Supporting Information

Room-Temperature Spin-Dependent Transport in Metalloporphyrin-Based Supramolecular Wires

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1. Break-junction single-molecule transport measurements

1.1. 1D histograms using a non-magnetized Ni tip: injecting from the Au substrate

Fig. S1.1 1D semi-log conductance histogram of the metal porphyrin wires (inset figure) bridging between the Au substrate and non-magnetized Ni tips. All conductance values have been extracted from Gaussian fits of the peaks. The applied bias was set to $-7.5$ mV.
1.2. 1D histograms using a non-magnetized Ni tip: injecting from the Ni tip

![Figures showing 1D histograms for Co-DPP, Ni-DPP, Cu-DPP, and Zn-DPP](image)

**Fig. S1.2** 1D semi-log conductance histogram of the metal porphyrin wires (inset figure) bridging between the Au substrate and non-magnetized Ni tips. All conductance values have been extracted from Gaussian fits of the peaks. The applied bias was set to +7.5 mV.
1.3. 1D histograms with non-functionalized magnetized Ni tip electrodes

Fig. S1.3 1D semi-log conductance histogram of the metal porphyrin wires (inset figure) bridging between the functionalized Au substrate and both α (blue) and β (orange) magnetically polarized Ni tips in the absence of the PyrMT axial ligand. Both histograms have been vertically offset for clarity. All conductance values have been extracted from Gaussian fits of the peaks. The applied bias was set to −7.5 mV.
1.4. 1D histograms of control experiments

Fig. S1.4 1D semi-log conductance histogram in the absence of molecule with both tip and surface functionalized with *PyrMT* groups (a) and in the absence of the *PyrMT* groups at the tip and substrate electrodes surfaces when [Cu(*DPP*)] is present in solution (b).
1.5. 1D histograms of rejected curves in the single-molecule experiments.

**Figure 1.5** 1D semi-log conductance histogram of the rejected curves for the single-molecule conductance histograms in main manuscript Figure 2. Both histograms have been vertically offset for clarity. The applied bias was set to $-7.5\text{ mV}$. 
1.6. 1D histograms under Ni tip magnetization and flowing current from tip to substrate.

Figure S1.6 Homologous 1D semi-log conductance histogram of those in the main manuscript Figure 2 under opposite Bias voltage, i.e. injecting the electrons from the nickel tip. All conductance values have been extracted from Gaussian fits of the peaks. The applied bias was set to +7.5 mV.
2. *Blinking* static charge transport measurements

Schematics of a static (blinking) STM break-junction experiment in Fig. S2.

**Fig. S2** Schematics describing the formation and breakdown of a static metalloporphyrin junction.
2.1. Samples of blinking events

Fig. S2.1 Representative individual “blink” traces corresponding to the formation of molecular junctions with the [Cu(DPP)] molecule showing the 3 conductance features labelled on the figure.
2.2. 2D conductance *blinking* maps using non magnetized Ni tips: injecting from the Au

**Fig. S2.2** 2D conductance *blinking* maps of the metalloporphyrins (figure insets) bridging between Au and non-magnetized Ni tips, obtained by accumulating hundreds of blinks at a common time origin and subtracted background. The 2D maps were normalized to a color scale versus the total number of counts, representing 100 counts the maximum and 0 counts the minimum. Applied voltage bias and initial setpoint currents were -7.5 mV and 7 nA, respectively.
2.3. Control blinking experiments

**Fig. S2.3** 2D conductance *blinking* maps for the experiments in the absence of molecule with both tip and surface functionalized with *PyrMT* groups (a) and in the absence of the *PyrMT* units at the tip and substrate electrodes surfaces when [Cu(DPP)] is present in solution (b).
2.4. Pulling during a molecular junction formation in a static STM break-junction experiment

(a) Pulling curves exerted during the static molecular junction formation (*blink*) showing mechanical resistance, confirming the molecular signature of the junction and its stability during the tip retraction. (b) Pulling exerted when the current is showing only the tunneling current background without a metalloporphyrin molecule bridged between the electrodes, which results in an exponential decay in the current without any mechanical resistance.

Fig. S2.4 (a) Pulling curves exerted during the static molecular junction formation (*blink*) showing mechanical resistance, confirming the molecular signature of the junction and its stability during the tip retraction. (b) Pulling exerted when the current is showing only the tunneling current background without a metalloporphyrin molecule bridged between the electrodes, which results in an exponential decay in the current without any mechanical resistance.
3. Characterization of the Ni tip magnetization

The magnitude of the magnetic polarization of the Ni tip was characterized before and after the STM experiment using SQUID magnetometry to ensure that the Ni magnetization persisted over the entire timeframe of the experiments (Fig. S3). The direction of the magnetized Ni tips was also characterized following the procedure used in previous works. [6] To avoid the Ni oxidation during magnetization and transport measurements under ambient conditions, the prepared Ni electrode was magnetically polarized and stored in strict anaerobic conditions before use. The Ni tip oxidation has been monitored during use by ex situ SEM-EDS electron microscopy. [6] Before functionalizing the Ni tip, it is transferred to the STM cell, and driven several times towards the Au surface to get a light Au coating that protects the tip apex surface against further oxidation throughout the timeframe of the single-molecule transport experiments and ensures the correct pyridin-4-yl-methanethiol functionalization via Au-S covalent chemistry.

Fig. S3 SQUID measurements of different demagnetization times of Ni tips. Inset shows different magnetization times for Ni tips using the setup described in the manuscript and compared to the magnetization value achieved by the SQUID.
4. Additional technical details of the single-molecule transport measurements

All glassware and PFTE homemade-STM cells were cleaned with piranha solution (3:1 H₂SO₄/H₂O₂ by volume) before usage, followed by rinsing with 18 MΩ cm⁻¹ Milli-Q water (Millipore). An Au (111) single crystal substrate (10 mm x 1 mm) of 99.99% purity and orientation accuracy < 0.1 degrees was purchased from MaTeck (Germany). Before each experiment, the Au(111) crystal substrate was electropolished to eliminate possible residual contamination and then annealed with a H₂ flame. The surfaces were then washed with Ar-purged ethanol and dried under a stream of Ar after which they were placed in 5 mM ethanol solution of pyridin-4-yl-methanethiol previously purged with Ar and protected from the light for 24 h. Polycrystalline Ni tips (99.99%, Godfellow, UK) were mechanically cut, coated with Au (see SI section S3), immersed in 5 mM ethanol solution of pyridin-4-yl-methanethiol previously purged with Ar and protected from light for 24 h. Next, the functionalized Ni tips were washed thoroughly with ethanol and dried under a stream of Ar and then magnetized for 2h (see SI section S3). To avoid the Ni tips oxidation under ambient conditions, they were magnetically polarized and stored under anaerobic conditions before use, as we report in previous works.[6] The Au (111) surface, after the functionalization step, was also washed thoroughly with ethanol and dried under a stream of Ar. The Au (111) surface was then assembled in the STM cell and filled with an 80 μL of pure mesitylene, where STM junction control experiments were firstly run. Next, few drops of an 8-12 nM mesitylene solution of the M-DPP were added to build the porphyrin-based supramolecular wires.

An STM-BJ method was employed to build and characterize charge transport through single-molecule wires built with the different metal complexes studied in this work. All experiments were carried out with a homemade PFTE-STM cell and a PicoSPM II microscope head controlled using a Picoscan 2500 electronics, all from Agilent (USA). The STM head was mechanically and electronically isolated. Data was acquired using a NI-DAQmx/BNC-2110 National Instruments (LabVIEW data acquisition System, USA) and analyzed with LabVIEW code. In a typical BJSTM, the STM tip is first brought to tunneling distance over a flat clean Au(111) surface area. The STM feedback is then turned off and the tip is driven into and out of contact with the substrate at 1 V/s. These 2-points feedback loop is used to collect thousands of current decays during the tip pulling cycles.[8] In order to minimize disruption of the tip and sample surface functionalization, the attained maximum current in the 2-points feedback loop was set to a low value well below saturation, which prevented the STM tip crashing against the substrate electrode. Because not every curve displayed plateau features corresponding to the molecular quantum conductance of the single-molecule bridge, we designed by LabVIEW code an automatic algorithm that identify and select curves containing them. The user defines the initial selection criteria that are fixed throughout all the experimental series.15-20% of the total collected current decays (~5000) display steps (plateaus),[6] [7, 9] and are used to determine the single molecule conductance using the expression $G = \frac{I_{\text{step}}}{U_{\text{bias}}}$ where $G$ is the conductance, $I$ is the current and $U$ is the potential.
difference between the two junction electrodes. The current decays are accumulated to form 1D semi-logarithmic conductance histograms. The observed peaks in the conductance histograms correspond to the observed plateaus in the current decays and provide averaged single-molecule conductance values. The bias voltage between the tip and substrate electrodes was set to −7.5 mV or +7.5 mV depending on the choice of applied current direction. In blinking static molecular conductance experiments when the target molecule is trapped between the functionalized electrodes, an abrupt jump of the tunneling current in the form of telegraphic blinks is observed.\(^{5b, 10a, 11}\) 2D conductance maps were built by the accumulation of hundreds of these individual blinks. No selection was applied to the data, so all blinking traces were used to build the histograms. In order to compare the lifetimes of the blinks in the 2D conductance maps, all the captures were set into a common time origin and subtracted background. The final STM tip pulling after the blinking was performed by externally controlling the piezo Z-position (see SI section 2.4).

5. Computational Details

Transport calculations were performed using the Siesta\(^{12}\) and Gollum\(^{13}\) codes with the molecule sandwiched between five Au layers with a 5 x 4 surface unit cell using the with the GGA+U functional (U = 4.0 eV) using the GGA exchange-correlation functional proposed by van Voorhis\(^{14}\) and coworkers to include dispersion effects. The +U methodology with PBE\(^{15}\) functional was employed to have semiquantitative conductance values because the energies of the frontier orbitals if they involve d metal orbitals are improved in comparison with common GGA functionals. A double-ζ basis set with polarization was combined with pseudopotentials. For Au atoms, two pseudopotentials have been employed: 11e\(^−\) pseudopotential for optimizations and 1e\(^−\) pseudopotential\(^{16}\) to calculate the transport properties. For the first-row transition metal atoms, a semicore pseudopotential was used, thus, the orbitals 3p were considered within the basis sets. To obtain the conductance value, we approximate \(G = T(E)G_0\) which should be suitable for very low biases. The accuracy reached with such approach allow to determine in a semiquantitative level the conductance values without any modification of the Fermi level to reproduce the experimental data.

For the periodic calculations of the [M\(^{II}\)(DPP)] in the hexacoordinated and pentacoordinated cases (Figure 5 red and blue dots), the optimization of the three molecules were obtained from DFT calculations (B3LYP\(^{17}\) functional with a TZVP\(^{18}\) basis for H, C, N and S and QZVP\(^{19}\) basis set for metal atoms by means of the Gaussian09\(^{20}\) package). The key structural parameter is the axial M-N distance with the pyridine ligand, d(Co-N) = 2.432 Å, d(Ni-N) = 2.306 Å, d(Cu-N) = 2.728 Å, d(Zn-N) = 2.494 Å. The previously optimized molecules were attached to 3 Au atoms to each S thiol end with a S-Au surface distance of 2.2 Å (hollow position). The distance of 4.0 Å between the [Zn\(^{II}\)(DPP)(PyrMT)] molecule plane to the Au surface (on top position) for the pentacoordinated system was previously reported.\(^{21}\) For other calculations in Figure 5 (green dots for I, II and III cases), the structure is fully optimized with the PBE+U approach implemented in the Siesta code fixing the Au electrode structure but allowing to optimize the interelectrode distance. All these
calculations were performed assuming an homolytic breaking of thiol S-H bond, thus, a triplet state was considered for the remaining S· radical groups.\[22\]

![Figure S5.1](image)

**Figure S5.1.** Graph (zoom in of Fig. 5) representing the experimental (black dots) and DFT calculated conductance values (green dots) for the three conductance feature I (A), II (B) and III (C) calculated using DFT optimized stacking structures (see Fig. 5) but the Zn case with only one axial ligand.

The Artaios[23]/Gaussian calculations were performed using the optimized structures with Siesta. In such periodic structures, the electrodes were cut to build discrete electrodes of enough size to interact with the PyrMT molecules and 2-layer width. All the periodic and discrete structures are provided as individual files as SI. These calculations were carried out using the TPSSh[24] functional and the LANL2DZ[25] basis set for all the atoms. In the case of the Ni-DPP system coordinated to the two axial PyrMT ligands, also the TPSSh functional was employed in the Gaussian code (see SI section 5) because it provides better estimation of the state energies than the B3LYP one.[26] TDDFT calculations were performed using the same TPSSh functional[24a] and Def2-TZVP basis set.

5.1 DFT calculations of high and low spin states of the [Ni(DPP)]/PyrMT system

The calculations were performed by optimizing the geometries for the S = 1 and S = 0 states with the Gaussian09 code (see Computational Details in the main text). We have employed the TPSSh functional because provides a better estimation of the state energies of transition metal complexes using just the [Ni(DPP)(PyrMT)$_2$] system without metal electrodes. The results indicate a small preference of 6 kcal/mol for the high spin state for the [Ni(DPP)(PyrMT)$_2$] complex with pseudooctahedral coordination with the two axial PyrMT ligands in a parallel orientation with metalloporphyrin plane (see HC in Fig. 5.1). It is well known the tendency of the Ni$^{II}$ complexes to change from low-spin S = 0 state in square planar coordination mode (14 kcal/mol more stable the [Ni(DPP)]) to high-spin S = 1 in octahedral systems with the PyrMT ligands in a perpendicular orientation respect to the metalloporphyrin (9 kcal/mol more stable). In this case, the position of the axial ligands is
strongly affected by the interaction with the electrodes and such interaction can modify the subtle energy difference between the two states to stabilize the $S = 0$ ground state as found experimentally by the lack of magnetoresistance effect that is not consistent with a $S = 1$ high-spin state.

The highest experimental conductance found for feature I in the [Zn$^{II}$$(DPP)$] system is counterintuitive for a closed shell system. As suggested from the above experimental results (Fig. S1.3), the strong pentacoordination character of Zn forces a top contact of the [Zn$^{II}$$(DPP)$] to the tip electrode via the bare metal, with an important reduction in the transmission pathway length and corresponding increase in conductance. The analysis of the interaction energies for the other three metals between the [M$^{II}$$(DPP)$] and the hexacoordinated $PyrMT$ ligands are collected in Table S5 showing a continuous decrease from features I to III due to the substitution of metal-$PyrMT$ interactions by porphyrin-$PyrMT$ contacts. The M-N distances for feature I are 2.505 (Co), 2.752 (Ni), 2.633 (Cu) and 2.759 Å (Zn). It is worth noting the long axial Ni-N distances favoring the low-spin state, in agreement with the experimental lack of magnetoresistance. Due to the d$^8$ electronic configuration, a short axial Ni-N distance would stabilize the triplet state which might result otherwise in a magnetoresistive junction.

Table S5.1. Calculated metalloporphyrine/PyrMT interaction energies (in kcal/mol) of the four optimized systems for the three observed conductance peaks (see Fig. 5).

|        | [Co$(DPP)$] | [Ni$(DPP)$] | [Cu$(DPP)$] | (Zn$(DPP)$) |
|--------|-------------|-------------|-------------|-------------|
| **HC** | -42.0       | -31.9       | -37.6       | -10.1*      |
| **MC** | -30.8       | -23.1       | -32.8       | -31.4       |
| **LC** | -18.6       | -18.2       | -18.6       | -19.7       |

*only one $PyrMT$ for pentacoordination
5.2 DOS and Transmission Spectra for all Systems.

| System | PDOS | T(E) |
|--------|------|------|
| [Co(DPP)] | ![PDOS](image1) | ![T(E)](image2) | HC | U=4eV | $6.84 \cdot 10^{-2} G_0$ |
|        | ![PDOS](image3) | ![T(E)](image4) | MC | U=4eV | $6.81 \cdot 10^{-3} G_0$ |
|        | ![PDOS](image5) | ![T(E)](image6) | LC | U=4eV | $4.50 \cdot 10^{-3} G_0$ |

**Fig. S5.2** Optimized structures at PBE+U level with the DOS and transmission curves for the [Co(DPP)] system and the calculated conductance value.
| [Ni(DPP)] | PDOS | T(E) |
|-----------|------|------|
| HC        | ![PDOS](image) | ![T(E)](image) |
| U=4eV     | $4.96 \cdot 10^{-2} G_0$ |
| MC        | ![PDOS](image) | ![T(E)](image) |
| U=4eV     | $6.66 \cdot 10^{-3} G_0$ |
| LC        | ![PDOS](image) | ![T(E)](image) |
| U=4eV     | $3.92 \cdot 10^{-3} G_0$ |

Fig. S5.3 Optimized structures at PBE+U level with the DOS and transmission curves for the [Ni(DPP)] system and the calculated conductance value.
**Table 1**

| [Cu(DPP)] | PDOS | T(E) |
|-----------|------|------|
| **HC**    | ![PDOS](image1) | ![T(E)](image2) |
| U=4eV     | 6.57·10⁻² G₀ |
| **MC**    | ![PDOS](image3) | ![T(E)](image4) |
| U=4eV     | 7.04·10⁻³ G₀ |
| **LC**    | ![PDOS](image5) | ![T(E)](image6) |
| U=4eV     | 5.06·10⁻³ G₀ |

**Fig. S5.4** Optimized structures at PBE+U level with the DOS and transmission curves for the [Cu(DPP)] system and the calculated conductance value.
Fig. S5.5 Optimized structures at PBE+U level with the DOS and transmission curves for the [Zn(DPP)] system and the calculated conductance value.
5.3 Hybrid functional calculations [Co(DPP)]/PyrMT and [Cu(DPP)]/(PyrMT) systems

In addition to periodic calculations, we performed more accurate molecular calculations with Artaios/Gaussian codes using a hybrid B3LYP orbital and non-periodic electrodes. Such hybrid functional calculations are employed as control to identify if PBE+U corrects the main deficiencies of the GGA functionals on the energy levels due to the self-interaction error. The transmission curves (Figure S5.6) are very similar to those of Figure 6 indicating that the PBE+U approach provides a sufficiently good description of the energy levels of the ground state of the studied systems.

Fig. S5.6 Transmission curves and frontier orbitals calculated with the hybrid meta-GGA TPSSh functional using Gaussian/Artaios codes for the [Co(DPP)] and [Cu(DPP)] systems.
5.4 TDDFT calculations \([\text{Co(DPP)}]/\text{PyrMT}\) and \([\text{Cu(DPP)}]/(\text{PyrMT})\) systems

To understand the spin polarization of \([\text{Co(DPP)}]\) and \([\text{Cu(DPP)}]\), we analyzed orbital and excitation energies for these systems in further detail. TPSSH density functional calculations for six, five and four coordinated systems show the presence of metal centered and ligand centered orbitals among the frontier manifold. Calculations locate most of the spin population in the metal center, being consistent with the presence of \(S=1/2\) metal centers associated with \(\text{LS-Co}^{II}\) and \(\text{Cu}^{II}\) ions (see Table 1).

**Table 5.2.** Löwdin spin populations for Cu and Co atoms in TPSSH/Def2-TZVP models and different coordination numbers by suppressing the axial \(\text{PyrMT}\) ligands.

| CN | Metal Co | Metal Cu |
|----|----------|----------|
| 4  | 1.08     | 0.61     |
| 5  | 1.03     | 0.63     |
| 6  | 0.99     | 0.65     |

Understanding the coexistence of ligand and metal dominated orbitals near the Fermi level is important to rationalize the origin of spin-polarized transport for \([\text{Co(DPP)}]\) and \([\text{Cu(DPP)}]\). Figure S5.7 shows the orbital energies and their metal contribution for the frontier orbitals. We observe that coordination number does not change the frontier orbital pattern dramatically, where several metal and ligand orbitals are identified in all cases. Regarding \([\text{Co(DPP)}]\), both alpha and beta HOMO orbitals are mainly ligand centered (black line without colored contribution next to it) while metal orbitals appear between HOMO-1 and HOMO-3, (black line next to an intense red (alpha) or (blue) beta line). The alpha LUMO has a significant metal contribution while beta LUMO is more ligand-centered. \([\text{Cu(DPP)}]\) shows ligand centered HOMO and HOMO-1 orbitals for both spin orientations while more stable orbitals start to show some metal contribution. The LUMO is always metal centered and corresponds to the \(d_{x^2-y^2}\) orbital. Such electronic structures are fully consistent with those obtained with the periodic and non-periodic calculations including the electrodes.
Fig. S5.7 Orbital energies for the [Co/Cu(DPP)(PyrMT)x] (x=0,1,2) systems. Alpha: red, beta: blue. The dashed line separates occupied from virtual orbitals. The intensity of the colored line indicates a larger metal contribution.

The analysis of Kohn-Sham orbital energies is often used to identify which orbitals are relevant for electron transport. In our case, the different nature of the frontier orbitals and their small energy differences recommends calculating low energy excitations to identify which electronic transitions are more energetically accessible. TD-DFT calculations were performed for all systems and are presented in Figures S5.8. The [Co(DPP)] spectra tend to have more than one allowed transition near 600 nm, while longer wavelengths feature several electric dipole forbidden transitions. Focusing on the lower energy ones, we observe a significant contribution of cobalt orbitals participating in d-d transitions (black vertical lines), metal-ligand (green) and ligand-metal (pink) charge transfer. Copper spectra show a similar
pattern, where allowed transactions appear at a slightly higher energy. Again, lowest energy excitations are dark and show a significant participation of ligand to metal charge transfer, confirming the participation of Cu orbitals in the low energy excited states of this system.

Fig. S5.8  TD-DFT spectrum (TPSSh functional and Def2-TZVP basis set) for [M(DPP)(PyrMT)] and [M(DPP)] (the [M(DPP)(PyrMT)_2] results are represent in Fig. 9). Each transition is represented by a vertical line, where colors indicate their transition composition (metal-metal: black; metal-ligand: green; ligand-metal: pink; ligand-ligand: orange). Furthermore, the spin polarization of the transition is represented in the figure, red: spin up, blue: spin down.
6. Synthesis of main reagents and metal complexes, [M\textsuperscript{II}(DPP)].

DPP was purchased and used as received from Frontier Scientific company. Pyridin-4-ylmethanethiol (PyrMT) and [M\textsuperscript{II}-DPP] (being M = Co\textsuperscript{II} and Zn\textsuperscript{II}), were synthesized following the works of Puigmarti-Luis et. al.\textsuperscript{[1]} and Song et. al.\textsuperscript{[2]} respectively. In addition, the characterization of the [Co(DPP)] is shown in our previous work.\textsuperscript{[27]} [Ni(DPP)] and [Cu(DPP)] were synthesized in a similar manner as it is described for the rest and summarized below.

[Ni(DPP)]
100 mg (216 mmol) of DPP were dissolved in 30 mL of DMF. Then, 128 mg (707 mmol) of nickel acetate were added and the reaction was stirred at 120 °C for 6h and then at room temperature overnight. An extraction Brine/Hexane was performed and the organic phase was dried with magnesium sulfate. The volatiles were removed under vacuum and the precipitate obtained was crystallized with CH\textsubscript{2}Cl\textsubscript{2} and MeOH, obtaining a red solid of [Ni(DPP)] (55 mg of, 47%). \textsuperscript{1}H NMR (300MHz CDCl\textsubscript{3}): ppm 9.96 (s, 2H, meso-H), 9.21 (d, 4H, J= 6Hz Pirrolic C-H), 8.96 (d, 4H, J=6Hz Pirrolic C-H), 8.10 (d, 4H, J=9Hz orto C-H) 7.76 (t, 4H, J=9Hz meta C-H). Uv-Vis (CH\textsubscript{2}Cl\textsubscript{2}, 25°C): \(\lambda_{max}\) nm 405, 516, 548. MALDI-TOF/MS: m/z (%) 518 (100) [M]+.

Figure S6.1. NMR spectra of: A) free DPP and B) [Ni(DPP)] in CDCl\textsubscript{3}
Figure S6.2 UV-Vis spectrum of the Q-bands area of [Ni(DPP)] in CH$_2$Cl$_2$.

Figure S6.3 A) Experimental MALDI spectrum of the [Ni(DPP)] and B) its theoretical isotopic distribution.

[Cu(DPP)]

40 mg (86.4 mmol) of DPP were dissolved into 10 ml of DMF and 48 mg (265 mmol) of solid copper acetate were added to the mixture. The mixture was stirred for 4h at 120°C. After this time, the solvent was removed and an extraction was performed with CH$_2$Cl$_2$/H$_2$O, the organic phase was dried with magnesium sulfate and the volatiles were removed under vacuum. The solid obtained was crystallized with CH$_2$Cl$_2$/MeOH obtaining 22 mg (47.5
mmol) obtaining a purple solid of [Cu(DPP)] with a yield of 55%. UV-Vis (CH$_2$Cl$_2$, 25°C): λ$_{\text{max}}$ nm 403, 528, 562. MALDI-TOF/MS: m/z (%) 523 (100) [M]+.

**Figure S6.4** UV-Vis spectrum of [Cu(DPP)] in CH$_2$Cl$_2$ (inset Q-bands area)

**Figure 6.5:** A) Experimental MALDI spectrum of the [Cu(DPP)] and B) its theoretical isotopic distribution.
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