

Supplementary material

for

Beyond the simple copper(II) coordination chemistry with quinaldinate and secondary amines

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Figure S1. Identification of the aged $[\text{Cu}(\text{quin})_2(\text{CH}_3\text{OH})]\cdot\text{CH}_3\text{OH}$ (**1**): (a) measured PXRD, (b) calculated pattern for $[\text{Cu}(\text{quin})_2(\text{H}_2\text{O})]$ [S1], and (c) calculated pattern for the new polymorph of $[\text{Cu}(\text{quin})_2(\text{H}_2\text{O})]$.

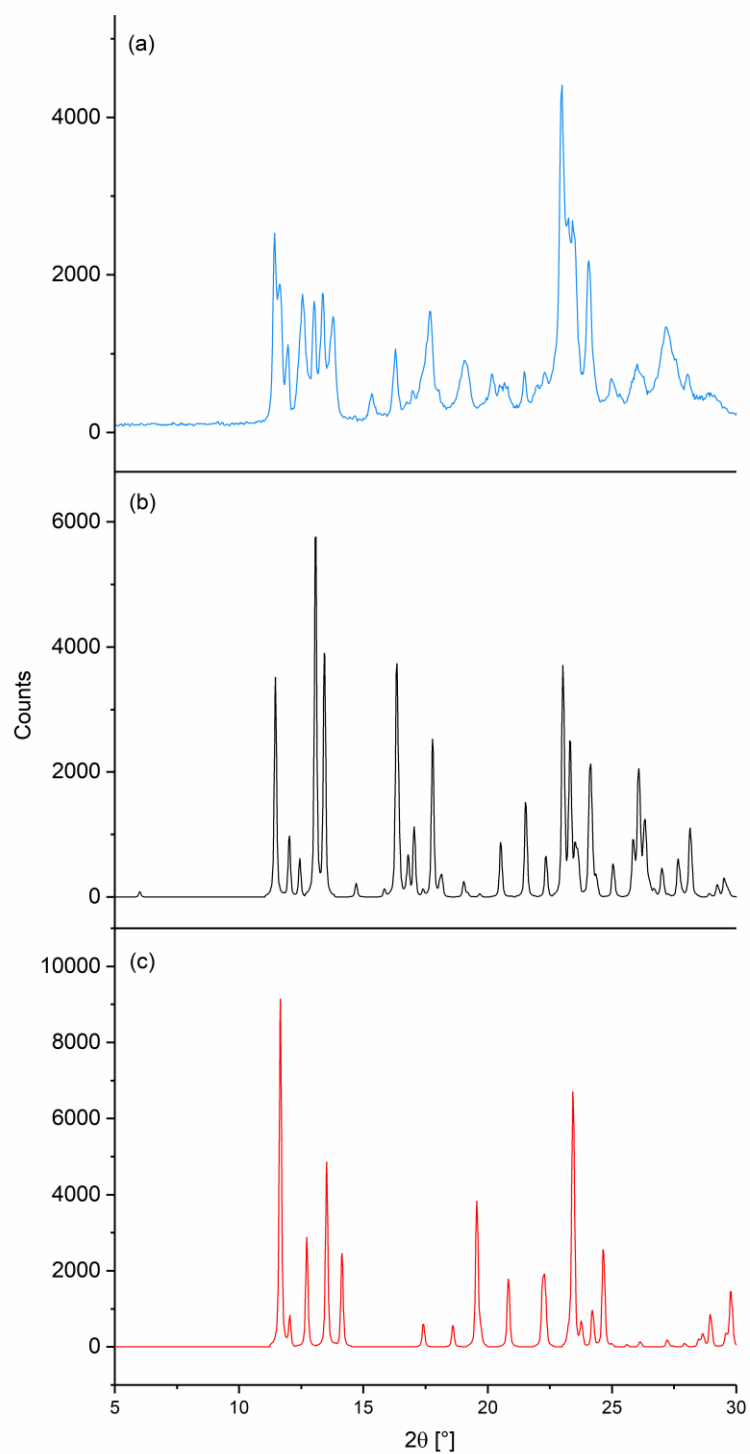
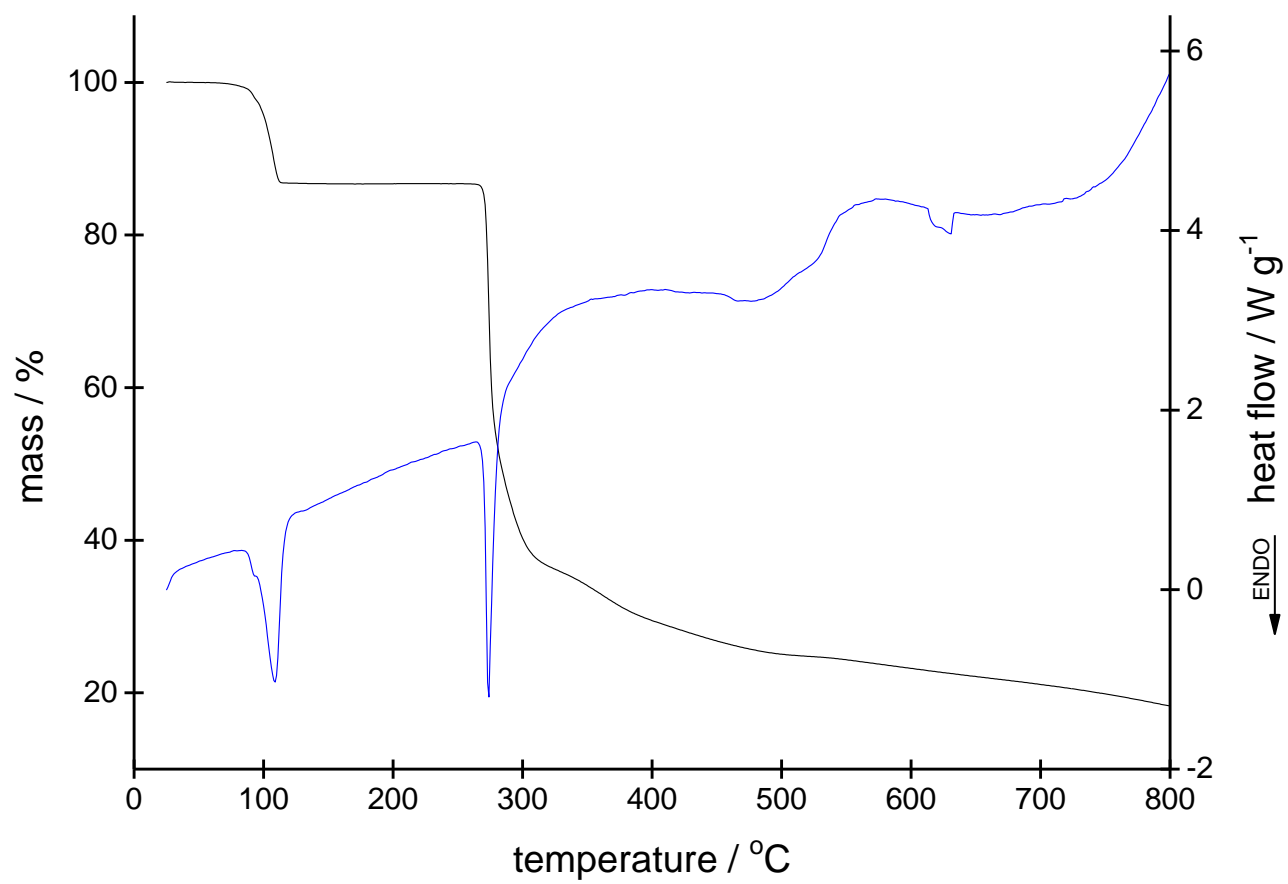


Figure S2. TG and DSC curves for $[\text{Cu}(\text{quin})_2(\text{CH}_3\text{OH})]\cdot\text{CH}_3\text{OH}$ (**1**).



A list of $\pi\cdots\pi$ stacking interactions in [Cu(quin)₂(CH₃OH)]·CH₃OH (1).

The labels *Cg*(3) and *Cg*(4) pertain to the centroids of the pyridine parts of the quinaldinates, *i.e.*, N(1)-C(11)-C(12)-C(13)-C(14)-C(19) and N(2)-C(21)-C(22)-C(23)-C(24)-C(29), respectively, and the label *Cg*(6) to the arene part of one quinaldinate, *i.e.*, C(24)-C(25)-C(26)-C(27)-C(28)-C(29). Parameters *Cg*⋯*Cg*, interplanar distance, dihedral and offset angles are as defined in reference [S2].

Table S1. $\pi\cdots\pi$ stacking interactions [Å, °] in [Cu(quin)₂(CH₃OH)]·CH₃OH (1).

$\pi\cdots\pi$ interactions	type	<i>Cg</i> ⋯ <i>Cg</i>	interplanar distance	dihedral angle	offset angle
<i>Cg</i> (4)⋯ <i>Cg</i> (4) [1− <i>x</i> , 1− <i>y</i> , 2− <i>z</i>]	pyridine⋯pyridine	3.6148(11)	3.3167(8)	0.02(10)	23.4
<i>Cg</i> (3)⋯ <i>Cg</i> (6) [− <i>x</i> , − <i>y</i> , 2− <i>z</i>]	pyridine⋯arene	4.0098(12)	2.9564(9)	20.83(10)	23.1

Figure S3. Overlay of the $[\text{Cu}(\text{quin})_2(\text{pyro})_2]$ molecules in **2**, done by Mercury [S3].

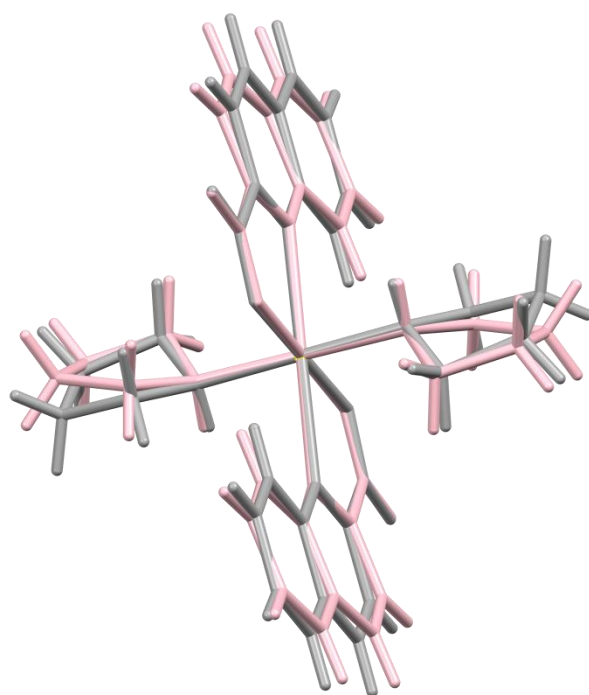


Table S2. Overlay parameters for pairs of complex molecules in **2**, **4** and **7**.^a

Compound	RMSD ^b	Max. distance ^c
2	0.2082	0.6469
4	0.2270	0.4844
7	0.1594	0.2959

^a Overlay was done by Mercury [S3].

^b Root-mean-square deviation.

^c Maximum distance in Å between two equivalent atoms in the overlaid molecules.

Figure S4. Chains in the structures of $[\text{Cu}(\text{quin})_2(\text{morph})_2]$ (**4**) (top) and $[\text{Cu}(\text{quin})_2(\text{pipe})_2]$ (**7**) (bottom).

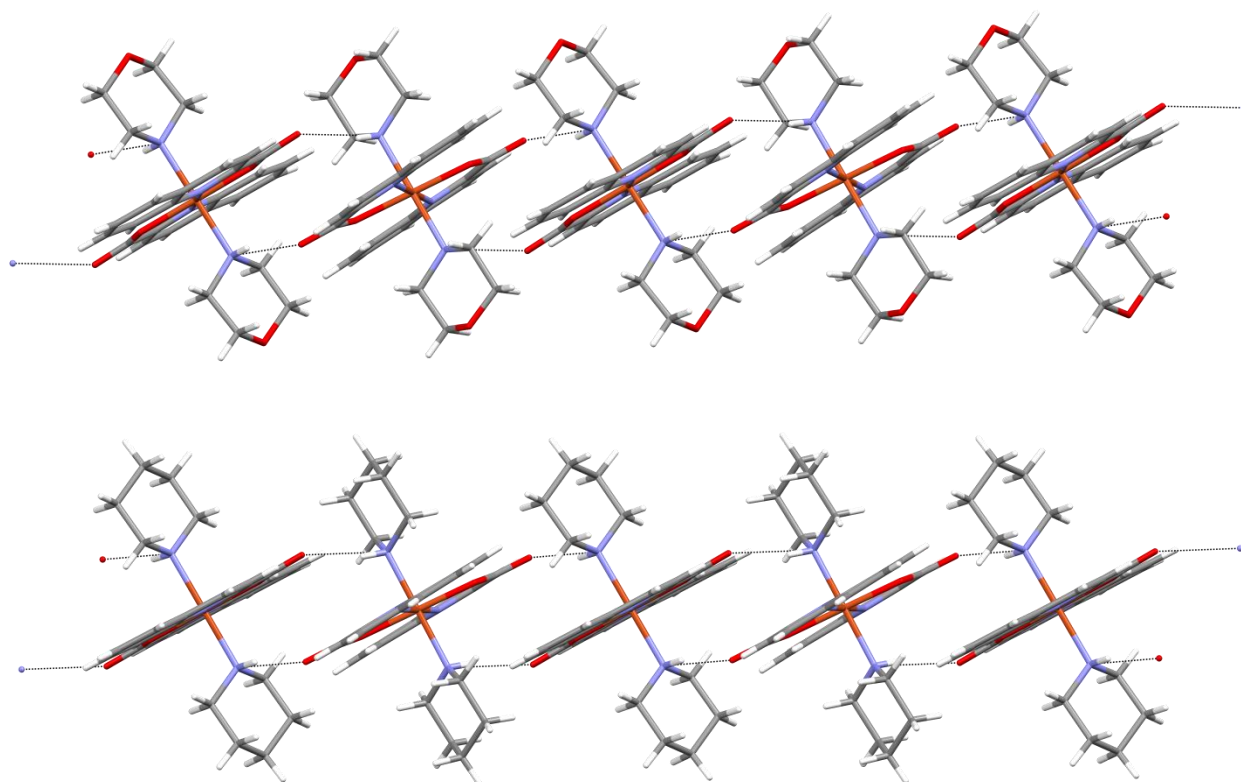


Figure S5. A view along the chains in the structure of $[\text{Cu}(\text{quin})_2(\text{pyro})_2]$ (**2**). The chains pack in a compact manner: each chain is surrounded by six adjacent ones.

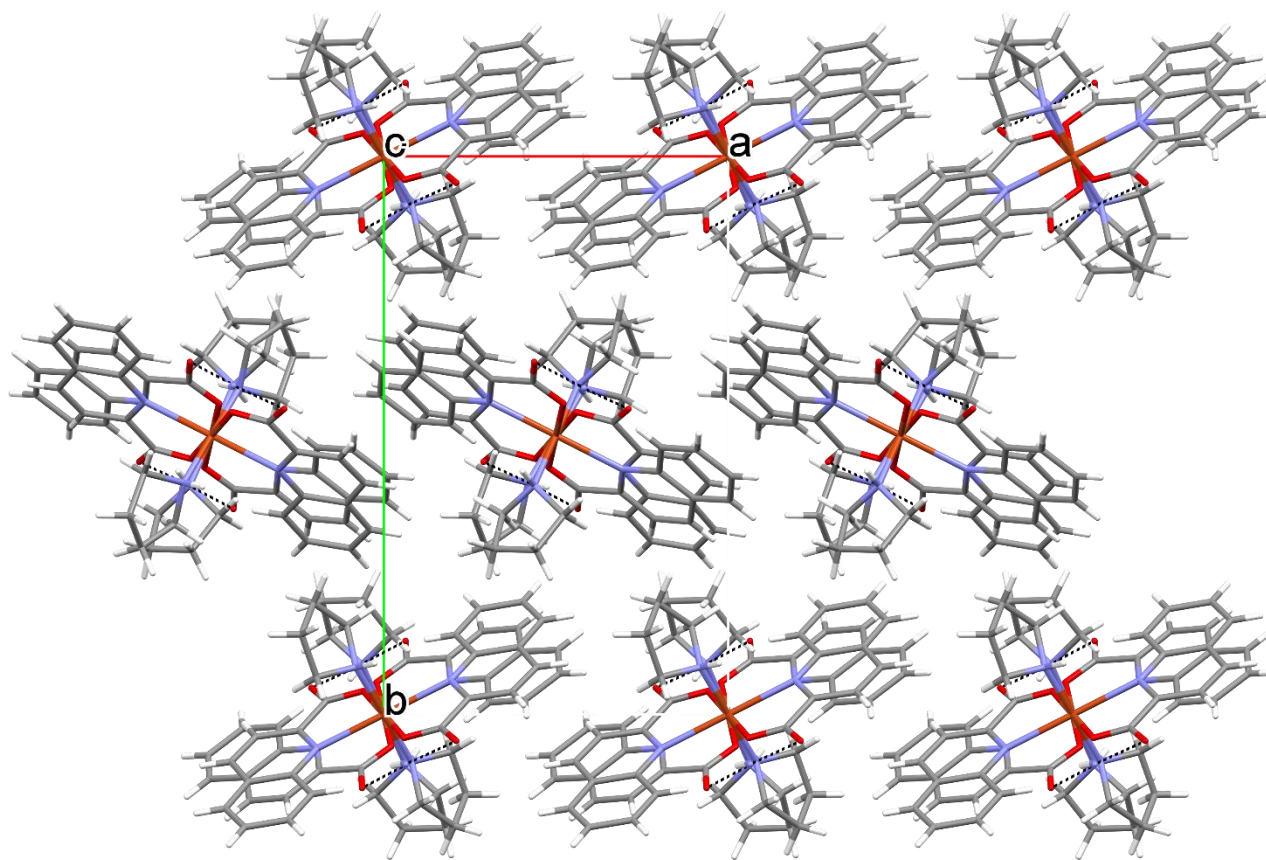


Figure S6. Packing in the structure of [Cu(quin)₂(pipe)] (**6**). Complex molecules are held together with the agency of $\pi\cdots\pi$ stacking interactions between pairs of quinaldinate rings.

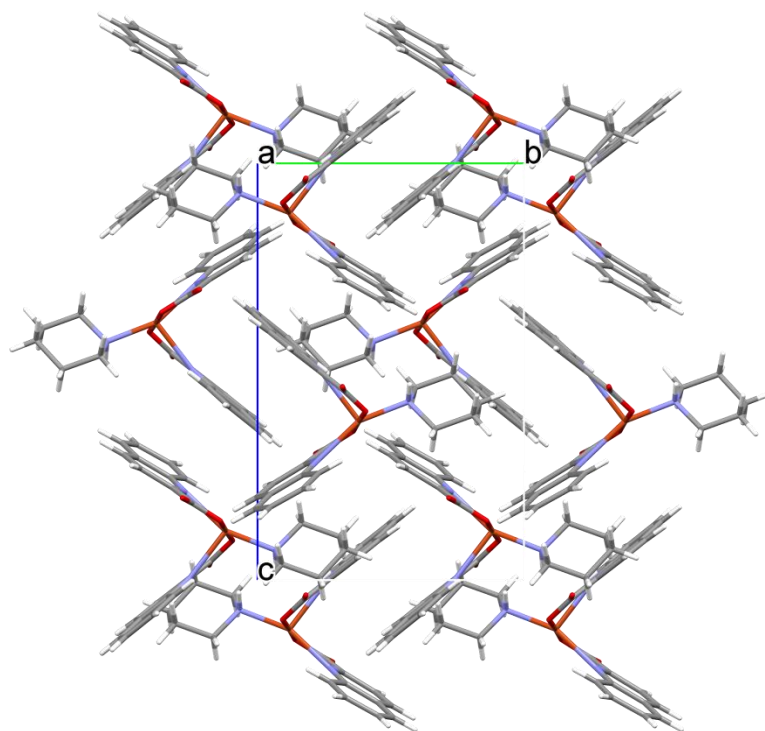


Table S3. Overlay parameters for the [Cu(quin)₂(pipe)₂] complex molecules in **7**, **8** and **9**.^a

Pairs of compounds	RMSD ^b	Max. distance ^c
7 and 8 ^d	0.1836	0.3717
	0.2458	0.4394
7 and 9 ^d	0.2452	0.4392
	0.2962	0.5059
8 and 9	0.0690	0.1281

^a Overlay was done by Mercury [S3].

^b Root-mean-square deviation.

^c Maximum distance in Å between two equivalent atoms in the overlaid molecules.

^d As there are two complex molecules in the asymmetric unit of **7**, two sets of parameters are given.

Figure S7. Packing motifs in $[\text{Cu}(\text{quin})_2(\text{pipe})_2]$ (**7**) (top) and $[\text{Cu}(\text{quin})_2(\text{pipe})_2] \cdot \text{CH}_3\text{CN}$ (**8**) (bottom). Both views are along the chains. Please note that $[\text{Cu}(\text{quin})_2(\text{pipe})_2] \cdot \text{CH}_3\text{CN}$ (**8**) and $[\text{Cu}(\text{quin})_2(\text{pipe})_2] \cdot \text{CH}_3\text{CH}_2\text{CN}$ (**9**) are isomorphous. The packing of chains in **8** and **9** creates hydrophobic channels.

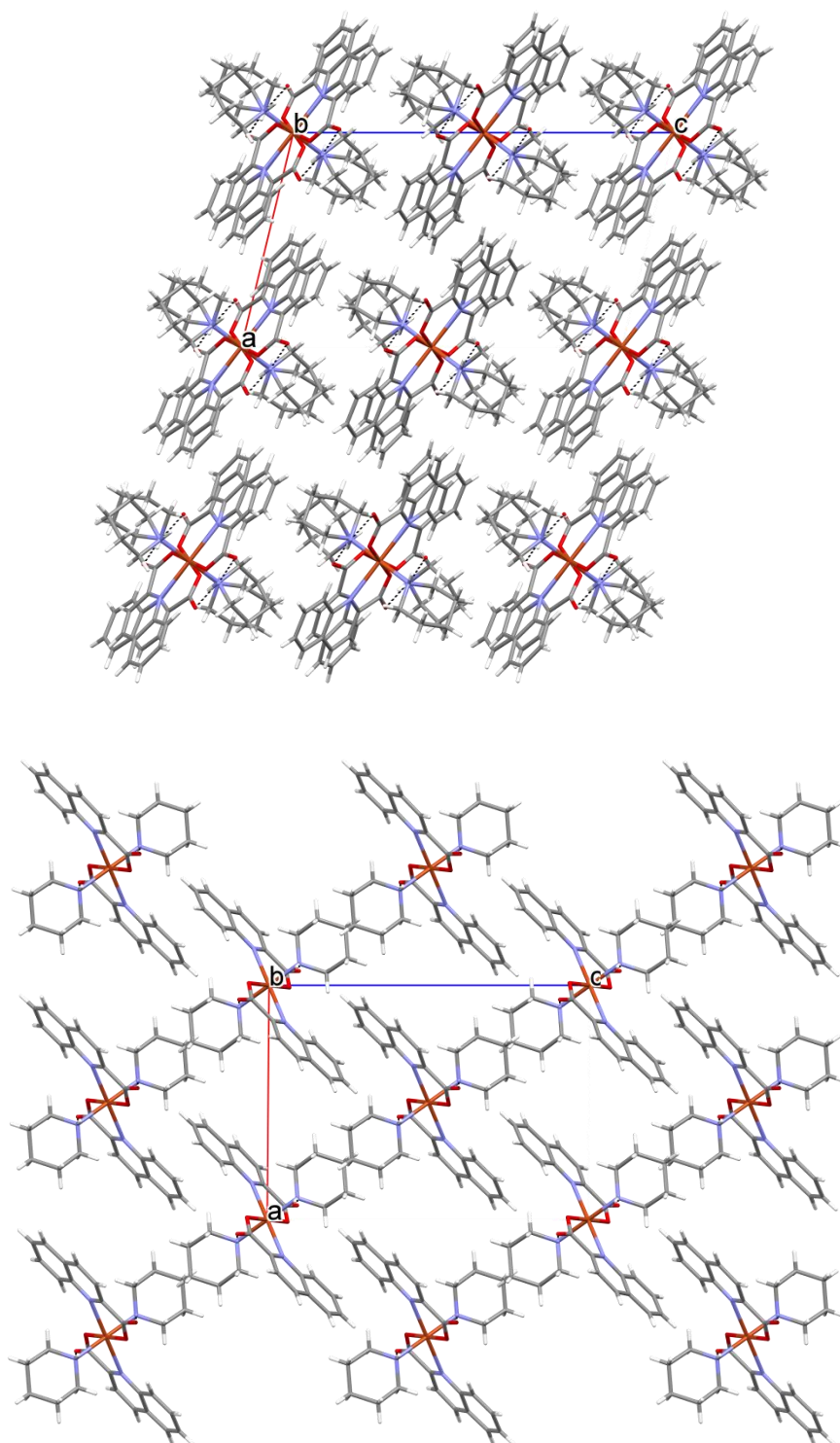
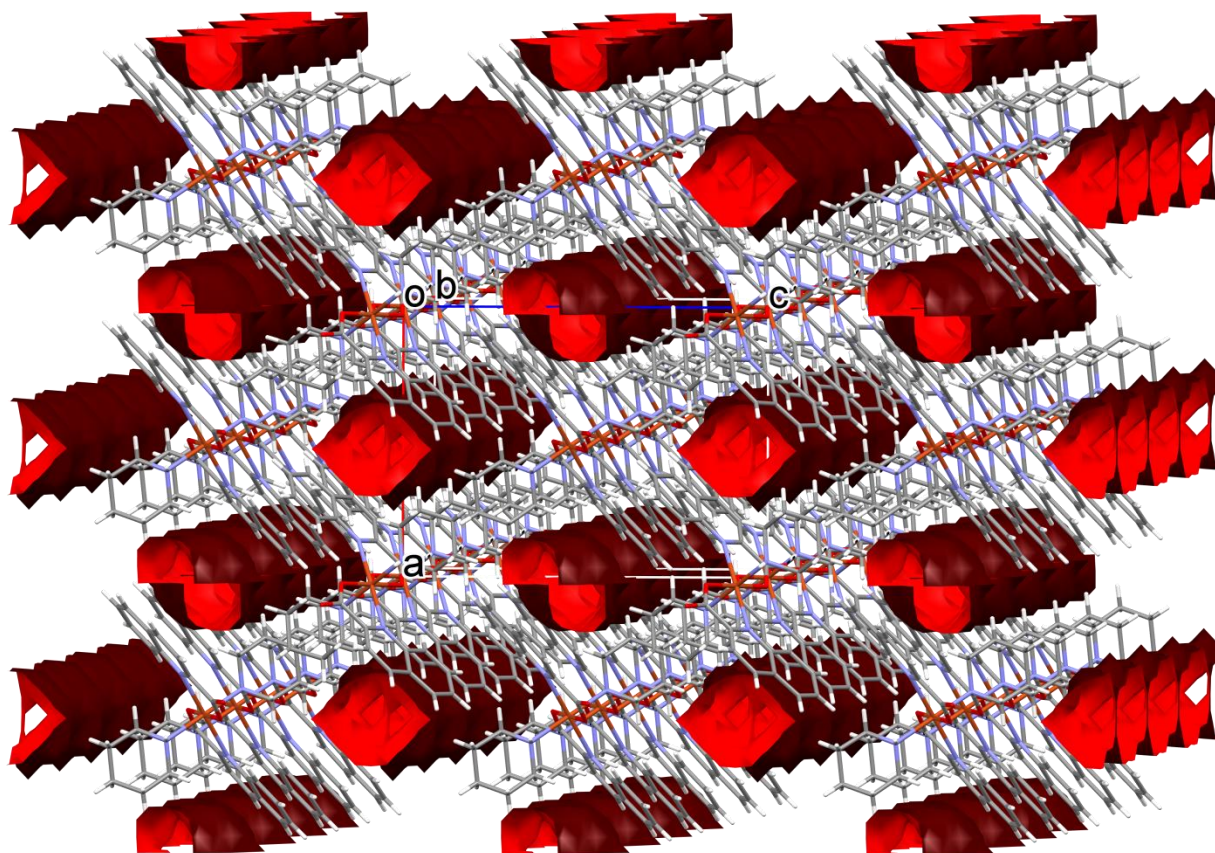


Figure S8. A view along the channels, shown in red colour, in the structure of $[\text{Cu}(\text{quin})_2(\text{pipe})_2] \cdot \text{CH}_3\text{CN}$ (**8**). Solvent molecules of crystallization that are accommodated in the channels are not shown.



A list of intermolecular interactions in [Cu(quin)₂(pipe)] (6).

The labels *Cg*(3) and *Cg*(4) pertain to the centroids of the pyridine parts of the quinaldinates, *i.e.*, N(1)-C(11)-C(12)-C(13)-C(14)-C(19) and N(2)-C(21)-C(22)-C(23)-C(24)-C(29), respectively, and the labels *Cg*(6) and *Cg*(7) to the corresponding arene parts, *i.e.*, C(14)-C(15)-C(16)-C(17)-C(18)-C(19) and C(24)-C(25)-C(26)-C(27)-C(28)-C(29), respectively. Parameters *Cg*...*Cg*, interplanar distance, dihedral and offset angles are as defined in reference [S2].

Table S4. Intermolecular interactions [Å, °] in [Cu(quin)₂(pipe)] (6).

$\pi\cdots\pi$ interactions	type	<i>Cg</i> ... <i>Cg</i>	interplanar distance	dihedral angle	offset angle
<i>Cg</i> (4)··· <i>Cg</i> (6) [<i>x</i> , 1/2− <i>y</i> , −1/2+ <i>z</i>]	pyridine···arene	3.7087(10)	3.5616(7)	11.77(8)	27.2
<i>Cg</i> (6)··· <i>Cg</i> (7) [<i>x</i> , 1/2− <i>y</i> , 1/2+ <i>z</i>]	arene···arene	3.9004(10)	3.4550(7)	11.41(8)	23.9
C–H··· π interactions	H··· <i>Cg</i>	C–H··· <i>Cg</i>	C··· <i>Cg</i>	X–H, π	
C(32)–H··· <i>Cg</i> (3) [<i>x</i> , 1+ <i>y</i> , <i>z</i>]	3.00	159	3.918(2)	67	
C(33)–H··· <i>Cg</i> (7) [<i>x</i> , 1+ <i>y</i> , <i>z</i>]	2.78	146	3.630(2)	60	

Figure S9. Hydrogen bonding pattern in (pyroH)[Cu(quin)₂Cl] (**3**): NH₂⁺...COO⁻ interactions link four pyrrolidinium cations with four complex anions into a cyclic supramolecular motif, described in graph set notation as $R_8^8(36)$ [S4]. Colour code: complex anions - grey, pyrrolidinium cations - gold.

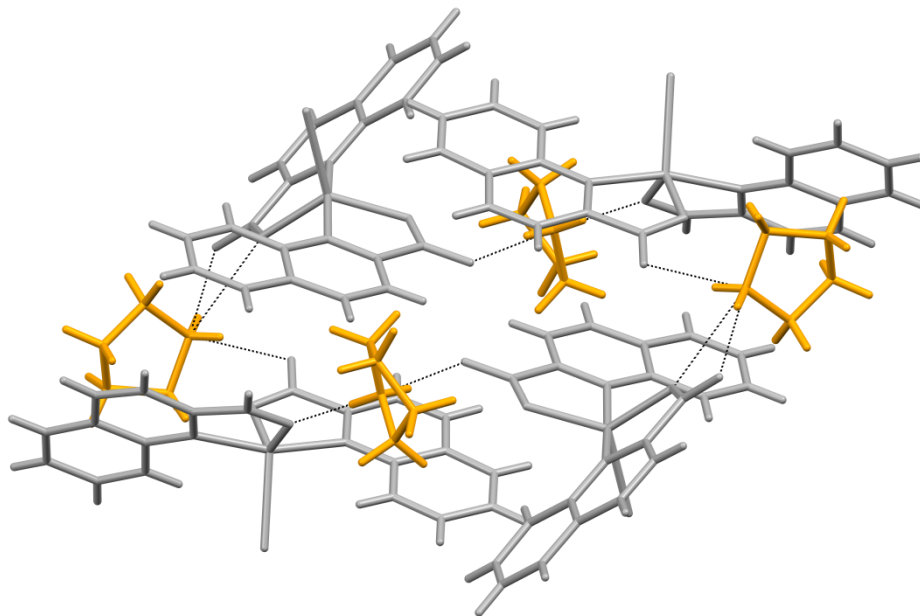


Figure S10. Hydrogen bonds in $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2](\text{morphCOO})_2$ (**5**): intricate pattern of H-bonds (dotted lines) links complex cations (light grey) and counteranions (gold) into infinite 2D array. The surface of the layers is covered with the hydrophobic part of the morphCOO^- anions. The layers stack along c -axis.

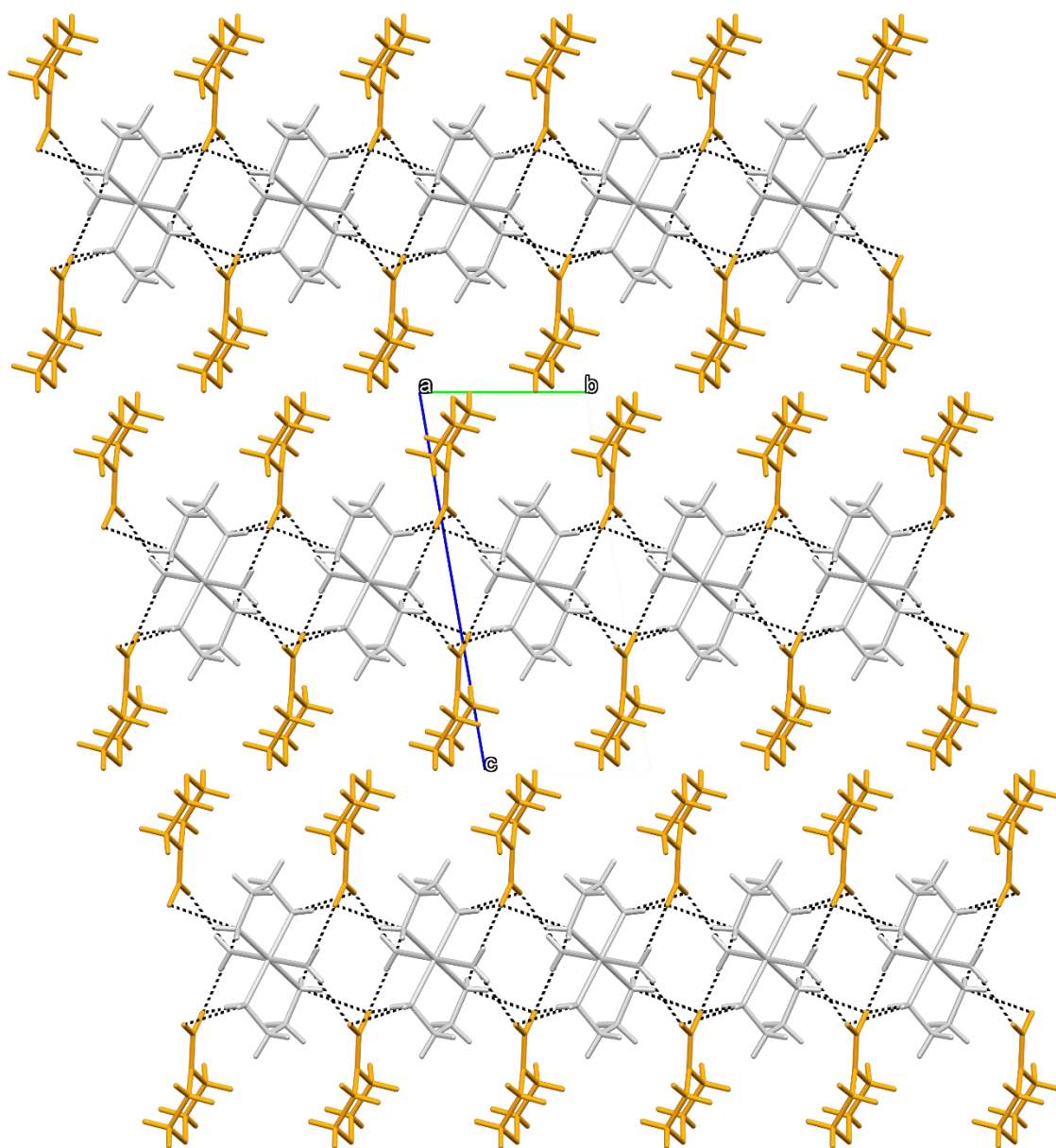


Figure S11. Packing arrangement in the structure of **10**.

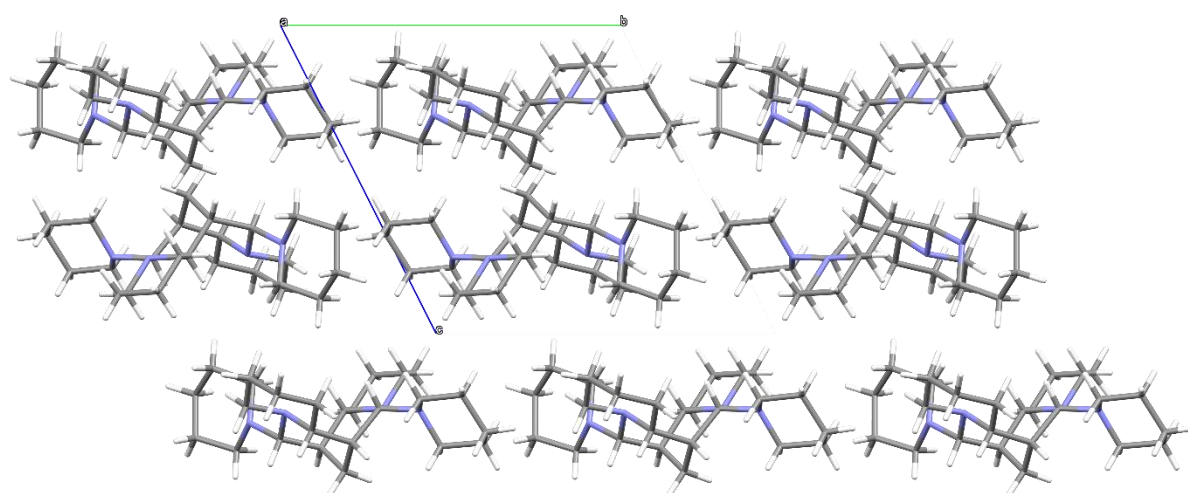


Table S5. Hydrogen bonds in compounds **1–11**.

Compound	Donor...acceptor	Description	Distance [Å]
[Cu(quin) ₂ (CH ₃ OH)]·CH ₃ OH (1)	O1M...O12[1-x, -y, 2-z]	CH ₃ OH(ligand)...COO ⁻	2.752(2)
	O2M...O22	CH ₃ OH...COO ⁻	2.743(2)
[Cu(quin) ₂ (pyro) ₂] (2)	N3...O22	NH(pyro)...COO ⁻	2.903(3)
	N4...O12[2-x, -y, 4-z]	NH(pyro)...COO ⁻	2.916(2)
(pyroH)[Cu(quin) ₂ Cl] (3)	N5...O11	NH ₂ ⁺ (pyroH ⁺)...COO ⁻	2.828(3)
	N5...O32	NH ₂ ⁺ (pyroH ⁺)...COO ⁻	2.730(3)
	N6...O22	NH ₂ ⁺ (pyroH ⁺)...COO ⁻	2.802(3)
	N6...O42[1-x, 1-y, 1-z]	NH ₂ ⁺ (pyroH ⁺)...COO ⁻	2.879(3)
[Cu(quin) ₂ (morph) ₂] (4)	N3...O22	NH(morph)...COO ⁻	2.924(4)
	N4...O12	NH(morph)...COO ⁻	2.952(4)
<i>trans</i> -[Cu(en) ₂ (H ₂ O) ₂](morphCOO) ₂ (5)	N1...O1[1+x, y, z]	NH ₂ ...H ₂ O	3.056(2)
	N1...O31	NH ₂ ...COO ⁻	3.001(2)
	N2...O31[x, -1+y, z]	NH ₂ ...COO ⁻	2.987(2)
	N2...O32[1+x, -1+y, z]	NH ₂ ...COO ⁻	2.907(2)
	O1...O31[-x, 2-y, 1-z]	H ₂ O...COO ⁻	2.7773(19)
	O1...O32	H ₂ O...COO ⁻	2.7447(18)
[Cu(quin) ₂ (pipe) ₂] (7)	N3...O22[2-x, 1-y, 1-z]	NH(pipe)...COO ⁻	2.924(2)
	N4...O12[2-x, -y, 1-z]	NH(pipe)...COO ⁻	2.994(2)
[Cu(quin) ₂ (pipe) ₂]·CH ₃ CN (8)	N2...O12[x, -1+y, z]	NH(pipe)...COO ⁻	3.0103(17)
[Cu(quin) ₂ (pipe) ₂]·CH ₃ CH ₂ CN (9)	N2...O12[x, -1+y, z]	NH(pipe)...COO ⁻	2.9973(17)
(pipeH)[Cu(quin) ₂ Cl] (11)	N5...O22[1-x, -y, 2-z]	NH ₂ ⁺ (pipeH ⁺)...COO ⁻	2.8505(18)
	N5...O42[1-x, -y, 2-z]	NH ₂ ⁺ (pipeH ⁺)...COO ⁻	2.8222(18)
	N6...O12	NH ₂ ⁺ (pipeH ⁺)...COO ⁻	2.7886(18)
	N6...O32[-x, 1-y, 2-z]	NH ₂ ⁺ (pipeH ⁺)...COO ⁻	2.8471(18)

Figure S12. Infrared spectrum of $[\text{Cu}(\text{quin})_2(\text{H}_2\text{O})]$.

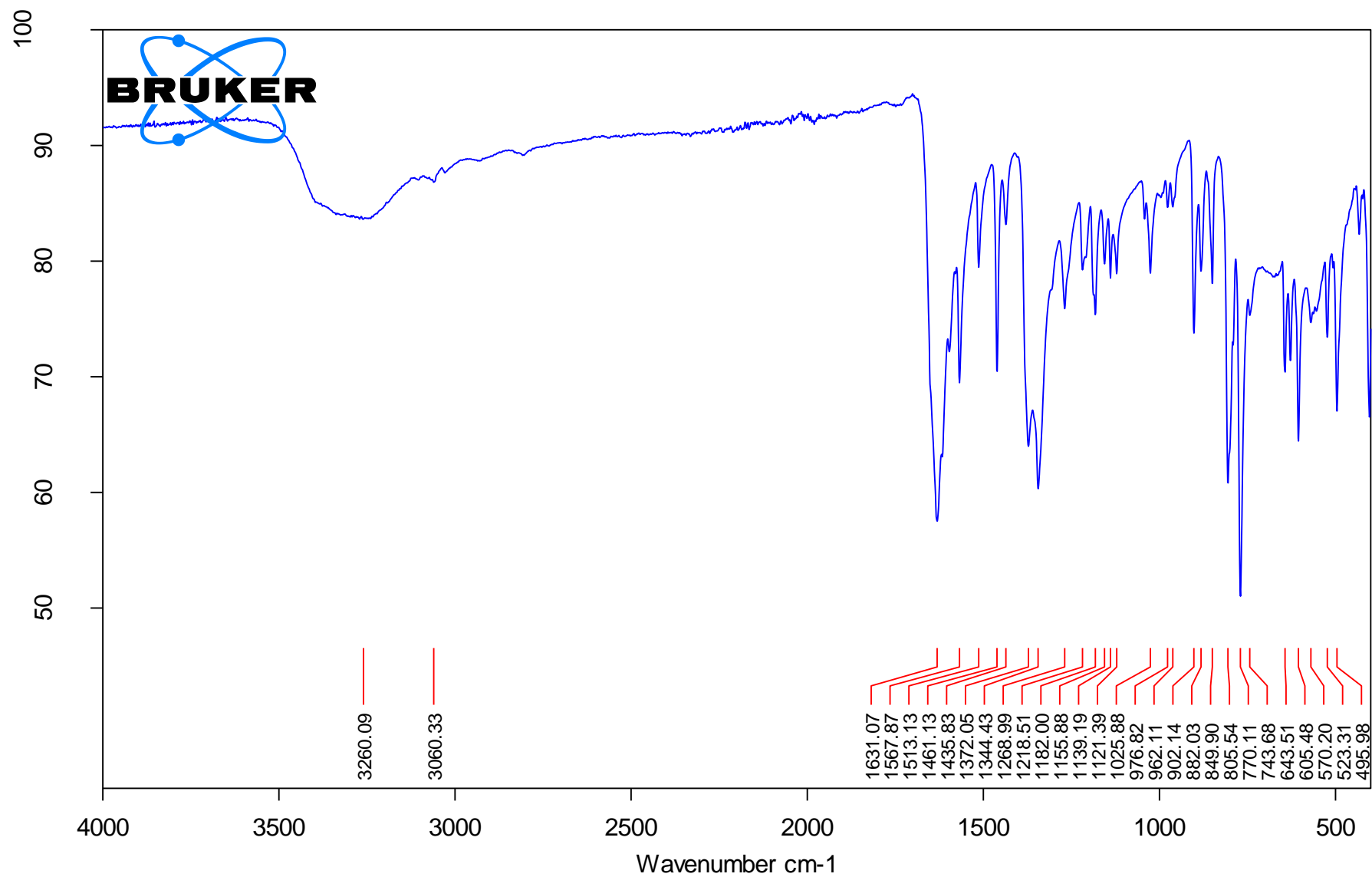


Figure S13. Infrared spectrum of $[\text{Cu}(\text{quin})_2(\text{CH}_3\text{OH})]\cdot\text{CH}_3\text{OH}$ (**1**).

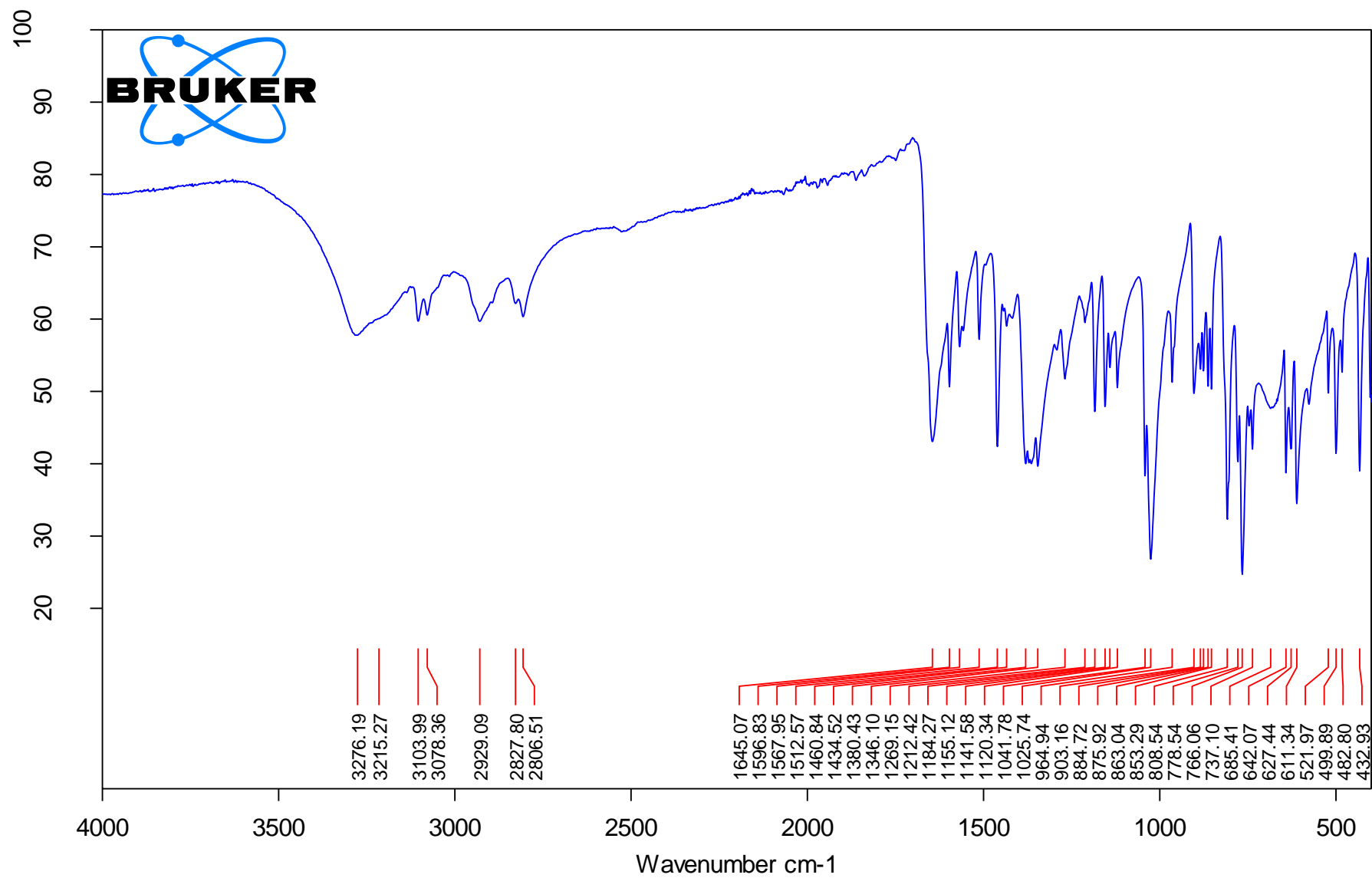


Figure S14. Infrared spectrum of $[\text{Cu}(\text{quin})_2(\text{pyro})_2]$ (**2**).

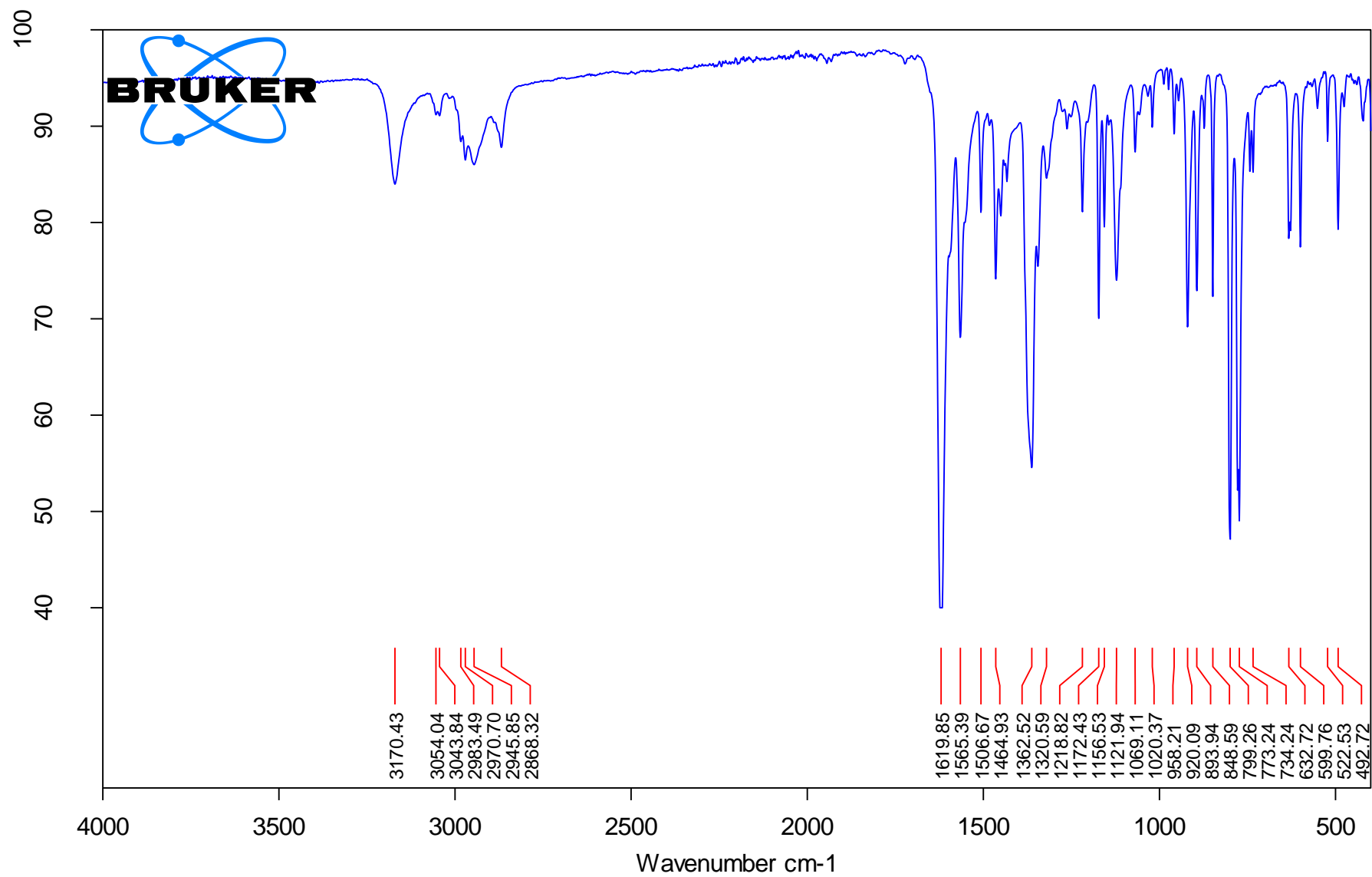


Figure S15. Infrared spectrum of (pyroH)[Cu(quin)₂Cl] (**3**).

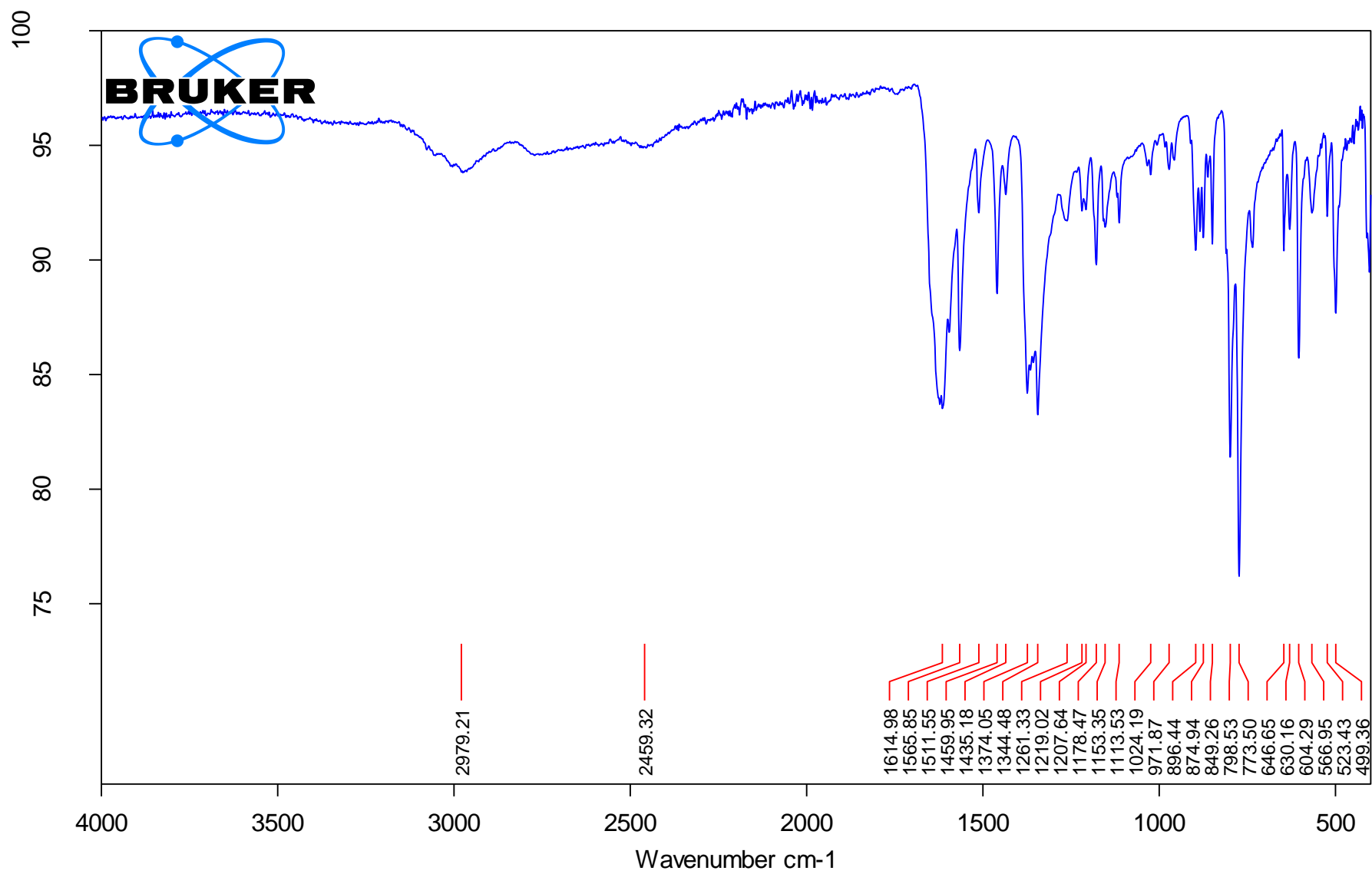


Figure S16. Infrared spectrum of $[\text{Cu}(\text{quin})_2(\text{morph})_2]$ (**4**).

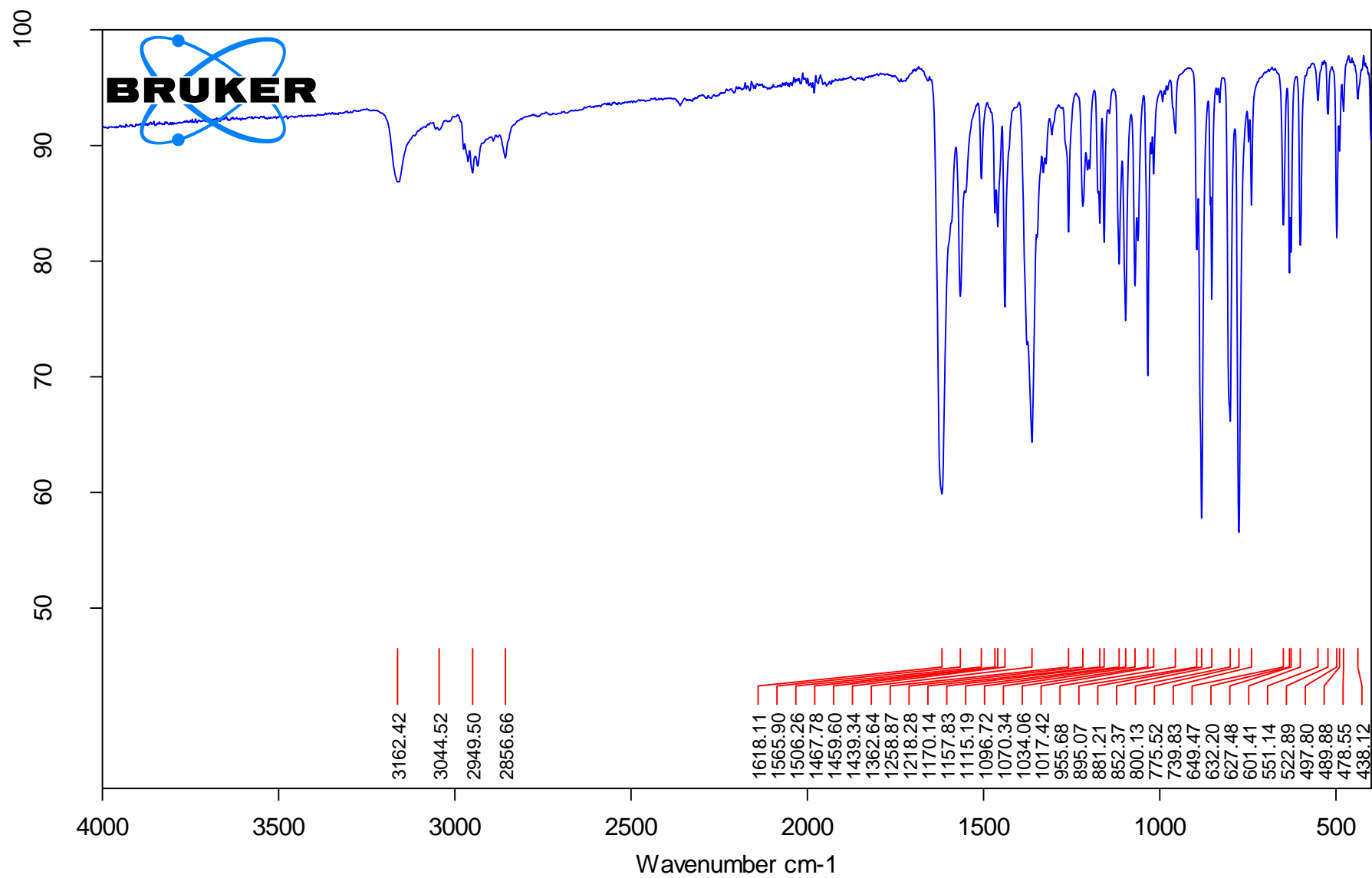


Figure S17. Infrared spectrum of [Cu(quin)₂(pipe)] (**6**).

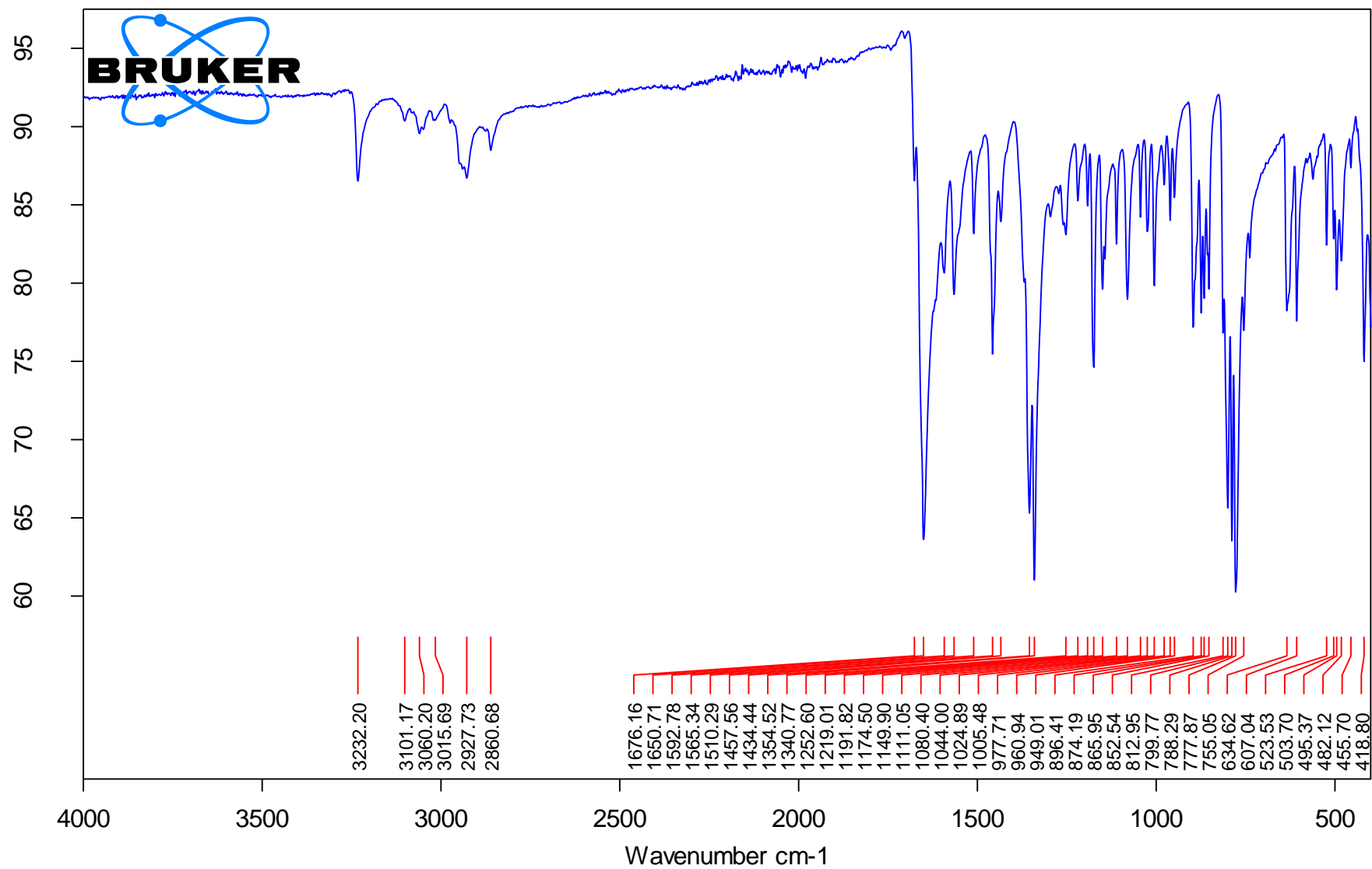


Figure S18. Infrared spectrum of $[\text{Cu}(\text{quin})_2(\text{pipe})_2]$ (**7**).

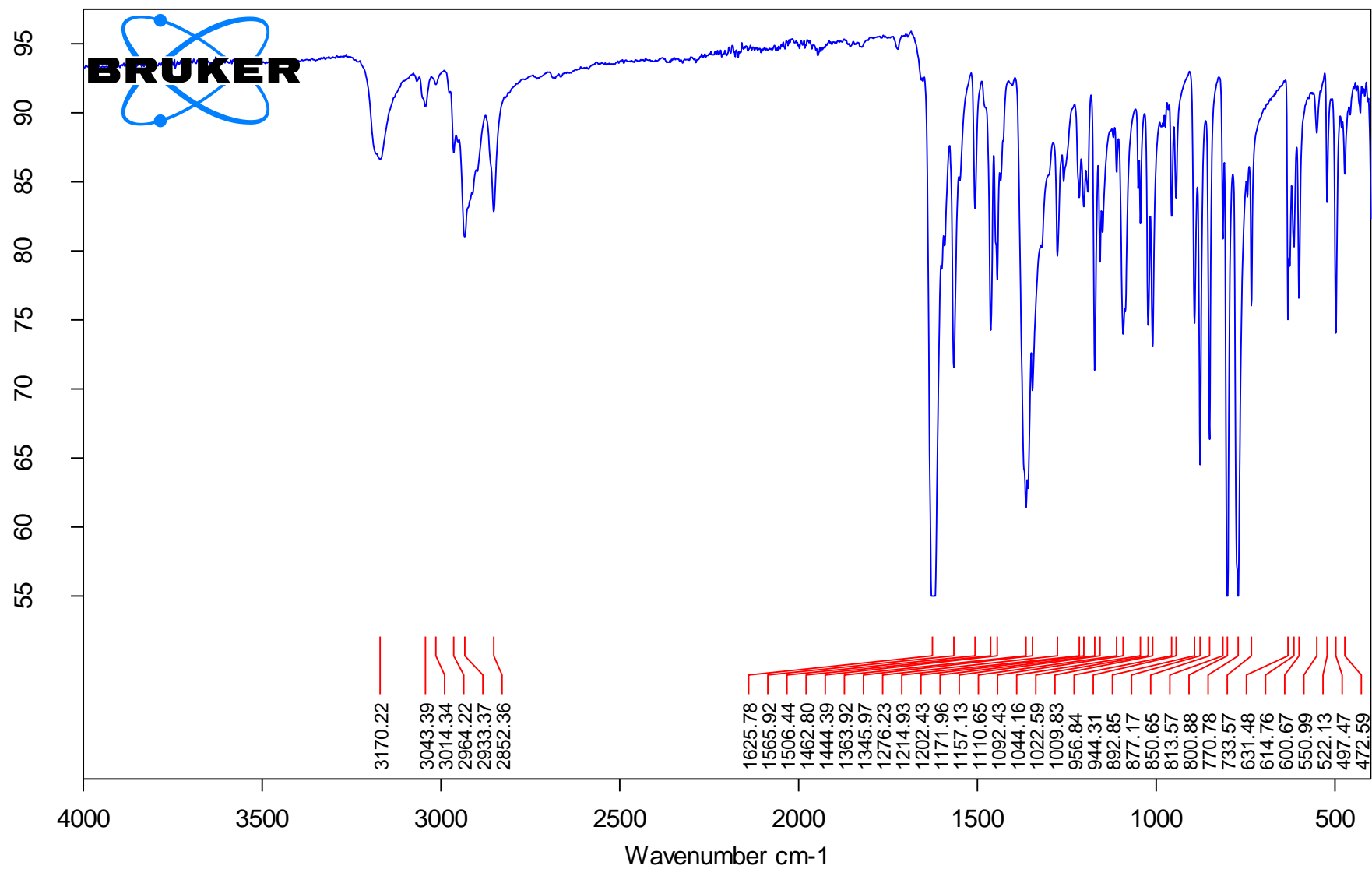


Figure S19. Infrared spectrum of $[\text{Cu}(\text{quin})_2(\text{pipe})_2] \cdot \text{CH}_3\text{CN}$ (**8**).

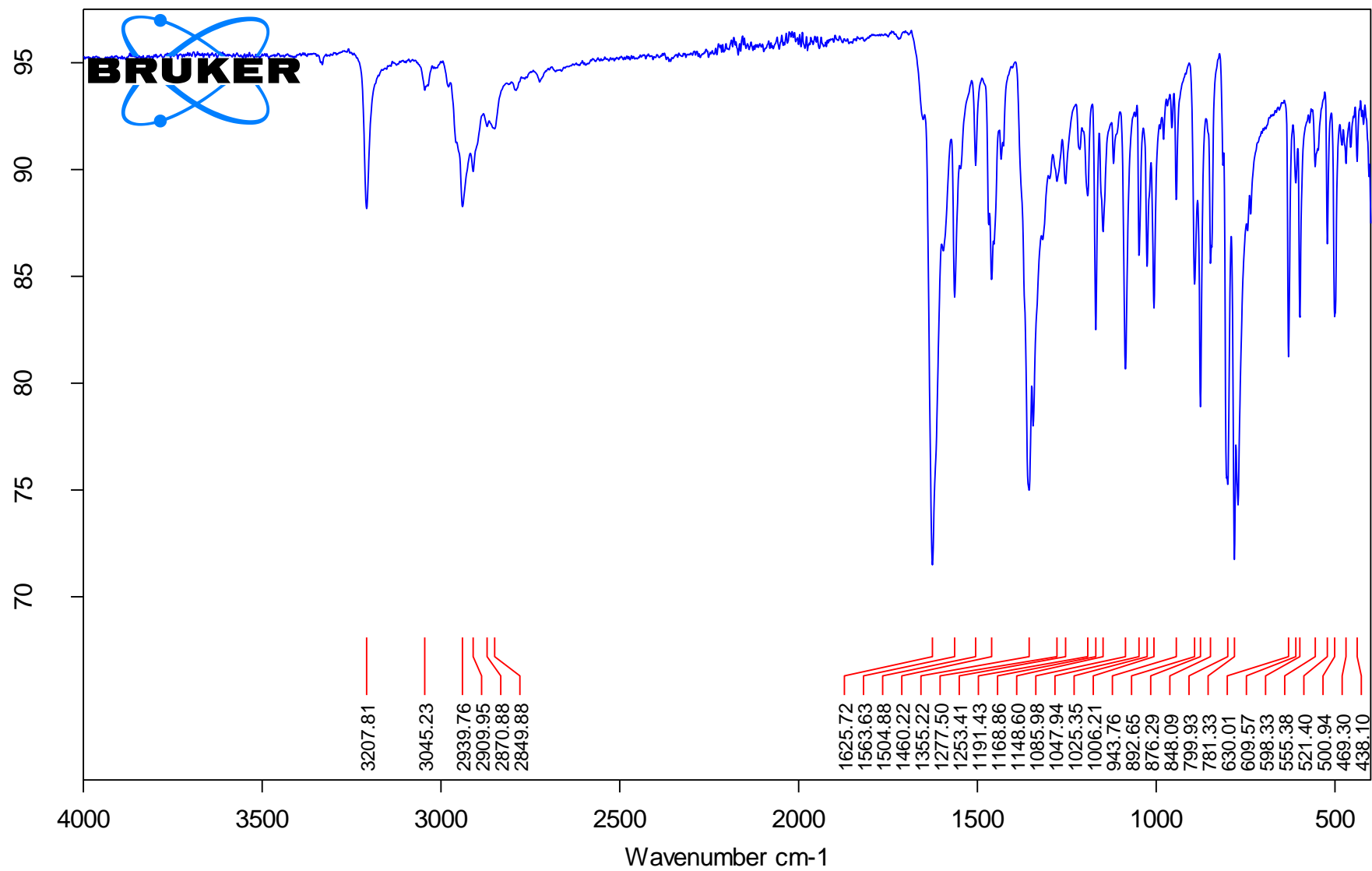


Figure S20. Infrared spectrum of $[\text{Cu}(\text{quin})_2(\text{pipe})_2] \cdot \text{CH}_3\text{CH}_2\text{CN}$ (**9**).

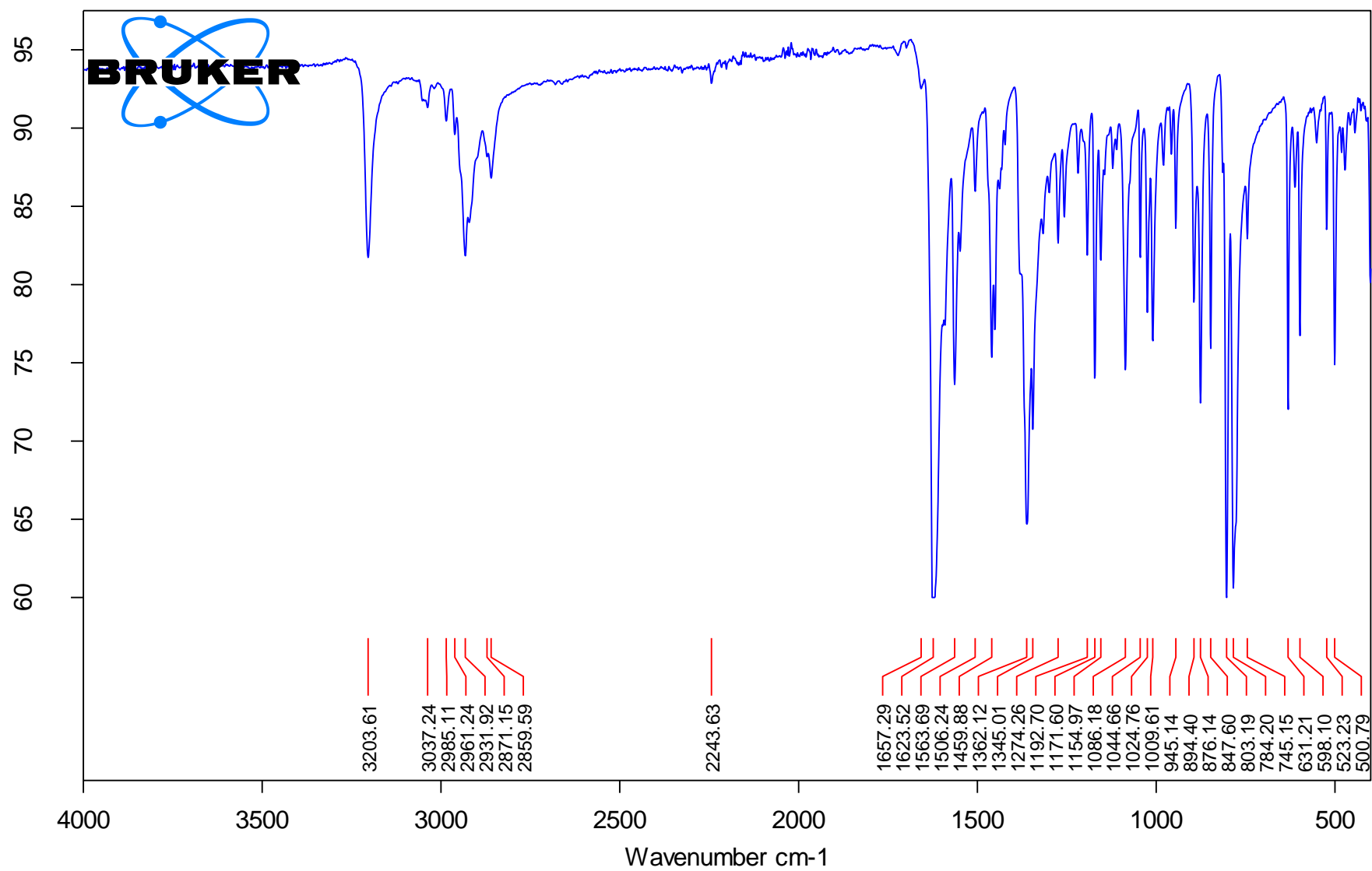
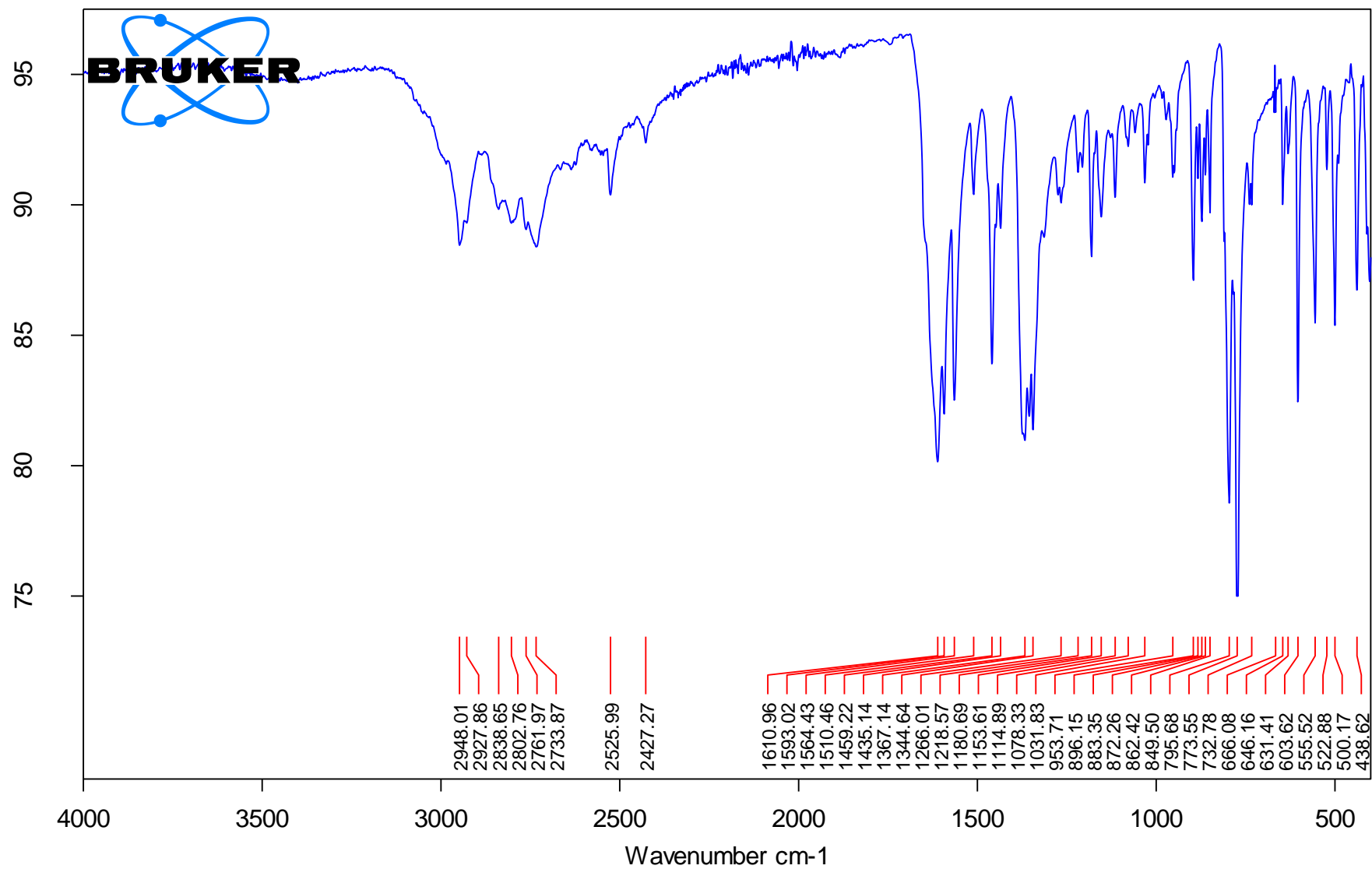


Figure S21. Infrared spectrum of (pipeH)[Cu(quin)₂Cl] (**11**).



References

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