Light-controlled switching of the spin state of iron(III)

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Controlled switching of the spin state of transition metal ions, particularly of FeII and FeIII, is a prerequisite to achieve selectivity, efficiency, and catalysis in a number of metalloenzymes. Here we report on an iron(III) porphyrin with a photochromic axial ligand which, upon irradiation with two different wavelengths reversibly switches its spin state between low-spin (S = 1/2) and high-spin (S = 5/2) in solution (DMSO-acetone, 2:598). The switching efficiency is 76% at room temperature. The system is neither oxygen nor water sensitive, and no fatigue was observed after more than 1000 switching cycles. Concomitant with the spin-flip is a change in redox potential by ~60 mV. Besides serving as a simple model for the first step of the cytochrome P450 catalytic cycle, the spin switch can be used to switch the spin-lattice relaxation time $T_1$ of the water protons by a factor of 15.
Spin-state switching is the key step in a number of enzymatic reactions, particularly in C-H activation processes. Controlled spin flips guide reactants and intermediates into reaction pathways with low barriers, and induce catalytic cycles leading to products that otherwise would be formed only under drastic reaction conditions. Cytochrome P450 is a particularly well-investigated example.1,2 Substrate binding to cytochrome P450 triggers a change in the spin state of the heme-bound Fe(III) from the resting state, low spin (S = 5/2), to high spin (S = 3/2). Concomitantly, the reduction potential changes, and a cascade of reactions follows, leading to the selective oxidation of alkyl and aromatic C-H bonds. Methane monooxygenases (MMOs) even catalyse oxygen insertion into saturated hydrocarbons, leading to the selective oxidation of alkyl and aromatic C-H bonds. Methane monooxygenases (MMOs) even catalyse oxygen insertion into saturated hydrocarbons.

Whereas spin-state switching in the solid state (spin-crossover mainly in Fe(II) complexes) is a well-investigated phenomenon, the first magnetically bistable compound in solution was published only recently (2011)9. Since then, research in the field considerably gained momentum7–10. The original molecular spin switches were based on Ni(II) porphyrins11–13. The square planar complexes are diamagnetic (S = 0), but turn paramagnetic (S = 1) upon coordination of axial ligands. Coordination/decoordination from the Ni ion was achieved by the use of photoswitchable axial ligands that were either covalently bound to the porphyrin or substituted in such a way that the cis configuration would not bind because of steric hindrance. A number of further transition metal ions change their spin state upon changing their coordination number, such as Fe2+11, Fe3+12, Co2+, Mn2+, and Mn3+, providing larger variations (Δμ) in their magnetic moments than Ni2+. Herein, we report the first photoswitchable, magnetically bistable Fe(III) porphyrin in solution that is stable at ambient conditions in solution, including moisture and air. Upon irradiation with light of 365 and 435 nm, the spin-state switches reversibly between low spin (S = 1/2) and high spin (S = 3/2), accompanied by a change in redox potential. The species involved and their spin states are characterized using several independent methods, and the mechanism is elucidated in detail.

**Results**

**Spectroscopic investigations.** In terms of redox behavior and spin states, iron is probably the most complicated and adaptable element in the periodic table. A number of different spin states are possible in every oxidation state, many of which are close in energy. More than 3000 papers have been published solely on iron porphyrins, particularly in view of their biological relevance. Several reviews summarize the field14,15. Iron(III) porphyrins exhibit four different spin states: low spin, S = 1/2, (dxy, dz2, dxz, dyz)1(δxy), low spin, S = 1/2, (dxy, dxz, dyz)1(δxy), intermediate spin, S = 3/2, (dxy, dxz, dyz)3(δxy), and high spin, S = 3/2, (dxy, dxz, dyz)3(δxy, dxz, dyz). Moreover, if the energy difference of intermediate spin (S = 3/2) and high spin (S = 3/2) is close to the spin-orbit coupling constant (which is mostly the case), linear combinations of high-spin and intermediate-spin states are formed, which have been coined admixed-spin states, S = a 3/2 + (1 − a) 3/2 (a = 0–1)16. The axial ligands and the nature of the porphyrin are the primary determinants of the spin state. Pure 4-coordinate Fe(III) porphyrins without axial coordination are intermediate spin (S = 3/2)17. Axial coordination of two oxygen ligands gives rise to an admixed-spin state (S = 3/2, 5/2) if they are weak, or a high-spin species (S = 5/2) if they are strong. Fe(III) porphyrins with two strong nitrogen ligands are low spin (S = 1/2). Besides their electronic properties, the steric bulk of axial ligands is decisive in controlling the spin state. Bulky substituents neighboring the coordinating nitrogen atom not only reduce the binding constant, but also favor the high-spin state18. If the counter-ion is weakly binding (e.g., ClO4−) and the axial ligands are weak, more basic porphyrins (i.e., electron-donating substituents) favor admixed-spin states, and less basic porphyrins (electron-withdrawing substituents) favor low-spin states. Strongly binding anions, such as chloride in the absence of axial ligands, favor the formation of high-spin complexes. Hydrogen bonding to the chloride weakens coordination and the spin-state changes to intermediate spin19. Upon judicious choice of the electronic and steric properties of the porphyrin and axial ligands, the complexes can be tuned in such a way that they are close to the S = 1/2 = S = 3/2 spin-crossover point20,21. In this region, small changes in ligand field strength or steric hindrance would switch the spin state of Fe(III). Since spin-state chemistry and axial ligand exchange processes of Fe(III) porphyrin complexes are very intricate, we used several independent methods to characterize our compounds in solution: (a) proton nuclear magnetic resonance (1H NMR) pyrrole shift and phenyl shifts, (b) ultraviolet–visible (UV–vis) absorption, (c) magnetic moments, and (d) electron paramagnetic resonance (EPR) spectroscopy. The largest change in spin state (ΔS = 2) in Fe(III) porphyrins is achieved upon switching between high spin (S = 5/2) and low spin (S = 1/2). In designing our molecular spin switch, we avoided admixed-spin (S = 3/2, 5/2) and intermediate-spin states (S = 3/2), not only because they reduce the change in magnetic moment (Δμ) but also because these species are sensitive to water and oxygen, and they are difficult to characterize (e.g., the 1H NMR pyrrole shift varies between +80 and −63 ppm)14. To achieve a reliable, robust, and large spin switch, we designed a system which would change the axial coordination between two strong oxygen ligands (high spin, S = 5/2) and two strong nitrogen ligands (low spin, S = 1/2) upon irradiation with two different wavelengths.

For our experiments, we chose the readily available Fe(III) tetraphenylporphyrin perchlorate (FeTPP(ClO4)) as the base porphyrin, and photoswitchable azopyridines as axial ligands (photodissociable ligands, PDLs). FeTPP(ClO4) is admixed-spin (S = 3/2, 5/2) in non-coordinating and weakly coordinating solvents11,22–24, and very sensitive towards water and oxygen25. In acetonitrile, a 6-coordinate complex (Fig. 1) is formed with two weakly binding acetonitrile molecules as axial ligands. The formation constants K′′ = 0.82 and K′′ = 1.08 L mol−1 have been determined by following the 1H NMR shifts of the phenyl protons upon titration of a solution of FeTPP(ClO4) in CD3CN with acetonitrile. (See Supplementary Figures 21, 24, 25, Supplementary Table 4, and Methods, Calculation of apparent equilibrium constants). Pyrrole shift (40.2 ppm), magnetic moment (4.5 B.M., see Methods, Magnetic susceptibility—Evans measurements) and EPR signals (medium-intensity, high-spin signals at g = 5.94 and 2.0, and a very small signal at g = 4.7–4.816 (see Supplementary Figures 36–37 and Methods, EPR spectroscopy) are indicative that the species is admixed spin with a substantial contribution of high spin. To generate a pure high-spin (S = 5/2) complex, and to increase ΔS upon switching, we added dimethyl sulfoxide (DMSO)–d6 to the solution which is known to form a 2:1 high-spin (S = 5/2) complex with FeTPP(ClO4) (Fig. 1 and Supplementary Figure 1)26. High-spin iron(III) porphyrins exhibit a typical Q band at ~690 nm (Supplementary Figure 19a). Upon titration with DMSO and monitoring the increase of the absorption at 686 nm, we...
Fig. 1 Determination of formation constants. Formation constants of high-spin FeTPP(DMSO)$_2$ClO$_4$ determined by following the absorption at 686 nm upon titration of the FeTPP(acetone)$_2$ClO$_4$ complex in acetone with DMSO. These values were confirmed by NMR titration.

Fig. 2 Design of the photodissociable ligand (PDL) based on photoswitchable phenyl azopyridine. Irradiation with UV light (365 nm) switches the trans isomer to the cis form. Visible light triggers reisomerization back to the trans form. The photostationary states (PSS) of the two processes are $trans/cis$ 75:25 (365 nm), and 6:94 (365 nm). The methoxy group in 4-position of the pyridine was introduced to increase the coordination strength, and to prevent the formation of the $\beta$ conformation of the cis isomer. The two t-Bu groups at the phenyl ring increase steric repulsion with the porphyrin in the cis form, however, have no effect on the coordination of the trans configuration.

determined the complex formation constants $K_1 = 5862 \text{ L mol}^{-1}$ and $K'_1 = 596 \text{ L mol}^{-1}$ (see Supplementary Figures 19b, 26-28). These formation constants were confirmed by NMR titration ($K_1 = 5372 \text{ L mol}^{-1}$ and $K'_1 = 580 \text{ L mol}^{-1}$) following the phenyl and pyrrole shifts (see Supplementary Figures 22, 29, 30, Supplementary Table 7, and Methods, Calculation of Apparent equilibrium constants)\textsuperscript{27,28}.

The magnetic moment of 5.8 B.M. (Evans, see Methods, Magnetic susceptibility—Evans measurements) and the EPR data (large-intensity, high-spin signals at $g = 5.92$ and 2.0, see Supplementary Figure 36 and Methods, Electron paramagnetic resonance (EPR) spectroscopy) confirm a high-spin $S = 5/2$ state for a solution of 0.2 mM FeTPP$^+$ and 47.12 mM DMSO-d$_6$ in acetone-d$_6$. The precise composition of the solution derived from $K_1$ and $K'_1$ is 0.01% FeTPP(acetone)$_2^+$, 3.5% FeTPP(acetone) (DMSO)$_2^+$, and 96.5% FeTPP(DMSO)$_2^+$. This stable solution, mainly consisting of high-spin FeTPP(DMSO)$_2$ClO$_4$, was used for further switching experiments with PDLs based on azopyridine.

Azopyridine-based PDL. The azopyridine was designed in such a way that it strongly coordinates to Fe(III) in its $trans$ configuration (Fig. 2), forming a low-spin $S = 1/2$ complex. However, upon switching to the $cis$ isomer under UV light, steric hindrance between the t-Bu groups and the porphyrin ring prevents binding (for the synthesis of the azopyridine see Supplementary Figure 41 and Methods, Synthesis)\textsuperscript{29,30}.

Irradiation with visible light (435 nm) regenerates the $trans$ isomer which returns to the coordination site. Conversion of the thermodynamically more stable $trans$ to the metastable $cis$ isomer with UV light is very efficient. The photostationary state (PSS) at 365 nm is 94% $cis$, and 6% $trans$, and the PSS of the back-reaction at 435 nm is 75% $trans$, and 25% $cis$ (see Supplementary Figure 5, Supplementary Table 1, and Methods, PSS of the phenyl azopyridine 2 and PSS of azopyridine). This incomplete conversion to the binding $trans$ isomer does not compromise the overall switching efficiency, because an excess of the ligand is used\textsuperscript{21}. Hence, the azopyridine is ideally suited as a PDL. The PSS are virtually the same in the presence of the porphyrin (Supplementary Figure 6, Supplementary Tables 1, 11, 12). Obviously, no quenching of the excited state of the azopyridine by the porphyrin occurs. Substitution of the pyridine ring in 4-position with a methoxy group was necessary to increase the binding constant, and to prevent the formation of the $\beta$ conformation of the $cis$ isomer (see Fig. 2 and Supplementary Figure 4). Thermal half-life of the metastable $cis$ isomer with 164 days at 27°C is very long (Supplementary Figure 7). In the presence of the Fe(III) porphyrin the half-life is reduced to 18 days which is still more than sufficient to serve as a...
photochemical switch (see Supplementary Figure 8 and Methods, Half-life ($t_{1/2}$) of cis azopyridine (cis-2)). With a strong Soret band of the Fe(III) porphyrin around 400 nm (Supplementary Figure 17), the photoexcitation may not be restricted to the PDL; the event of the Fe(III) porphyrin getting excited, at least partially, cannot be rigorously excluded while irradiating at 365 or 435 nm. The porphyrin in its excited state does not seem to have a noticeable impact on the photoisomerization mechanism of the PDL, since the PSS of the ligand remains largely unaffected by the presence or absence of the porphyrin. However, a slightly longer irradiation time is required for the PDL to arrive at its PSS in the presence of the strongly absorbing porphyrin.

Discussion

The light-driven spin-state switching experiments with our electronically fine-tuned Fe(III) porphyrin system and the sterically and electronically designed axial ligand were monitored by several methods: NMR, UV–vis, EPR, Evans, and potentiometry, to unanimously determine the structure and magnetic properties of the species involved in the spin-state switching process.

In contrast to acetone/DMSO, axial ligand exchange of DMSO/azopyridine is slow on the NMR time scale. Upon titration of the high-spin acetone/DMSO solution of FeTPPClO$_4$ (0.2 mM FeTPP$^+$, 47.12 mM DMSO-$d_6$ in acetone-$d_6$) with the PDL, the signal of the pyrrole protons at 68.6 ppm decreases and a new signal at −14.7 ppm appears (Supplementary Figure 2). Unfortunately, the high-spin signal at 68.6 ppm is very broad, and integration of the NMR signals is not sufficiently accurate to derive a binding model, and to accurately determine coordination constants. We therefore monitored the titration by UV–vis spectroscopy (Supplementary Figure 20). High-spin ($S = 5/2$) FeTPP$^+$ complexes exhibit characteristic bands (Q bands) at 690 nm (Supplementary Figure 19a) and low-spin ($S = 1/2$) FeTPP$^+$ does not absorb above 650 nm (Supplementary Figure 20a). The decreasing absorption at 686 nm as a function of added azopyridine yields a binding isotherm (Supplementary Figure 20b), which was analyzed by non-linear optimization (see Methods, Calculation of apparent equilibrium constants). A binding model that includes all conceivable species should consider the starting complex FeTPP(DMSO)$_2$$^+$, the mixed complex FeTPP(DMSO)(azopy)$^+$, and the 1:2 complex FeTPP(azopy)$_2$$^+$. The solution of the initial DMSO complex FeTPP(DMSO)$_2$$^+$ has been thoroughly characterized (see above), the properties of the pure low-spin 1:2 complex FeTPP(azopy)$_2$$^+$ can be determined by dissolving FeTPPClO$_4$ in pure 4-methoxyazopyridine. However, the properties of the mixed complex cannot be directly determined, since it is not a stable species. It is not known whether coordination of a single strong nitrogen ligand to FeTPP$^+$ is sufficient to induce a spin switch to the low-spin state. We therefore synthesized a strapped porphyrin, in which one of the two axial binding sites is sterically shielded (Fig. 3, see Methods, Syntheses). The chloride complex (similar to FeTPPCl) is high spin as indicated by the pyrrole proton shifts (81.6, 78.0 ppm), and by the magnetic moment (5.87 B.M., see Methods, Magnetic susceptibility—Evans measurements). Note that in contrast to FeTPP$^+$, the structure of the strapped porphyrin does not exhibit a fourfold symmetry axis and the eight pyrrole protons are not symmetry equivalent. Upon addition of $N$-methyl-imidazole, the chloride is replaced by the strong nitrogen ligand. The coordination of a second ligand is prevented by the bridge. Magnetic moment (2.49 B.M.) and the pyrrole proton shifts (−7.92, −10.05, −22.15, and −23.28 ppm) clearly indicate that the complex is low spin ($S = 1/2$) with a slow exchange of the ligand on the NMR time scale (see Supplementary Figures 42–43 and Methods, Synthesis). Hence, coordination of one nitrogen ligand is sufficient to induce the spin switch.

Based on the properties of the strapped porphyrin, we assume that the mixed complex FeTPP(DMSO)(azopy)$^+$ is low spin as well. Further evidence for the low-spin state of the mixed complex is provided by the fact that the fitting of the binding isotherm is considerably superior with the assumption that the spin change is induced by the coordination of the first azopyridine ligand (see Supplementary Figures 31–33 and Methods, Calculation of apparent equilibrium constants). Based on this model, both binding constants $K_1$ and $K_2$ can be accurately determined by UV–vis titration of the DMSO complex with the azopyridine (see above). According to the analysis of the binding isotherm, the first DMSO ligand is replaced by azopyridine with $K_1 = 314 \text{ L mol}^{-1}$ and the second with $K_2 = 868 \text{ L mol}^{-1}$ (Fig. 4 and Supplementary Table 10). Thus, azopyridine is a much stronger ligand than DMSO and displacement of the second DMSO is much more favorable than expulsion of the first DMSO ligand. Therefore, the concentration of the mixed (DMSO/azopyridine) complex is always small. This is favorable for our spin switching efficiency, because the isomerization of one azopyridine ligand should facilitate the replacement of the second by DMSO leading to an efficient conversion to the high-spin FeTPP(DMSO)$_2$$^+$ complex.

Spectroscopic parameters as well as magnetic properties consistently prove that the addition of azopyridine converts the high-spin ($S = 5/2$) FeTPP(DMSO)$_2$$^+$ to a low-spin ($S = 1/2$) complex. Upon addition of 75 equivalents of trans azopyridine to a solution of 0.1 mM FeTPP$^+$, and 25.87 mM DMSO-$d_6$ in acetone$-d_6$, the EPR high-spin signals at $g = 5.92$ and 2.0 are reduced to approximately 3% of their initial intensity (see Supplementary
The situation is rather complicated since both azopyridine ligands rebind to the axial coordination sites replacing the azopyridine. In NMR, (see Methods, Calculation of apparent equilibrium constants). Upon irradiation with light of 435 nm, the cis azopyridine returns to its strongly binding trans configuration (24.5% cis, 75.5% trans), and replaces the DMSO ligands. At the PSS (365 nm) the solution contains 81.4% high-spin FeTPP(DMSO)2\(^{+}\), 11.3% low-spin FeTPP(azopy)(DMSO)\(^{+}\), and 4.3% low-spin FeTPP(azopy)\(^{2-}\) and (very small amounts of the acetonitrile complexes, for a detailed list see Table 1). Upon irradiation with light of 435 nm, the cis azopyridine to FeTPP(DMSO)\(^{+}\) is low spin.

Figure 36 and Methods, EPR spectroscopy), and the UV–vis absorption at 686 nm almost completely vanished (Supplementary Figure 20a). According to Evans measurements (see Methods, Magnetic susceptibility—Evans measurements), the effective magnetic moment of the solution is 2.1 B.M. The high-spin pyrrole proton signal at 68.8 ppm disappeared, and a new signal at −14.7 ppm (typical for low-spin FeTPP\(^{+}\) complexes) appeared (Supplementary Figure 2). Unfortunately, only a very low intensity large \(g_{\text{max}}\) signal for the low-spin complex at \(g = 3.4\) was visible in the EPR spectrum in frozen acetone (Supplementary Figure 36), most probably because of solubility problems, and aggregation. In frozen CH\(_3\)Cl\(_2\) however, the low-spin signal is visible more clearly (Supplementary Figures 37–38). More detailed information about the exact composition of the solution can be derived from the binding constants: \(K_1\), \(K_2\), and \(K_3\). In a solution of 0.2 mM FeTPP\(^{+}\), 47.12 mM DMSO–\(d_6\), and 15 mM trans azopyridine in acetone–\(d_6\), the following species are in equilibrium: 0.00066% FeTPP(acetone)\(_2\)\(^{+}\), 0.17% FeTPP(acetone)(DMSO)\(^{+}\), 4.7% FeTPP(DMSO)\(_2\)\(^{+}\), 11.9% FeTPP(DMSO)(azopy)\(^{+}\), and 83.2% FeTPP(azopy)\(^{2-}\). The species with at least one strong nitrogen ligand (azopyridine), and that with two strong oxygen ligands (DMSO), add up to 95.1% low-spin and 4.7% high-spin porphyrin, respectively, which is consistent with the EPR observations.

This solution that is predominantly low spin was subjected to irradiation with light of 365 nm. The trans azopyridine isomerizes to the cis configuration with a conversion rate of 94.4% cis (determined by \(^1\)H NMR, Supplementary Figure 5) in the PSS. Isomerization, in turn, leads to increasing steric demand, and dissociation of the cis azopyridine ligand. The binding constant of cis azopyridine to FeTPP\(^{+}\) was too low to be determined. Addition of a solution of 94% cis and 6% trans azopyridine to an acetonitrile–\(d_6\) or acetone–\(d_6\)/DMSO–\(d_6\) solution of FeTPP\(^{+}\) does not change the \(^1\)H NMR spectrum beyond what would be expected from the coordination of the residual trans isomer (6%) (see Supplementary Figure 3b and Methods, Switching experiments in NMR.). Hence, cis azopyridine is a much weaker ligand than DMSO (in contrast to the trans isomer); therefore, DMSO rebinds to the axial coordination sites replacing the azopyridine. The situation is rather complicated since both azopyridine ligands must be replaced by DMSO to switch the spin state. Mixed complexes, such as FeTPP(DMSO)(azopyridine)\(^{+}\) in the equilibrium, have to be considered as well. The exact composition of the solution in the PSS can be calculated from the binding constants of DMSO (\(K_4\), \(K_5\)), and trans azopyridine (\(K_6\), \(K_7\)) to FeTPP\(^{+}\) determined by NMR and UV–vis titration (see above), and the cis/trans ratio of azopyridine at the PSS, determined by \(^1\)H NMR (Supplementary Figure 6). At the PSS (365 nm) the solution contains 81.4% high-spin FeTPP(DMSO)\(_2\)\(^{+}\), 11.3% low-spin FeTPP(azopy)(DMSO)\(^{+}\), and 4.3% low-spin FeTPP(azopy)\(^{2-}\) and (very small amounts of the acetonitrile complexes, for a detailed list see Table 1).

To investigate the fatigue resistance of the spin switch, we irradiated the above solution with 365 and 435 nm in an alternating sequence and monitored the \(^1\)H NMR spectrum as a function of the number of switching cycles (Fig. 6a and Supplementary Figure 35b). After 5 min irradiation of the NMR tube with 365 nm (light-emitting diode (LED), 12 × 400 mW), the low-spin signal at −14.7 ppm disappeared, and the broad high-spin signal at 66.8 ppm appeared. Upon irradiation of the NMR tube with 435 nm (LED, 12 × 380 mW), the high-spin signal disappeared and the low-spin signal reappeared. There was no observable change in the \(^1\)H NMR spectrum after 1000 switching cycles under ambient conditions (air, moisture, 300 K, Supplementary Figure 3a).
where \( \Delta T_1 \) is the difference of \( T_1 \) with and without relaxation agent and \( c \) the concentration of the relaxation agent. High-spin FeTPP\(^+\) has a larger magnetic moment than low-spin FeTPP\(^+\) and therefore exhibits a larger relaxivity. Low-spin FeTPP\(^+\) (\( S = 1/2 \)) is not completely diamagnetic; however, both axial coordination sites are occupied by strong nitrogen ligands which prevent a fast exchange with the solvent on the NMR time scale (inner sphere relaxation). The low magnetic moment as well as the blockage of axial coordination sites lead to a considerably smaller relaxivity \( R_1 \) of the low-spin complex. The relaxivity values \( R_1 \) and relaxation times \( T_1 \) of a 2.0 mM solution of the high-spin FeTPP\(^+\) complex in an acetone-\( d_6 \)/DMSO-\( d_6 \) solution containing 1% acetone and 1% water are given in Table 2. The relaxivity \( R_1 \) of acetone, and water with FeTPP\(^+\) in the high-spin state is 12.9, and 17.7 times higher than in the low-spin state. The relaxation time \( T_1 \) changes from 5.05 to 1.68 s (acetone), and from 0.56 to 0.04 s (water) upon low-spin to high-spin conversion (Table 2). Thus, the efficiency in relaxivity switching is considerably higher than in a previous Ni\(^2+\) porphyrin-based system\(^5\).

In nature, upon binding of a substrate to cytochrome P450 in its low-spin, 6-coordinate resting state, the axial water ligand is released and a 5-coordinate high-spin Fe(III) porphyrin is formed\(^2\). Concomitant with the spin flip is a change in redox potential\(^37\). A similar trend has been observed by Walker et al.\(^38\) who investigated a number of iron porphyrins (as models of cytochromes) including FeTPP\(^+\) in N,N-dimethylformamide in the presence and absence of pyridine ligands. Switching of the azopyridine ligand from the \( \text{trans} \) to the \( \text{cis} \) configuration should lead to a shift of the reduction potential. Typical cyclic voltammograms (CVs) obtained for the Fe(III)/Fe(II) redox couple for the low-spin FeTPP\(^+\) complex before and after irradiation at 365 nm for 20 min are shown in Fig. 6b. The low-spin complex was found to exhibit a well-defined \( 1e^- \) oxidation–reduction curve with a half-wave potential of 82±4 mV (vs. standard hydrogen

Table 1 Photostationary states of the PDL and different possible complexes of FeTPP\(^+\)

|                     | PSS 435 nm (%) | PSS 365 nm (%) |
|---------------------|---------------|---------------|
| \( \text{trans azopy} \) | 75.5          | 5.6           |
| \( \text{cis azopy} \)   | 24.5          | 94.4          |
| FeTPP(azopy)\(^+\)(DMSO)\(^-\) | 77.2          | 14.7          |
| FeTPP(azopy)\(^+\)(DMSO)\(^-\) | 4.4           | 11.3          |
| FeTPP(DMSO)\(^-\)\(^+\)  | 7.8           | 81.4          |
| FeTPP(acetone)(DMSO)\(^+\) | 0.3           | 2.9           |
| FeTPP(acetone)\(^+\)\(^-\) | 0.001         | 0.01          |

At the photostationary state generated upon irradiation with light of 435 nm (PSS 435 nm), the combined concentration of low-spin species is 91.9%, and at PSS 365 nm this concentration decreases to 15.7%. Hence, the switching efficiency is 76.2%.

Fig. 5 Light-induced spin switching of iron(III) porphyrin (FeTPP\(^+\)) using azopy as a PDL. The composition of the solution is calculated from the binding constants \( K_1, K_2 \) and \( K_1, K_2 \), and is listed for the photostationary states (PSS) at 435 and 365 nm in Table 1. The calculations are based on the assumption that \( \text{cis} \) azopyridine does not coordinate to FeTPP\(^+\), and that FeTPP(DMSO)(azopy)\(^+\) is a low-spin complex
potential (SHE)). After 30 min under 435 nm illumination, the Fe (III)/Fe(II) reduction potential almost returns to its value before the 365 nm illumination (Fig. 6b). If the electrochemical experiments are performed strictly under nitrogen, the switching is reversible (see Supplementary Figure 39 and Methods, Electrochemical measurements). Under air obviously the reduced Fe(II) species reacts with oxygen and the reaction becomes irreversible. This work presents the first light-controlled molecular spin switch based on Fe(III). Starting complex is the readily accessible, admixed-spin ($S = \frac{3}{2}, \frac{5}{2}$) Fe(III) tetraphenylporphyrin perchlorate. In an acetone/DMSO solution it forms a well-defined high-spin ($S = \frac{5}{2}$) complex with two axial DMSO ligands. The spin switching process is induced by a photoswitchable azopyridine ligand. This ligand is designed in such a way that it coordinates to the iron porphyrin in its trans configuration with a binding constant 180 times stronger than DMSO, forming a low-spin ($S = \frac{1}{2}$) complex with two axial trans azopyridine ligands. Upon irradiation with 365 nm, the trans isomer of the azopyridine ligand photoisomerizes to the cis configuration with a conversion ratio of 94.4%. The cis isomer is sterically hindered and does not bind to the iron porphyrin, and thus is replaced by DMSO, regenerating the high-spin state. This ligand exchange/spin switching process is reversible. Light (435 nm) converts the cis azopyridine back to the trans form, which again replaces the DMSO ligands. No fatigue or side reactions have been observed after more than 1000 switching cycles under air and moisture at room temperature.

Alongside the spin-state flipping, several properties change reversibly. The capability of reducing the NMR proton relaxation time (relaxivity) changes by a factor of more than 10. Properly designed iron(III) porphyrins could therefore be used as functional contrast agents in MRI. Upon switching the spin state from $S = \frac{1}{2}$ to $S = \frac{5}{2}$, the redox potential shifts to more positive values. The active center of cytochrome P450 contains a low spin Fe(III) porphyrin in its resting state. The iron(III) center undergoes a spin flip upon substrate binding, leading to a change in redox potential, which in turn triggers a cascade of reactions.

### Table 2: Relaxivities and relaxation times of the solvent protons

| Relaxity $R_1$ (mM$^{-1}$s$^{-1}$) | Relaxation time $T_1$ (s) |
|-----------------------------------|--------------------------|
|                                   | Acetone | Water | Acetone | Water |
| (i) High spin                     | 0.219   | 10.6  | 1.68    | 0.037  |
| (ii) Low spin                     | 0.017   | 0.6   | 5.05    | 0.564  |

Relaxivities $R_1$ and relaxation times $T_1$ of a solution of 2.0 mM FeTPP$^+$ and 47.12 mM DMSO-d$_6$, (i) without and (ii) with 15 mM trans azopyridine in acetone-d$_6$, containing 1% acetone and 1% water.

**Fig. 6** Switching of the properties of iron porphyrin FeTPP$^+$. 
(a) Long-term stability (1000 switching cycles) of a solution of 0.2 mM FeTPPClO$_4$, 47.12 mM DMSO-d$_6$, and 15 mM azopyridine in acetone-d$_6$ at 300 K upon irradiation with 365 and 435 nm in an alternating sequence (left) sections of $^1$H NMR spectra between 54 and 78 ppm (high-spin region) and (right) between −18 and −3 ppm (low-spin region). 
(b) Light-induced switching of the redox potential of a solution containing 0.2 mM FeTPPClO$_4$, 40 mM tetrabutylammonium perchlorate as the supporting electrolyte and 47.2 mM DMSO in acetone (see Methods, Electrochemical measurements). Blue: cyclic voltammogram before irradiation; red: after irradiating with 365 nm for 20 min; black: after irradiation of the above with 435 nm light for 30 min. The experiment was performed using a platinum disk working electrode, platinum counter electrode, and Ag/AgNO$_3$ 0.01M reference electrode at a scan rate of 50 V/s (see Methods, Electrochemical measurements).
which finally leads to selective C-H oxidation.\textsuperscript{1,2} Spin state switching is also a crucial step in the conversion of methane to methanol by methanotrophic bacteria, using Fe\textsuperscript{3+}-containing enzymes (MMOs).\textsuperscript{39} Nature obviously uses spin flipping to solve difficult catalytic problems that are not susceptible to simple transition state lowering on a given spin-state energy hypersurface.

Control of the spin state might as well be used as a key step in a number of particularly obstinate cases of catalysis in artificial systems, or even industrial processes. We believe that our results could provide a contribution towards this end.

**Methods**

**General experimental procedure.** All reactions were carried out in high air-dried glassware with magnetic stirring under nitrogen atmosphere (when required) using commercially available reagent-grade solvents (dried when necessary, but without purification), and all evaporation were carried out under reduced pressure on Büchi rotary evaporator or Heidolph rotary evaporator below 50 °C, unless otherwise noted. Yields refer to chromatographically and spectroscopically homogeneous materials, unless otherwise stated. Most reagents were purchased from Sigma-Aldrich, ABCR, Alfa Aesar, or Merck and were used as received. Solvents (reagent grade) were purchased from Sigma -Aldrich, ABCR, and Merck. Specific experimental conditions are provided under each section below.

The high-resolution (HR) mass spectra were measured with an APEX 3 FT-ICR with a 7.05 T magnet by co. Bruker Daltonics, Electron impact and matrix-assisted laser desorption/ionization (MALDI) mass spectra were measured with a Bi 4700 FT-ICR mass spectrometer with an A531-G Golden-Gate-Diamond-ATR-unit. Signals were additionally labeled with br.

**Infrared spectra.** Infrared spectra were measured on a Perkin-Elmer 1610 Series FT-IR spectrometer with an ATR accessory on a Bruker 500 MHz NMR spectrometer in acetone-

**NMR investigations.** Long-term \textsuperscript{1}H NMR switching experiments were performed on a Bruker 500 MHz NMR spectrometer in acetone-

**Evans measurements:** The paramagnetic susceptibility of admixed-spin complex FeTPP(acetonitrile),\textsuperscript{1,2} high-spin and low-spin complexes FeTPP(DMSO),\textsuperscript{3,4} and FeTPP(azopyridine),\textsuperscript{3} were determined via the standard Evans measurements using \textsuperscript{1}H NMR spectroscopy. An NMR tube with a coaxial insert, both sealable, was used. For the admixed-spin complex FeTPP(acetonitrile),\textsuperscript{1,2} the outer tube was filled with a 0.2 mM solution of paramagnetic FeTPPClO\textsubscript{4} in acetone-

**Magnetic susceptibility:**

\[ \chi = \frac{\mu_B}{4\pi} \chi_M + \chi_{dia} \]

\[ \chi_M = \frac{3\delta M}{4\pi mf} + \frac{4\pi}{3} [d_0 - d_1] \chi_{dia} \]

\[ \chi_{dia} = \frac{3\delta M}{4\pi fm} \]

\[ \delta M = \frac{3\delta M}{4\pi fm} \chi_{dia} \]

\[ \mu_B = 9.274 \times 10^{-24} \text{ } \text{J} \text{ } \text{T}^{-1} \text{ } \text{mol}^{-1} \]

\[ \chi_{dia} = \frac{3\delta M}{4\pi fm} \]

...
For a 0.2 mM solution of the high-spin complex FeTPP(DMSO)$_2$, $\delta_d = 5.78$ Hz, $\chi_{T2} = 0.0138$ cm$^2$ mol$^{-1}$, and $\mu_{EFF} = 5.76$ B.M.

For a 0.2 mM solution of low-spin complex FeTPP(azopy)$_2$, $\delta_d = 0.00186$ cm$^2$ mol$^{-1}$, $\mu_{EFF} = 2.11$ B.M.

For a 0.2 mM solution of amidix-spin complex FeTPP(acetone)$_2$, $\delta_d = 3.53$ Hz, $\chi_{T2} = 0.00825$ cm$^2$ mol$^{-1}$, and $\mu_{EFF} = 4.50$ B.M.

For a 0.721 mM solution of 5,15-strapped iron(III) porphyrin chloride 17, $\delta_d = 24.8$ Hz, $\chi_{T2} = 0.01434$ cm$^2$ mol$^{-1}$, and $\mu_{EFF} = 5.87$ B.M.

For a 1.63 mM solution of 5, 15-strapped iron(III) porphyrin methylimidazole 18, $\delta_d = 8.79$ Hz, $\chi_{T2} = 0.00258$ cm$^2$ mol$^{-1}$, and $\mu_{EFF} = 2.49$ B.M.

Relaxivity measurements: The relaxation time of acetone and water were determined by NMR using a Bruker AC 300 (Supplementary Table 6) in acetone-$_d_6$ and FeTPP(DMSO)$_2$ + 1 acetonic. The longitudinal (or spin-lattice) relaxation time ($T_1$) of acetone and water were obtained by an inversion recovery pulse sequence. The integral of the acetone and water signals were observed as a function of the delay time (Supplementary Figure 8). See Supplementary Table 3 for the calculated values of $T_1$. The transverse (or spin–spin) relaxation time $T_2$ was determined by a spin echo pulse sequence. The integral of the DMSO signal was observed as a function of the spin echo ($n$) with an echo time ($\tau$) of 10 ms (Supplementary Figure 12). The efficiency of paramagnetic ions in shortening the relaxation time of solvent protons may be determined based on relaxation ($R_1$ and $R_2$). The plot of the relaxation rate ($1/T_1$ or $1/T_2$) vs. the concentration of the paramagnetic species shows a linear relation and the slope is defined as relaxivity, $R_1$ and $R_2$.

**UV-vis and far-vis spectroscopy investigations.** UV–vis and far–vis absorption spectra were recorded on a Perkin–Elmer Lambda 14 spectrophotometer using quartz cells of 1 cm path length. Spectrophotometric grade solvents (2.0 mL) were used in the UV–vis and far–vis absorption spectroscopy of the spin-state changes: To a solution of FeTPP(acetone)$_2$ in acetone, containing DMSO–$_d_6$ at fixed at 25 °C using a water–flow system connected to a thermostat. For a 0.2 mM solution of the high-spin complex FeTPP(DMSO)$_2$, $\delta_d = 5.78$ Hz, $\chi_{T2} = 0.0138$ cm$^2$ mol$^{-1}$, and $\mu_{EFF} = 5.76$ B.M.

For a 0.2 mM solution of low-spin complex FeTPP(azopy)$_2$, $\delta_d = 0.00186$ cm$^2$ mol$^{-1}$, $\mu_{EFF} = 2.11$ B.M.

For a 0.2 mM solution of amidix-spin complex FeTPP(acetone)$_2$, $\delta_d = 3.53$ Hz, $\chi_{T2} = 0.00825$ cm$^2$ mol$^{-1}$, and $\mu_{EFF} = 4.50$ B.M.

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**Calculating the apparent equilibrium constants.** The optical changes accompanying the spin-state changes were used to derive the corresponding apparent equilibrium constants. The model equations were as shown in Supplementary Table 2. The equations were then solved for the $K_{eff}$ and $K_{app}$ values.

The binding constants obtained from the UV–vis experiments ($K_{app} = 5862$ L mol$^{-1}$, $K_{app} = 596.1$ L mol$^{-1}$), were used to fit the solutions of the phenyl and pyrrole protons of FeTPPClO$_4$ to a binding model. The fitting of the UV–vis absorption spectra was performed using the program Equilibrium Speciation Tool 3.3 based on Newton–Raphson method and the reported hybrid generic algorithm, in combination with Excel’s Solver.

**Absorption changes for the titration of a 0.1 mM solution of FeTPPClO$_4$ in acetone with DMSO–$_d_6$ (see Supplementary Figure 19) were analyzed using both 1:1 and 2:1 binding models.** Both models were tested and their fitting has been compared: (a) No intermediate (mixed complex) is formed during ligand exchange (very strong cooperativity of ligand exchange). (b) Formation of only the mixed complex (no double ligand exchange, which is very unlikely because DMSO is known to form 1:1 complexes with FeTPP(acetone)$_2$) (c) absorption of the mixed complex FeTPP(acetone)$_2$ + DMSO–$_d_6$ is identical to the absorption of FeTPP(acetone)$_2$; (d) absorption of the mixed complex FeTPP(acetone)$_2$ + DMSO–$_d_6$ is identical to the absorption of FeTPP(DMSO)$_2$; (e) the absorption of the mixed complex is in between FeTPP(acetone)$_2$ and FeTPP(DMSO)$_2$. The 5372 L mol$^{-1}$ (sum of squared residuals) values are (a) 1.5 × 10$^{-5}$, (b) 8.1 × 10$^{-5}$, and (c) 2.9 × 10$^{-5}$. This suggests formation of an intermediate species FeTPP(acetone)(DMSO)$^+$ according to model (d) or (e). Model (e) is in accordance with the absorption observed in Supplementary Figure 19, which shows a near isosbestic point at 621 nm but a different behavior above 750 nm.

In Supplementary Table 6, the composition of the corresponding solutions is given for the switching experiments (see above).

**Calculation of apparent equilibrium constants.** The optical changes accompanying the spin-state changes were used to derive the corresponding apparent equilibrium constants. The model equations were as shown in Supplementary Table 2. The equations were then solved for the $K_{eff}$ and $K_{app}$ values. The results the main component in pure acetone-$_d_6$ (1.3600 mM) is complex FeTPP(acetone)$_2$; (±939, see Supplementary Table 5). Absorption changes for the titration of a 0.1 mM solution of FeTPPClO$_4$ in acetone with DMSO–$_d_6$ (see Supplementary Figure 19) were analyzed using both 1:1 and 2:1 binding models. Both models were tested and their fitting has been compared: (a) No intermediate (mixed complex) is formed during ligand exchange (very strong cooperativity of ligand exchange). (b) Formation of only the mixed complex (no double ligand exchange, which is very unlikely because DMSO is known to form 1:1 complexes with FeTPP(acetone)$_2$) (c) absorption of the mixed complex FeTPP(acetone)$_2$ + DMSO–$_d_6$ is identical to the absorption of FeTPP(acetone)$_2$; (d) absorption of the mixed complex FeTPP(acetone)$_2$ + DMSO–$_d_6$ is identical to the absorption of FeTPP(DMSO)$_2$; (e) the absorption of the mixed complex is in between FeTPP(acetone)$_2$ and FeTPP(DMSO)$_2$. The 5372 L mol$^{-1}$ (sum of squared residuals) values are (a) 1.5 × 10$^{-5}$, (b) 8.1 × 10$^{-5}$, and (c) 2.9 × 10$^{-5}$. This suggests formation of an intermediate species FeTPP(acetone)(DMSO)$^+$ according to model (d) or (e). Model (e) is in accordance with the absorption observed in Supplementary Figure 19, which shows a nearly isosbestic point at 621 nm but a different behavior above 750 nm.

In Supplementary Table 6, the composition of the corresponding solutions is given for the switching experiments (see above). The most likely model was stepwise coordination of two 1:1 complexes. The pyrrole protons were not visible over the complete range of the titration, and thus could not be used for analysis (see Supplementary Figure 21 and Supplementary Table 4).

**Formation of FeTPP(acetone)$_2$ and FeTPP(acetone)$_2$ClO$_4$ with K'$_{app}$ = 0.865 L mol$^{-1}$ and K'$_{app}$ = 1.077 L mol$^{-1}$ is the most likely model.** The observed and calculated shifts are given in Supplementary Table 4 and are depicted in Supplementary Figure 24. The composition of the corresponding solutions is given in Supplementary Table 5 and shown in Supplementary Figure 25. Based on these results the main component in pure acetone-$_d_6$ is FeTPP(acetone)$_2$; (±939, see Supplementary Table 5).
EPR spectroscopy. Sample solutions of Fe(II) porphyrin complexes were vacuum-sealed in EPR quartz-glass tubes. X-band (~9.5 GHz) continuous wave (CW) EPR experiments in acetone samples in a Bruker ESP 380E spectrometer equipped with an Oxford Instruments Ltd. ICTC liquid He flow system and temperature controller. X-band CW EPR spectra on samples in CH2Cl2 were recorded at 4.8 K using a Bruker ELEXYS E500 spectrometer equipped with an Oxford Instruments Ltd. ESR 900 liquid He flow cryostat and an ICTC temperature controller. All spectra were recorded by subtraction of a background spectrum of the resonator with an empty sample tube. X-band EPR experiments at liquid He temperatures were performed on various Fe(III) porphyrin complexes dissolved in acetone or CH2Cl2 to verify their properties of acetone, possibly promoting agglomeration of the complexes. Magnetic interactions between the iron centers and concomitant enhanced relaxation rates prevent that electron spin echoes can be detected, while their CW signals shall be measured.

Hence, dichloromethane (CH2Cl2), which possesses more favorable glassing properties of acetone, possibly promoting agglomeration of the complexes. The experiments were conducted inside a glovebox at room temperature. EPR and UV are currently underway and shall be reported in due course.

Syntheses. Synthesis of porphyrin 1: Tetraphenylporphyrin and FeTPPCLI were synthesized as reported43. FeTPPCLI (1) was prepared via a modified literature method42. The toluene complex obtained after crystallization from toluene was dissolved in dichromethane (purified over basic alumina) and the solvent was removed in vacuo. This procedure was repeated several times until no toluene signals were visible in 1HNMR.

HR masses of FeTPPCLI (1) with different ligands (see Supplementary Figure 40): (a) acetone: 784.24952 (calc.), 784.24989 (found) for C23H21N2O2Fe; (b) 4-methoxypyridine: 886.27132 (calc.), 886.27059 (found) for C24H23N2O2Fe; (c) DMSO: 822.17801 (calc.), 822.17609 (found) for C19H17N2O2FeS.

Synthesis of azopyridine 2, general strategy: The azopyridine 2 was synthesized in three steps from commercially available 3,5-di-tert-butylpyrane and 3-amino-4-chloropyridine 8 as shown in Supplementary Figure 41. Oxidation of the aniline 5 to the corresponding nitrosobenzene 6 was achieved using oxone in a mixture of water and CH2Cl2. Base-mediated coupling of the nitrosobenzene 6 with the aminopyridine 8 afforded the azo-product 9, which on dechlorination–methylation resulted in the azo-compound 2.

Synthesis of nitrosobenzene 6: To a solution of Oxone® (12.9 g, 39.9 mmol) in water (100 mL) was added a solution of 3,5-di-tert-butylpyrane 5 (2.00 g, 9.74 mmol) in CH2Cl2 (40 mL) and the resulting mixture was stirred at room temperature for 5 h. The formation of the nitroso compound was evident by a change in color of the solution to light green. After 5 h, the phases were separated and the aqueous phase was extracted with CH2Cl2 (2 x 25 mL). The organic phases were combined, dried over anhydrous MgSO4, and evaporated under reduced pressure. The temperature during evaporation was maintained at 30 °C. The crude solid thus obtained was purified by column chromatography (silica gel, 2.5 CH2Cl2/ pentane as eluent) to afford the nitroso compound 6 as a light green solid. The yield was 2.38 mmol (45% of theoretical yield).

Electrochemical measurements. The electrochemical measurements were performed on an Autolab PGSTAT204 potentiostat equipped with a 3-electrode setup. A platinum disk (5 mm diameter) was used as the working electrode, a platinum wire as the counter electrode and a Ag/AgNO3 0.01 M in acetonitrile was used as the reference electrode. The reference electrode was separated from the working system and temperature controller. X-band CW EPR spectra on samples in CH2Cl2 were recorded at 4.8 K using a Bruker ELEXYS E500 spectrometer equipped with an Oxford Instruments Ltd. ESR 900 liquid He flow cryostat and an ICTC temperature controller. All spectra were recorded by subtraction of a background spectrum of the resonator with an empty sample tube. X-band EPR experiments at liquid He temperatures were performed on various Fe(III) porphyrin complexes dissolved in acetone or CH2Cl2 to verify their spin states.

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The synthesised porphyrin 17, general strategy: The ether bridge 15 was synthesized in two steps from commercially available chemicals with a yield of 24%. The meso-phenyl dipropylamine 14 was synthesized with a yield of 81%. The stripped iron porphyrin 17 was prepared from 14 and 15 in two steps (see Supplementary Figure S1).

Synthesis of meso-phenyl dipropylamine 14[47]. Pyrrole 13 (24.0 mL, 347 mg mol) and benzaldehyde 12 (850 mg, 8.00 mmol) were dissolved under nitrogen atmosphere and stirred for 15 min. TFA (150 µL) was added and the mixture was stirred at room temperature for 25 min. Subsequently, 200 mL of DCM were added and the mixture was washed with a 0.1 M potassium hydroxide solution (120 mL) and twice with water (120 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. A brown solid was obtained (30.0 mg, 34.3 µmol, 92%). m.p.: 372 °C; 1H NMR (600 MHz, CDCl3, 300 K): δ 8.83 (s, 3H, OCPh3); 4.03 (s, 4H, -CH2); 3.99 (s, 4H, -CH2); 3.29 (s, 4H, -CH2); 2.81 (s, 4H, -CH2); 2.63 (m, 8H, -CH); 2.28 (s, 4H, -CH2); 1.71 (t, J = 5.5 Hz, 3H, C(3)3); 1.17 (t, J = 5.5 Hz, 3H, C(3)3) ppm; 13C NMR (150 MHz, CDCl3, 300 K): δ = 128.9 (C-3), 128.7 (C-3), 128.6 (C-3), 128.5 (C-3), 128.4 (C-3); δ = 28.3 (CH(2)), 34.8 (CH(2)); 77.6 (C-Ph); 69.7 (C(3)3); 68.0 (C(3)3); 67.9 (C(3)3); 67.8 (C(3)3); 66.9 (C(3)3); 43.1 (s, 4H, -H-10); 4.27 (t, J = 4.7 Hz, 4H, -H-4); 3.95 (s, J = 4.7 Hz, 4H, -H-9) ppm; 13C NMR (150 MHz, CDCl3, 300 K): δ = 189.1 (C-1), 161.1 (C-3), 135.9 (C-5), 128.3 (C-7), 125.2 (C-2), 121.1 (C-6), 112.8 (C-4), 82.4 (C-8), 68.0 (C-8, C-9), 58.9 (C-10) ppm; HRMS (EI): 382.14257 (calc.), 382.14146 (found) for C22H32O4N2; FT-IR (film): ν=2921 (w), 1597 (m), 1442 (m), 1336 (m), 1243 (m), 1099 (m), 801 (m), 719 (m), 659 (m), 541 (m), 463 (s), 436 (w), 418 (w), 408 (s) cm⁻¹. Due to the highly diluted NMR samples, the large number of quaternary C-atoms and the paramagnetism, 13C NMR spectroscopy of 17 did not provide sufficient signal intensities. Therefore, the 13C NMR spectrum was not analyzable.

Synthesis of 5,15-strapped iron(III) porphyrin chloride 18: The 5,15-strapped iron(III) porphyrin chloride 17 (1.82 mg, 1.63 µmol) was dissolved in 400 µL dichloromethane-d2. To this solution 1-methylimidazole (5.48 mg, 66.8 µmol) dissolved in 80 µL of dichloromethane-d2 was added. 11H NMR (500 MHz, CDCl3, 300 K): δ = -7.92 (s, 2H, H-pyrophe; -10.05 (s, 2H, H-pyrophe); -22.15 (s, 2H, H-pyrophe); -23.28 (s, 2H, H-pyrophe) ppm; HRMS (ESI): 292.15585 (calc.), 292.15557 (found) for C22H32N2O4Cl; Due to the highly diluted NMR samples, the large number of quaternary C-atoms and the paramagnetism, 13C NMR spectroscopy of 18 did not provide sufficient signal intensities. Therefore, the 13C NMR spectrum was not analyzable.

Data availability
All the data that support the findings of this study are available within its article and its Supplementary Information files, or from the corresponding author on reasonable request.

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Author contributions
R.H. and S.S. designed the experiments; S.S. performed the photoswitching, electrochemistry, and relaxivity experiments; S.S. and B.K. performed titration experiments; K.S. analyzed the binding isotherms; F.D.S. assisted in the NMR data acquisition and interpretation; M.P. synthesized and investigated the strapped porphyrin and performed electrochemistry experiments together with S.S. and O.R.; T.L., D.G., and W.S measured the EPR spectra; Evans measurements have been performed by B.K., S.S., and M.P.; R.H. supervised the project; and S.S. and R.H. wrote the manuscript.

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