Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Table S1. Crystallographic data and single-crystal XRD experiment details.

Structure identifier	**2**	**3**	**4**
Empirical formula	$C_{24}H_{38}Br_2CuN_{12}O_9$	$C_{24}H_{40}Br_2CuN_{12}O_{10}$	$C_{24}H_{40}Br_2CuN_{12}O_{10}$
Formula weight, g/mol	862.02	880.04	880.04
Temperature, K	150	150	200
Crystal system, space group	monoclinic, *Cc*	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
a, Å	30.7828(17)	11.262(3)	7.5931(19)
b, Å	5.6317(3)	7.5904(17)	9.5094(19)
c, Å	20.8991(12)	21.555(4)	13.177(3)
α, °	90	90	103.046(8)
β, °	100.075(2)	94.803(7)	106.647(9)
γ, °	90	90	94.822(8)
Volume, Å^3	3567.2(3)	1836.0(7)	876.7(4)
Z / Z′	4 / 1	2 / ½	1 / ½
ρ_{calc}, g/cm^3	1.605	1.592	1.667
μ, mm^{-1}	2.916	2.837	2.970
F(000)	1748.0	894.0	447.0
Crystal size, mm^3	0.55×0.04×0.03	0.28×0.25×0.19	0.10×0.04×0.005
Radiation	MoKα, λ = 0.71073		
2Θ range for data collection,°	4.378 to 55.748	3.792 to 61.352	4.454 to 50.05
Index ranges	$-40 \le h \le 40$ $-6 \le k \le 7$ $-27 \le l \le 27$	$-16 \le h \le 16$ $-10 \le k \le 10$ $-28 \le l \le 30$	$-9 \le h \le 9$ $-11 \le k \le 8$ $-15 \le l \le 15$
Reflections collected / independent	27621 / 8500	32014 / 5628	8450 / 3083
R_{int} / R_σ	0.0389 / 0.0455	0.0374 / 0.0253	0.0769 / 0.1200
Data / restraints / parameters	8500 / 2 / 438	5628 / 0 / 231	3083 / 0 / 225
Goodness-of-fit on F^2	1.028	1.037	0.973
Final R_1 / wR_2 for $I \ge 2\sigma(I)$	0.0331 / 0.0754	0.0248 / 0.0575	0.0479 / 0.0751
Final R_1 / wR_2 for all data	0.0497 / 0.0815	0.0317 / 0.0602	0.1019 / 0.0885
Largest diff. peak/hole, e/Å^3	0.79 / –0.44	0.45 / –0.39	0.47 / –0.52

Table S2. Experimental data of bond lengths of **2**–**4**; bond lengths of **1** and L are taken from CCDC.

		2	**3**	**4**	**1**	L
Br1	Cu1	2.7804(6)	2.9383(5)	2.9652(9)	2.4904(4)	
Br1	Cu1'	2.8514(6)			3.0447(5)	
Cu1	N11	2.005(4)	2.0003(13)	2.013(4)	1.9625(36)	
Cu1	N21	2.020(4)	2.0211(12)	2.027(4)		
Cu1	N31	2.014(4)				
Cu1	N41	2.019(4)				
N11	N12	1.382(6)	1.3726(18)	1.376(5)	1.3709(51)	1.3669(19)
N21	N22	1.378(6)	1.3772(17)	1.372(5)		
N31	N32	1.375(6)				
N41	N42	1.375(6)				
N11	C11	1.310(7)	1.3208(18)	1.322(6)	1.3161(60)	1.3235(22)
N21	C21	1.323(7)	1.3235(19)	1.316(6)		
N31	C31	1.308(7)				
N41	C41	1.312(7)				
N12	C13	1.335(7)	1.3428(19)	1.346(6)	1.3405(63)	1.3329(22)
N22	C23	1.341(7)	1.3520(18)	1.342(6)		
N32	C33	1.352(7)				
N42	C43	1.342(7)				
N13	C13	1.353(7)	1.346(2)	1.344(6)	1.3547(69)	1.3518(21)
N23	C23	1.348(8)	1.3486(19)	1.339(6)		
N33	C33	1.341(7)				
N43	C43	1.347(7)				
C11	C12	1.406(8)	1.399(2)	1.399(7)	1.3928(64)	1.3871(22)
C21	C22	1.398(8)	1.409(2)	1.404(6)		
C31	C32	1.402(8)				
C41	C42	1.404(8)				
C12	C13	1.390(8)	1.400(2)	1.402(7)	1.3891(61)	1.4164(22)

C22	C23	1.396(8)	1.399(2)	1.384(6)		
C32	C33	1.410(8)				
C42	C43	1.406(8)				
C12	C14	1.446(9)	1.444(2)	1.448(7)	1.4467(63)	1.4430(24)
C22	C24	1.432(9)	1.453(2)	1.455(6)		
C32	C34	1.438(9)				
C42	C44	1.449(9)				
C15	C16	1.509(11)	1.502(2)	1.449(8)	1.4952(93)	1.4923(25)
C25	C26	1.474(11)	1.503(3)	1.500(7)		
C35	C36	1.518(10)				
C45	C46	1.509(11)				
O11	C14	1.208(8)	1.2198(19)	1.200(6)	1.2068(64)	1.2159(20)
O21	C24	1.228(8)	1.211(2)	1.207(5)		
O31	C34	1.239(8)				
O41	C44	1.223(8)				
O12	C14	1.354(8)	1.3372(19)	1.360(6)	1.3451(62)	1.3364(20)
O22	C24	1.343(8)	1.3461(19)	1.329(6)		
O32	C34	1.329(8)				
O42	C44	1.337(8)				
O12	C15	1.455(7)	1.4512(17)	1.456(6)	1.4512(62)	1.4509(22)
O22	C25	1.484(8)	1.447(2)	1.454(6)		
O32	C35	1.441(7)				
O42	C45	1.445(8)				

’ –x, –y, –z for **1** and –x, 1–y, 1–z for L

Table S3. Experimental data of valence angles of **2**–**4**; valence angles of **1** and L are taken from CCDC.

			2	**3**	**4**	**1**	L
Cu1	Br1	Cu1[1]	179.52(3)				
Br1	Cu1	Br1[2]	179.52(3)	180	180		
N11	Cu1	Br1	91.70(12)	91.41(4)	88.54(13)		
N21	Cu1	Br1	89.93(12)	90.96(4)	89.99(13)		
N31	Cu1	Br1	93.16(12)	88.59(4)	91.46(13)		
N41	Cu1	Br1	88.79(12)	89.04(4)	90.01(13)		
N11	Cu1	Br1[2]	87.84(12)				
N21	Cu1	Br1[2]	89.92(13)				
N31	Cu1	Br1[2]	87.30(12)				
N41	Cu1	Br1[2]	91.36(12)				
N11	Cu1	N21	91.10(17)	90.40(5)	90.42(17)		
N11	Cu1	N31	175.13(12)	180	180		
N11	Cu1	N41	88.83(18)	89.60(5)	89.58(16)		
N21	Cu1	N31	89.13(18)	89.61(5)	89.58(16)		
N21	Cu1	N41	178.71(12)	180	180		
N31	Cu1	N41	91.05(17)				
Cu1	N11	N12	125.2(3)	123.05(9)	121.8(3)	124.705(259)	
Cu1	N21	N22	123.7(3)	119.41(9)	119.6(3)		
Cu1	N31	N32	124.7(3)				
Cu1	N41	N42	124.4(3)				
Cu1	N11	C11	129.7(4)	130.86(10)	133.0(4)	130.090(311)	
Cu1	N21	C21	130.9(4)	135.22(10)	134.7(3)		
Cu1	N31	C31	129.2(3)				
Cu1	N41	C41	129.7(4)				
N11	N12	C13	111.3(4)	111.57(12)	112.4(4)	111.3(3)	103.96(13)
N21	N22	C23	111.3(4)	112.03(12)	111.2(4)		
N31	N32	C33	111.5(4)				
N41	N42	C43	111.6(4)				
N12	N11	C11	104.9(4)	105.63(12)	104.5(4)	105.2(3)	113.6(1)
N22	N21	C21	105.2(4)	105.37(11)	105.5(4)		
N32	N31	C31	106.0(4)				
N42	N41	C41	105.9(4)				

N12	C13	C12	107.4(5)	106.48(13)	106.1(5)	107.0(4)	111.09(14)
N22	C23	C22	107.1(5)	105.96(13)	107.1(4)		
N32	C33	C32	105.8(5)				
N42	C43	C42	106.2(5)				
N11	C11	C12	112.2(5)	111.25(13)	112.2(4)	111.9(4)	106.50(14)
N21	C21	C22	111.7(5)	111.15(13)	111.3(4)		
N31	C31	C32	111.6(5)				
N41	C41	C42	111.3(5)				
C11	C12	C13	104.1(5)	105.07(12)	104.8(5)	104.6(4)	104.79(14)
C21	C22	C23	104.7(5)	105.49(12)	104.8(4)		
C31	C32	C33	105.0(5)				
C41	C42	C43	105.0(5)				
N12	C13	N13	122.9(6)	123.55(14)	124.2(5)	123.6(4)	121.77(14)
N22	C23	N23	122.9(6)	122.28(14)	122.4(4)		
N33	C33	N32	124.2(6)				
N42	C43	N43	124.0(6)				
N13	C13	C12	129.6(6)	129.96(14)	129.7(5)	129.4(4)	127.15(15)
N23	C23	C22	130.0(6)	131.75(14)	122.4(4)		
N33	C33	C32	130.0(5)				
N43	C43	C42	129.7(6)				
C13	C12	C14	126.0(5)	124.94(13)	123.2(5)	125.76(4)	126.71(15)
C23	C22	C24	125.0(6)	125.35(14)	124.4(4)		
C33	C32	C34	126.0(5)				
C43	C42	C44	124.1(6)				
C11	C12	C14	129.9(6)	129.77(14)	131.6(5)	129.6(4)	128.44(15)
C21	C22	C24	130.3(6)	129.15(14)	130.6(4)		
C31	C32	C34	129.0(6)				
C41	C42	C44	130.9(6)				
O11	C14	O12	123.9(6)	123.56(14)	124.6(5)	124.1(5)	123.58(15)
O21	C24	O22	123.4(6)	123.91(14)	123.8(5)		
O31	C34	O32	123.2(6)				
O41	C44	O42	122.7(6)				
O11	C14	C12	125.1(6)	123.56(14)	124.3(5)	124.4(4)	123.83(15)
O21	C24	C22	123.6(6)	124.61(15)	122.7(5)		
O31	C34	C32	124.0(6)				
O41	C44	C42	124.3(6)				
O12	C14	C12	111.0(6)	112.16(13)	110.9(5)	111.6(4)	112.58(14)
O22	C24	C22	112.9(6)	111.48(13)	113.4(4)		
O32	C34	C32	112.7(6)				
O42	C44	C42	113.0(6)				
C14	O12	C15	115.8(5)	115.99(12)	114.4(4)	116.1(4)	116.94(13)
C24	O22	C25	115.4(6)	116.00(13)	115.8(4)		
C34	O32	C35	117.2(5)				
C44	O42	C45	115.2(6)				
O12	C15	C16	105.4(5)	107.15(13)	108.1(5)	106.4(5)	106.62(13)
O22	C25	C26	106.8(7)	106.74(16)	108.3(4)		
O32	C35	C36	106.2(6)				
O42	C45	C46	107.1(6)				

For **3** and **4** X3n=X1n', X4n=X2n'.

Table S4. Experimental data of torsion angles of **2**–**4**; torsion angles of **1** and L are taken from CCDC.

				2	**3**	**4**	**1**	L
Br1	Cu1	N11	C11	38.7(5)	23.65(14)	–156.2(5)	–68.8(4)	
Br1	Cu1	N21	C21	–141.5(5)	–173.86(15)	171.4(5)		
Br1	Cu1	N31	C31	41.3(5)				
Br1	Cu1	N41	C41	–139.5(5)				
C11	C12	C14	O11	–175.9(6)	–176.68(16)	–174.9(6)	177.9(5)	–173.74(17)
C21	C22	C24	O21	–172.6(6)	–175.70(16)	170.5(6)		
C31	C32	C34	O31	–179.4(6)				

C41	C42	C44	O41	–176.1(7)				
C12	C14	O12	C15	–175.5(5)	178.90(12)	–175.0(5)	–179.5(4)	–179.29(13)
C22	C24	O22	C25	–176.5(5)	–179.84(14)	174.3(5)		
C32	C34	O32	C35	–177.2(5)				
C42	C44	O42	C45	–178.7(6)				
C14	O12	C15	C16	–179.1(5)	179.27(13)	–175.8(5)	–178.5(5)	175.87(14)
C24	O22	C25	C26	177.9(6)	–176.30(15)	–171.2(5)		
C34	O32	C35	C36	–179.2(5)				
C44	O42	C45	C46	175.7(6				

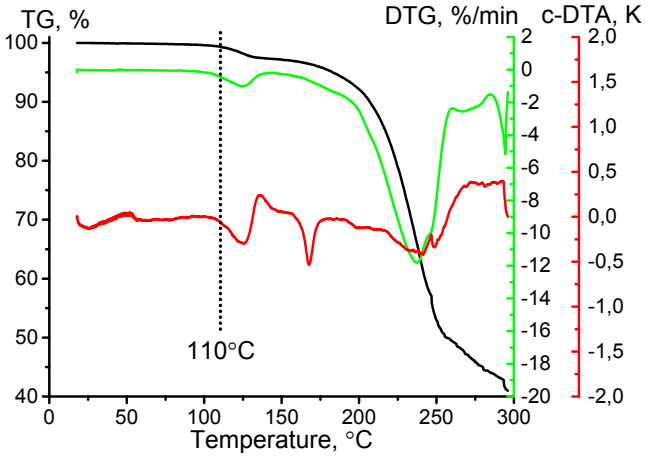

Fig. S1. TG, DTG and c-DTA curves of polycrystalline **2**.

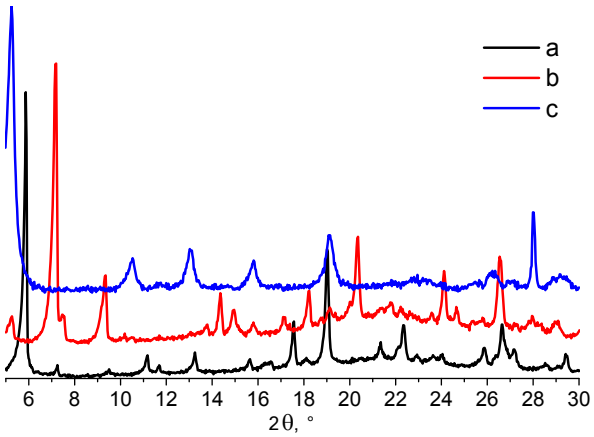

Fig. S2. XRD spectra at 300 K of samples **2** (a), **2** annealed at 110°C (b) and **1** (c).

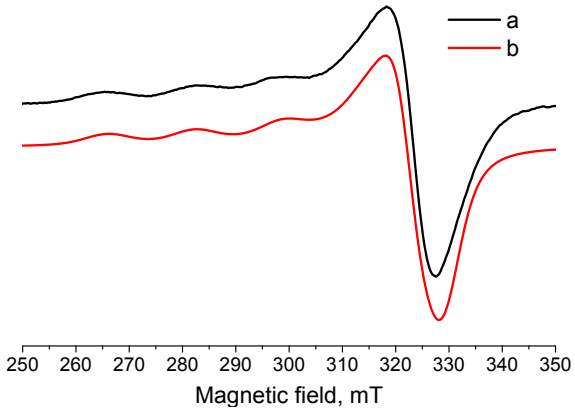

Fig. S3. X-band EPR spectra of polycrystalline **3** at 300 K: a-experimental; b-simulated.

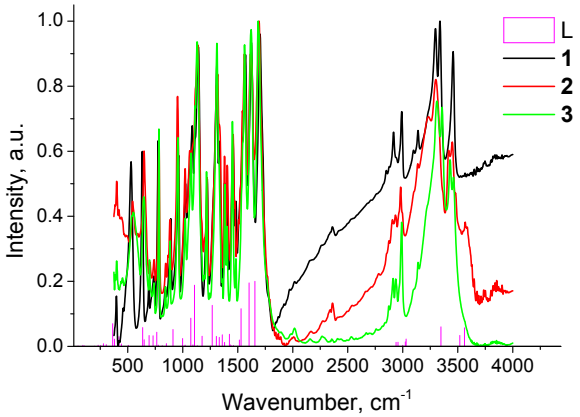

Fig. S4. Experimental IR-spectra of polycrystalline samples **1** (in KBr), **2** (in oil), and **3** (in oil) at 300K and calculated by ADF IR-spectrum of L. *Line at 3460 cm^{-1} (sample **1**) corresponds to KBr(H_2O).*