

Electronic Supplementary Information (ESI)

Synthesis and properties of five unexpected copper complexes with ring-cleavage of 3,6-di-2-pyridyl-1,2,4,5-tetrazine by one pot *in situ* hydrothermal reaction

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Figure S1. FT-IR spectroscopy of the compound **1**.

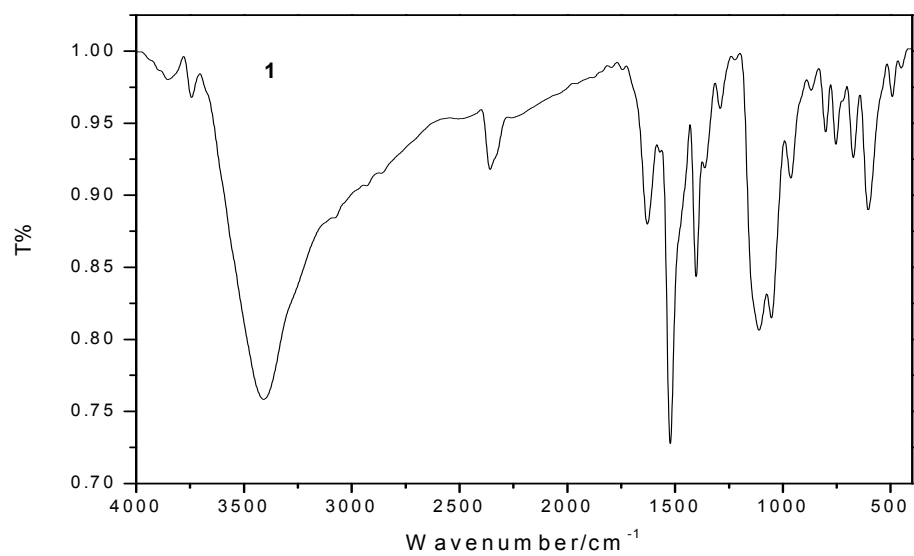


Figure S2. FT-IR spectroscopy of the compound **2**.

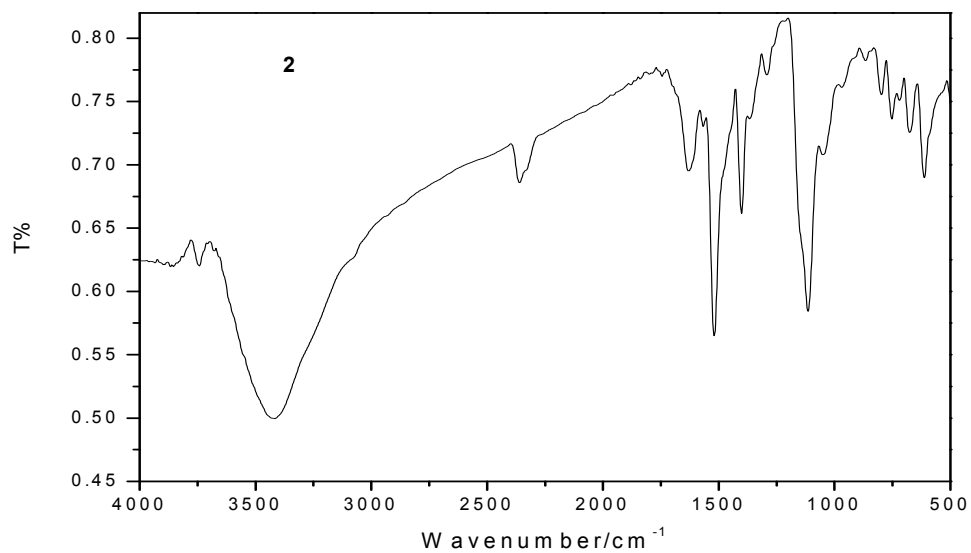


Figure S3. FT-IR spectroscopy of the compound **3**.

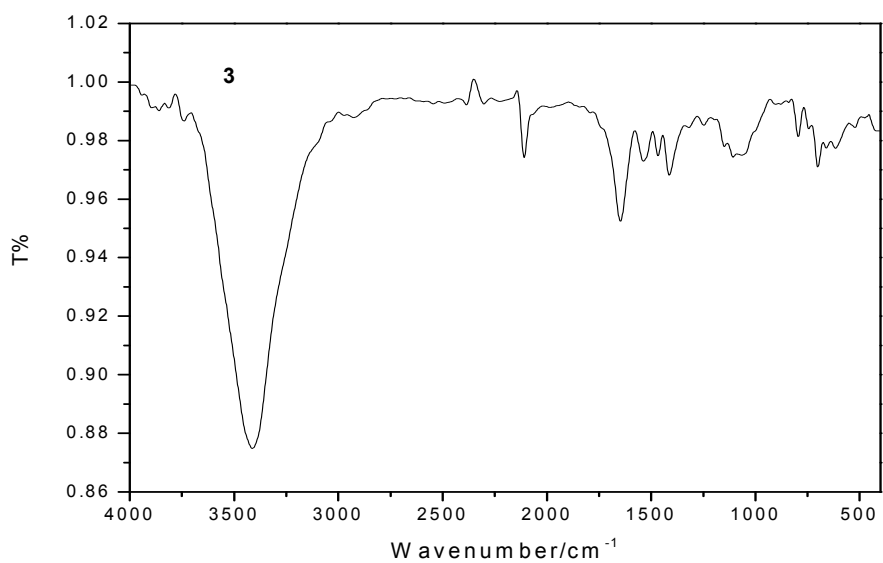


Figure S4. FT-IR spectroscopy of the compound **4**.

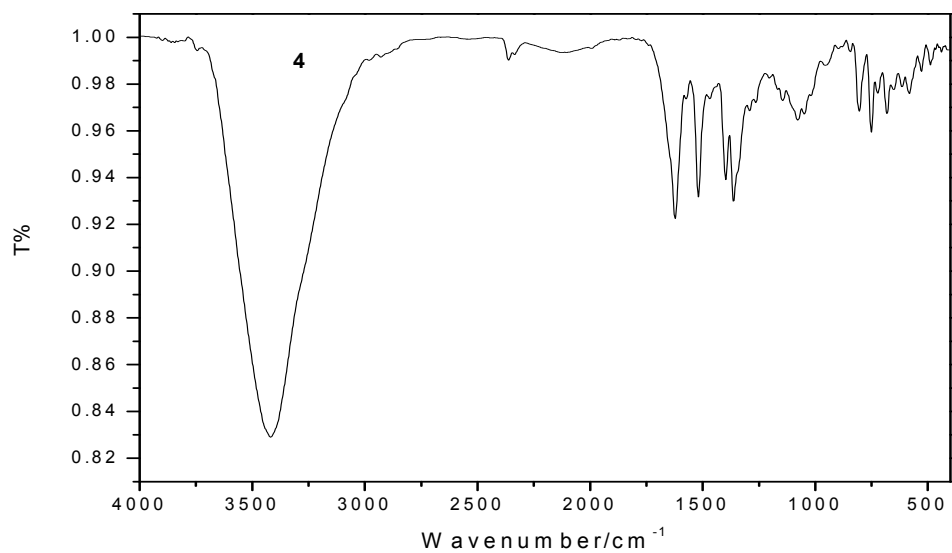


Figure S5a. UV absorbance spectra of **1** (in acetonitrile /water (1:3) with 120 °C), **2** (in acetonitrile /water (3:1) with 120 °C), **3** (in acetonitrile /water (1:3) with 60 °C), **4** (in acetonitrile /water (1:3) with 120 °C), DPTZ in acetonitrile /water (1:3) solution with room temperature.

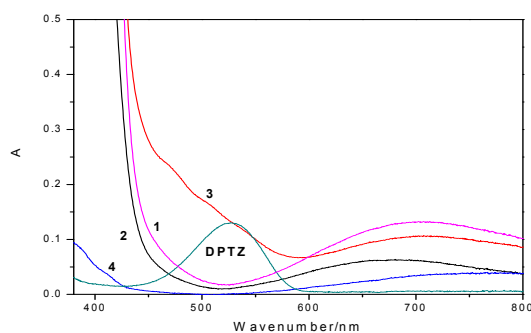


Figure S5b. UV absorbance spectra of DPTZ in acetonitrile /water (1:3) solution, a: room temperature. b: 60 °C. c: 120 °C.

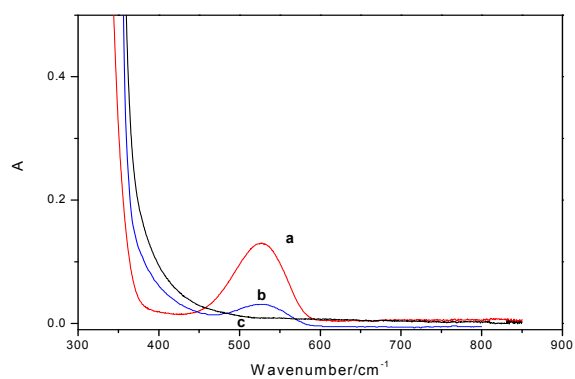


Figure S5c. The diffuse reflect solid-state UV/Vis spectra of **1**, **2**, **3**, **4** and DPTZ.

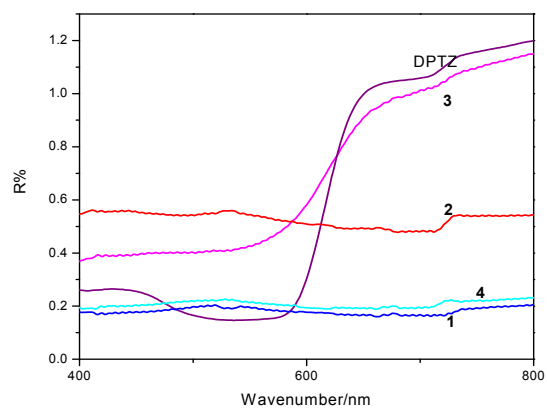


Figure S5d. XPS spectra of compound **3**.

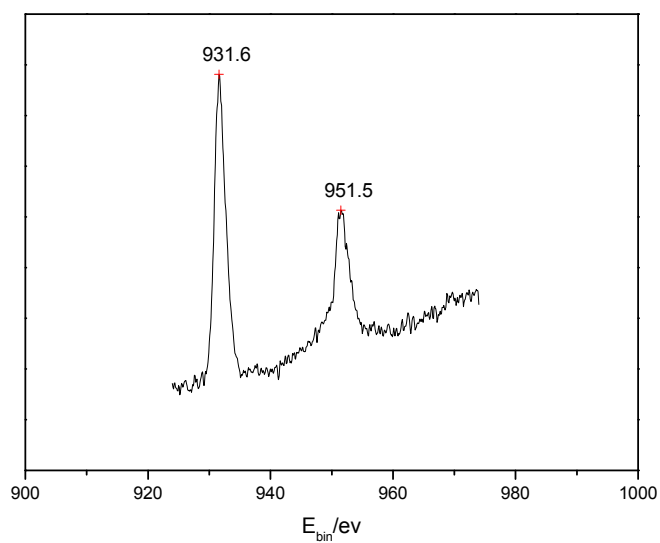
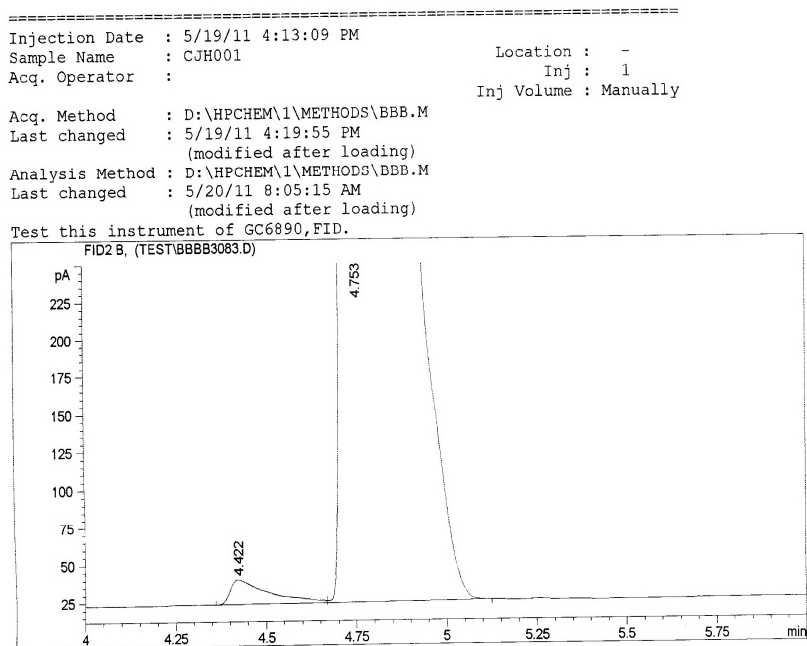


Figure S5e. The GC analysis of methanol.



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Area Percent Report
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Sorted By	:	Signal
Multiplier	:	1.0000
Dilution	:	1.0000

Signal 1: FID2 B,

Figure S6. Powder x-ray diffraction patterns of compound 1.

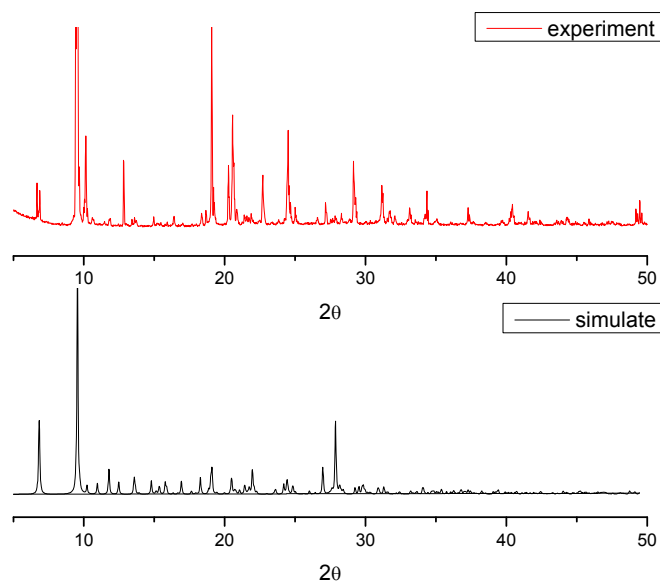


Figure S7. Powder x-ray diffraction patterns of compound **2**

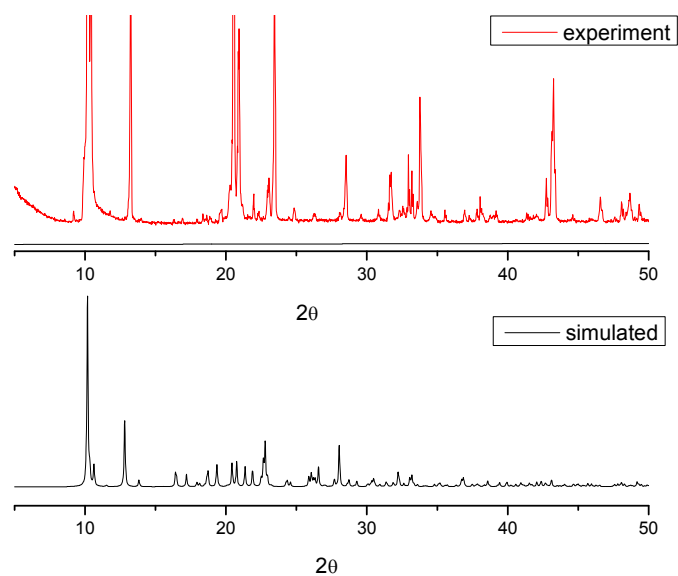


Figure S8. Powder x-ray diffraction patterns of compound **3**

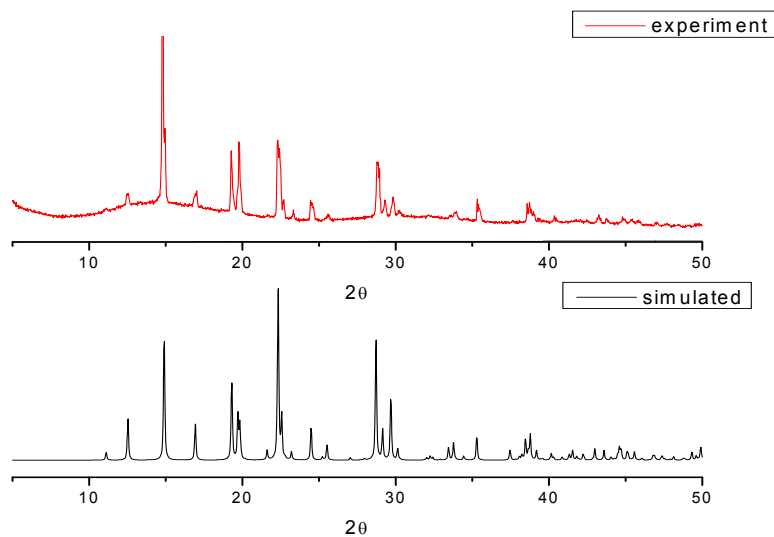


Figure S9. Powder x-ray diffraction patterns of compound **4**

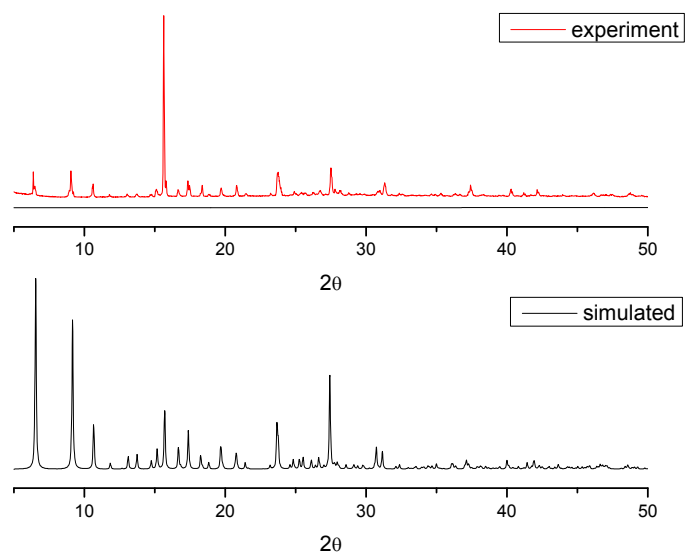


Figure S10. The curves of TGA of **1**, **2**, **3** and **4**

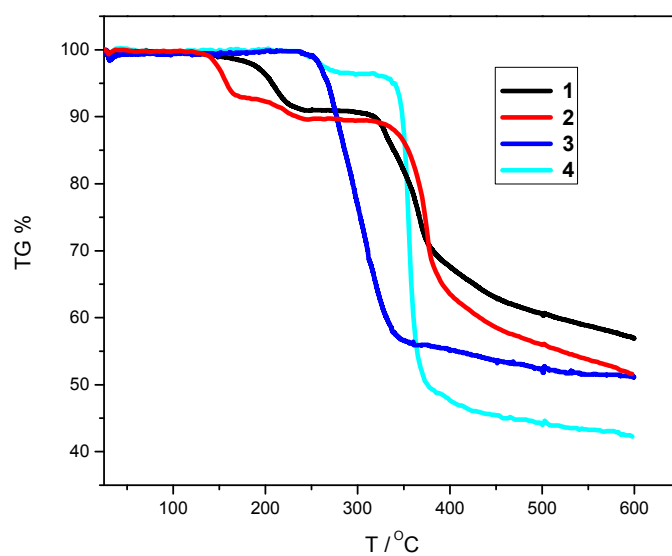


Table S1. Selected bond lengths (Å) and angles (deg) for compound **1**

Cu1-N2	1.916(3)	Cu1-O10	1.955(2)	Cu1-O3	1.955(3)	Cu1-N1	1.962(3)
Cu1-O10	2.301(3)	Cu2-N7	1.903(3)	Cu2-O11	1.938(2)	Cu2-O4	1.956(3)
Cu2-N6	1.977(3)	Cu2-O11	2.345(3)	Cu3-O6	1.922(3)	Cu3-N5	1.984(3)
Cu3-O5	1.994(3)	Cu3-N3	2.015(3)	Cu3-O14	2.375(3)	Cu4-O7	1.924(3)
Cu4-N9	1.984(3)	Cu4-N8	2.026(3)	Cu4-O8	2.021(3)	Cu4-O9	2.275(3)
N2-N3	1.404(4)						
O3-Cu1-N1		163.11(12)		N2-Cu1-N1		82.42(12)	
N2-Cu1-N1		82.42(12)		N7-Cu2-O4		81.19(12)	
N5-Cu3-O5		91.23(12)		O6-Cu3-N3		95.30(12)	
N5-Cu3-N3		81.90(12)		O5-Cu3-N3		171.92(12)	

Table S2. selected bond lengths (Å) and angles (deg) for compound **2**

O7-Cu1	2.281(3)	Cu1-O6	1.935(2)	Cu1-O5	1.983(2)	Cu1-N1	1.989(3)
Cu1-N2	2.013(3)	Cu1-O7	2.281(3)	Cu2-N3	1.923(3)	Cu2-O4	1.953(3)
Cu2-O8	1.950(3)	Cu2-N4	1.995(3)	Cu2-O3	2.331(3)		
O5- Cu1- N1		89.52(12)		O6- Cu1- N2		96.95(11)	
O5- Cu1- N2		170.44(11)		N1- Cu1- N2		82.00(12)	
N1- Cu1- O7		101.00(11)		N2- Cu1- O7		95.54(10)	
N3- Cu2- O4		176.78(14)		N3- Cu2- O8		81.27(11)	
O4- Cu2- O8		96.01(13)		N3- Cu2- N4		81.86(11)	
O4- Cu2- N4		100.92(14)		O8- Cu2- N4		162.69(11)	
N3- Cu2- O3		95.18(11)		O4- Cu2- N4		100.92(14)	

Table S3. Selected bond lengths (Å) and angles (deg) for compound **3**

Cu1-C7	1.892(3)	Cu1-N3	1.926(3)	Cu1-N1	2.241(3)	Cu1-N2	2.365(3)
C7-Cu1-N3		147.65(15)		C7-Cu1-N1		106.99(13)	
N3-Cu1-N1		102.35(11)		C7-Cu1-N2		100.20(13)	
N3-Cu1-N2		100.77(12)		N1-Cu1-N2		73.86(10)	

Table S4. Selected bond lengths (Å) and angles (deg) for compound **4**

Cu1-O7	1.945(3)	Cu1-O6	1.951(3)	Cu1-N5	1.982(4)	Cu1-N2	1.998(3)
O1-Cu1	2.357(3)	Cu2-O3	1.889(3)	Cu2-N1	1.916(4)	Cu2-N3	2.016(4)
O7-Cu1-O6		90.65(13)		O7-Cu1-N5		161.29(14)	
O6- Cu1-N5		91.43(15)		O7-Cu1-N2		93.45(14)	
O6-Cu1-N2		169.99(15)		N5-Cu1-N2		81.80(15)	
O7-Cu1-O1		96.81(12)		N1-Cu2-N3		81.22(16)	
N5-Cu1-O1		101.83(13)		N2- Cu1-O1		97.11(13)	
O3-Cu2-N1		177.41(16)		O3-Cu2-N3		98.07(16)	