

Supporting Information

Cuprophilic Interactions in Highly Luminescent Dicopper(I)-NHC-Picolyl Complexes – Fast Phosphorescence or Thermally Activated Delayed Fluorescence?

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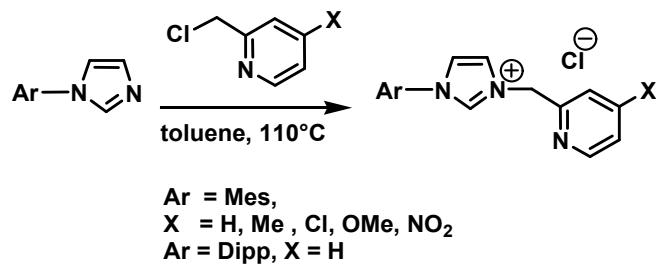
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Synthesis and characterization

Preparation of IMesPic·HCl and $[\text{Cu}_2\text{Cl}_2(\text{IMesPic})_2]$ (**2**) was performed as previously described.¹
² Compound $[\text{CuCl}(\text{IMesPic})]$ (**6**) was isolated upon allowing for longer crystallization times. Except otherwise stated, solvents and reagents were used as received. For complex synthesis, monodistilled water was used as solvent. NMR spectra were recorded with a Bruker AVANCE 400 spectrometer (¹H at 400 MHz, ¹³C at 100 MHz) at 298 K. Data are reported as chemical shifts (δ) in ppm. Residual solvent signals were used as internal references (¹H, ¹³C). Electrospray (positive mode) high resolution mass spectra were recorded on a Q-TOF microspectrometer (Waters), using internal (H_3PO_4) and external lock masses (leucine enkephalin $[\text{M} + \text{H}]^+$: m/z = 556.2766). Elemental analyses were performed at the Service de Microanalyse, Université Henry Poincaré, Vandoeuvre-les-Nancy, France.

General procedure for imidazolium salt synthesis:² 4-R-2-picolyl chloride hydrochloride (5 mmol)³ was suspended in 10 mL toluene and the resulting suspension was treated with 3 mL of saturated aqueous K_2CO_3 . The organic phase was transferred in a screw-cap pressure vial containing 1-aryl-imidazole⁴ (1 eq.). The resulting solution was heated with stirring at 110 °C for 1-3 days during which the desired product precipitates from the reaction mixture. The solid was collected by filtration and washed with toluene and *n*-pentane. The filtrate was concentrated to 5 mL and heated again for 1-3 days to yield a second crop of solid material.



IMesPic^{Me}·HCl: beige solid, 74% yield. ¹H NMR (400 MHz, CDCl_3) : δ 10.62 (s, 1H, NCHN), 8.40 (d, $J=4.9$ Hz, 1H, CH_{py}), 8.06 (broad, 1H, CH_{py}), 7.81 (s, 1H, CH_{imid}), 7.29 (m, 1H, H_{py}), 7.08 (s, 1H, CH_{imid}), 7.01 (s, 2H, CH_{Ar}), 6.13 (s, 2H, CH_2), 2.40 (s, 3H, $\text{CH}_{3\text{py}}$), 2.35 (s, 3H, CH_3), 2.06 (s, 6H, CH_3). ¹³C NMR (100 MHz, CDCl_3): δ =152.3 (C_{qpy}), [149.6, 149.1, (C_{qpy} , CH_{py})], 141.2 (CH_{imid}), 138.3 (C_{qAr}), 134.3 (C_{qAr}), 130.8 (C_{qAr}), 129.8 (CH_{Ar}), [125.9, 125.0, 123.8, 122.7 (CH_{py} , CH_{imid})], 53.8(CH_2), 21.6(CH_3), 17.5(CH_3). HRMS (ESI, +): calcd for $[\text{C}_{19}\text{H}_{22}\text{N}_3]^+$: 292.1808, found 292.1779.

IMesPic^{Cl}·HCl: beige solid, 80% yield. ¹H NMR (400 MHz, CDCl_3) : δ 10.53 (s, 1H, NCHN), 8.43 (d, $J=5.1$ Hz, 1H, CH_{py}), 7.99 (d, 1H, $J=1.8$ Hz, CH_{py}), 7.96 (s, 1H, CH_{imid}), 7.30 (dd, $J_1=5.1$ Hz, $J_2=1.8$ Hz, 1H, CH_{py}), 7.12 (s, 1H, CH_{imid}), 7.00 (s, 2H, CH_{Ar}), 6.23 (s, 2H, CH_2), 2.34 (s, 3H, CH_3), 2.06 (s, 6H, CH_3). ¹³C NMR (100 MHz, CDCl_3): δ =154.3 (C_{qpy}), 150.3 (CH_{py}), 145.3 ($\text{C}_{\text{py-Cl}}$), 141.1 (CH_{imid}), 138.5 (C_{qAr}), 134.1 (C_{qAr}), 130.6 (C_{qAr}), 129.7 (CH_{Ar}), [124.1(2C), 123.9, 122.6, (CH_{py} , CH_{imid})], 53.8(CH_2), 21.6(CH_3), 17.5(CH_3). HRMS (ESI, +): calcd for $[\text{C}_{18}\text{H}_{19}\text{N}_3\text{Cl}^+]$: 312.1262, found 312.1239.

IMesPic^{OMe}·HCl: In the case of this compound, a brown impure material was isolated. Purification was performed by treating the crude product dissolved in 40 mL H_2O with activated charcoal. Filtration over celite and evaporation yielded a beige solid (46% yield). ¹H NMR (400

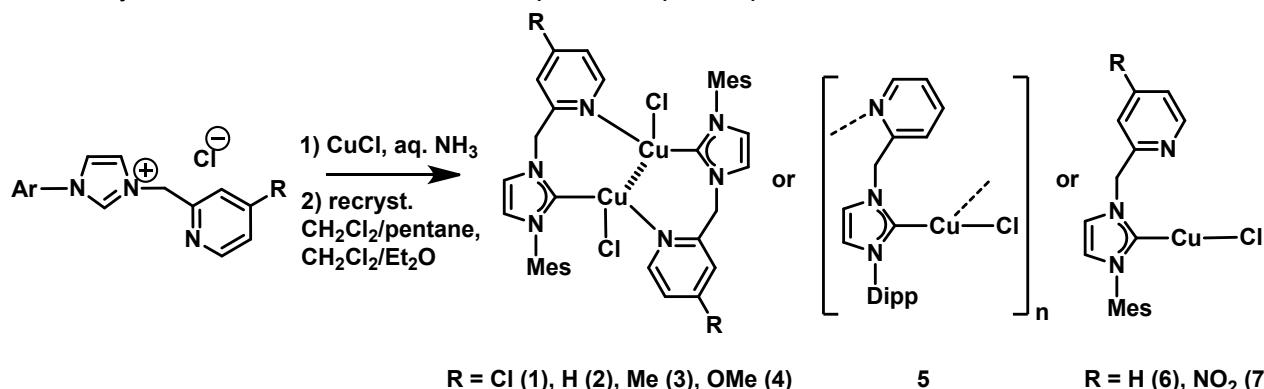
MHz, CDCl₃) : δ 10.41 (s, 1H, NCHN), 8.30 (d, *J*=5.7 Hz, 1H, CH_{py}), 8.06 (s, 1H, CH_{imid}), 7.66 (d, *J*=2.4 Hz, 1H, CH_{ipy}), 7.10 (s, 1H, CH_{imid}), 6.98 (s, 2H, CH_{Ar}), 6.78 (dd, *J*₁=5.7 Hz, *J*₂=2.4 Hz, 1H, CH_{py}), 6.02 (s, 2H, CH₂), 3.90 (s, 3H, OCH₃), 2.33 (s, 3H, CH₃), 2.04 (s, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): 167.7, 153.9, 149.6, 141.3 (CH_{imid}), 138.4 (C_{qAr}), 134.3 (C_{qAr}), 130.8 (C_{qAr}), 129.9 (CH_{Ar}), 124.1 (CH_{imid}), 122.8 (CH_{imid}), 111.5 (CH_{py}), 110.5 (CH_{py}). HRMS (ESI, +): calcd for [C₁₉H₂₂N₃O⁺]: 308.1757, found 308.1744.

IMesPic^{NO₂}·HCl: off-white solid, 64% yield. ¹H NMR (400 MHz, CDCl₃): δ 10.80 (s, 1H, NCHN), 8.85 (d, *J*=5.3 Hz, 1H, CH_{py}), 8.61 (d, 1H, *J*=2.0 Hz, CH_{py}), 8.04 (dd, *J*₁=5.3 Hz, *J*₂=2.0 Hz, 1H, CH_{py}), 7.98 (broad, 1H, CH_{imid}), 7.16 (m, 1H, CH_{imid}), 7.03 (s, 2H, CH_{Ar}), 6.52 (s, 2H, CH₂), 2.37 (s, 3H, CH₃), 2.10 (s, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): 156.6 (C_{qpy}), 154.4. (C_{qpy}), 151.9, (CH_{py}), 141.3 (CH_{imid}), 138.9 (C_{qAr}), 134.3 (C_{qAr}), 130.8 (C_{qAr}), 129.8 (CH_{Ar}), 124.6 (CH_{imid}), 123.0 (CH_{imid}), 116.4 (CH_{py}), 116.2 (CH_{py}), 53.2 (CH₂), 21.1(CH₃), 17.5(CH₃). HRMS (ESI, +): calcd for [C₁₈H₁₉N₃Cl⁺]: 323.1503, found 323.1508.

IDippPic·HCl: beige solid, 82% yield. Characterisation data identical to a literature report.⁵

General procedure for the preparation of copper(I) complexes: The respective imidazolium chloride (0.5 mmol) was dissolved/suspended in 5 mL of water. Copper(I) chloride (0.6 mmol, 1.2 eq.) was added and the reaction mixture was degassed by bubbling argon for 5 min. Then, 214.0 μ L of aqueous ammonia (14.0 mol L⁻¹, 6 eq.) were added with a syringe and the reaction vessel was degassed for 1 more minute. The mixture was stirred vigorously for 1 h at RT. The reaction mixture was transferred to a separating funnel containing 5 mL dichloromethane. Extraction was performed three times, during which the aqueous layer turned a deep blue colour, characteristic of a Cu(II)-ammine complex. The combined organic phases were dried over K₂CO₃ (this agent also absorbing traces of Cu^{II}), filtered and the volatiles were evaporated. The crude product was first purified by recrystallisation by layering a concentrated solution of the product in dichloromethane with n-pentane. Single crystals suitable for X-ray diffraction studies were obtained by recrystallisation by slow diffusion of degassed and dried diethyl ether into a concentrated solution of the respective complex in dried dichloromethane.

The isolated copper(I) complexes **1-7** are, in the solid state, insensitive to moisture, and only moderately sensitive to air and light. However, in solution equilibrium between species of various nuclearity exists, and we observe decomposition upon exposure to air.



[Cu₂Cl₂(IMesPic^{Cl})₂]·CH₂Cl₂ (1**):** yellow solid, 91% yield ¹H NMR (500 MHz, DMSO-d₆, 343 K): δ [9.01 (d, 1H, *J*=4.7 Hz), 8.09 (s, 1H), 7.90 (m, 2H), 7.75 (s, 1H), all CH, py/Imid], 7.48 (s, 2H,

CH, Mes), 6.08 (broad, 2H, CH₂, pic), 2.78 (s, 3H, CH₃, Mes), 2.48 (s, 6H, CH₃, Mes). ¹³C NMR (100 MHz, CDCl₃, 343 K) : δ 157.6 (C_q, py), 150.5 (CH, py), 143.4, (C-Cl, py), 138.5 (C_q, Mes), 135.5 (C_q, Mes), 135.2(C_q, Mes), 128.6 (CH, Mes), [122.9, 122.5 (2C), 121.7 (CH), py/Imid)], 54.4 (CH₂, pic), 20.2 (CH₃, Mes), 16.8 (CH₃, Mes). Elemental analysis: Calcd for [Cu₂Cl₂(IMesPic^{Cl})]. CH₂Cl₂: C, 52.63, H, 4.42, N, 10.23 ; found C 52.43, H 4.47, N 10.25

[Cu₂Cl₂(IMesPic^{Me})₂]·CH₂Cl₂ (3): beige solid, 49% yield ¹H (400 MHz, CDCl₃): ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.7-6.8 (very broad signals, CH_{py}, Imid), 5.50 (m, 2H, CH₂), 2.35-2.32 (m, 6H, CH₃, py/Mes), 2.01 (s, 6H, CH₃, Mes), CH₂Cl₂ signal also detected. Very broad ¹H NMR spectra were recorded at RT as well as 343 K common NMR solvents, possibly due to the presence of multiple species in solution interconverting in the NMR timescale. Elemental analysis: Calcd for [Cu₂Cl₂(IMes^{Me}Pic)₂]⁻/3 CH₂Cl₂: C 48.49, H 4.74, N 8.34 ; found C 48.66, H 4.60, N 8.66.

[Cu₂Cl₂(IMesPic^{OMe})₂]·CH₂Cl₂ (4) off-white solid, 71% yield. ¹H NMR (500 MHz, DMSO-d₆, 343 K): δ [8.79 (d, 1H, J=4.8 Hz), 7.99 (broad, 1H), 7.68 (broad, 1H), 7.44 (broad, 1H), 7.34 (broad, 1H), CH, py/Imid], 7.42 (s, 2H, CH, Mes), 5.83 (broad, 2H, CH₂, pic), 4.33 (s, 3H, CH₃, OMe), 2.75 (s, 3H, CH₃, Mes), 2.44 (s, 6H, CH₃, Mes), CH₂Cl₂ signal also detected. Compound excessively oxydisable in solution: no satisfactory ¹³C NMR spectrum could be recorded. HRMS (ESI, +): calcd for C₂₁H₂₄CuN₄O ([Cu(ACN)(IMesPic^{OMe})]⁺): 411.1241, found 411.1262.

[CuCl(IDippPic)]_∞ (5): off-white solid, 98% yield. ¹H NMR (500 MHz, CDCl₃, 343 K): δ 8.61 (broad, 1H, CH, py), 7.74 (t, 1H, J=7.5 Hz, CH, py), 7.47-7.39 (m, 2H, CH, Mes/py), 7.31 (m, 2H, CH, Imid/py), 7.25 (d, 2H, J=7.5 Hz, CH, Mes), 6.93 (s, 1H, CH, Imid), 5.55 (s, 2H, CH₂, pic), 2.38 (hept, J=6.8Hz, 2H, CH, iPr), 1.23 (d, J=6.8Hz, 6H, CH₃, iPr), 1.11 (d, J=6.8Hz, 6H, CH₃, iPr). ¹³C NMR (400 MHz, CDCl₃, 343 K): δ 155.2 (C_q, py), 149.8 (CH, py), 145.7(C_q, Mes), 137.5 (CH, py), 134.5 (C_q, Mes), 130.4 (CH, Mes), 124.1 (CH, Mes), [123.6, 123.4 122.5, 121.2 (CH, Imid/py)], 56.8 (CH₂, pic), 28.3 (CH, iPr), 24.3 (CH₃, iPr), 24.1 (CH₃, iPr). Elemental analysis: Calcd for [CuCl(IDippPic)]_∞: C 60.28, H 6.02, N 10.04 ; found C 60.51, H 6.07, N 9.90.

[CuCl(IMesPic^{NO2})] (6): beige solid 70% yield. ¹H NMR (400 MHz, acetone-d₆): δ 8.99 (d, J=5.3 Hz, 1H, CH, py), 8.13 (dd, J₁=5.3 Hz, J₂=1.8 Hz, 1H, CH, py), 8.04 (broad, 1H, CH, py), 7.72 (broad, 1H, CH, Imid), 7.38 (broad, 1H, CH, Imid), 7.03 (s, 2H, CH, Mes), 5.83 (s, 2H, CH₂, pic), 2.32 (s, 3H, CH₃, Mes), 2.04 (s, 6H, CH₃, Mes, overlaid with solvent signal). ¹³C NMR (100 MHz, CDCl₃): 159.0 (C_q, py), 154.7(C_q, py), 152.5 (CH, py), 139.9, (C_q, Mes), 135.2 (C_q, Ar), 134.6 (C_q, Mes), 129.6 (CH, Mes), 123.3 (CH, Imid), 121.9 (CH, Imid), 116.3 (CH, py), 114.5 (CH, py), 56.2 (CH₂, pic), 21.1 (CH₃, Mes), 18.0 (CH₃, Mes). HRMS (ESI, +): calcd for [C₁₈H₁₈N₄OCu⁺]: 385.0754, found 385.0726.

Photophysical measurements

The photoluminescence studies were carried out on crystalline samples of **1-7**, of which the respective unit cell was determined for several crystals of the bulk sample before the measurements in order to exclude impurities or polymorphs being responsible for the photophysical properties. Absorption spectra of **1**, **4** and **7**, and emission and excitation measurements of **1** in dichloromethane at room temperature (Figure S1) confirm that the dimers are in equilibrium with other species of different nuclearity, as described in the literature, thus accounting for the different photophysical properties compared to the solid state. For this reason we have focussed on the study of the crystalline material in order to develop structure-property relationships. Excitation and emission spectra were recorded on a FLSP920 Edinburgh Instruments spectrometer, equipped with a 450 W Xenon lamp, double monochromators for the excitation and emission pathways, and photomultiplier (PMT-R928) as detector. The emission was collected at right angles to the excitation source with the emission wavelength selected using a double grated monochromator and detected by a R928-P PMT. The excitation and emission spectra were fully corrected using the standard corrections supplied by the manufacturer for the spectral power of the excitation source and the sensitivity of the detector. Low temperature measurements were performed with an Optistat cryostat.

The luminescence lifetimes were measured either via time correlated single photon counting (TCSPC) using a 374 nm pulsed ps laser diode (5 mW), or using a μ F900 pulsed 60 W xenon microsecond flashlamp, with a repetition rate of 100Hz, and a multichannel scaling module. For TCSPC mode, the instrument response function (IRF) was measured using a scattering sample and setting the monochromator at the emission wavelength of the excitation light source. The resulting intensity decay is a convolution of the luminescence decay with the IRF and iterative deconvolution of the IRF with a decay function and non-linear least squares analysis was used to analyse the convoluted data. In case of bi-exponential decays, the amplitude weighted average lifetime $\tau_{av} = (A_1\tau_1 + A_2\tau_2)/(A_1+A_2)$ has been used for temperature dependent lifetime plots.

Determination of the absolute quantum yield was performed as described in the literature.⁶ First, the diffuse reflection of the sample was determined under excitation. Second, the emission was measured for this excitation wavelength. Integration over the reflected and emitted photons by use of an Ulbricht sphere allows calculating the absolute quantum yield.

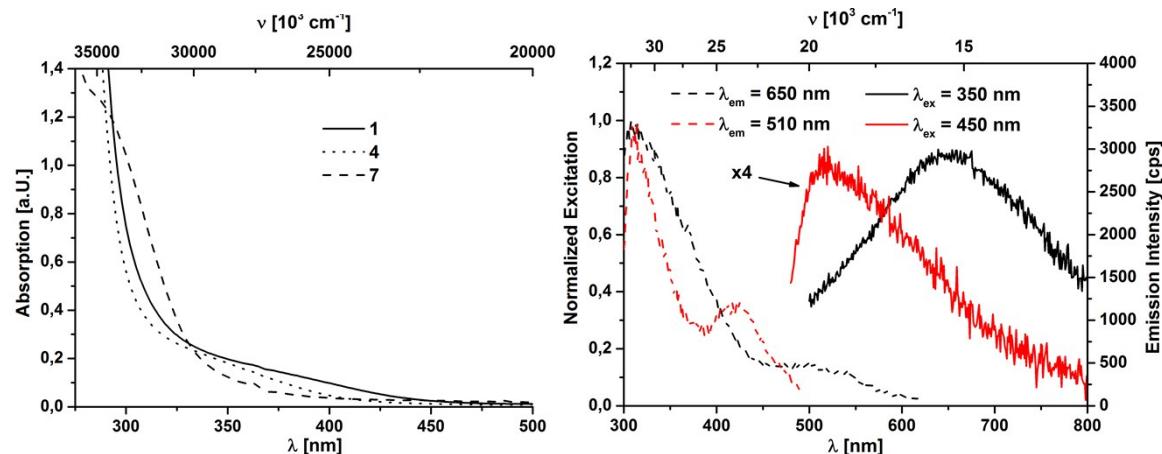


Figure S1. Absorption of **1, **4** and **7** (left), and emission and excitation spectra of **1** (right) in degassed dichloromethane at room temperature.**

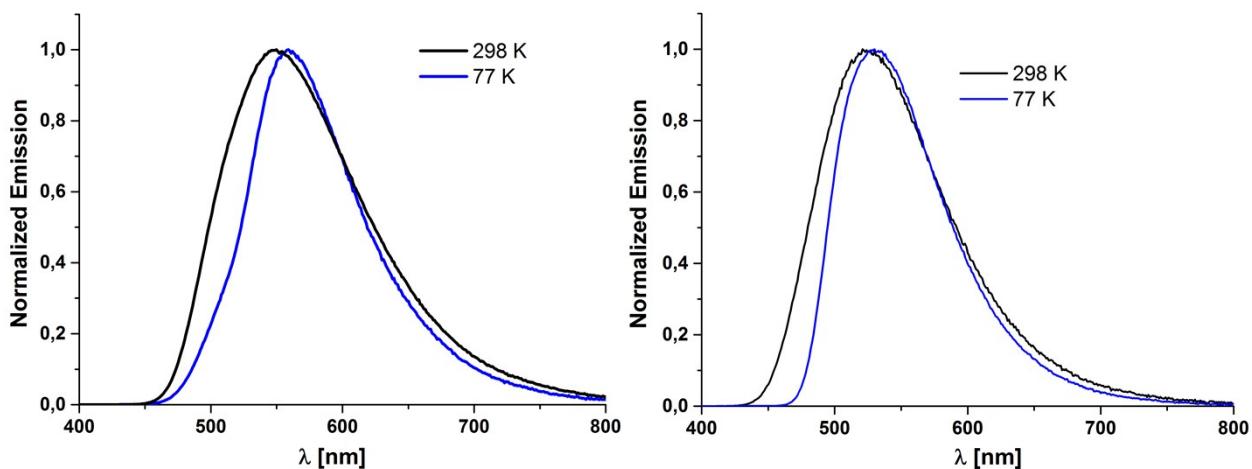


Figure S2. Emission spectra of 1 (left) and 2 (right) in the solid state at 298 K and 77 K.

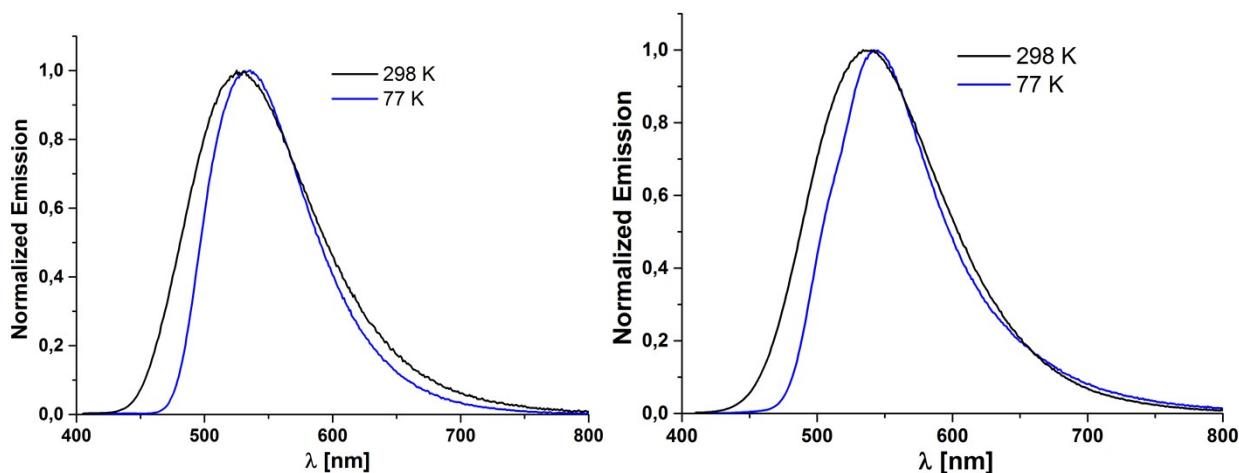


Figure S3. Emission spectra of 3 (left) and 4 (right) in the solid state at 298 K and 77 K.

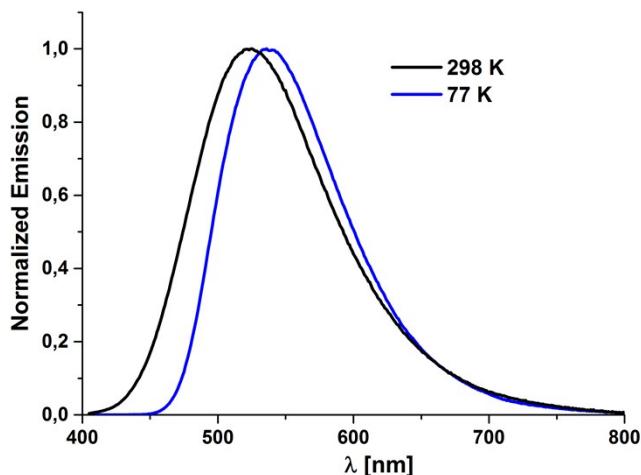


Figure S4. Emission spectra of 5 in the solid state at 298 K and 77 K.

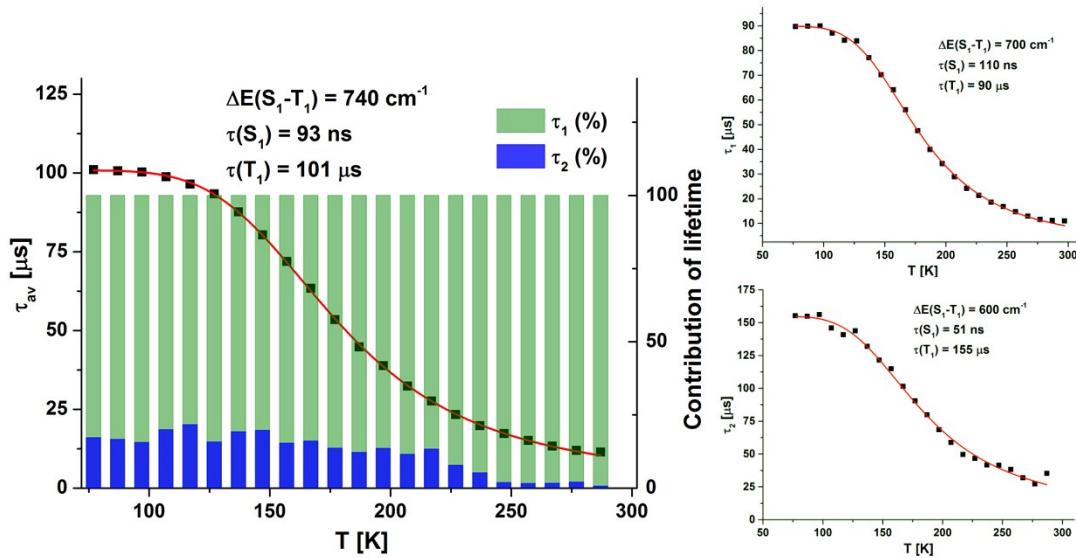


Figure S5. Temperature dependence of the average lifetime of **1**, including the respective lifetime contributions (left), and of the two lifetime components (right).

Computational studies

Calculations (gas-phase) were performed with the ORCA 3.0.2 program suite.⁷ Geometry optimisations of the ground state S_0 for compounds **1-4** were carried out with the PBE0⁸⁻¹⁴ functional as implemented in ORCA. The def2-TZVP^{15, 16} basis set was used for all atoms together with the auxiliary basis set def2-TZVP/J in order to accelerate the computations within the framework of RI approximation. Relativistic effects were accounted for by employing the ZORA¹⁷ method and van der Waals interactions have been considered by an empirical dispersion correction (Grimme-D3).^{18, 19} TD-DFT calculations were performed with the same functional employing a COSMO model for dichloromethane. Representations of molecular orbitals and transition densities were produced with orca_plot as provided by ORCA 3.0.2 and with gOpenMol 3.00.^{20, 21} The NBO analysis was carried out with the NBO 6.0 program.²²

Table S1. Cartesian coordinates of the optimised ground state S_0 of **1**.

C	1.736353	0.272058	-4.403294
C	2.919172	-1.888621	-3.942981
C	1.772363	-1.114747	-3.845455
C	4.283046	-3.927682	-3.443441
C	-1.461831	-0.560953	-3.836428
C	3.006080	-3.147831	-3.361638
C	-2.172444	0.470365	-3.331552
C	0.684812	-1.652385	-3.154339
C	1.889141	-3.654743	-2.710489
C	0.706043	-2.928092	-2.603457
C	-0.495279	-3.483337	-1.911733
C	-0.497908	0.035996	-1.877483
C	5.054938	-0.501442	-1.262025
C	3.779843	0.031474	-1.235473
C	-1.987733	1.906896	-1.290927
C	5.329391	-1.570069	-0.428850
C	-4.338243	2.073528	-0.411997
C	-3.091823	1.471876	-0.374339
C	4.332896	-2.063379	0.399085
C	3.085868	-1.462856	0.360542

C	-5.330666	1.589658	0.426539
C	-3.778909	-0.006452	1.239425
C	-5.053043	0.528579	1.268249
C	1.977924	-1.907757	1.267831
C	0.510961	3.466096	1.923142
C	0.495169	-0.038063	1.873137
C	-0.695010	2.919331	2.613178
C	-1.873693	3.653225	2.717475
C	-0.683019	1.643075	3.163474
C	-2.995008	3.152763	3.366089
C	2.159050	-0.501749	3.330275
C	-4.268097	3.939325	3.443807
C	-1.774878	1.112044	3.852557
C	1.451412	0.526658	3.845269
C	-2.916784	1.893514	3.948138
C	-1.749436	-0.275948	4.407953
H	0.870601	0.430568	-0.501023
H	2.636151	0.473327	-4.984673
H	4.450592	-4.314839	-4.452722
H	-1.580589	-1.125638	-4.744883
H	3.781365	-1.481541	-4.462171
H	-3.047407	0.974784	-3.704616
H	1.671234	1.016408	-3.601037
H	5.138857	-3.297383	-3.189583
H	4.273472	-4.778735	-2.761741
H	-1.323971	-3.608719	-2.614357
H	1.936244	-4.639882	-2.256884
H	5.812075	-0.086014	-1.912676
H	-2.303815	2.743621	-1.913780
H	3.509051	0.887779	-1.844382
H	-0.278936	-4.455005	-1.467783
H	-0.853508	-2.834524	-1.109559
H	-4.535051	2.893712	-1.089614
H	-1.106003	2.220636	-0.723422
H	1.097060	-2.210843	0.693556
H	4.526900	-2.889915	1.069749
H	0.854879	2.822863	1.110219
H	0.306877	4.446652	1.493277
H	-3.506184	-0.857868	1.854158
H	-5.807205	0.120367	1.926858
H	2.289918	-2.753932	1.879869
H	-1.913937	4.638621	2.263805
H	1.345363	3.568724	2.622600
H	-4.256479	4.783912	2.754119
H	-5.127450	3.310620	3.198166
H	-1.681872	-1.018712	3.604387
H	3.029199	-1.016104	3.701007
H	-4.430952	4.337036	4.449761
H	-3.782789	1.491848	4.465207
H	1.568956	1.078992	4.761438
H	-2.654595	-0.474116	4.982091
H	-0.889504	-0.440125	5.061908
C\	1.587942	2.557220	-1.308436
C\	6.900037	-2.273608	-0.407212
C\	-6.900184	2.295695	0.407594
C\	-1.597473	-2.541487	1.298744
Cu	0.980274	0.416710	-0.726217
Cu	-0.984498	-0.400501	0.716461
N	-0.448492	-0.810706	-2.936349
N	-1.561924	0.823016	-2.149271
N	2.808628	-0.439916	-0.453194
N	-2.811362	0.456490	0.447699
N	1.553233	-0.834426	2.139747
N	0.444587	0.794554	2.942981

Table S2. Cartesian coordinates of the optimised triplet state T₁ of 1.

C	1.946284	0.240912	-3.791360
C	2.591485	-2.123063	-3.253695
C	1.632120	-1.123595	-3.265198
C	3.373972	-4.460336	-2.793315
C	-1.205685	0.324967	-3.622738
C	2.303537	-3.412615	-2.814891
C	-1.988693	1.246760	-3.016006
C	0.355682	-1.443433	-2.789590
C	1.003805	-3.707199	-2.432213
C	0.000195	-2.740230	-2.426225
C	-1.404458	-3.118837	-2.069025
C	-0.964069	0.080698	-1.403453
C	5.184653	0.552470	-1.382264
C	3.844102	0.847840	-1.218728
C	-2.525564	1.741219	-0.582982
C	5.673332	-0.584325	-0.761105
C	-4.813298	1.053016	0.134532
C	-3.470139	0.786654	0.055281
C	4.825143	-1.370730	0.003020

C	3.497509	-0.992178	0.106068
C	-5.670771	0.130464	0.729883
C	-3.777442	-1.281552	1.097116
C	-5.117591	-1.070192	1.223566
C	2.528119	-1.774787	0.949584
C	1.416924	3.290767	2.188867
C	0.987935	0.020106	1.580558
C	-0.004814	2.902784	2.454196
C	-1.022290	3.845651	2.326118
C	-0.373468	1.612326	2.821854
C	-2.350020	3.527268	2.571562
C	2.041077	-0.987952	3.291449
C	-3.437570	4.532507	2.346372
C	-1.684389	1.271196	3.169137
C	1.231052	-0.040041	3.815851
C	-2.657932	2.249263	3.030188
C	-2.027060	-0.086401	3.694739
H	1.492713	0.393010	-4.775292
H	3.022828	0.365401	-3.910237
H	3.611850	-4.807084	-3.803116
H	-1.030763	0.120104	-4.664102
H	3.596322	-1.884334	-3.588785
H	-2.630537	2.004760	-3.429319
H	1.570535	1.032214	-3.139764
H	4.298211	-4.067067	-2.362709
H	3.066576	-5.328240	-2.209111
H	-1.664531	-4.062787	-2.552289
H	0.752332	-4.717180	-2.124615
H	5.830174	1.193592	-1.967160
H	-3.046931	2.610248	-0.978544
H	3.396254	1.733100	-1.660062
H	-1.514402	-3.259330	-0.990439
H	-2.123828	-2.364014	-2.383721
H	-5.198260	1.982287	-0.268135
H	-1.754849	2.085874	0.118378
H	1.746593	-2.221104	0.327316
H	5.197542	-2.248524	0.514364
H	2.121494	2.585082	2.628714
H	1.609880	3.334958	1.113438
H	-3.319651	-2.193869	1.458280
H	-5.744010	-1.823051	1.682715
H	3.035960	-2.582119	1.473947
H	-0.762634	4.846330	1.995692
H	1.617695	4.279369	2.606672
H	-3.078783	5.377718	1.757864
H	-4.278006	4.076978	1.817211
H	-1.494280	-0.881540	3.173716
H	2.694778	-1.696626	3.769015
H	-3.825277	4.923905	3.291492
H	-3.688778	1.991479	3.249676
H	1.047601	0.253297	4.834629
H	-3.095129	-0.277171	3.595763
H	-1.767050	-0.161993	4.756033
Cl	1.017569	2.668272	-1.303274
Cl	7.333349	-1.007116	-0.907694
Cl	-7.358212	0.456016	0.865243
Cl	-0.701609	-2.683640	1.452823
Cu	0.928967	0.781320	-0.171306
Cu	-1.019454	-0.800795	0.321201
N	-0.591632	-0.393339	-2.623822
N	-1.827781	1.074552	-1.669906
N	3.015164	0.087482	-0.510731
N	-2.916769	-0.379430	0.536721
N	1.883940	-0.927341	1.929346
N	0.603125	0.570913	2.756812

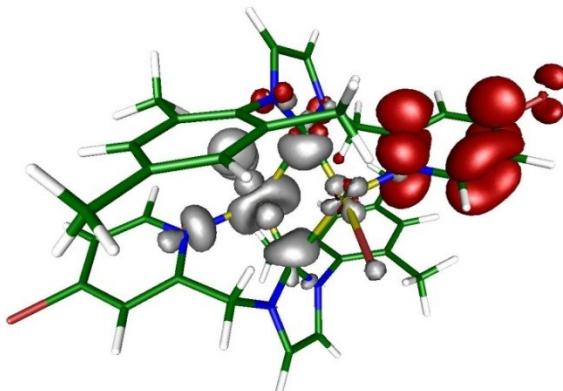


Figure S6. Electron (red) and hole (grey) of the DFT-(PBE0-D3BJ/def2-TZVP)-optimized T₁ state of 1.

Table S3. TD-DFT results for the first 50 singlet and triplet excitations from the optimised ground state S_0 of 1.

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

State	Energy (cm ⁻¹)	Wavelength (nm)	fosc	T2 (au**2)	TX (au)	TY (au)	TZ (au)
1	21144.0	472.9	0.104022560	1.61963	-1.22946	0.32451	0.05254
2	21718.0	460.4	0.000002262	0.00003	-0.00379	-0.00443	0.00060
3	24383.3	410.1	0.000017163	0.00023	0.00923	0.01152	-0.00371
4	24730.8	404.4	0.008941209	0.11902	-0.28954	-0.17688	0.06250
5	25720.3	388.8	0.003799649	0.04863	-0.21564	-0.04186	0.01956
6	25719.8	388.8	0.000003142	0.00004	-0.00603	-0.00138	-0.00141
7	27500.6	363.6	0.002827093	0.03384	-0.17558	0.05200	-0.01759
8	27643.3	361.8	0.069964402	0.83322	0.87144	-0.25801	0.08512
9	29577.9	338.1	0.000004773	0.00005	-0.00529	-0.00434	-0.00250
10	29648.6	337.3	0.018288132	0.20307	-0.40574	-0.13249	0.14452
11	29764.9	336.0	0.0000175051	0.00194	-0.03968	-0.01454	0.01227
12	29773.1	335.9	0.010694856	0.11826	-0.21280	0.14527	-0.22775
13	30681.4	325.9	0.013169719	0.14131	-0.12672	-0.14675	0.32205
14	31032.8	322.2	0.000084841	0.00094	-0.00988	0.01624	-0.02403
15	30949.3	323.1	0.009670581	0.10287	-0.21432	0.12478	-0.20338
16	31723.2	315.2	0.000046714	0.00048	0.00171	-0.02042	0.00805
17	31244.1	320.1	0.016931367	0.17840	0.27088	-0.18135	-0.26859
18	31330.6	319.2	0.000763651	0.00802	0.06521	-0.03478	-0.05062
19	31396.5	318.5	0.003325180	0.03487	0.01132	-0.18621	0.00791
20	31931.7	313.2	0.000048980	0.00050	-0.00262	-0.01902	0.01168
21	32328.7	309.3	0.000038216	0.00039	-0.00496	0.01710	0.00850
22	32380.3	308.8	0.003246999	0.03301	-0.08648	-0.14934	-0.05684
23	32573.9	307.0	0.000366680	0.00371	0.03014	-0.04738	-0.02351
24	32508.3	307.6	0.020413704	0.20673	-0.39754	0.18618	0.11842
25	33150.8	301.7	0.000079682	0.00079	-0.02674	0.00806	0.00339
26	33090.1	302.2	0.000004401	0.00004	-0.00302	-0.00206	0.00552
27	33174.8	301.4	0.001814934	0.01801	-0.12757	-0.04151	0.00380
28	33551.5	298.0	0.015743074	0.15447	0.24295	-0.14303	0.27385
29	33666.7	297.0	0.000241214	0.00236	-0.03125	0.01271	-0.03494
30	34538.3	289.5	0.004284307	0.04084	0.11966	-0.00670	0.16271
31	34583.2	289.2	0.000094576	0.00090	-0.01478	-0.00109	-0.02609
32	34620.9	288.8	0.012925510	0.12291	0.34012	0.03771	0.07620
33	34539.4	289.5	0.000790993	0.00754	0.08055	0.02470	0.02099
34	35664.5	280.4	0.013086973	0.12080	0.04341	0.33655	0.07520
35	35480.2	281.8	0.000422103	0.00392	0.04509	-0.04340	0.00019
36	35555.6	281.2	0.001217763	0.01128	-0.09396	0.01982	-0.04531
37	35498.3	281.7	0.000914215	0.00848	-0.08067	0.02981	0.03290
38	35667.9	280.4	0.002346163	0.02165	-0.13666	0.03089	0.04500
39	35918.9	278.4	0.000012709	0.00012	-0.01036	0.00231	0.00196
40	36392.0	274.8	0.008437147	0.07632	-0.04230	0.26405	-0.06938
41	36252.7	275.8	0.000071928	0.00065	0.00362	-0.01190	-0.02233
42	36457.7	274.3	0.023071132	0.20833	0.17911	0.22799	0.35252
43	36469.1	274.2	0.000190555	0.00172	-0.01940	-0.01291	-0.03431
44	36540.7	273.7	0.011818769	0.10648	-0.29442	0.12613	-0.06235
45	36481.5	274.1	0.001403914	0.01267	-0.08692	-0.06897	-0.01891
46	36432.4	274.5	0.011950934	0.10799	0.31247	0.08674	0.05317
47	36898.0	271.0	0.000010229	0.00009	-0.00838	-0.00242	-0.00389
48	37342.3	267.8	0.0002633361	0.00232	-0.00958	-0.02181	0.04188
49	37302.2	268.1	0.002092301	0.01847	0.04681	0.07329	-0.10442
50	37575.1	266.1	0.011752178	0.10297	-0.12269	-0.15529	-0.25258
51	20561.1	486.4	spin forbidden (mult=3)				
52	20664.4	483.9	spin forbidden (mult=3)				
53	24204.5	413.1	spin forbidden (mult=3)				
54	24878.3	402.0	spin forbidden (mult=3)				
55	25517.4	391.9	spin forbidden (mult=3)				
56	26123.8	382.8	spin forbidden (mult=3)				
57	26741.7	373.9	spin forbidden (mult=3)				
58	26786.4	373.3	spin forbidden (mult=3)				
59	27820.5	359.4	spin forbidden (mult=3)				
60	28569.1	350.0	spin forbidden (mult=3)				
61	30011.6	333.2	spin forbidden (mult=3)				
62	30147.7	331.7	spin forbidden (mult=3)				
63	30516.0	327.7	spin forbidden (mult=3)				
64	30628.8	326.5	spin forbidden (mult=3)				
65	31101.8	321.5	spin forbidden (mult=3)				
66	31120.3	321.3	spin forbidden (mult=3)				
67	31190.5	320.6	spin forbidden (mult=3)				
68	31238.1	320.1	spin forbidden (mult=3)				
69	31579.5	316.7	spin forbidden (mult=3)				
70	31648.2	316.0	spin forbidden (mult=3)				
71	32158.5	311.0	spin forbidden (mult=3)				
72	32236.2	310.2	spin forbidden (mult=3)				
73	32759.5	305.3	spin forbidden (mult=3)				
74	32877.4	304.2	spin forbidden (mult=3)				
75	32922.1	303.7	spin forbidden (mult=3)				
76	32959.5	303.4	spin forbidden (mult=3)				
77	33067.2	302.4	spin forbidden (mult=3)				
78	33119.4	301.9	spin forbidden (mult=3)				
79	33473.0	298.7	spin forbidden (mult=3)				
80	33680.3	296.9	spin forbidden (mult=3)				
81	33900.7	295.0	spin forbidden (mult=3)				
82	34149.7	292.8	spin forbidden (mult=3)				

83	34242.1	292.0	spin forbidden (mult=3)
84	34275.7	291.8	spin forbidden (mult=3)
85	34703.7	288.2	spin forbidden (mult=3)
86	34737.5	287.9	spin forbidden (mult=3)
87	34872.8	286.8	spin forbidden (mult=3)
88	34891.3	286.6	spin forbidden (mult=3)
89	35386.7	282.6	spin forbidden (mult=3)
90	35456.2	282.0	spin forbidden (mult=3)
91	35592.3	281.0	spin forbidden (mult=3)
92	36016.2	277.7	spin forbidden (mult=3)
93	36048.9	277.4	spin forbidden (mult=3)
94	36109.4	276.9	spin forbidden (mult=3)
95	36219.6	276.1	spin forbidden (mult=3)
96	36235.5	276.0	spin forbidden (mult=3)
97	36307.0	275.4	spin forbidden (mult=3)
98	36382.1	274.9	spin forbidden (mult=3)
99	36537.3	273.7	spin forbidden (mult=3)
100	36636.1	273.0	spin forbidden (mult=3)

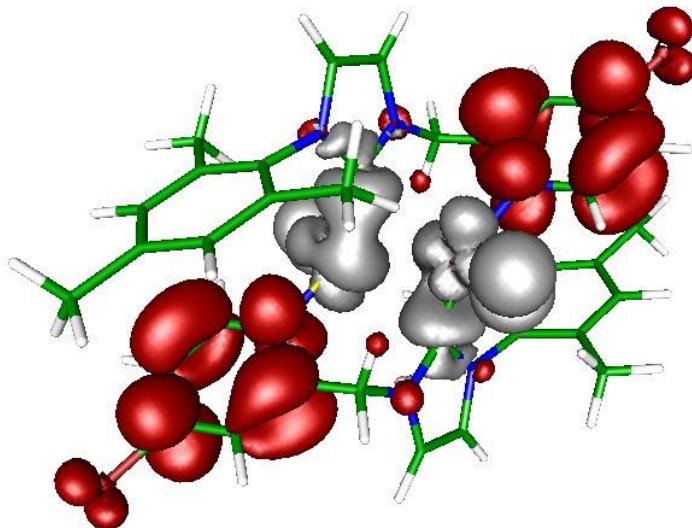


Figure S7. Electron density difference for the transition $S_0 \rightarrow S_1$ of 1.

Table S4. Cartesian coordinates of the optimised ground state S_0 of 2.

C	3.048006	-0.168399	-3.095064
C	3.995974	2.112134	-2.607262
C	4.881740	4.445074	-2.230573
C	3.519457	0.887084	-2.146656
C	4.452432	3.096425	-1.739949
C	-0.849751	2.273999	-1.714664
C	0.307951	4.500309	-1.492672
C	-4.181073	-1.326947	-1.425226
C	0.053667	3.230604	-1.000841
C	1.146585	5.344864	-0.783916
C	-3.088958	2.483172	-0.619586
C	-1.475981	-3.598000	-0.692549
C	3.506307	0.678891	-0.771003
C	4.483172	2.815821	-0.379274
C	-1.788412	-4.876141	-0.267197
C	-1.892542	0.602229	-0.236159
C	-4.126906	-1.604878	0.043384
C	-3.838247	1.686064	0.169433
C	4.014915	1.615181	0.131081
C	3.715757	-1.669855	0.002420
C	1.678549	4.899240	0.412053
C	-4.584782	-2.807750	0.557773
C	1.770166	-0.583275	0.401687
C	-3.620484	-0.663846	0.941733
C	1.366734	3.622812	0.842755
C	-1.264654	-5.323712	0.931650
C	2.964545	-2.464123	0.792392
C	-0.177038	-3.208504	1.161508
C	4.062701	1.333625	1.599200

C	-0.433100	-4.479385	1.649096
C	-4.545836	-3.085969	1.918771
C	0.722353	-2.251873	1.880320
C	-4.962797	-4.437064	2.413461
C	-3.625689	-0.870007	2.317677
C	-4.091655	-2.097497	2.782421
C	-3.155049	0.189306	3.262166
H	3.248210	0.133483	-4.123561
H	4.003384	2.297923	-3.676848
H	5.129797	4.436060	-3.293187
H	3.559968	-1.116607	-2.915845
H	4.078962	5.174093	-2.080809
H	-1.286951	2.743988	-2.596299
H	1.975849	-0.370728	-2.991485
H	-0.152292	4.818183	-2.420389
H	-4.639850	-2.162977	-1.952916
H	-0.304186	1.384044	-2.049479
H	-3.186322	-1.154582	-1.849735
H	5.750789	4.809526	-1.679376
H	-4.772958	-0.432052	-1.636335
H	-1.833849	-3.201238	-1.636334
H	-3.286299	3.461383	-1.023759
H	-2.426713	-5.503966	-0.875349
H	-4.971029	-3.556018	-0.127448
H	4.703910	-1.804344	-0.402123
H	4.872096	3.560124	0.308788
H	-4.825707	1.818817	0.576207
H	2.322871	5.527065	1.013804
H	3.160260	-3.441621	1.199036
H	-5.833280	-4.807704	1.868637
H	1.731138	3.228320	1.784941
H	4.644453	0.432037	1.809792
H	4.529070	2.163723	2.129616
H	3.065359	1.170721	2.021488
H	0.175397	-1.361523	2.211372
H	-4.156314	-5.160857	2.258494
H	0.021039	-4.798866	2.579260
H	1.155693	-2.720922	2.764297
H	-2.082639	0.390730	3.158865
H	-5.203548	-4.428557	3.477743
H	-3.665865	1.137206	3.078452
H	-4.092156	-2.281778	3.852277
H	-3.356366	-0.108342	4.291669
Cl	-0.561369	-1.024432	-2.905622
Cl	0.454696	1.050521	3.069304
Cu	-0.703028	-0.847643	-0.624780
Cu	0.593602	0.876664	0.789767
N	-1.920261	1.799484	-0.865564
N	2.972841	-0.530191	-0.227458
N	-0.709716	-2.770851	0.017657
N	0.594198	2.794586	0.140298
N	-3.093850	0.546342	0.394530
N	1.796293	-1.778552	1.034931
H	-1.490428	-6.317161	1.301651
H	1.371899	6.336846	-1.158132

Table S5. Cartesian coordinates of the optimised triplet state T₁ of 2.

C	3.259220	-0.287145	-3.024151
C	4.205892	1.981752	-2.503858
C	5.036549	4.330368	-2.101870
C	3.693738	0.766636	-2.058029
C	4.621207	2.974364	-1.625803
C	-1.143154	2.458623	-1.739183
C	0.052103	4.650728	-1.693127
C	-4.112373	-1.354580	-1.341516
C	-0.170313	3.413793	-1.158194
C	1.033654	5.505765	-1.161384
C	-3.128120	2.584869	-0.204130
C	-1.422780	-3.613653	-0.950763
C	3.603406	0.580212	-0.680524
C	4.598781	2.702598	-0.263858
C	-1.715765	-4.895578	-0.516403
C	-1.984631	0.647614	-0.282366
C	-4.022944	-1.654555	0.121880
C	-3.772387	1.710725	0.597750
C	4.093928	1.513822	0.235745

C 3.580735 -1.781537 0.167376
 C 1.686433 5.059635 0.015237
 C -4.446070 -2.882523 0.607312
 C 1.728066 -0.537587 0.391959
 C -3.539708 -0.719199 1.040700
 C 1.416806 3.831695 0.527971
 C -1.351095 -5.261242 0.765844
 C 2.700167 -2.488178 0.908863
 C -0.414556 -3.084383 1.038631
 C 4.087483 1.246464 1.707158
 C -0.677051 -4.342610 1.553844
 C -4.406117 -3.194000 1.960075
 C 0.388504 -2.067770 1.789618
 C -4.800844 -4.562245 2.423820
 C -3.553615 -0.962139 2.412550
 C -3.982199 -2.212836 2.846980
 C -3.137041 0.085198 3.396201
 H 3.480539 0.025954 -4.044572
 H 4.259608 2.159465 -3.573201
 H 5.336265 4.325800 -3.151227
 H 3.777464 -1.232009 -2.841623
 H 4.196355 5.023171 -1.991490
 H -1.732587 2.937816 -2.521537
 H 2.187364 -0.498513 -2.953758
 H -0.546965 4.956183 -2.545318
 H -4.759954 -2.079549 -1.834675
 H -0.647231 1.581345 -2.176336
 H -3.134335 -1.381955 -1.831161
 H 5.863584 4.724717 -1.508578
 H -4.517541 -0.355964 -1.520288
 H -1.666780 -3.275260 -1.952175
 H -3.324925 3.619355 -0.427766
 H -2.216894 -5.588267 -1.179756
 H -4.818950 -3.619997 -0.096344
 H 4.580905 -2.011782 -0.155493
 H 4.955716 3.452926 0.433534
 H -4.669026 1.816328 1.183029
 H 2.388463 5.697933 0.539393
 H 2.773929 -3.471765 1.339667
 H -5.683530 -4.921511 1.891327
 H 1.872770 3.486043 1.447060
 H 4.634284 0.329789 1.944877
 H 4.564812 2.068704 2.238647
 H 3.075897 1.132642 2.106533
 H -0.175101 -1.146449 1.950214
 H -3.995666 -5.276525 2.225406
 H -0.340945 -4.599949 2.550988
 H 0.691310 -2.444794 2.766350
 H -2.092210 0.383325 3.261808
 H -5.013908 -4.586566 3.493694
 H -3.730101 0.994982 3.287769
 H -3.983593 -2.419561 3.912767
 H -3.278220 -0.280519 4.413559
 Cl -0.211706 -1.172868 -2.992289
 Cl 0.489104 1.200453 2.637508
 Cu -0.815470 -0.714620 -0.910008
 Cu 0.753395 1.132217 0.398325
 N -2.062902 1.909715 -0.744705
 N 2.967266 -0.589119 -0.138846
 N -0.810201 -2.719046 -0.181268
 N 0.546978 2.938419 -0.070274
 N -3.064035 0.527811 0.537481
 N 1.578216 -1.700721 1.044919
 H -1.568087 -6.253037 1.145357
 H 1.225583 6.482115 -1.583452

Table S6. TD-DFT results for the first 50 singlet and triplet excitations from the optimised ground state S_0 of 2.

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

State	Energy (cm ⁻¹)	Wavelength (nm)	fosc	T2 (au**2)	TX (au)	TY (au)	TZ (au)
1	23063.7	433.6	0.081488717	1.16317	0.19701	1.05492	-0.10724
2	23411.2	427.1	0.000196585	0.00276	0.00920	0.05164	-0.00366
3	25593.1	390.7	0.000003586	0.00005	0.00057	-0.00670	0.00098
4	25756.5	388.3	0.011119556	0.14213	0.03767	0.32352	0.18985

5	27532.3	363.2	0.014633949	0.17498	0.18784	0.36031	0.09937
6	27718.9	360.8	0.000000052	0.00000	0.00026	-0.00062	-0.00040
7	28039.3	356.6	0.000001595	0.00002	0.00293	-0.00235	0.00215
8	28108.1	355.8	0.052114843	0.61039	-0.02318	0.75365	-0.20461
9	30193.5	331.2	0.021147881	0.23058	0.34730	-0.08649	0.32013
10	30387.4	329.1	0.000010611	0.00011	0.01044	0.00015	0.00242
11	30452.7	328.4	0.000039454	0.00043	0.01052	0.01774	0.00095
12	30478.3	328.1	0.010151834	0.10966	-0.01547	0.32787	-0.04375
13	30938.8	323.2	0.009112586	0.09696	-0.06781	0.28623	0.10218
14	31510.9	317.4	0.000051497	0.00054	0.01257	-0.01914	-0.00369
15	31778.2	314.7	0.000026991	0.00028	-0.00151	0.01424	-0.00864
16	31713.7	315.3	0.011749054	0.12196	-0.14573	0.30554	-0.08587
17	32141.7	311.1	0.000120296	0.00123	0.01744	0.02887	-0.00973
18	32213.6	310.4	0.011661578	0.11918	-0.25468	-0.21784	0.08281
19	32523.1	307.5	0.000040754	0.00041	0.01212	0.01612	0.00241
20	32646.2	306.3	0.000039884	0.00040	-0.01187	0.01546	0.00471
21	32870.9	304.2	0.005713213	0.05722	-0.14050	0.18341	0.06197
22	33133.4	301.8	0.016461283	0.16356	-0.29154	-0.25410	-0.11831
23	33185.4	301.3	0.000036823	0.00037	0.01587	0.01048	0.00189
24	33369.0	299.7	0.000152551	0.00151	-0.00247	-0.03287	0.02045
25	33764.3	296.2	0.010697760	0.10431	0.04999	0.27776	-0.15702
26	33950.5	294.5	0.002045069	0.01983	-0.05248	0.12819	-0.02538
27	34207.3	292.3	0.000851210	0.00819	-0.02137	0.07485	0.04618
28	34212.1	292.3	0.004119448	0.03964	0.06517	-0.17239	-0.07533
29	34490.9	289.9	0.0000969611	0.00093	-0.01947	0.01529	-0.01767
30	34864.8	286.8	0.011541814	0.10898	0.09142	-0.17323	0.26574
31	33891.7	295.1	0.017080434	0.16591	0.36647	-0.15063	-0.09445
32	33678.4	296.9	0.005813607	0.05683	0.21632	-0.09635	-0.02744
33	35758.7	279.7	0.010432364	0.09605	0.20470	-0.15006	0.17783
34	35864.5	278.8	0.000062122	0.00057	0.01775	0.01448	-0.00674
35	35883.9	278.7	0.000015336	0.00014	0.00984	0.00404	-0.00526
36	36024.7	277.6	0.004191346	0.03830	-0.11887	-0.13604	0.07527
37	35984.5	277.9	0.005929978	0.05425	0.13812	0.16443	-0.09019
38	36711.3	272.4	0.001761927	0.01580	0.03052	-0.06843	0.10093
39	36753.0	272.1	0.003006123	0.02693	-0.07155	-0.04194	-0.14159
40	36858.3	271.3	0.000013325	0.00012	0.00162	0.01030	0.00322
41	37380.6	267.5	0.002530484	0.02229	0.01498	0.14369	0.03763
42	37259.1	268.4	0.000421447	0.00372	0.01045	-0.05876	-0.01275
43	37115.3	269.4	0.000456516	0.00405	-0.05426	0.03315	0.00252
44	37308.8	268.0	0.009552193	0.08429	0.02911	-0.27762	-0.07979
45	37500.9	266.7	0.019511426	0.17129	0.35903	-0.20413	0.02675
46	37780.2	264.7	0.001446784	0.01261	-0.09959	0.04257	-0.02960
47	37956.4	263.5	0.000109455	0.00095	0.02793	-0.00294	-0.01267
48	38289.9	261.2	0.018468324	0.15879	-0.26503	0.12927	0.26802
49	37802.3	264.5	0.021421949	0.18656	0.37728	-0.04619	-0.20514
50	37218.1	268.7	0.004828616	0.04271	0.15594	0.11644	0.06955
51	22363.2	447.2	spin forbidden (mult=3)				
52	22424.1	445.9	spin forbidden (mult=3)				
53	24757.5	403.9	spin forbidden (mult=3)				
54	25830.2	387.1	spin forbidden (mult=3)				
55	26014.7	384.4	spin forbidden (mult=3)				
56	26895.7	371.8	spin forbidden (mult=3)				
57	27361.4	365.5	spin forbidden (mult=3)				
58	27963.9	357.6	spin forbidden (mult=3)				
59	28777.4	347.5	spin forbidden (mult=3)				
60	29143.5	343.1	spin forbidden (mult=3)				
61	30134.0	331.9	spin forbidden (mult=3)				
62	30741.8	325.3	spin forbidden (mult=3)				
63	31239.1	320.1	spin forbidden (mult=3)				
64	31614.4	316.3	spin forbidden (mult=3)				
65	31657.4	315.9	spin forbidden (mult=3)				
66	31699.2	315.5	spin forbidden (mult=3)				
67	31835.8	314.1	spin forbidden (mult=3)				
68	31891.4	313.6	spin forbidden (mult=3)				
69	32194.0	310.6	spin forbidden (mult=3)				
70	32379.9	308.8	spin forbidden (mult=3)				
71	32653.8	306.2	spin forbidden (mult=3)				
72	32740.0	305.4	spin forbidden (mult=3)				
73	32934.5	303.6	spin forbidden (mult=3)				
74	33190.9	301.3	spin forbidden (mult=3)				
75	33438.3	299.1	spin forbidden (mult=3)				
76	33508.7	298.4	spin forbidden (mult=3)				
77	33583.4	297.8	spin forbidden (mult=3)				
78	33596.4	297.7	spin forbidden (mult=3)				
79	34095.3	293.3	spin forbidden (mult=3)				
80	34166.1	292.7	spin forbidden (mult=3)				
81	34396.4	290.7	spin forbidden (mult=3)				
82	34426.6	290.5	spin forbidden (mult=3)				
83	34476.3	290.1	spin forbidden (mult=3)				
84	34632.7	288.7	spin forbidden (mult=3)				
85	34681.8	288.3	spin forbidden (mult=3)				
86	34759.5	287.7	spin forbidden (mult=3)				
87	35243.3	283.7	spin forbidden (mult=3)				
88	35275.4	283.5	spin forbidden (mult=3)				
89	35657.5	280.4	spin forbidden (mult=3)				
90	35886.6	278.7	spin forbidden (mult=3)				
91	36162.6	276.5	spin forbidden (mult=3)				
92	36220.4	276.1	spin forbidden (mult=3)				
93	36472.9	274.2	spin forbidden (mult=3)				
94	36507.0	273.9	spin forbidden (mult=3)				
95	36540.9	273.7	spin forbidden (mult=3)				
96	36591.7	273.3	spin forbidden (mult=3)				
97	36668.5	272.7	spin forbidden (mult=3)				
98	36676.9	272.7	spin forbidden (mult=3)				

99 36756.9 272.1 spin forbidden (mult=3)
 100 36815.7 271.6 spin forbidden (mult=3)

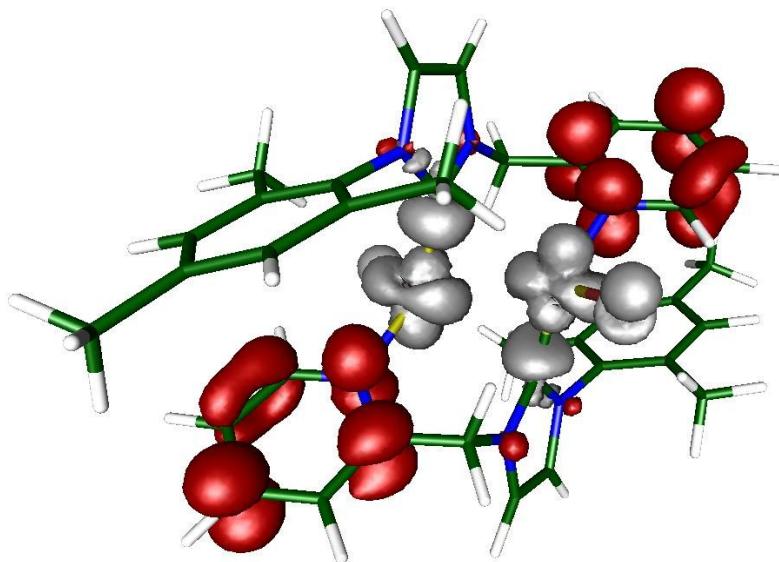


Figure S8. Electron density difference for the transition $S_0 \rightarrow S_1$ of 2.

Table S7. Cartesian coordinates of the optimised ground state S_0 of 3.

C	3.26238194437714	-1.51808141275242	-2.49140827518422
C	4.11289227382956	0.77599185179600	-3.04000749948248
C	4.94843301912860	3.03164128202789	-3.75279514432453
C	3.61365446716934	-0.11825941095118	-2.10038964643967
C	4.45392131645656	2.07971941822660	-2.70716340124365
C	-0.54342838923017	2.61506392162794	-1.57048416992035
C	-0.05410031461079	4.97169082267404	-0.82578962637241
C	-3.64188520734726	-1.45695159223313	-1.63704013775076
C	0.02267786881384	3.60670227296414	-0.59748887690813
C	0.36765215765803	5.87013038220189	0.14659834323189
C	-2.93065893964931	2.53928641322991	-0.85197574706957
C	-0.90112553148891	-3.35869810285477	-1.09886496171358
C	3.45928671505164	0.34282587558034	-0.79369102838707
C	4.33381818914920	2.47955031967852	-1.38199355962730
C	-1.22338745383438	-4.67843558773430	-0.85266078270397
C	-1.6252487997843	0.75379195207597	-0.36406027016086
C	-3.72569658313835	-1.64143265770724	-0.15752171780487
C	-3.68798355754053	1.67213158650498	-0.15191445228432
C	3.86131502083554	1.61856727625204	-0.40092020001339
C	3.69110328961888	-1.43875084348549	0.89947625013008
C	0.88837377340327	5.32962881405988	1.31626301683871
C	-4.18986989083904	-2.82592420689081	0.39196137373087
C	1.61353453662278	-0.60458948079667	0.54989751214345
C	-3.35245567078448	-0.62077280653307	0.71681654768036
C	0.93839720440154	3.95950417640663	1.47324226892198
C	-1.08432441226210	-5.19277334879634	0.43126940833317
C	2.84661699121482	-2.10363986925226	1.71679283829933
C	-0.27261758682467	-3.02764931712318	1.07694510604153
C	3.86677880055844	2.02459803172546	1.03877180683073
C	-0.58442448099834	-4.33665698523695	1.40462731008672
C	-4.28977290823078	-3.00528174392073	1.76545201801344
C	0.37027430928520	-2.08629247359331	2.0507925270969
C	-4.73928429244008	-4.32433973017927	2.31276216287118
C	-3.46749772364691	-0.74242490327032	2.09911405423687
C	-3.94315658060594	-1.95171183776566	2.60058981825102
C	-3.09576309386731	0.37655470922433	3.01966202432879
H	3.76196429338407	-1.78713189714130	-3.42249063354994
H	4.24298644768714	0.43501124196174	-4.06215400471588
H	5.53484330217496	2.51168509106682	-4.51269099314899
H	3.55076799420922	-2.23786424641406	-1.72367846802556
H	4.11333669122191	3.52140352980219	-4.26379946705435

H	-0.85440392528272	3.10836124126660	-2.49159046259559
H	2.18060754177400	-1.59952327748642	-2.64688668310500
H	-0.47542373065576	5.33229761847738	-1.75759134253003
H	-3.96496808901615	-2.36107630819094	-2.15254818265102
H	0.17448572573659	1.83202482469421	-1.82892252256984
H	-2.62699866470397	-1.21099108695857	-1.96407310185374
H	5.56986010079421	3.81289104549024	-3.31200887437017
H	-4.28357131303948	-0.63426306841835	-1.96485780646683
H	-0.97519695664944	-2.91429712511641	-2.08651978918116
H	-3.16575767136458	3.50501932058566	-1.26605910168094
H	-1.57850381562559	-5.30323076624668	-1.66397197138082
H	-4.47960734328232	-3.63303673347649	-0.27326498667517
H	4.75503412203367	-1.52015568824342	0.75979977289226
H	4.64419161115535	3.47914928780703	-1.09376541515090
H	-4.72000421222381	1.71578083793303	0.14997695489148
H	1.23132461316551	5.97219055840566	2.11884278317190
H	3.03155406692862	-2.88566672466329	2.43271825078390
H	-5.55567629978000	-4.74249828084797	1.72068292096418
H	1.28827222912435	3.49972244095705	2.39165725944135
H	4.64939205478471	1.48709235986370	1.58278443082517
H	4.06460529861280	3.09219590824845	1.13976202380931
H	2.92696884129192	1.79367540366850	1.54694922243215
H	-0.26863412537690	-1.22423372974333	2.26781927810206
H	-3.91816064926659	-5.04732012955943	2.28325907491670
H	-0.41741686440773	-4.68966737019996	2.41661547853823
H	0.58871385387270	-2.58298762001026	3.00121071907623
H	-0.202515794039394	0.60649428307219	2.98156838541784
H	-5.07664077417766	-4.24252210724348	3.34737870954629
H	-3.62093735861704	1.29890607247702	2.76051774563337
H	-4.0472263456102	-2.06446852915447	3.67540096405755
H	-3.34938219876598	0.11850195068573	4.04814853117862
Cl	-0.06766036927844	-0.59655376377268	-2.88906750338107
Cl	0.55145301398651	1.15727304511016	3.29082248906230
Cu	-0.11368652601825	-0.48541640619909	-0.54779782454188
Cu	0.59063704484402	1.11137322333783	1.02631501584697
N	-1.69042448245468	1.95791005184953	-0.97815531187961
N	2.92820761351440	-0.54108735395434	0.19052223119968
N	-0.45966075157002	-2.54047106653022	-0.14751812150596
N	0.51879542842219	3.10648893665524	0.53660052882692
N	-2.87550859181799	0.59396917681322	0.1397996662288
N	1.60065222748990	-1.58094261868908	1.49839194433572
C	0.212103212199	7.34668642936770	-0.01868195669228
H	-0.09293552097311	7.61132545976267	-0.3158405679940
H	-0.55054363073485	7.72181826110750	0.66867733742902
H	1.13969024337256	7.87031559320728	0.22210310439706
C	-1.44342215160719	-6.61083282569264	0.73720823311092
H	-0.89370859086170	-7.29973171032103	0.09185053076163
H	-1.22146235755734	-6.86585039091552	1.77420086791580
H	-2.50779837719566	-6.78672507366437	0.55682797102992

Table S8. Cartesian coordinates of the optimised ground state T₁ of 3.

C	2.84630450915167	-1.91542867695450	-2.27623838447025
C	3.65068532016916	0.35014047200245	-2.96305893798557
C	4.44446295548528	2.56506362926412	-3.83168514207077
C	3.22904590206578	-0.50339673383767	-1.95016119008570
C	4.04228437818493	1.657335805247760	-2.70936518295780
C	-0.25969524968618	2.90197349946677	-1.56590838338090
C	-0.129522212536929	5.15097620303029	-0.43589939737946
C	-3.52258831828130	-1.76185497176696	-1.00832335366664
C	0.15082628495752	3.793013350420769	-0.42935461447966
C	0.13173001459176	5.91584614766896	0.69398092928128
C	-2.71313209999053	2.35960157371532	-1.65576625718901
C	-0.63220839287184	-3.48464990537967	-1.91000147744052
C	3.20692017888884	0.00149639779673	-0.64878788659335
C	4.05509565161961	2.10040778153051	-1.39171997016417
C	-0.66460412852063	-4.84385278201763	-1.97076618788814
C	-1.41998451201493	1.22009437471784	-0.20949780118313
C	-3.51328077306107	-1.39269415410331	0.44140979935372
C	-3.51985298209553	1.52012059451742	-0.97031728594656
C	3.65429811826116	1.28685345175618	-0.34098660577309
C	3.37947374809617	-1.55143801266764	1.31592961575025
C	0.70638232454919	5.26102903012170	1.77914930209586
C	-3.91165972028999	-2.31288690183954	1.40420327830702
C	1.34916012458244	-1.095665578251603	0.48075196194232
C	-3.16878464316505	-0.11288868052289	0.87401538103387
C	0.95148972824573	3.90251790396798	1.70618575315841
C	-0.46420622504079	-5.62348087764176	-0.80227775485419
C	2.47844751489824	-2.31757998133967	1.97341119997929
C	-0.28901527726193	-3.53003764504089	0.39934332060402
C	3.74502437888308	1.75313110549047	1.07677547569487
C	-0.28829396146793	-4.91062101444991	0.37905395645694
C	-3.99662806391921	-1.97485797727433	2.74824445629414
C	-0.01039861609876	-2.74469553800859	1.62837765686531
C	-4.43003214880836	-2.98432462771512	3.76731785607058
C	-3.26155807271868	0.27829494877821	2.21084245592942
C	-3.68144463109011	-0.67627571757762	3.12845704349086
C	-2.94953457162929	1.67082576867619	2.66561525235538
H	3.49031019547843	-2.29991908064578	-3.06891266411014

H	3.67354410506515	-0.02453838602718	-3.98160565158048
H	4.97393043764225	2.01681180685380	-4.61311435521118
H	2.92907475008556	-2.57611490259182	-1.41394834426908
H	3.56592706766688	3.02436880269541	-4.29645799973095
H	-0.49676279113380	3.47815797366318	-2.45893881122239
H	1.81624831744309	-1.97069004497962	-2.64030110915587
H	-0.57795541838724	5.60608662615936	-1.31269091271421
H	-4.49067656617944	-1.50949703356845	-1.45513635919483
H	0.52202256992341	2.18102649927491	-1.81357758191701
H	-3.36745531848748	-2.83335983939478	-1.13423424705121
H	5.08970540752310	3.37086857460288	-3.47967425703277
H	-2.75570727170212	-1.24012431901903	-1.58005217943382
H	-0.76542741024548	-2.87433702290944	-2.79476992777318
H	-2.93180142136116	3.05668254195866	-2.4456344630826019
H	-0.83115968476772	-5.32191581450936	-2.92944821770714
H	-4.17140380678566	-3.31739219517985	1.08654359499856
H	4.44564253927416	-1.46358659160382	1.43056204907666
H	4.39457238718677	3.10725622855647	-1.16982903409773
H	-4.57859098925465	1.34081371601197	-1.03533130826010
H	0.94301288540766	5.80041794199817	2.68903221316981
H	2.61147492705643	-3.02525318233977	2.77296296819675
H	-5.03598948897896	-3.76841839343709	3.31125282839256
H	1.34727344820388	3.34931055427333	2.55166933539653
H	4.59322971146139	1.28054786199711	1.58192628439934
H	3.89618956615975	2.83213840417018	1.11761899168704
H	2.85155733897732	1.49929459649445	1.65054181658538
H	-0.77825816851180	-1.98144319579773	1.81641820533016
H	-3.56683175320179	-3.46562227205558	4.23784615337381
H	-0.13812151555207	-5.44062823789453	1.31571919992510
H	0.07341859064223	-3.38674832880009	2.50300267114240
H	-1.89318378477594	1.76047005412746	2.93876285254917
H	-5.01351275083620	-2.51440591802459	4.56131000923655
H	-3.16019963367123	2.40878120902418	1.89028193794965
H	-3.77615021939941	-0.38776571754538	4.17056124926157
H	-3.54414890595170	1.91774474742925	3.54621059128237
Cl	-0.52057969062007	-0.29348586611654	-2.90671578667760
Cl	0.65394514518835	0.81880209287977	3.08857842962627
Cu	-0.00992790852586	-0.88392384093050	-0.84275276902703
Cu	0.02505726917171	0.91829032540894	0.9883865217251
N	-1.44457756904805	2.16394855792603	-1.7358437182453
N	2.67504129977067	-0.81244565869923	0.39217356335813
N	-0.42693316661954	-2.79166364248800	-0.75603696038079
N	0.67656292376589	3.17397140089986	0.62662572095547
N	-2.71426355279817	0.83741879942414	-0.08782939207915
N	1.24914253444854	-2.02782281016540	1.44519575427345
C	-0.23304986530398	7.36300658834988	0.7627457362897
H	-0.55876171410697	7.74585019085703	-0.20046709440139
H	-1.05045156216603	7.51161477396598	1.47789377154633
H	0.60638199129373	7.96609321972108	1.12061029092962
C	-0.42089313579298	-7.11070944133758	-0.87596291389488
H	0.34874643586377	-7.44936809346328	-1.57813328324942
H	-0.19699841891953	-7.55397127313498	0.09632868559801
H	-1.36904304122424	-7.53100735423284	-1.23321579011795

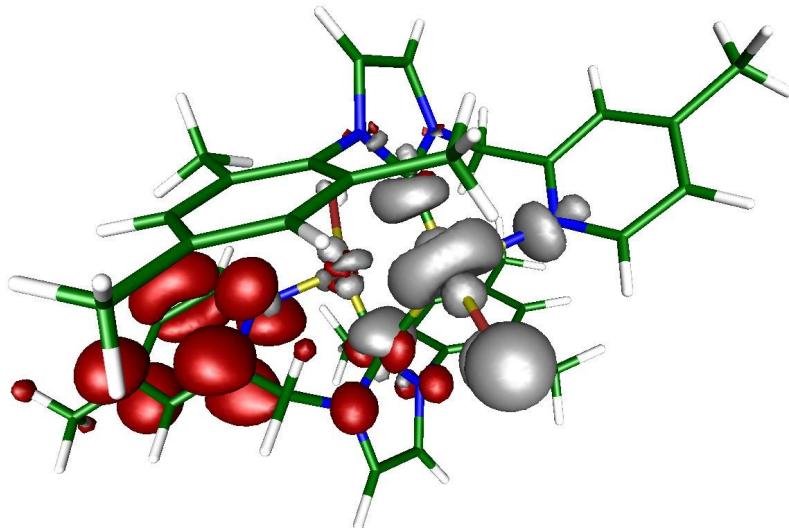


Figure S9. Electron (red) and hole (grey) of the DFT-(PBE0-D3BJ/def2-TZVP)-optimized T₁ state of 3.

Table S9. TD-DFT results for the first 10 singlet and triplet excitations from the optimised ground state S_0 of 3.

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS							
State	Energy (cm ⁻¹)	Wavelength (nm)	fosc	T2 (au**2)	TX (au)	TY (au)	TZ (au)
1	22554.6	443.4	0.031190481	0.45526	-0.07254	0.67081	0.00400
2	25566.9	391.1	0.034602113	0.44555	0.00355	0.66506	0.05694
3	26141.4	382.5	0.010398459	0.13095	-0.01464	-0.34578	0.10570
4	26235.9	381.2	0.022497464	0.28230	-0.17053	0.48101	0.14780
5	26742.4	373.9	0.012019199	0.14796	0.23914	0.29616	0.05537
6	28620.0	349.4	0.001462571	0.01682	0.00191	-0.03299	0.12543
7	28865.5	346.4	0.004194775	0.04784	-0.06167	0.08399	-0.19231
8	28917.9	345.8	0.012232363	0.13926	0.33625	-0.14772	0.06613
9	30508.4	327.8	0.006501832	0.07016	0.19241	-0.15269	-0.09912
10	29771.3	335.9	0.003797395	0.04199	-0.17354	-0.01347	-0.10814
11	23324.0	428.7	spin forbidden (mult=3)				
12	24387.9	410.0	spin forbidden (mult=3)				
13	25634.2	390.1	spin forbidden (mult=3)				
14	26173.0	382.1	spin forbidden (mult=3)				
15	27323.3	366.0	spin forbidden (mult=3)				
16	28014.4	357.0	spin forbidden (mult=3)				
17	28430.7	351.7	spin forbidden (mult=3)				
18	29007.2	344.7	spin forbidden (mult=3)				
19	29803.0	335.5	spin forbidden (mult=3)				
20	30615.0	326.6	spin forbidden (mult=3)				

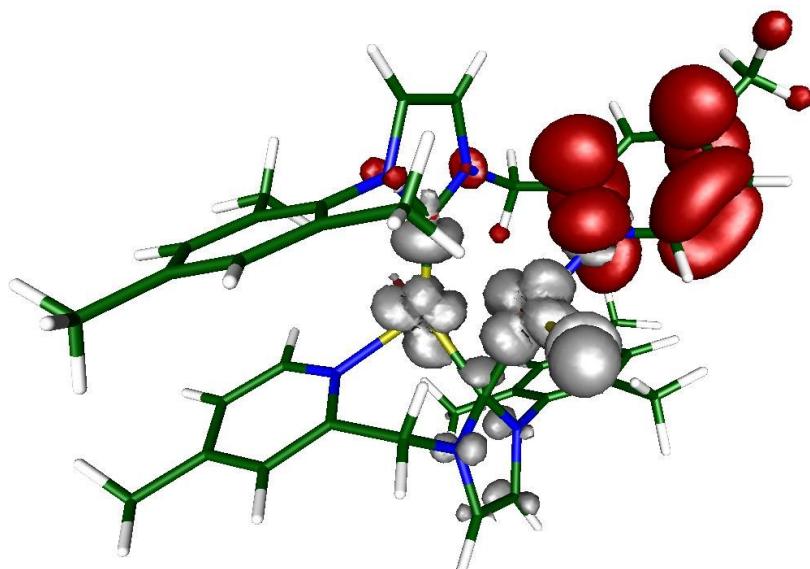


Figure S10. Electron density difference for the transition $S_0 \rightarrow S_1$ of 3.

Table S10. Cartesian coordinates of the optimised ground state S_0 of 4.

C	2.891083	-0.301316	-2.868452
C	4.086227	1.877626	-2.497110
C	5.212246	4.114896	-2.253903
C	3.502657	0.725622	-1.974372
C	4.657378	2.846149	-1.684231
C	-1.282794	2.495511	-1.648704
C	0.022943	4.615515	-1.762593
C	-4.128777	-1.205921	-1.303656
C	-0.185509	3.389108	-1.171784
C	2.284746	7.426709	-1.536115
C	1.077722	5.411112	-1.325241
C	-3.181232	2.653912	-0.014655
C	-1.192949	-3.508097	-1.107025
C	3.504837	0.577768	-0.590926
C	4.675638	2.634949	-0.310836
C	-1.351719	-4.851865	-0.816495
C	-2.035118	0.711266	-0.146586
C	-4.023468	-1.584915	0.140293
C	-3.810124	1.764533	0.780979
C	4.097460	1.511296	0.260302
C	3.534458	-1.681854	0.445721
C	1.849696	4.955089	-0.263906
C	-4.398420	-2.855857	0.549652
C	-1.294622	-7.566727	-0.098371
C	1.599427	-0.507265	0.488661
C	-3.564569	-0.695156	1.115972
C	1.545832	3.719228	0.279472
C	-1.042432	-5.290017	0.464757
C	2.659438	-2.373830	1.203802
C	-0.418663	-3.047329	0.996221
C	4.083876	1.319113	1.742461
C	-0.580814	-4.356267	1.390610
C	-4.339256	-3.249434	1.879501
C	0.268309	-2.041377	1.871158
C	-4.691411	-4.657304	2.253777
C	-3.552259	-1.024293	2.468906
C	-3.938330	-2.313470	2.825418
C	-3.139785	-0.028270	3.506896
H	3.154671	-0.104649	-3.907933
H	4.087424	2.016435	-3.573587
H	5.392018	4.033794	-3.326716
H	3.232935	-1.306349	-2.610711
H	4.504955	4.935333	-2.095833
H	-1.915630	3.025798	-2.360997
H	1.798267	-0.311597	-2.791376
H	-0.616243	4.967736	-2.561918
H	-4.826964	-1.870069	-1.813907
H	-0.861218	1.618880	-2.158846
H	-3.162642	-1.261838	-1.815278
H	6.148393	4.397440	-1.767537
H	-4.482281	-0.179617	-1.425799
H	-1.410677	-3.112083	-2.094721
H	2.213634	8.322004	-2.149599
H	-3.394007	3.690002	-0.215269
H	-1.704649	-5.523287	-1.586164
H	3.262583	6.959108	-1.689137
H	-0.553659	-7.467756	-0.896447
H	-4.750782	-3.559918	-0.197808
H	4.559144	-1.883695	0.185386
H	2.167492	7.696985	-0.482196
H	5.135509	3.374283	0.338265
H	-4.691616	1.864629	1.389752
H	-2.298384	-7.535715	-0.533704
H	2.668790	5.526797	0.148068
H	-1.150793	-8.513937	0.417367
H	2.761161	-3.318675	1.709499
H	-5.564130	-5.004768	1.697192
H	2.100352	3.341518	1.129068
H	4.579273	0.387971	2.029678
H	4.600239	2.140603	2.238909
H	3.061345	1.268499	2.133750
H	-0.331237	-1.137548	2.003427
H	-3.865925	-5.334792	2.013264
H	-0.304295	-4.679897	2.386000
H	0.495471	-2.455809	2.853044
H	-2.100749	0.298293	3.382979
H	-4.906726	-4.755136	3.319249
H	-3.746891	0.877656	3.455390
H	-3.920480	-2.588461	3.875622
H	-3.267211	-0.451974	4.503533
Cl	-0.683422	-0.739041	-3.052798
Cl	0.359792	1.602328	2.858976
Cu	-0.824267	-0.632367	-0.757847
Cu	0.543372	1.064773	0.651338
N	-2.119205	1.986266	-0.584649
N	2.871919	-0.550929	0.015850
N	-0.742038	-2.616932	-0.230310
N	0.576627	2.928174	-0.172740
N	-3.103159	0.582744	0.682061

N	1.498258	-1.634086	1.229010
O	1.244558	6.577539	-1.963720
O	-1.120613	-6.563490	0.881241

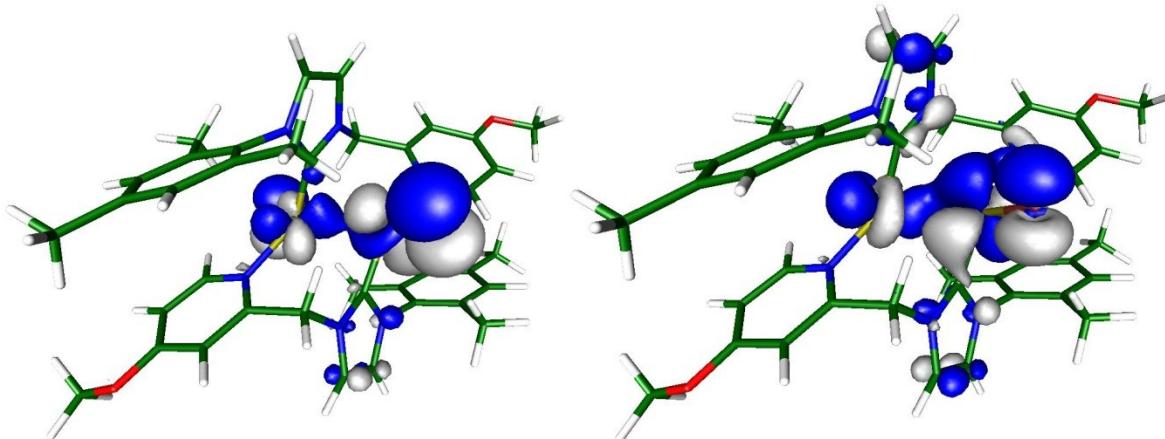


Figure S11. HOMO-6 (left) and HOMO-7 of 4 showing the dispersion interaction between the two copper atoms (isovalue = 0.026).

Table S11. Cartesian coordinates of the optimised triplet state T₁ of 4.

C	3.407527	-1.582827	-2.698371
C	4.122098	0.759796	-3.207600
C	4.841520	3.066909	-3.888412
C	3.670189	-0.170236	-2.280255
C	4.391241	2.076867	-2.858636
C	0.047142	2.551426	-1.743375
C	0.104196	4.866973	-0.795492
C	-3.449533	-1.465363	-1.466694
C	0.367588	3.513923	-0.661166
C	-0.130462	7.857497	1.221006
C	0.179373	5.702999	0.301947
C	-2.430284	2.299492	-1.454300
C	-0.968997	-3.533927	-1.263731
C	3.490495	0.267212	-0.965957
C	4.251336	2.451840	-1.530034
C	-1.553795	-4.746395	-0.949928
C	-1.065540	0.838650	-0.379233
C	-3.385792	-1.514668	0.025363
C	-3.205243	1.566219	-0.631142
C	3.829367	1.555978	-0.555419
C	3.779447	-1.587962	0.646626
C	0.531474	5.138109	1.543136
C	-3.856820	-2.619513	0.714638
C	-2.837947	-7.071900	-0.059789
C	1.694960	-0.781007	0.377880
C	-2.883293	-0.435901	0.761441
C	0.759364	3.784772	1.602090
C	-1.498286	-5.178648	0.371337
C	2.957456	-2.316619	1.433789
C	-0.254309	-3.207529	0.885791
C	3.853082	1.958041	0.884680
C	-0.791313	-4.405980	1.291051
C	-3.843743	-2.675208	2.102965
C	0.491582	-2.327032	1.850238
C	-4.297798	-3.917356	2.803575
C	-2.914966	-0.426891	2.155809
C	-3.392024	-1.565952	2.803965
C	-2.494393	0.775873	2.939464
H	3.949141	-1.807692	-3.617436
H	4.271665	0.437512	-4.232969
H	5.432424	2.583032	-4.668085
H	3.714961	-2.300064	-1.935827
H	3.984763	3.544062	-4.374486
H	-0.154133	3.059915	-2.685541
H	2.339615	-1.727895	-2.891129
H	-0.173657	5.277697	-1.758975
H	-3.741472	-2.435896	-1.868128
H	0.831058	1.804406	-1.910000
H	-2.495069	-1.173653	-1.913116
H	5.444483	3.856012	-3.436331
H	-4.186499	-0.730462	-1.802104
H	-0.982506	-3.139843	-2.275361
H	-0.452624	8.829937	0.851655
H	-2.688583	3.108522	-2.115667

H -2.045315 -5.315922 -1.725458
 H 0.855379 7.956224 1.687947
 H -2.200535 -7.516058 -0.829925
 H -4.246717 -3.460349 0.150359
 H 4.842092 -1.642567 0.486994
 H -0.845189 7.498905 1.968483
 H 4.504583 3.463160 -1.228667
 H -4.270309 1.582402 -0.473693
 H -3.621129 -6.474795 -0.535981
 H 0.620607 5.728369 2.443407
 H -3.294621 -7.859292 0.535944
 H 3.165596 -3.133295 2.102953
 H -5.128828 -4.388767 2.274637
 H 1.011809 3.306539 2.541987
 H 4.827800 1.708113 1.318272
 H 3.709991 3.033905 0.986800
 H 3.098001 1.460611 1.490543
 H -0.121690 -1.474060 2.151626
 H -3.488194 -4.652661 2.842490
 H -0.690118 -4.747076 2.313857
 H 0.751557 -2.877443 2.752858
 H -1.424551 0.757417 3.171235
 H -4.617811 -3.711761 3.826515
 H -2.682881 1.692796 2.380566
 H -3.432495 -1.570189 3.889076
 H -3.039768 0.822026 3.883321
 Cl 0.038956 -0.844818 -3.134783
 Cl 1.162958 0.819003 3.005578
 Cu 0.095104 -0.773036 -0.887071
 Cu 0.558613 0.957912 0.824607
 N -1.143303 1.836390 -1.329772
 N 2.996063 -0.662702 0.001913
 N -0.370534 -2.755487 -0.368221
 N 0.679381 2.957109 0.548133
 N -2.391123 0.682977 0.041487
 N 1.699206 -1.809197 1.258777
 O -0.094125 7.010599 0.098435
 O -2.076913 -6.292224 0.840986

Table S12. TD-DFT results for the first 100 singlet and triplet excitations from the optimised ground state S_0 of 4.

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

State	Energy (cm ⁻¹)	Wavelength (nm)	fosc	T2 (au**2)	TX (au)		TZ (au)
1	25406.5	393.6	0.094327725	1.22228	0.31759	1.05854	0.03002
2	25668.8	389.6	0.004465745	0.05727	-0.08006	-0.16602	0.15265
3	26628.2	375.5	0.005555116	0.06868	-0.15070	0.18963	-0.10004
4	25834.6	387.1	0.000246766	0.00314	-0.04649	-0.01899	0.02495
5	27749.4	360.4	0.003560605	0.04224	-0.05822	0.19369	0.03656
6	29084.3	343.8	0.013581290	0.15373	0.32472	0.11764	0.18561
7	28649.5	349.0	0.006386624	0.07339	-0.14535	0.20574	0.09967
8	29933.9	334.1	0.003511157	0.03862	-0.17314	0.02575	-0.08931
9	30260.2	330.5	0.013349096	0.14523	0.07647	-0.34654	0.13890
10	30253.4	330.5	0.009756168	0.10616	0.01317	-0.27118	-0.18015
11	30629.6	326.5	0.003248004	0.03491	0.14777	0.10057	0.05438
12	31671.2	315.7	0.004171055	0.04336	-0.00852	0.20799	0.00502
13	31872.2	313.8	0.057473113	0.59365	0.11971	-0.74173	0.17075
14	31908.0	313.4	0.004219902	0.04354	0.16129	0.12472	0.04439
15	31991.9	312.6	0.006711770	0.06913	-0.04732	0.25861	-0.00351
16	32485.1	307.8	0.003867905	0.03920	0.03635	0.03690	-0.19109
17	31513.3	317.3	0.003298756	0.03446	-0.17071	-0.06663	-0.02969
18	32784.4	305.0	0.001700309	0.01707	-0.07969	-0.05845	0.08548
19	33087.6	302.2	0.006626158	0.06593	0.01405	0.11150	0.23087
20	33617.7	297.5	0.011114526	0.10884	0.26778	-0.17983	0.06927
21	32348.5	309.1	0.002914299	0.02966	0.14285	0.08860	-0.03743
22	33297.1	300.3	0.001253315	0.01239	-0.04888	-0.08711	0.04912
23	34284.2	291.7	0.001374715	0.01320	0.06981	0.09027	0.01340
24	34393.1	290.8	0.016077993	0.15390	-0.35026	0.17241	-0.03863
25	34511.5	289.8	0.005055995	0.04823	-0.04847	-0.02430	0.21281
26	34770.7	287.6	0.006227102	0.05896	0.23304	0.06612	0.01674
27	34768.2	287.6	0.008382617	0.07937	-0.06427	-0.26226	0.08037
28	35021.6	285.5	0.003574846	0.03360	0.11240	-0.11475	0.08834
29	35368.8	282.7	0.006210064	0.05780	-0.07790	0.22655	0.02022
30	35282.3	283.4	0.011079004	0.10338	0.02840	0.27012	-0.17206
31	35894.8	278.6	0.001584254	0.01453	-0.06883	-0.08060	-0.05741
32	35694.3	280.2	0.002113198	0.01949	0.05488	-0.12836	-0.00080
33	35663.0	280.4	0.006772487	0.06252	-0.22431	-0.11042	0.00305
34	35670.3	280.3	0.000083884	0.00077	-0.02261	-0.01606	0.00223
35	36405.7	274.7	0.014888740	0.13464	-0.34864	0.10255	0.05070
36	36458.0	274.3	0.015656740	0.14138	0.33615	0.11361	-0.12439
37	36063.5	277.3	0.000550200	0.00502	-0.04965	0.04434	-0.02431
38	36943.9	270.7	0.022489110	0.20040	-0.33427	0.29768	0.00702

39	37175.1	269.0	0.014043585	0.12437	-0.31508	0.15540	0.03070
40	36711.0	272.4	0.000399456	0.00358	0.00994	0.05754	-0.01316
41	37157.9	269.1	0.005207728	0.04614	-0.09136	-0.19440	-0.00071
42	37392.6	267.4	0.005727560	0.05043	-0.08093	0.20310	0.05126
43	35857.4	278.9	0.005197084	0.04772	0.20892	-0.01844	-0.06104
44	37936.3	263.6	0.014975646	0.12996	-0.22111	-0.15168	0.24097
45	37805.7	264.5	0.005647983	0.04918	-0.14033	0.08680	0.14818
46	37758.3	264.8	0.002192338	0.01911	0.10863	0.06217	-0.05872
47	37968.7	263.4	0.004476797	0.03882	0.06037	0.18754	-0.00069
48	37023.4	270.1	0.001352795	0.01203	0.02175	-0.10483	0.02381
49	38094.9	262.5	0.002465883	0.02131	0.12221	-0.00474	0.07971
50	38258.5	261.4	0.010717059	0.09222	-0.27927	0.05176	0.10746
51	37426.8	267.2	0.000896317	0.00788	-0.00929	0.00272	0.08826
52	38163.7	262.0	0.003836960	0.03310	-0.06632	-0.01521	0.16873
53	38804.7	257.7	0.026517553	0.22497	0.34325	-0.14454	-0.29370
54	38160.7	262.0	0.000228605	0.00197	0.03858	-0.01671	0.01429
55	39099.9	255.8	0.000724015	0.00610	0.00060	0.07596	0.01805
56	38262.3	261.4	0.005062827	0.04356	-0.12285	0.16099	0.05049
57	38977.2	256.6	0.001809137	0.01528	-0.12292	0.00871	-0.00974
58	39004.4	256.4	0.005749469	0.04853	-0.21173	0.03842	0.04715
59	39530.8	253.0	0.006201351	0.05164	0.20730	-0.00018	-0.09311
60	39888.4	250.7	0.008421962	0.06951	-0.06992	0.21588	0.13423
61	39488.7	253.2	0.020202122	0.16842	-0.33131	0.15386	0.18704
62	40182.6	248.9	0.012494423	0.10237	-0.31081	0.06069	-0.04557
63	40016.7	249.9	0.005632404	0.04634	-0.08118	-0.19617	-0.03559
64	40579.7	246.4	0.005166596	0.04192	-0.19702	-0.05531	0.00618
65	40627.7	246.1	0.005287762	0.04285	0.19177	0.07233	-0.02898
66	40551.7	246.6	0.008856493	0.07190	-0.08624	0.25311	0.01993
67	40094.3	249.4	0.001339003	0.01099	0.04143	-0.09185	-0.02901
68	40436.4	247.3	0.005571136	0.04536	-0.18725	-0.07125	0.07224
69	39743.3	251.6	0.000104636	0.00087	-0.00731	-0.00231	-0.02843
70	40865.0	244.7	0.003588025	0.02891	-0.09419	-0.12898	-0.05830
71	41307.8	242.1	0.001478835	0.01179	-0.08238	-0.04411	0.05526
72	41543.8	240.7	0.006311837	0.05002	0.18248	-0.10252	-0.07878
73	40194.0	248.8	0.003514059	0.02878	-0.02125	-0.16788	0.01216
74	41566.6	240.6	0.009832574	0.07787	0.27121	0.05309	-0.03871
75	41651.0	240.1	0.025907975	0.20478	-0.41135	0.18344	0.04378
76	40479.8	247.0	0.001359011	0.01105	-0.00135	-0.08545	0.06123
77	41889.1	238.7	0.002293325	0.01802	0.01215	-0.05380	-0.12240
78	41356.5	241.8	0.022085200	0.17581	0.31414	-0.27379	0.04649
79	42109.7	237.5	0.001607236	0.01257	0.04388	0.10167	0.01744
80	42165.7	237.2	0.003402451	0.02656	-0.14172	0.07967	-0.01154
81	40465.9	247.1	0.007414012	0.06032	-0.20030	-0.10992	0.09008
82	42102.0	237.5	0.008080204	0.06318	0.05107	0.23800	-0.06270
83	42152.5	237.2	0.003847272	0.03005	-0.15874	-0.01114	0.06875
84	42098.7	237.5	0.002896841	0.02265	-0.09108	0.11982	0.00050
85	42171.1	237.1	0.001403927	0.01096	-0.01507	-0.08851	-0.05384
86	42393.7	235.9	0.020338827	0.15794	0.38073	-0.10845	-0.03502
87	40905.6	244.5	0.000269859	0.00217	-0.04648	0.00078	0.00327
88	42958.5	232.8	0.002907883	0.02228	-0.10602	0.02869	-0.10110
89	40986.4	244.0	0.000442199	0.00355	-0.04559	0.03405	0.01771
90	42876.6	233.2	0.004242190	0.03257	-0.09743	-0.13350	-0.07251
91	42856.3	233.3	0.002236707	0.01718	0.09383	0.08905	-0.02120
92	43229.0	231.3	0.0025757952	0.01962	0.12638	0.02798	-0.05351
93	43397.6	230.4	0.001544375	0.01172	-0.10627	0.00596	0.01965
94	43143.9	231.8	0.002157666	0.01646	0.12540	-0.02570	0.00885
95	43359.4	230.6	0.005715560	0.04340	0.13610	-0.07077	-0.14094
96	43727.5	228.7	0.008542885	0.06432	-0.22135	-0.09756	0.07619
97	43486.4	230.0	0.003057133	0.02314	0.12972	0.04974	-0.06199
98	43661.8	229.0	0.005385333	0.04061	0.01920	-0.19143	-0.05991
99	42924.2	233.0	0.002929320	0.02247	-0.04075	-0.13412	0.05308
100	43030.0	232.4	0.005517087	0.04221	0.18114	0.06808	-0.06902
101	23639.8	423.0	spin forbidden (mult=3)				
102	25294.0	395.3	spin forbidden (mult=3)				
103	25752.3	388.3	spin forbidden (mult=3)				
104	26854.0	372.4	spin forbidden (mult=3)				
105	27852.9	359.0	spin forbidden (mult=3)				
106	28405.8	352.0	spin forbidden (mult=3)				
107	28808.4	347.1	spin forbidden (mult=3)				
108	29510.7	338.9	spin forbidden (mult=3)				
109	30052.9	332.7	spin forbidden (mult=3)				
110	30287.0	330.2	spin forbidden (mult=3)				
111	30713.0	325.6	spin forbidden (mult=3)				
112	30850.5	324.1	spin forbidden (mult=3)				
113	31220.9	320.3	spin forbidden (mult=3)				
114	31496.2	317.5	spin forbidden (mult=3)				
115	31547.3	317.0	spin forbidden (mult=3)				
116	31864.1	313.8	spin forbidden (mult=3)				
117	32376.3	308.9	spin forbidden (mult=3)				
118	32475.1	307.9	spin forbidden (mult=3)				
119	32738.1	305.5	spin forbidden (mult=3)				
120	32993.1	303.1	spin forbidden (mult=3)				
121	33155.9	301.6	spin forbidden (mult=3)				
122	33337.1	300.0	spin forbidden (mult=3)				
123	33509.8	298.4	spin forbidden (mult=3)				
124	33676.7	296.9	spin forbidden (mult=3)				
125	33880.6	295.2	spin forbidden (mult=3)				
126	33950.2	294.5	spin forbidden (mult=3)				
127	34044.0	293.7	spin forbidden (mult=3)				
128	34519.7	289.7	spin forbidden (mult=3)				
129	34640.1	288.7	spin forbidden (mult=3)				
130	34852.5	286.9	spin forbidden (mult=3)				
131	35053.2	285.3	spin forbidden (mult=3)				
132	35446.9	282.1	spin forbidden (mult=3)				

133	35608.4	280.8	spin forbidden (mult=3)
134	35691.0	280.2	spin forbidden (mult=3)
135	35830.0	279.1	spin forbidden (mult=3)
136	35943.4	278.2	spin forbidden (mult=3)
137	35974.8	278.0	spin forbidden (mult=3)
138	36212.0	276.2	spin forbidden (mult=3)
139	36306.2	275.4	spin forbidden (mult=3)
140	36369.9	275.0	spin forbidden (mult=3)
141	36412.8	274.6	spin forbidden (mult=3)
142	36494.7	274.0	spin forbidden (mult=3)
143	36606.7	273.2	spin forbidden (mult=3)
144	36692.5	272.5	spin forbidden (mult=3)
145	36756.0	272.1	spin forbidden (mult=3)
146	36841.7	271.4	spin forbidden (mult=3)
147	36870.9	271.2	spin forbidden (mult=3)
148	36970.5	270.5	spin forbidden (mult=3)
149	37168.5	269.0	spin forbidden (mult=3)
150	37254.3	268.4	spin forbidden (mult=3)
151	37320.1	268.0	spin forbidden (mult=3)
152	37363.4	267.6	spin forbidden (mult=3)
153	37502.1	266.7	spin forbidden (mult=3)
154	37669.2	265.5	spin forbidden (mult=3)
155	37735.8	265.0	spin forbidden (mult=3)
156	37863.3	264.1	spin forbidden (mult=3)
157	37962.3	263.4	spin forbidden (mult=3)
158	38073.1	262.7	spin forbidden (mult=3)
159	38133.1	262.2	spin forbidden (mult=3)
160	38295.9	261.1	spin forbidden (mult=3)
161	38366.5	260.6	spin forbidden (mult=3)
162	38429.4	260.2	spin forbidden (mult=3)
163	38655.7	258.7	spin forbidden (mult=3)
164	38769.3	257.9	spin forbidden (mult=3)
165	38875.3	257.2	spin forbidden (mult=3)
166	38921.8	256.9	spin forbidden (mult=3)
167	38983.1	256.5	spin forbidden (mult=3)
168	39160.4	255.4	spin forbidden (mult=3)
169	39234.9	254.9	spin forbidden (mult=3)
170	39384.1	253.9	spin forbidden (mult=3)
171	39498.1	253.2	spin forbidden (mult=3)
172	39576.0	252.7	spin forbidden (mult=3)
173	39742.3	251.6	spin forbidden (mult=3)
174	39790.8	251.3	spin forbidden (mult=3)
175	39891.6	250.7	spin forbidden (mult=3)
176	39958.3	250.3	spin forbidden (mult=3)
177	40044.5	249.7	spin forbidden (mult=3)
178	40272.9	248.3	spin forbidden (mult=3)
179	40379.1	247.7	spin forbidden (mult=3)
180	40471.4	247.1	spin forbidden (mult=3)
181	40656.8	246.0	spin forbidden (mult=3)
182	40836.8	244.9	spin forbidden (mult=3)
183	40980.3	244.0	spin forbidden (mult=3)
184	41069.9	243.5	spin forbidden (mult=3)
185	41098.0	243.3	spin forbidden (mult=3)
186	41209.3	242.7	spin forbidden (mult=3)
187	41322.8	242.0	spin forbidden (mult=3)
188	41442.1	241.3	spin forbidden (mult=3)
189	41539.9	240.7	spin forbidden (mult=3)
190	41560.4	240.6	spin forbidden (mult=3)
191	41711.7	239.7	spin forbidden (mult=3)
192	41985.3	238.2	spin forbidden (mult=3)
193	42103.6	237.5	spin forbidden (mult=3)
194	42154.3	237.2	spin forbidden (mult=3)
195	42178.8	237.1	spin forbidden (mult=3)
196	42327.2	236.3	spin forbidden (mult=3)
197	42361.1	236.1	spin forbidden (mult=3)
198	42481.9	235.4	spin forbidden (mult=3)
199	42592.3	234.8	spin forbidden (mult=3)
200	42707.3	234.2	spin forbidden (mult=3)

X-ray crystallography

Crystals suitable for single-crystal X-ray diffraction were selected, coated in perfluoropolyether oil, and mounted on MiTeGen sample holders. Diffraction data were collected on a Nonius Kappa three circle diffractometer utilizing graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) from a rotating anode tube run at 50 V and 30 mA. The diffractometer is equipped with a Bruker ApexII area detector and an open flow N₂ Cryoflex II (Bruker) device, the measurement was performed at 100 K. For data reduction, the Bruker Apex2 software suite (Bruker AXS) was used. Subsequently, utilizing Olex2²³ or ShelX²⁴ the structures were solved using the Olex2.solve²⁵ charge-flipping algorithm or ShelXT²⁶, and were subsequently refined with Olex2.refine²⁵ using Gauss-Newton minimization or ShelXL. All non-hydrogen atom positions were located from the Fourier maps and refined anisotropically. Hydrogen atom positions were calculated using a riding model in geometric positions and refined isotropically, where possible to determine unambiguously.

Table S13. Selected crystallographic data for $2 \cdot 2 \text{ CH}_2\text{Cl}_2$ and $3 \cdot 2 \text{ CH}_2\text{Cl}_2$ at different temperatures.

	$2 \cdot 2 \text{ CH}_2\text{Cl}_2$	$2 \cdot 2 \text{ CH}_2\text{Cl}_2$	$3 \cdot 2 \text{ CH}_2\text{Cl}_2$	$3 \cdot 2 \text{ CH}_2\text{Cl}_2$
CCDC	1038476	1038475	1038478	1038477
Empirical formula	C ₃₈ H ₄₂ Cl ₆ Cu ₂ N ₆	C ₃₈ H ₄₂ Cl ₆ Cu ₂ N ₆	C ₄₀ H ₄₆ Cl ₆ Cu ₂ N ₆	C ₄₀ H ₄₆ Cl ₆ Cu ₂ N ₆
Formula weight	922.55	922.55	950.61	950.61
T [K]	100	290	102	290
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1	P-1
a [\AA]	8.1887(6)	8.2153(8)	8.3293(13)	8.3056(14)
b [\AA]	10.9691(7)	11.1662(10)	10.9929(17)	11.1055(19)
c [\AA]	11.3579(8)	11.5343(11)	11.7343(18)	11.873(2)
α [°]	85.0163(15)	85.272(3)	86.079(5)	86.315(6)
β [°]	85.1738(16)	84.430(3)	89.732(6)	89.284(6)
γ [°]	77.5551(15)	77.543(3)	77.869(5)	77.720(6)
V [\AA^3]	990.21(12)	1026.24(17)	1047.9(3)	1067.9(3)
Z	1	1	1	1
ρ_{calc} [g/cm ³]	1.547	1.493	1.506	1.478
μ [mm ⁻¹]	1.516	1.463	1.435	1.408
F(000)	472.0	472.0	488.0	488.0
Crystal size [mm ³]	0.338 × 0.289 × 0.160	0.546 × 0.431 × 0.310	0.404 × 0.356 × 0.138	0.255 × 0.162 × 0.110
Radiation / λ [\AA]	MoK α / 0.71073			
2 Θ range for data collection [°]	3.608 - 53.49	3.554 - 53.574	3.48 - 53.436	3.438 - 53.576
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -13 ≤ l ≤ 14	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected	11434	13923	15195	12827
Independent	4210 [$R_{\text{int}} = 0.0207$,	4388 [$R_{\text{int}} = 0.0236$,	4437 [$R_{\text{int}} = 0.0360$,	4523 [$R_{\text{int}} = 0.0326$,

reflections	$R_\sigma = 0.0213]$	$R_\sigma = 0.0256]$	$R_\sigma = 0.0411]$	$R_\sigma = 0.0502]$
Data/restraints/ parameters	4210/0/238	4388/0/238	4437/0/248	4523/0/248
Goodness-of-fit on F^2	1.040	1.161	1.146	1.045
Final R indexes [$ I \geq 2\sigma(I)$]	$R_1 = 0.0237,$ $wR_2 = 0.0606$	$R_1 = 0.0337,$ $wR_2 = 0.0973$	$R_1 = 0.0363,$ $wR_2 = 0.1043$	$R_1 = 0.0451,$ $wR_2 = 0.1163$
Final R indexes [all data]	$R_1 = 0.0256,$ $wR_2 = 0.0618$	$R_1 = 0.0467,$ $wR_2 = 0.1175$	$R_1 = 0.0491,$ $wR_2 = 0.1225$	$R_1 = 0.0823,$ $wR_2 = 0.1458$
Largest diff. peak/hole [e Å ⁻³]	0.37/-0.39	0.62/-0.61	0.83/-0.60	0.59/-0.57

Table S14. Selected crystallographic data for **1 · 2 CH₂Cl₂, 4 · 2 CH₂Cl₂, and 5-7.**

	1 · 2 CH₂Cl₂	4 · 2 CH₂Cl₂	7	5
CCDC	1038479	1038480	1038481	1038482
Empirical formula	C ₃₈ H ₄₀ Cl ₈ Cu ₂ N ₆	C ₄₀ H ₄₆ Cl ₆ Cu ₂ N ₆ O ₂	C ₃₆ H ₃₆ Cl ₂ Cu ₂ N ₈ O ₄	C ₂₁ H ₂₅ ClCuN ₃
Formula weight	991.44	982.61	842.71	418.43
T [K]	100	100	100	100
Crystal system	triclinic	triclinic	orthorhombic	monoclinic
Space group	P-1	P-1	P ₂ 12 ₁ 2 ₁	P2 ₁ /c
a [Å]	8.253(3)	8.292(2)	9.0636(13)	9.5545(5)
b [Å]	10.948(3)	10.995(3)	9.6375(13)	8.8034(5)
c [Å]	11.802(4)	12.277(4)	20.925(3)	23.9329(12)
α [°]	85.792(9)	84.743(9)	90	90
β [°]	89.721(9)	86.680(8)	90	96.6239(16)
γ [°]	78.477(9)	78.394(8)	90	90
V [Å ³]	1041.9(6)	1090.9(5)	1827.8(4)	1999.61(18)
Z	1	1	2	4
ρ _{calc} [g/cm ³]	1.580	1.496	1.531	1.390
μ [mm ⁻¹]	1.570	1.384	1.361	1.235
F(000)	504.0	504.0	864.0	872.0
Crystal size [mm ³]	0.450 × 0.436 × 0.130	0.338 × 0.296 × 0.184	0.426 × 0.218 × 0.118	0.236 × 0.135 × 0.106
Radiation / λ [Å]	MoKα / 0.71073	MoKα / 0.71073	MoKα / 0.71073	MoKα / 0.71073
2θ range for data collection [°]	3.46 - 53.966	3.334 - 53.528	4.654 - 53.472	3.426 - 53.55
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -14 ≤ l ≤ 15	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -26 ≤ l ≤ 26	-12 ≤ h ≤ 12, -11 ≤ k ≤ 11, -30 ≤ l ≤ 30
Reflections collected	14284	13159	22052	26675
Independent reflections	4444 [<i>R</i> _{int} = 0.0295, <i>R</i> _σ = 0.0270]	4622 [<i>R</i> _{int} = 0.0248, <i>R</i> _σ = 0.0270]	3874 [<i>R</i> _{int} = 0.0292, <i>R</i> _σ = 0.0253]	4269 [<i>R</i> _{int} = 0.0345, <i>R</i> _σ = 0.0234]
Data/restraints/parameters	4444/198/247	4622/204/257	3874/204/238	4269/0/239
Goodness-of-fit on <i>F</i> ²	1.186	1.208	1.061	1.058
Final <i>R</i> indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0256, <i>wR</i> ₂ = 0.0808	<i>R</i> ₁ = 0.0347, <i>wR</i> ₂ = 0.1015	<i>R</i> ₁ = 0.0228, <i>wR</i> ₂ = 0.0597	<i>R</i> ₁ = 0.0296, <i>wR</i> ₂ = 0.0720
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0295, <i>wR</i> ₂ = 0.0952	<i>R</i> ₁ = 0.0410, <i>wR</i> ₂ = 0.1153	<i>R</i> ₁ = 0.0246, <i>wR</i> ₂ = 0.0605	<i>R</i> ₁ = 0.0343, <i>wR</i> ₂ = 0.0744
Largest diff. peak/hole [e Å ⁻³]	0.62/-0.58	1.00/-0.70	0.31/-0.28	0.46/-0.32
Flack parameter			0.061(4)	

	6
CCDC	1431818
Empirical formula	C ₃₆ H ₃₈ Cl ₂ Cu ₂ N ₆
Formula weight	752.70
T [K]	100(2)
Crystal system	Monoclinic
Space group	P2 ₁ /n
a [Å]	10.0169(4)
b [Å]	15.9690(6)
c [Å]	10.7209(4)
α [°]	90
β [°]	95.0560(10)
γ [°]	90
V [Å ³]	1708.24(11)
Z	2
ρ _{calc} [g/cm ³]	1.463
μ [mm ⁻¹]	1.437 ??
F(000)	776
Crystal size [mm ³]	0.800 x 0.600 x 0.350
Radiation / λ [Å]	MoKα / 0.71073 Å
2θ range for data collection [°]	4.588 - 52.088
	-10<=h<=12, -
Index ranges	19<=k<=19, -
	13<=l<=13
Reflections collected	12547
Independent reflections	3371 [R _{int} = 0.0175, R _σ = 0.0134]
Data/restraints/ parameters	3371 / 0 / 211
Goodness-of-fit on F ²	1.043
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0210, wR ₂ = 0.0532
Final R indexes [all data]	R ₁ = 0.0230, # wR ₂ = 0.0541
Largest diff. peak/hole [e Å ⁻³]	0.334 / -0.278
Flack parameter	

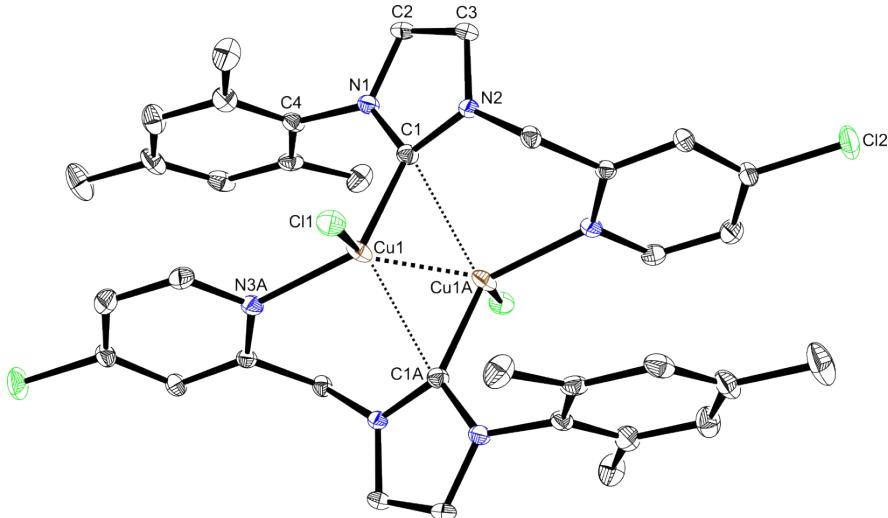


Figure S12. Molecular structure of $\mathbf{1} \cdot 2 \text{CH}_2\text{Cl}_2$ in the solid state; displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms and CH_2Cl_2 are omitted for clarity. Selected bond lengths [\AA], atom···atom distances [\AA], and bond angles [$^\circ$]: $\text{Cu1-C1} = 1.9462(19)$, $\text{Cu1-Cl1} = 2.3407(7)$, $\text{Cu1-N3A} = 2.0453(16)$, $\text{C1-N1} = 1.366(2)$, $\text{C1-N2} = 1.357(2)$; $\text{Cu1}\cdots\text{Cu1A} = 2.5226(8)$, $\text{Cu1}\cdots\text{C1A} = 2.5483(19)$; $\text{C1-Cu1-Cu1A} = 68.13(6)$, $\text{N1-C1-N2} = 103.48(15)$.

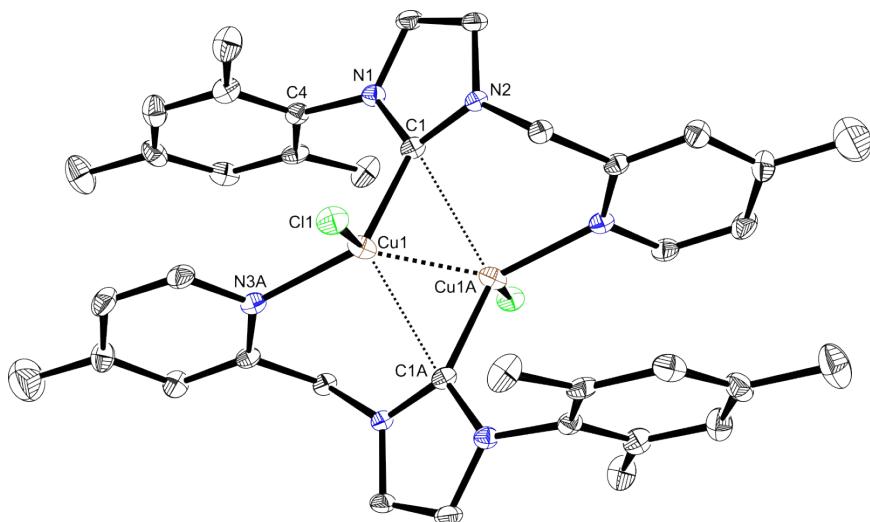


Figure S13. Molecular structure of $\mathbf{3} \cdot 2 \text{CH}_2\text{Cl}_2$ in the solid state; displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms and CH_2Cl_2 are omitted for clarity. Selected bond lengths [\AA], atom···atom distances [\AA], and bond angles [$^\circ$]: $\text{Cu1-C1} = 1.945(3)$, $\text{Cu1-Cl1} = 2.3762(8)$, $\text{Cu1-N3A} = 2.049(2)$, $\text{C1-N1} = 1.378(3)$, $\text{C1-N2} = 1.367(3)$; $\text{Cu1}\cdots\text{Cu1A} = 2.5668(8)$, $\text{Cu1}\cdots\text{C1A} = 2.593(3)$; $\text{C1-Cu1-Cu1A} = 68.58(8)$, $\text{N1-C1-N2} = 103.2(2)$.

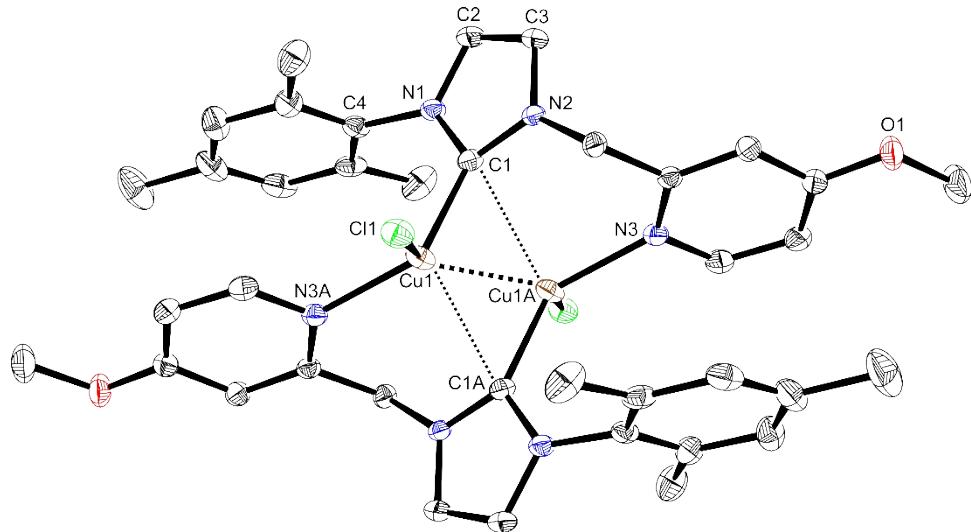


Figure S14. Molecular structure of **4 · 2 CH₂Cl₂ in the solid state;** displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms and CH₂Cl₂ are omitted for clarity. Selected bond lengths [Å], atom···atom distances [Å], and bond angles [°]: Cu1–C1 = 1.940(2), Cu1–Cl1 = 2.3620(8), Cu1–N3A = 2.032(2), C1–N1 = 1.366(3), C1–N2 = 1.357(3); Cu1···Cu1A = 2.5744(9), Cu1···C1A = 2.621(3); C1–Cu1–Cu1A = 69.35(7), N1–C1–N2 = 103.68(19).

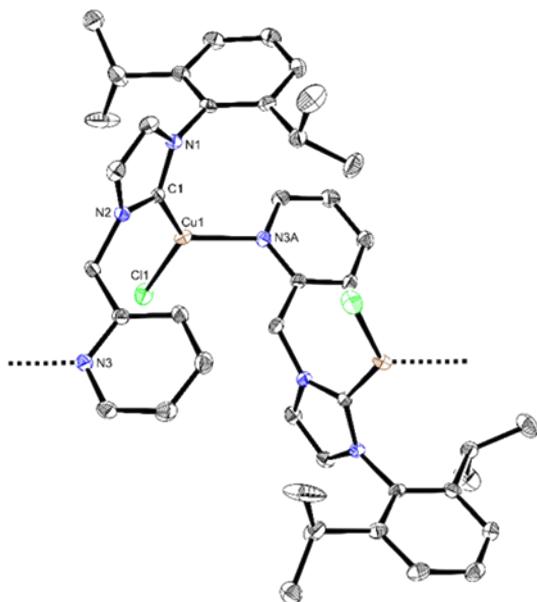


Figure S15. Molecular structure of **5 in the solid state;** displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

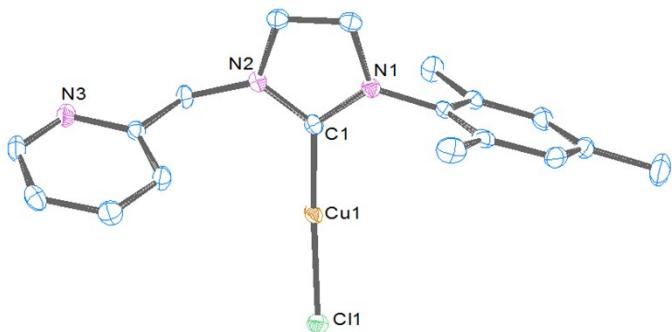


Figure S16. Molecular structure of 6 in the solid state; displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

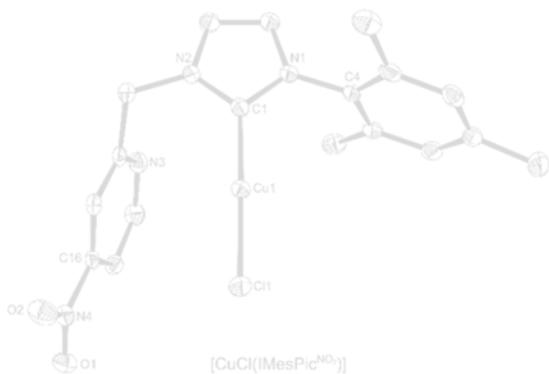


Figure S17. Molecular structure of 7 in the solid state; displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

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