Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

On the fly multi-modal observation of ligand synthesis and complexation of Cu complexes in flow with 'benchtop' NMR and mass spectrometry

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Supporting Information (SI)

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1. Chemicals and Instrumentation Section

Chemicals: All chemicals were supplied by *Fisher Chemicals*, *Sigma Aldrich* and *Lancaster Chemicals Ltd*. and were used without further purification.

CNH Microanalysis: Carbon, nitrogen and hydrogen content (%) were determined by the microanalysis services within the Department of Chemistry, University of Glasgow using an EA 1110 CHNS CE-440 Elemental Analyzer.

Single crystal X-Ray diffraction: Single crystal datasets and unit cells were collected at 150K unless stated otherwise on the following instrument: Bruker Apex II Quasar x-ray Diffractometer with enhanced X-ray beam (λMo-Kα = 0.71073 Å, T = 150 K, monochromated graphite). Structure solution and refinement were carried out with SHELXS-97[1] and SHELXL-97[2] via WinGX.[3]

[1] G. Sheldrick, *Acta Crystallogr. A* **1990**, *46*, 467-473.
[2] G. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112-122.
[3] L. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837-838.

The CIF file for compounds 2, 3, 4, and 5 where submitted to CSD@Cambridge and allocated the numbers CCDC 1011858-1011863 respectively.

Sherwood Scientific Magnetic Susceptibility Balance Mark 1:

Magnetic susceptibility measurements were carried out on manually powdered single-crystalline samples. Pascal's constants were used to determine the necessary diamagnetic corrections.

Microsaic systems 4000 MiD, spraychip® (electrospray ionisation source);

Mass analyzer - ionchip® quadrupole mass spectrometer
Direct flow rate – 0.2 µL min^{-1}– 2 µL min^{-}
Split flow rate – up to 2.0 mL min^{-1}
Make-up flow – 1 mL min^{-1}, 50 : 50 MeOH : H_2O
Attenuation – 1000

Ionisation mode – positive
Tip voltage – 850 V
Nebulizer (N2) flow – 2.5 L min^{-1}

Vacuum interface voltage – 40 V
Tube lens voltage – 10 V
Plate lens voltage – 5 V
Ion guide voltage – 1 V
Count time – 0.20 ms
Mass range - *m/z* 50-800 with ionchip®150
Mass accuracy - +/- *m/z* 0.3 in full scan
Mass resolution – *m/z* 0.7 +/- 0.1 FWHM

Masscape® software was used for control of sample methods and data analysis

NMR: high field NMR data was recorded on a Bruker Advanced 400 MHz.

Bench top NMR: Spinsolve Magritek, 43 MHz, Spinsolve purchased from Magritek.

Fourier-transform infrared spectroscopy (FT-IR): The materials were prepared without any treatment and the powder of the compound was placed in the machine directly. FT-IR spectra were collected in transmission mode using a Shimadzu FT-IR 8400S spectrophotometer. Wavenumbers ($\tilde{\upsilon}$) are given in cm^{-1} and intensities are described as vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = sharp or vsh = very sharp.

ATR-infrared spectroscopy flow cell (flow ATR-IR): IR spectra were collected in-line employing a Nicolet IS-5 from Thermo Scientific and a ZnSe Golden Gate ATR from Specac equipped with a flow cell. The resolution was set at 4 cm^{-1} and 16-80 scans were recorded.

Raman spectroscopy: The materials were prepared without any treatment and the crystal was placed in the machine directly. The LabRAM HR system is equipped with a Ventus 532 laser system, 100 mW, 532 nm; Helium Cadmium IK3201R-F, 20 mW, 325 nm. It uses a Synapse CCD detection system, and has the following objectives: 15x for UV; 10x, 50x and 100x for visible.

Ultra violet visible spectroscopy (UV-vis): UV-vis spectra were collected using a Jasco V-670 spectrophotometer in transmission mode. UV-vis spectra of the compounds were collected from solid state.

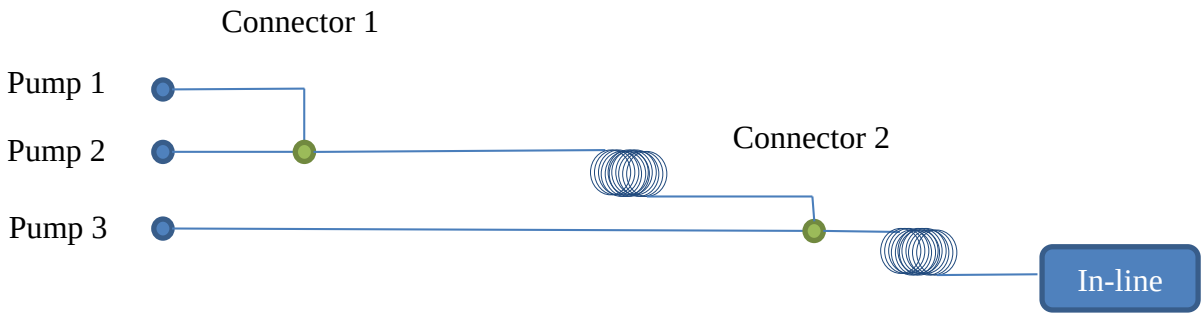
Device Setups All solutions were pumped by means of C-3000 syringe pumps from Tricontinent equipped with 5 mL syringes and 3-way solenoid valve. An in-house developed *LabVIEW*™ application was employed to program the pumps to deliver the desired flow-rates.

2. Flow set-up description

The flow set-up utilised consists of 6 pumps, 2 flow reactors, 2 mixing manifolds and 2 in-line flow analytics, flow ESI-MS and flow NMR, in order to follow the reaction progress in real-time (**Figure S1**).

Figure S1: **Top**: flow set-up for the experiments in flow with the ESI-MS. **Bottom**: flow set-up for the flow NMR

The pumps deliver the dissolved starting material through the reaction system, using polytetrafluoroethylene (PTFE) coil tubing with an internal diameter (ID) of about 0.80 mm [Omnifit labware (Diba), PTFE, 1/16″ (1.6 mm) OD and 0.8 mm ID] and standard connectors made of polyfluoroelastomer (FPM) and Polyether Ether Ketone (PEEK). The same coil tubing as used to build the two flow reactors for this system: the coil tubing length results in a total volume of 2.10 mL for the first reactor (V_{R1}) and 0.70 mL for the second reactor (V_{R2}). The first reactor inlet was connected to the 2 syringe pumps containing the starting material solutions used in the first step (the ligand synthesis); the outlet of the first reactor was connected to the second manifold with the other syringe pump outlet containing the salt solution. The output of this second manifold was connected to the second reactor used in the second step, which is the synthesis of the complex; and the output of V_{R2} was connected to the in-line analytics (**Scheme S1**).

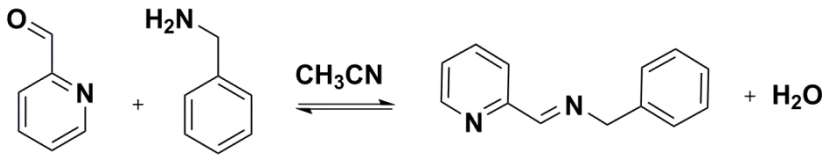


Scheme S1. Scheme of flow set-up

The connectors at the two manifolds and relevant to the syringe pumps outlets were equipped with check valves (made of PEEK with a Chemraz® O-ring, which is compatible with organic solvents and compounds) to prevent potential backflow issues. A LabVIEW™-based PC interface was used to control the experiments in terms of flow rates and volume of the reactants.

3. One pot flow-syntheses with the bidentate ligand (L^1)

3.1 Synthesis of bidentate ligand $C_{13}H_{12}N_2$ (L^1)



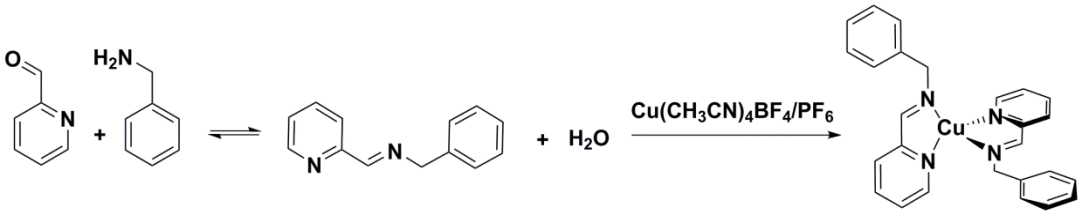
In each experiment, 2-pyridinecarboxaldehyde (1.07 g, 10 mmol), and benzylamine (1.07 g, 10 mmol) were dissolved each in acetonitrile or methanol (25 mL) resulting in 2 equimolar solutions with a concentration of 0.4 M. In each experiment 2-pyridinedicarboxaldehyde (3.55 mL) and benzylamine (3.55 mL) were pumped with F_{r1} and F_{r2} respectively to a 3-way connector resulting in a total flow rate of F_{r3}. The flow rates and residence times relative to each experiment are reported in **Table S1**. In the **Experiments 1-7** of **Table S1** the output, a colorless solution was introduced in the flow NMR tube - resulting in a total reactor volume of 2.1 mL - and its ^{1}H-NMR was collected (see **Figure S2**). In the **Experiment 8** of **Table S1** both flow reactors V_{R1} and V_{R2} were used to perform the ligand synthesis, resulting in a total reactor volume of 2.8 mL, and the output of it was connected to a flow ESI-MS (see **Figure S1**).

Table S1. Flow conditions regarding the synthesis of ligand L^1.

Experiment	F_{r1} (mL min^{-1})	F_{r2} (mL min^{-1})	F_{r3} (mL min^{-1})	t_R (min)
1	0.050	0.050	0.100	21.000
2	0.105	0.105	0.210	10.000
3	0.210	0.210	0.420	5.000
4	0.320	0.320	0.640	3.281
5	0.640	0.640	1.280	1.641
6	0.900	0.900	1.800	1.167
7	1.200	1.200	2.400	0.875
8	0.140	0.140	0.280	10.000

^{1}H-NMR: (CH_3CN, 43 MHz): δ = two broad signals corresponding to the imine and aromatic protons are present between 8.76 and 8.39 ppm, and between 8.18 and 7.19 ppm; at 4.82 ppm is present a broad signal corresponding to the C*H*$_2$ protons of the benzyl group. **^{1}H-NMR:** (CD_3CN, 400 MHz): δ = 8.63 (ddd, 1H, ^3J = 4.9 *Hz*, ^4J = 1.7 *Hz*, ^5J = 0.9 *Hz*, C*H*Ar), 8.49 (bs, 1H, C*H*N), 8.00 (dt, 1H, ^3J_d= 7.9 *Hz,* ^3J_t = 0.9 *Hz*, C*H*Ar), 7.77 (tdd, 1H, ^3J_t = 7.7 *Hz,* ^4J = 1.7 *Hz*, ^5J = 0.6 *Hz*, C*H*Ar) 7.39-7.33 (m, 5H, C*H*Ar), 7.30-7.27 (m, 1H, C*H*Ar), 4.83 (s, 2H, C*H*$_2$) ppm. **^{13}C-NMR:** (CD_3CN, 100 MHz): δ = 163.6 (CHN), 155.5 (C_qAr), 150.2 (CHAr), 140.2 (C_qAr), 137.3 (CHAr), 129.2 (CHAr), 128.8 (CHAr), 127.7 (CHAr), 125.7 (CHAr), 121.3 (CHAr), 65.1 (CH_2) ppm. **MS-ESI:** *m/z* 197.2 $(L^1-H)^+$.

3.2 Synthesis of complex $[Cu(L^1)_2]$ (1)



2-pyridinecarboxaldehyde (1.07 g, 10 mmol), benzylamine (1.07 g, 10 mmol) and copper(I)tetrakisacetonitrile tetrafluoroborate (786.4 mg, 2.50 mmol) or copper(I)tetrakisacetonitrile hexafluorophosphate (0.93 g, 2.50 mmol) were dissolved in acetonitrile (25 mL) resulting in 3 solutions having a concentration of 0.4 M, 0.4 M and 0.1 M respectively. 2-pyridinecarboxaldehyde (3.55 mL) and benzylamine (3.55 mL) were pumped with the same flow rate F_{r1} and F_{r2} to a 3 way connector. The output, a colorless reaction solution, had a total flow rate F_{r3} and was further mixed at flow rate F_{r4} (the same flow rate of the ligand) with the copper(I)tetrakisacetonitrile tetrafluoroborate solution or copper(I)tetrakisacetonitrile hexafluorophosphate (5 mL), for a total flow rate of F_{r5}. In each experiment, the flow rates of the 2 equimolar solutions were chosen in order to keep the ligand : metal ratio as 2 : 1. The complexation of **L^1** with copper(I)tetrakisacetonitrile tetrafluoroborate was investigated using different flow conditions; different flow rates and residence time relative to each of these experiments are reported in **Table S2**.

Table S2. Flow conditions regarding the synthesis of complex **1**.

Exper.	F_{r1} (mL min^{-1})	F_{r2} (mL min^{-1})	F_{r3} (mL min^{-1})	F_{r4} (mL min^{-1})	F_{r5} (mL min^{-1})	t_{R1} (min)	t_{R2} (min)
1	0.050	0.050	0.100	0.100	0.200	21.000	3.500
2	0.105	0.105	0.210	0.210	0.420	10.000	1.667
3	0.320	0.320	0.640	0.640	1.280	3.281	0.547
4	0.640	0.640	1.280	1.280	2.560	1.641	0.273
5	0.900	0.900	1.800	1.800	3.600	1.167	0.194

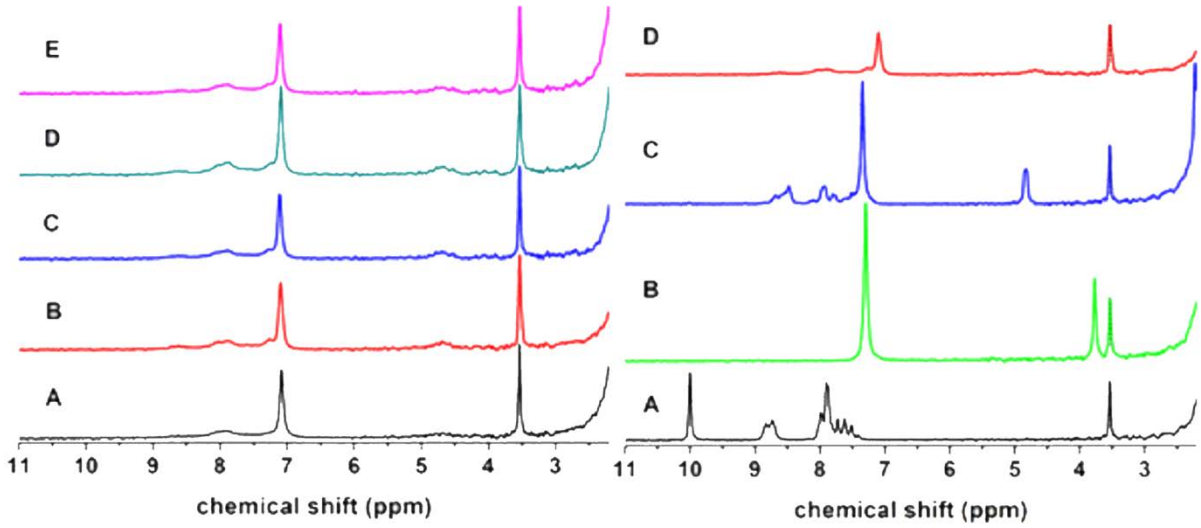


Figure S2. Normalized spectra**. Left**: Comparison of ^{1}H-NMR spectra collected in-line during the synthesis in flow of compound **1** at different flow rates; **A)** 0.2 mL min^{-1}, **B)** 0.42 mL min^{-1}, **C)** 1.28 mL min^{-1}, **D)** 2.56 mL min^{-1}, **E)** 3.6 mL min^{-1}. **Right**: Comparison of ^{1}H-NMR spectra collected in-line during the synthesis in flow of compound **1**; **A)** 2-pyridinecarboxaldehyde, **B**) benzylamine, **C)** *N*-(2-pyridinylmethylene)-benzenemethanamine (**L^{1}**), **D)** complex **1**.

Experiment 2 of **Table S2** was repeated connecting the output of the second flow reactor to a flow ESI-MS, and mass spectra were collected in real-time to follow the reaction progress (See **Figure S3**).

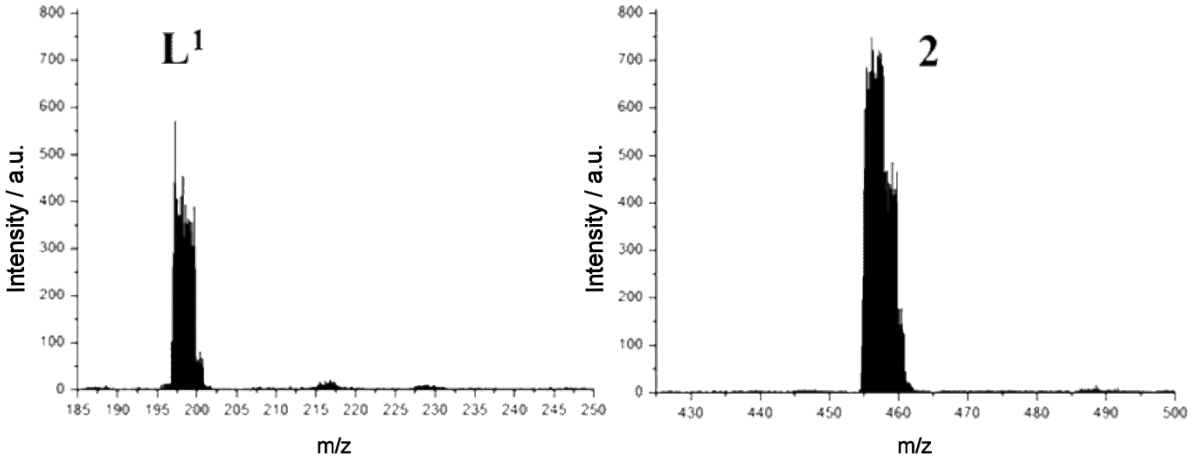


Figure S3. ESI-MS spectra of the ligand **L^1, left** (m/z 197.2) and the complex **1 right** (m/z 455.4) synthesised in flow and measured in-line.

^{1}H-NMR: (CH_3CN, 43 MHz): δ two broad signals corresponding to the imine and aromatic protons are present between 8.78 and 8.52 ppm, and between 8.21and 6.93 ppm; between 4.81 and 4.56 ppm is present a broad signal corresponding to the C*H*$_2$ protons of the benzyl group. **^{1}H-NMR:** (CH_3CN, 400 MHz): δ = 8.63 (bs, 2H, C*H*N), 8.02 (bs, 4H, C*H*Ar), 7.80 (bs, 2H, C*H*Ar), 7.50 (bs, 2H, C*H*Ar), 7.10 (bs, 10H, C*H*Ar), 4.68 (bs, 4H, C*H*$_2$) ppm. **MS-ESI:** *m/z* 455.4 $[Cu(L^1)_2]^+$.

3.3 $[Cu_2(L^1)_4(\mu\text{-}CO_3)](BF_4)_2$ (2) & $[Cu_3(L^1)_6(\mu\text{-}CO_3)](PF_6)_2(OH)_2$ (3)

Both the complexations of **L^1** with copper(I)tetrakisacetonitrile or copper(I)tetrakisacetonitrile hexafluorophosphate gave a brown reaction mixture, but from the first synthetic process the monomer **1** gave a green crystalline product (**2**), resulting in the dimeric aggregation of this complex after standing at 7 °C for 14 days (50.2 mg, 43.8 µmol, 9 %); whilst from the latter, the monomer **1** gave a green blue crystalline product (**3**), resulting in the trimeric aggregation of the complex **1** after standing at 18 °C for 4 days (7.20 mg, 4.11 µmol, 1 %).

$[Cu_2(L^1)_4(\mu\text{-}CO_3)](BF_4)_2$ (2): Solid IR solid: (cm^{-1}) 3074 (C-H, aromatic, w), 1634 (s), 1597 (s), 1021 (b). **Elemental analysis:** calcd (%) for $C_{53}H_{48}B_2Cu_2F_8N_8O_3$ = C 55.56, H 4.22, N 9.78; found = C 55.60, H 4.22, N 9.78. **Magnetic susceptibility:** μ_{eff} = 3.07 B.M. (χ_M = 6.84 cm mol^{-1}, μ_{so} = 2.83 B. M., 2 unpaired electrons). **Crystallography data:** see **Table S3**. **MS-ESI:** *m/z* 455.4 $[Cu(L)_2]^+$.

$[Cu_3(L^1)_6(\mu\text{-}CO_3)](PF_6)_2(OH)_2$ (3): Solid IR: (cm^{-1}) 3076 (C-H, aromatic, w), 1640 and 1603 (s), 1345 (s), 1282(s), 1050. **Elemental analysis:** calcd (%) for $C_{79}H_{74}Cu_3F_{12}N_{12}O_5P_2$ = C 54.16, H 4.26, N 9.59; found = C 53.86, H 4.02, N 9.49. **Magnetic susceptibility:** μ_{eff} = 3.73 B.M. (χ_M = 5.99 cm mol^{-1}, μ_{so} = 3.87 B. M., 3 unpaired electrons). **Crystallography data:** See **Table S3**. **MS-ESI:** *m/z* 455.4 $[Cu(L)_2]^+$.

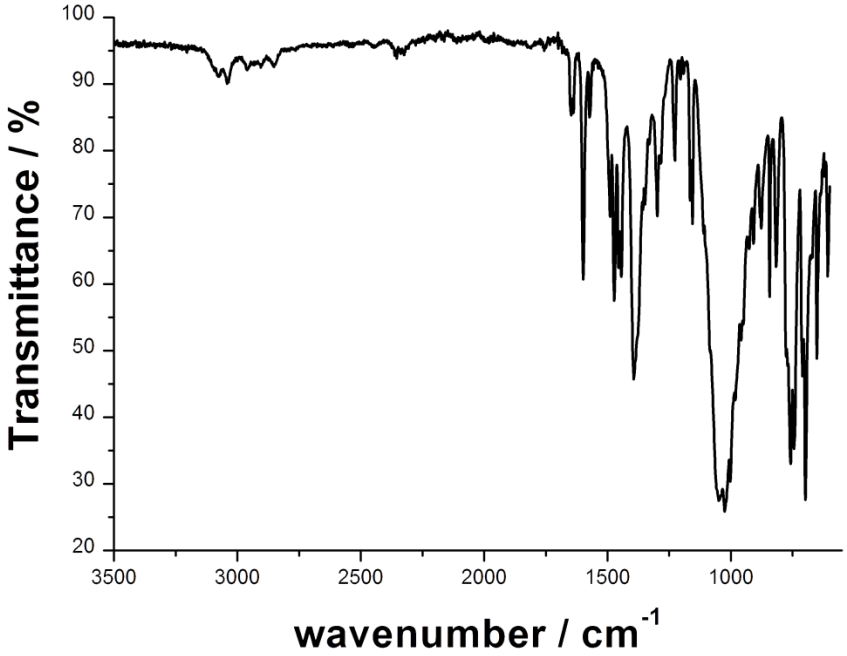


Figure S4. IR (solid) of $[Cu_2(L^1)_4(\mu\text{-}CO_3)](BF_4)_2$ **(2)**

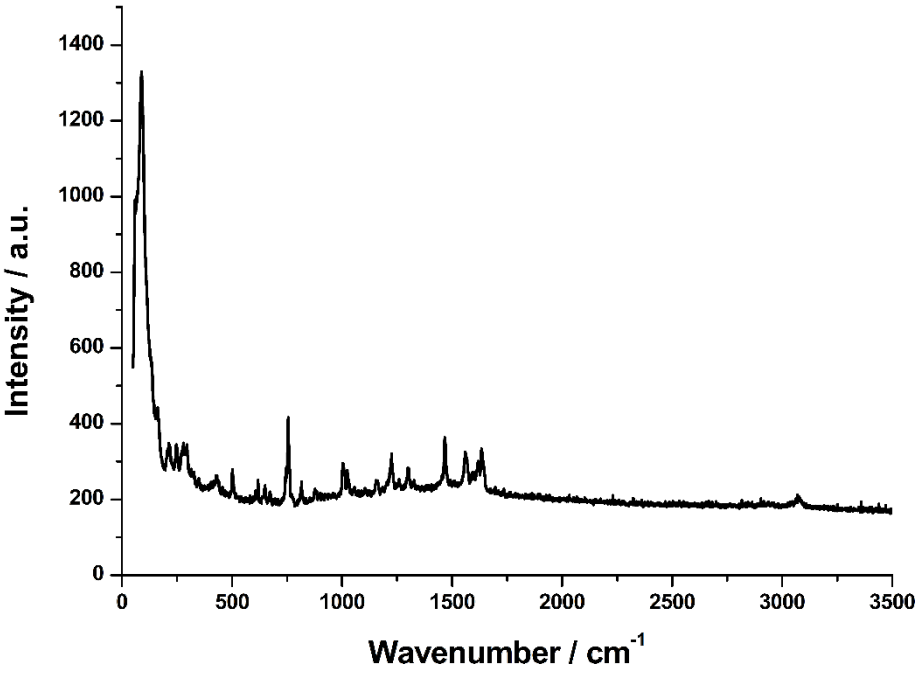


Figure S5. Raman (solid) of $[Cu_2(L^1)_4(\mu\text{-}CO_3)](BF_4)_2$ **(2)**

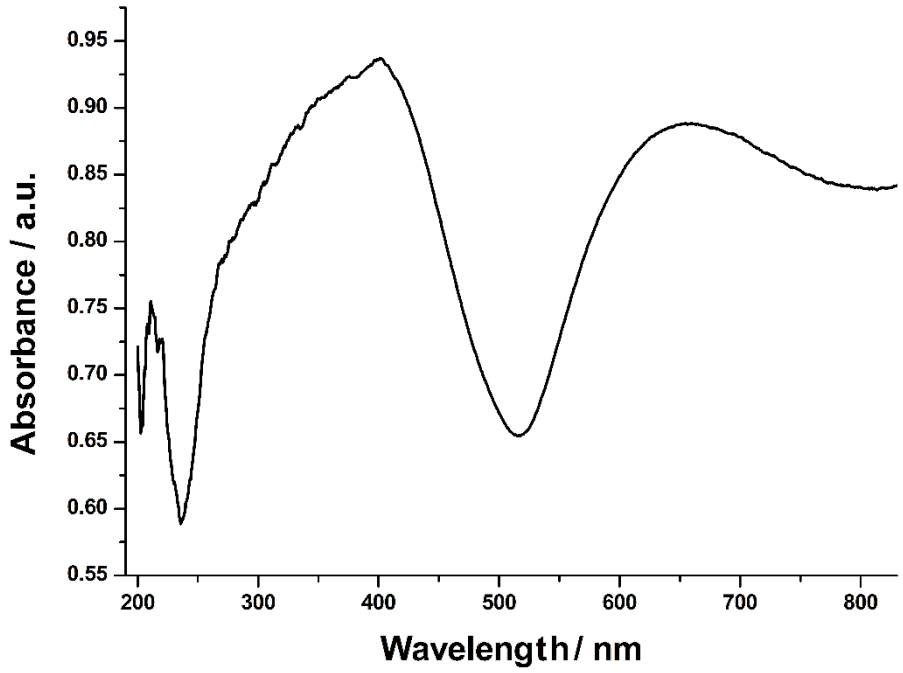


Figure S6. UV-vis (solid) of $[Cu_2(L^1)_4(\mu\text{-}CO_3)](BF_4)_2$ **(2)**

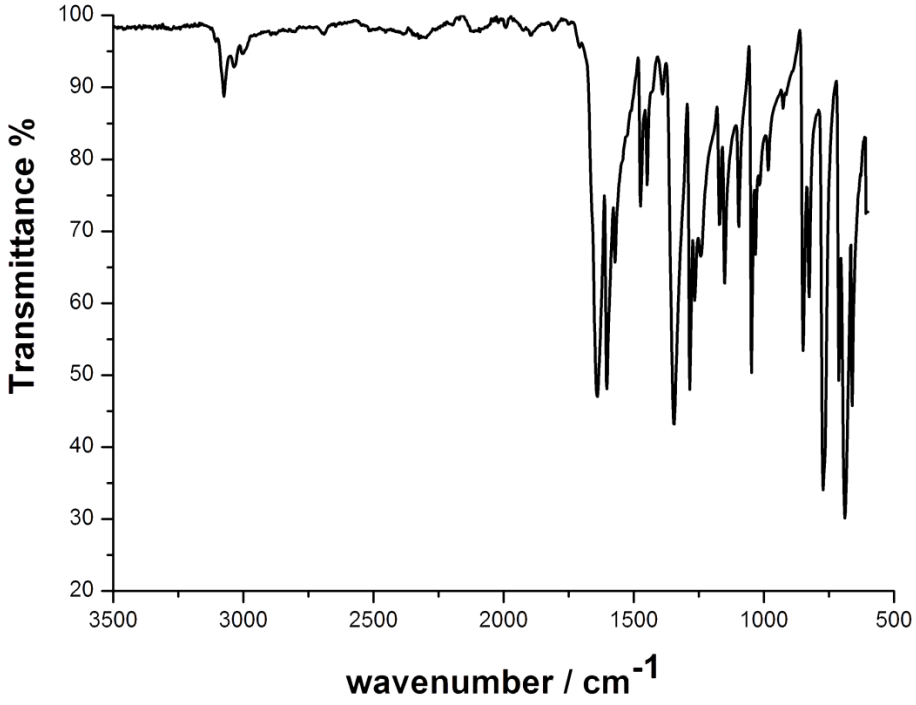


Figure S7. IR (solid) of $[Cu_3(L^1)_6(\mu\text{-}CO_3)](PF_6)_2(OH)_2$ **(3**)

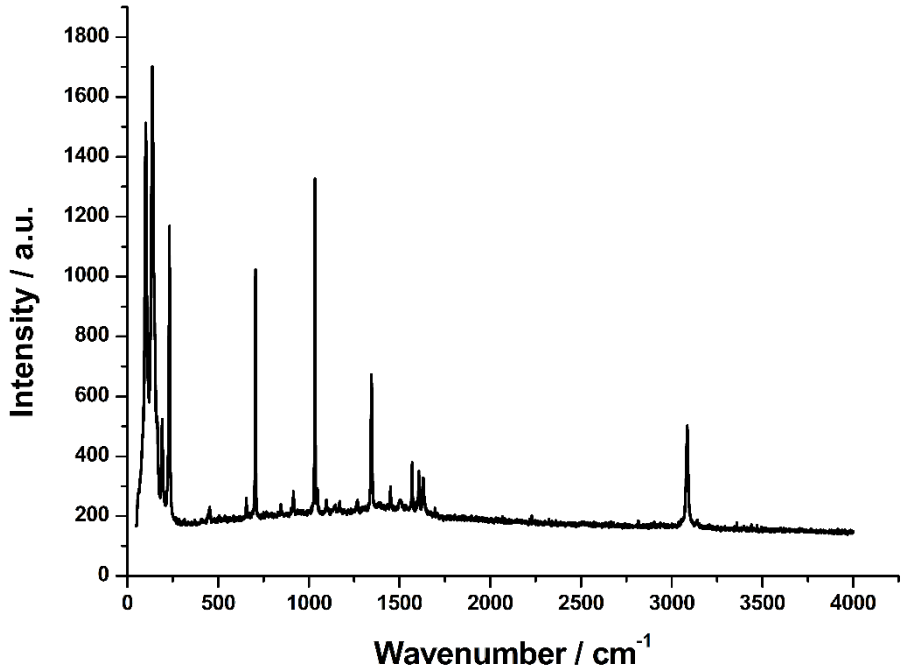


Figure S8. Raman (solid) of $[Cu_3(L^1)_6(\mu\text{-}CO_3)](PF_6)_2(OH)_2$ **(3)**

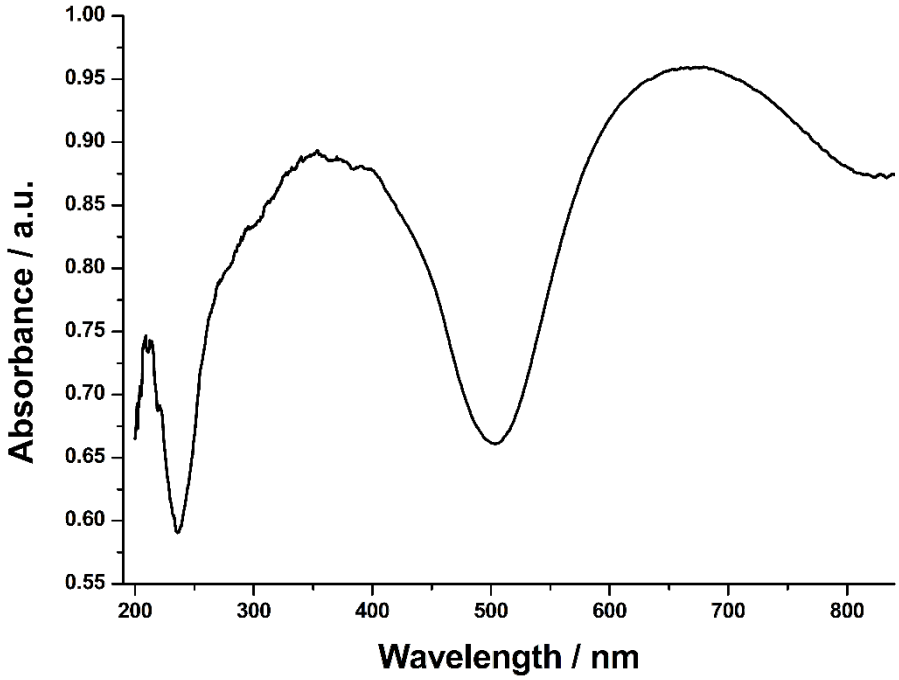


Figure S9. UV-vis (solid) of $[Cu_3(L^1)_6(\mu\text{-}CO_3)](PF_6)_2(OH)_2$ **(3)**

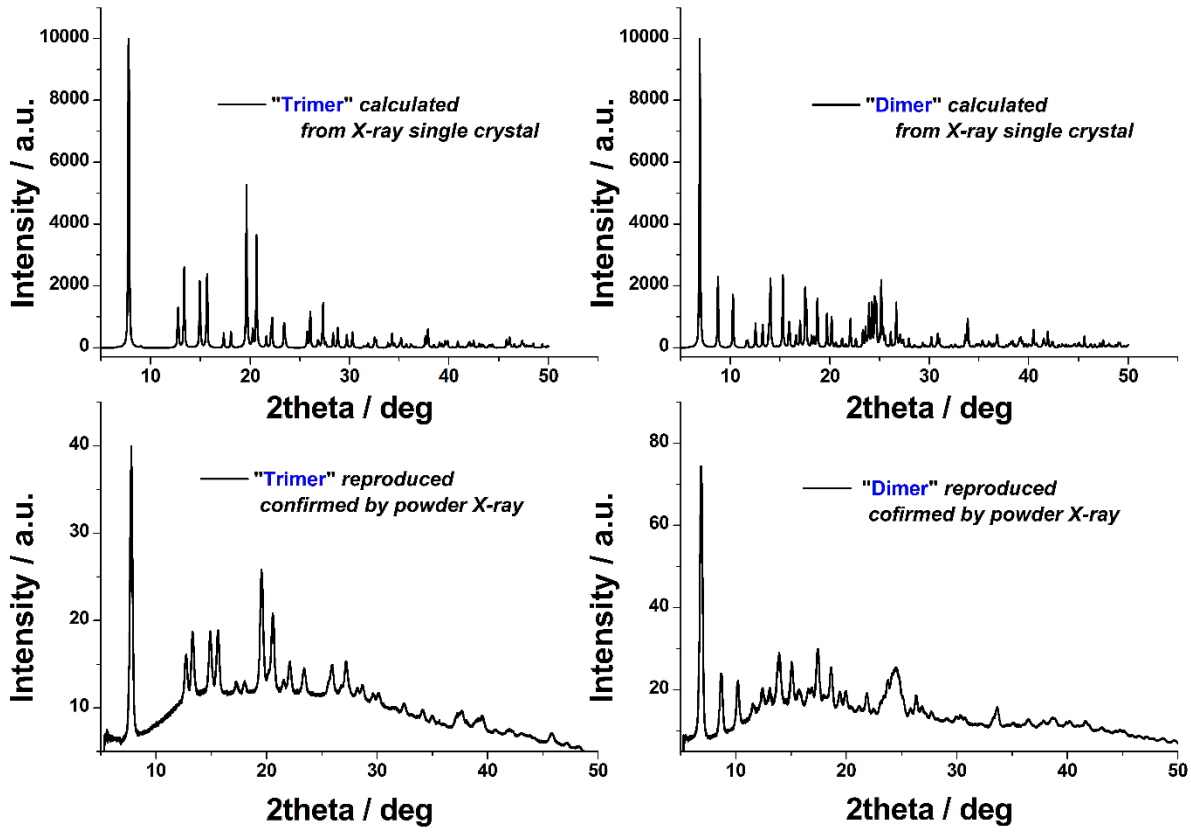
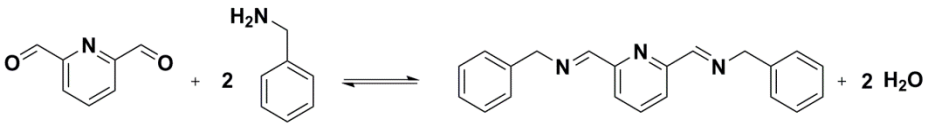


Figure S10. PXRD: **top left**: simulated pattern from single crystal $[Cu_2(L^1)_4(\mu\text{-}CO_3)](BF_4)_2$ **(2), top right**, simulated pattern from single crystal $[Cu_3(L^1)_6(\mu\text{-}CO_3)](PF_6)_2(OH)_2$ (**3**), **bottom left** PXRD measurement of reproduced material **(2)**, **bottom right**, PXRD measurement of reproduced material **(3)**

4. One-pot flow-syntheses with the tridentate ligand

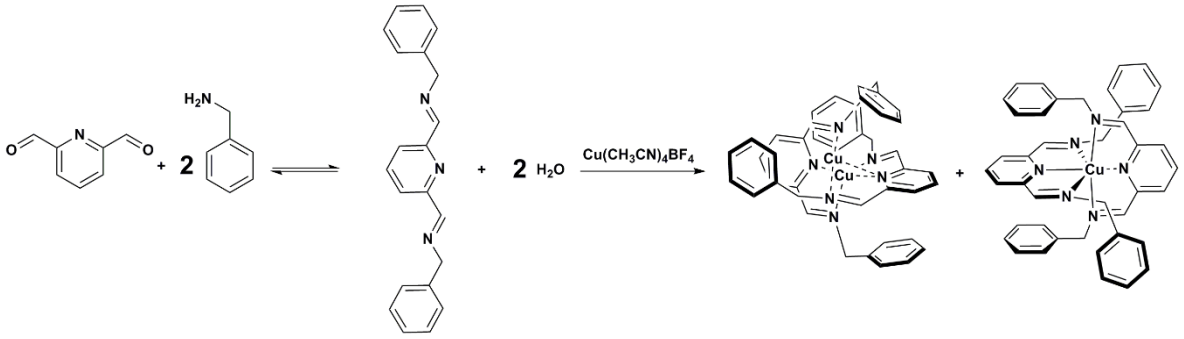
4.1 Synthesis of tridentate ligand $C_{21}H_{19}N_3$ (L^2)



2,6-pyridinedicarboxaldehyde (337.8 mg, 2.5 mmol), and benzylamine (275.1 mg, 2.5 mmol) were dissolved in acetonitrile (5 mL) resulting in 2 equimolar solutions with a concentration of 0.5 M. In each experiment 2,6-pyridinedicarboxaldehyde (2 mL) and benzylamine (4 mL) were pumped with flow rates of 0.155 mL min^{-1} (F_{r1}) and 0.310 mL min^{-1} (F_{r2}) respectively to a 3 way connector. These flow rates were chosen in order to keep the aldehyde : amine ratio as 1 : 2. The output, a colorless reaction solution, had a total flow rate of 0.465 mL min^{-1} (F_{r3}) and residence time of about 4.5 minutes (t_{R1}) and was introduced in the flow NMR tube and the ^{1}H-NMR was collected. This experiment was also repeated and monitored with a flow ESI-MS; in this case both flow reactors V_{R1} and V_{R2} were used to perform the ligand synthesis, resulting in a total reactor volume of 2.8 mL, and the output of it was connected to a flow ESI-MS. To keep the same t_{R1}, the flow reaction conditions were modified: F_{r1} = 0.205 mL min^{-1}, F_{r2} = 0.410 mL min^{-1} and F_{r3} = 0.615 mL min^{-1}.

^{1}H-NMR: (CH_3CN, 43 MHz): δ = two broad signals corresponding to the imine and aromatic protons are present as broad signals at 8.50, 7.98 and 7.34 ppm; at 4.86 and 3.86 ppm are present two broad signals corresponding to the C*H*$_2$ protons of the benzyl group of the ligand and residual unreacted benzylamine respectively. **^{1}H-NMR:** (CD_3CN, 400 MHz): δ = 8.50 (s, 2H, C*H*N), 8.04 (d, 2H, ^3J = 7.8 *Hz*, C*H*Ar), 7.86 (t, 1H, ^3J = 7.8 *Hz*, C*H*Ar), 7.38-7.34 (m, 8H, C*H*Ar), 7.31-7.26 (m, 2H, C*H*Ar), 4.86 (s, 4H) ppm. **^{13}C-NMR:** (CD_3CN, 100 MHz): δ = 163.1 (*C*HN), 155.3 (C_qAr), 140.0 (C_qAr), 138.1 (CHAr), 129.2 (CHAr), 128.9 (CHAr), 127.8 (CHAr), 122.5 (CHAr), 65.0 (CH_2) ppm. **MS-ESI:** *m/z* 314.4 $(L^2+H)^+$.

4.2 $[Cu_2(L^2)_2](BF_4)_2$ (4) & $[Cu(L^2)_2](BF_4)_2 \cdot CH_3CN$ (5)



2,6-pyridinedicarboxaldehyde (337.8 mg, 2.5 mmol), benzylamine (275.1 mg, 2.5 mmol) and copper(I)tetrakisacetonitrile tetrafluoroborate (157.28 mg, 0.5 mmol) were dissolved in acetonitrile (5 mL), resulting in a concentration of 0.5 M, 0.5 M and 0.1 M respectively. 2-pyridinecarboxaldehyde (2 mL) and benzylamine (4 mL) were pumped with flow rates of 0.155 mL min^{-1} (F_{r1}) and 0.310 mL min^{-1} (F_{r2}) respectively to a 3 way connector (as described for the ligand synthesis). The output, a colorless reaction solution, had a total flow rate of 0.465 mL/min (F_{r3}) and residence time of about 4.5 minutes (t_{R1}) and was further mixed at the flow rate of 0.3875 mL min^{-1} (F_{r4}), with the copper(I)tetrakisacetonitrile tetrafluoroborate solution (3.25 mL), for a total flow rate of 0.8525 mL min^{-1} (F_{r5}) and residence time of about 0.82 minutes (t_{R2}). The flow rates of the solutions were chosen in order to keep the aldehyde : amine ratio to 1 : 2 and the ligand : metal ratio to 2 : 1. The output, a brown reaction solution was introduced in the flow NMR tube and the ^{1}H-NMR was collected (**Figure S11**).

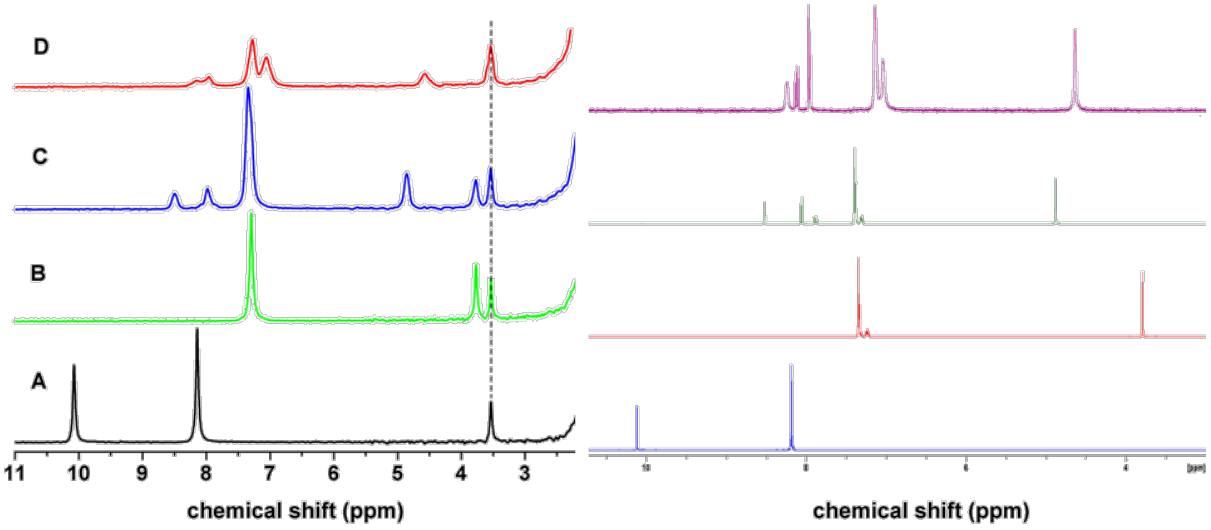


Figure S11. left: Flow ^{1}H-NMR (43 MHz), **Right**: High field ^{1}H-NMR(400 MHz); **A)** 2,6-pyridinedicarboxaldehyde, **B)** benzylamine, **C)** 2,6-bis(*N*-benzyliminomethyl)pyridine (**L^2**), **D)** complex **5.**

^{1}H-NMR: (CH_3CN, 43 MHz): δ two broad signals corresponding to the imine and aromatic protons are present between 8.30 and 7.86 ppm and between 7.41 and 6.88 ppm; at 4.57 ppm is present t broad signal corresponding to the CH_2 protons of the benzyl group. **^{1}H-NMR:** (CD_3CN, 400 MHz): δ = 8.22 (bs, 4H, C*H*N), 8.10 (t, 2H, ^{3}J = 7.7 *Hz*, C*H*Ar), 7.94 (d, 4H, ^{3}J = 7.7 *Hz*, C*H*Ar), 7.11 (bs, 12H, C*H*Ar), 7.02 (bs, 8H, C*H*Ar), 4.62 (bs, 8H, CH_2) ppm. **^{13}C-NMR:** (CD_3CN, 100 MHz): δ = 160.4 (*C*HN), 151.5 (C_qAr), 139.1 (CHAr), 138.1 (C_qAr), 129.4 (CHAr), 128.9 (CHAr), 128.2 (CHAr), 127.4 (CHAr), 63.7 (CH_2) ppm.

The same experiment, with the same reaction conditions was repeated to follow the progress of the reaction by ESI-MS (**Figure S12**). Brown crystals (**4**) were obtained after standing at 25 °C for 4 days; from the same solution mixture a green crystalline product (**5**) was obtained after standing for a further 6 days. **ESI-MS:** *m/z* 689.4 $[Cu(L^2)_2]^+$ (**5**), 376.2 $[Cu_2(L^2)_2]^{2+}$ (4).

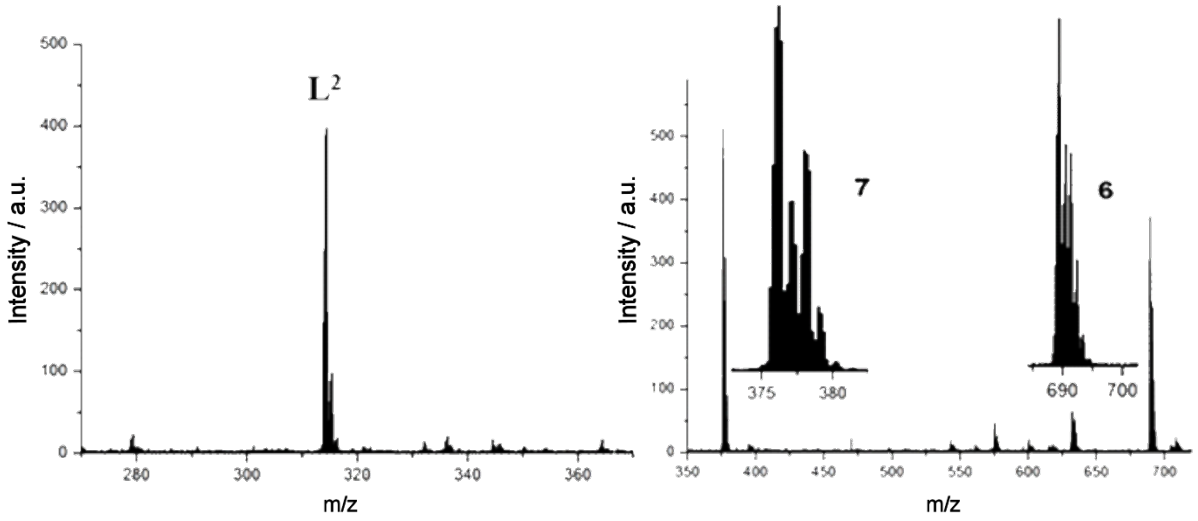


Figure S12. **Left*:*** ESI-MS spectra of ligand **L²** (m/z 314.4), **right:** compound **4** ($[Cu_2(L^2)_2]^{2+}$ m/z 376.2) and compound **5** ($[Cu(L^2)_2]^+$ m/z 689.4)**.**

5. Crystallographic details

Table S3: Crystallographic details

	2	**3**
chemical formula	$C_{53}H_{48}B_2Cu_2F_8N_8O_3$	$C_{79}H_{74}Cu_3F_{12}N_{12}O_5P_2$
formula mass	1145,69	1752.06
crystal system	Monoclinic	Trigonal
space group	$P2_1/c$	$R\text{-}3c$
a (Å)	7.5600(6)	13.8259(10)
b (Å)	20.2225(16)	13.8259(10)
c (Å)	16.4909(12)	68.225(10)
α (deg)	90	90
β (deg)	94.726(5)	90
γ (deg)	90	120
V (Å^3)	2512.6(3)	11294(2)
Z	2	6
Density (Mg/m^3)	1.514	1.546
μ (mm^{-1}) (Mo-$K\alpha$)	0.930	0.974
F(000)	1172	5382
Crystal size (mm^3)	0.080 * 0.040 * 0.040	0.090 * 0.050 * 0.040
ϑ range (deg)	2.014 – 24.987	2.078 – 25.985
data collected	31718	26387
unique data (R_{int})	4393 (0.1129)	2447(0.0724)
Refined parameters	352	203
S	1.325	1.056
R_1 [$I > 2\sigma(I)$]	0.078	0.044
wR_2 (all data)	0.166	0.141
Extrema (e$^-$/Å^3)	0.45, -0.58	0.36, -0.37
CCDC number	1011863	1011858

Table S3: Crystallographic details (continued)

	4	**5**
chemical formula	$C_{42}H_{38}B_2Cu_2F_8N_6$	$C_{44}H_{41}B_2Cu_1F_8N_7$
formula mass	927.48	905.00
crystal system	Triclinic	Orthorhombic
space group	P-1	$P2_12_12_1$
a (Å)	10.9622(5)	11.5185(8)
b (Å)	11.7396(6)	18.7898(14)
c (Å)	18.0232(9)	19.2943(14)
α (deg)	72.041(2)	90
β (deg)	80.116(2)	90
γ (deg)	62.834(2)	90
V (Å^3)	1961.73(17)	4175.9(5)
Z	2	4
Density (Mg/m^3)	1.570	1.439
μ (mm^{-1}) (Mo-$K\alpha$)	1.163	0.601
F(000)	944	1860
Crystal size (mm^3)	0.090 * 0.050 *0.040	0.080 * 0.060 * 0.030

ϑ range (deg)	2.021 – 25.999	2.059 – 25.988
data collected	27260	31700
unique data (R_{int})	7689(0.0670)	8009 (0.0321)
Refined parameters	541	560
S	1.028	1.030
R_1 [$I > 2\sigma(I)$]	0.0396	0.033
wR_2 (all data)	0.1043	0.086
Extrema ($e^-/Å^3$)	1.560, -0.644	0.676, -0.292
CCDC number	1011861	1011860