Electronic Supplementary Information

Templated metalophilicity: synthesis of halometallic double salts directed by a dicopper(I) hydrazinyl-tetraimine nanocation

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1.Experimental details

1.1. Materials and Methods

Organic reagents used in the syntheses were purchased in Sigma-Aldrich while inorganic salts were purchased in POCH chemicals (Gliwice, Poland). Ethanol (92%) was purchased in POLMOS (Poland). ATR-FTIR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with an iD5 diamond ATR attachment (automatic baseline correction). The absorbance UV-VIS spectra were recorded on a Shimadzu UV-VIS-NIR UV-3600 spectrophotometer. Electronic diffuse reflectance spectra were measured in $BaSO_4$ pellets with $BaSO_4$ as a reference using UV-3600 UV-VIS-NIR spectrophotometer equipped with ISR-260 attachment. The luminescence spectra were measured on PerkinElmer LS55 spectrofluorimeter. Measurements in solution were taken after deoxygenation with pure Ar. Solid state fluorescence spectra were measured at room temperature using PerkinElmer LS55 fluorimeter in 45^o geometry (with respect to incident light) with solid samples attached to a glass plates. The presented data for solid luminescence were background-corrected for scattering effects and smoothed using Savitzky-Golay method. Microanalyses on carbon, hydrogen and nitrogen were performed using an Elemental Vario MICRO Cube elemental analyser. The electrochemical experiments were conducted on AUTOLAB/PGSTAT 128N potentiostat/galvanostat (Metrohm, Switzerland) in a three-electrode system with a silver chloride reference electrode, a platinum plate auxiliary electrode and a corresponding carbon paste working electrode. The carbon paste electrode (CPE) was prepared analogously to a published procedure using graphite powder (Sigma-Aldrich) and nujol.[1] All measurements were carried out in 0.3M aqueous solution of sulphuric acid *vs* Ag/AgCl/saturated KCl aqueous solution at room temperature.

1.2 Data collection and refinement details for 1-3 and rpaz, Powder X-Ray diffraction

Diffraction intensity data for single crystals of the new compounds were collected on a (supernova) KappaCCD (Nonius) diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). Corrections for Lorentz, polarisation and absorption effects [Nonius, 1997-2000; Otwinowski and Minor, 1997] were applied. The structure was solved by direct methods using SIR-92 program package [Altomare, et al, 1994] and refined using a full-matrix least square procedure on F^2 using SHELXL-97 [Sheldrick, 1997]. Anisotropic displacement parameters for all non-hydrogen atoms and isotropic temperature factors for hydrogen atoms were introduced. In the structure, the hydrogen atoms connected to carbon atoms were included in calculated positions from the geometry of molecules, whereas hydrogen atoms of water molecules were included from the difference maps and were refined with isotropic thermal parameters. The figures were made using ToposPRO[2], Olex2,[3] Mercury[4] and Crystal Explorer[5] software [Brandenburg and Putz, 1997–2000]. CCDC 1412615-1412617, 1555068 contain the supplementary crystallographic data for 1, 2, 3 and r*paz* ligand. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Powder X-ray diffraction (PXRD) patterns were recorded at room temperature (295 K) on a Rigaku Miniflex 600 diffractometer with Cu-K a radiation (λ=1.5418 Å) in a range from 3° to 45° with a 0.02° step at a scan speed of 1° min^{-1}. The presented powder patterns were background corrected using DASH. The simulated diffraction patterns for the single-crystal structures of 1-3 were calculated in Mercury using default parameters of simulation for λ=1.5418 Å.

1.3 Synthesis

All the synthetic operations have been done under Ar atmosphere. Ethanolic aqueous (92% of ethanol) solution was used as a solvent for all the syntheses, except 2. The fresh 2-hydrazinopyridine (97%) and phthalaldehyde (+98%) we used as supplied from Sigma-Aldrich.

1.3.1 Synthesis of $[Cu_2(dih)_2]_2[Cu_4Cl_8]\cdot EtOH$ (1)

0.50 mmol of phthalaldehyde and 1.00 mmol of 2-hydrazinopyridine were dissolved in 10 mL of deaerated ethanol and heated under reflux and argon for 5 minutes. Small amounts of yellow condensation product have precipitated. To this slurry mixture, 0.50 mmol of $CuCl_2$ was added. The dark red clear solution was then transferred under argon to a vial, sealed and thermostated at 353 K for two hours. The red crystalline product was collected by vacuum filtration and washed with acetone. Yield 53.0 mg (20.1%). Elemental analysis calculated for $[Cu_2(dih)_2]_2[Cu_4Cl_8]\cdot EtOH$, $C_{74}H_{70}Cl_8Cu_8N_{24}O$; 2103.51 g·mol^{-1}: C, 42.25; H, 3.35; N, 15.98%. Found: C, 41.72; H, 3.47; N, 15.72%. ATR-FTIR: ν, cm^{-1} 740(w), 756(w), 765(m), 863(vw), 910(vw), 917(vw), 926(vw), 954(vw), 1008(w), 1045(vw), 1075(w), 1100(w), 1107(w), 1130(w), 1149(w), 1162(vw), 1198(vw), 1252(m), 1274(w), 1287(w), 1333(w), 1361(vw), 1399(vw), 1426(m), 1449(w), 1480(vs), 1527(s), 1551(vw), 1559(w), 1575(m), 1612(vs), 2882(vw), 2922(w), 2945(w), 2972(w), 3034(w), 3076(w), 3128(w), 3176(w), 3206(w), 3445(vw).

1.3.2 Synthesis of $[Cu_2(dih)_2]_2[Cu_2MnCl_8]\cdot 2H_2O$ (2)

0.25 mmol (34 mg) of phthalaldehyde and 0.50 mmol (55 mg) of 2-hydrazinopyridine were dissolved in 15 mL of deaerated 2-propanol and heated under reflux and argon for 10 minutes. To this mixture, 0.25 mmol (45 mg) of $CuCl_2$ and 0.25 mmol (49 mg) of $MnCl_2$ were added in a stepwise manner, where $MnCl_2$ was added 10 min after $CuCl_2$. The mixture was then transferred under argon to a vial, sealed and thermostated at 353 K for two hours. The red crystalline product was collected by vacuum filtration and washed with 2-propanol. Yield 55 mg (44%), Elemental analysis calculated for $[Cu_2(dih)_2]_2[Cu_2MnCl_8]\cdot 2H_2O$, $C_{72}H_{68}Cl_8Cu_6MnN_{24}O_2$; 2021.32 g·mol^{-1}: C, 42.78; H, 3.39; N, 16.63%. Found: C, 41.98; H, 3.56; N, 15.57%.μ_B=5.3 (room temperature). The single crystals suitable for XRD analysis were grown in ethanolic solution in analogous way, however the crop contains also the phase 1.

1.3.3 Synthesis of $[Cu_2(dih)_2]_2[LaCl_6][CuCl_2]\cdot EtOH$ (3)

0.13 mmol of phthalaldehyde and 0.25 mmol of 2-hydrazinopyridine were dissolved in 8 mL of deaerated ethanol, sealed and thermostated for 15 min at 353 K. Subsequently, to the resulting yellow solution 0.13 mmol of $CuCl_2$ was added. After 10 min 0.13 mmol of tris(hydroxymethyl)aminomethane and 0.13 mmol of $LaCl_3$ were added. The resulting mixture was sealed under argon and thermostated at 373.0 K for two hours. Large, red single crystals of 3 were separated from the white powdery side-product by vacuum filtration at G2 filter, washed with ethanol and dried in air. The single crystals for X-ray diffraction were selected from the bulk product. Yield 27.0 mg (40.0%). Elemental analysis calculated for $[Cu_2(dih)_2]_2[LaCl_6][CuCl_2]\cdot EtOH$, $C_{74}H_{70}Cl_8Cu_5LaN_{24}O$; 2051.78 g·mol^{-1}: C, 43.32; H, 3.44; N, 16.38%. Found: C, 44.40; H, 3.45; N, 16.29%. ATR-FTIR: ν, cm^{-1} 740(vw), 746(vw), 756(w),

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767(w), 875(vw), 907(vw), 912(vw), 929(vw), 956(vw), 1008(vw), 1043(w), 1075(w), 1099(vw), 1109(vw), 1129(w), 1148(w), 1198(vw), 1252(w), 1275(w), 1283(w), 1337(w), 1362(vw), 1375(vw), 1425(m), 1448(w), 1479(vs), 1526(m), 1552(w), 1576(w), 1614(vs), 2886(vw), 2927(vw), 2965(w), 2981(w), 3037(w), 3080(vw), 3105(vw), 3133(w), 3218(m), 3233(m), 3383(vw).

1.3.4 Synthesis of the ligand rpaz (4)

Ethanolic solution (5 mL) containing dissolved 67 mg of phthalaldehyde (0.50 mmol) and 109 mg of 2-hydrazinopyridine (1.00 mmol) was thermostated at 353.0 K for 2h. The yellow product was collected by vacuum filtration after cooling the solution to the room temperature. Single crystals suitable for X-ray diffraction experiment were grown analogously, but the solution was kept at room temperature for one month. Yield 90 mg (59%). Elemental analysis calculated for *rpaz*, $C_{18}H_{20}N_6O_2$; 352.4 g·mol^{-1}: C, 68.34; H, 5.10; N, 26.56%. Found: C, 67.80; H, 4.73; N, 26.26%. ATR-FTIR: ν, cm^{-1} 762m, 1141m, 1285m, 1300m, 1314s, 1436vs, 1458m, 1538s, 1574s, 1584s, 1597vs, 2936m, 2987m, 3013m, 3053m, 3194m.

Table S1. Crystal data and experimental details for 1-3.

Compound	**1**	**2**	**3**
Chem.	$C_{38}H_{33}Cl_4Cu_4N_{12}O$	$C_{36}H_{32}Cl_4Cu_3Mn_{0.5}N_{12}$	$C_{38}H_{38}Cl_4Cu_{2.5}La_{0.5}N_{12}O$
***M*$_r$**	1069.72	992.62	1048.91
Cryst. system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
T (K)	120	120	120
***a* (A)**	11.785 (5)	11.6842 (3)	11.8200 (3)
***b* (A)**	12.353 (5)	12.3404 (4)	12.8808 (3)
***c* (A)**	15.745 (5)	15.7885 (3)	15.6470 (4)
α (°)	112.037 (5)	112.226 (3)	111.058 (2)
β (°)	103.923 (5)	102.317 (2)	104.035 (2)
γ (°)	98.618 (5)	98.889 (3)	99.087 (2)
V (Å^3)	1987.5 (13)	1988.00 (10)	2076.29 (10)
Z	2	2	2
C. size (mm)	0.40x0.10x0.05	0.25x0.18x0.06	0.40x0.15x0.07
***D*$_{calc}$ (g cm^{-3})**	1.788	1.658	1.678
μ (mm^{-1})	2.43	2.06	2.08
No. Refl. coll./indep.	27615/9247	53005/11473	29487/9771
***R*$_1$ (I>2σ(I))^a**	0.0437	0.0731	0.0500
***w*R(*F*^{2})^a**	0.122	0.226	0.141

[a] Parameters definition: $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $wR(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0808P)^2 + 2.6927P]$; $P = (F_o^2 + 2F_c^2)/3$.

Table S2. Crystal data and refinement parameters for *rpaz.*

Crystal data

$C_{18}H_{16}N_6$	D_x = 1.339 Mg m^{-3}
M_r = 316.37	Mo *Kα* radiation, λ = 0.71073 Å
Monoclinic, $P2_1/c$	μ = 0.09 mm^{-1}
a = 10.1182 (2) Å	*T* = 298 K
b = 12.9469 (3) Å	0.36 × 0.33 × 0.22 mm
c = 12.1513 (4) Å	
β = 99.671 (2)°	
V = 1569.19 (7) Å^3	
Z = 4	
F(000) = 664	

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.1065P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.130$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.76$	$\Delta\rho_{max} = 0.16$ e Å^{-3}
3577 reflections	$\Delta\rho_{min} = -0.13$ e Å^{-3}
234 parameters	Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
0 restraints	Extinction coefficient: 0.042 (5)

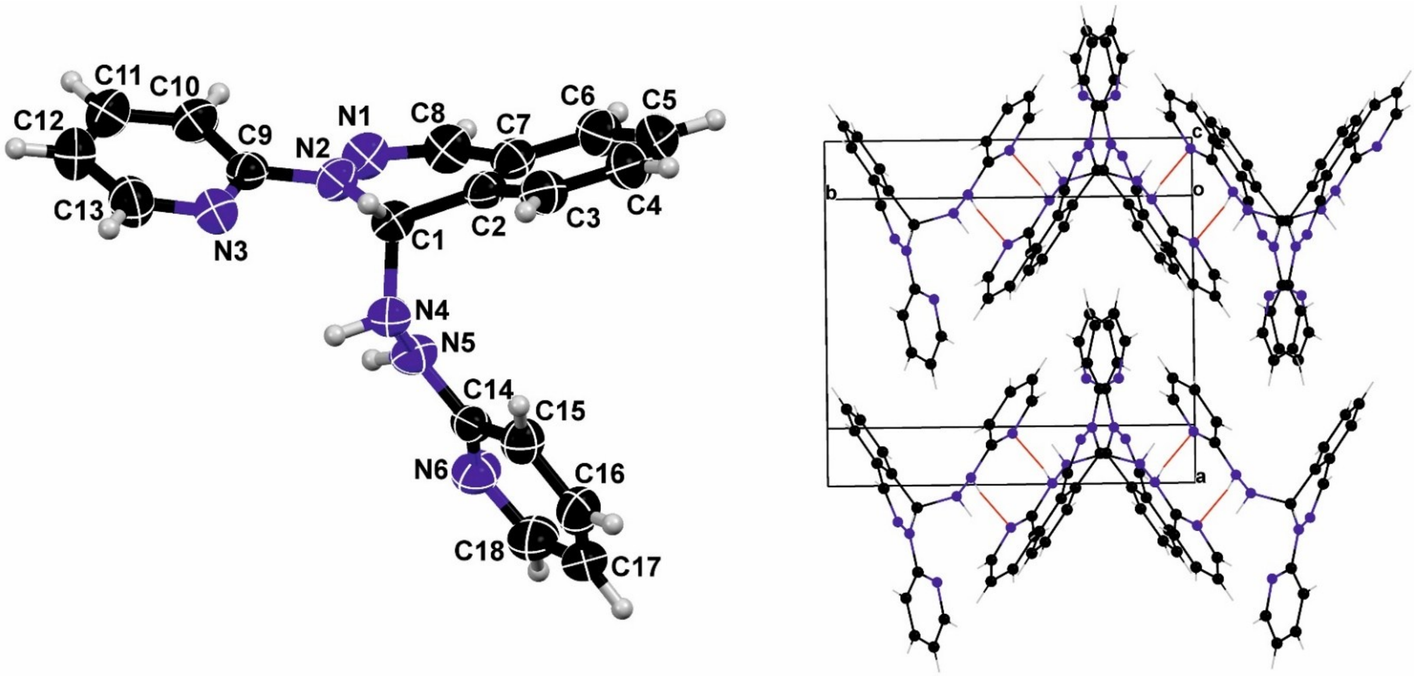

Figure S1. The molecular structure with labelling of atoms and crystal packing of the ligand *rpaz*. The thermal ellipsoids represent 50% of displacement probability.

Table S3. Hydrogen Bonds for 1-3

D—H···A	D—H	H···A	D···A	D—H···A
N5b—H5b···Cl1$^{\mathrm{v}}$	0.98 (2)	2.27 (3)	3.181 (3)	154 (4)
N2b—H2b···Cl4$^{\mathrm{vi}}$	0.69 (4)	2.55 (4)	3.226 (4)	169 (4)
N5—H6b···Cl3$^{\mathrm{vii}}$	0.89 (4)	2.56 (5)	3.403 (3)	158 (4)
C1a—H3b···Cl2$^{\mathrm{viii}}$	0.91 (4)	2.80 (4)	3.596 (4)	146 (3)
C18b—H18b···Cl2	0.95	2.89	3.487 (4)	122
C12b—H12b···Cl3	0.95	2.74	3.593 (4)	150
N2—H2a···Cl1$^{\mathrm{v}}$	0.96 (2)	2.39 (2)	3.306 (3)	160 (3)
C10a—H10a···Cl4$^{\mathrm{vii}}$	0.95	2.98	3.854 (4)	153
C8a—H8a···Cl3$^{\mathrm{vii}}$	0.92 (4)	2.60 (4)	3.485 (4)	160 (3)
O1—H1c···Cl4	0.84	2.49	3.191 (12)	141

(1)

Symmetry codes: (v) −x+1, −y+2, −z+1; (vi) −x+1, −y+1, −z; (vii) x−1, y−1, z; (viii) x−1, y, z.

(2)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C17*a*—H17*a*···Cl2^{iv}	0.95	2.95	3.582 (5)	125
C17*b*—H17*b*···Cl1	0.95	2.75	3.580 (5)	147
N5*b*—H5*bb*···Cl4^{v}	1.00 (2)	2.25 (3)	3.219 (4)	164 (6)
C8*b*—H8*b*···Cl4^{v}	1.02 (5)	2.89 (5)	3.727 (5)	140 (4)
C8*a*—H8*a*···Cl1^{vi}	0.78 (7)	2.74 (7)	3.457 (5)	154 (6)
N5*a*—H5*aa*···Cl1^{vi}	1.00 (2)	2.36 (4)	3.330 (4)	162 (9)
C1*a*—H1*a*···Cl2^{vii}	0.80 (7)	2.89 (7)	3.586 (5)	146 (6)
N2*b*—H2*b*···Cl3^{viii}	0.98 (5)	2.38 (10)	3.165 (4)	137 (10)
N2*a*—H2*a*···Cl3^{ix}	1.00 (2)	2.37 (4)	3.326 (4)	160 (8)

Symmetry codes: (iv) *x*, *y*−1, *z*; (v) −*x*+1, −*y*+2, −*z*+2; (vi) *x*+1, *y*, *z*; (vii) *x*+1, *y*−1, *z*; (viii) −*x*+1, −*y*+1, −*z*+1; (ix) −*x*+1, −*y*, −*z*+1.

(3)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12*a*—H12*a*···Cl3^{v}	0.95	2.76	3.616 (5)	151
C13*a*—H13*a*···O1^{v}	0.95	2.51	3.316 (6)	142
C17*b*—H17*b*···Cl1^{vi}	0.95	2.93	3.639 (5)	132
O1—H1*c*···N2*a*^{vii}	0.84	2.10	2.807 (5)	141
C20—H20*a*···Cl3	0.99	2.92	3.630 (7)	129
N5*b*—H5*bbb*···Cl3^{i}	0.98 (2)	2.34 (3)	3.277 (4)	159 (5)
N2*a*—H2*a*···O1^{viii}	0.99 (2)	1.83 (2)	2.807 (5)	169 (6)
N2*b*—H2*b*···Cl2^{ix}	0.99 (2)	2.39 (4)	3.314 (4)	154 (6)
C1*a*—H1*a*···O1^{viii}	1.04 (2)	2.52 (4)	3.402 (6)	142 (4)
C1*b*—H1*b*···Cl1^{iii}	1.04 (2)	2.77 (3)	3.675 (4)	145 (4)
N5*a*—H5*aa*···Cl2	0.99 (2)	2.21 (3)	3.196 (4)	170 (8)
C8*b*—H8*b*···Cl3^{i}	1.02 (1)	2.62 (3)	3.532 (4)	149 (3)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*, −*z*+1; (v) −*x*, −*y*+1, −*z*+1; (vi) −*x*, −*y*, −*z*+1; (vii) *x*, *y*−1, *z*−1; (viii) *x*, *y*+1, *z*+1; (ix) *x*, *y*−1, *z*.

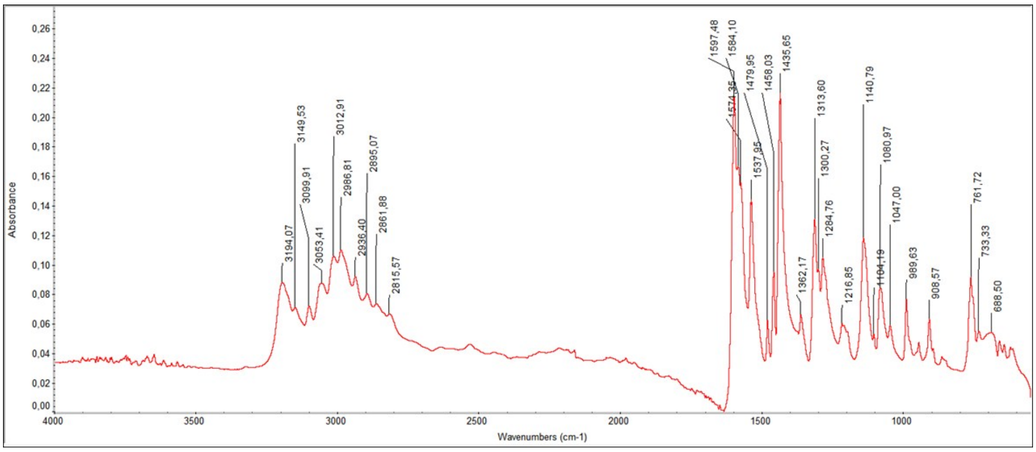

Figure S2. The ATR FTIR spectrum of *rpaz*.

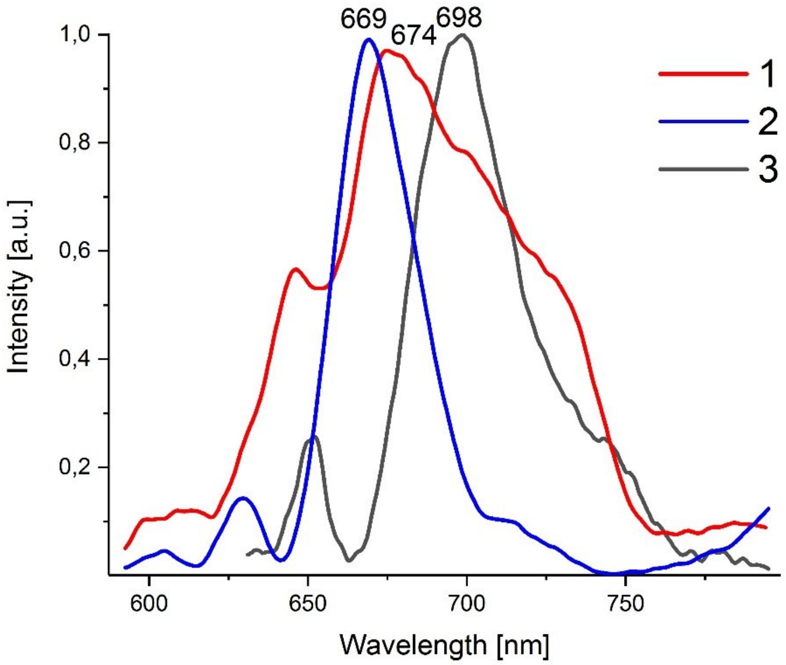

Figure S3. Luminescence spectra of 1-3 after excitation 550, 530 and 560 nm (1-3, respectively). Room temperature.

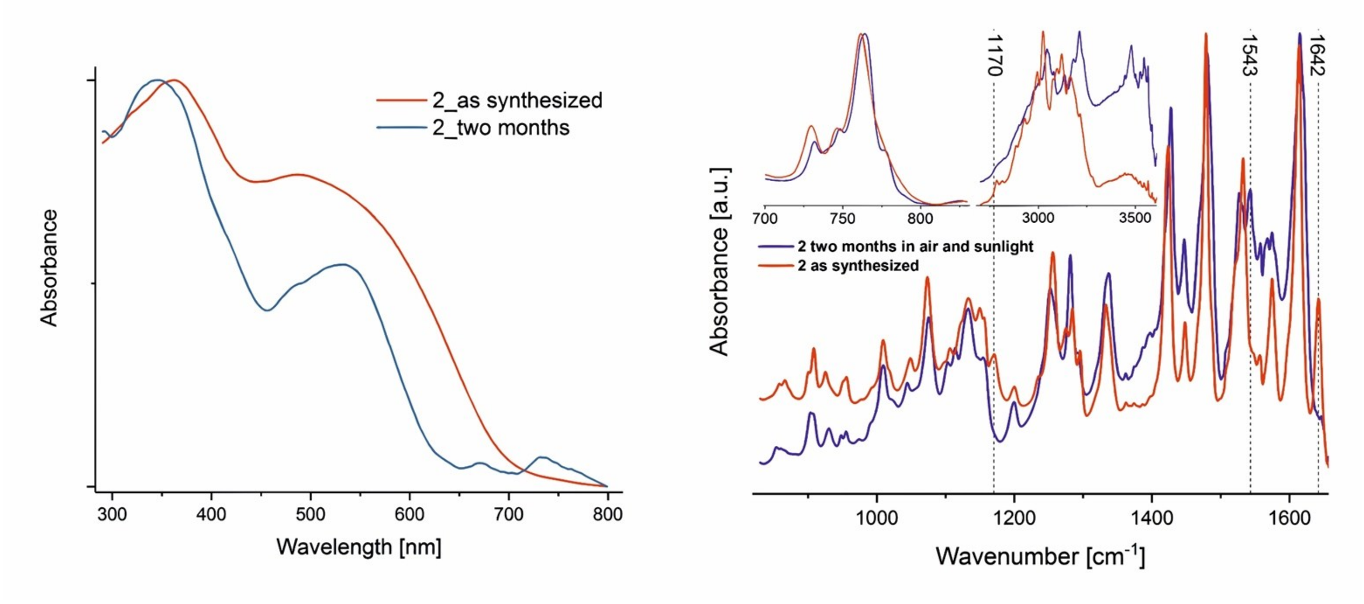

Figure S4. The Diffuse Reflectance UV-VIS and ATR-FTIR spectra of 2 as synthesized and after two months. Room temperature.

Table S4. Bond Valence Summation calculation results for 2.[6]

Atom no.	Valence state assumed	Bond Valence Sum	Deviation from assumed valence state [%]
Cu1a	+1	0,991	1
Cu1b	+1	0,889	11
Cu3	+1	1,334	33
Mn1	+2	1,852	7

Notes and references

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