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New Kagomé Lattice Coordination Polymer Based on Bismuth and Pyridine-2,5-dicarboxylate: Structure and Photoluminescent Properties

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X-ray Crystallography details of $\text{Bi}(\text{pydc})_2 \cdot (\text{H}_3\text{O}^+)(\text{H}_2\text{O})_{0.83}$.

Table S1. Crystal data and structure refinement of $\text{Bi}(\text{pydc})_2 \cdot (\text{H}_3\text{O}^+)(\text{H}_2\text{O})_{0.83}$.

Table S2. Representative bond lengths (Å) and bond angles ($^\circ$) of $\text{Bi}(\text{pydc})_2 \cdot (\text{H}_3\text{O}^+)(\text{H}_2\text{O})_{0.83}$.

Figure S1. (a) Environment of bismuth and the one independent ligand (labeled) of the compound. Displacement ellipsoids drawn at the 30% probability level. Disordered guests in channels omitted. Symmetry codes: (i) $x-y, -y, -z+1/2$ (ii) $-x+1, -x+y, -z+1/2$ (iii) $-y+1, x-y, z$ (iv) $-x+y+1, -x+1, z$. (b) Slightly distorted bi-capped octahedra formation of the compound. Bi = blue, O = red, N = dark blue, (c) ideal bi-capped octahedra.

Figure S2. 3D structure formation of the compound showing disordered water and hydronium ions inside the channel. Bi = blue, O = red, N = dark blue, C = black.

Figure S3. An optical image of the crystals showing plate-like crystals.

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sample holder with mother liquor, 2) Pressing down on the crystals (with mother liquor), 3) Ground crystals with mother liquor, 4) Dried and ground crystal.

Figure S5. Fluorescence spectra comparison of: 1 = the compound with mother liquor, 2 = the dried compound; ex = excitation curve, em = emission curve.

Figure S6. Excitation (Ex) spectra of the as received H₂pydc ligand (a, purple) and of the compound (b, blue).

Figure S7. UV/Vis spectra of the as received H₂pydc ligand (a, purple) and of the compound (b, blue).

X-ray Crystallography details of $\text{Bi}(\text{pydc})_2 \cdot (\text{H}_3\text{O}^+)(\text{H}_2\text{O})_{0.83}$.

Crystals of the compound formed as abundant large colorless hexagonal plates. The crystals are not stable outside the crystallization medium, but crack and lose crystallinity within seconds of removal from the mother liquor. X-ray intensity data were collected at 295(2) K from a crystal sealed along with a drop of the mother liquor inside a glass capillary, using a Bruker SMART APEX diffractometer (Mo K α radiation, λ = 0.71073 Å).¹ Raw area detector data frame processing and corrections for absorption effects were performed with the SAINT+ and SADABS programs.¹ Final unit cell parameters were determined by least-squares refinement of 6918 reflections from the data set. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL.²

The compound crystallizes in the trigonal system. The space group R-3c (No. 167) was indicated by the pattern of systematic absences in the intensity data, and confirmed by obtaining a reasonable solution and refinement of the structure. The asymmetric unit of the crystal consists of (formally half of) a bismuth(III) ion located on a crystallographic two-fold axis of rotation, one $\text{C}_7\text{H}_3\text{NO}_4^{2-}$ ligand and several chemically featureless electron density peaks located in channels running along the crystallographic c axis. This disordered distribution of electron density was modeled as variably occupied oxygen atoms of water molecules and/or hydronium ions. Only interstitial (channel) peaks with electron density concentrations larger than the arbitrarily chosen value of 1.0 $\text{e}^-/\text{\AA}^3$ were added to the refinement. Each such peak was assigned with a fixed isotropic displacement parameter value of 0.15 $\text{\AA}^2$, and was retained only if its site occupancy refined to greater than 15% and it was chemically sensible. With this model, five peaks remain, O1S – O5S, giving a composition of ca. 1.8 channel oxygen atoms per bismuth. As formulated, the crystal is not electroneutral, but has one excess negative charge per formula unit. It is likely that the charge balancing species is the hydronium ion (one per bismuth), which is disordered among water molecules and other unknown occupants of the channels. No hydrogen atoms could be located in difference maps because of the disorder. It should be noted that because of the strong correlation between site occupation factors and displacement parameters, and of course because of the disorder, the reported composition should be regarded as approximate. All non-hydrogen atoms of the metal-organic framework were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The largest residual electron density peak of 1.20 $\text{e}^-/\text{\AA}^3$ is located 0.82 Å from the bismuth atom. Calculations using PLATON³ show that in the absence of the disordered channel guests, there is a solvent-accessible void volume of 6760.9 $\text{\AA}^3$, corresponding to 54.3% of the total unit cell volume.

1SMART Version 5.630, SAINT+ Version 6.45 and SADABS Version 2.10. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.

2Sheldrick, G.M. *Acta Cryst.* 2008, **A64**, 112-122.

3(a) Spek, A. L. *Acta Crystallogr., Sect A* 1990, **46**, C34. (b) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, Spek, A. L. 1998.

Table S1. Crystal data and structure refinement of $\text{Bi}(\text{pydc})_2 \cdot (\text{H}_3\text{O}^+)(\text{H}_2\text{O})_{0.83}$.

Compound	$\text{Bi}(\text{pydc})_2 \cdot (\text{H}_3\text{O}^+)(\text{H}_2\text{O})_{0.83}$
Empirical formula	$\text{C}_{14} \text{H}_{10.66} \text{Bi} \text{N}_2 \text{O}_{9.83}$
Formula weight	573.21
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	R -3 c
Unit cell dimensions	$a = 16.7164(3) \text{ Å} \quad \alpha = 90^\circ$ $b = 16.7164(3) \text{ Å} \quad \beta = 90^\circ$ $c = 51.487(2) \text{ Å} \quad \gamma = 120^\circ$
Volume	$12459.9(7) \text{ Å}^3$
Z	18
Density (calculated)	1.375 Mg/m^3
Absorption coefficient	6.404 mm^{-1}
F(000)	4866
Crystal size	$0.22 \times 0.20 \times 0.06 \text{ mm}^3$
Theta range for data collection	1.61 to 25.02°
Index ranges	$-19 \leq h \leq 19, -19 \leq k \leq 19, -61 \leq l \leq 61$
Reflections collected	59,233
Independent reflections	2458 [R(int) = 0.0541]
Completeness to theta	100.0 %
Max. and min. transmission	1.0000 and 0.5022
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameter	2458 / 0 / 126
Goodness-of-fit on F^2	1.134
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0382, wR2 = 0.1206$
R indices (all data)	$R1 = 0.0459, wR2 = 0.1277$

Table S2. Representative bond lengths (Å) and bond angles (°) of $\text{Bi}(\text{pydc})_2 \cdot (\text{H}_3\text{O}^+)(\text{H}_2\text{O})_{0.83}$.

Bi(1)-O(1)	2.336(5)	N(1)#1-Bi(1)-O(3)#3	79.5(2)
Bi(1)-O(1)#1	2.337(5)	O(3)#2-Bi(1)-O(3)#3	131.3(3)
Bi(1)-N(1)	2.448(5)	O(1)-Bi(1)-O(4)#2	82.41(18)
Bi(1)-N(1)#1	2.448(5)	O(1)#1-Bi(1)-O(4)#2	121.94(17)
Bi(1)-O(3)#2	2.508(5)	N(1)-Bi(1)-O(4)#2	77.8(2)
Bi(1)-O(3)#3	2.509(5)	N(1)#1-Bi(1)-O(4)#2	161.3(2)
Bi(1)-O(4)#2	2.637(7)	O(3)#2-Bi(1)-O(4)#2	49.99(17)
Bi(1)-O(4)#3	2.637(7)	O(3)#3-Bi(1)-O(4)#2	102.6(2)
O(1)-Bi(1)-O(1)#1	134.7(3)	O(1)-Bi(1)-O(4)#3	121.94(17)
O(1)-Bi(1)-N(1)	67.41(16)	O(1)#1-Bi(1)-O(4)#3	82.40(18)
O(1)#1-Bi(1)-N(1)	80.45(17)	N(1)-Bi(1)-O(4)#3	161.3(2)
O(1)-Bi(1)-N(1)#1	80.45(17)	N(1)#1-Bi(1)-O(4)#3	77.8(2)
O(1)#1-Bi(1)-N(1)#1	67.41(16)	O(3)#2-Bi(1)-O(4)#3	102.6(2)
N(1)-Bi(1)-N(1)#1	88.8(3)	O(3)#3-Bi(1)-O(4)#3	49.99(17)
O(1)-Bi(1)-O(3)#2	127.03(18)	O(4)#2-Bi(1)-O(4)#3	117.9(4)
O(1)#1-Bi(1)-O(3)#2	73.45(17)		
N(1)-Bi(1)-O(3)#2	79.5(2)	Symmetry transformations used to generate equivalent atoms: #1 x-y,-y,-z+1/2 #2 -y+1,x-y,z #3 -x+1,-x+y,-z+1/2 #4 -x+y+1,-x+1,z	
N(1)#1-Bi(1)-O(3)#2	140.48(17)		
O(1)-Bi(1)-O(3)#3	73.45(17)		
O(1)#1-Bi(1)-O(3)#3	127.02(17)		
N(1)-Bi(1)-O(3)#3	140.49(17)		

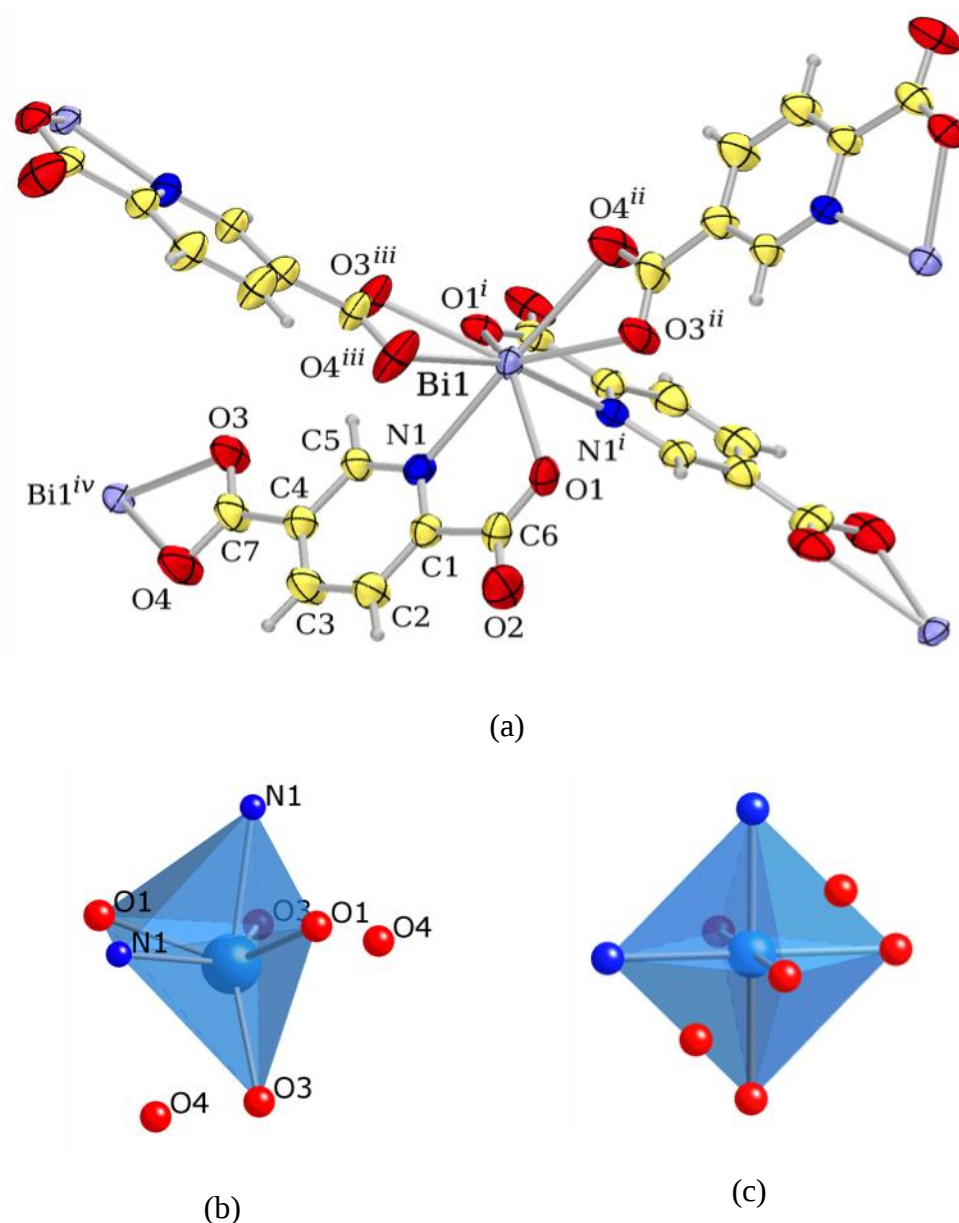


Figure S1. (a) Environment of bismuth and the one independent ligand (labeled) of the compound. Displacement ellipsoids drawn at the 30% probability level. Disordered guests in channels omitted. Symmetry codes: (i) $x-y, -y, -z+1/2$ (ii) $-x+1, -x+y, -z+1/2$ (iii) $-y+1, x-y, z$ (iv) $-x+y+1, -x+1, z$. (b) Slightly distorted bi-capped octahedra formation of the compound. Bi = blue, O = red, N = dark blue, (c) ideal bi-capped octahedra.

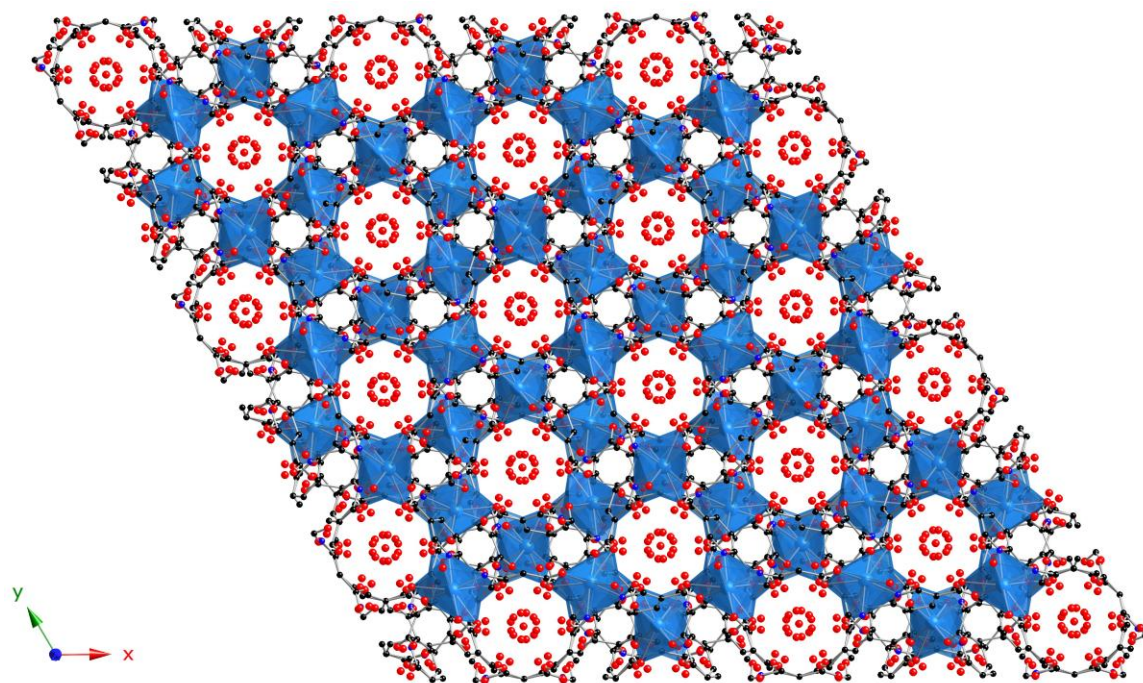


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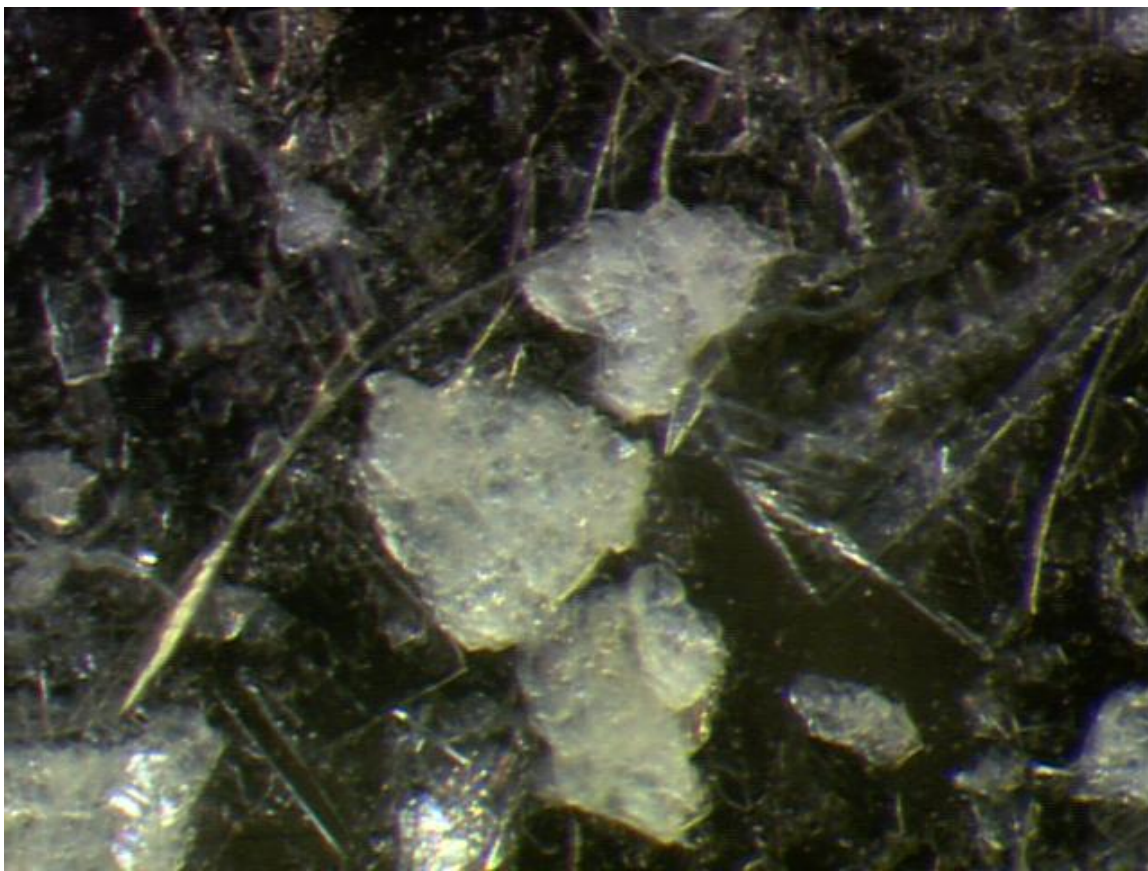


Figure S3. An optical image of the crystals showing plate-like crystals.

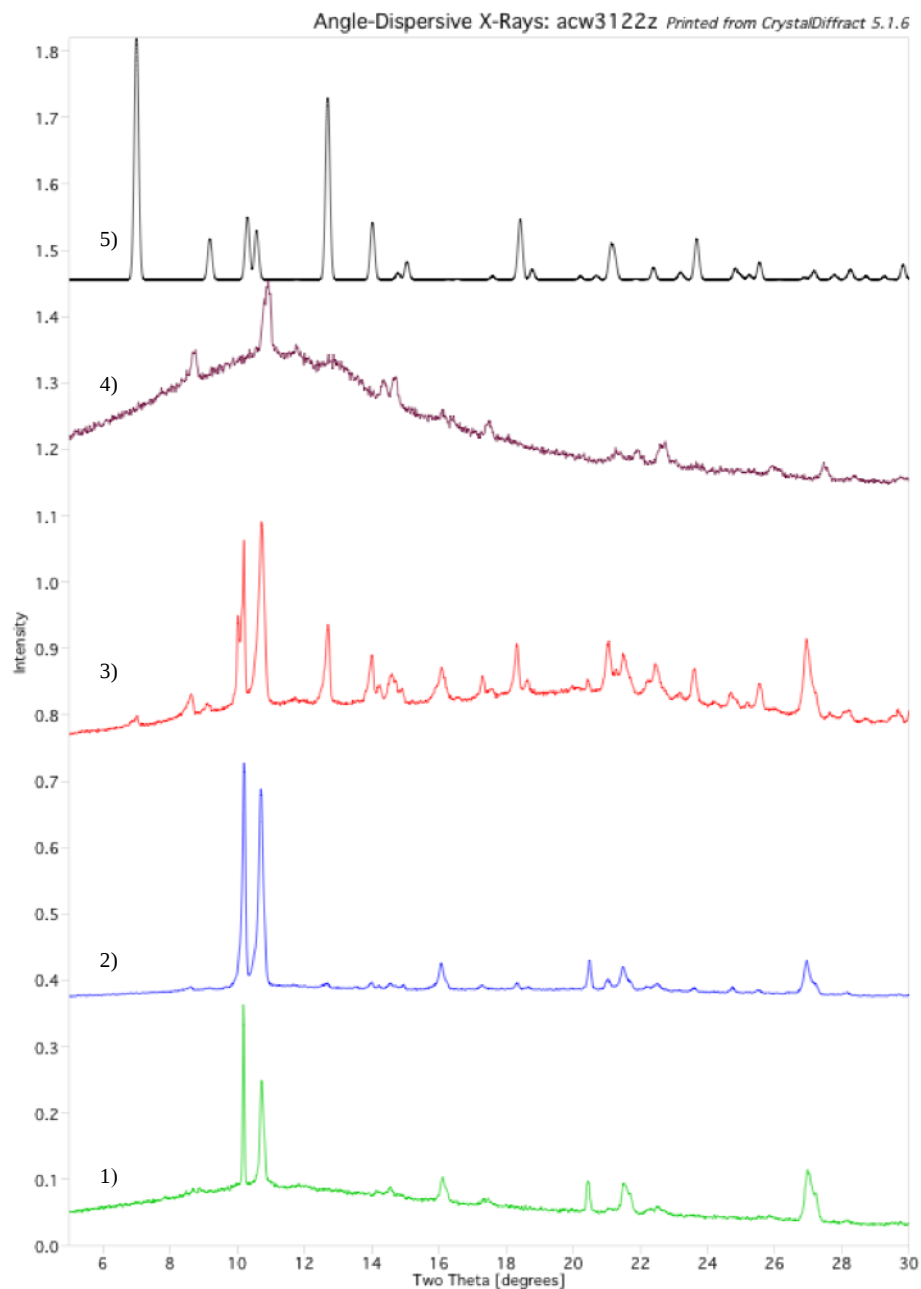


Figure S4. X-Ray Powder Diffraction comparison between calculated (top, #5) and observed (bottom, #1-4) patterns of the compound: 1) Placing the crystals onto the sample holder with mother liquor, 2) Pressing down on the crystals (with mother liquor), 3) Ground crystals with mother liquor, 4) Dried and ground crystal.

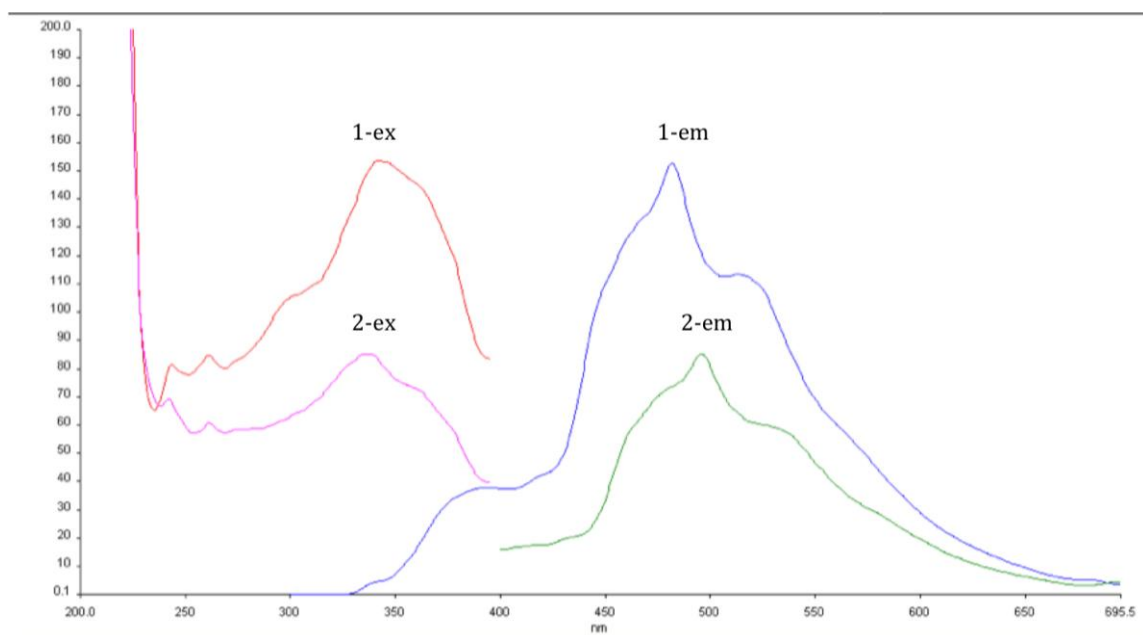


Figure S5. Fluorescence spectra of $\text{Bi(pydc)}_2 \cdot (\text{H}_3\text{O}^+)(\text{H}_2\text{O})_{0.83}$: Data 1 were collected by placing the as grown crystals together with the mother liquor into the fluorescence instrument sample holder. Data 2 were collected by placing the dried crystals into the fluorescence instrument sample holder; ex = excitation curve, em = emission curve.

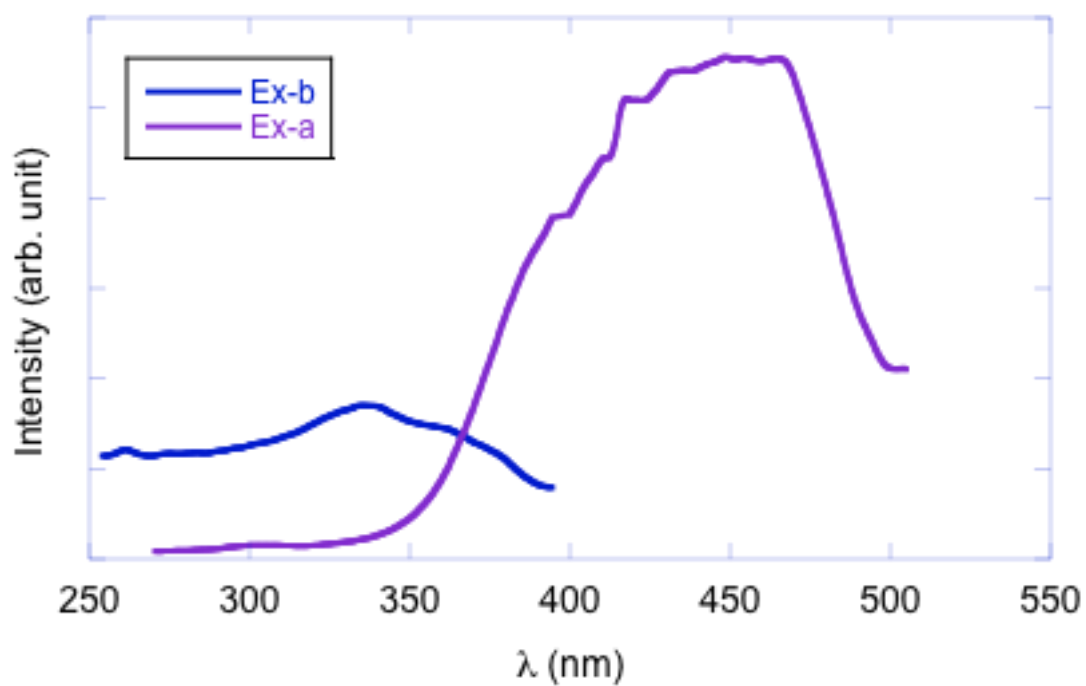


Figure S6. Excitation (Ex) spectra of the as received H₂pydc ligand (a, purple) and of the compound (b, blue).

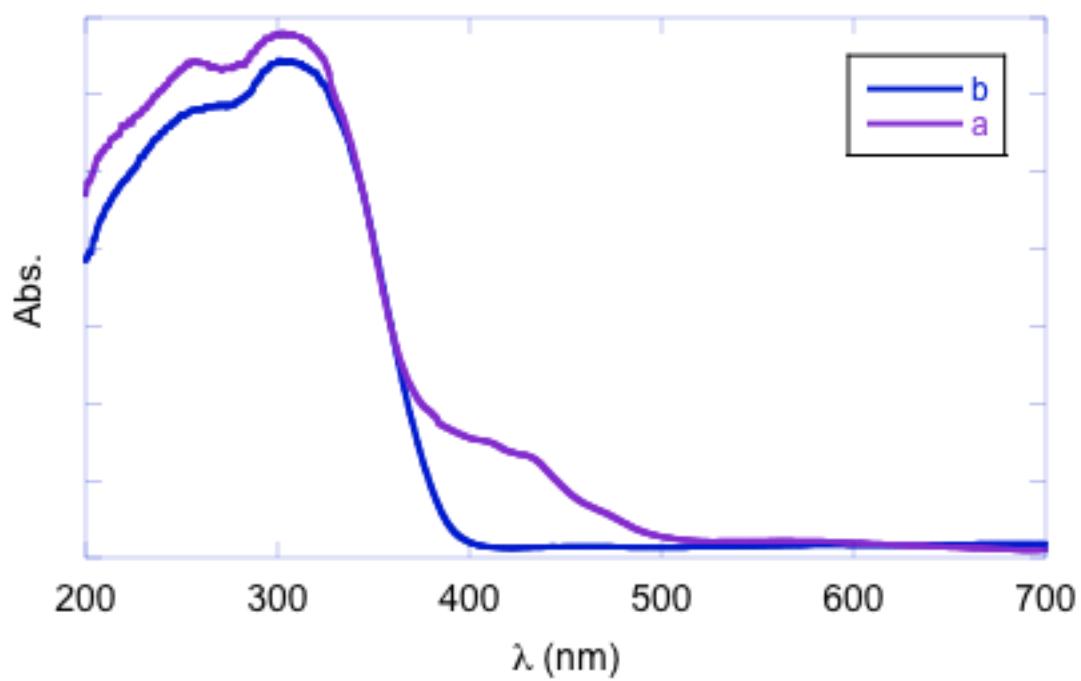


Figure S7. UV/Vis spectra of the as received H_2pydc ligand (a, purple) and of the compound (b, blue).