

Electronic Supporting Information

For

A Reversible Nanoswitch as ON/OFF Photocatalyst

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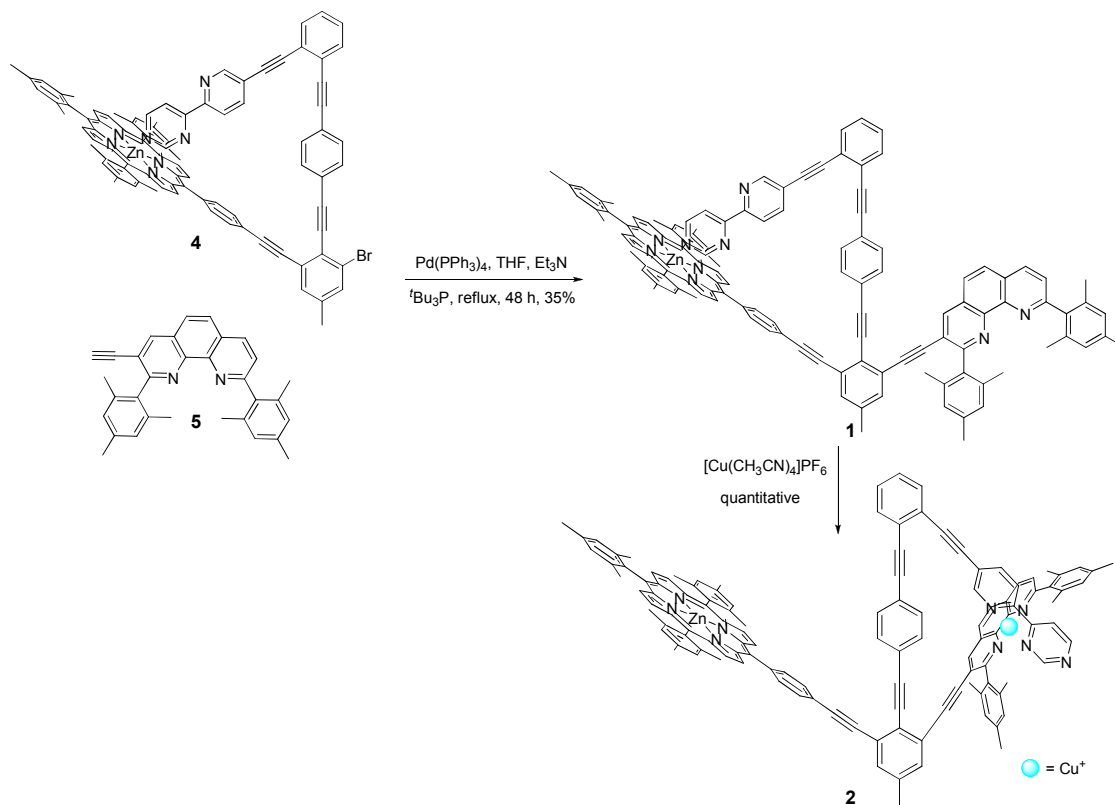
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Synthesis

General Information

All commercially available reagents were used without further purification and all solvents for column chromatography distilled prior to use. Thin-layer chromatography was performed using thin-layer chromatography plates (silica gel 60 F₂₅₄, Merck). Silica gel 60 was used for column chromatography. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance 400 MHz spectrometer using the deuterated solvent as the lock and residual solvent as the internal reference. In ¹H NMR assignments, the chemical shift (in ppm) is given first, followed, in brackets, by the multiplicity of the signal (s: singlet, d: doublet, t: triplet, dd: doublet of doublets, ddd: doublet of doublet of doublets, td: triplet of doublets, m: multiplet, bs: broad singlet), the value of the coupling constants in Hertz (Hz), the number of protons implied, and finally the assignment of the proton wherever possible. Numbering of the carbon atoms of the molecular formulae shown in the experimental section is only used for the assignments of the NMR signals and is not in accordance with IUPAC nomenclature rules. Anhydrous tetrahydrofuran (THF) and benzene were distilled over potassium. Diethyl ether was distilled over sodium/benzophenone. Triethyl amine was dried over calcium hydride. Melting points of solid compounds were measured on a Büchi (BÜCHI 510) melting point apparatus and remained uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 1750. Electro-spray ionisation mass spectra (ESI-MS) were recorded on a Thermo-Quest LCQ Deca. Microanalyses were performed on a Euro elemental analyser from EuroVector.

Synthetic Scheme and Synthetic procedures



Scheme S1. Synthesis of ligand **1** and formation of complex **2**.

14/13-H), 2.60 (s, 6 H, t-H), 2.62 (s, 3 H, v-H), 2.87 (d, $^3J = 5.6$ Hz, 1 H, b-H), 3.32 (d, $^5J = 1.2$ Hz, 1 H, a-H), 6.63 (dd, $^3J = 5.6$ Hz, $^5J = 1.2$ Hz, 1 H, c-H), 6.75 (s, 1 H, n-H), 6.97 (s, 2 H, 9/10-H), 7.03 (s, 2 H, 10/9-H), 7.28 (s, 4 H, q-H), 7.29 (s, 2 H, r-H), 7.32 (td, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz, 1 H, h/i-H), 7.37 (td, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz, 1 H, i/h-H), 7.44 (d, $^3J = 8.4$ Hz, 2 H, k/l-H), 7.47 (dd, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz, 1 H, g/j-H), 7.52 (s, 1 H, m-H), 7.59-7.60 (m, 2 H, j/g, 8-H), 7.62-7.69 (m, 3 H, d-, l/k-H), 7.70 (dd, $^3J = 8.4$ Hz, $^4J = 2.0$ Hz, 1 H, e-H), 7.88 (d, $^3J = 8.8$ Hz, 1 H, 5/6-H), 7.89 (d, $^3J = 8.0$ Hz, 2 H, o/p-H), 7.96 (d, $^3J = 8.8$ Hz, 1 H, 6/5-H), 8.02 (d, $^3J = 8.0$ Hz, 2 H, p/o-H), 8.35 (d, $^3J = 8.0$ Hz, 1 H, 7-H), 8.50 (dd, $^4J = 2.0$ Hz, $^5J = 0.8$ Hz, 1 H, f-H), 8.58 (s, 1 H, 4-H), 8.63 (d, $^3J = 4.4$ Hz, 2 H, β -H), 8.69 (d, $^3J = 4.4$ Hz, 2 H, β -H), 8.71 (d, $^3J = 4.4$ Hz, 2 H, β -H), 8.72 (d, $^3J = 4.4$ Hz, 2 H, β -H) ppm.

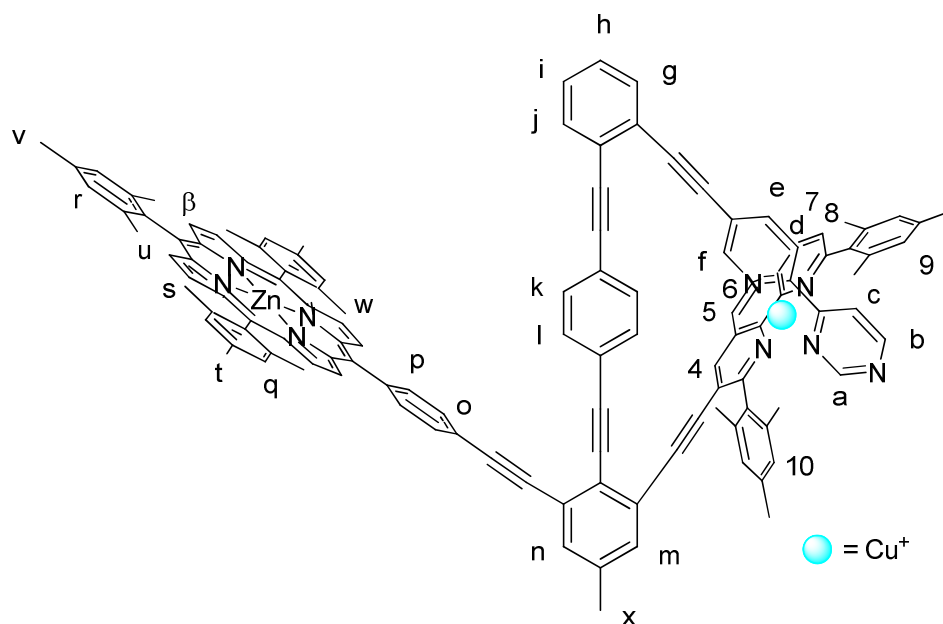
^{13}C NMR (100 MHz, CDCl_3): $\delta = 20.2, 20.6, 21.1$ (2C), 21.2, 21.5 (2C), 21.8, 21.9, 88.7, 89.5, 89.8, 89.9, 91.0, 93.4, 93.7, 93.9 (2C), 96.5, 115.0, 118.2, 118.4, 118.5, 120.0, 120.9, 121.8, 122.3, 123.0, 123.8, 124.0, 124.4, 125.2, 125.5, 125.7, 126.2, 126.4, 126.8, 127.0, 127.5, 127.6 (3C), 128.1, 128.2, 128.5, 128.9, 129.6, 130.5, 130.8, 131.2, 131.5, 131.6 (3C), 132.1, 132.9, 133.4, 134.1, 135.9, 136.1, 136.4, 136.9, 137.1, 137.2, 137.3, 137.6, 138.2, 138.5, 139.0, 139.2, 139.3, 139.5 (2C), 144.0, 145.0, 145.9, 148.8, 149.3, 149.9 (2C), 150.6, 151.2, 151.4, 152.8, 160.6, 161.0, 162.1 ppm.

ESI-MS: m/z (%): 1735.5 (100) [$\mathbf{1} + \text{H}^+$], calcd. 1735.7; see also Figure S20.

UV-vis absorption: $\lambda_{\text{max}} = 429$ nm, $\epsilon = 4.54 \times 10^5$ L mol $^{-1}$ cm $^{-1}$ (Soret band).

Elemental analysis: Calcd for $\text{C}_{121}\text{H}_{91}\text{N}_9\text{Zn}$: C, 83.69; H, 5.28; N, 7.26.
Found: C, 83.48; H, 5.34; N, 7.07.

Formation of complex **2** = [(**1**)Cu]PF₆



To a mixture of [Cu(CH₃CN)₄]PF₆ (1.23 mg, 3.30 μmol) and **1** (5.73 mg, 3.30 μmol) in an NMR tube, CD₂Cl₂ was added. The mixture was sonicated for 2-3 minutes to solubilise compound **1** and then analysed by NMR, ESI-MS and UV-vis. For other measurements the solvent was removed.

Yield: Quantitative. Melting point: Above 300 °C.

IR (KBr): $\nu = 3045, 2916, 2852, 2375, 2281, 2213, 1630, 1582, 1545, 1459, 1408, 1379, 1334, 1201, 1062, 997, 842, 798, 724, 635, 556, 477 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CD₂Cl₂): $\delta = 1.09$ (s, 3 H, CH₃), 1.64 (s, 3 H, CH₃), 1.71 (s, 3 H, CH₃), 1.79 (s, 6 H, s/w-H), 1.80 (s, 6 H, w/s-H), 1.82 (s, 6 H, u-H), 1.84 (s, 3 H, CH₃), 1.86 (s, 3 H, CH₃), 1.94 (s, 3 H, CH₃), 2.42 (s, 3 H, x-H), 2.61 (s, 9 H, v-, t-H), 5.93 (s, 1 H, 9/10-H), 6.16 (s, 1 H, 9/10-H), 6.26 (s, 1 H, 9/10-H), 6.37 (s, 1 H, 9/10-H), 7.28-7.31 (m, 10 H, q-, r-, a-, b-, k/l-H), 7.37-7.39 (m, 5 H, h-, i-, m/n-, l/k-H), 7.46-7.49 (m, 1 H, g/j-H), 7.54 (s, 1 H, n/m-H), 7.61-7.63 (m, 1 H, j/g-H), 7.67 (d, ³J = 4.8 Hz, 1 H, c-H), 7.85 (d, ³J = 8.4 Hz, 1 H, 8-H), 7.88 (d, ³J = 8.4 Hz, 1 H, d-H), 7.90 (d, ³J = 8.4 Hz, 2 H, o/p-H), 8.10 (dd, ³J = 8.4 Hz, ⁴J = 2.0 Hz, 1 H, e-H), 8.13 (s, 1 H, f-H), 8.20 (d, ³J = 8.4 Hz, 2 H, p/o-H), 8.21 (d, ³J = 8.8 Hz, 1 H, 5/6-H), 8.24 (d, ³J = 8.8 Hz, 1 H, 6/5-H), 8.67

(d, $^3J = 8.4$ Hz, 1 H, 7-H), 8.68 (d, $^3J = 4.4$ Hz, 2 H, β -H), 8.70 (d, $^3J = 4.4$ Hz, 2 H, β -H), 8.72 (d, $^3J = 4.4$ Hz, 2 H, β -H), 8.84 (d, $^3J = 4.4$ Hz, 2 H, β -H), 9.00 (s, 1 H, 4-H) ppm.

^{13}C NMR (100 MHz, DMF- d_7): $\delta = 19.5, 20.0, 20.1, 20.6, 20.8, 21.3$ (2C), 21.7 (2C), 88.9, 89.0, 89.7, 89.8, 90.1, 93.4, 93.6, 94.1, 95.0, 97.6, 118.3, 118.7, 118.8, 119.3, 122.0 (2C), 123.2, 123.5, 123.7, 124.1, 125.1, 125.4, 125.5, 125.8, 126.3, 126.9, 127.5, 127.7, 127.8, 127.9, 128.3 (2C), 129.1, 129.9, 130.5 (2C), 130.8, 131.2, 131.3, 132.3 (2C), 132.5, 132.7, 133.0, 133.2, 133.9, 135.3, 135.6, 135.7, 135.8, 136.0, 137.9 (2C), 138.2, 138.3, 138.4, 138.6, 139.4 (2C), 140.1, 140.2, 140.5, 141.2, 142.3, 143.7, 144.4, 145.0, 149.0, 150.0, 150.1 (2C), 150.2, 151.7, 157.2, 157.6, 158.5, 159.4, 159.9 ppm.

ESI-MS: m/z (%): 1799.4 (100) $[\text{Cu}(\mathbf{1})]^+$. calcd 1799.6; see also Figure S21.

UV-vis absorption: $\lambda_{\text{max}} = 422$ nm, $\epsilon = 5.09 \times 10^5$ L mol $^{-1}$ cm $^{-1}$ (Soret band).

Elemental analysis: Calcd for $\text{C}_{121}\text{H}_{91}\text{CuF}_6\text{N}_9\text{PZn}\cdot\text{CHCl}_3$: C, 70.98; H, 4.49; N, 6.11.
Found: C, 71.39; H, 4.45; N, 6.57.

Photoisomerisation Experiment S1

A argon saturated solution of *trans*-**3** (10.0 mg, 54.8 μmol , $\lambda_{\text{max}} = 315 \text{ nm}$) in 2 mL of toluene was irradiated at 300 nm with high pressure mercury vapor lamp for 2 h in a quartz cell. The resulting mixture was analysed by ^1H NMR which indicated a 66 : 34 mixture of *cis* to *trans*. The mixture was subjected to column chromatography over flash silica using 10% ethylacetate in hexane as eluent. The received pure *cis*-**3** was used for a further photoisomerisation reaction.

Photoisomerisation Experiment S2

Photoinduced isomerisation experiments were performed in dichloromethane using a quartz cell. Prior to the all experiments, dichloromethane was degassed and kept under argon. All experiments were performed with a high pressure mercury vapor lamp.

Model study with *cis*-**3**

A solution of zinc tetraphenylporphyrin (Zn**TPP**) (140 μmg , 0.206 μmol , 0.10 mM) and *cis*-**3** (37.5 μmg , 0.206 μmol) in 2.0 mL of degassed dichloromethane was put in a quartz cell under argon and irradiated at 419 nm light for 30 min. 72% of *cis*-**3** was converted to *trans*-**3** as determined from the NMR (Figure S12).

Model study with *cis*-stilbene

Zn**TPP** (138 μmg , 0.203 μmol , 0.10 mM) and *cis*-stilbene (36.6 μmg , 0.203 μmol) in 2.0 mL of degassed dichloromethane was put in a quartz cell under argon and irradiated at 419 nm light for 30 min. No conversion was observed from the ^1H NMR spectra (Figure S13).

Photoinduced isomerisation of *cis*-stilbene with **1** and **2**

1 (349 μmg , 0.201 μmol , 0.10 mM) and *cis*-stilbene (36.2 μmg , 0.201 μmol) in 2.0 mL of degassed dichloromethane was put in a quartz cell under argon and irradiated at 419 nm light for 30 min. From ^1H NMR, no conversion was obtained (Figure S16). A similar experiment was performed with **2**, obtained after adding $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{B}(\text{C}_6\text{F}_5)_4$ (182

μg, 0.201 μmol). Irradiation was performed in degassed dichloromethane under argon at 419 nm for 30 min. No formation of *trans*-isomer was detected in the ¹H NMR as with **1** (Figure S17).

Photoinduced isomerisation of *cis*-**3** with **1** and **2**

Cis-**3** (37.9 μg, 0.208 μmol) was added to **1** (361 μg, 0.208 μmol, 0.10 mM) and placed in a quartz cell. The mixture was dissolved in degassed 2.0 mL of dichloromethane and irradiated for 30 min at 419 nm light under argon. The ¹H NMR depicts no isomerisation to *trans*-**3** (Figure S14).

Photoisomerisation of **2** was checked separately: A mixture of [Cu(CH₃CN)₄]B(C₆F₅)₄ (190 μg, 0.210 μmol) and **1** (365 μg, 0.210 μmol, 0.10 mM) was irradiated at 419 nm for 30 min under argon using degassed DCM as solvent. Irradiation led to 72% conversion of the *cis*-**3** as depicted from the ¹H NMR integration values (Figure S15).

Photoinduced isomerisation of *cis*-**3** and *cis*-stilbene with **1** and **2**

A mixture of **1** (355 μg, 0.204 μmol, 0.10 mM), *cis*-**3** (37.2 μg, 0.204 μmol) and *cis*-stilbene (36.8 μg, 0.204 μmol) was irradiated at 419 nm for 30 min in DCM. No isomerisation was observed from ¹H NMR (Figure S18).

A degassed DCM solution 0.10 mM of **2** (491 μg, 0.206 μmol), *cis*-**3** (37.5 μg, 0.206 μmol) and *cis*-stilbene (37.1 μg, 0.206 μmol) was irradiated for 30 min at 419 nm. The ¹H NMR showed 72% of conversion of *cis*-**3** whereas no conversion was obtained for *cis*-stilbene at all (Figure S19).

Reversibility and Catalysis Experiment

The catalytic experiment was performed with 25 mol% of the switch. A 0.10 mM solution of **2** (485 μg, 0.203 μmol) and *cis*-**3** (37.0 μg, 0.203 μmol) was irradiated in degassed DCM for 20 min at 419 nm. ¹H NMR shows 45% of the *trans*-**3** isomer (Figure S20). Cyclam (40.7 μg, 0.203 μmol) was added to the mixture to generate **1**. Irradiation of the solution under similar condition did not produce any *trans*-**3** as observed from integration (Figure S20).

NMR Spectra:

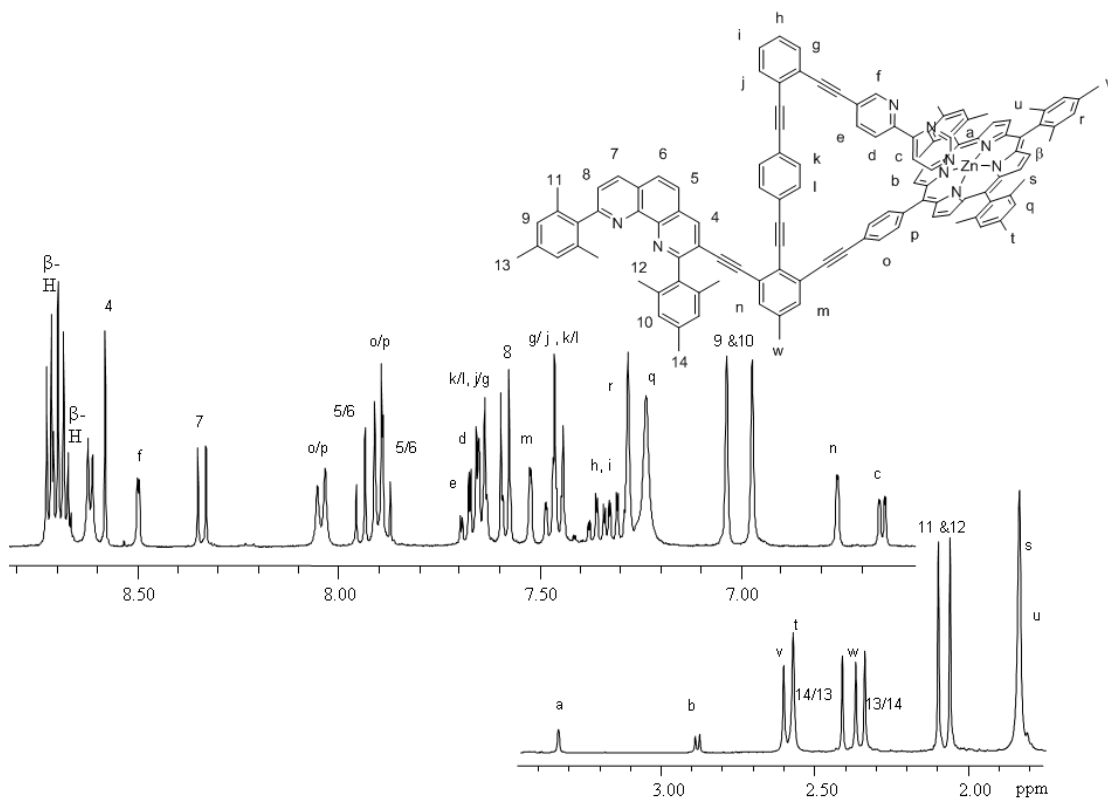


Figure S1. Partial ^1H NMR (400 MHz, CD_2Cl_2 , 298 K) of compound **1**.

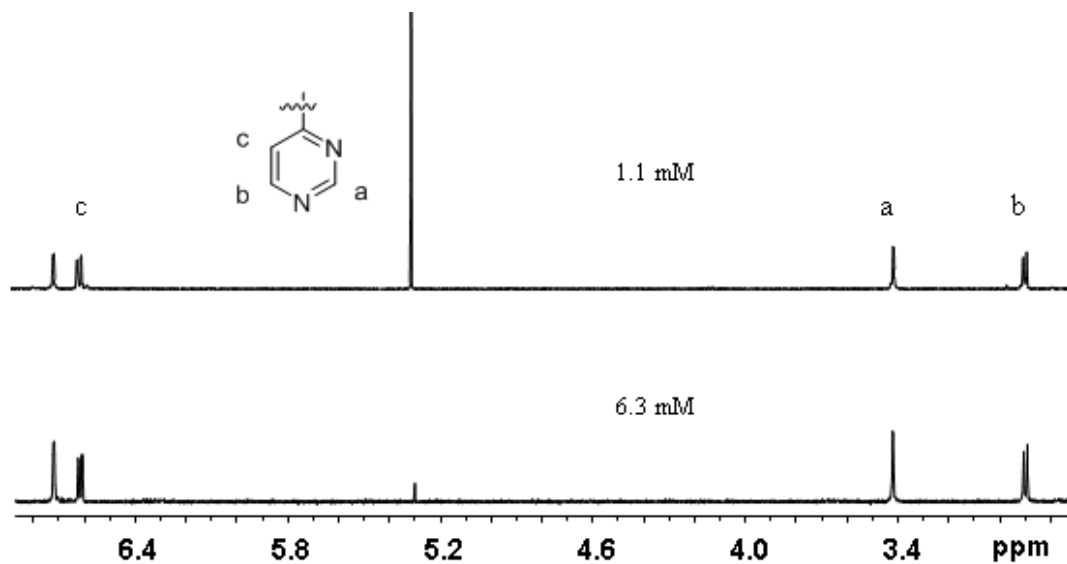


Figure S2. Partial ^1H NMR (400 MHz, CDCl_3 , 298 K) of compound **1** at different concentrations.

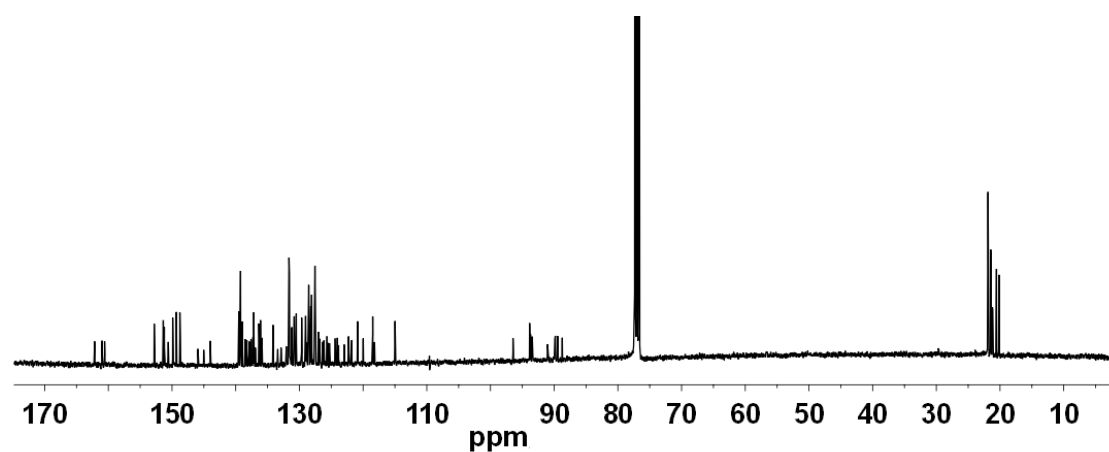


Figure S3. ^{13}C NMR (100 MHz, CDCl_3 , 298 K) of compound **1**.

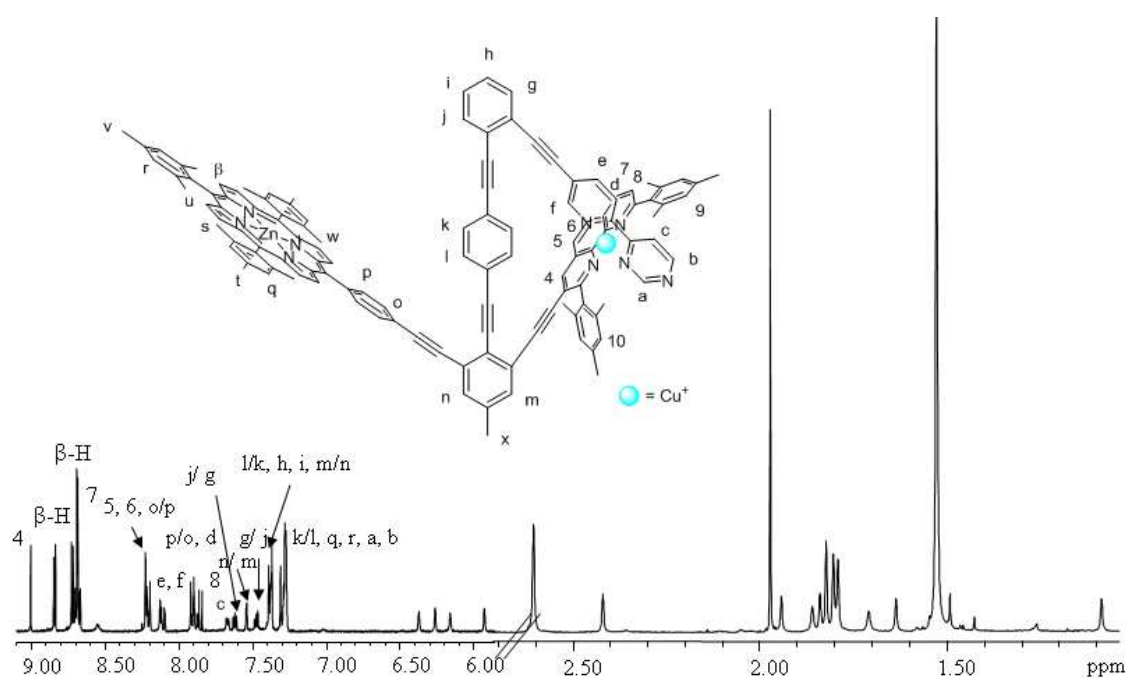


Figure S4. Partial ^1H NMR (400 MHz, CD_2Cl_2 , 298 K) of **2** = $[\text{Cu}(\mathbf{1})]\text{PF}_6$.

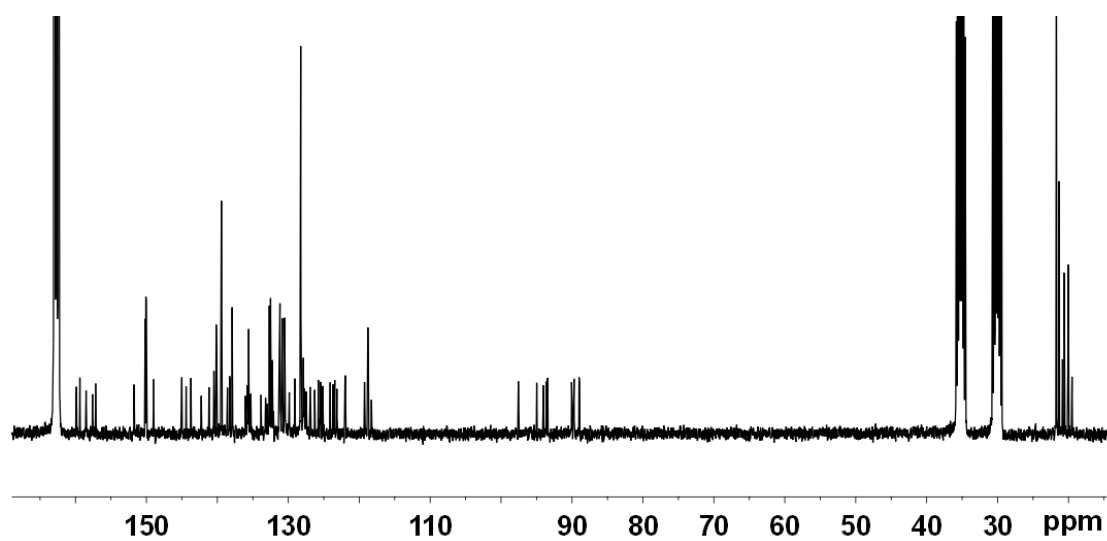


Figure S5. Partial ^{13}C NMR (100 MHz, DMF- d_7 , 298 K) of **2** = $[\text{Cu}(\mathbf{1})]\text{PF}_6$.

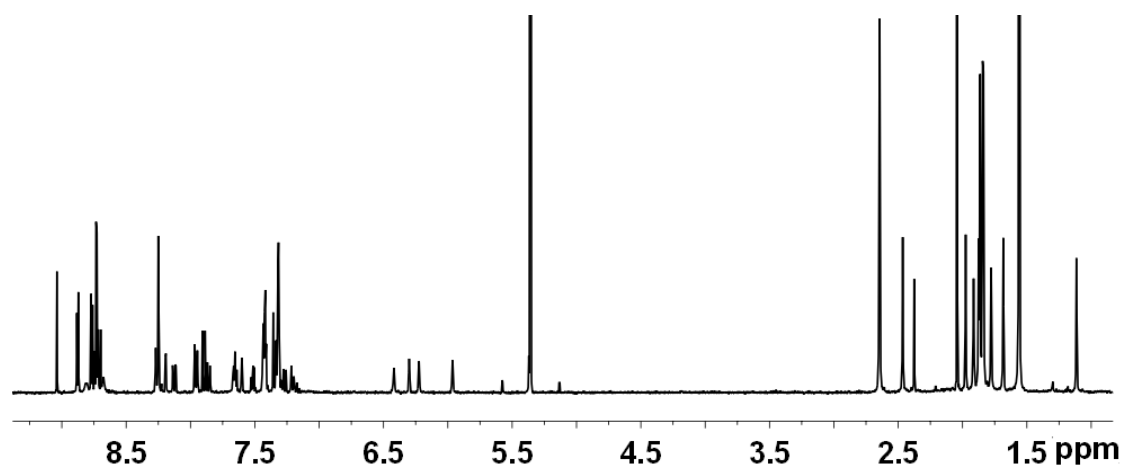


Figure S6. Partial ^1H NMR (400 MHz, CD_2Cl_2 , 298 K) of $[\text{Cu}(\mathbf{1})]\text{B}(\text{C}_6\text{F}_5)_4$.

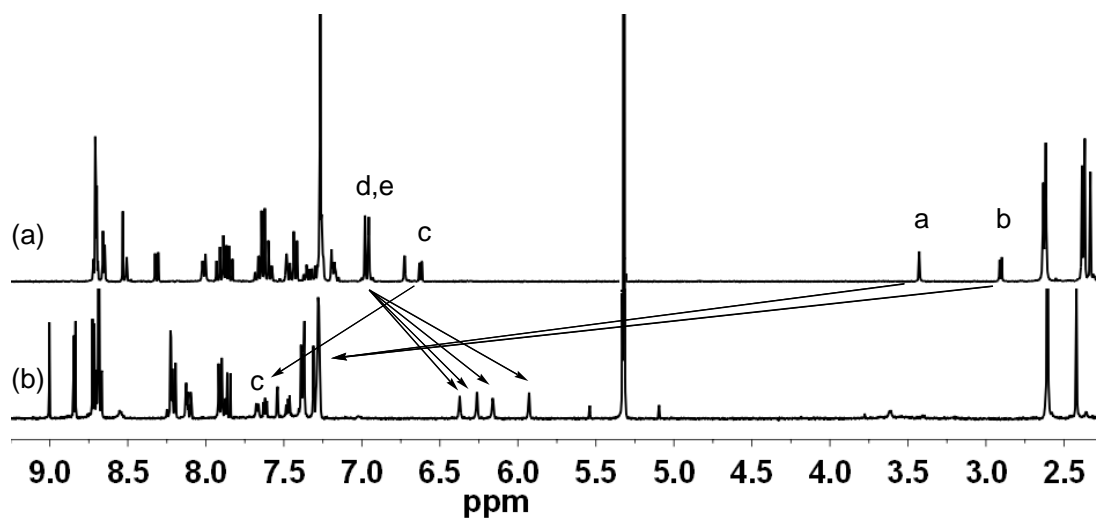


Figure S7. Partial ^1H NMR of (a) **1** (400 MHz, CDCl_3 , and (b) **2** (400 MHz, CD_2Cl_2).

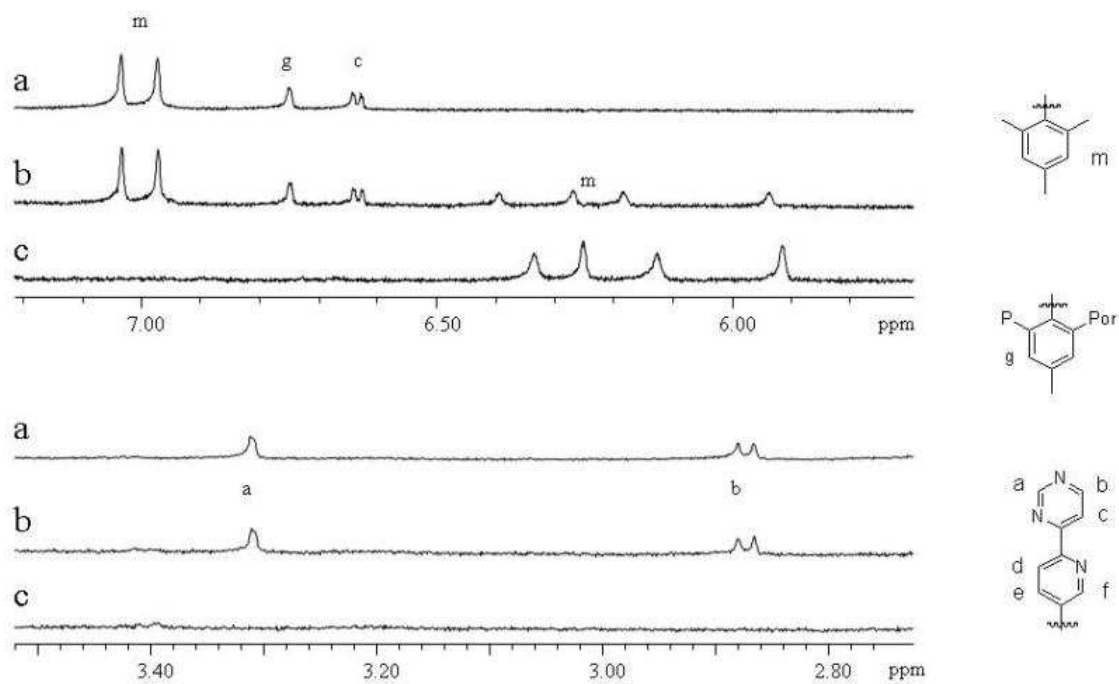


Figure S8. Partial ^1H NMR (400 MHz, CD_2Cl_2 , 298 K) of a titration of compound **1** (1.5 mM) against Cu^+ : (a) compound **1**; (b) compound **1** + 0.5 equiv. of Cu^+ ; (c) compound **1** + 1.0 equiv. of Cu^+ .

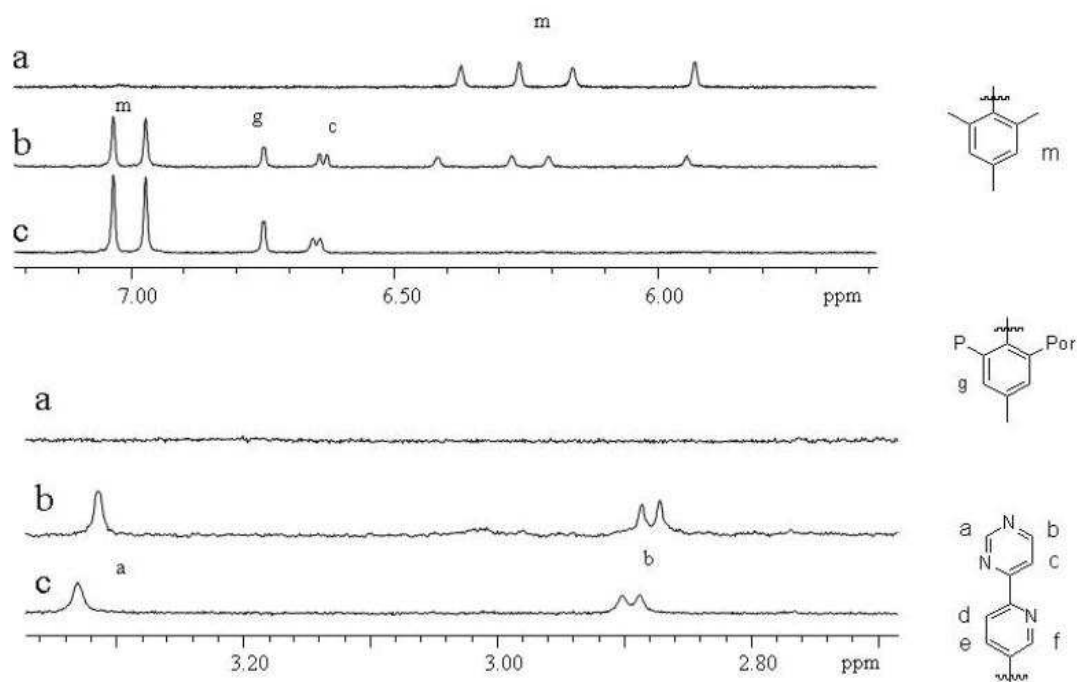


Figure S9. Partial ^1H NMR (400 MHz, CD_2Cl_2 , 298 K) of the titration of complex $[\text{Cu}(\mathbf{1})]^+$ (1.2 mM) vs. cyclam: (a) complex $[\text{Cu}(\mathbf{1})]^+$; (b) complex $[\text{Cu}(\mathbf{1})]^+$ + 0.5 equiv. of cyclam; (c) complex $[\text{Cu}(\mathbf{1})]^+$ + 1.0 equiv. of cyclam.

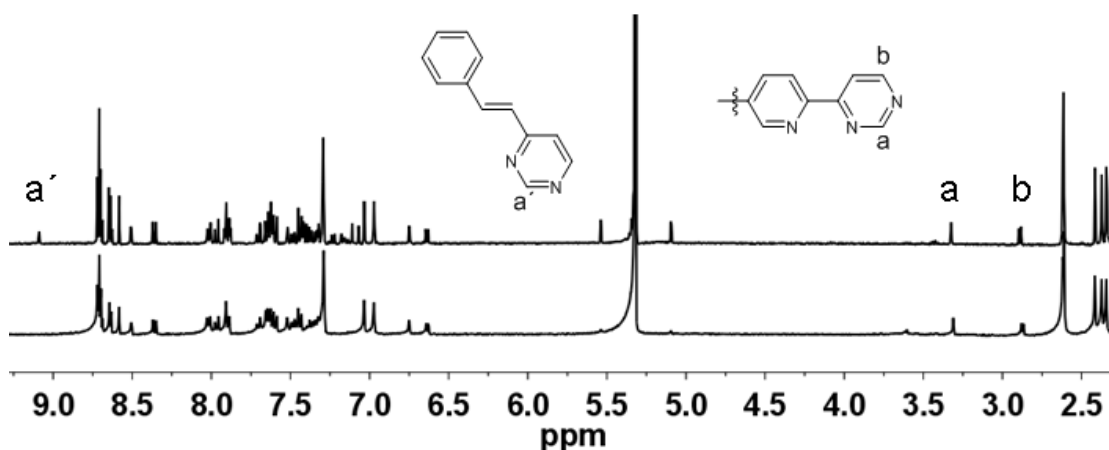


Figure S10. Partial ^1H NMR (400 MHz, CD_2Cl_2 , 298 K) spectrum of (bottom) $\mathbf{1}$ and (top) $\mathbf{1}$ after addition of one equiv. of *trans*- $\mathbf{3}$ (0.18 mM). The unchanged shifts of protons a-H and b-H after addition of *trans*- $\mathbf{3}$ indicate that the system remains self-locked.

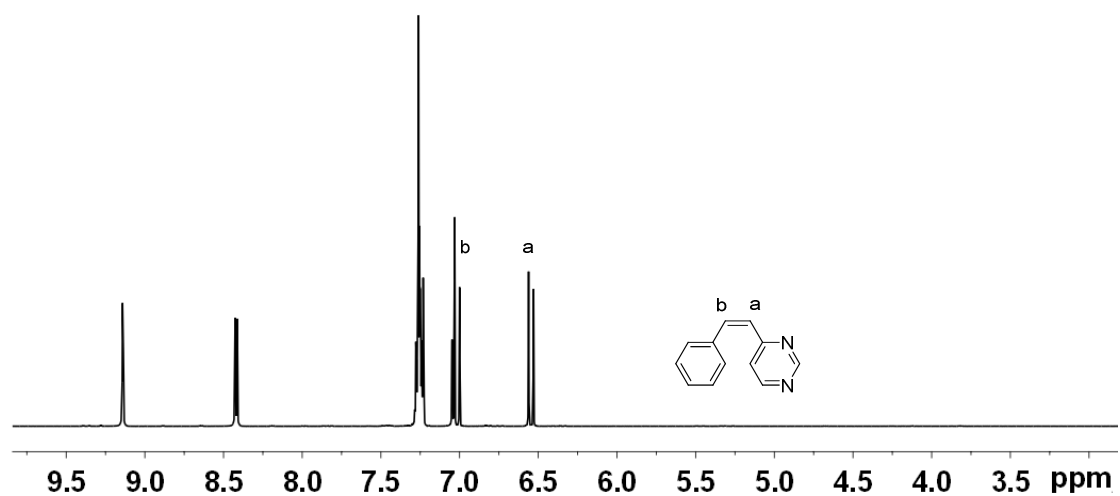


Figure S11. ¹H NMR (400 MHz, CDCl₃, 298 K) of *cis*-3.

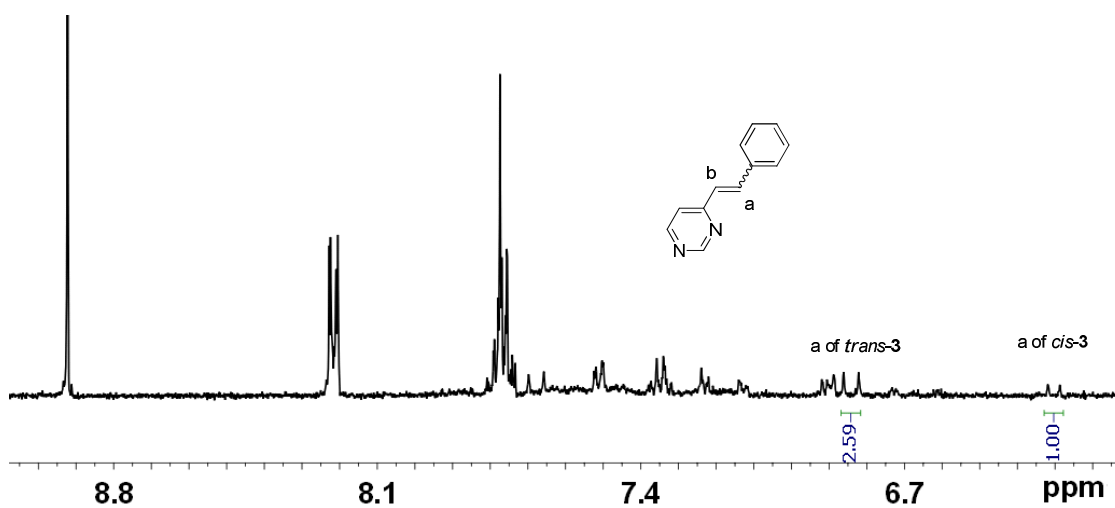


Figure S12. Partial ¹H NMR (400 MHz, CD₂Cl₂, 298 K) spectrum showing the ratio of *cis*- to *trans*-3 after irradiation of pure *cis*-3 (0.10 mM) in presence of zinc tetraphenylporphyrin (1: 1) at 419 nm for 30 min in DCM.

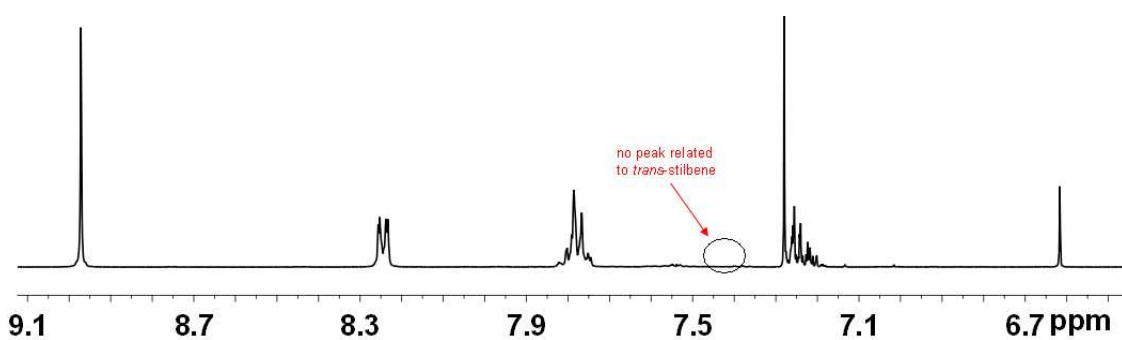


Figure S13. ¹H NMR (400 MHz, CD₂Cl₂, 298 K) of the mixture of ZnTPP and *cis*-stilbene (1: 1) after irradiation at 419 nm light for 30 min in dichloromethane at 0.10 mM (no conversion observed).

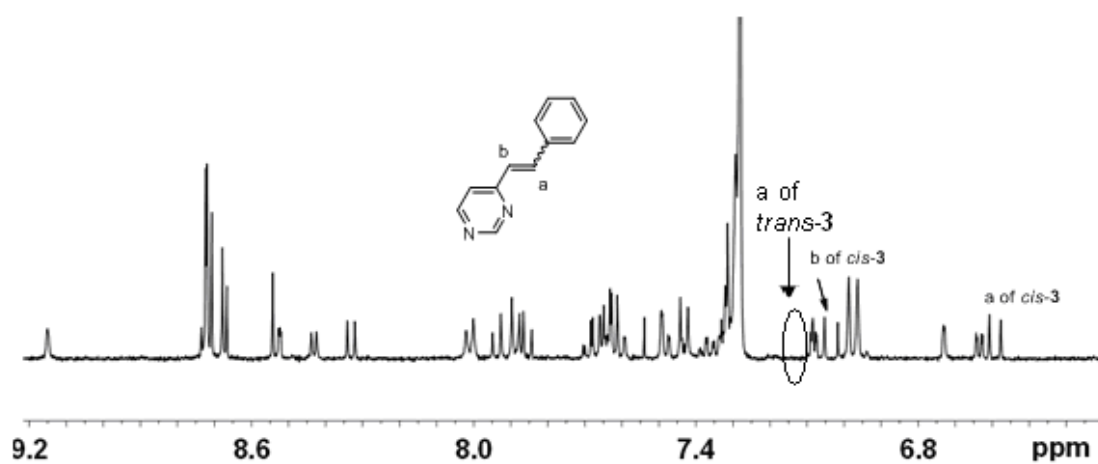


Figure S14. Partial ¹H NMR (400 MHz, CD₂Cl₂, 298 K) of *cis*-**3** (0.10 mM) after irradiation in presence of **1** (1: 1) at 419 nm for 30 min (0.10 mM). No *trans*-**3** was generated.

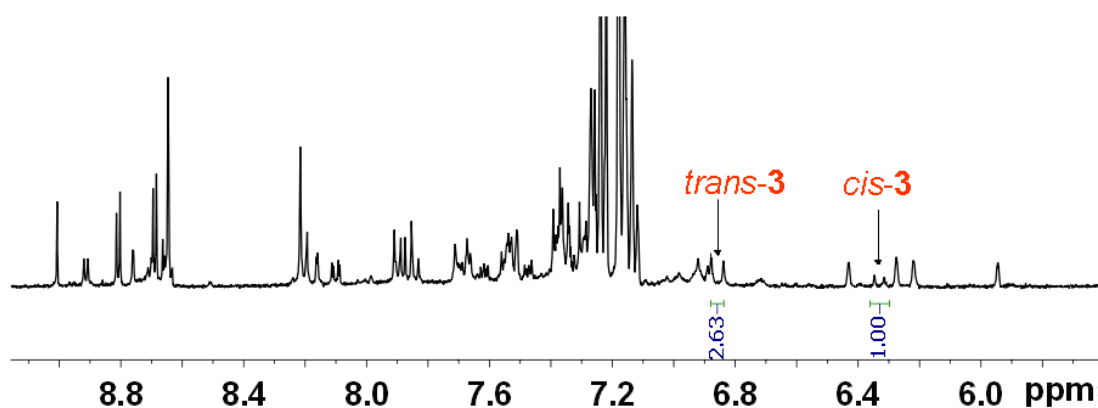


Figure S15. Partial ¹H NMR (400 MHz, CD₂Cl₂, 298 K) of the reaction mixture after irradiation of pure *cis*-**3** (0.10 mM) in presence of **2** (1: 1) at 419 nm for 30 min. 72% of *trans*-**3** was formed from pure *cis*-**3**.

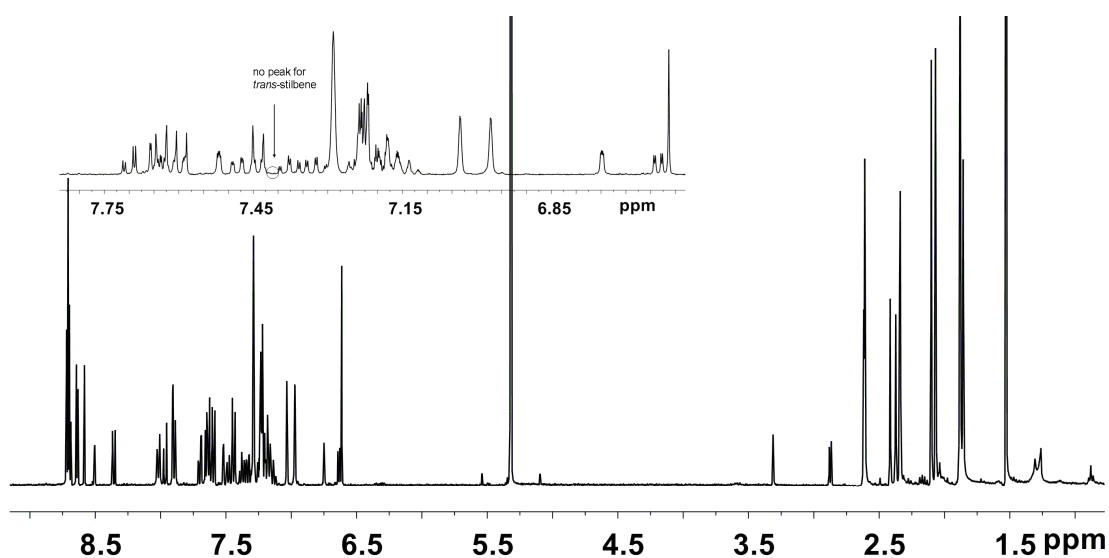


Figure S16. ¹H NMR (400 MHz, CD₂Cl₂, 298 K) of a mixture of **1** and *cis*-stilbene (1: 1) after irradiation at 419 nm for 30 min in dichloromethane at 0.10 mM (no conversion observed). The aromatic region shows no peak at 7.37 ppm corresponding to *trans*-stilbene.

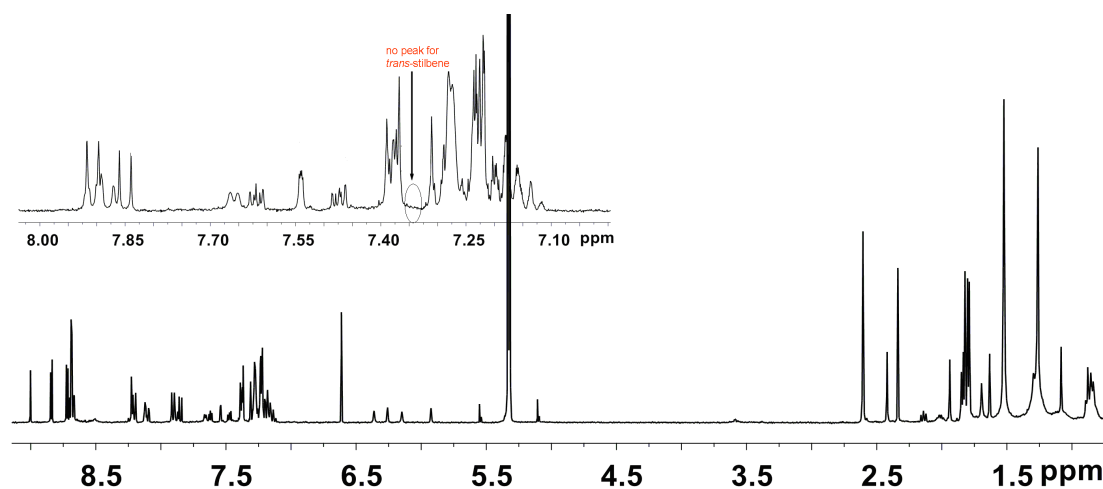


Figure S17. ^1H NMR (400 MHz, CD_2Cl_2 , 298 K) of the mixture of **2** and *cis*-stilbene (1: 1) after irradiation at 419 nm for 30 min in dichloromethane at 0.10 mM (no conversion observed). The aromatic region shows no peak at 7.37 ppm corresponding to the *trans*-stilbene.

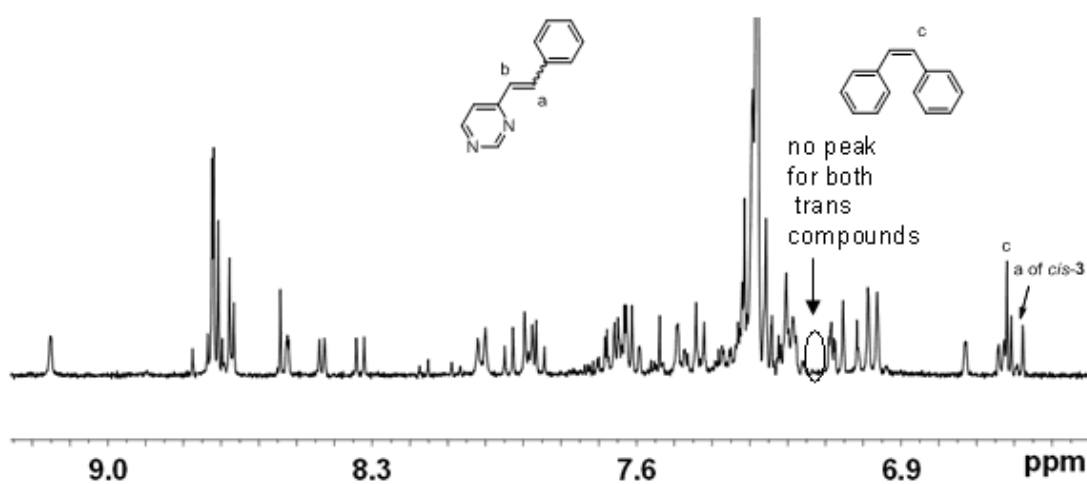


Figure S18. Partial ^1H NMR (400 MHz, CD_2Cl_2 , 298 K) of the reaction mixture after irradiating *cis*-**3** (0.10 mM) and *cis*-stilbene in presence of **1** (1: 1: 1) at 419 nm for 30 min in DCM.

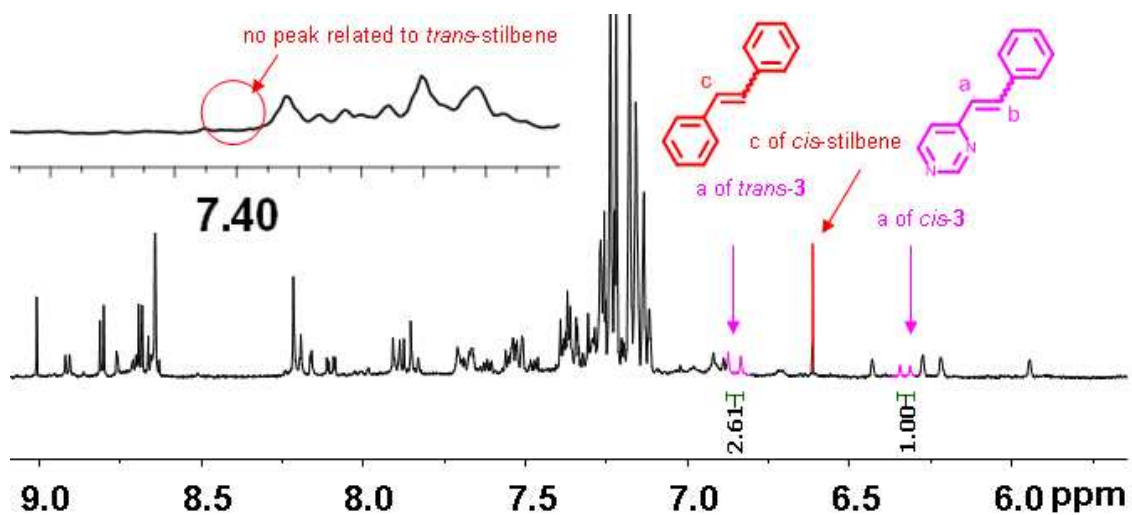


Figure S19. Partial ^1H NMR (400 MHz, CD_2Cl_2 , 298 K) of the reaction mixture after irradiating *cis*-**3** (0.10 mM) and *cis*-stilbene in presence of **2** (1: 1: 1) at 419 nm for 30 min in DCM. 72% of *trans*-**3** is formed.

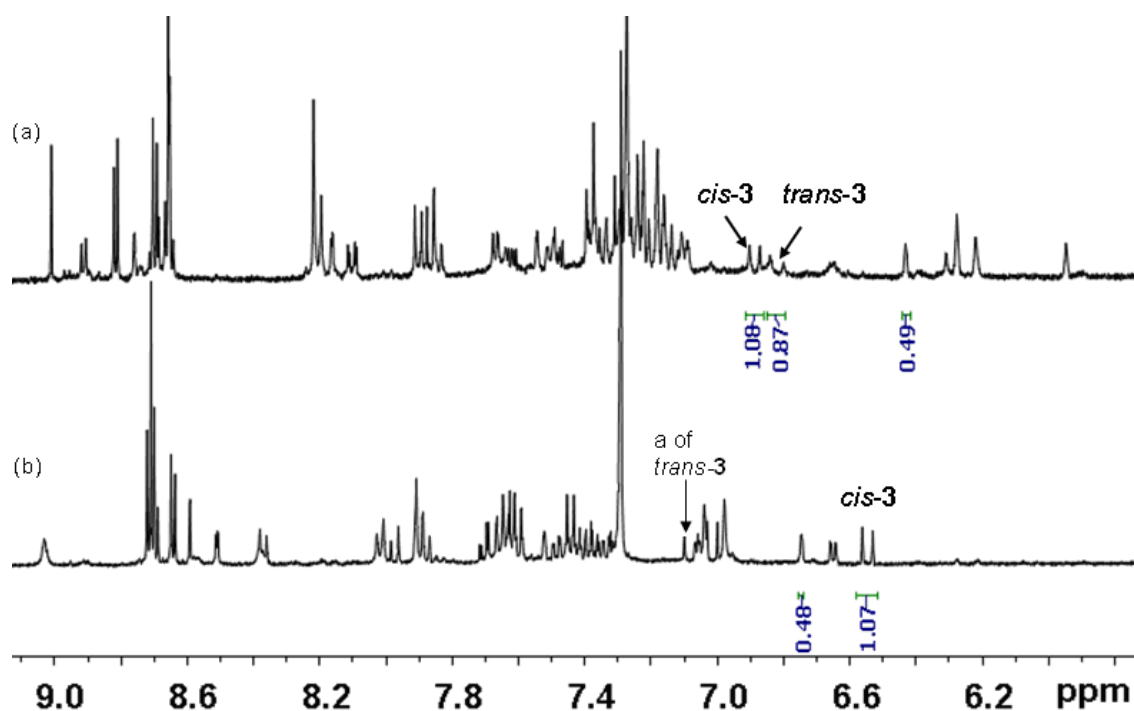


Figure S20. Partial ^1H NMR (400 MHz, CD_2Cl_2 , 298 K) of experiments checking for ON/OFF operation. (a) Reaction mixture A obtained after irradiation of pure cis-3 for 20 min at 419 nm in DCM in presence of **2** (4:1); (b) Reaction mixture after irradiation (for 20 min at 419 nm in DCM) of solution A in presence of cyclam (in order to produce **1** from **2**). Because **1** is coordinated to cis- and trans-3 , the NMR shifts of **3** appear at different positions in the two spectra. No further conversion of cis-3 is seen.

ESI-MS Spectra:

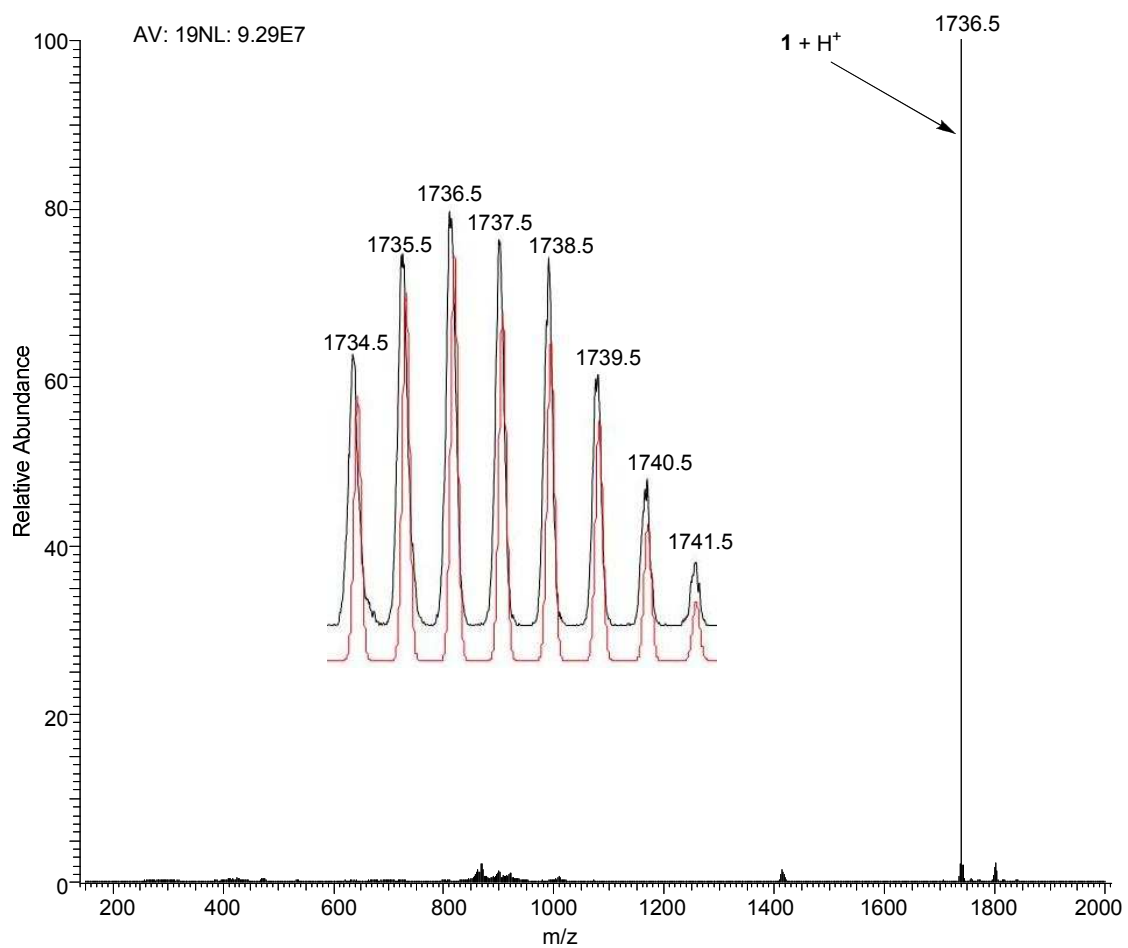


Figure S21. ESI-MS spectrum of complex $[1 + H]^+$.

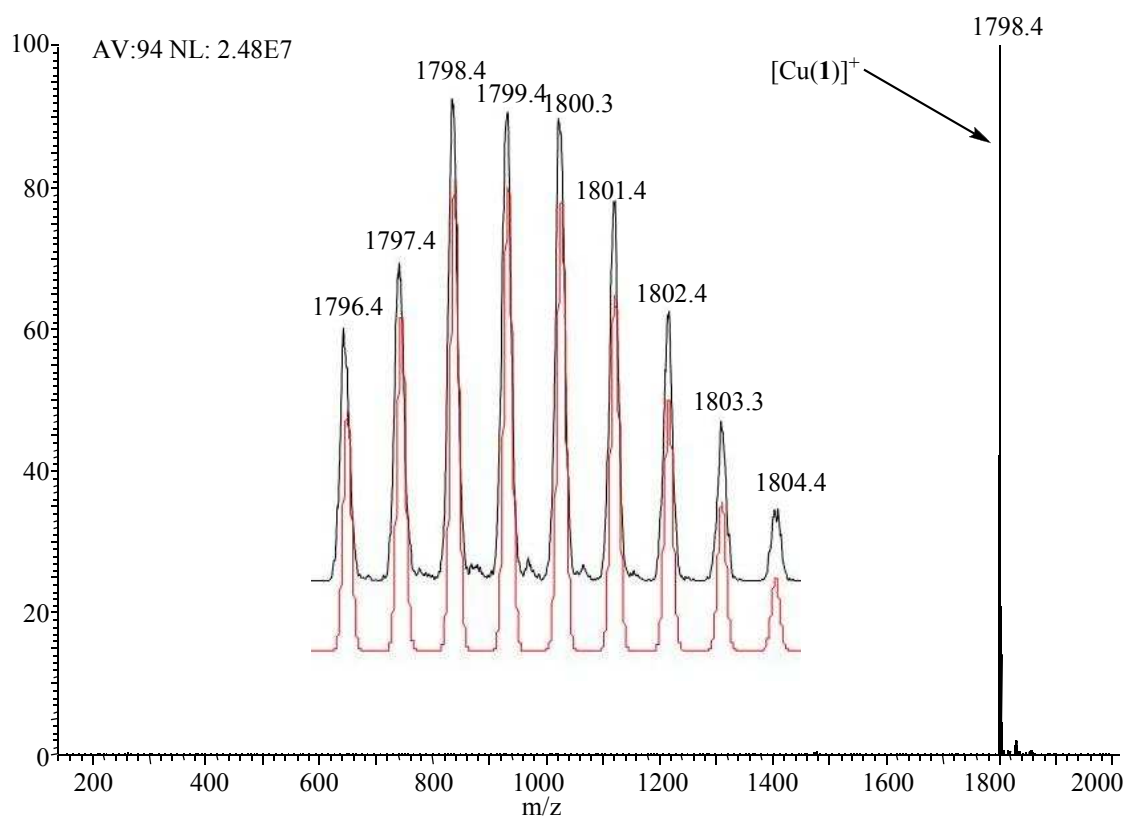


Figure S22. ESI-MS spectrum of complex **2** = [Cu(1)]⁺.

UV-vis Spectra:

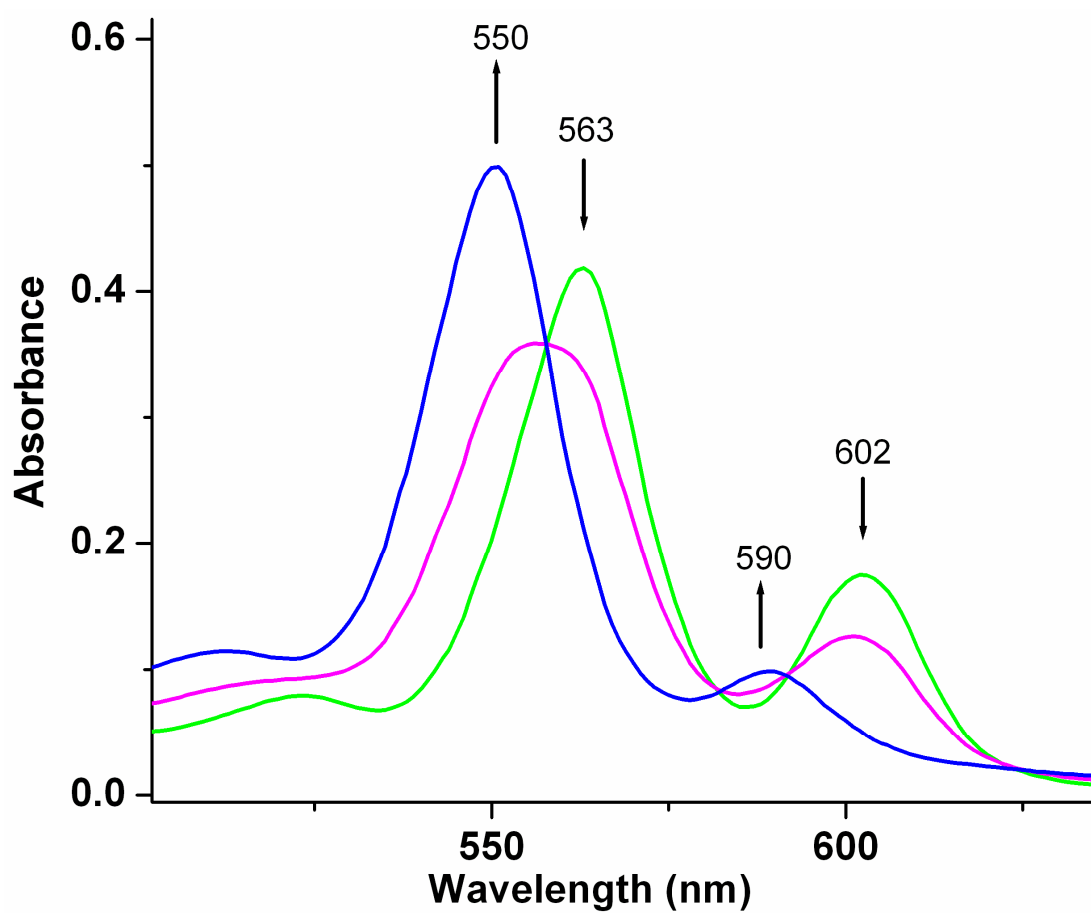


Figure S23. UV-Vis titration of **1** (0.1 mM) with 0, 0.5 and 1 equiv. of Cu^+ (2.5 mM) in DCM at 298 K monitoring the Q band. After addition of > 1 equiv. of Cu^+ , the intensity at 550 nm remains constant.

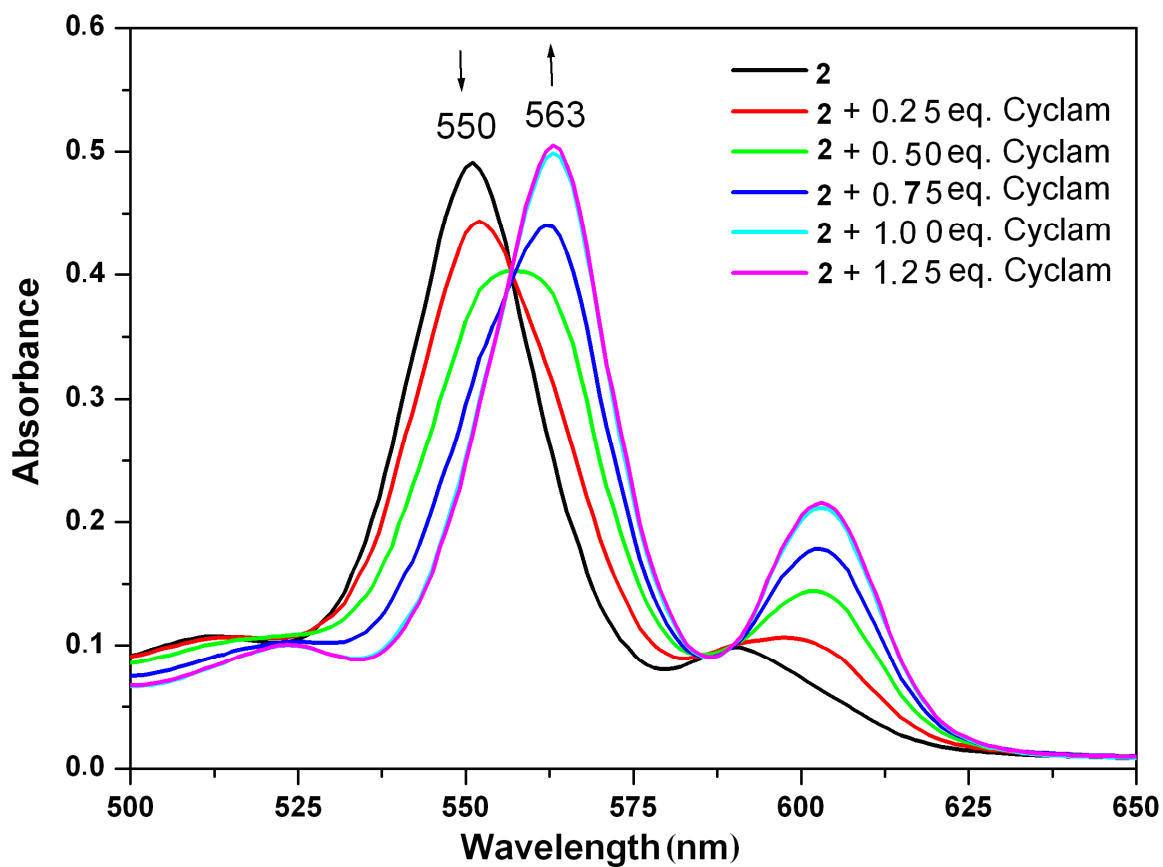


Figure S24. UV-vis titration of **2** (10 mM) with cyclam (2.5 mM) in DCM at 298 K at the Q band. After addition of 1 equivalent of cyclam, the intensity at 563 nm remains constant.

Binding Constant Measurements:

Log *K* of **1** and [Cu(CH₃CN)₄]PF₆

A UV-Vis titration was used to determine the binding constant between **1** and Cu⁺. A solution of **1** at 10⁻⁶ M was titrated with a 10⁻⁴ M solution of Cu⁺ in dichloromethane. UV-vis titrations were analysed by the nonlinear curve-fitting method. Δ*A* values were monitored at 430 nm. The equation^[1] used for the fitting is

$$\Delta A = (L \cdot (1 + K \cdot X + K \cdot A) - \text{SQRT}(L^2(K \cdot X + K \cdot A + 1)^2 - 4 \cdot K \cdot 2 \cdot A \cdot X \cdot L^2)) / 2 \cdot K \cdot A$$

with *X* and *A* representing [Guest]_{total} and [Host]_{total}, respectively; *L* denoting Δ*A* at 100% complexation; *L* and *K* are parameters.

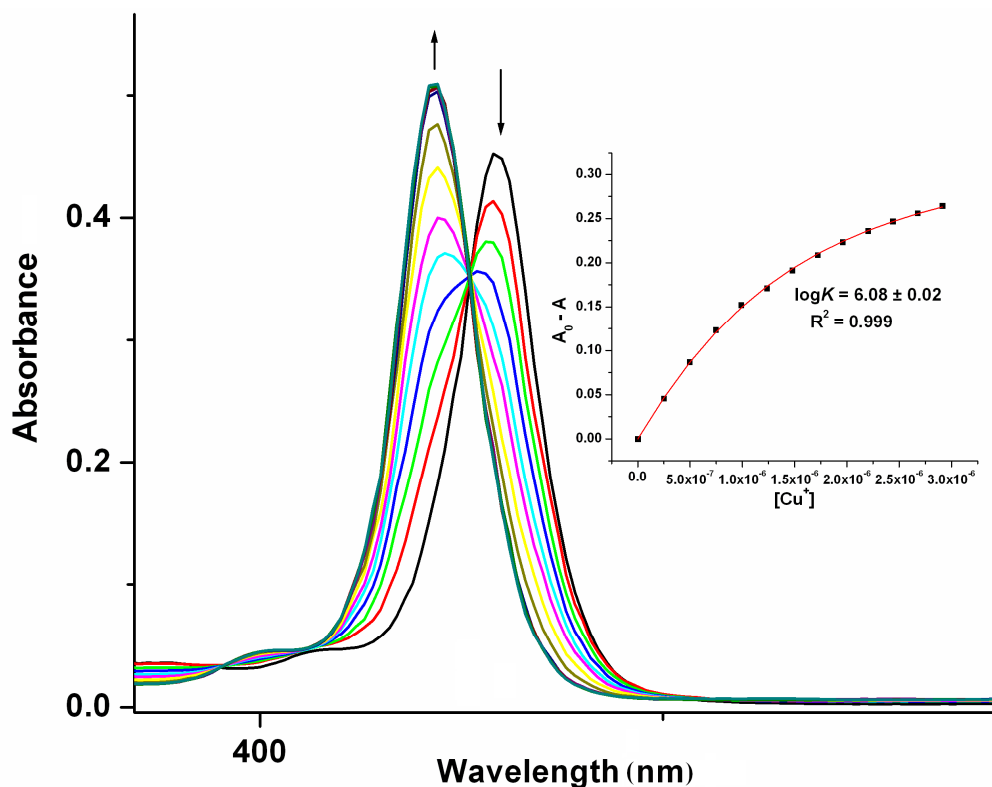


Figure S25. Curve-fitting for determination of binding constant between **1** and Cu⁺.

Log K of **2** and *trans*-**3**

The binding constant was determined from a UV-vis titration. A solution of **2** (10^{-4} M) was titrated with a 2.5×10^{-3} M solution of *trans*-**3** in dichloromethane. It was analysed by the nonlinear curve-fitting method. ΔA value was monitored at 550 nm.

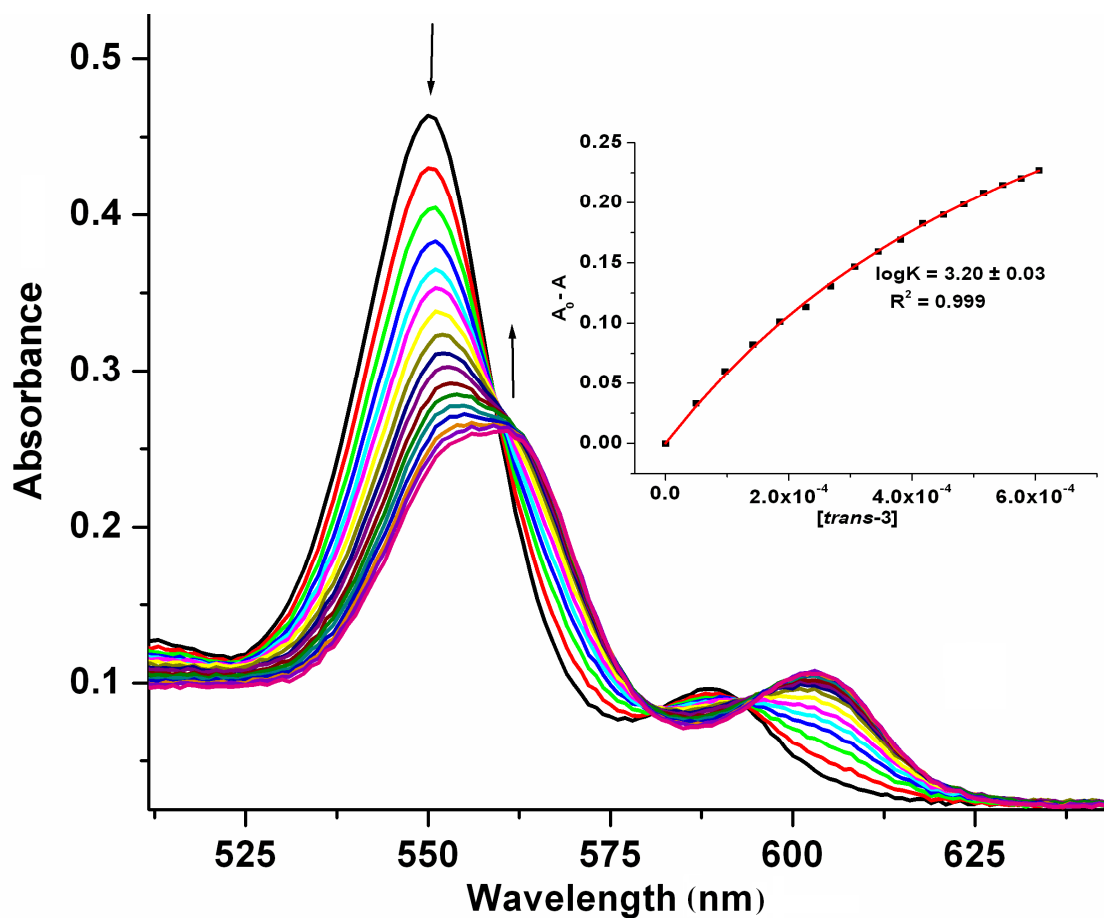


Figure S26. Curve-fitting for determination of binding constant between **2** and *trans*-**3**.

Log *K* of **1** and *trans*-**3**

To determine the binding constant between **1** and *trans*-**3**, the UV-vis titration method was not suitable because both **1** and [(**1**)(*trans*-**3**)] absorb at the same wavelength. Thus, NMR was used. A 0.135 mM solution of **1** was prepared in CDCl₃ in an NMR tube. In another vessel, a 0.162 M stock solution of *trans*-**3** was prepared in the same solvent. Small aliquots of the solution of *trans*-**3** were added. After each addition, the ¹H NMR was recorded and the peak at 3.32 ppm was monitored for data analysis. The binding constant was determined using nonlinear curve-fitting applying the following equation:^[2]

$$Y=Y_0+DY*\left(\frac{K*(P+x)+1-\text{SQRT}\left(\left(K*(P+x)+1\right)^2-4*K*K*P*x\right)}{2*K*P}\right)$$

with Y = Measured Chemical shift; Y₀ = Chemical shift of empty host solution; DY = Maximal change in chemical shift: the difference in chemical shift of a fully occupied host and an empty host; K = Binding constant; P = Total host concentration; x = Total guest concentration.

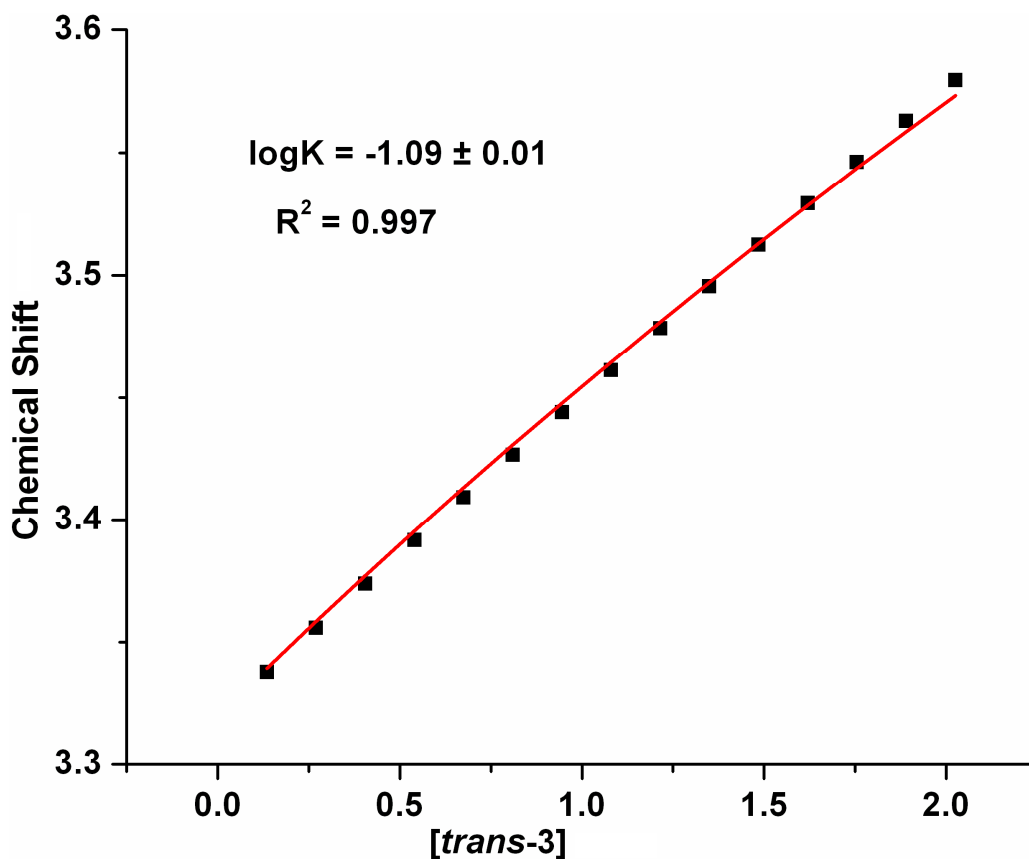


Figure S27. Curve-fitting for determining the binding constant between **1** and *trans*-**3**.

Log K of 2 and *cis*-3:

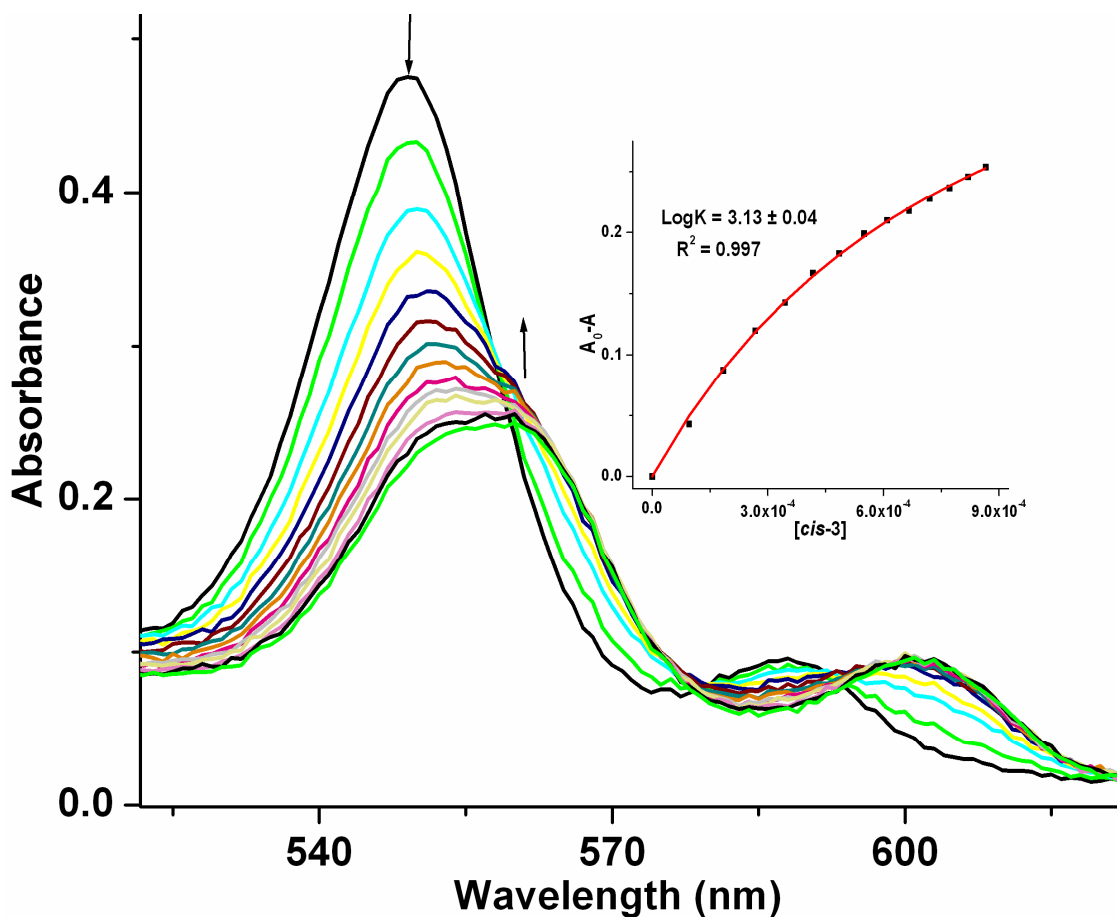


Figure S 28. Curve-fitting for determination of binding constant between 2 and *cis*-3.

References:

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- [2] Y. R. Hristova, M. M. J. Smulders, J. K. Clegg, B. Breiner and J. R. Nitschke, *Chem. Sci.*, 2011, **2**, 638.