## Supporting Information

for

# Selective detection of DABCO using a supramolecular interconversion as fluorescence reporter 

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## Experimental details and characterization data

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## 1. Synthesis (general remarks)

### 1.1 General remarks on instrumentation and chemicals

All solvents were dried by distillation prior to use while commercial reactants $(\mathbf{4}, \mathbf{9}, \mathbf{1 0})$ were utilized without any further purification. A Bruker Avance $(400 \mathrm{MHz})$ spectrometer was employed to measure ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra using a deuterated solvent as the lock and residual protiated solvent as internal reference $\left(\mathrm{CDCl}_{3}: \delta_{\mathrm{H}} 7.26 \mathrm{ppm}, \delta_{\mathrm{C}} 77.0 \mathrm{ppm} ; \mathrm{CD}_{2} \mathrm{Cl}_{2}: \delta_{\mathrm{H}} 5.32 \mathrm{ppm}, \delta_{\mathrm{C}} 53.8 \mathrm{ppm}\right.$, THF- $d_{8}:$ $\left.\delta_{\mathrm{H}} 1.72 \mathrm{ppm}, 3.58 \mathrm{ppm}, \delta_{\mathrm{C}} 25.3 \mathrm{ppm}, 67.2 \mathrm{ppm}\right)$. The following abbreviations were used to define NMR peak patterns: $\mathrm{s}=$ singlet, $\mathrm{d}=$ doublet, $\mathrm{t}=$ triplet, $\mathrm{br}=$ broad, $\mathrm{m}=$ multiplet. The coupling constants are given in hertz $(\mathrm{Hz})$ and, wherever possible, assignment of protons is made. The carbons in the molecular skeletons are mostly not numbered following the IUPAC nomenclature rules; it was exclusively done for assigning NMR signals. All electrospray ionization (ESIMS) spectra were recorded on a Thermo-Quest LCQ deca and the theoretical isotopic distributions of the mass signals were calculated using the IsoPro 3.0 software. Melting points of compounds were measured on a Büchi 510 instrument and are not corrected. Infrared spectra were recorded on a Varian 1000 FTIR instrument. Elemental analysis was performed using the EA-3000 CHNS analyzer. UV-vis spectra were recorded on a Cary Win 50 ( 298 K ) spectrometer. Binding constants were determined through

UV-vis titrations assuming a $1: 1$ binding scheme or with the SPECFIT $/ 32^{\mathrm{TM}}$ global analysis system by Spectrum Software Associates (Marlborough, MA). Column chromatography was performed either on silica gel ( $60-400 \mathrm{mesh}$ ) or neutral alumina (Fluka, 0.05-0.15 mm, Brockmann Activity 1). Merck silica gel ( 60 F 254 ) or neutral alumina ( 150 F 254 ) sheets were used for thin layer chromatography (TLC). All metal-ligand complexes were prepared directly in the NMR tube using $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ as solvent. Compounds $\mathbf{8},{ }^{1} \mathbf{1 3},{ }^{1} \mathbf{1 4},{ }^{2}$ and $\mathbf{1 5}^{\mathbf{3}}$ were synthesized according to literature known procedures.

### 1.2 General remarks on synthetic schemes




3

2



10





4

Chart S1: Ligands used in the present study.


Scheme S1. Synthetic scheme used in the preparation of ligands 1 and 2.


Scheme S2. Synthetic scheme used in the preparation of porphyrin 3.

## 2. Synthesis and characterization of ligands

## Synthesis of ligand 1



Under an argon atmosphere porphyrin $\mathbf{1 4}^{2}(200 \mathrm{mg}, 197 \mu \mathrm{~mol})$ and phenanthroline $\mathbf{1 3}^{1}(263 \mathrm{mg}$, $493 \mu \mathrm{~mol})$ were dissolved in 15 mL of dry DMF and 15 mL of trimethylamine. Subsequently, the solution was deaerated by bubbling nitrogen through the solution for 1 h . Then the solution was charged with $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(23.0 \mathrm{mg}, 19.7 \mu \mathrm{~mol})$ and heated at $75^{\circ} \mathrm{C}$ for 24 h . The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, $\mathrm{DCM}, R_{\mathrm{f}}=0.4$ ) furnishing 210 mg of $\mathbf{1}$ as red solid ( $110 \mu \mathrm{~mol}, 56 \%$ ); Mp: $>300^{\circ} \mathrm{C}$. IR (KBr): $\tilde{v}=$ $536,576,602,622,753,815,876,903,938,992,1119,1191,1255,1285,1347,1390,1436,1473$, 1518, 1605, 2191, 2201, 2362, 2891, 2858, $3077 \mathrm{~cm}^{-1} .{ }^{\mathbf{1}} \mathbf{H}$ NMR ( $400 \mathbf{M H z}, \mathbf{C D}_{2} \mathbf{C l}_{2}$ ): $\delta=1.79$ (s, $12 \mathrm{H}, \mathrm{b}-\mathrm{H}), 2.14(\mathrm{~s}, 12 \mathrm{H}, \mathrm{e}-\mathrm{H}), 2.55(\mathrm{~s}, 12 \mathrm{H}, \mathrm{f}-\mathrm{H}), 2.62(\mathrm{~s}, 6 \mathrm{H}, \mathrm{a}-\mathrm{H}), 3.71(\mathrm{~s}, 12 \mathrm{H}, \mathrm{g}-\mathrm{H}), 3.88(\mathrm{~s}, 6 \mathrm{H}$, i-H), $6.28(\mathrm{~s}, 4 \mathrm{H}, \mathrm{h}-\mathrm{H}), 7.29(\mathrm{~s}, 4 \mathrm{H}, \mathrm{m}-\mathrm{H}), 7.51\left(\mathrm{~d},{ }^{3} \mathrm{~J}=8.0 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{c}-\mathrm{H}\right), 7.61\left(\mathrm{~d},{ }^{3} J=8.0 \mathrm{~Hz}, 2 \mathrm{H}, 8-\right.$ H), 7.93 (d, $\left.{ }^{3} J=8.4 \mathrm{~Hz}, 2 \mathrm{H}, 5 / 6-\mathrm{H}\right), 7.95\left(\mathrm{~d},{ }^{3} J=8.4 \mathrm{~Hz}, 2 \mathrm{H}, 6 / 5-\mathrm{H}\right), 8.14\left(\mathrm{~d},{ }^{3} J=8.0 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{d}-\mathrm{H}\right)$, $8.83\left(\mathrm{~d},{ }^{3} J=8.0 \mathrm{~Hz}, 2 \mathrm{H}, 7-\mathrm{H}\right), 8.65(\mathrm{~s}, 2 \mathrm{H}, 4-\mathrm{H}), 8.72\left(\mathrm{~d},{ }^{3} J=4.8 \mathrm{~Hz}, 4 \mathrm{H}, \beta_{2}-\mathrm{H}\right), 8.82\left(\mathrm{~d},{ }^{3} J=4.8 \mathrm{~Hz}\right.$, $\left.4 \mathrm{H}, \beta_{1}-\mathrm{H}\right) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR ( $\mathbf{1 0 0} \mathbf{~ M H z}, \mathbf{C D}_{2} \mathbf{C l}_{2}$ ): $\delta=18.7,21.1,21.5,21.7,55.8,56.3,87.8,91.2$, $95.7,113.1,119.6,119.7,120.1,122.0,126.0,127.1,127.4,127.6,127.9,128.3,129.3,129.9,131.1$, $132.3,133.9,134.3,134.9,135.8,137.9,139.0,139.4,139.4,139.9,143.9,145.4,146.3,150.01$, 150.2, 156.1, 159.3, 162.0, 162.6, 162.0 ppm. ESI-MS: $m / z(\%)=1921.4(50)[1+H]^{+}, 961.8$ (100) $[1+2 \mathrm{H}]^{2+}$. Elemental analysis: Calcd. for $\mathrm{C}_{116} \mathrm{H}_{94} \mathrm{Br}_{2} \mathrm{~N}_{8} \mathrm{O}_{6} \mathrm{Zn}: \mathrm{C}, 72.52 ; \mathrm{H}, 4.93$; N, 5.83. Found: C, 72.31; H, 5.12; N, 5.74.

## Synthesis of Ligand 2:



Porphyrin $\mathbf{1 4}^{2}(100 \mathrm{mg}, 98.5 \mu \mathrm{~mol})$ and 4-ethynyl-2,6-dimethylpyridine $\left(\mathbf{1 5}^{3}, 32.3 \mathrm{mg}, 246 \mu \mathrm{~mol}\right)$ were loaded into sealed tube. After the addition of dry triethylamine ( 10 mL ) and dry DMF ( 10 mL ), the mixture was deaerated by bubbling nitrogen through it for 30 min . Then, solid $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(12 \mathrm{mg}$, $9.85 \mu \mathrm{~mol}$ ) was added under a steady flow of nitrogen and the mixture stirred at $75^{\circ} \mathrm{C}$ for 24 h . After completion, the solvents were evaporated under reduced pressure. The residue was dissolved in DCM $(50 \mathrm{~mL})$ and washed with water ( 100 mL ). After drying over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, the solvent was removed and the crude product was purified by column chromatography $\left(\mathrm{SiO}_{2}\right)$ using DCM as eluent to afford $52.0 \mathrm{mg}(51.0 \mu \mathrm{~mol}, 52 \%)$ of the desired product $\mathbf{2}$ as a violet solid (silica gel, $\mathrm{DCM}, R_{\mathrm{f}}=0.5$ ). Mp: $>300{ }^{\circ} \mathrm{C}$. IR (KBr): $\tilde{v}=506,616,748,790,863,989,1038,1094,1246,1390,1469,1581,2155$, 2221, 2896, 2955, 3013, 3058, $\mathrm{cm}^{-1}{ }^{\mathbf{1}} \mathbf{H}^{\mathbf{H}} \mathbf{N M R}\left(\mathbf{4 0 0} \mathbf{~ M H z}, \mathbf{C D}_{\mathbf{2}} \mathbf{C l}_{2}\right): \delta=1.82(\mathrm{~s}, 12 \mathrm{H}, \mathrm{b}$ ' -H ), $2.55(\mathrm{~s}$, $\left.12 \mathrm{H}, \mathrm{f}^{\prime}-\mathrm{H}\right), 2.62(\mathrm{~s}, 6 \mathrm{H}, \mathrm{a}-\mathrm{H}), 7.22$ (s, 4H, e'-H), 7.30 ( $\mathrm{s}, 4 \mathrm{H}, \mathrm{m}$ '-H), 7.93 (d, ${ }^{3} \mathrm{~J}=8.0 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{c}$ '-H), $8.24\left(\mathrm{~d},{ }^{3} J=8.0 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{d} \cdot-\mathrm{H}\right), 8.74\left(\mathrm{~d},{ }^{3} J=4.8 \mathrm{~Hz}, 4 \mathrm{H}, \beta^{\prime}{ }_{2}-\mathrm{H}\right), 8.90\left(\mathrm{~d},{ }^{3} J=4.8 \mathrm{~Hz}, 4 \mathrm{H}, \beta^{\prime}{ }_{1}-\mathrm{H}\right) \mathrm{ppm}$. ${ }^{13} \mathbf{C}$ NMR ( $\mathbf{1 0 0} \mathbf{~ M H z}, \mathbf{C D}_{2} \mathbf{C l}_{2}$ ): $\delta=21.5,21.7,24.5,88.4,92.8,119.7,119.9,121.9,122.2,127.9$, 130.4, 131.2, 131.8, 132.4, 134.9, 138.0, 139.2, 139.4, 144.0, 150.1, 150.3, 158.4 ppm. ESI-MS: $m / z$ $(\%)=1019.7(100)[2+\mathrm{H}]^{+}$; Elemental analysis: Calcd. for $\mathrm{C}_{68} \mathrm{H}_{54} \mathrm{~N}_{6} \mathrm{Zn} \bullet \mathrm{H}_{2} \mathrm{O}: \mathrm{C}, 78.64 ; \mathrm{H}, 5.43 ; \mathrm{N}$, 8.09. Found C, 78.46; H, 5.37; N, 8.22.

## Synthesis of porphyrin $3^{4}$



Under a nitrogen atmosphere, $\mathrm{Rh}_{2}(\mathrm{CO})_{4} \mathrm{Cl}_{2}(47.0 \mathrm{mg}, 121 \mu \mathrm{~mol})$ and $5,10,15,20$-tetraphenylporphyrin ( $50.0 \mathrm{mg}, 81.3 \mu \mathrm{~mol}$ ) were dissolved in anhydrous $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$. After the addition of anhydrous $\mathrm{NaOAc}(198 \mathrm{mg}, 2.42 \mathrm{mmol})$ stirring was continued for 45 min . Avoiding any exposure to air, the reaction mixture was concentrated under vacuum ( 5 min , to remove residual acetic acid), a new portion of $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ was added, and the procedure was repeated. The reaction mixture was dissolved in dry benzene $(10 \mathrm{~mL})$ and $\mathrm{I}_{2}(21.0 \mathrm{mg}, 121 \mu \mathrm{~mol})$ was added. The progress of oxidation was monitored by UV-vis analysis and TLC. As soon as the reaction was completed ( 45 min ), the mixture was transferred to a silica column and the product was eluted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. After evaporation under vacuum $42.0 \mathrm{mg}(50.4 \mu \mathrm{~mol}, 62 \%)$ of reddish product 3 (silica gel, DCM, $R_{\mathrm{f}}=0.4$ ) were obtained. Mp: $>300^{\circ} \mathrm{C}$. IR (KBr): $\tilde{v}=3058,3013,2955,2896,1581,1469,1390$, 1246, 1094, 1038, 989, 863, 790, 748, 616, $506 \mathrm{~cm}^{-1} .{ }^{\mathbf{1}} \mathbf{H} \mathbf{N M R}\left(\mathbf{4 0 0} \mathbf{~ M H z}, \mathbf{C D}_{\mathbf{2}} \mathbf{C l}_{2}\right): \delta=7.74-7.84$ (m, 12H, p-,r-H), 8.11-8.30 (m, 8H, q-H), 8.89 (s, 8H, $\beta-\mathrm{H}$ ) ppm.

## 3. Synthesis and characterization of model complexes

General procedure: All solid compounds were placed in an NMR tube and then dissolved in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$. Subsequently, the NMR spectra were recorded at 298 K.

## Model complex $11=[\mathrm{Cu}(\mathbf{8})(9)]^{+}$



In an NMR tube, compound $\mathbf{8}(1.33 \mathrm{mg}, 2.21 \mu \mathrm{~mol})$, 4-bromo-2,6-dimethylpyridine $(\mathbf{9}, 412 \mu \mathrm{~g}$, $2.21 \mu \mathrm{~mol})$, and $\left[\mathrm{Cu}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{4}\right] \mathrm{PF}_{6}(825 \mu \mathrm{~g}, 2.21 \mu \mathrm{~mol})$ were mixed in $500 \mu \mathrm{~L}$ of $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at room temperature. Yield: Quantitative. ${ }^{\mathbf{1}} \mathbf{H}$ NMR ( $\mathbf{4 0 0} \mathbf{~ M H z}, \mathbf{C D}_{2} \mathbf{C l}_{2}$ ): $\delta=1.94(\mathrm{~s}, 6 \mathrm{H}, \mathrm{e}-\mathrm{H}), 2.17(\mathrm{~s}, 6 \mathrm{H}$, $\left.\mathrm{f}^{\prime}-\mathrm{H}\right), 2.38(\mathrm{~s}, 6 \mathrm{H}, \mathrm{f}-\mathrm{H}), 3.60(\mathrm{~s}, 6 \mathrm{H}, \mathrm{g}-\mathrm{H}), 3.73(\mathrm{~s}, 3 \mathrm{H}, \mathrm{i}-\mathrm{H}), 5.98(\mathrm{~s}, 2 \mathrm{H}, \mathrm{h}-\mathrm{H}), 7.24\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{e}^{\prime}-\mathrm{H}\right)$, $7.88\left(\mathrm{~d},{ }^{3} J=8.0 \mathrm{~Hz}, 1 \mathrm{H}, 3 / 8-\mathrm{H}\right), 7.91\left(\mathrm{~d},{ }^{3} J=8.0 \mathrm{~Hz}, 1 \mathrm{H}, 8 / 3-\mathrm{H}\right), 8.14(\mathrm{~s}, 2 \mathrm{H}, 5-6-\mathrm{H}), 8.60\left(\mathrm{~d},{ }^{3} \mathrm{~J}=\right.$ $8.0 \mathrm{~Hz}, 1 \mathrm{H}, 4 / 7-\mathrm{H}), 8.70\left(\mathrm{~d},{ }^{3} J=8.0 \mathrm{~Hz}, 1 \mathrm{H}, 7 / 4-\mathrm{H}\right) \mathrm{ppm}$. ESI-MS: $m / z(\%)=853.8(100)[\mathrm{Cu}(8)(9)]^{+}$.

## Model complex $12=\left[\operatorname{DABCO}(10)_{2}\right]$



In an NMR tube $\operatorname{DABCO}(\mathbf{4}, 150 \mu \mathrm{~g}, 1.34 \mu \mathrm{~mol})$ and $\operatorname{ZnTPP}(\mathbf{1 0}, 1.81 \mathrm{mg}, 2.68 \mu \mathrm{~mol})$ were mixed in $500 \mu \mathrm{~L}$ of $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at room temperature. Yield: Quantitative. ${ }^{1} \mathbf{H} \mathbf{N M R}\left(\mathbf{4 0 0} \mathbf{~ M H z}, \mathbf{C D}_{2} \mathbf{C l}_{2}\right): \delta=$ -4.67 (s, 12H, CH2-DABCO), 7.63-7.79 (m, 24H, a-c-H), 7.86-8.09 (m, 16H, b-H), 8.67 (s, 16H, $\beta-$ H) ppm .

## Model complex $7=\left[\operatorname{DABCO}(3)_{2}\right]$



In an NMR tube DABCO $(4,110 \mu \mathrm{~g}, 0.982 \mu \mathrm{~mol})$ and porphyrin $3(1.65 \mathrm{mg}, 1.96 \mu \mathrm{~mol})$ were mixed in $500 \mu \mathrm{~L}$ of $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at room temperature. Yield: Quantitative. ${ }^{1} \mathbf{H}$ NMR ( $\mathbf{4 0 0} \mathbf{~ M H z}, \mathbf{C D}_{2} \mathbf{C l}_{2}$ ): $\delta=$ $-5.55\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{CH}_{2}-\mathrm{DABCO}\right), 7.61-7.67\left(\mathrm{~m}, 8 \mathrm{H}, \mathrm{a} / \mathrm{a}^{\prime}-\mathrm{H}\right), 7.67-7.72\left(\mathrm{~m}, 8 \mathrm{H}, \mathrm{a}^{\prime}-/ \mathrm{a}-\mathrm{H}\right), 7.74-7.80(\mathrm{~m}$, 16H, b-H), 7.86-7.90 (m, 8H, c-H) ppm.

## 4. Synthesis and characterization of supramolecular architectures

Synthesis of complex $5=\left[\mathrm{Cu}_{4}(\mathbf{1})_{2}(2)_{2}\right]^{4+}$


In an NMR tube, ligand $1(911 \mu \mathrm{~g}, 0.474 \mu \mathrm{~mol})$, ligand $2(483 \mu \mathrm{~g}, 0.474 \mu \mathrm{~mol})$, and $\left[\mathrm{Cu}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{4}\right] \mathrm{PF}_{6}(353 \mu \mathrm{~g}, 0.948 \mu \mathrm{~mol})$ were dissolved in $500 \mu \mathrm{~L}$ of $\mathrm{CD}_{2} \mathrm{Cl}_{2}$. Yield: Quantitative. ${ }^{1} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathbf{C D}_{2} \mathbf{C l}_{2}$ ): $\delta=1.79$ (s, 24H, b-H), 1.80 (s, 24H, b'-H), 2.16 (s, 24H, e-H), 2.27 (s, 24H, f'-H), $2.44(\mathrm{~s}, 24 \mathrm{H}, \mathrm{f}-\mathrm{H}), 2.59(\mathrm{~s}, 12 \mathrm{H}, \mathrm{a}-\mathrm{H}), 2.61(\mathrm{~s}, 12 \mathrm{H}, \mathrm{a}-\mathrm{H}), 3.70(\mathrm{~s}, 24 \mathrm{H}, \mathrm{g}-\mathrm{H}), 3.82(\mathrm{~s}$, $12 \mathrm{H}, \mathrm{i}-\mathrm{H}), 6.08$ (s, $8 \mathrm{H}, \mathrm{h}-\mathrm{H}$ ), 7.22 (s, $8 \mathrm{H}, \mathrm{e}^{\prime}-\mathrm{H}$ ), 7.29 ( $\mathrm{s}, 16 \mathrm{H}, \mathrm{m}-, \mathrm{m}^{\prime}-\mathrm{H}$ ), 7.54 (d, ${ }^{3} J=8.0 \mathrm{~Hz}, 8 \mathrm{H}, \mathrm{c}-$ H), 7.96-7.80 (m, 12H, 8-, c'-H), $8.18\left(\mathrm{~d},{ }^{3} J=8.0 \mathrm{~Hz}, 8 \mathrm{H}, \mathrm{d}-\mathrm{H}\right), 8.22\left(\mathrm{~d},{ }^{3} \mathrm{~J}=8.4 \mathrm{~Hz}, 4 \mathrm{H}, 5 / 6-\mathrm{H}\right)$, $8.24\left(\mathrm{~d},{ }^{3} J=8.4 \mathrm{~Hz}, 4 \mathrm{H}, 6 / 5-\mathrm{H}\right), 8.28\left(\mathrm{~d},{ }^{3} J=8.0 \mathrm{~Hz}, 8 \mathrm{H}, \mathrm{d} \cdot-\mathrm{H}\right), 8.67\left(\mathrm{~d},{ }^{3} J=8.0 \mathrm{~Hz}, 4 \mathrm{H}, 7-\mathrm{H}\right), 8.76$ (d, $\left.{ }^{3} J=4.8 \mathrm{~Hz}, 8 \mathrm{H}, \beta_{2}-\mathrm{H}\right), 8.78\left(\mathrm{~d},{ }^{3} \mathrm{~J}=4.8 \mathrm{~Hz}, 8 \mathrm{H}, \beta^{\prime}{ }_{2}-\mathrm{H}\right), 8.83\left(\mathrm{~d},{ }^{3} \mathrm{~J}=4.8 \mathrm{~Hz}, 8 \mathrm{H}, \beta_{1}-\mathrm{H}\right), 8.90(\mathrm{~d}$, $\left.{ }^{3} J=4.8 \mathrm{~Hz}, 8 \mathrm{H}, \beta^{\prime}{ }_{1}-\mathrm{H}\right), 8.98(\mathrm{~s}, 4 \mathrm{H}, 4-\mathrm{H}) \quad \mathrm{ppm}$. ESI-MS: $m / z(\%)=1534.5(100)\left[\mathrm{Cu}_{4}(\mathbf{1})_{2}(\mathbf{2})_{2}\right]^{4+}$. Elemental analysis: Calcd for $\mathrm{C}_{368} \mathrm{H}_{296} \mathrm{Br}_{4} \mathrm{Cu}_{4} \mathrm{~F}_{24} \mathrm{~N}_{28} \mathrm{O}_{12} \mathrm{P}_{4} \mathrm{Zn}_{4} \bullet 2 \mathrm{H}_{2} \mathrm{O}: \mathrm{C}, 65.44 ; \mathrm{H}, 4.48$; N, 5.81. Found C, 65.19; H, 4.56; N, 5.74.

## Synthesis of complex $6=\left[\mathrm{Cu}_{2}(\mathbf{1})(2) \mathrm{DABCO}\right]^{2+}$



In an NMR tube, ligand $1(911 \mu \mathrm{~g}, 0.474 \mu \mathrm{~mol})$, ligand $2(483 \mu \mathrm{~g}, 0.474 \mu \mathrm{~mol})$, DABCO (4) (53.1 $\mu \mathrm{g}$, $0.474 \mu \mathrm{~mol})$ and $\left[\mathrm{Cu}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{4}\right] \mathrm{PF}_{6}(353 \mu \mathrm{~g}, 0.948 \mu \mathrm{~mol})$ were dissolved in $500 \mu \mathrm{~L}$ of $\mathrm{CD}_{2} \mathrm{Cl}_{2}$. Yield: Quantitative; ${ }^{\mathbf{1}} \mathbf{H}$ NMR ( $\mathbf{4 0 0} \mathbf{~ M H z}, \mathbf{C D}_{\mathbf{2}} \mathbf{C l}_{2}$ ): $\delta=-[5.12-5.05]\left(\mathrm{m}, 6 \mathrm{H}, \mathrm{CH}_{2}, \mathrm{DABCO}\right),-[4.92-4.85]$ ( $\mathrm{m}, 6 \mathrm{H}, \mathrm{CH}_{2}, ~ \mathrm{DABCO}$ ), -0.63 ( $\mathrm{s}, 6 \mathrm{H}, \mathrm{f}_{1}{ }^{\prime}-/ \mathrm{f}_{2}{ }^{\prime}-\mathrm{H}$ ), 1.26 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{b}-\mathrm{H}$ ), 1.29 (br s, 6H, b-H), 1.30 (s, 3H, b-H), 1.44 (s, 6H, f $\mathrm{f}^{\prime}-/ \mathrm{f}_{1}{ }^{\prime}-\mathrm{H}$ ), $2.03\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{a}^{\prime}-\mathrm{H}\right.$ ), 2.23 (s, 6H, a-H), $2.40(\mathrm{~s}, 6 \mathrm{H}, \mathrm{du}-\mathrm{H}), 2.45$ (s, 6H, du-H), 2.52 (s, 6H, du-H), 2.53 (s, 6H, du-H), 2.62 (s, 6H, b-H), 2.67 (s, 6H, b-H), 3.78 (s, 6H, g1$\left./ \mathrm{g}_{2}-\mathrm{H}\right), 3.79\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{g}_{2}-\mathrm{g}_{1}-\mathrm{H}\right), 3.90(\mathrm{~s}, 6 \mathrm{H}, \mathrm{i}-\mathrm{H}), 6.26\left(\mathrm{~d},{ }^{4} J=1.9 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{h}_{1}-/ \mathrm{h}_{2}-\mathrm{H}\right), 6.30\left(\mathrm{~d},{ }^{4} J=1.9\right.$ $\left.\mathrm{Hz}, 2 \mathrm{H}, \mathrm{h}_{2}-/ \mathrm{h}_{1}-\mathrm{H}\right), 6.49\left(\mathrm{~d},{ }^{3} J=8.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{s}-\mathrm{H}\right), 6.56\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{e}_{1}{ }^{\prime} / \mathrm{e}_{2}{ }^{\prime}-\mathrm{H}\right), 6.99\left(\mathrm{~d},{ }^{3} \mathrm{~J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{s}-\right.$ H), $7.09(\mathrm{~s}, 2 \mathrm{H}, \mathrm{m}-\mathrm{H}), 7.17(\mathrm{~s}, 2 \mathrm{H}, \mathrm{m}-\mathrm{H}), 7.19\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{m}{ }^{\prime}-\mathrm{H}\right), 7.24\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{m}{ }^{\prime}-\mathrm{H}\right), 7.30\left(\mathrm{~d},{ }^{3} \mathrm{~J}=8.0\right.$ $\mathrm{Hz}, 2 \mathrm{H}, \mathrm{s}-\mathrm{H}), 7.32\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{e}_{2}{ }^{\prime} / \mathrm{e}_{1}{ }^{\prime}-\mathrm{H}\right), 7.36\left(\mathrm{~d},{ }^{3} \mathrm{~J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{s}-\mathrm{H}\right), 7.54\left(\mathrm{~d},{ }^{3} \mathrm{~J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{s}-\mathrm{H}\right)$, $7.62-7.66(\mathrm{~m}, 4 \mathrm{H}, \mathrm{s}-\mathrm{H}), 7.71\left(\mathrm{~d},{ }^{3} J=4.8 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H}\right), 7.80\left(\mathrm{~d},{ }^{3} J=8.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{s}-\mathrm{H}\right), 7.91\left(\mathrm{~d},{ }^{3} J=\right.$ $4.8 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H}), 8.04\left(\mathrm{~d},{ }^{3} \mathrm{~J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}, 8-\mathrm{H}\right), 8.15\left(\mathrm{~d},{ }^{3} J=4.8 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H}\right), 7.17-7.26(\mathrm{~m}, 12 \mathrm{H}$, $[4 \beta, 5,6]-\mathrm{H}), 8.30\left(\mathrm{~d},{ }^{3} J=4.8 \mathrm{~Hz}, 2 \mathrm{H}, \beta-\mathrm{H}\right), 8.71\left(\mathrm{~d},{ }^{3} \mathrm{~J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}, 7-\mathrm{H}\right), 8.83(\mathrm{~s}, 2 \mathrm{H}, 4-\mathrm{H}) \mathrm{ppm} ;$ ESI-MS: $m / z(\%)=1589.4(100)\left[\mathrm{Cu}_{2}(\mathbf{1})(\mathbf{2}) \mathrm{DABCO}\right]^{2+}$. Elemental analysis: Calcd. for $\mathrm{C}_{184} \mathrm{H}_{148} \mathrm{Br}_{2} \mathrm{Cu}_{2} \mathrm{~F}_{12} \mathrm{~N}_{14} \mathrm{O}_{6} \mathrm{P}_{2} \mathrm{Zn}_{2} \bullet \mathrm{CH}_{3} \mathrm{CN}$ : C, 65.71; H, 4.48; $\mathrm{N}, 6.18$. Found: C, 65.38; H, 4.41; N , 6.32.

## 5. Model studies

Guest and metal-dependent two-fold completive self-sorting was tested by mixing ligand $\mathbf{8}(1.33 \mathrm{mg}$, $2.21 \mu \mathrm{~mol}$ ), 4-bromo-2,6-dimethylpyridine ( $\mathbf{9}, 412 \mu \mathrm{~g}, 2.21 \mu \mathrm{~mol}$ ), ZnTPP ( $\mathbf{1 0}, 3.00 \mathrm{mg}, 4.41 \mu \mathrm{~mol}$ ), $\operatorname{DABCO}(4,248 \mu \mathrm{~g}, 2.21 \mu \mathrm{~mol})$ and $\left[\mathrm{Cu}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{4}\right] \mathrm{PF}_{6}(825 \mu \mathrm{~g}, 2.21 \mu \mathrm{~mol})$ in a ratio of 1:1:2:1:1 in $500 \mu \mathrm{~L}$ of $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at room temperature. The ${ }^{1} \mathrm{H}$ NMR spectrum was compared with those of the
individual ligands and complexes. Accordingly, $\mathbf{1 1}=[\mathrm{Cu}(\mathbf{8})(\mathbf{9})]^{+}$and $1 \mathbf{2}=\left[\mathrm{DABCO}(\mathbf{1 0})_{2}\right]$ were formed quantitatively.


To the above reaction mixture rhodium porphyrin $3(3.71 \mathrm{mg}, 4.41 \mu \mathrm{~mol})$ was added at room temperature. The ${ }^{1} \mathrm{H}$ NMR spectrum was compared with those of the individual NMRs attesting formation of complexes $[\mathrm{Cu}(\mathbf{8})(\mathbf{9})]^{+},\left[\mathrm{DABCO}(\mathbf{3})_{2}\right]$ and free ZnTPP . This study clearly indicates double self-sorting phenomena.




Figure S1. ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , 298 K ) of (a) ligand $\mathbf{8}$; (b) complex $\mathbf{1 1}=[\mathrm{Cu}(\mathbf{8})(\mathbf{9})]+$; (c) $\mathrm{ZnTPP}(\mathbf{1 0})$; (d) complex 12 $=\left[\operatorname{DABCO}(10)_{2}\right]$; (e) rhodium porphyrin 3; (f) complex $\mathbf{7}=\left[\mathrm{DABCO}(\mathbf{3})_{2}\right]$; (g) formation of $\mathbf{1 1}$ and $\mathbf{1 2}$ after mixing of $\mathbf{8}, \mathbf{9}, \mathbf{1 0}, \mathrm{DABCO}$ and $\left[\mathrm{Cu}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{4}\right] \mathrm{PF}_{6}$ in a ratio of $1: 1: 2: 1$; (h) formation of $\mathbf{1 1}$ and $\mathbf{7}$ as well as free porphyrin $\mathbf{1 0}$ after mixing of porphyrin 3 (2 equiv.) and mixture of $\mathbf{1 1}$ and $\mathbf{1 2}$.

## 6. Selectivity and guest-induced structural rearrangement

pyrazine, 2-chloropyrazine
1,4-dimethylpiperazine,
anthracene, pyrene, coronene, perylene,
perylene-3,4,9,10-tetracarboxylic dianhydride,
DABCO
$\left[\mathrm{Cu}_{4}(1)_{2}(2)_{2}\right]^{4+} \longrightarrow 2 \times\left[\mathrm{Cu}_{2}(1)(2)(\mathrm{DABCO})\right]^{2+}$
Rectangle
Sandwich

Guest selectivity and structural rearrangement was tested by mixing ligand $\mathbf{1}(736 \mu \mathrm{~g}, 0.383 \mu \mathrm{~mol})$, ligand $2(390 \mu \mathrm{~g}, 0.383 \mu \mathrm{~mol}),\left[\mathrm{Cu}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{4}\right] \mathrm{PF}_{6}(284 \mu \mathrm{~g}, 0.766 \mu \mathrm{~mol})$, pyrazine $(30.0 \mu \mathrm{~g}$, $0.383 \mu \mathrm{~mol}$ ), 2-chloropyrazine ( $43.8 \mu \mathrm{~g}, 0.383 \mu \mathrm{~mol}$ ), 1,4-dimethylpiperizine ( $43.7 \mu \mathrm{~g}, 0.383 \mu \mathrm{~mol}$ ), anthracene ( $68.2 \mu \mathrm{~g}, 0.383 \mu \mathrm{~mol}$ ), pyrene ( $77.4 \mu \mathrm{~g}, 0.383 \mu \mathrm{~mol}$ ), coronene ( $115 \mu \mathrm{~g}, 0.383 \mu \mathrm{~mol}$ ), perylene-3,4,9,10-tetracarboxylic dianhydride ( $150 \mu \mathrm{~g}, 0.383 \mu \mathrm{~mol}$ ), and DABCO ( $42.8 \mu \mathrm{~g}$, $0.383 \mu \mathrm{~mol})$ in $500 \mu \mathrm{~L}$ of $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at room temperature followed by measurement of the ${ }^{1} \mathrm{H}$ NMR spectrum. The main part of the spectrum agreed with that of complex $\left[\mathrm{Cu}_{2}(\mathbf{1})(\mathbf{2}) \mathrm{DABCO}\right]^{2+}$ with the rest of the signals representing free guests in solution.


Figure S2. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, 298 \mathrm{~K}$ ) of (a) complex 5 and pyrazine in a ratio of 1:1; (b) complex 5, pyrazine and DABCO in a ratio of 1:1:1, furnishing complex 6 and leaving the pyrazine free; (c) complex 5 and 2-chloropyrazine in a ratio of $1: 1$; (d) complex 5 and 1,4-dimethylpiperizine in a ratio of 1:1; (e) complex 5, pyrazine, 2-chloropyrazine, 1,4dimethylpiperizine, anthracene, pyrene, coronene, perylene-3,4,9,10-tetracarboxylic dianhydride and DABCO in a ratio of 1:1:1:1:1:1:1:1:1 furnishing complex 6 and free ligands.

## 7. NMR spectra: ${ }^{1} \mathrm{H}$ NMR, ${ }^{13} \mathrm{C}$ NMR, ${ }^{1} \mathrm{H},{ }^{1} \mathrm{H}$ COSY



Figure S3. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(400 \mathrm{MHz}, 298 \mathrm{~K})$.


Figure S4. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(100 \mathrm{MHz}, 298 \mathrm{~K})$.


Figure S5. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(400 \mathrm{MHz}, 298 \mathrm{~K})$.


Figure S6. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(100 \mathrm{MHz}, 298 \mathrm{~K})$.


Figure S7. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{3}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(400 \mathrm{MHz}, 298 \mathrm{~K})$.


Figure S8. ${ }^{1} \mathrm{H}$ NMR spectrum of complex $\mathbf{1 1}=[\mathrm{Cu}(\mathbf{8})(\mathbf{9})]^{+}$in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(400 \mathrm{MHz}, 298 \mathrm{~K})$.


Figure S9. ${ }^{1} \mathrm{H}$ NMR spectrum of complex $\mathbf{1 2}=\left[(\mathbf{4})(\mathbf{1 0})_{3}\right]$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(400 \mathrm{MHz}, 298 \mathrm{~K})$.


Figure S10. ${ }^{1} \mathrm{H}$ NMR spectrum of complex $7=\left[(\mathbf{3})_{2}(\mathbf{4})\right]$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(400 \mathrm{MHz}, 298 \mathrm{~K})$.


Figure S11. ${ }^{1} \mathrm{H}$ NMR spectrum of complex $\mathbf{5}=\left[\mathrm{Cu}_{4}(\mathbf{1})_{\mathbf{2}}(\mathbf{2})_{2}\right]^{4+}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(400 \mathrm{MHz}, 298 \mathrm{~K})$.


Figure S12. ${ }^{1} \mathrm{H},{ }^{1} \mathrm{H}$ COSY spectrum of complex $\mathbf{5}=\left[\mathrm{Cu}_{4}(\mathbf{1})_{2}(\mathbf{2})_{2}\right]^{4+}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(400 \mathrm{MHz}, 298 \mathrm{~K})$.


Figure S13. ${ }^{1} \mathrm{H}$ NMR spectrum of complex $\mathbf{6}=\left[\mathrm{Cu}_{2}(\mathbf{1})(\mathbf{2}) \mathrm{DABCO}\right]^{2+}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(400 \mathrm{MHz}, 298 \mathrm{~K})$.


Figure S14. ${ }^{1} \mathrm{H},{ }^{1} \mathrm{H}$ COSY spectrum of complex $\mathbf{6}=\left[\mathrm{Cu}_{2}(\mathbf{1})(\mathbf{2})(\mathbf{4})\right]^{2+}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(400 \mathrm{MHz}, 298 \mathrm{~K})$.


Figure S15. ${ }^{1} \mathrm{H},{ }^{1} \mathrm{H}$ ROESY spectrum of complex $\mathbf{6}=\left[\mathrm{Cu}_{2}(\mathbf{1})(\mathbf{2})(\mathbf{4})\right]^{2+}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(400 \mathrm{MHz}, 298 \mathrm{~K})$.

## 8. ESIMS spectra



Figure S16. ESI-MS of $\mathbf{1}$ after protonation.


Figure S17. ESIMS of $\mathbf{2}$ after protonation.


Figure S18. ESIMS of complex 11.


Figure S19. ESIMS of complex $5=\left[\mathrm{Cu}_{4}(\mathbf{1})_{2}(\mathbf{2})_{2}\right]^{4+}$.


Figure S20. ESIMS of complex $6=\left[\mathrm{Cu}_{2}(\mathbf{1})(\mathbf{2})(\mathbf{4})\right]^{2+}$.

## 9. UV-vis data

## Measurement of binding constants

The UV-vis titration technique was used to determine the binding constants of complexes. The full data of a selected wavelength region was analyzed using the SPECFIT/32 global analysis system (Spectrum Software Associates, Marlborough, MA).


Figure S21. UV-vis spectra of $\mathbf{1 0}\left(1.15 \times 10^{-5} \mathrm{M}\right)$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ upon addition of DABCO (4) $\left(1.10 \times 10^{-4} \mathrm{M}\right)$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at 298 K to afford the complex $\mathbf{1 2}=\left[\mathrm{DABCO}(\mathbf{1 0})_{2}\right]$. The wavelength region $500-700 \mathrm{~nm}$ was analyzed. Result for $\left[\operatorname{DABCO}(10)_{2}\right]: \log \beta=7.20 \pm 0.15$.


Figure S22. UV-vis spectra of $\mathbf{3}\left(5.10 \times 10^{-6} \mathrm{M}\right)$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ upon addition of DABCO $(\mathbf{4})\left(4.08 \times 10^{-4} \mathrm{M}\right)$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at 298 K to afford the complex $7=\left[\mathrm{DABCO}(3)_{2}\right]$. The wavelength region $450-700 \mathrm{~nm}$ was analyzed. Result for $\left[\operatorname{DABCO}(3)_{2}\right]: \log \beta=9.60 \pm 0.35$.


Figure S23. UV-vis spectra of $\mathbf{8}\left(3.20 \times 10^{-5} \mathrm{M}\right)$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ upon addition of $\left[\mathrm{Cu}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{4}\right] \mathrm{PF}_{6}\left(5.30 \times 10^{-3} \mathrm{M}\right)$ in $\mathrm{CH}_{3} \mathrm{CN}$ at 298 K to afford the complex $[\mathrm{Cu}(8)]^{+}$. The wavelength region $200-400 \mathrm{~nm}$ was analyzed. Result for $[\mathrm{Cu}(\mathbf{8})]^{+}: \log K=5.64 \pm 0.11$.


Figure S24. UV-vis spectra of $[\mathrm{Cu}(\mathbf{8})]^{+}\left(3.10 \times 10^{-5} \mathrm{M}\right)$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ upon addition of $9\left(4.15 \times 10^{-3} \mathrm{M}\right)$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at 298 K to afford the complex $[\mathrm{Cu}(\mathbf{8})(\mathbf{9})]^{+}$. The wavelength region $200-400 \mathrm{~nm}$ was analyzed. Result for $[\mathrm{Cu}(\mathbf{8})(\mathbf{9})]^{+}$: $\log K=4.60 \pm 0.21$.


Figure S25. UV-vis spectra of rectangle $5\left(4.50 \times 10^{-6} \mathrm{M}\right)$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ upon addition of DABCO (4) (4.50 $\times 10^{-4}$ M ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at 298 K to afford the complex 6 . The wavelength region $470-700 \mathrm{~nm}$ was analyzed.


Figure S26. UV-vis analysis of the reversible interconversion between the structure $5\left(4.70 \times 10^{-6} \mathrm{M}\right)$ and $\mathbf{6}(4.70 \times$ $\left.10^{-6} \mathrm{M}\right)$ by addition/removal of guest DABCO (4) by porphyrin $3\left(2.50 \times 10^{-3} \mathrm{M}\right)$.

## 10. Fluorescence data



Figure S27. Emission spectra of state I (complex 5) and state II (complex 6) ( $\left.\lambda_{\mathrm{ex}}=557 \mathrm{~nm}\right)$.


Figure S28. Emission spectroscopy ( $\lambda_{\mathrm{ex}}=557 \mathrm{~nm}$ ) was used to analyze the guest selectivity. All listed guests were sequentially added to complex 5 (state I). In absence of added DABCO, no change in the emission was noted. Even the fluorescence intensity did not change. When lastly DABCO was added the fluorescence spectrum of state II (complex 6) was generated as indicated by the shift of the emission wavelength to 618 nm .

## 11. DOSY NMR

## Calculation of hydrodynamic radius from

a) The diffusion coefficient $D$ (of complex $\mathbf{5}$ and $\mathbf{6}$ ) was obtained from the DOSY spectrum and the corresponding hydrodynamic radius was calculated from the Stokes-Einstein equation.

$$
r=\mathrm{k}_{\mathrm{B}} T / 6 \eta \pi D
$$

b) Radius of the architectures were calculated from their optimized structures at B3LYP/6$31 G(d)$ level.


Figure S29. DOSY NMR spectrum $\left(600 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 298 \mathrm{~K}\right)$ of rectangle $\mathbf{5}=\left[\mathrm{Cu}_{4}(\mathbf{1})_{2}(\mathbf{2})_{2}\right]\left(\mathrm{PF}_{6}\right)_{4}$.


Figure S30. DOSY NMR spectrum $\left(600 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 298 \mathrm{~K}\right)$ of complex $\mathbf{6}=\left[\mathrm{Cu}_{2}(\mathbf{1})(\mathbf{2}) \mathrm{DABCO}\right]\left(\mathrm{PF}_{6}\right)_{2}$.

## 12. Calculated structures



Figure S31. DFT-optimized (B3LYP/6-31G(d)) structure of rectangle 5. The calculated hydrodynamic radius is $21.5 \AA$.


Figure 32. (a) DFT-optimized (B3LYP/6-31G(d)) structure of complex 6 (top view). (b) Side view and calculated hydrodynamic radius from the corresponding structure is $12.3 \AA$.

## 13. References

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