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Spin Switching with Triazolate-Strapped Ferrous Porphyrins

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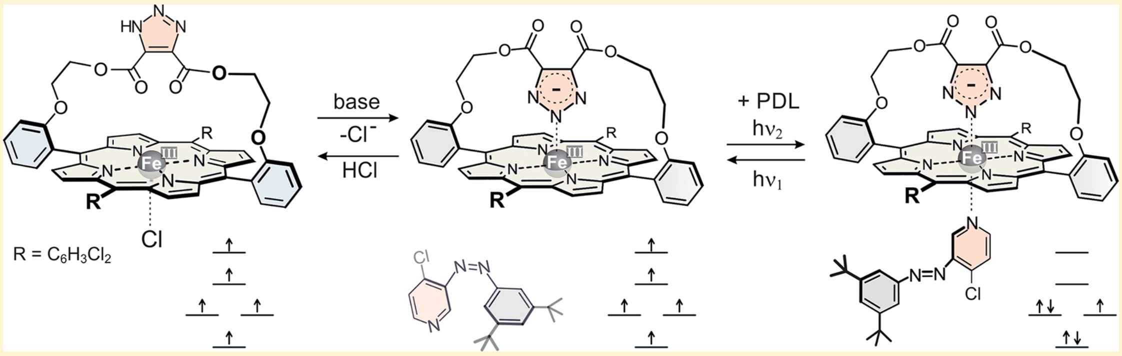
Supporting Information



ABSTRACT: Fe(III) porphyrins bridged with 1,2,3-triazole ligands were synthesized. Upon deprotonation, the triazolate ion coordinates to the Fe(III) ion, forming an overall neutral high-spin Fe(III) porphyrin in which the triazolate serves both as an axial ligand and as the counterion. The second axial coordination site is activated for coordination and binds *p*-methoxypyridine, forming a six-coordinate low-spin complex. Upon addition of a phenylazopyridine as a photodissociable ligand, the spin state of the complex can be reversibly switched with ultraviolet and visible light. The system provides the basis for the development of switchable catalase- and peroxidase-type catalysts and molecular spin switches.

INTRODUCTION

Ferrous porphyrins with anionic ligands serving both as an axial ligand and as counterions are abundant in nature. They act as catalysts in selective CH activation (cytochrome P450),[1−4] hydrogen peroxide decomposition (catalases),[5] oxidation of a variety of substrates with hydrogen peroxide (peroxidases),[6] and a number of further biologically important processes (Figure 1).[7−9]

Controlled spin switching is essential for the function of these enzymes.[10] During its catalytic cycle, cytochrome P450 switches between the six-coordinate low-spin resting state and the five-coordinate high-spin state.[11] Spin state control, particularly of iron complexes, is also a prerequisite in a number of further biocatalytic processes such as C−H activation by methane monooxygenases.[12] The design of artificial systems whose spin states are responsive to external stimuli is the first step toward molecular machine-type catalysts[13] that perform particularly difficult processes such as conversion of hydrocarbons to alcohols under ambient conditions.[14] Single-molecule spin state switching is also the prerequisite to molecular spintronics,[15] responsive contrast agents,[16,17] and a number of further applications.[18] Recently, we presented the first artificial ferrous porphyrin system that changes its spin state between high-spin ($S = {}^{5}/_{2}$) and low-spin ($S = {}^{1}/_{2}$) states upon irradiation with light.[19] However, the complex consists of six components [Fe(III)porphyrin, the counterion, two oxygen ligands, and two nitrogen ligands] that are in equilibrium in solution. Notwithstanding the high switching efficiency (76%), caused by the multicomponent character, the system is quite sensitive to changes in composition and environment. Here we report a novel two-component system, which includes a covalent triazole-porphyrin unit and only one separate ligand.

Fe(III)tetraphenylporphyrin chloride (FeTPPCl) is commercially available and in principle meets the structural requirements for spin switching. The FeTPPCl is five-coordinate and a high-spin complex with a chloride ion serving as the counterion and axial ligand (Figure 2).[19] However, the chloride ligand is strongly bound, and the second axial coordination site binds only very strong nitrogen ligands, such as 1-methylimidazole (Figure 2a). Moreover, the mixed chloride/imidazole complex is still a high-spin complex.[20,21] Upon replacement of the chloride ligand in FeTPPCl with azide (FeTPPN$_3$), the iron(III) ion is closer to its spin crossover point. The azide complex FeTPPN$_3$ is also five-coordinate and high-spin, but in contrast to FeTPPCl, it is considerably more apt to bind a second axial ligand, leading to a low-spin complex (Figure 2b).[9,22,23]

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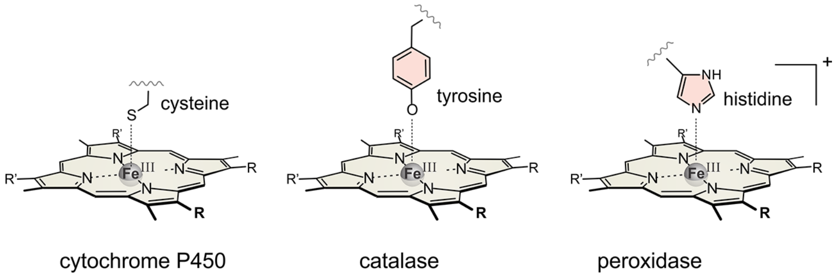

Figure 1. Heme units of ferrous porphyrin-containing enzymes.

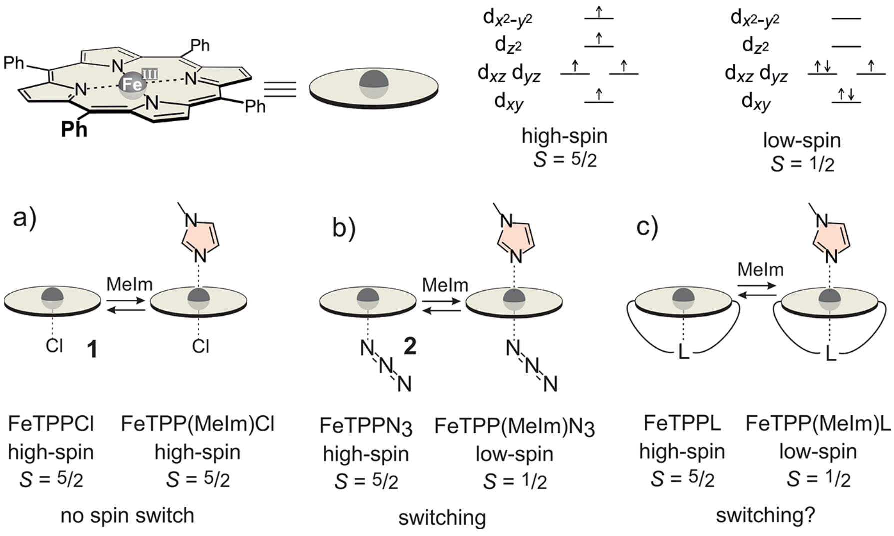

Figure 2. Spin states of Fe(III)porphyrins with one anionic axial ligand, with and without 1-methylimidazole as the second axial ligand: (a) with a chloride ligand (**1**), (b) with azide (**2**), and (c) schematic representation of a ferrous porphyrin strapped with an anionic ligand (target structure for spin switching).

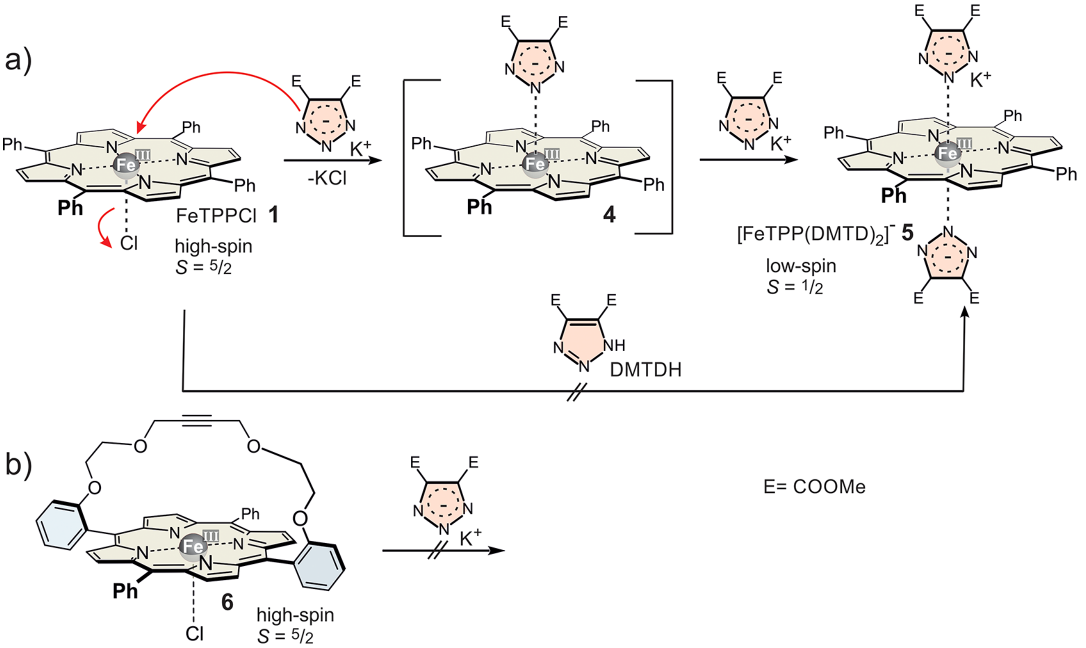

Figure 3. Coordination of Fe(III)porphyrin chloride with triazole (DMTDH) and triazolate (DMDT$^-$). (a) FeTPPCl **1** reacts with triazolate but not with triazole to form a 2:1 complex. (b) Strapped porphyrin **3** does not react with the triazolate anion.

However, $FeTPPN_3$ **2** has several disadvantages. The azide ligand is easily replaced with Cl^- forming FeTPPCl **1** and with OH^- leading to the μ-oxo compound $(FeTPP)_2O$.[24] To avoid these problems, we designed a strapped porphyrin including an anionic ligand L^- in the bridge (Figure 2c), complying with the following preconditions. (1) L^- should be strongly binding. (2)

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The five-coordinate complex should be high-spin. (3) The free axial coordination site should bind ligands with a low or medium ligand field strength. (4) Binding of the second axial ligand should induce a spin switch to the low-spin state.

■ RESULTS AND DISCUSSION

Several Fe(III)porphyrins with covalently linked anionic ligands are known.[25−29] However, strapped anionic nitrogen ligands have not been realized so far. Among the noncovalently coordinated nitrogen ligands, imidazolate, isocyanate,[30] and azide[22] are the most common.[31] Unfortunately, azide and isocyanate cannot be tethered to the porphyrin because there is no free valence available to form a covalent bond. Imidazolate anions suffer from the fact that only one position is available to attach a tether (the C atom distant from the coordinating N atom) and imidazolates are easily protonated ($\mathrm{p}K_\mathrm{a} = 14.3$);[32] hence, the corresponding complexes would not be water stable. We therefore considered triazoles as anionic ligands for strapping from positions 4 and 5. The parent triazole has a $\mathrm{p}K_\mathrm{a}$ of 8.8.[33] The 4,5-diester substituted triazole unit should be considerably more acidic ($\mathrm{p}K_\mathrm{a} \sim 5$) and when coordinated to Fe(III) should be inert to protonation (water stable) at neutral pH.

To test whether triazolates are suitable anionic ligands for an integration into the bridge of a strapped porphyrin, we performed preliminary experiments with 4,5-dimethyl-1,2,3-triazole-4,5-dicarboxylate (DMTDH) (Figure 3). In a preliminary experiment, a solution of iron(III) tetraphenylporphyrin chloride (FeTPPCl **1**, 100 μM) in acetonitrile was treated with an 1000-fold excess of the 4,5-dimethyl-1,2,3-triazole-4,5-dicarboxylate (DMTDH). Changes in nuclear magnetic resonance (NMR) or ultraviolet (UV) spectra were not observed, indicating that there is no coordination of the free ligand DMTDH to the Fe(III) ions. Obviously, the coordination power of neutral DMTDH is insufficient for coordination. However, upon deprotonation of the triazole (DMTDH) with solid K_2CO_3, the color of the FeTPPCl/DMTDH solution changes from brown to yellow and the UV−visible (UV−vis) spectrum exhibits characteristic absorption bands of low-spin FeTPPL_2 (550 nm, 575 nm shoulder, 640 nm) (Figure 3; see Figure S2).[34] Resonances in the NMR spectrum at −14 ppm further confirm the $[\mathrm{FeTPP(DMTD)}_2]^-$ low-spin state. Density functional theory (DFT) calculations verify that the triazolate anion coordinates from its nitrogen at position 2 to the Fe(III) ion forming a symmetrical complex (Figure S1). An FeTPP-(DMTD) (1,1 complex) is very unlikely, because it is known that FeTPP^+ cations with one anionic nitrogen ligand are high-spin (see Figure 3a).[10,11,35−37] The triazolate (DMTD^-), however, does not coordinate to a strapped, Fe(III)porphyrin **6** whose second axial coordination side is sterically shielded (Figure 3b).[8] This lack of reactivity proves that the triazolate has to attack from the opposite axial side to replace the chloride ligand. We conclude that a strapped triazolate should thus bind to the Fe(III) ion.

The DFT model reactions predict that an $-\mathrm{O}-\mathrm{CH}_2-\mathrm{CH}_2-$ or $-\mathrm{O}-\mathrm{CH}_2-\mathrm{CH}_2-\mathrm{CH}_2-$ chain connecting the ester function of the DMTDH with the *ortho* position of the *meso* phenyl rings should provide a suitable preorientation of the central nitrogen atom of DMTD^- for coordination with Fe(III) [**7** and **8** (panels b and c of Figure 4, respectively)]. As compared to a structurally similar reference compound (Figure 4a) with an unconstrained triazolate ligand and optimal coordination geometry, structure **7** with the short tether exhibits a somewhat shorter Fe−N coordination bond, and compound **8** with the longer tether has a longer Fe−N distance. Obviously, the tether in structure **7** is somewhat too small, pulling the triazolate ligand toward the Fe(III) ion, while the tether in **8** is slightly too long. A conformational analysis of **7** revealed that the tethers are still flexible. The $\mathrm{O}-\mathrm{CH}_2-\mathrm{CH}_2-\mathrm{O}$ units adopt *gauche* and *anti* conformations, which are similar in energy (Figure S1). Nevertheless, the geometry fit is quite good, and **7** and **8** were selected as target structures for synthesis.

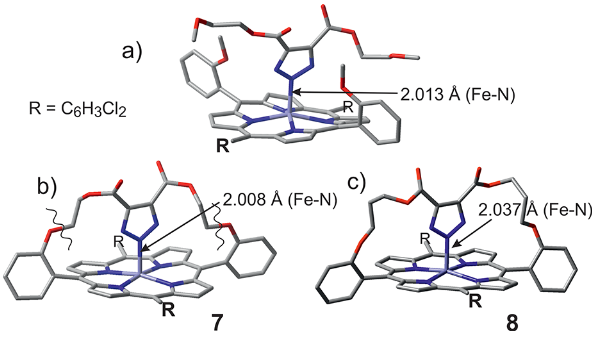

Figure 4. PBE/def2svp-optimized structures of triazolate-strapped target compounds (b) **7** and (c) **8** and (a) a structural reference with a corresponding non-covalently attached ligand. Hydrogen atoms and the *meso* 2,5-dichlorophenyl substituents have been omitted for the sake of clarity. The bond lengths of the Fe−N coordination bonds indicate the accuracy of the fit of the tether lengths. The reference compound exhibits the optimum Fe−N distance because the porphyrin and the ligand were optimized without further geometry constraints. The reference compound (a) was constructed by cutting the structure in panel b at the wavy lines and complementing the free valences by methyl groups.

Conceptually, three strategies for synthesizing strapped porphyrins (capped,[38] hindered,[1] or bridged porphyrins[39]) are possible: (a) bridging a prefabricated porphyrin, e.g., reaction of a 5,15-bis(2-hydoxyphenyl) porphyrin with a chainlike building block with a leaving group at both ends, and (b and c) using building blocks that already include the bridge to prepare the porphyrin (mixed aldehyde synthesis). There are two options for the latter strategy:[1,40] (b) using a bridged bis-aldehyde and 2 equiv of dipyrromethane[1,40−42] or (c) using a bridged bisdipyrromethane and 2 equiv of an aldehyde (see Figure 5).[43]

Synthetic pathway a was not successful. Therefore, we pursued strategy b. Salicylaldehyde (**9**) and chloroethanol (**10a**) were reacted to give 2-(2-hydroxyethoxy)benzaldehyde (**11a**).[44] Acetylene dicarboxylic acid (**12**) with **11a** yields dialdehyde **13a** (85%). Dialdehyde **13a** was used in Lindsay-type cyclization reactions with different 5-substituted dipyrromethanes[45] to afford acetylene-bridged strapped porphyrins (see Figure 6, bottom right) with yields of ≤35%.

The yield of **15b** is low (1%) because of severe scrambling.[46] The main product is tetraphenylporphyrin (TPP). **15c** is formed in a 15% yield. A crystal structure analysis reveals a strained structure with an approximate C_2 symmetry. The acetylene unit is not exactly linear, and the porphyrin ring is distorted toward a ruffled-type geometry (see Figure 5 and Figure S7).

We also prepared an analogously strapped porphyrin **15e** with longer $-\mathrm{O}-\mathrm{CH}_2-\mathrm{CH}_2-\mathrm{CH}_2-$ bridges (extended by an additional CH_2 group) in a 35% yield, which is more than double compared to that of **15c**, obviously because the longer bridge imposes less strain. A similar trend albeit with lower yields was observed with the bis(pentafluoro)-substituted strapped

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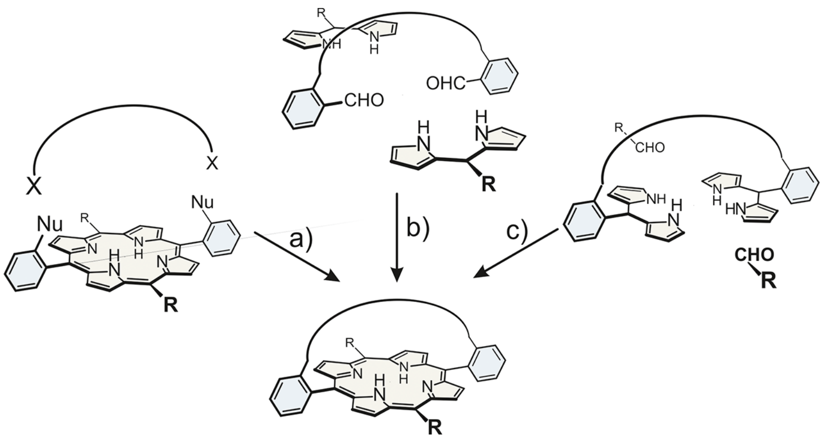

Figure 5. Three strategies for synthesizing strapped porphyrins.

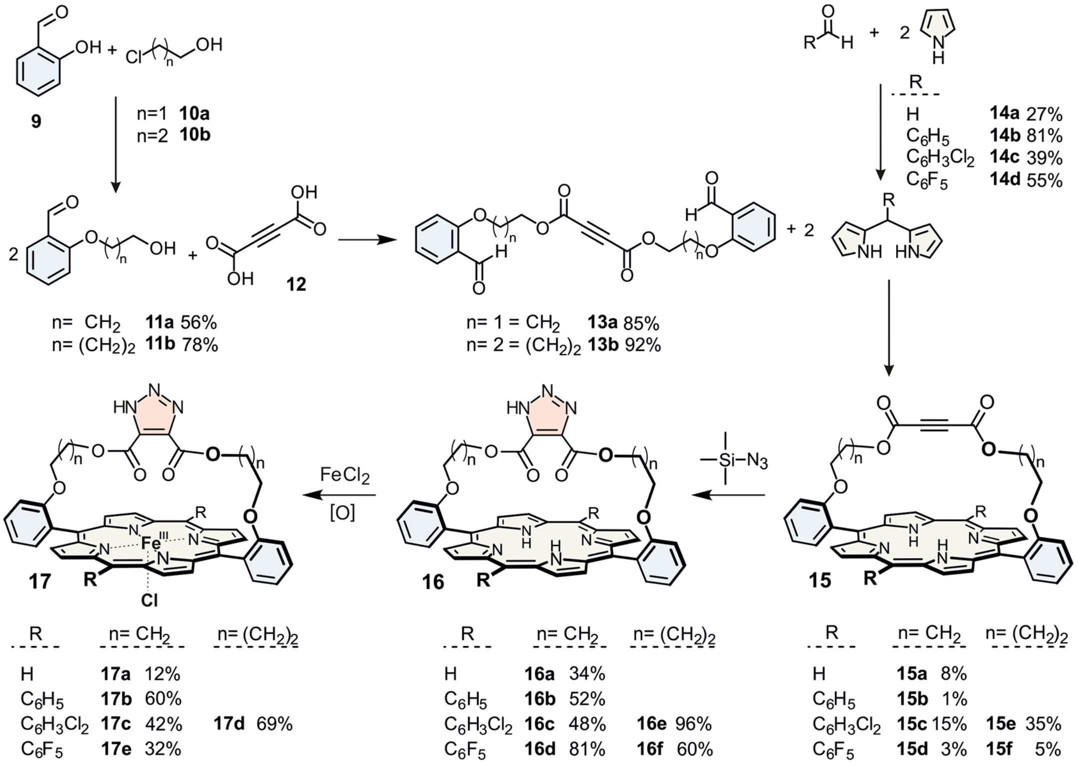

Figure 6. Stepwise synthesis of the strapped porphyrins (Figure 5, pathway b).

porphyrins **15d** (3%) and **15f** (5%). Scrambling was not detected in any strapped porphyrin except **15b**.

Electron deficient acetylenes are known to undergo 1,3-dipolar cycloaddition with azide.[47] Reaction of the strapped porphyrins **15a−f** with trimethylsilyl azide afforded the corresponding triazoles **16a−f**, respectively, in moderate to excellent yields (34−96%). A crystal structure analysis of **16e** confirms the structural assignment. The porphyrin ring is planar, which is in agreement with our assumption that the bridge does not impose strain (see Figure 8).

The X-ray structure of **16e** shows an orientation of the "strap" markedly different from that in **15c** (Figure 7). Due to the bulky triazole unit, the orientation of the ester groups is inverted with respect of the porphyrin plane, and the carbonyl oxygens in **16e** point toward the porphyrin plane. This *esters-in* conformation creates a larger steric demand (see Figure S8 for van der Waals plots) of the strap toward the porphyrin plane and is compensated by tilting of the strap toward one of the dichlorobenzene substituents of the porphyrin skeleton (Figure

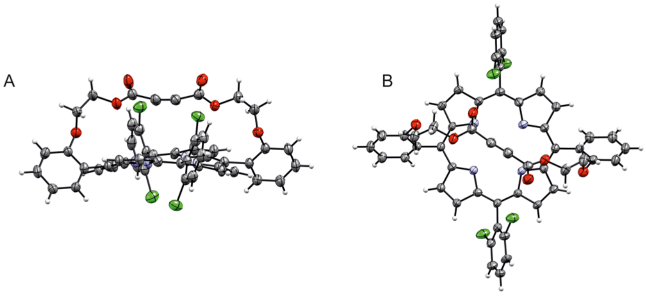

Figure 7. Crystal structure of **15c**, with thermal ellipsoids shown at the 50% probability level: (A) side view and (B) top view (for a van der Waals plot, see Figure S7).

8B) by 26° from orthogonality. The triazole hydrogen is located at position N2 and not at N3 as this is usually the case. This might be due to the strong hydrogen bond (N−H···O, 1.76 Å; N···O, 2.75 Å; N−H···O angle, 175°) to the solvent diisopropyl ether.

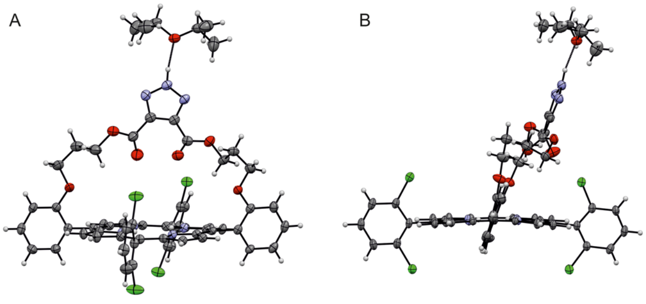

Figure 8. Crystal structure of **16e** with thermal ellipsoids shown at the 50% probability level. (A) Front view and (B) side view showing the tilting of the strap.

Upon a solution of the free base porphyrins with $FeCl_2$ in acetonitrile being heated to 80 °C under nitrogen and subsequent oxidation upon exposure to air, the Fe(III)-porphyrins were obtained in 12−69% yields.[48] NMR analysis reveals that all iron(III) porphyrins are high-spin ($S = ^5/_2$). The pyrrole protons resonate at 70−80 ppm, which is characteristic for high-spin Fe(III)porphyrins.[49] No signals were observed at 0 to −30 ppm, which would indicate the formation of low-spin ($S = ^1/_2$) complexes.[50] Obviously, the strapped, protonated triazole units do not coordinate to the Fe^{3+} ion, in agreement with the corresponding free protonated triazoles [DMTDH (Figure 3)]. To confirm the noncoordinating behavior of the triazole unit, trifluoroacetic acid was added. If coordinated, the triazole should decoordinate upon protonation. Changes in the UV−vis spectrum were not observed.

Because the free triazole ligand DMTDH coordinates to FeTPPCl after deprotonation (Figure 3), a similar intramolecular coordination was expected for the deprotonated, strapped DMTDH ligand in **17c**. Upon addition of K_2CO_3 to chloride complex **17c**, the four high-spin signals of the pyrrole protons at 85.7, 83.0, 80.2, and 78.4 ppm change to form two broad signals at 78.9 and 84.9 ppm (Figure S3). No signals are visible in the low-spin range, and the magnetic moment was determined to be 5.62 μ_B (see the Supporting Information, page S27), confirming the high-spin $S = ^5/_2$ state for a solution of 0.77 mM **17c** with K_2CO_3 in acetone-d_6. Characteristic changes are also observed in the UV−vis spectrum. A strong Q-band at 576 nm appears, which is typical for five-coordinate nitrogen Fe(III)TPP complexes (see Figure 9).[51] Protonation of five-coordinate strapped triazolate complex **18** with HCl leads back to chloride complex **17c** (Figure 9).

The *p*-methoxypyridine acts both as a base and as a ligand (Figure 9b). Upon addition of 100 equiv of *p*-methoxypyridine, triazole is deprotonated and replaces the chloride. Starting from both **17c** and **18**, the same six-coordinate complex **20** is formed. The pyrrole proton chemical shifts (−0.61 and −26.08 ppm) clearly indicate that complex **20** is low-spin ($S = ^1/_2$) (see Figure 9 and Figure S5), being in agreement with the magnetic moment of 2.56 μ_B (see Supporting Information, page S27). Hence, the overall neutral five-coordinate, strapped triazolate complex **18** performs spin switching upon coordination to an additional axial anion (Figure 9a) as well as to a neutral nitrogen ligand (Figure 9b).

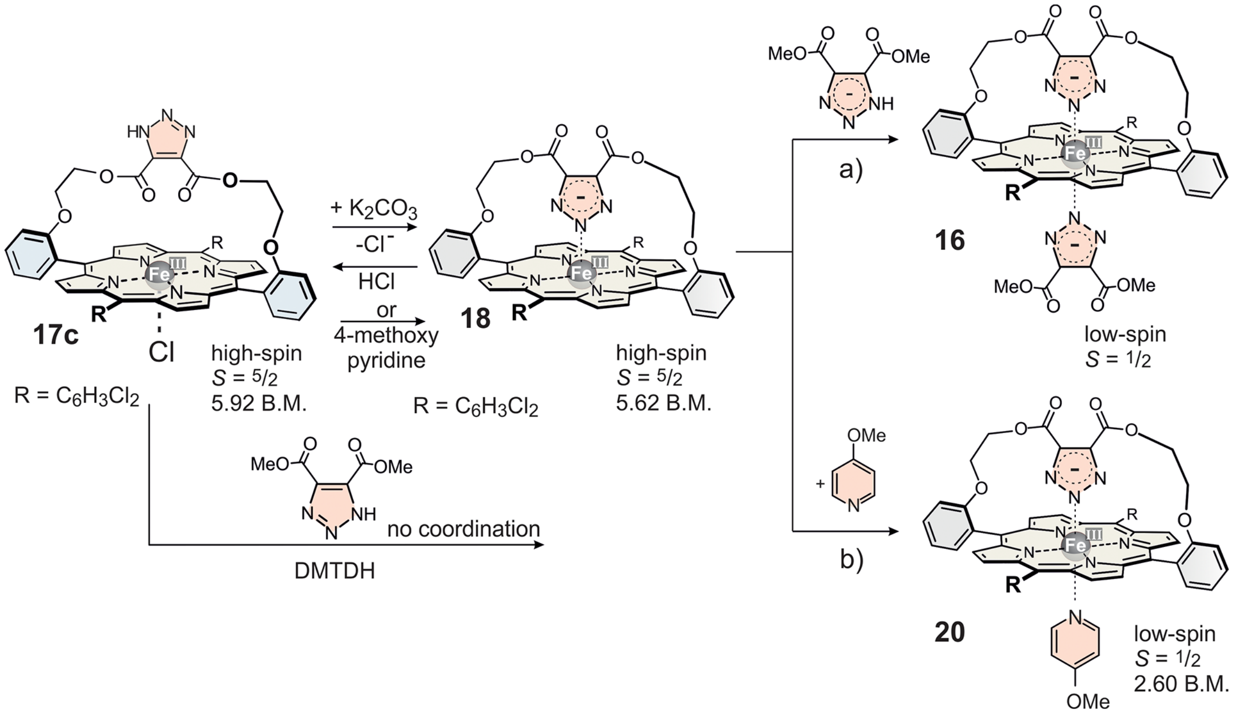

Figure 9. Switching the spin state of triazole-strapped porphyrins. Deprotonation of the triazole leads to coordination of the triazolate, the spin state remaining high-spin ($S = ^5/_2$). Additional coordination of an external ligand, (a) triazolate ($DMTD^-$) or (b) *p*-methoxypyridine, switches the spin state to low-spin ($S = ^1/_2$). The change in coordination number, charge, and spin state leads to a change in the UV spectrum of **16** that makes it similar to that of **5** (see Figure 3 and Figures S2 and S4).

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As with the addition of methoxypyridine to **17c** (Figure 9), the addition of the photodissociable ligand (PDL)[52−54] *trans*-4-methoxy-3-(3,5-di-*tert*-butylphenyl)azopyridine (50 equiv) leads to the formation of a low-spin complex. Upon irradiation with 365 nm, the ligand isomerizes from the *trans* to the *cis* configuration. However, the ligand remains coordinated. Obviously, the steric hindrance in the *cis* geometry is not sufficient to overcome the electronically strong binding power. We therefore applied *trans*-4-chloro-3-(3,5-di-*tert*-butylphenyl)-azopyridine **22** (50 equiv) as a weaker photodissociable ligand. **22** leads to the formation of a low-spin complex **21** with the typical ^1H NMR signals at −26.6 ppm and a magnetic moment of 3.44 μ_B (Figure 10). The magnetic moment is higher than expected for a pure low-spin complex, because coordination is incomplete and **22** is a weaker ligand than *p*-methoxypyridine (Figure 9, complex **20**). Irradiation for 15 min (20.0 mW/cm^2) with UV light (365 nm) switches the *trans*-azopyridine to the *cis* configuration (PSS = 72% *cis*, 28% *trans*), which in turn gives rise to a decrease in the intensity of the low-spin signals and an increase in the magnetic moment to 4.3 μ_B (see Supporting Information, page S27). Irradiation for 15 min (20.0 mW/cm^2) with 430 nm light restores the low-spin signals in ^1H NMR (PSS = 86% *trans*, 14% *cis*) (see Figure S6). We attribute the change in magnetic moment to the dissociation of the ligand in the *cis* configuration and recoordination of the *trans* isomer. The moderate spin state switching efficiency (~25%) is mainly due to the low photochemical *trans*−*cis* conversion of ligand **22**.

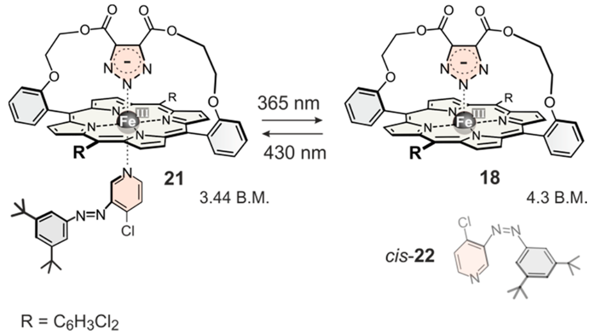

Figure 10. Assumed mechanism of spin state switching of strapped ferrous porphyrin **21** in the presence of photodissociable ligand **22**.

Further improvement of the switching efficiency must involve a covalently attached, photoswitchable ligand according to the “record player” design.[55−57]

■ CONCLUSION

In summary, we report on the design, synthesis, and investigation of an Fe(III)-based molecular ($S = {}^5/_2 \rightleftarrows S = {}^1/_2$) spin switch. The two-component system includes an Fe(III)porphyrin with a covalently attached triazolate unit and a separate pyridine ligand. The triazole is strapped to the porphyrin in such a way that the nitrogen lone pair in position 2 of the corresponding triazolate is placed in an optimal geometry to coordinate to the Fe(III) ion. Upon deprotonation of the triazole, the triazolate anion coordinates and serves as both the counterion and the axial ligand. The acidity of the ester-substituted triazole is sufficient for facile deprotonation, and the ligand field strength of the resulting triazolate is strong enough to coordinate. However, the coordination power is still in a range that preserves the high-spin state and allows coordination of pyridines to the remaining axial site, which in turn leads to a spin switch to the low-spin state. Upon addition of a photoswitchable ligand, the spin state of the complex can be reversibly switched with light. Our five-coordinate high-spin complexes **18** might serve as model compounds for a number of natural iron(III)-porphyrins, such as cytochrome P450, and as potential photoswitchable catalases. Further potential applications include responsive contrast agents[16,58] and spintronics.[15]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00349.

> All one-dimensional NMR spectra, UV−vis spectra, ESI-MS, MALDI-MS, Evans measurements, experimental data of the spin switch, data of the crystal structure, and DFT calculation (PDF)

Accession Codes

CCDC 1884544 and 1885475 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Momenteau, M.; Mispelter, J.; Loock, B.; Bisagni, E. Both-faces hindered porphyrins. Part 1. Synthesis and characterization of basket-handle porphyrins and their iron complexes. *J. Chem. Soc., Perkin Trans. 1* **1983**, *1*, 189−196.

(2) Andrioletti, B.; Ricard, D.; Boitrel, B. Cyclam-strapped porphyrins and their iron (III)−copper (II) complexes as models for the resting state of cytochrome c oxidase. *New J. Chem.* **1999**, *23*, 1143−1150.

(3) Kozuch, S.; Leifels, T.; Meyer, D.; Sbaragli, L.; Shaik, S.; Woggon, W. D. New synthetic models of cytochrome P450: How different are they from the natural species? *Synlett* **2005**, No. 4, 675−684.

(4) Konishi, K.; Oda, K.; Nishida, K.; Aida, T.; Inoue, S. Asymmetric Epoxidation of Olefins Catalyzed by Manganese Complexes of Chiral “Strapped” Porphyrins with Diastereotopic Faces. A Novel Strategy for Stereochemical Modeling of the Active Site of Cytochrome P-450. *J. Am. Chem. Soc.* **1992**, *114*, 1313−1317.

(5) Maté, M. J.; Murshudov, G.; Bravo, J.; Melik-Adamyan, W.; Loewen, P. C.; Fita, I. Heme catalases. In *Handbook of Metalloproteins*;

Messerschmidt, A., Huber, R., Poulos, T., Widghardt, K., Eds.; Wiley & Sons: Chichester, U.K., 2001; pp 486−502.

(6) Veitch, N. C. Horseradish peroxidase: a modern view of a classic enzyme. *Phytochemistry* **2004**, *65*, 249−259.

(7) Collman, J. P.; Lee, V. J.; Kellen-Yuen, C. J.; Zhang, X.; Ibers, J. A.; Brauman, J. I. Threitol-strapped manganese porphyrins as enantioselective epoxidation catalysts of unfunctionalized olefins. *J. Am. Chem. Soc.* **1995**, *117*, 692−703.

(8) Gunter, M. J.; Hockless, D. C. R.; Johnston, M. R.; Skelton, B. W.; White, A. H. Self-assembling porphyrin [2]-catenanes. *J. Am. Chem. Soc.* **1994**, *116*, 4810−4823.

(9) Morgan, B.; Dolphin, D. Synthesis and structure of biomimetic porphyrins Synthesis and structure of biomimetic porphyrins. *Struct. Bonding (Berlin)* **1987**, *64*, 115−203.

(10) Rydberg, P.; Sigfridsson, E.; Ryde, U. On the role of the axial ligand in heme proteins: a theoretical study. *JBIC, J. Biol. Inorg. Chem.* **2004**, *9*, 203−223.

(11) Meunier, B.; de Visser, S. P.; Shaik, S. Mechanism of oxidation reactions catalyzed by cytochrome P450 enzymes. *Chem. Rev.* **2004**, *104*, 3947−3980.

(12) Baik, M.-H.; Newcomb, M.; Friesner, R. A.; Lippard, S. J. Mechanistic studies on the hydroxylation of methane by methane monooxygenase. *Chem. Rev.* **2003**, *103*, 2385−2419.

(13) De, S.; Pramanik, S.; Schmittel, M. A Toggle Nanoswitch Alternately Controlling Two Catalytic Reactions. *Angew. Chem., Int. Ed.* **2014**, *53*, 14255−14259.

(14) Nagababu, P.; Yu, S. S.-F.; Maji, S.; Ramu, R.; Chan, S. I. *Catal. Sci. Technol.* **2014**, *4*, 930−935.

(15) Ferrando-Soria, J.; et al. Molecular magnetism, quo vadis? A historical perspective from a coordination chemist viewpoint. *Coord. Chem. Rev.* **2017**, *339*, 17−103.

(16) Dommaschk, M.; Peters, M.; Gutzeit, F.; Schuett, C.; Naether, C.; Soennichsen, F. D.; Tiwari, S.; Riedel, C.; Boretius, S.; Herges, R. Photoswitchable Magnetic Resonance Imaging Contrast by Improved Light-Driven Coordination-Induced Spin State Switch. *J. Am. Chem. Soc.* **2015**, *137*, 7552−7555.

(17) Heitmann, G.; Schuett, C.; Groebner, J.; Huber, L.; Herges, R. Azoimidazole functionalized Ni-porphyrins for molecular spin switching and light responsive MRI contrast agents. *Dalton Trans.* **2016**, *45*, 11407−11412.

(18) Herges, R.; Jansen, O.; Tuczek, F.; Venkatamarani, S. Transition metal complexes with photosensitive tethered ligands as visible light-induced spin-crossover magnetic molecular switches. PCT Int. Appl. WO 2012022299 A1 20120223, 2012.

(19) Shankar, S.; Peters, M.; Steinborn, K.; Krahwinkel, B.; Sönnichsen, F. D.; Grote, D.; Sander, W.; Lohmiller, T.; Rüdiger, O.; Herges, R. Light-controlled switching of the spin state of iron(III). *Nat. Commun.* **2018**, *9*, 4750.

(20) Byers, W.; Cossham, J. A.; Edwards, J. O.; Gordon, A. T.; Jones, J. G.; Kenny, E. T. P.; Mahmood, A.; McKnight, J.; Sweigart, D. A.; Tondreau, G. A.; Wright, T. Hydrogen Bonding in Metalloporphyrins. Mechanistic Study of the Reactions of (Tetraphenylporphinato) iron (111) Azide with Imidazole and N-Methylimidazole. *Inorg. Chem.* **1986**, *25*, 4767−4774.

(21) Bond, A. M.; Sweigart, D. A. Low temperature electrochemistry of metalloporphyrins in dichloromethane: characterization of transient species. *Inorg. Chim. Acta* **1986**, *123*, 167−173.

(22) Adams, K. M.; Rasmussen, P. G.; Scheidt, W. R.; Hatano, K. Structure and properties of an unsymmetrically substituted six-coordinate iron (III) porphyrin. *Inorg. Chem.* **1979**, *18*, 1892−1899.

(23) Zhang, Y.; Hallows, W. A.; Ryan, W. J.; Jones, J. G.; Carpenter, G. B.; Sweigart, D. A. Models for Steric Interactions in Heme Proteins. Structures of the Five-Coordinate Complex Iron(III) Tetraphenylporphyrin Azide and Its Six-Coordinate 1:1 Adducts with 1-Methylimidazole and 1,2-Dimethylimidazole. *Inorg. Chem.* **1994**, *33*, 3306−3312.

(24) Evans, D. R.; Reed, C. A. Reversal of H2O and OH- Ligand Field Strength on the Magnetochemical Series Relative to the Spectrochemical Series. Novel 1-equiv Water Chemistry of Iron(III) Tetraphenylporphyrin Complexes. *J. Am. Chem. Soc.* **2000**, *122*, 4660−4667.

(25) Meyer, D.; Leifels, T.; Sbaragli, L.; Woggon, W.-D. Reactivity of a new class of P450 enzyme models. *Biochem. Biophys. Res. Commun.* **2005**, *338*, 372−377.

(26) Higuchi, T.; Hirobe, M. Four recent studies in cytochrome P450 modelings: A stable iron porphyrin coordinated by a thiolate ligand; a robust ruthenium porphyrin-pyridine N-oxide derivatives system; polypeptide-bound iron porphyrin; application to drug metabolism studies. *J. Mol. Catal. A: Chem.* **1996**, *113*, 403−422.

(27) Staubli, B.; Fretz, H.; Piantini, U.; Woggon, W.-D. Synthetic Models of the Active Site of Cytochrome P-450. 1st Communication. The Synthesis of a Doubly-Bridged Iron(II)-Porphyrin Carrying a Tightly Bound Thiolate Ligand. *Helv. Chim. Acta* **1987**, *70*, 1173−1193.

(28) Narula, C. K.; Janik, J. Fr.; Duesler, E. N.; Paine, R. T.; Schaeffer, R. Convenient Synthesis, Separation, and X-ray Crystal Structure Determinations of 1(e),3(e),5(e)-Trimethylcycloborazane and 1(e),3(e),5(a)-TrimethylcycIoborazane. *Inorg. Chem.* **1986**, *25*, 3346−3349.

(29) Hawker, C. J.; Fréchet, J. M. J. Preparation of Polymers with Controlled Molecular Architecture. A New Convergent Approach to Dendritic Macromolecules. *J. Am. Chem. Soc.* **1990**, *112*, 7638−7647.

(30) Geiger, D. K.; Chunplang, V.; Scheidt, W. R. Control of Spin State in (Porphinato)iron(III) Complexes. A New Crystalline Phase of (Isothiocyanato) (pyridine) (meso -tetraphenylporphine)iron(III) with Two Magnetically Distinct Sites. *Inorg. Chem.* **1985**, *24*, 4736−4741.

(31) Hamza, M. S. A.; Pratt, J. M. Hemes and hemoproteins. Part 10. Co-ordination of imidazole and other azoles by the iron (III) porphyrin microperoxidase-8. *J. Chem. Soc., Dalton Trans.* **1994**, 1367−1371.

(32) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1975; Vol. 2 (Amines).

(33) Wichems, D. N.; Nag, S.; Mills, J.; Fishbein, J. C. Evidence for intermediates and a change in rate-limiting step in the aminolysis of the carcinogen N-methyl-N'-nitro-N-nitrosoguanidine by cyclic amines. *J. Am. Chem. Soc.* **1992**, *114*, 8846−8851.

(34) Walker, F. A.; Lo, M.-W.; Ree, M. T. Electronic Effects in Transition Metal Porphyrins. The Reactions of Imidazoles and Pyridines with a Series of Para-Substituted Tetraphenylporphyrin Complexes of Chloroiron(III). *J. Am. Chem. Soc.* **1976**, *98*, 5552−5560.

(35) Doeff, M. M.; Sweigart, D. A. Hydrogen bonding in metalloporphyrin reactions. Reaction of (tetraphenylporphinato) iron (III) chloride and N-methylimidazole. *Inorg. Chem.* **1982**, *21*, 3699−3705.

(36) Tondreau, G. A.; Sweigart, D. A. Hydrogen bonding in metalloporphyrin reactions. Reaction of (tetraphenylporphinato) iron (III) chloride and imidazole. *Inorg. Chem.* **1984**, *23*, 1060−1065.

(37) Adams, K. M.; Rasmussen, P. G.; Scheidt, R.; Hatano, K. Structure and properties of an unsymmetrically substituted six-coordinate iron(III) porphyrin. *Inorg. Chem.* **1979**, *18*, 1892−1999.

(38) Ganesh, K. N.; Sanders, J. K. M. Quinone-capped metalloporphyrins: synthesis and co-ordination chemistry. *J. Chem. Soc., Chem. Commun.* **1980**, 1129−1131.

(39) Battersby, A. R.; Hamilton, A. D. Synthesis of a doubly-bridged oxygen-carrier which shows reduced affinity for carbon monoxide. *J. Chem. Soc., Chem. Commun.* **1980**, 117−119.

(40) Meyer, D.; Woggon, W.-D. Synthesis and characterization of a new family of iron porphyrins. *Chimia* **2005**, *59*, 85−87.

(41) Almog, J.; Baldwin, J. E.; Crossley, M. J.; Debernardis, J. F.; Dyer, R. L.; Huff, J. R.; Peters, M. K. Synthesis of “capped porphyrins. *Tetrahedron* **1981**, *37*, 3589−3601.

(42) Shao, X.-B.; Jiang, X.-K.; Wang, X.-Z.; Li, Z.-T.; Zhu, S.-Z. A novel strapped porphyrin receptor for molecular recognition. *Tetrahedron* **2003**, *59*, 4881−4889.

(43) Gonçalves, D. P. N.; Sanders, J. K. M. Synthesis of new strapped porphyrins via a bisdipyrromethane condensation. *Synlett* **2007**, *2007*, 0591−0594.

(44) He, J.; Zheng, J.; Liu, J.; She, X.; Pan, X. N-heterocyclic carbene catalyzed nucleophilic substitution reaction for construction of benzopyrones and benzofuranones. *Org. Lett.* **2006**, *8*, 4637−4640.

(45) Littler, B. J.; Miller, M. A.; Hung, C.-H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. Refined synthesis of 5-substituted dipyrromethanes. *J. Org. Chem.* **1999**, *64*, 1391−1396.

(46) Geier, G. R.; Littler, B. J.; Lindsey, J. S. Investigation of porphyrin-forming reactions. Part 3.1 The origin of scrambling in dipyrromethane + aldehyde condensations yielding trans-A2B2-tetraarylporphyrins. *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 701−711.

(47) Taherpour, A. A.; Kheradmand, K. One-pot microwave-assisted solvent free synthesis of simple alkyl 1, 2, 3-triazole-4-carboxylates by using trimethylsilyl azide. *J. Heterocycl. Chem.* **2009**, *46*, 131−133.

(48) Evans, S.; Lindsay Smith, J. R. The oxidation of ethylbenzene and other alkylaromatics by dioxygen catalysed by iron (III) tetrakis (pentafluorophenyl) porphyrin and related iron porphyrins. *J. Chem. Soc., Perkin Trans. 2* **2000**, *2*, 1541−1552.

(49) Reed, C. A.; Guiset, F. A "Magnetochemical" Series. Ligand Field Strengths of Weakly Binding Anions Deduced from S = 3/2, 5/2 Spin State Mixing in Iron(III) Porphyrins. *J. Am. Chem. Soc.* **1996**, *118*, 3281−3282.

(50) Nakamura, M. Dissociation rates of axially coordinated imidazoles and formation constants of low spin ferric complexes derived from tetraphenylporphyrin and tetramesitylporphyrin. *Inorg. Chim. Acta* **1989**, *161*, 73−80.

(51) Quinn, R.; Nappa, M.; Valentine, J. S. New five-and six-coordinate imidazole and imidazolate complexes of ferric tetraphenylporphyrin. *J. Am. Chem. Soc.* **1982**, *104*, 2588−2595.

(52) Schuett, C.; Heitmann, G.; Wendler, T.; Krahwinkel, B.; Herges, R. Design and Synthesis of Photodissociable Ligands Based on Azoimidazoles for Light-Driven Coordination-Induced Spin State Switching in Homogeneous Solution. *J. Org. Chem.* **2016**, *81*, 1206−1215.

(53) Thies, S.; Sell, H.; Schuett, C.; Bornholdt, C.; Naether, C.; Tuczek, F.; Herges, R. Light-Induced Spin Change by Photodissociable External Ligands: A New Principle for Magnetic Switching of Molecules. *J. Am. Chem. Soc.* **2011**, *133*, 16243−16250.

(54) Thies, S.; Sell, H.; Bornholdt, C.; Schuett, C.; Koehler, F.; Tuczek, F.; Herges, R. Light-Driven Coordination-Induced Spin-State Switching: Rational Design of Photodissociable Ligands. *Chem. - Eur. J.* **2012**, *18*, 16358−16368.

(55) Venkataramani, S.; Jana, U.; Dommaschk, M.; Soennichsen, F. D.; Tuczek, F.; Herges, R. Magnetic Bistability of Molecules in Homogeneous Solution at Room Temperature. *Science* **2011**, *331*, 445−448.

(56) Heitmann, G.; Schuett, C.; Herges, R. Spin State Switching in Solution with an Azoimidazole-Functionalized Nickel(II)-Porphyrin. *Eur. J. Org. Chem.* **2016**, *2016* (22), 3817−3823.

(57) Heitmann, G.; Schuett, C.; Groebner, J.; Huber, L.; Herges, R. Azoimidazole functionalized Ni-porphyrins for molecular spin switching and light responsive MRI contrast agents. *Dalton Trans.* **2016**, *45*, 11407−11412.

(58) Calvete, M. J. F.; Pinto, S. M. A.; Pereira, M. M.; Geraldes, C. F. G. C. Metal coordinated pyrrole-based macrocycles as contrast agents for magnetic resonance imaging technologies: Synthesis and applications. *Coord. Chem. Rev.* **2017**, *333*, 82−107.

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