Supporting Information for

Structural transformations of layered structures constructed from Cu(II)–chloranilate monomer compounds

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Crystallographic Data Collection and Refinement of Structures

A suitable crystal was chosen and mounted on a glass fiber with epoxy resin. Data collection was carried out on a Rigaku R-AXIS RAPID II for **1** and **2** with graphite-monochromated Mo(Kα) radiation (λ = 0.71075 Å). Crystallographic data are given in Table S1 and S2. The structures were solved by direct methods (Rigaku Crystal Structure crystallographic software package of Molecular Structure Corporation). Full-matrix least squares refinements (SHELXL-2016) were carried out with anisotropic thermal parameters for all non-hydrogen atoms.

Table S1. Crystal data and structural refinement of compound **1**

	1 (100K)	**1** (200K)	**1** (295K)
CCDC No.	1521434	1521428	1521424
Empirical Formula	$C_{28}H_{44}Cl_4CuN_2O_{10}$	$C_{28}H_{44}Cl_4CuN_2O_{10}$	$C_{28}H_{44}Cl_4CuN_2O_{10}$
Formula Weight	773.99	773.99	773.99
Crystal Color, Habit	violet, platelet	violet, platelet	violet, platelet
Crystal Dimensions	0.25 X 0.10 X 0.05 mm	0.25 X 0.10 X 0.05 mm	0.25 X 0.10 X 0.05 mm
Crystal System	Monoclinic	Monoclinic	Monoclinic
Lattice Type	C-centered	C-centered	C-centered
Lattice Parameters	a = 9.7962(4) Å b = 16.0447(8) Å c = 11.0491(5) Å β = 90.9641(14)° V = 1736.42(14) Å^3	a = 9.8160(16) Å b = 16.032(3) Å c = 11.2106(17) Å β = 91.082(4)° V = 1763.9(5) Å^3	a = 9.8642(19) Å b = 16.051(3) Å c = 11.379(2) Å β = 91.283(5)° V = 1801.3(6) Å^3
Space Group	C2/m (#12)	C2/m (#12)	C2/m (#12)
Z value	2	2	2
D_{calc}	1.480 g/cm^3	1.457 g/cm^3	1.427 g/cm^3
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated	MoKα (λ = 0.71075 Å) graphite monochromated	MoKα (λ = 0.71075 Å) graphite monochromated
Temperature	-173.0°C	-70.0°C	22.0°C
Residuals: R1 (I>2.00σ(I))	0.058	0.062	0.075
Residuals: R (All reflections)	0.087	0.100	0.127
Residuals: wR2 (All reflections)	0.171	0.151	0.243
Goodness of Fit Indicator	1.038	1.107	1.076

Table S2. Crystal data and structural refinement of compound **2**

	2 (100K)	**2** (200K)	**2** (250K)	**2** (295K)
CCDC No.	1521436	1521432	1521426	1521430
Empirical Formula	$C_{26}H_{38}Cl_4CuN_2O_9$	$C_{26}H_{38}Cl_4CuN_2O_9$	$C_{26}H_{38}Cl_4CuN_2O_9$	$C_{26}H_{38}Cl_4CuN_2O_9$
Formula Weight	727.92	727.92	727.92	727.92
Crystal Color, Habit	violet, block	violet, block	violet, block	violet, block
Crystal Dimensions	0.40 X 0.20 X 0.15 mm	0.40 X 0.20 X 0.15 mm	0.40 X 0.20 X 0.15 mm	0.40 X 0.20 X 0.15 mm
Crystal System	Triclinic	Triclinic	Triclinic	Triclinic
Lattice Type	Primitive	Primitive	Primitive	Primitive
Lattice Parameters	a = 9.9958(4) Å b = 12.3264(5) Å c = 14.0179(6) Å α= 67.9707(16) ^{o} β = 89.4411(15) ^{o} γ = 87.1956(13) ^{o} V = 1599.09(12) Å^3	a = 9.9903(3) Å b = 12.3925(3) Å c = 14.1213(3) Å α = 68.4083(7) ^{o} β = 89.2403(9) ^{o} γ = 86.7971(11) ^{o} V = 1623.02(7) Å^3	a = 9.9963(3) Å b = 12.4259(4) Å c = 14.1763(5) Å α = 68.7310(14) ^{o} β = 88.9340(12) ^{o} γ = 86.718(1) ^{o} V = 1638.25(9) Å^3	a = 10.064(5) Å b = 12.559(6) Å c = 14.362(7) Å α = 69.311(8) ^{o} β = 88.594(7) ^{o} γ = 86.781(7) ^{o} V = 1695.6(15) Å^3
Space Group	P-1 (#2)	P-1 (#2)	P-1 (#2)	P-1 (#2)
Z value	2	2	2	2
D_{calc}	1.512 g/cm^3	1.490 g/cm^3	1.476 g/cm^3	1.426 g/cm3
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated	MoKα (λ = 0.71075 Å) graphite monochromated	MoKα (λ = 0.71075 Å)graphite monochromated	MoKα (λ = 0.71075 Å)graphite monochromated
Temperature	-173.0^{o}C	-73.0^{o}C	-23.0^{o}C	22.0 ^{o}C
Residuals: R1 (I>2.00σ(I))	0.031	0.034	0.039	0.056
Residuals: R (All reflections)	0.037	0.041	0.049	0.084
Residuals: wR2 (All reflections)	0.090	0.098	0.128	0.171
Goodness of Fit Indicator	1.096	1.080	1.082	1.044

Table S3. Geometric parameters (Å, º) in compound **1** (at 100K).

Cu1—O1	1.963 (3)	C5—H5B	0.9800
Cu1—O1^{i}	1.963 (3)	C5—H5C	0.9800
Cu1—O1^{ii}	1.963 (3)	C6—C7	1.487 (10)
Cu1—O1^{iii}	1.963 (3)	C6—H6A	0.9900
Cl1—C2	1.741 (3)	C6—H6B	0.9900
O1—C1	1.270 (5)	C7—C8	1.489 (10)
O2—C3	1.235 (5)	C7—H7A	0.9900
O3—C4	1.423 (8)	C7—H7B	0.9900
O3—H3	0.8400	C8—C9	1.510 (11)
N1—C6	1.499 (11)	C8—H8A	0.9900
N1—H1A	0.9100	C8—H8B	0.9900
N1—H1B	0.9100	C9—C10	1.504 (13)
N1—H1C	0.9100	C9—H9A	0.9900
C1—C2	1.380 (6)	C9—H9B	0.9900
C1—C1^{iii}	1.539 (6)	C10—C11	1.450 (12)
C2—C3	1.403 (6)	C10—H10A	0.9900
C3—C3^{iii}	1.559 (6)	C10—H10B	0.9900
C4—C5	1.558 (10)	C11—H11A	0.9800
C4—H4A	0.9900	C11—H11B	0.9800
C4—H4B	0.9900	C11—H11C	0.9800
C5—H5A	0.9800		
O1—Cu1—O1^{i}	96.35 (14)	C7—C6—H6A	108.7
O1—Cu1—O1^{ii}	180.0	N1—C6—H6A	108.7
O1^{i}—Cu1—O1^{ii}	83.65 (14)	C7—C6—H6B	108.7
O1—Cu1—O1^{iii}	83.65 (14)	N1—C6—H6B	108.7
O1^{i}—Cu1—O1^{iii}	180.0	H6A—C6—H6B	107.6
O1^{ii}—Cu1—O1^{iii}	96.35 (14)	C6—C7—C8	115.5 (7)
C1—O1—Cu1	113.03 (19)	C6—C7—H7A	108.4
C4—O3—H3	109.5	C8—C7—H7A	108.4
C6—N1—H1A	109.5	C6—C7—H7B	108.4
C6—N1—H1B	109.5	C8—C7—H7B	108.4
H1A—N1—H1B	109.5	H7A—C7—H7B	107.5
C6—N1—H1C	109.5	C7—C8—C9	115.9 (8)
H1A—N1—H1C	109.5	C7—C8—H8A	108.3
H1B—N1—H1C	109.5	C9—C8—H8A	108.3
O1—C1—C2	125.7 (3)	C7—C8—H8B	108.3
O1—C1—C1^{iii}	115.13 (18)	C9—C8—H8B	108.3
C2—C1—C1^{iii}	119.1 (2)	H8A—C8—H8B	107.4

C1—C2—C3	122.7 (3)	C10—C9—C8	111.8 (8)
C1—C2—Cl1	119.0 (3)	C10—C9—H9A	109.2
C3—C2—Cl1	118.3 (3)	C8—C9—H9A	109.2
O2—C3—C2	125.8 (3)	C10—C9—H9B	109.2
O2—C3—C3^{iii}	116.09 (18)	C8—C9—H9B	109.2
C2—C3—C3^{iii}	118.1 (2)	H9A—C9—H9B	107.9
O3—C4—C5	97.3 (6)	C11—C10—C9	119.8 (8)
O3—C4—H4A	112.3	C11—C10—H10A	107.4
C5—C4—H4A	112.3	C9—C10—H10A	107.4
O3—C4—H4B	112.3	C11—C10—H10B	107.4
C5—C4—H4B	112.3	C9—C10—H10B	107.4
H4A—C4—H4B	109.9	H10A—C10—H10B	106.9
C4—C5—H5A	109.5	C10—C11—H11A	109.5
C4—C5—H5B	109.5	C10—C11—H11B	109.5
H5A—C5—H5B	109.5	H11A—C11—H11B	109.5
C4—C5—H5C	109.5	C10—C11—H11C	109.5
H5A—C5—H5C	109.5	H11A—C11—H11C	109.5
H5B—C5—H5C	109.5	H11B—C11—H11C	109.5
C7—C6—N1	114.2 (9)		
Cu1—O1—C1—C2	−178.1 (3)	Cl1—C2—C3—O2	0.6 (5)
Cu1—O1—C1—C1^{iii}	1.4 (4)	C1—C2—C3—C3^{iii}	−0.9 (6)
O1—C1—C2—C3	−178.3 (3)	Cl1—C2—C3—C3^{iii}	−179.2 (3)
C1^{iii}—C1—C2—C3	2.2 (6)	N1—C6—C7—C8	66.6 (9)
O1—C1—C2—Cl1	0.0 (5)	C6—C7—C8—C9	179.7 (7)
C1^{iii}—C1—C2—Cl1	−179.5 (3)	C7—C8—C9—C10	168.2 (10)
C1—C2—C3—O2	179.0 (3)	C8—C9—C10—C11	−171.8 (12)

Symmetry codes: (i) x, −y+1, z; (ii) −x+1, −y+1, −z+1; (iii) −x+1, y, −z+1.

Table S4. Geometric parameters (Å, o) in compound **2** (at 100K).

Cu1—O1	1.9362 (12)	C16—H16B	0.9900
Cu1—O6	1.9425 (12)	C17—C18	1.519 (2)
Cu1—O5	1.9431 (12)	C17—H17A	0.9900
Cu1—O2	1.9653 (12)	C17—H17B	0.9900
Cu1—O9	2.2328 (14)	C18—C19	1.520 (3)
Cl1—C3	1.7272 (17)	C18—H18A	0.9900
Cl2—C6	1.7272 (17)	C18—H18B	0.9900
Cl3—C9	1.7281 (17)	C19—C20	1.517 (3)
Cl4—C12	1.7319 (17)	C19—H19A	0.9900
O1—C1	1.290 (2)	C19—H19B	0.9900
O2—C2	1.269 (2)	C20—H20A	0.9800
O3—C4	1.252 (2)	C20—H20B	0.9800
O4—C5	1.233 (2)	C20—H20C	0.9800
O5—C7	1.288 (2)	C21—C22	1.509 (4)
O6—C8	1.286 (2)	C21—H21A	0.9900
O7—C10	1.229 (2)	C21—H21B	0.9900
O8—C11	1.241 (2)	C22—C23	1.544 (4)
O9—C13	1.425 (2)	C22—H22A	0.9900
O9—H1	0.71 (3)	C22—H22B	0.9900
N1—C15	1.486 (2)	C23—C24	1.490 (5)
N1—H2	0.91 (3)	C23—H23A	0.9900
N1—H3	0.88 (2)	C23—H23B	0.9900
N1—H4	0.86 (2)	C24—C25	1.487 (5)
N2—C21	1.508 (3)	C24—H24A	0.9900
N2—H2A	0.9100	C24—H24B	0.9900
N2—H2B	0.9100	C25—C26	1.572 (5)
N2—H2C	0.9100	C25—H25A	0.9900
C1—C6	1.370 (2)	C25—H25B	0.9900
C1—C2	1.520 (2)	C26—H26A	0.9800
C2—C3	1.394 (2)	C26—H26B	0.9800
C3—C4	1.404 (2)	C26—H26C	0.9800
C4—C5	1.545 (2)	C27—C28	1.518 (12)
C5—C6	1.427 (2)	C27—H27A	0.9900
C7—C12	1.375 (2)	C27—H27B	0.9900
C7—C8	1.517 (2)	C28—C29	1.490 (13)
C8—C9	1.374 (2)	C28—H28A	0.9900
C9—C10	1.434 (2)	C28—H28B	0.9900
C10—C11	1.557 (2)	C29—C30	1.538 (15)

C11—C12	1.417 (2)	C29—H29A	0.9900
C13—C14	1.510 (3)	C29—H29B	0.9900
C13—H13A	0.9900	C30—C31	1.503 (15)
C13—H13B	0.9900	C30—H30A	0.9900
C14—H14A	0.9800	C30—H30B	0.9900
C14—H14B	0.9800	C31—C32	1.541 (17)
C14—H14C	0.9800	C31—H31A	0.9900
C15—C16	1.519 (2)	C31—H31B	0.9900
C15—H15A	0.9900	C32—H32A	0.9800
C15—H15B	0.9900	C32—H32B	0.9800
C16—C17	1.522 (2)	C32—H32C	0.9800
C16—H16A	0.9900		
O1—Cu1—O6	96.04 (5)	C16—C17—H17A	108.7
O1—Cu1—O5	171.52 (5)	C18—C17—H17B	108.7
O6—Cu1—O5	84.36 (5)	C16—C17—H17B	108.7
O1—Cu1—O2	83.95 (5)	H17A—C17—H17B	107.6
O6—Cu1—O2	172.51 (5)	C17—C18—C19	112.72 (16)
O5—Cu1—O2	94.55 (5)	C17—C18—H18A	109.0
O1—Cu1—O9	94.47 (6)	C19—C18—H18A	109.0
O6—Cu1—O9	95.96 (5)	C17—C18—H18B	109.0
O5—Cu1—O9	93.91 (5)	C19—C18—H18B	109.0
O2—Cu1—O9	91.51 (5)	H18A—C18—H18B	107.8
C1—O1—Cu1	112.56 (10)	C20—C19—C18	113.88 (18)
C2—O2—Cu1	112.38 (11)	C20—C19—H19A	108.8
C7—O5—Cu1	112.24 (10)	C18—C19—H19A	108.8
C8—O6—Cu1	112.66 (11)	C20—C19—H19B	108.8
C13—O9—Cu1	127.92 (13)	C18—C19—H19B	108.8
C13—O9—H1	109 (2)	H19A—C19—H19B	107.7
Cu1—O9—H1	112 (2)	C19—C20—H20A	109.5
C15—N1—H2	111.7 (15)	C19—C20—H20B	109.5
C15—N1—H3	109.3 (15)	H20A—C20—H20B	109.5
H2—N1—H3	111 (2)	C19—C20—H20C	109.5
C15—N1—H4	108.9 (15)	H20A—C20—H20C	109.5
H2—N1—H4	112 (2)	H20B—C20—H20C	109.5
H3—N1—H4	104 (2)	N2—C21—C22	108.9 (2)
C21—N2—H2A	109.5	N2—C21—H21A	109.9
C21—N2—H2B	109.5	C22—C21—H21A	109.9
H2A—N2—H2B	109.5	N2—C21—H21B	109.9
C21—N2—H2C	109.5	C22—C21—H21B	109.9

H2A—N2—H2C	109.5	H21A—C21—H21B	108.3
H2B—N2—H2C	109.5	C21—C22—C23	111.1 (2)
O1—C1—C6	124.67 (15)	C21—C22—H22A	109.4
O1—C1—C2	114.98 (14)	C23—C22—H22A	109.4
C6—C1—C2	120.34 (15)	C21—C22—H22B	109.4
O2—C2—C3	124.75 (15)	C23—C22—H22B	109.4
O2—C2—C1	115.37 (15)	H22A—C22—H22B	108.0
C3—C2—C1	119.88 (15)	C24—C23—C22	117.4 (3)
C2—C3—C4	120.85 (15)	C24—C23—H23A	107.9
C2—C3—Cl1	120.04 (13)	C22—C23—H23A	107.9
C4—C3—Cl1	119.10 (13)	C24—C23—H23B	107.9
O3—C4—C3	125.59 (16)	C22—C23—H23B	107.9
O3—C4—C5	115.05 (15)	H23A—C23—H23B	107.2
C3—C4—C5	119.36 (15)	C25—C24—C23	114.1 (3)
O4—C5—C6	124.91 (16)	C25—C24—H24A	108.7
O4—C5—C4	116.93 (15)	C23—C24—H24A	108.7
C6—C5—C4	118.17 (15)	C25—C24—H24B	108.7
C1—C6—C5	121.24 (15)	C23—C24—H24B	108.7
C1—C6—Cl2	119.59 (13)	H24A—C24—H24B	107.6
C5—C6—Cl2	119.17 (13)	C24—C25—C26	114.0 (3)
O5—C7—C12	124.23 (15)	C24—C25—H25A	108.7
O5—C7—C8	115.38 (14)	C26—C25—H25A	108.7
C12—C7—C8	120.36 (15)	C24—C25—H25B	108.7
O6—C8—C9	125.56 (15)	C26—C25—H25B	108.7
O6—C8—C7	114.86 (14)	H25A—C25—H25B	107.6
C9—C8—C7	119.57 (15)	C25—C26—H26A	109.5
C8—C9—C10	122.09 (15)	C25—C26—H26B	109.5
C8—C9—Cl3	119.53 (13)	H26A—C26—H26B	109.5
C10—C9—Cl3	118.37 (13)	C25—C26—H26C	109.5
O7—C10—C9	125.34 (15)	H26A—C26—H26C	109.5
O7—C10—C11	116.98 (15)	H26B—C26—H26C	109.5
C9—C10—C11	117.68 (14)	C28—C27—H27A	110.4
O8—C11—C12	124.34 (15)	C28—C27—H27B	110.4
O8—C11—C10	117.71 (14)	H27A—C27—H27B	108.6
C12—C11—C10	117.95 (14)	C29—C28—C27	114.1 (10)
C7—C12—C11	122.02 (15)	C29—C28—H28A	108.7
C7—C12—Cl4	119.60 (13)	C27—C28—H28A	108.7
C11—C12—Cl4	118.29 (13)	C29—C28—H28B	108.7
O9—C13—C14	110.22 (19)	C27—C28—H28B	108.7

O9—C13—H13A	109.6	H28A—C28—H28B	107.6
C14—C13—H13A	109.6	C28—C29—C30	115.5 (11)
O9—C13—H13B	109.6	C28—C29—H29A	108.4
C14—C13—H13B	109.6	C30—C29—H29A	108.4
H13A—C13—H13B	108.1	C28—C29—H29B	108.4
C13—C14—H14A	109.5	C30—C29—H29B	108.4
C13—C14—H14B	109.5	H29A—C29—H29B	107.5
H14A—C14—H14B	109.5	C31—C30—C29	105.5 (13)
C13—C14—H14C	109.5	C31—C30—H30A	110.6
H14A—C14—H14C	109.5	C29—C30—H30A	110.6
H14B—C14—H14C	109.5	C31—C30—H30B	110.6
N1—C15—C16	111.72 (15)	C29—C30—H30B	110.6
N1—C15—H15A	109.3	H30A—C30—H30B	108.8
C16—C15—H15A	109.3	C30—C31—C32	108.9 (13)
N1—C15—H15B	109.3	C30—C31—H31A	109.9
C16—C15—H15B	109.3	C32—C31—H31A	109.9
H15A—C15—H15B	107.9	C30—C31—H31B	109.9
C15—C16—C17	110.92 (15)	C32—C31—H31B	109.9
C15—C16—H16A	109.5	H31A—C31—H31B	108.3
C17—C16—H16A	109.5	C31—C32—H32A	109.5
C15—C16—H16B	109.5	C31—C32—H32B	109.5
C17—C16—H16B	109.5	H32A—C32—H32B	109.5
H16A—C16—H16B	108.0	C31—C32—H32C	109.5
C18—C17—C16	114.06 (15)	H32A—C32—H32C	109.5
C18—C17—H17A	108.7	H32B—C32—H32C	109.5
Cu1—O1—C1—C6	171.34 (14)	O5—C7—C8—C9	179.81 (15)
Cu1—O1—C1—C2	−7.96 (18)	C12—C7—C8—C9	−2.2 (2)
Cu1—O2—C2—C3	−176.78 (14)	O6—C8—C9—C10	−178.31 (16)
Cu1—O2—C2—C1	4.03 (18)	C7—C8—C9—C10	2.6 (3)
O1—C1—C2—O2	2.6 (2)	O6—C8—C9—Cl3	1.9 (3)
C6—C1—C2—O2	−176.68 (16)	C7—C8—C9—Cl3	−177.15 (12)
O1—C1—C2—C3	−176.59 (15)	C8—C9—C10—O7	−178.66 (17)
C6—C1—C2—C3	4.1 (3)	Cl3—C9—C10—O7	1.1 (2)
O2—C2—C3—C4	177.40 (16)	C8—C9—C10—C11	1.3 (2)
C1—C2—C3—C4	−3.4 (3)	Cl3—C9—C10—C11	−178.96 (12)
O2—C2—C3—Cl1	−1.2 (3)	O7—C10—C11—O8	−6.2 (2)
C1—C2—C3—Cl1	177.97 (12)	C9—C10—C11—O8	173.84 (15)
C2—C3—C4—O3	−179.69 (17)	O7—C10—C11—C12	174.19 (16)
Cl1—C3—C4—O3	−1.1 (3)	C9—C10—C11—C12	−5.7 (2)

C2—C3—C4—C5	−0.1 (3)	O5—C7—C12—C11	175.24 (16)
Cl1—C3—C4—C5	178.53 (12)	C8—C7—C12—C11	−2.5 (3)
O3—C4—C5—O4	2.4 (2)	O5—C7—C12—Cl4	−1.3 (2)
C3—C4—C5—O4	−177.28 (16)	C8—C7—C12—Cl4	−179.10 (12)
O3—C4—C5—C6	−177.19 (16)	O8—C11—C12—C7	−173.19 (16)
C3—C4—C5—C6	3.2 (2)	C10—C11—C12—C7	6.4 (2)
O1—C1—C6—C5	179.83 (16)	O8—C11—C12—Cl4	3.4 (2)
C2—C1—C6—C5	−0.9 (3)	C10—C11—C12—Cl4	−177.04 (11)
O1—C1—C6—Cl2	−0.7 (3)	Cu1—O9—C13—C14	−79.2 (2)
C2—C1—C6—Cl2	178.58 (12)	N1—C15—C16—C17	173.44 (14)
O4—C5—C6—C1	177.92 (17)	C15—C16—C17—C18	−175.89 (15)
C4—C5—C6—C1	−2.6 (3)	C16—C17—C18—C19	178.33 (17)
O4—C5—C6—Cl2	−1.6 (3)	C17—C18—C19—C20	−178.49 (19)
C4—C5—C6—Cl2	177.96 (12)	N2—C21—C22—C23	179.6 (2)
Cu1—O5—C7—C12	176.58 (14)	C21—C22—C23—C24	69.3 (4)
Cu1—O5—C7—C8	−5.54 (18)	C22—C23—C24—C25	59.4 (5)
Cu1—O6—C8—C9	−174.50 (14)	C23—C24—C25—C26	166.1 (4)
Cu1—O6—C8—C7	4.60 (17)	C27—C28—C29—C30	−61.7 (15)
O5—C7—C8—O6	0.7 (2)	C28—C29—C30—C31	−69.5 (16)
C12—C7—C8—O6	178.62 (15)	C29—C30—C31—C32	−172.0 (13)

Symmetry codes: (i) −x, −y+1, −z+1; (ii) x+1, y, z; (iii) −x+2, −y, −z+1; (iv) −x+1, −y, −z+1.

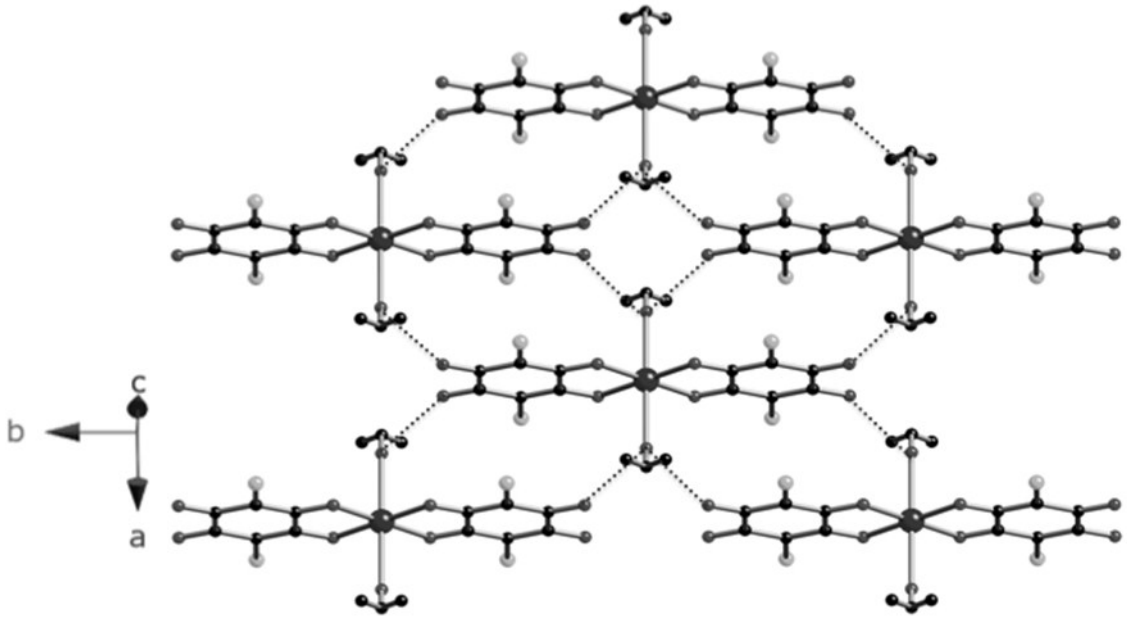


Fig. S1. Sheet structure of $\{[Cu(CA)_2(EtOH)_2]^{2-}\}_n$.

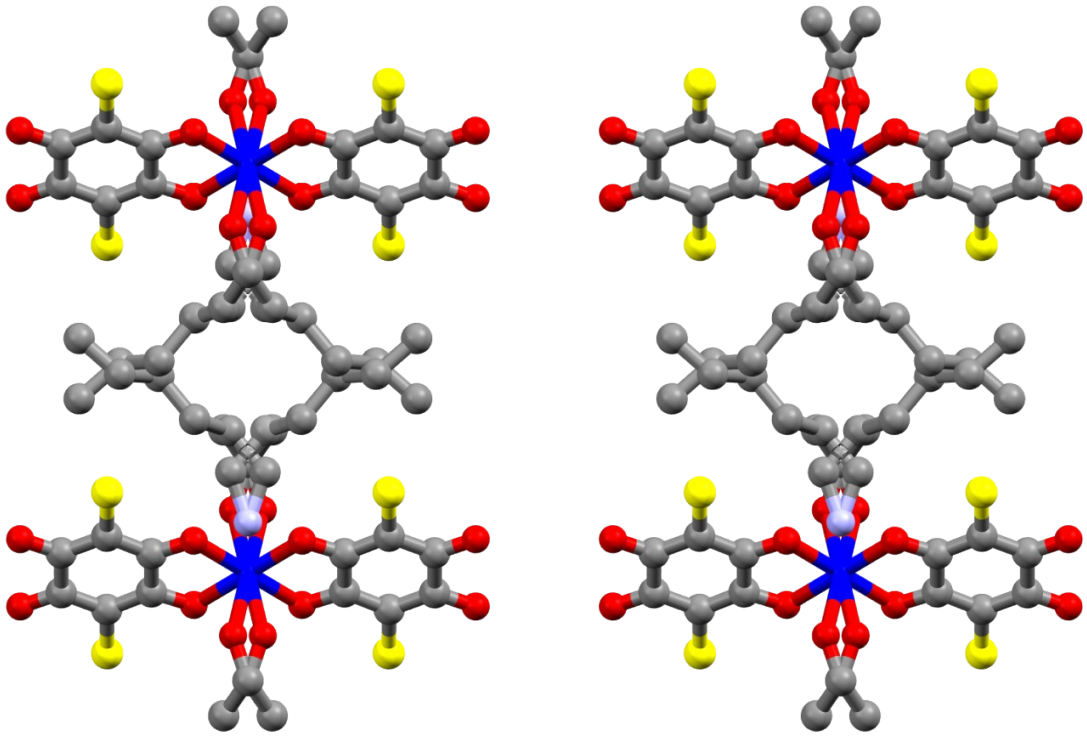


Fig. S2. The assembled structure of **1** (at 100 K).

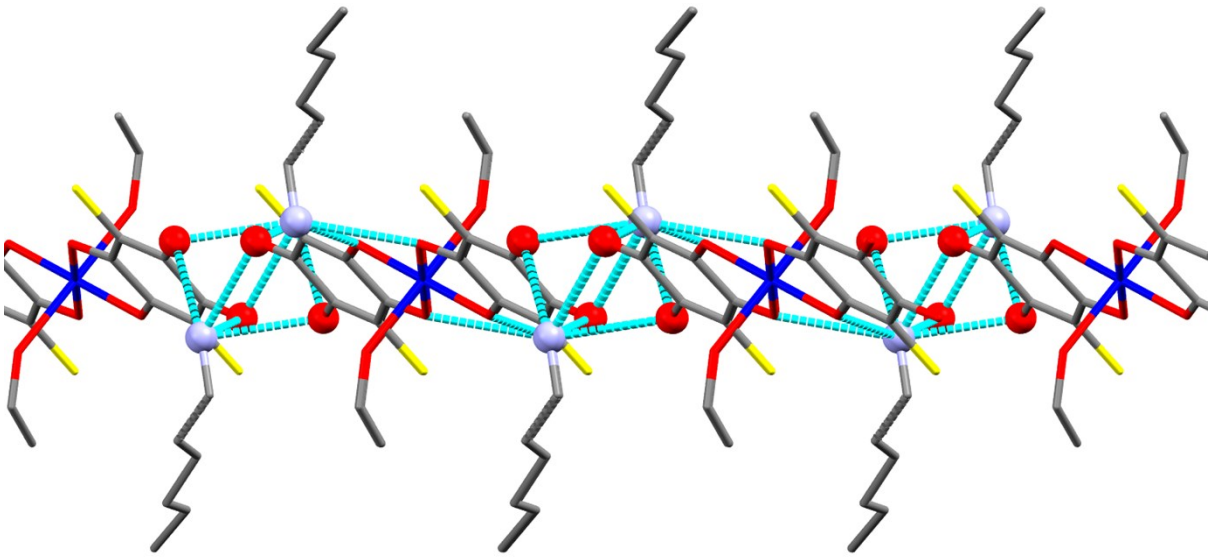


Fig. S3. Perspective view of the structure showing the formation of hydrophobic environment between the layers (in the horizontal direction of ab-plane). Light blue dotted lines denote H-bonding network of $[Cu(CA)_2(EtOH)_2]^{2-}$ and Hha^+ in the layer.

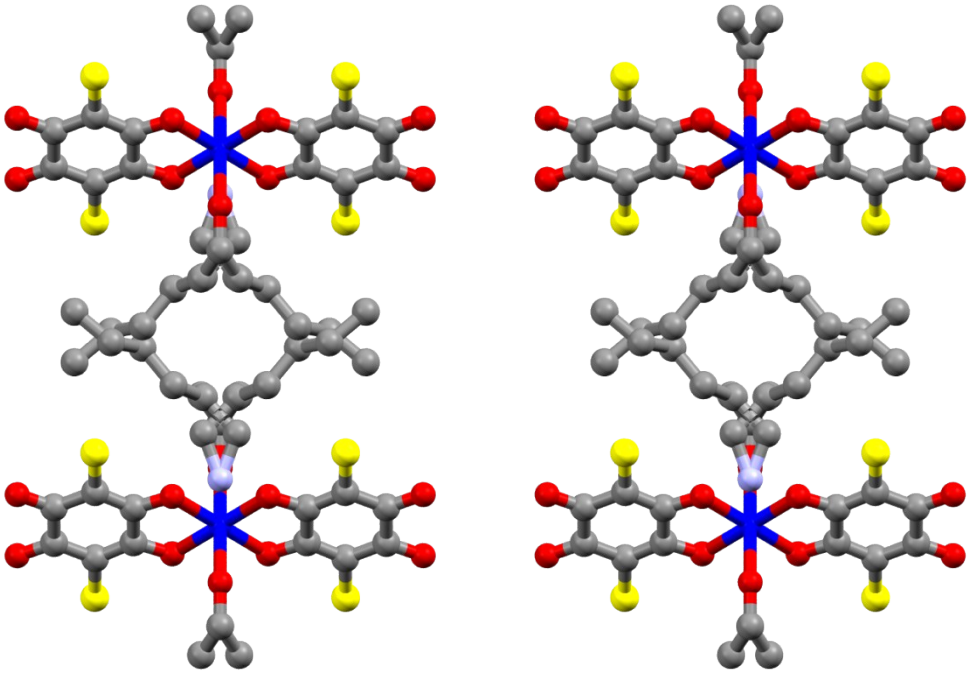


Fig. S4. The assembled structure of **1** (at 295 K).

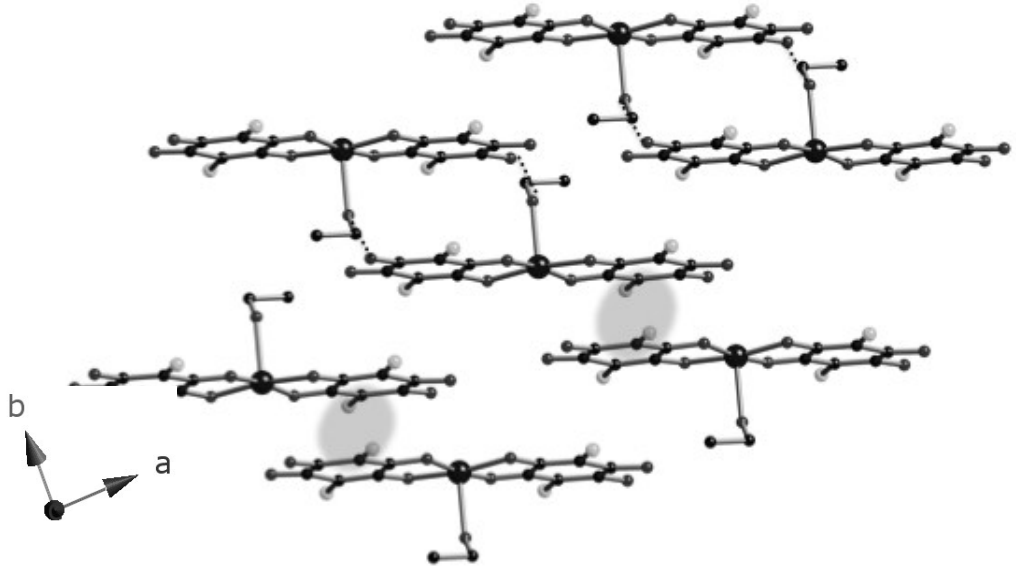


Fig. S5. Sheet structure of $\{[Cu(CA)_2(EtOH)]^{2-}\}_n$ in **2**.

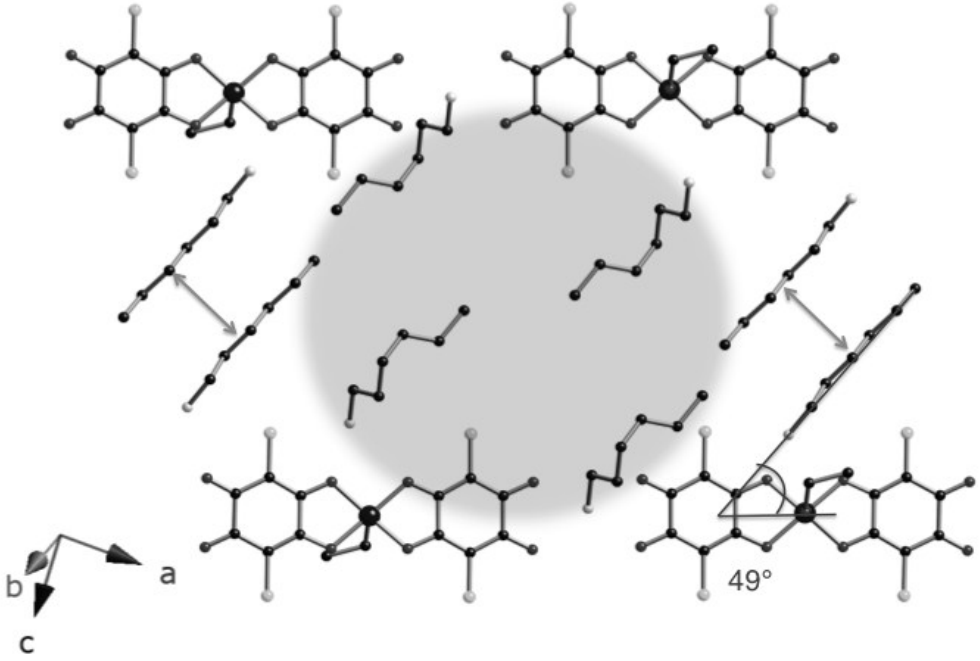


Fig. S6. The assembled structure of **2** (at 100 K).

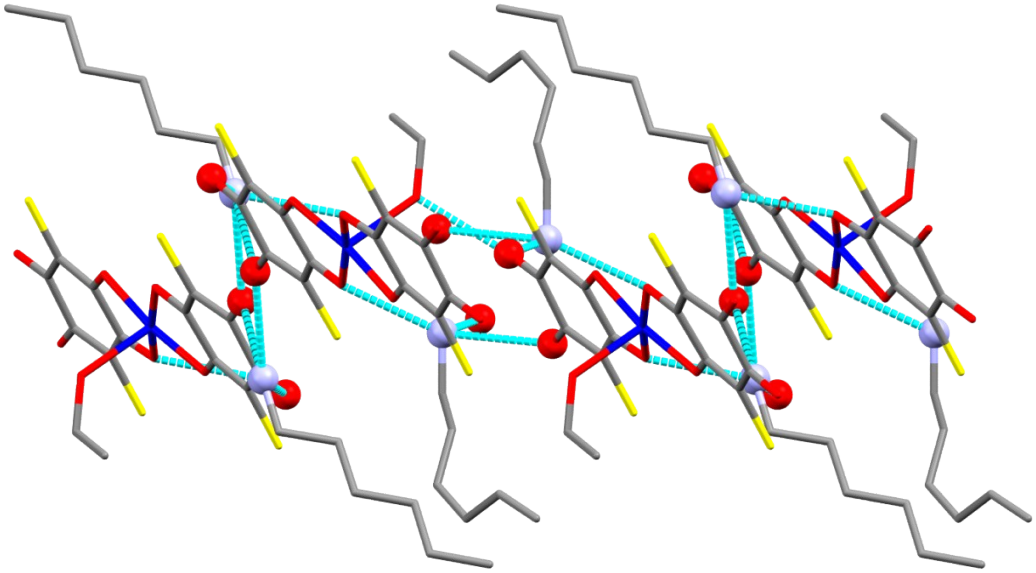


Fig. S7. Perspective view of the structure showing the formation of hydrophobic environment between the layers (in the horizontal direction of ab-plane). Light blue dotted lines denote H-bonding network of $[Cu(CA)_2(EtOH)]^{2-}$ and Hha^+ in the layer.

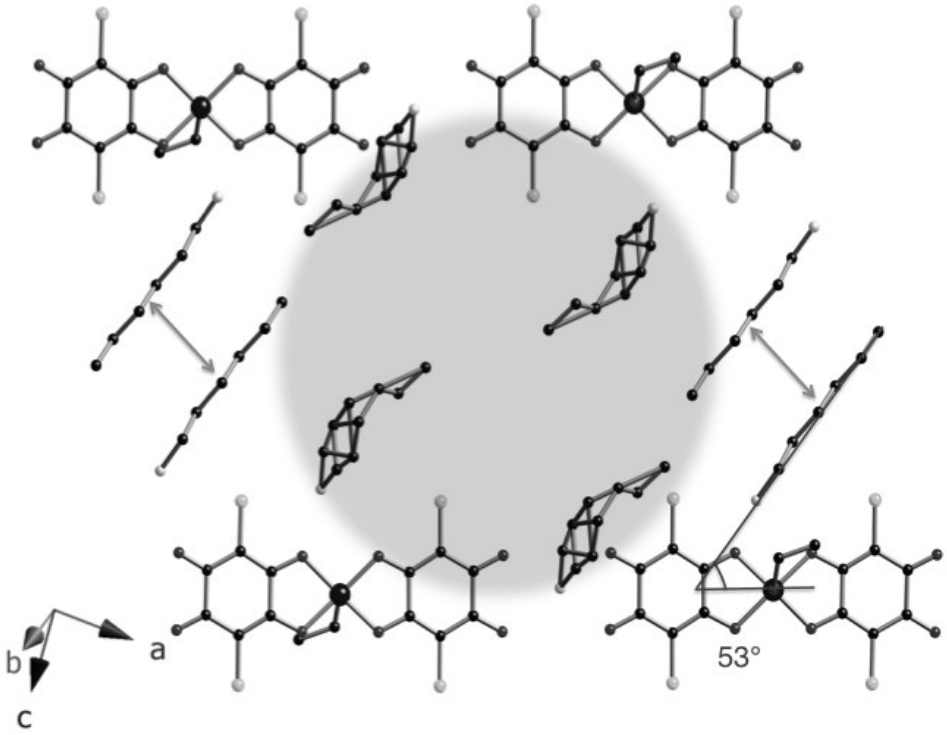


Fig. S8. The assembled structure of **2** (at 295 K).

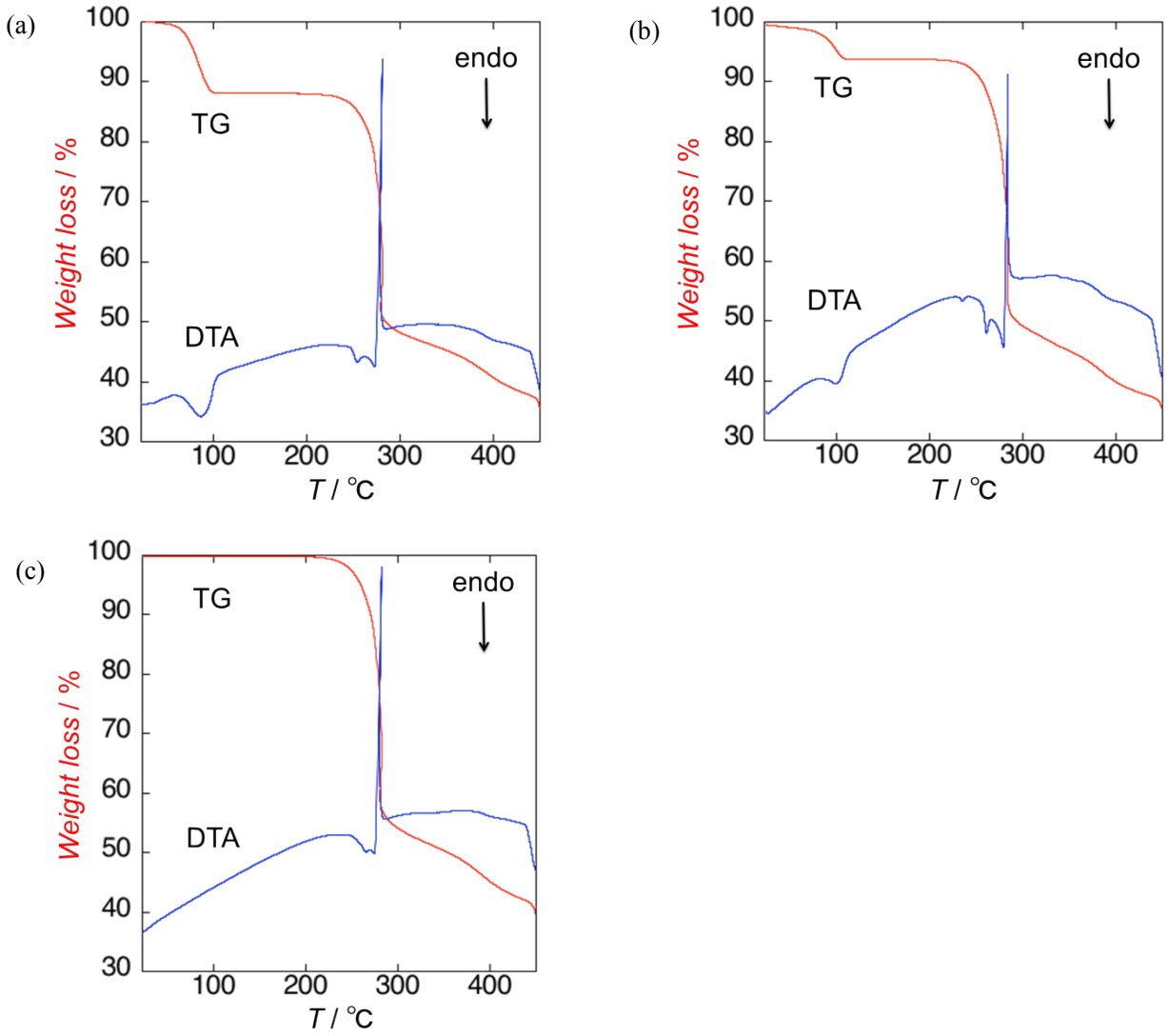


Fig. S9. Thermogravimetric analyses data for **1** (a), **2** (b) and **3** (c).

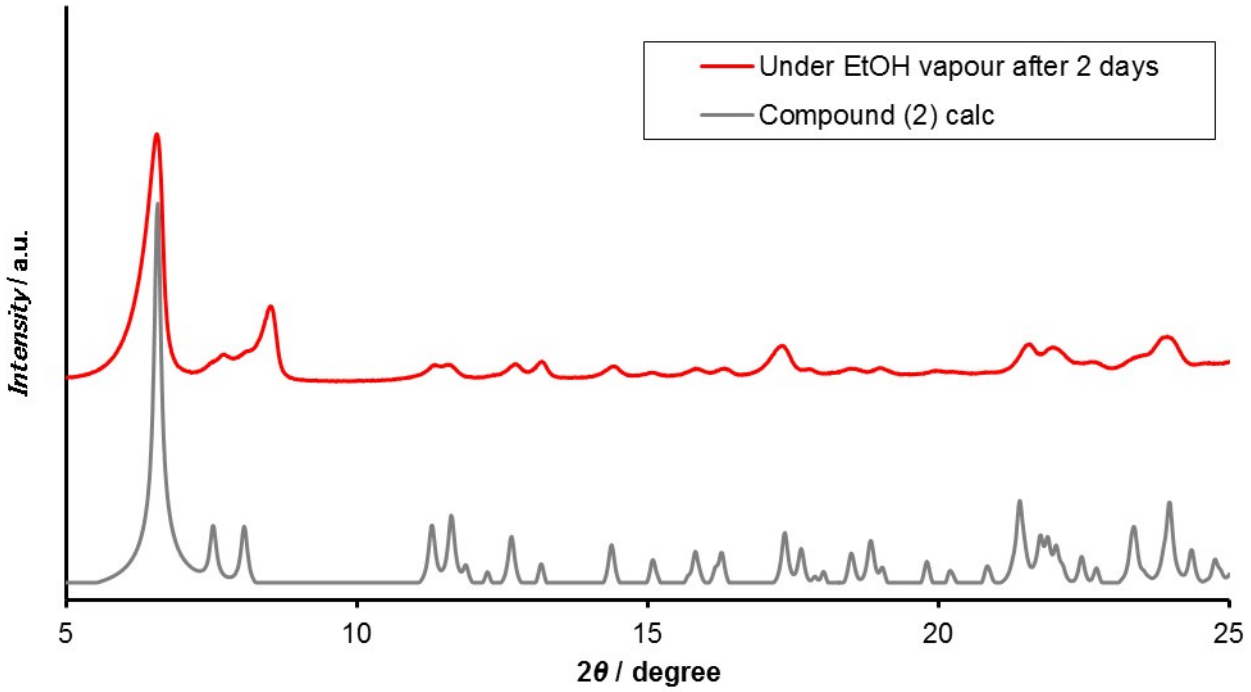


Fig. S10. PXRD change under EtOH vapor after 2 days (at RT) for **2**.

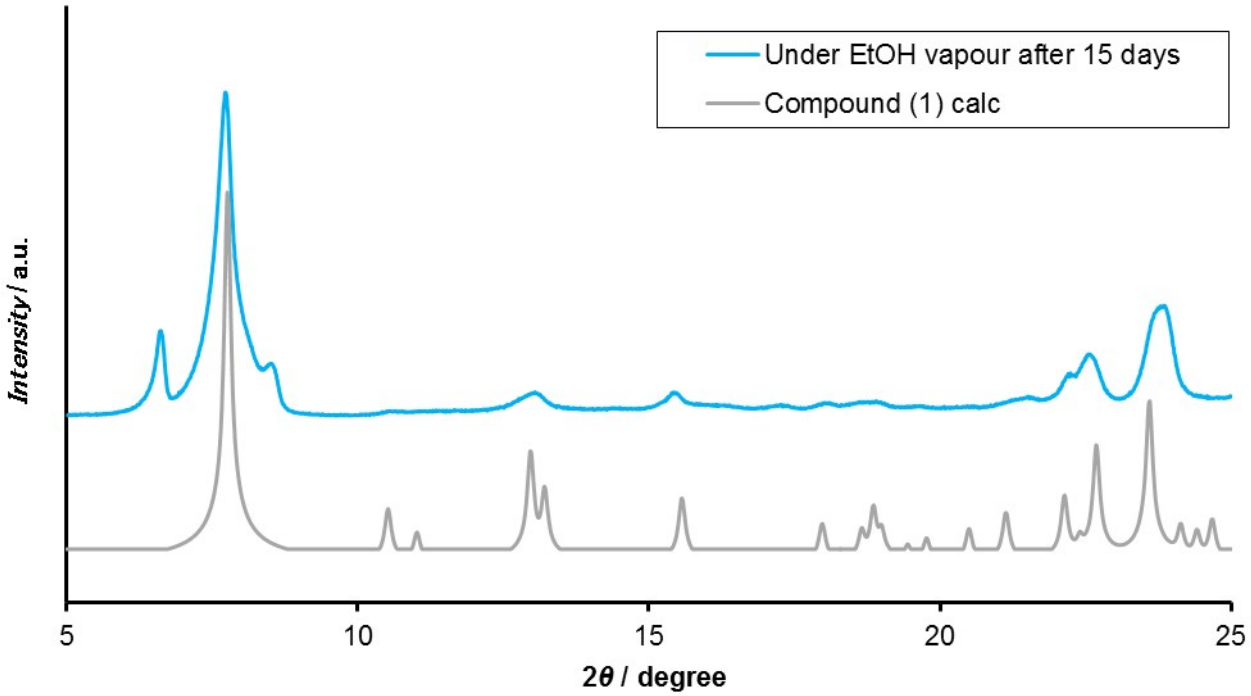


Fig. S11. PXRD change under EtOH vapor after 15 days (at RT) for **1**.

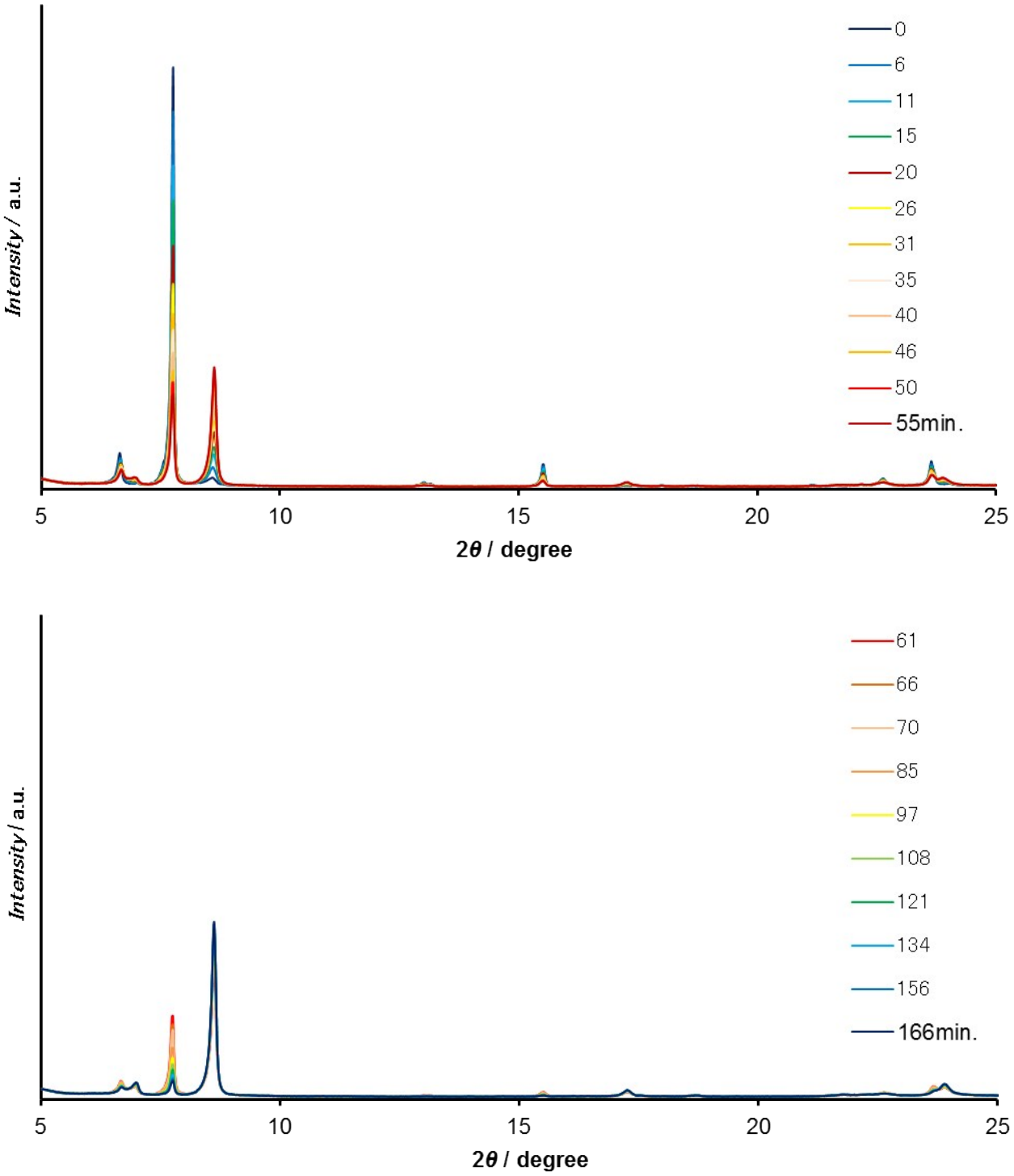


Fig. S12. Time-series variations of XRD patterns of **1** at RT.

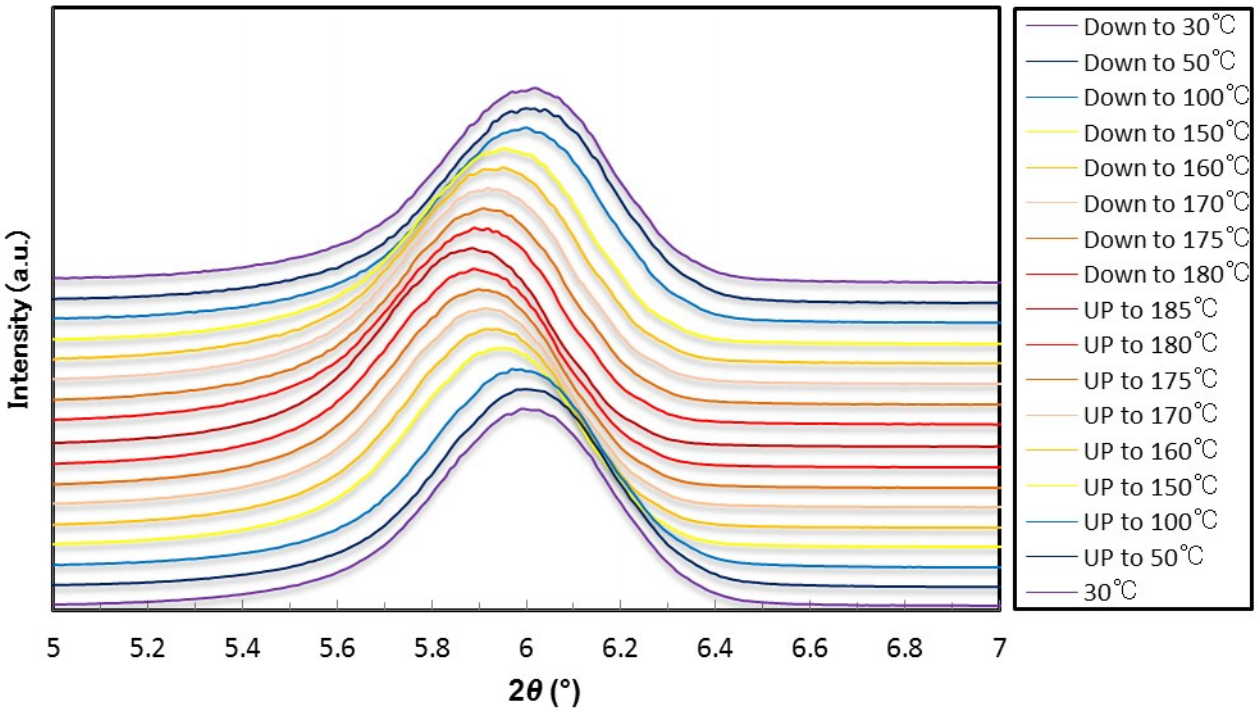


Fig. S13. Temperature dependence of the PXRD of **3**.

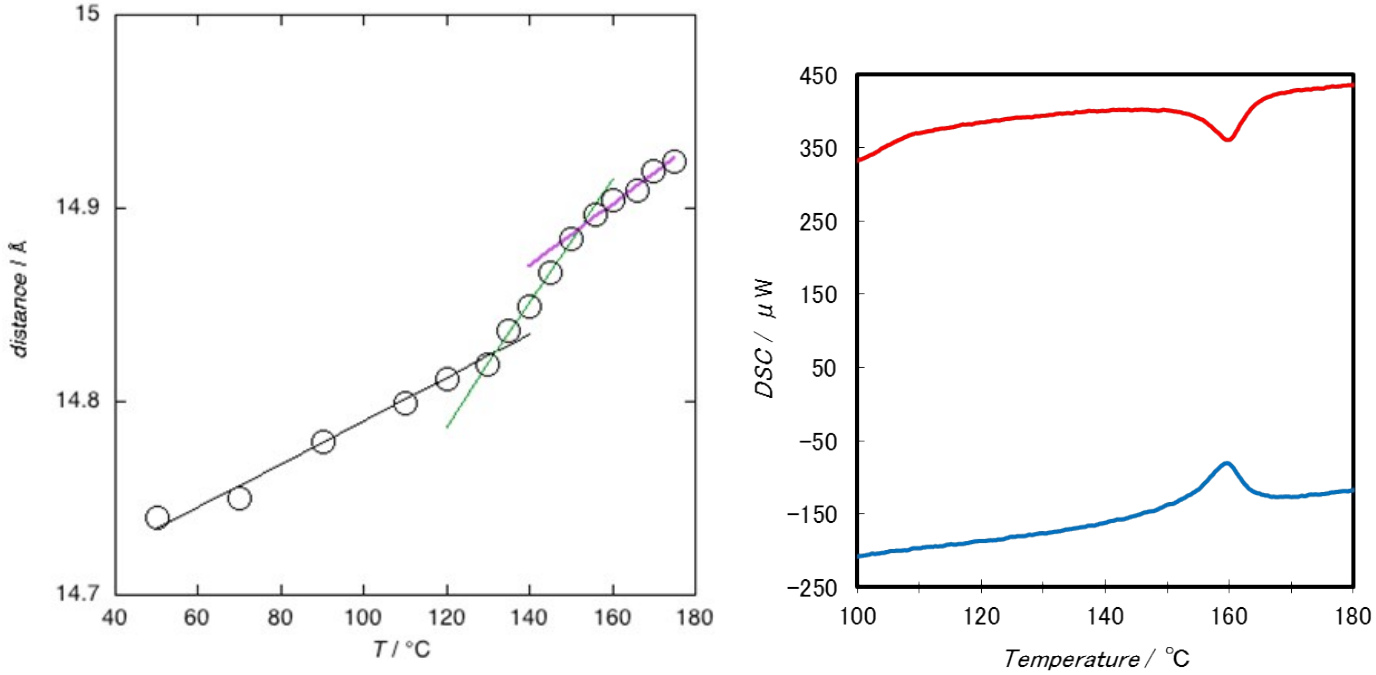


Fig. S14. Temperature dependence of 001 diffraction and DSC trace of **3**.

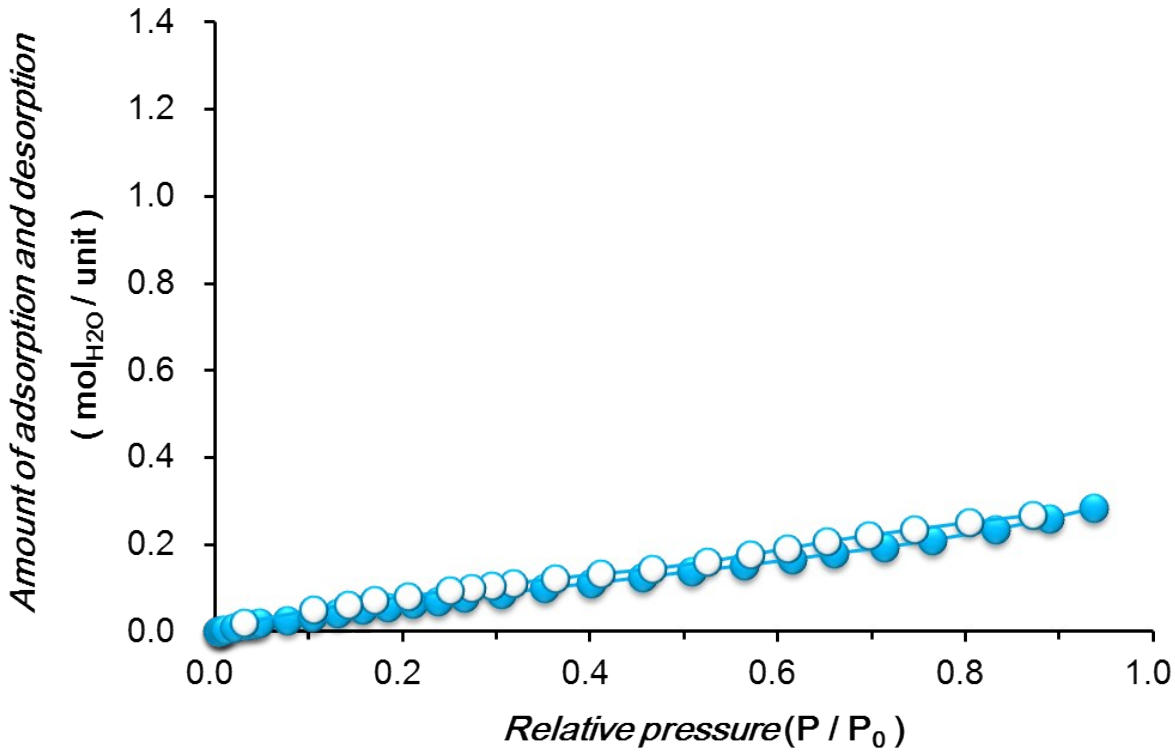


Fig. S15. Water adsorption/desorption isotherms of **1** (blue). Filled and open symbols represent adsorption and desorption, respectively. Solid lines are drawn to guide the eyes.

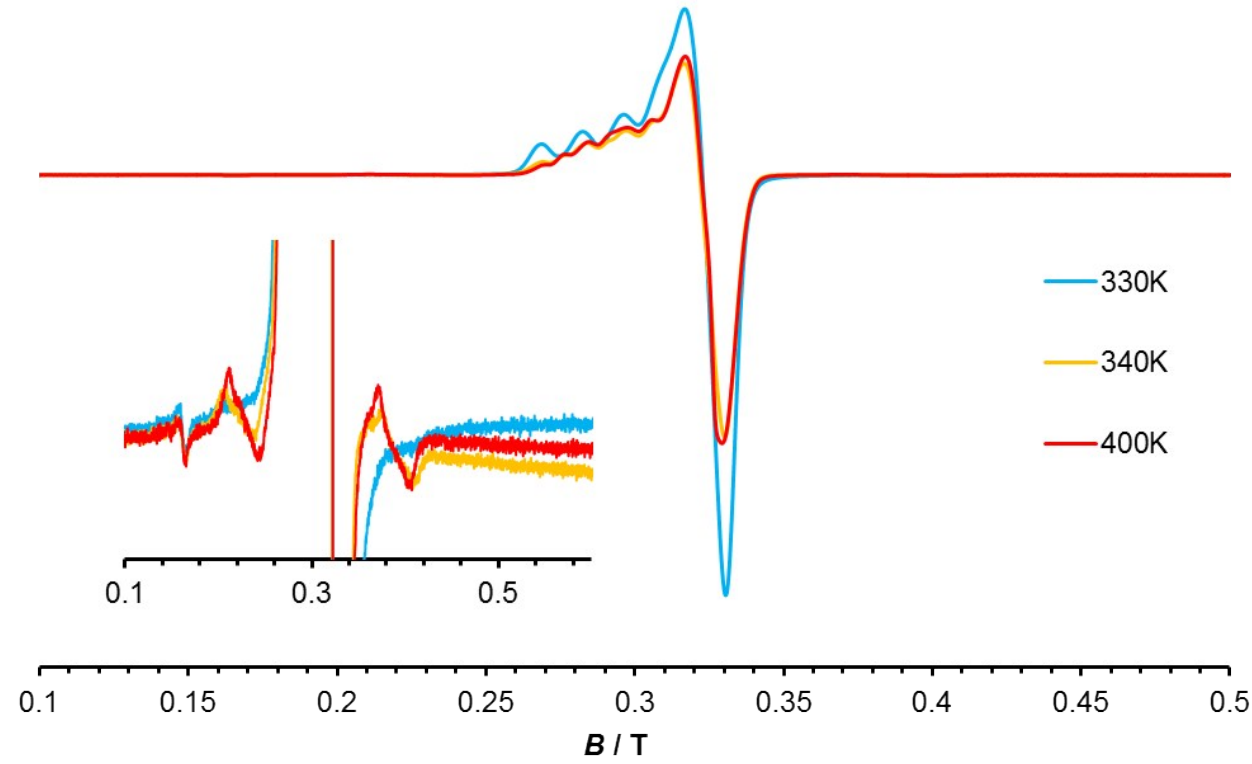


Fig. S16. Temperature dependence of ESR spectra of **1**.

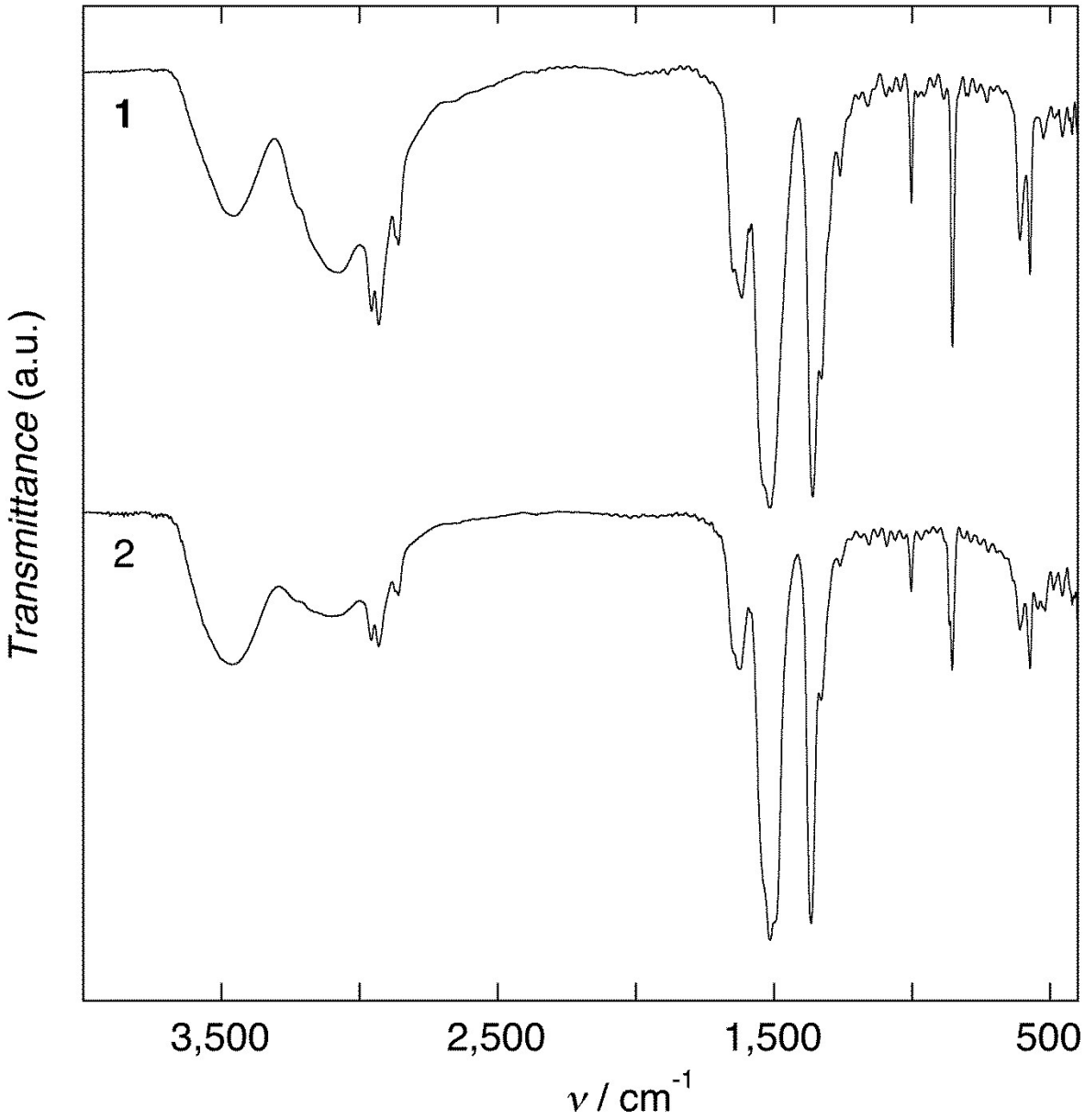


Fig. S17. FT-IR spectra of **1** and **2**.

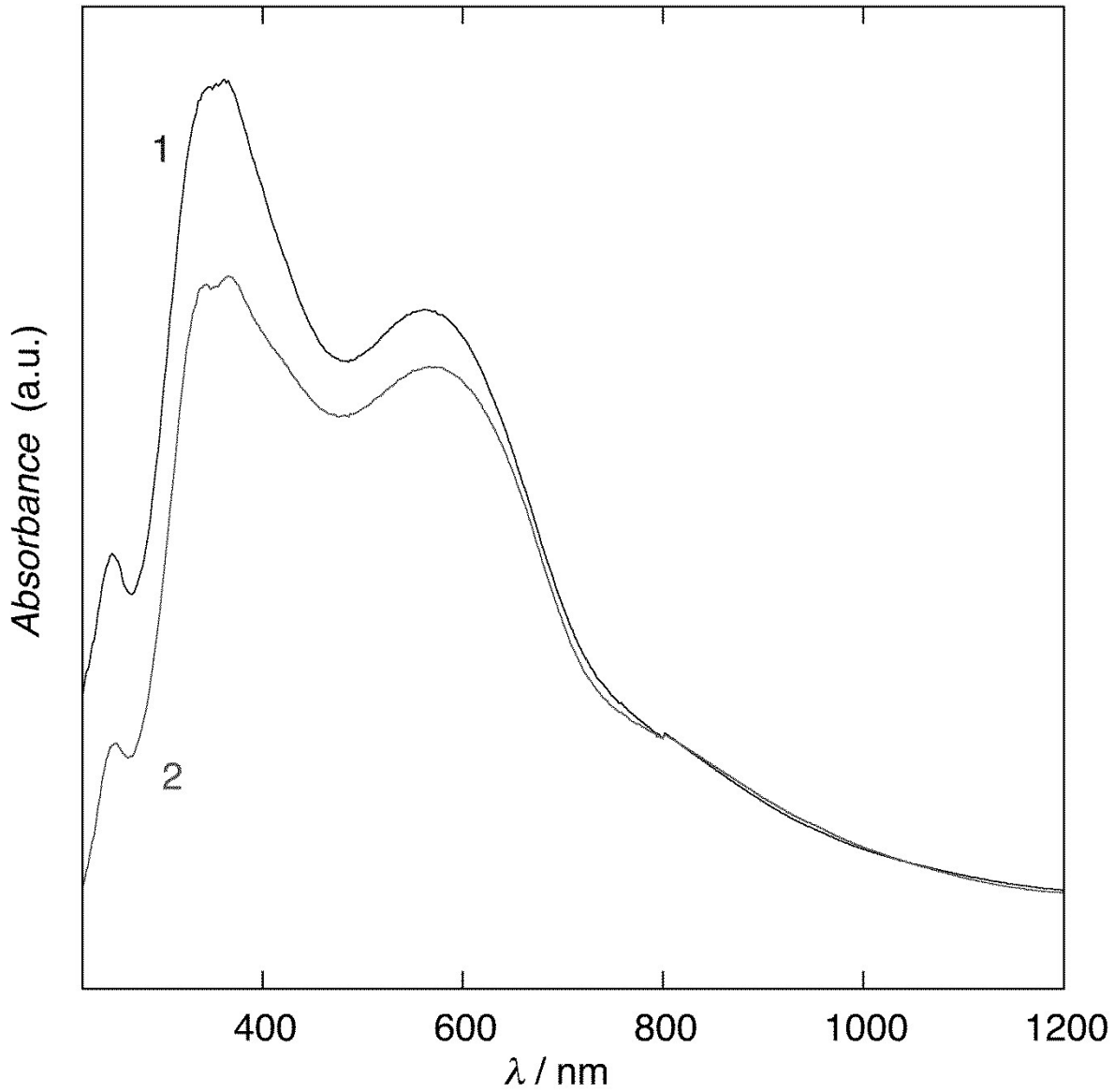
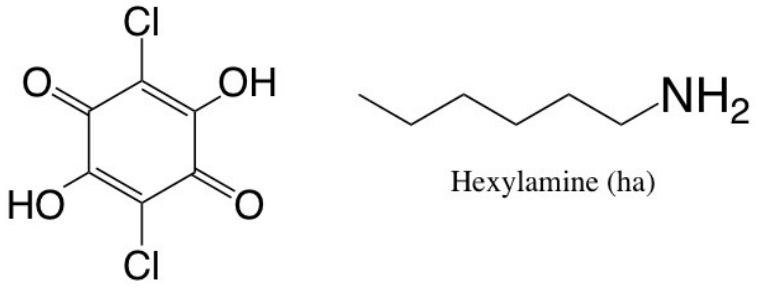


Fig. S18. UV and visible spectra of **1** and **2**.



Chloranilic acid (H_2CA)

Hexylamine (ha)

Fig. S19. Structural formula of Chloranilic acid and Hexylamine.