,-z+1/2	0.901	1.646	2.537	169.48
O_{1W}-H_{1WA}..O_{2W}	-x+1,+y-1/2,-z+1/2	0.965	1.720	2.668	166.59
C_{1A}-H_{1AA} ...O_1	-x+1,+y+1/2,-z+1/2	0.930	2.994	3.697	133.61
O_{2W}-H_{2WB}...O_1	-x+1,+y+1/2,-z+1/2	1.042	1.822	2.796	153.84
C_{10A}-H_{10A} ...N_2	-x+2,-y+1,-z+1	0.930	2.537	3.279	137.03
C_{1A}-H_{1AA} ...O_3	-x+2,-y+1,-z+1	0.930	2.579	3.028	110.18
O_{2W}-H_{2WA}...O_3	-x+2,-y+1,-z+1	0.921	1.936	2.842	167.05
O_{2W}-H_{2WA}...O_4	-x+2,-y+1,-z+1	0.921	2.785	3.545	140.54
C_{10A}-H_{10A} ...N_1	-x+2,-y+1,-z+1	0.930	2.936	3.363	109.50
C_{3A}-H_{3AA} ...O_4	x,-y+1/2,+z-1/2	0.930	2.809	3.282	112.67
O_{1W}-H_{1WB}...O_4	x,-y+1/2,+z-1/2	0.866	1.827	2.673	165.06
C_{2A}-H_{2AA} ...O_4	x,-y+1/2,+z-1/2	0.930	2.557	3.156	122.51
C_{9A}-H_{9AA}..O_{1W}	x+1,-y+1/2,+z+1/2	0.930	2.542	3.441	162.53

Table S5. Selected hydrogen bonding distances (Å) and angles (deg) for the **Complex 5**

D-H….A	Symmetry operation	D-H (Å)	A…H (Å)	D….A (Å)	<D-H-A(deg)
C_{23}-H_{23}…O_3	x, y, z	0.95	2.480	2.784	98.49
C_9-H_9....O_1	x, y, z	0.95	2.673	3.144	111.19
C_{13}-H_{13}....N_4	x, y, z	0.95	2.837	3.303	111.30
C_{21}-H_{21}….O_4	x, y, z	0.95	2.449	2.754	98.45
C_{12}-H_{12}….O_5	x, y, z	0.95	2.494	3.412	162.33
O_4-H_{5A}…O_7	x, +y, +z-1	0.84	1.741	2.555	162.48
C_9-H_9….O_8	x+1, +y, +z	0.95	2.805	3.743	169.64
C_{19}-H_{19}….N_3	-x+1, -y+1,-z+1	0.95	2.904	3.329	108.40
C_{10}-H_{10}….O_4	x+1, +y, -z+1	0.95	2.702	3.627	164.96
C_5-H_5….O_2	x, +y+1, +z	0.95	2.774	3.470	130.86
C_1-H_{1C}….O_3	-x+2, -y+1, -z+1	0.98	2.867	3.673	140.13
C_1-H_{1C}….O_6	-x+2, -y+1, -z+2	0.98	2.706	3.165	109.12

Table S6 Selected Bond angle & Bond length of Complex **2**

Bond angle (˚)				Bond length (Å)	
N_1 -Cu_1 -O_1	**83.3(2)**	N_1 -Cu_1 -N_{2A}	**98.8(2)**	Cu_1 N_1	**1.932(6)**
N_1 -Cu_1 -N_{1A}	**168.5(2)**	O_1 -Cu_1 -N_{2A}	**166.7(2)**	Cu_1 O_1	**1.976(5)**
O_1 -Cu_1 -N_{1A}	**93.0(2)**	N_{1A}-Cu_1-N_{2A}	**82.4(2)**	Cu_1 N_{1A}	**1.989(6)**
				Cu_1 N_{2A}	**2.009(6)**

Table S7 Selected Bond angle & Bond length of Complex **3**

Bond angle (˚)				Bond length (Å)	
N_1 -Cu_1 -N_{1A}	**160.8(4)**	O_2 -Cu_1 -N_1'	**167.4(4)**	Cu_1 N_1	**1.972(10)**
N_1 -Cu_1 -O_2	**80.7(3)**	N_1 -Cu_1 -N_{2A}	**112.1(4)**	Cu_1 N_{1A}	**2.006(9)**
N_{1A} -Cu_1 -O_2	**84.6(3)**	N_{1A} -Cu_1 -N_{2A}	**80.4(4)**	Cu_1 O_2	**2.015(8)**
N_1 -Cu_1 -$N_{1'}$	**96.8(3)**	O_2 -Cu_1 -N_{2A}	**90.6(3)**	Cu_1 $N_{1'}$	**2.028(10)**
N_{1A} -Cu_1 -N_1'	**94.8(4)**	$N_{1'}$ -Cu_1 -N_{2A}	**101.8(4)**	Cu_1 N_{2A}	**2.235(10)**

Table S9 Selected Bond angle & Bond length of Complex **4**

Bond angle (˚)				Bond length (Å)	
N_1 -Cu_1 -O_3	**82.32(12)**	N_{1A} -Cu_1 -N_{2A}	**81.58(13)**	Cu_1 N_1	**1.939(3)**
N_1 -Cu_1 -N_{1A}	**164.74(13)**	N_1 -Cu_1 -N_2	**95.71(12)**	Cu_1 O_3	**1.978(3)**
O_3 -Cu_1 -N_{1A}	**91.09(12)**	O_3 -Cu_1 -N_2	**109.32(12)**	Cu_1 N_{1A}	**1.992(3)**
N_1 -Cu_1 -N_{2A}	**99.52(13)**	N_{1A} -Cu_1 -N_2	**99.46(12)**	Cu_1 N_{2A}	**2.026(3)**
O_3 -Cu_1 -N_{2A}	**158.13(13)**	N_{2A} -Cu_1 -N_2	**92.25(12)**	Cu_1 N_2	**2.352(3)**

Table S10 Selected Bond angle & Bond length of Complex **5**

Bond angle (˚)				Bond length (Å)	
N_2 Cu_1 N_4	**168.15(18)**	O_1 Cu_1 N_3	**160.34(17)**	Cu_1 N_2	**1.941(4)**
N_2 Cu_1 O_1	**81.77(17)**	N_2 Cu_1 N_1	**94.67(16)**	Cu_1 N_4	**1.995(5)**
N_4 Cu_1 O_1	**94.21(18)**	N_4 Cu_1 N_1	**97.18(16)**	Cu_1 O_1	**1.996(4)**
N_2 Cu_1 N_3	**98.67(19)**	O_1 Cu_1 N_1	**109.87(16)**	Cu_1 N_3	**2.027(5)**
N_4 Cu_1 N_3	**81.38(19)**	N_3 Cu_1 N_1	**89.72(17)**	Cu_1 N_1	**2.376(4)**

Table S11: The Cu-N_{axial} distances and magnetic nature of complex 1-5

Complex	Distance (Cu-N_{ax}) in Å	Observed J value (cm^{-1})	Magnetic nature
1	**2.409(5)**	+1.41	**Ferromagnetic**
2	**2.513(7)**	+15.3	**Ferromagnetic**
3	**2.353 (3)**	-6.4	**Antiferromagnetic**
4	**2.376(4)**	+5.4	**Ferromagnetic**
5	**2.23(1)** **2.21(1)**	-68	**Antiferromagnetic**

Table S12: Torsion angle (50°- 120°) dependent magnetic exchange of copper compounds.

Compound (CSD REFCODE)	Magnetic study (J value)	Torsion angle(τ)	References
$C_{34}H_{22}Cu_2N_8O_5$ (POVPUN)	Ferromagnetic +15 cm^{-1}	69.52°, 75.28°	*Eur.J.Inorg.Chem*.2014,**34,**5874–5884
$C_{92}H_{80}Cu_2N_8$ (OLIWAI)	Ferromagnetic +16.3 cm^{-1}	78.90°, 80.16°	*Angew. Chem. Int. Ed,* 2011, **50,**1420 –1424
$C_{118}H_{120}B_2Cu_2F_8N_8O_4$ (DOFRIB)	Ferromagnetic +67 cm^{-1} (From DFT)	74.82°, 84.71°	*J. Am. Chem. Soc*. 2013, **135,** 13892−13899
$C_{38}H_{70}Cl_6Cu_2N_8O_{12}$ (JOBCUO)	Antiferromagnetic -300 cm^{-1}	4.3° – 58.55°	*Inorg. Chem*. 2014, **53**, 3290−3297
$C_{239}H_{165}Cu_{16}N_{51}O_{19}$ (JOBCIO)	Magnetic study was not reported.	16.3°-51.2°	*Inorg. Chem*. 2014, **53**, 3290−3297
$C_{35}H_{64}Cl_6Cu_2N_8O_{11}$ (ADIMAB)	Magnetic study was not reported.	54.88-63.41	*Chem. Eur. J*. 2002, **8(1),** 247-258

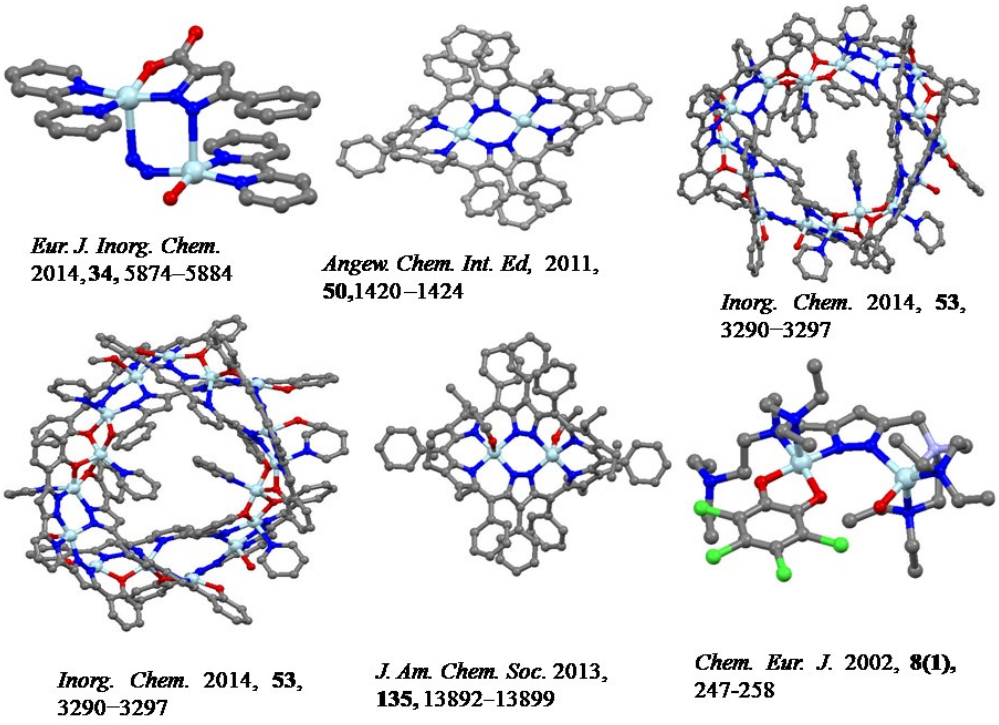

Figure S1. Structure of the all copper compounds having torsion angle in the range 50°-120° from CSD search.

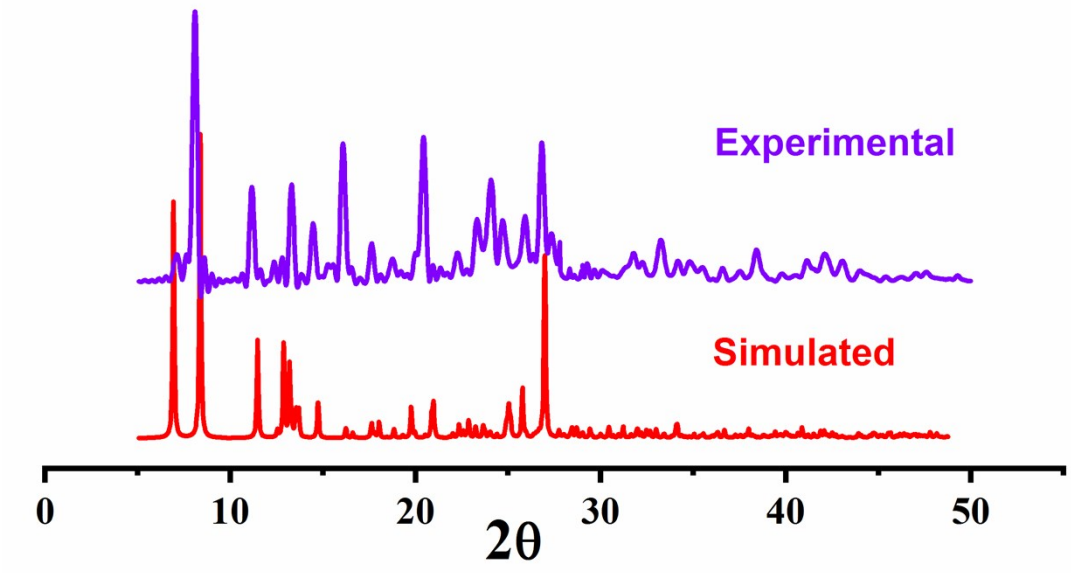

Figure S2: Powder pattern of complex **1**.

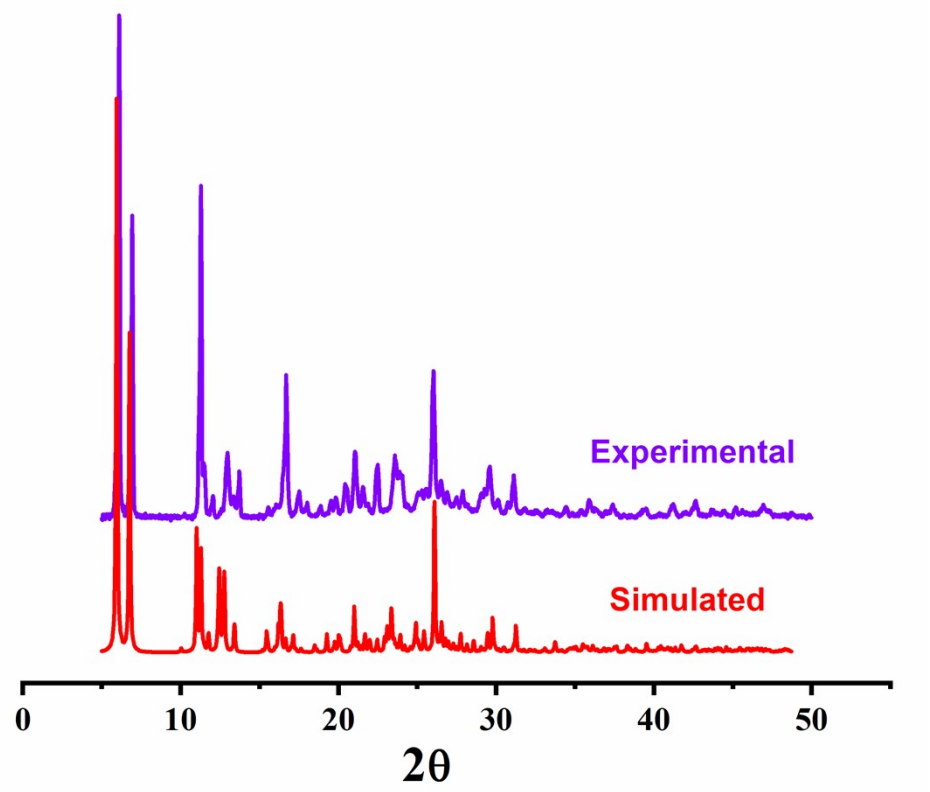

Figure S3: Powder pattern of complex **2**.

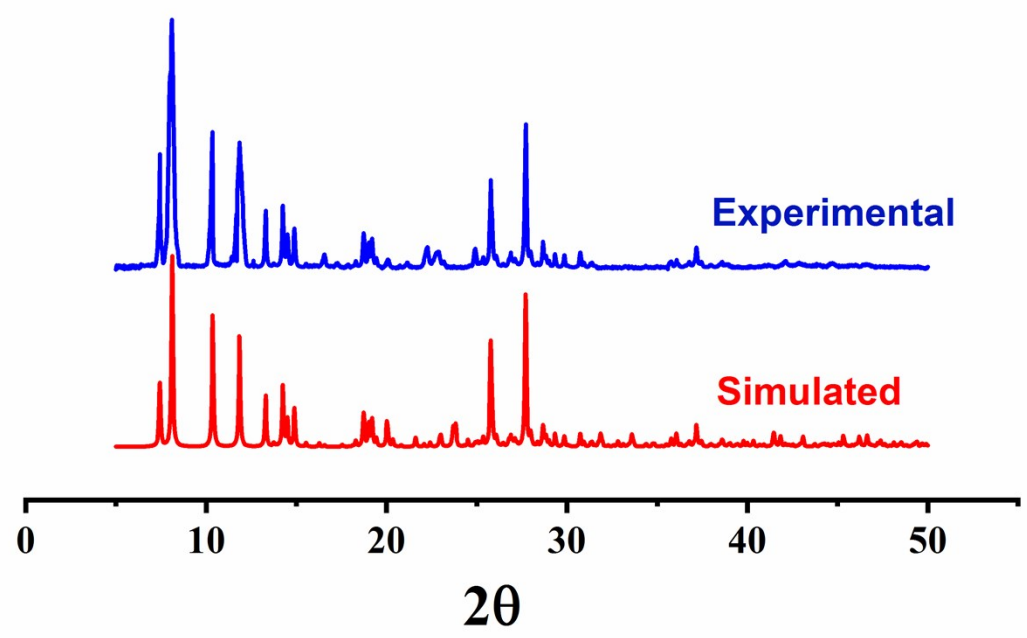

Figure S4: Powder pattern of complex **3**.

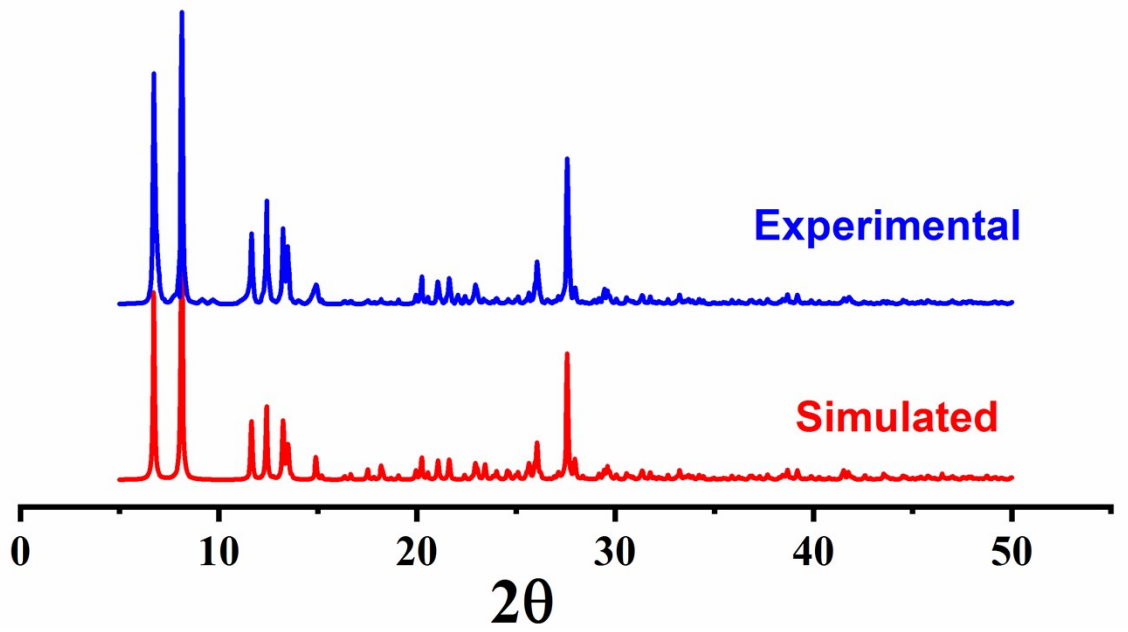

Figure S5: Powder pattern of complex **4**.

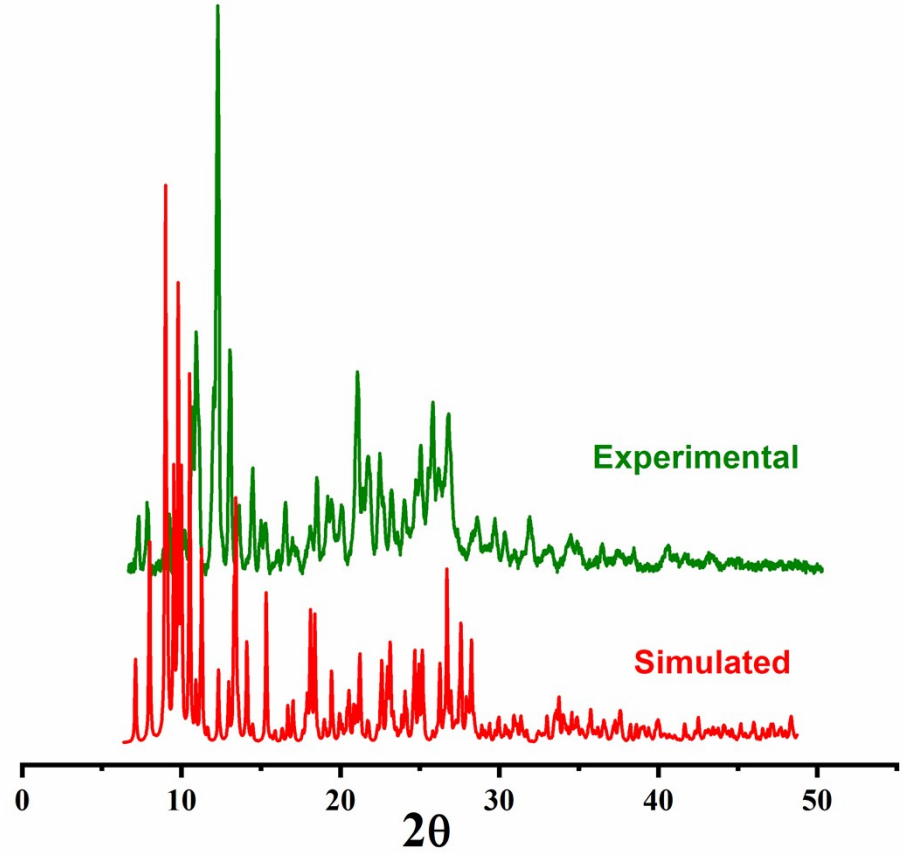

Figure S6: Powder pattern of complex **5**.

Interatomic (Cu-Cu) distance and H-bonding pattern of complex 1-5:

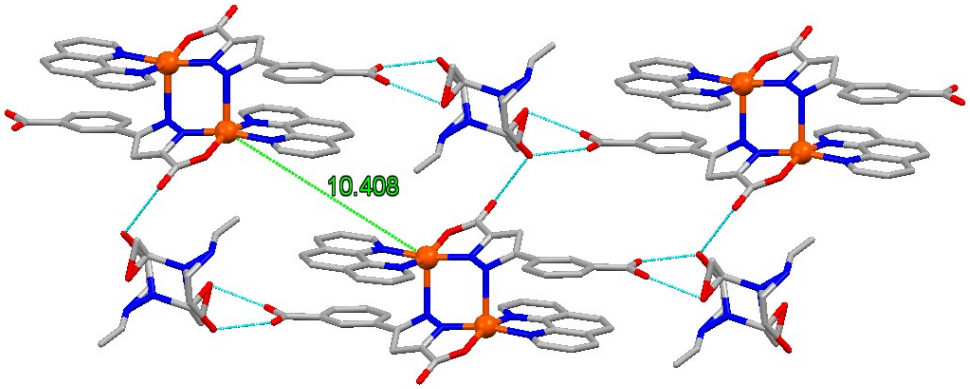

Figure S7: Interatomic (Cu-Cu) distance of Complex **1.**

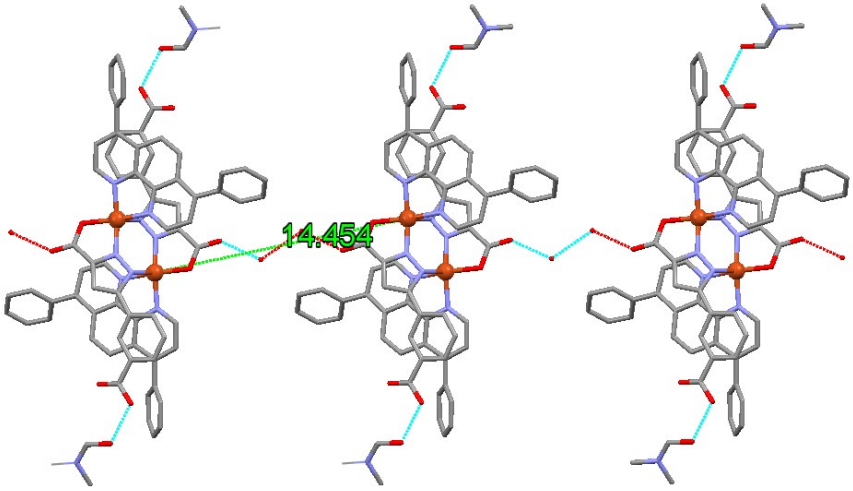

Figure S8: Interatomic (Cu-Cu) distance of Complex **2**.

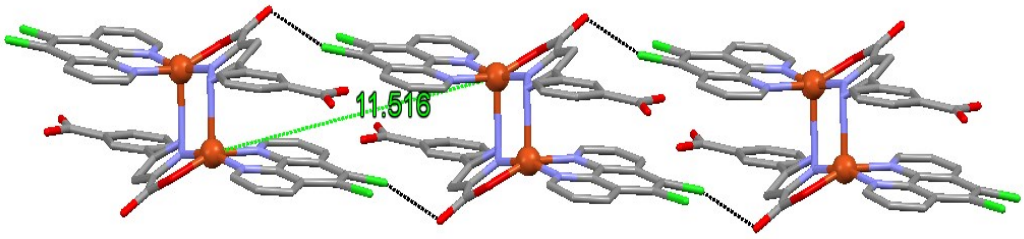

Figure S9: Interatomic (Cu-Cu) distance of Complex **3**.

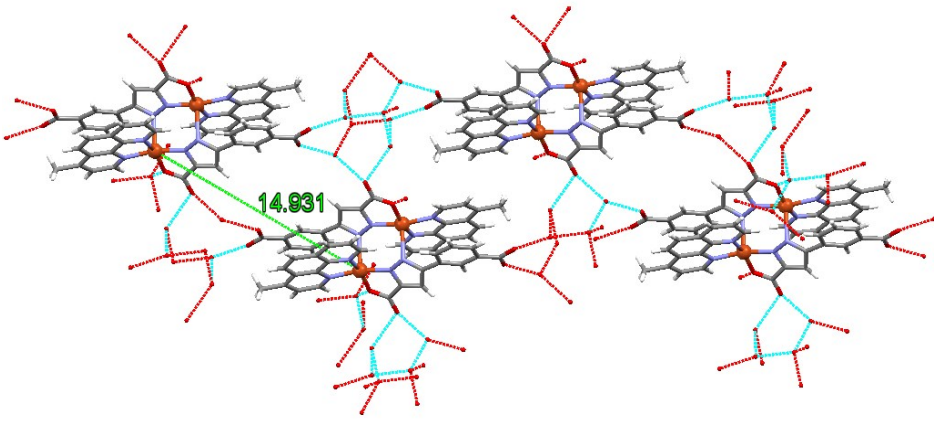

Figure S10: Interatomic (Cu-Cu) distance of Complex **4**.

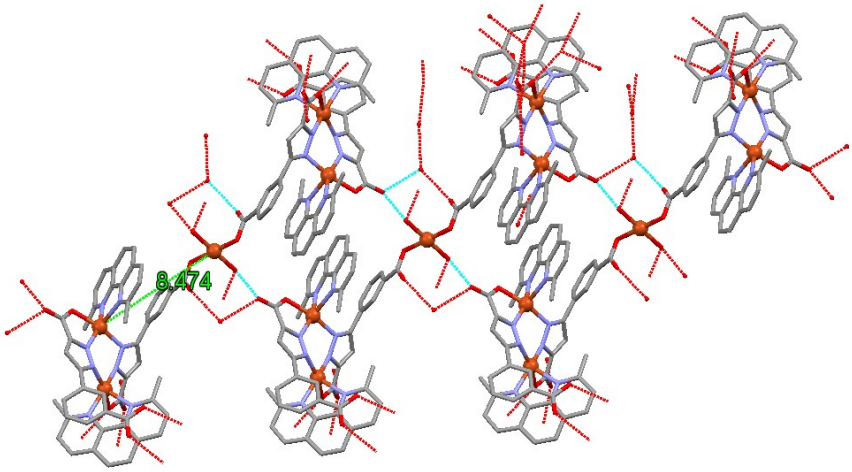

Figure S11: Interatomic (Cu-Cu) distance of Complex **5**.

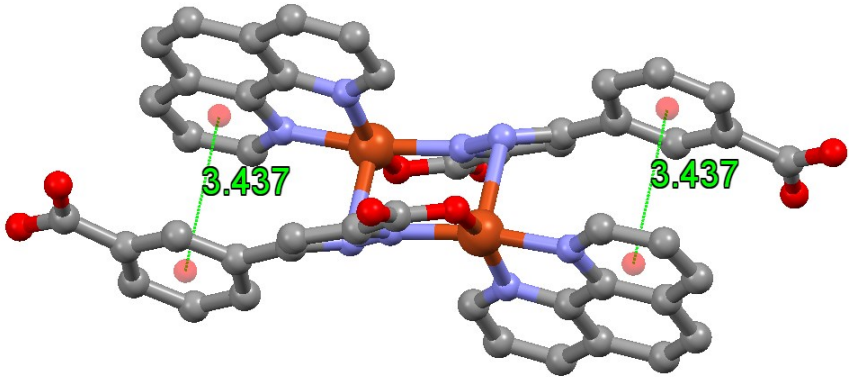

Figure S12: Representation of π-π stacking of complex **1**.

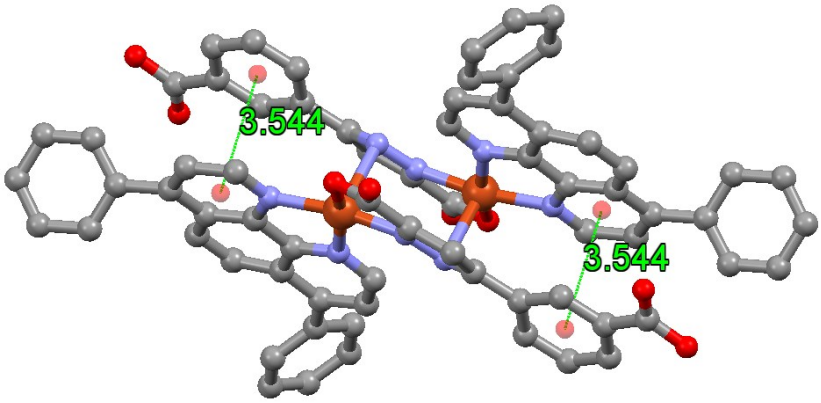

Figure S13: Representation of π-π stacking of complex **2**.

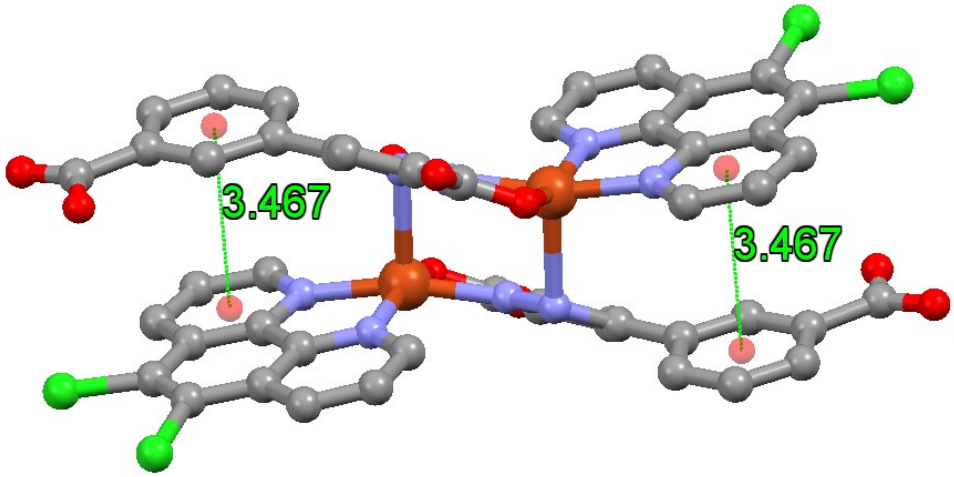

Figure S14: Representation of π-π stacking of complex **3**.

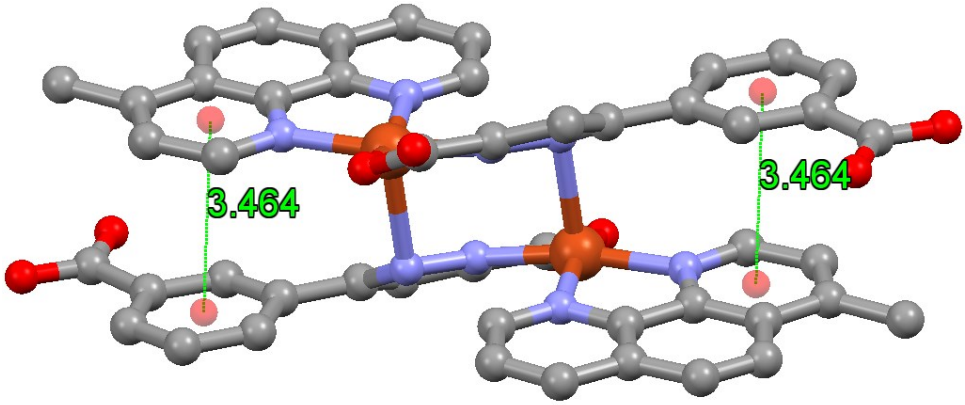

Figure S15: Representation of π-π stacking of complex **4**.

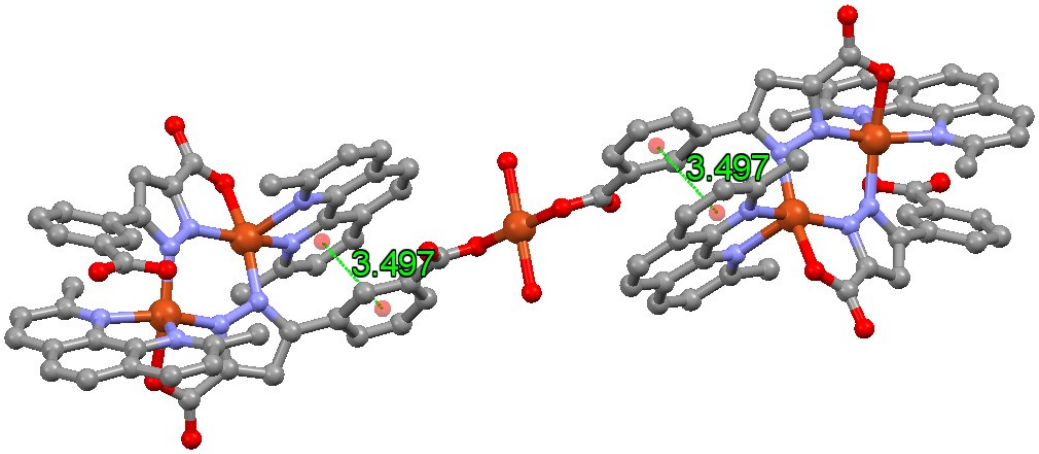

Figure S16: Representation of π-π stacking of complex **5**.

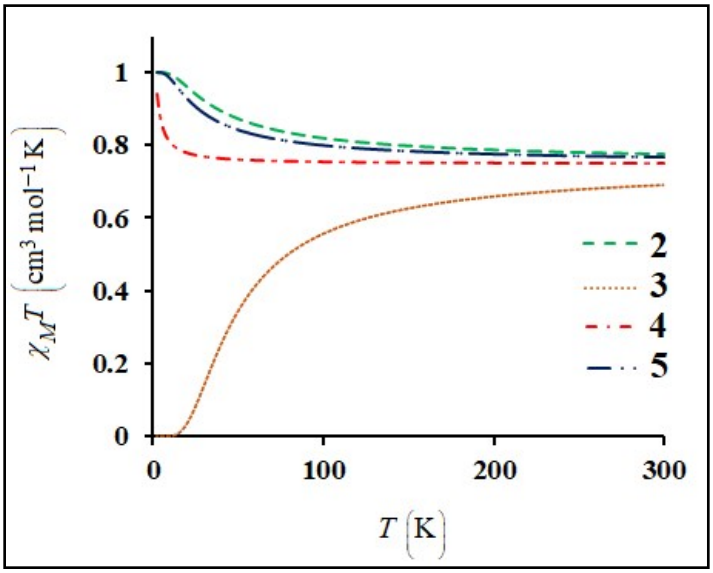

Figure S17. Computationally calculated molar magnetic susceptibility (χ_M) at different temperatures.

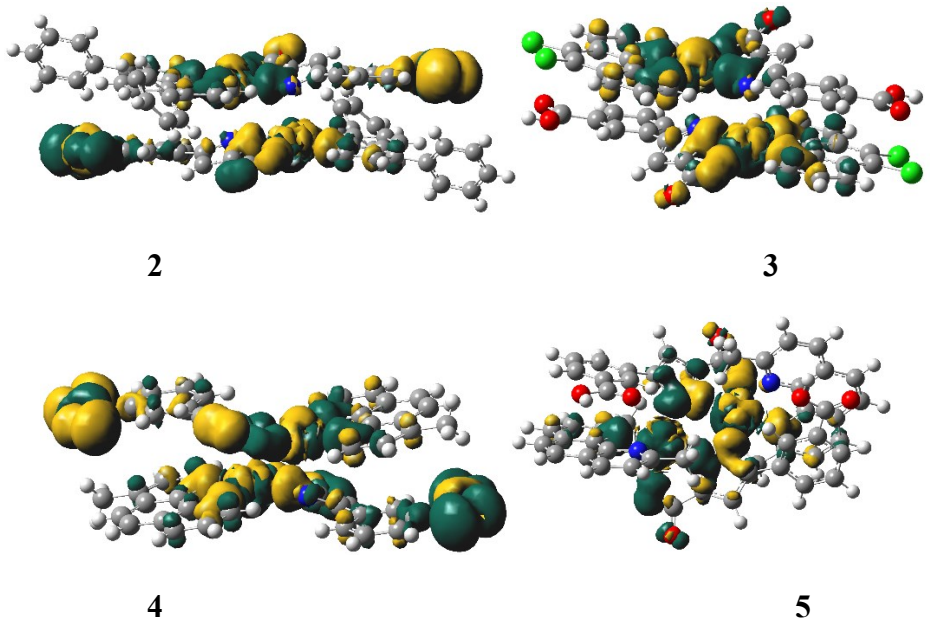

Figure S18. Spin density plots at broken symmetry state. The isovalues are of ±0.002 a.u. Green refers the positive density while the yellow refers the negative density.

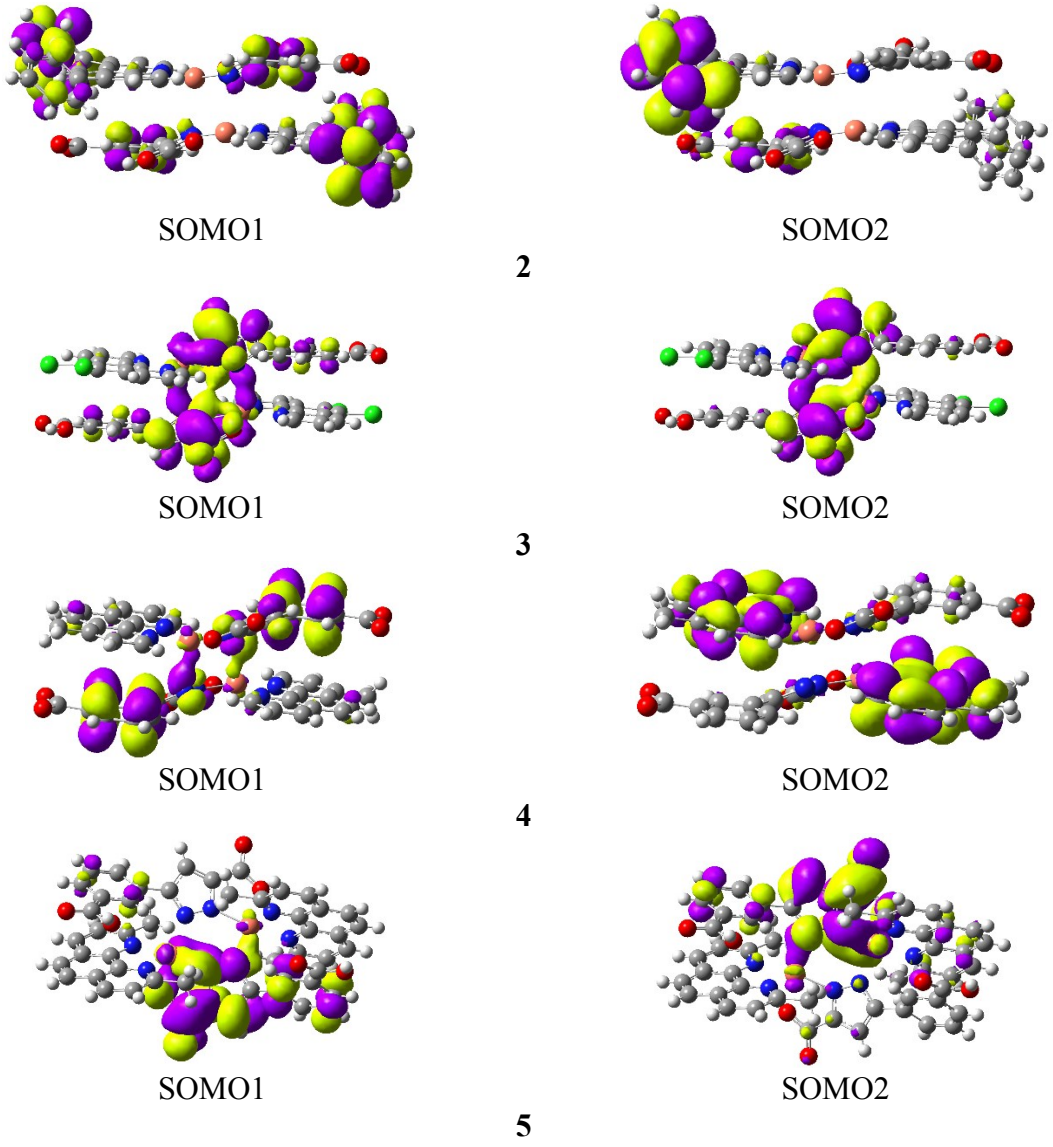

Figure S19. The singly occupied molecular orbitals (SOMOs) with isovalues of ±0.03 a.u. The purple color indicates the positive sign whereas yellow color refers negative sign.