Supporting Information for

Quantifying the Exchange Coupling in Linear Copper Porphyrin Oligomers

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1 Experimental Details

1.1 Synthetic Procedures

Dry toluene and THF were obtained by passing the solvents through columns of alumina, under nitrogen. Diisopropylamine (DIPA) was distilled from CaH_2 and kept over activated molecular sieves (3 Å, 8–12 mesh). Unless specified otherwise, all other solvents were used as commercially supplied. Flash chromatography was carried out on silica gel 60 under positive pressure. Analytical thin-layer chromatography was carried out on aluminum-backed silica gel 60 F254 plates.

All UV-vis-NIR spectra were recorded in solution using a Perkin-Lambda 20 spectrometer (1 cm path length quartz cell).

Unless stated otherwise, ¹H NMR spectra were recorded at 298 K using a Bruker AV400 (400 MHz) instrument. ¹H NMR spectra are reported in ppm; coupling constants are given in Hertz, to the nearest 0.1 Hz. The solvent used was CDCl₃. The presence of the paramagnetic Cu(II) centers in some of the oligomers drastically complicates the interpretation of the ¹H NMR spectra. Many signals cannot be observed at all due to shortening of the relaxation times. Some signals can be observed but, due to broadening, cannot be accurately integrated and therefore the calculated integration, rather than the experimentally observed integrations, will be reported below.

MALDI-TOF mass spectra were carried out using a Waters MALDI Micro MX spectrometer.

Size exclusion chromatography (SEC) was carried out using Bio-Beads S-X1, 200-400 mesh (Bio Rad). Analytical and semi-preparative GPC was carried out on a Shimadzu Recycling GPC system equipped with a LC-20 AD pump, SPD-20A UV detector and a set of JAIGEL 3H (20×600 mm) and JAIGEL 4H (20×600 mm) columns in toluene/1%pyridine as eluent at a flow rate of 3.5 mL/min.

1.1.1 Synthesis of $P1_{2H}$

P1_{Zn} (280 mg, 0.12 mmol) was dissolved in CHCl₃ (40 mL). Trifluoroacetic acid (0.47 mL) was mixed with CHCl₃ (5 mL) to give a 10 % solution. The TFA solution was added dropwise to the porphyrin solution and the reaction mixture was stirred at room temperature for 15 minutes. The reaction mixture was passed through a short plug of silica gel (CHCl₃) and the solvent was removed to give the title compound as a dark oil (260 mg, 96 %).



¹**H NMR** (400 MHz, CDCl₃, 298 K): δ_{H} (ppm) 9.61 (4H, d, J = 4.7 Hz, H2), 8.78 (4H, d, J = 4.7 Hz, H3), 8.24 (4H, m, H4), 8.00 (2H, m, H6), 1.80–0.82 (234H, m, H1/H5), -2.11 (2H, s, H7).

MALDI-TOF: m/z = 2207 (C₁₄₄H₂₅₀N₄Si₆, M⁺ requires 2206).

1.1.2 Synthesis of $P1_{Cu}$

P1_{2H} (150 mg, 0.068 mmol) was dissolved in CHCl₃ (30 mL). Cu(OAc)₂ \cdot H₂O (494 mg, 2.72 mmol) was dissolved in MeOH (5 mL), added to the reaction mixture and stirred at 60 °C for 15 minutes. The mixture was allowed to cool to room temperature and passed through a short plug of silica gel (CHCl₃). The solvent was removed to give the title compound as a dark oil (110 mg, 71 %).



¹**H NMR** (400 MHz, CDCl₃, 298 K): $\delta_{\rm H}$ (ppm) broad, 1.80–0.61 (234H, m, H1/H2).

MALDI-TOF: m/z = 2266.7 (C₁₄₄H₂₄₈CuN₄Si₆, M⁺ requires 2266.7).



 λ_{max} (CHCl₃) / nm log(ε) : 434 (5.58), 567 (4.20), 610 (4.53).

Figure S1: MALDI-MS spectrum of $P1_{Cu}$, obtained from the EPSRC National Mass Spectrometry Facility, Swansea. The mass of the molecular ion matches well with that expected for $P1_{Cu}$: m/z = 2266.7 (C₁₄₄H₂₄₈CuN₄Si₆, M⁺ requires 2266.7).





A solution of $Cu(OAc)_2 \cdot H_2O$ (1.25 mg, 6.20 μ mol) in MeOH (200 μ L) was added to a solution of free base **P2**_{(2H)2} (6.0 mg, 1.60 μ mol) in DCM (2 mL). The mixture was stirred overnight, then passed over a short SiO₂ plug to afford, following evaporation of the solvent, the product **P2**_{Cu2} as a dark green oily solid (4.0 mg, 66%).

¹**H NMR** (400 MHz, CDCl₃, 298 K): $\delta_{\rm H}$ (ppm) broad, 8.02–7.75 (m), 1.76–0.68 (m).

MALDI-TOF: m/z = 3966.9 (C₂₅₂H₄₁₈Cu₂N₈Si₁₀, M⁺ requires 3966.9).

 λ_{\max} (CHCl₃) / nm log(ε) : 453 (5.56), 482 (5.30), 568 (4.40), 634 (4.87), 687 (5.00).



Figure S2: MALDI-MS spectrum of $P2_{Cu2}$, obtained from the EPSRC National Mass Spectrometry Facility, Swansea. The mass of the molecular ion matches well with that expected for $P2_{Cu2}$: m/z = 3966.9 (C₂₅₂H₄₁₈Cu₂N₈Si₁₀, M⁺ requires 3966.9).



Figure S3: GPC trace (toluene/pyridine, 100/1, v/v) of P2_{Cu2}. GPC column: JAIGEL 3H (20×600 mm) and JAIGEL 4H (20×600 mm) columns; flow rate: 3.5 mL/min; retention time: 66.9 min; detection wavelength: 590 nm.

1.1.4 Synthesis of $P3_{Cu3}$



A solution of $Cu(OAc)_2 \cdot H_2O(1.31 \text{ mg}, 6.20 \,\mu\text{mol})$ in MeOH (170 μ L) was added to a solution of free base **P3**_{(2H)3} (6.0 mg, 1.09 μ mol) in CHCl₃ (3 mL). The mixture was stirred overnight, then passed over a short SiO₂ plug to afford, following evaporation of the solvent, the product **P3**_{Cu3} as a dark green oily solid (3.3 mg, 55 %).

¹**H NMR** (400 MHz, CDCl₃, 298 K): $\delta_{\rm H}$ (ppm) broad, 1.67–0.55 (m).

MALDI-TOF: m/z = 5668.1 (C₃₆₀H₅₈₈Cu₃N₁₂Si₁₄, M⁺ requires 5668.1).

 λ_{\max} (CHCl₃) / nm log(ε) : 449 (5.45), 485 (5.24), 569 (4.45), 702 (5.00).



Figure S4: MALDI-MS spectrum of $P3_{Cu3}$, obtained from the EPSRC National Mass Spectrometry Facility, Swansea. The mass of the molecular ion matches well with that expected for $P3_{Cu3}$: m/z = 5668.1 ($C_{360}H_{588}Cu_3N_{12}Si_{14}$, M⁺ requires 5668.1).



Figure S5: GPC trace (toluene/pyridine, 100/1, v/v) of P3_{Cu3}. GPC column: JAIGEL 3H (20×600 mm) and JAIGEL 4H (20×600 mm) columns; flow rate: 3.5 mL/min; retention time: 64.9 min; detection wavelength: 590 nm.

1.1.5 Synthesis of $P1'_{Cu}$

P1_{Cu} (131 mg, 0.057 mmol) was dissolved in CHCl₃ (3.5 mL) and CH₂Cl₂ (13 mL). Tetra-*n*-butylammonium fluoride (86 μ L, 1.0 M solution in THF, 0.086 μ mol) was added to the stirred solution. The progress of the reaction was monitored by TLC (petrol ether) until an optimal mixture was reached (approx. 30 min). The mixture was immediately passed through a short plug of silica gel (CHCl₃) and the solvent was removed to give the title compound as a purple oil (48 mg, 42 %).



¹**H NMR** (400 MHz, CDCl₃, 298 K): $\delta_{\rm H}$ (ppm) broad, 1.70–0.68 (195H, m, H1/H2).

MALDI-TOF: m/z = 1986 (C₁₂₆H₂₁₀CuN₄Si₅, M⁺ requires 1985).



1.1.6 Synthesis of $P3_{Cu2}$

 $P1'_{Cu}$ (48.0 mg, 24.2 μ mol) and $P1''_{Zn}$ (8.2 mg, 8.2 μ mol) were dissolved in CHCl₃ (3 mL). A catalyst solution was prepared by dissolving PdCl₂(PPh₃)₂ (2.6 mg, 3.6 μ mol), Cul (2.5 mg, 13.3 μ mol) and 1,4-benzoquinone (7.5 mg, 69.2 μ mol) in CHCl₃ (1.7 mL) and diisopropylamine (84 μ L). The catalyst solution was added to the porphyrin solution and the reaction mixture was stirred at room

temperature for 1 hour. The crude reaction mixture was passed through a short plug of silica gel (1% pyridine in CHCl₃), passed over a size exclusion column on Biobeads SX-1 (1% pyridine in toluene), and finally the oligomers were separated by recycling GPC (1% pyridine in toluene) to give $P3_{Cu2}$ as a dark oily substance (7.7 mg, 28%).

¹**H NMR** (400 MHz, CDCl₃, 298 K): $\delta_{\rm H}$ (ppm) 9.82 (m, H3), 8.95 (m, H4), 8.29 (m, H5), 8.02 (m, H6), 7.89 (m, H2), 1.59–1.18 (m, H1), 1.01–0.73 (m, H1).

MALDI-TOF: m/z = 5668.6 (C₃₆₀H₅₈₈Cu₂N₁₂Si₁₄Zn, M⁺ requires 5670.1).

 λ_{\max} (CHCl₃) / nm log(ε) : 427 (5.42), 450 (5.60), 490 (5.42), 572 (4.57), 614 (4.64), 727 (5.20).



Figure S6: MALDI-MS spectrum of $P3_{Cu2}$. The mass of the molecular ion matches well with that expected for $P3_{Cu2}$: m/z = 5668.6 ($C_{360}H_{588}Cu_2N_{12}Si_{14}Zn$, M⁺ requires 5670.1).



Figure S7: GPC trace (toluene/pyridine, 100/1, v/v) of P3_{Cu2}. GPC column: JAIGEL 3H (20×600 mm) and JAIGEL 4H (20×600 mm) columns; flow rate: 3.5 mL/min; retention time: 64.3 min; detection wavelength: 590 nm.

1.2 EPR Sample Preparation

The purity of the compounds was verified by NMR, UV-vis and recycling GPC. All EPR samples were prepared at concentrations of roughly $0.2 \,\text{mM}$ in either deuterated or regular toluene. The solutions were subsequently degassed by the freeze-pump-thaw method, backfilled with argon and closed with a rubber septum. For storage in liquid nitrogen the rubber septum was removed. The frozen samples were directly inserted into the EPR resonator for the measurements at either 100 K (cw) or 15 K (pulsed).

1.3 Cw EPR

The continuous wave EPR spectra were recorded on a Bruker EMX spectrometer equipped with a liquid nitrogen flow cryostat. The measurements were performed in frozen toluene at a temperature of 100 K (or 298 K). The modulation frequency was set to 100 kHz and the modulation amplitude to 5 G at a microwave power of 0.5 mW (26 dB). After data acquisition, the individual spectra were baseline corrected, using the spectrum of pure solvent as a reference to compensate for resonator background signals, normalized and frequency corrected to a common value of 9.39 GHz for direct comparison.

1.4 ENDOR

Davies ENDOR measurements at 15 K were carried out at Q-band frequencies (34.0 GHz) on a Bruker ELEXSYS E580 pulsed EPR spectrometer equipped with a Bruker EN 5107D2 resonator and an Oxford Instruments liquid helium flow cryostat (CF935). All experimental ENDOR spectra were obtained using the pulse sequence $\pi - T - \pi/2 - \tau - \pi - \tau$ – echo with $\pi/2$ and π pulse lengths of 20 and 40 ns, respectively, and an evolution period T of 27 μ s during which a 25 μ s RF π pulse was applied. The inter-pulse delay τ for the detection sequence was chosen to be 220 ns. The whole echo signal was integrated and recorded as a function of the RF frequency in stochastic mode with an RF increment of 0.1 MHz. The RF power was adjusted based on a nutation experiment.

2 Complementary EPR Measurements

Figure S8 shows a comparison of the X-band cw EPR spectra of $P1_{Cu}$ and CuTPP recorded at 100 K and 298 K. It can be seen that the isotropic limit is reached at room temperature for CuTPP since no further changes in the spectral shape are observed when increasing the temperature further and the spectrum can be simulated with purely isotropic parameters. On the contrary, in the case of $P1_{Cu}$, the tumbling is still too slow at 298 K for any anisotropic contributions to average out (the spectrum of $P1_{Cu}$ at room temperature resembles the spectrum of CuTPP recorded at 200 K). Since the isotropic limit cannot be reached for $P1_{Cu}$, due to the bulky side and end groups, anisotropic contributions cannot be neglected and a straightforward isolation of the contribution of J to the spectrum is hence not possible. Spectral simulations are therefore best performed in the solid state and need to account for both, D and J.



Figure S8: Comparison of the X-band continuous wave EPR spectra recorded at 100 K and room temperature (298 K) in toluene for **P1**_{Cu} (*left*) and **CuTPP** (*right*).

A comparison of the frozen solution cw EPR spectra of $P1_{Cu}$, $P2_{Cu2}$, and $P3_{Cu2}$ in toluene (100 K) reveals that, to a first approximation, the exchange coupling in the presently studied linear copper porphyrin oligomers is only effective between nearest neighbors (cf. Figure S9). If the copper ion in the central porphyrin unit of a copper porphyrin trimer is replaced by a zinc ion in $P3_{Cu2}$, the corresponding EPR spectrum resembles that of a copper porphyrin monomer, indicating that the spin-spin interaction in conjugated linear copper porphyrin oligomers at a distance of 2.7 nm is not strong enough to affect the appearance of the cw EPR spectrum.*

To get an idea about the changes in the nitrogen hyperfine coupling constants in $P2_{Cu2}$ as compared to $P1_{Cu}$, ¹⁴N Davies ENDOR spectra were recorded for the two samples at 15 K. Figure S10 shows a comparison of the obtained ENDOR spectra recorded at Q-band frequencies for two different magnetic field positions, corresponding to the *xy* and *z* orientations of the electronic **g**-tensor. The ENDOR spectra for $P1_{Cu}$ and corresponding simulations to determine the hyperfine coupling parameters have been discussed before [2]. Since no major differences in the hyperfine coupling constants are observed between $P1_{Cu}$ and $P2_{Cu2}$, it seems safe to assume in all simulations that the hyperfine coupling constants stay the same between $P1_{Cu}$ and $P2_{Cu2}$.

^{*}It has been shown that the situation is different in cyclic porphyrin oligomers, where the bent geometry favors orbital overlap (J), especially in sufficiently rigid structures [1].



Figure S9: Comparison of the continuous wave EPR spectra of $P1_{Cu}$, $P2_{Cu2}$, and $P3_{Cu2}$ recorded at X-band in frozen toluene- d_8 at 100 K.

The nitrogen hyperfine coupling constants in the copper porphyrin monomer are of the order of 50 MHz. If the exchange coupling in the dimer was significantly larger than the hyperfine couplings, one should theoretically expect the hyperfine couplings to be halved in the dimer since, due to the coupling between the two spin centers, the spin density should be evenly spread over both units. The fact that the hyperfine couplings remain unchanged despite the presence of J with a magnitude greater than 50 MHz might be explained by the large copper hyperfine coupling $A_{||}$ of the order of 600 MHz present in these systems.



Figure S10: Comparison of the ¹⁴N Davies ENDOR spectra of **P1**_{Cu} and **P2**_{Cu2} recorded at Q-band at magnetic field positions corresponding to the *xy* (*left*) or *z* (*right*) orientation of the electronic **g**-tensor.

3 Details of the Spinach Simulations

The following strategies, implemented in Spinach [3], were employed in order to make the time domain simulation of the dimer spectrum manageable:

- System level state space restriction [4]. Correlations between an electron located on one of the porphyrin units and the nuclei located on the other porphyrin unit were dropped from the basis set. Nuclei located on different porphyrin units were also assumed to stay uncorrelated. This reduces the Liouville space dimension from 688747536 to 3359216 since the biggest order of spin correlation that must be included under these assumptions is seven. The validity of this assumption may be demonstrated by partitioning the system trajectory into contributions from different levels of spin coherence and correlation [5]. Even in P1_{Cu}, several coherence orders may in practice be ignored. In P2_{Cu2}, the population of the seven-spin correlation subspace stays below 5% of the total at all times and it may reasonably be expected that higher levels of spin correlation can be ignored altogether, along with multiple coherence orders that stay unpopulated to very high accuracy (Figure S11).
- 2. Full symmetry factorization [6]. The copper hyperfine coupling constants in this system are very large and anisotropic, but the ¹⁴N hyperfine coupling tensors can be assumed to be approximately isotropic as confirmed by the fit of the cw EPR spectrum of $P1_{Cu}$. Constraining them to be isotropic produces a very reasonable fit. For the purposes of the simulation this signifies that two groups of nuclei have S_4 permutation symmetry each and the full symmetry group of the system is $S_4 \times S_4$. Spinach auto-generates character tables for product groups [3] and a full symmetry factorization is therefore possible over 576 elements and 25 irreducible representations. Because only the fully symmetric irreducible representation is required for Liouville space simulations [6], the state space dimension is reduced further from 3359216 to 253424.
- 3. Trajectory level state space restriction [7]. Because the initial condition in our time-domain simulation is very sparse (L
 + state on the electrons), and there are multiple hidden conservation laws in high-field EPR Hamiltonians of symmetric systems with multiple isotropic couplings [6], trajectory level basis pruning algorithms in Spinach [6, 7] were able to reduce the state space dimension further: the zero track elimination module [7] reports that the actual trajectory is confined to a 1916-dimensional sub-space of the 253424-dimensional space produced at the previous stage. Matrix-matrix and matrix-vector operations involving arrays of dimension 1916 are realistic, but rather slow.
- 4. Sparse GPU processing. A workstation with two *Tesla K40c* coprocessor cards was used for the simulations. Spinach supports sparse CUDA exponentiation, which in this case results in an about ten-fold acceleration relative to a 32-core CPU simulation. This brings the simulation time for a single spin system orientation down to several seconds.

With all of these measures in place, a simulation involving a 10-point conformational grid (spanning a quadrant of the full circle) and an 800-point spherical averaging grid (a two-angle REPUL-



Figure S11: State space population analysis for the powder averaged spin system trajectories following an ideal 90° pulse on the electrons. Individual curves correspond to the 2-norm of the projection of the density matrix into the subspaces with specific spin coherence or correlation orders. *Top left*: P1_{Cu}, populations of the seven possible orders of spin correlation. *Top right*: P1_{Cu}, populations of the major coherence orders present. *Bottom left*: P2_{Cu2}, populations of the major coherence orders present. P2_{Cu2}, populations of the major coherence orders present.

SION set [8] spanning an octant of the full sphere) takes a few hours on a 32-core workstation with 256 GB of memory and two *Tesla K40c* coprocessor cards.

4 Complementary Simulation Data

Dipolar convolution was used in the main part of the manuscript do demonstrate that the spectral broadening observed for $P2_{Cu2}$, as compared to the reference spectrum of $P1_{Cu}$, cannot be accounted for if only dipolar broadening (*D*) is considered. The result shows that exchange coupling is substantial and that its effect needs to be considered in the simulations to satisfactorily describe the shape of the EPR spectrum of $P2_{Cu2}$.

Additional simulations using *Spinach* were carried out to support these conclusions. In Figure S12 (*left*) the simulated spectra for $P1_{Cu}$, $P2_{Cu2}$ including only the effect of D and $P2_{Cu2}$ including the influence of both D and J (parameters as indicated in the main text) are compared. The comparison shows that the lack of hyperfine structure observed experimentally in the cw EPR spectrum of $P2_{Cu2}$ can only be explained if the effect of a significant exchange coupling is included in the simulations.

Figure S12 (*right*) shows a comparison of the *Spinach* simulations carried out for different values of *J*. The spectra shown in the figure have been simulated with parameters of (i) $C_1 = C_2 = 0$, (ii) $C_1 = 15$ MHz, $C_2 = 25$ MHz, (iii) $C_1 = 30$ MHz, $C_2 = 50$ MHz, with reference to equation (1) in the main text, and the experimental spectrum is shown in the background in light gray. The fit corresponding to the doubled *J*-coupling parameters with respect to those indicated in the main text – parameter set (iii) – clearly cannot satisfactorily reproduce the relative peak heights as well as the field position of the intensity maximum providing a good estimate for an upper limit on *J*.



Figure S12: Comparison of the spectra simulated using *Spinach* for $P1_{Cu}$, $P2_{Cu2}$ including only the effect of D and $P2_{Cu2}$ including the influence of both D and J (*left*) and $P2_{Cu2}$ using different *J*-values, as indicated (*right*). The experimental data is shown in the background in light gray.

5 DFT Calculations

5.1 Hyperfine coupling

DFT calculations of the hyperfine coupling constants of $P1_{Cu}$ and $P2_{Cu2}$ were performed in ORCA (Version 3.0) [9]. The aryl side groups were replaced by phenyl groups and the end groups by a proton to simplify the calculations. The TPSSh exchange correlation functional was used in combination with the def2-TZVP basis set on H, C, and N and the CP(PPP) basis set on Cu. The RI approximation was employed using the def2-TZVP/J auxiliary basis set. Effects of spin-orbit coupling were accounted for by the one-centre approximation of the mean field approach, SOMF(1X). Fermi contact, dipolar and orbital contributions were summed up in the specified **A**-tensors. In the dimer, the hyperfine couplings were calculated for the triplet spin state and the results were multiplied by two to obtain the indicated values.

The calculated hyperfine coupling constants amount to:

 $\textbf{P1}_{\textbf{Cu}}: \ \textbf{A}_{\textbf{Cu}} = [-15 \ -602]; \ \textbf{A}_{\textbf{N}} = [41 \ 43 \ 55]$

P2_{Cu2}: $A_{Cu} = [-10 - 604]$; $A_N = [44 \ 44 \ 56]$

and indicate that the hyperfine coupling constants are not expected to change significantly between monomer and dimer, in agreement with the ENDOR results (cf. **Figure S10**).



Figure S13: Visualization of the calculated spin density for $P1_{Cu}$.

5.2 Exchange coupling

Several DFT functionals have been tested to explore the variation in exchange coupling calculated for the planar and perpendicular conformations of $P2_{Cu2}$. A reduced model was used, where the aryl side groups and end groups were replaced by hydrogen atoms. In all cases, the atoms within a porphyrin macrocycle were found to be (approximately) co-planar and the dimer exhibited either an approximate D_{2h} (planar) or D_{2d} (perpendicular) symmetry, although the geometry optimizations were conducted without symmetry. The calculations were done using Gaussian09/D.01. The SCF convergence criteria were set to 10^{-8} (default) and 10^{-12} for geometry optimizations and single-point calculations, respectively.

The exchange coupling Hamiltonian in the form of Equation (S1) has been used in all calculations.

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 \tag{S1}$$

The exchange coupling parameter J was computed using the broken-symmetry approach and the Yamaguchi formalism

$$J = \frac{E_{BS} - E_T}{\langle S_T^2 \rangle - \langle S_{BS}^2 \rangle}$$
(S2)

where E_{BS} is the energy of the broken symmetry (singlet) state, E_T is the energy of the triplet state, and $\langle S_{BS}^2 \rangle$ and $\langle S_T^2 \rangle$ are expectation values of S^2 for the broken symmetry and triplet states.

Reviews and benchmarks have shown that pure GGA functionals (like BP86 or BLYP) overestimate the antiferromagnetic coupling in exchange coupled dimers, which is also observed in our case (**Table S1**).[10, 11] Introduction of Hartree-Fock (HF) exchange in hybrid functionals reduces the antiferromagnetic coupling and increases ferromagnetism. This trend is also observed for the hybrid functional we have tested (B3LYP [12] has 20% HF exchange, while M06-2X [13] has 54% HF exchange). Recently, range-separated (aka long-range corrected) functionals have been developed, including CAM-B3LYP [14] and ω B97X-D [15]. In these functionals, the non-Coulomb exchange varies as a function of distance. Such functionals have improved the description of charge delocalization, minimizing the self-interaction error. All range separated functionals and M06-2X predict ferromagnetic coupling in the range of 10–100 MHz for the planar structure, whereas *J* for the perpendicular structure is very close to zero (on the level of the numerical accuracy). From the spin density distribution of the broken-symmetry solution **Figure S14** one can see that the spin density on the butadiyne linker is localized on the p_z orbitals, where *z* is perpendicular to the corresponding porphyrin plane. These orbitals become orthogonal for the twisted structure, which explains the much reduced exchange coupling.

Figure S14: Spin density distribution of the broken-symmetry solution (contour value 10⁻⁶) shown for the planar (*left*) and perpendicular (*right*) structures of **P2_{Cu2}** computed at the CAM-B3LYP/6-31G(d) level.

Based on the results presented in **Table S1**, the analysis of the exchange coupling modulation due to low energy vibrational modes has been performed using the range-separated CAM-B3LYP functional on a $P2_{Cu2}$ structure with phenyl side groups. Note that introduction of the phenyl side groups causes a small distortion of the porphyrin structure from planarity. The maximum variation

Table S1: Exchange coupling constants (MHz) computed using various DFT functionals (6-31G(d) basis
set) for the two optimized conformations of $P2_{Cu2}$ using the reduced model (i.e., no phenyl side
groups).

	BP86	B3LYP	M06-2X	ω B97XD	CAM-B3LYP
Planar	-530	-1	11	55	88
Perpendicular	-72	-14	-1	-6	5

Table S2: Variation of the exchange coupling ΔJ (MHz) due to vibrational modes evaluated at DDNC=4, computed using CAM-B3LYP/6-31G* for eight low-lying vibrations of the structure with phenyl side groups. The harmonic frequencies $\hbar\omega$ (cm⁻¹) have been corrected using the computed energies at DDNC=4, marked as $\hbar\omega'$ (cm⁻¹).

Mode	$\hbar\omega(cm^{-1})$	$\hbar\omega'(cm^{-1})$	$\Delta J(MHz)$
1	1.5	17	-38
2	5.5	46	12
3	5.9	52	5
4	6.3	83	16
5	12.7	71	7
6	24.4	206	-28
7	24.6	221	7
8	25.0	135	-24

in J upon distortion of the minimum structure along certain of its energetically low-lying normal modes is presented in **Table S2**. The animations of the vibrations are attached as separate files. In order to quantify the displacements along the normal modes, we express the harmonic potential U in terms of the dimensionless displacement of nuclear coordinates (DDNC) q.

$$U = \frac{1}{2}m\omega^2 x^2 = \frac{\hbar\omega}{2}q^2 \tag{S3}$$

The effects of the distortion along the normal modes have been evaluated at DDNC=4 (limiting step in the animations). The vibrational frequencies have been corrected using the energy at the DDNC=4 displacement (Table S2).

The largest variation in exchange coupling is caused by the energetically lowest vibrational mode that corresponds to the rotation about the butadiyne linker. The relaxed surface scan shows that this vibration is anharmonic (or rather sinusoidal) with a very low energy barrier below 100 cm^{-1} . Another low-lying vibration that modulates J significantly is mode #6, corresponding to the distortion of both porphyrin macrocycles out of their planar structure in an antisymmetric manner (see animations attached). The symmetric partner of this vibration (mode #7) does not cause a significant change in J. The symmetric in-plane rotation of the porphyrin macrocycles (mode #8) distorting the linker also causes significant modulation of J. The amplitudes of these vibrations are small compared to the almost free rotation of the porphyrin planes about the butadiyne linker, which is assumed to be the dominant source of the distribution in J values observed by EPR.

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