JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

ARTICLE

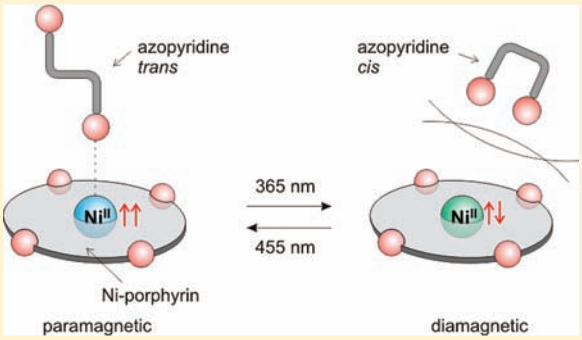
pubs.acs.org/JACS

Light-Induced Spin Change by Photodissociable External Ligands: A New Principle for Magnetic Switching of Molecules

Steffen Thies,[†] Hanno Sell,[†] Christian Schütt,[†] Claudia Bornholdt,[†] Christian Näther,[‡] Felix Tuczek,[‡] and Rainer Herges*,[†]

[†]Otto-Diels-Institut für Organische Chemie, Christian-Albrechts-Universität, Otto-Hahn-Platz 4, D-24098 Kiel, Germany
[‡]Institut für Anorganische Chemie, Christian-Albrechts-Universität, Otto-Hahn-Platz 6/7, D-24098 Kiel, Germany

S *Supporting Information*



ABSTRACT: Magnetic bistability in spin-crossover materials generally is a collective phenomenon that arises from the cooperative interaction of a large number of microscopic magnetic moments within the crystal lattice in the solid state. We now report on individual molecules in homogeneous solution that are switched between the diamagnetic and paramagnetic states at room temperature by light-driven coordination-induced spin-state switching (LD-CISSS). Switching of the coordination number (and concurrently of the spin state) was achieved by using Ni−porphyrin as a square-planar platform and azopyridines as photodissociable axial ligands. The square-planar Ni−porphyrin is diamagnetic (low-spin, $S = 0$), and all complexes with axial ligands are paramagnetic (high-spin, $S = 1$). Association constants were determined for all conceivable 1:1 and 1:2 porphyrin/azopyridine complexes. The binding constants of the trans azopyridines are larger than those of the corresponding cis isomers. Thus, upon irradiation with UV light (365 nm, trans → cis) and visible light (455 nm, cis → trans), switching of the magnetic properties was achieved. Upon substitution of the azopyridines at the 4- and 4′-positions with larger substituents, the difference in trans and cis association constants, and thus the switching efficiency, was increased. A photoinduced, reversible switching between 20 and 68% paramagnetic Ni species in solution was achieved with isopropyl substituents at room temperature.

INTRODUCTION

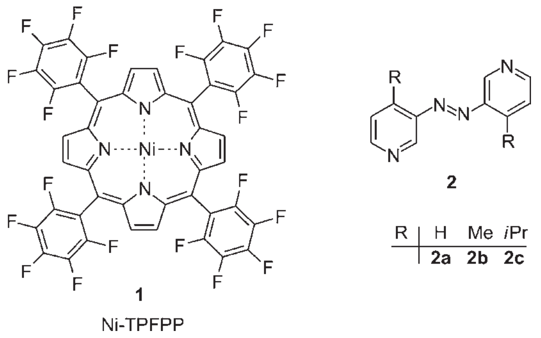
Octahedral complexes of first-row transition metals with d^4-d^7 configurations exist in different spin states depending on their ligand-field strengths.[1] This phenomenon is by far most frequently observed in Fe(II) complexes. Ligands with weak donor character favor the high-spin state, and complexes with a strong ligand field prefer the low-spin state. In complexes with ligands of medium donor strength, an entropy-driven spin crossover from low-spin to high-spin is observed. Cooperative interactions in the solid state may give rise to a more or less pronounced hysteresis and to bistable behavior.[2] Such a spin change may also be induced by light [light-induced excited-spin-state trapping (LIESST)].[3−6] Cooperative effects in the solid state again determine the lifetime of the excited state.[2] In the mid-1990s, Zarembowitch, Boillot, and co-workers published the first attempts to establish bistable properties without cooperative effects.[7−9] In the so-called ligand-driven light-induced spin change (LD-LISC) approach, one or several photochromic ligands are used to switch the ligand-field strength in metal complexes [usually Fe(II) compounds].[10−15] Upon light-induced trans−cis isomerization of styryl- and azopyridines, the ligand-field strength is changed, and thereby the equilibrium between the high-spin and low-spin states is shifted.

Besides control of the ligand-field strength, in principle, a change in coordination number could also be used to change the spin state. In case of Ni(II), increasing the coordination number from 4 to 5 (or 6) leads to a transition from the diamagnetic state ($S = 0$) to the paramagnetic state ($S = 1$).[16] The main advantage over changing the ligand-field strength (LD-LISC) is the fact that the coordination number is a "digital" parameter. Magnetic properties that are defined by switching the coordination number should be much more robust with respect to the environment, such as changes in temperature or solvent.

To demonstrate the principle of our light-driven, coordination-induced spin-state switching (LD-CISSS) concept, we initially chose Ni(II) as the transition-metal cation. The advantage of Ni(II) over Fe(II) is its stability in the oxidation state II under air. Moreover, the spin change in Ni(II) is easier to understand using qualitative molecular orbital theory, and the electronic states can be more accurately and more reliably calculated with ab initio and density functional theory (DFT) methods. Ni(II) in square-planar coordination is always diamagnetic (low-spin, $S = 0$), and it is always paramagnetic (high-spin, $S = 1$) in an octahedral, hexacoordinate ligand field.[17] However, there are examples of pentacoordinate (square-pyramidal) Ni(II) complexes for both spin states (high- and low-spin). It is evident from the literature

Received: July 28, 2011
Published: September 02, 2011

Scheme 1. Ni(II)-Tetrakis(pentafluorophenyl)porphyrin (1) and the 4,4′-Disubstituted 3-Azopyridines 2a−c Used as Axial Ligands



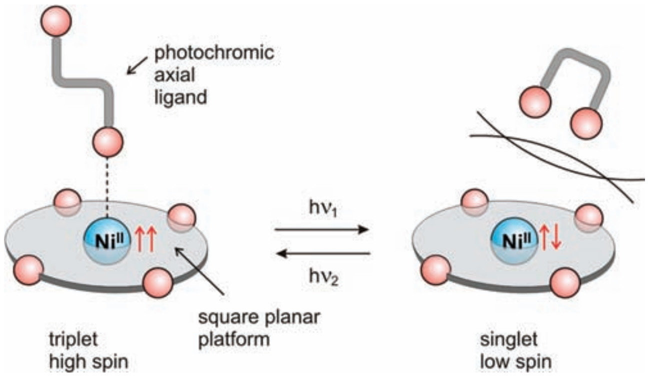


Figure 1. Schemetic representation of the spin-state switching of square-planar Ni(II) complexes by light-induced association and dissociation of a photochromic axial ligand.

and from our own investigations that the high-spin state is preferred in pentacoordinate complexes if the ligands in the square-planar environment are electron-withdrawing and the axial ligand is electron-rich (a strong σ donor). In such a complex, switching between the high-spin and low-spin states should occur if the axial ligand is coordinated (pentacoordinate, $S = 1$) or dissociated (tetracoordinate, $S = 0$).[18]

We chose Ni(II)-tetrakis(pentafluorophenyl)porphyrin (Ni-TPFPP) (**1**) as the square-planar platform complex (Scheme 1). The porphyrin framework is a planar and chemically robust aromatic π system, and the electron-withdrawing pentafluorophenyl groups ensure that the coordination of only *one* axial ligand is sufficient to switch the spin state of the complex (see below).

When a solution of **1** in toluene is titrated with pyridine, the spin state gradually changes from diamagnetic to paramagnetic. The spin change can be followed visually as a change in color from red to yellow-ocher. The measured magnetic moment of the high-spin complex, $\mu = 2.9\ \mu_B$[18] as determined by Evans measurements, is in good agreement with the theoretically expected value (2.9−3.4 μ_B; variations are due to the contribution of the orbital moment).[19] As expected, the spin change is already induced upon binding of the first axial ligand. With a value of 8.2 $L\cdot mol^{-1}$ (25 °C, toluene-d_8), the corresponding association constant K_{1s} is smaller than the association constant of the second pyridine. ($K_2 = 22.4\ L\cdot mol^{-1}$).[18] Therefore, the concentration of the pentacoordinate Ni(II) complex with only one pyridine ligand is small at all mixing ratios of porphyrin and ligand.[20] To switch the coordination number between 4 and 5 in a controlled fashion, we recently designed a molecular system with a phenylazopyridine covalently bound to Ni-tris(pentafluorophenyl)porphyrin.[21] The geometry of the azoporphyrin was chosen in such a way that the azopyridine ligand in the cis configuration coordinates to the central Ni ion but in the trans form does not bind ("record player" design). When the azopyridine is switched between the cis and trans configurations using light of two different wavelengths, the coordination number and consequently the spin state of the nickel ion change.

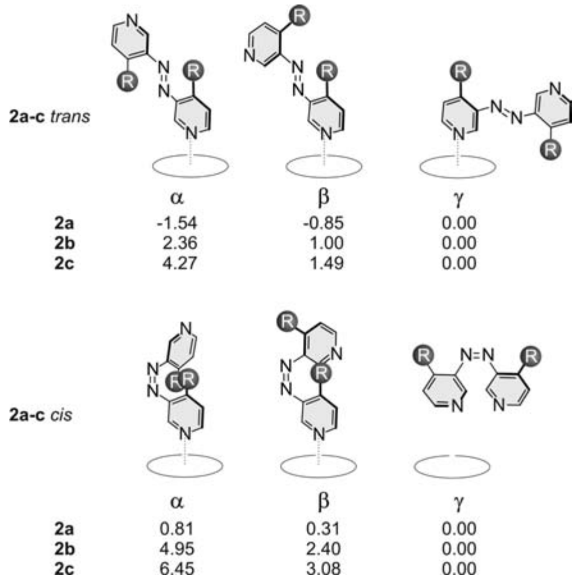
RESULTS AND DISCUSSION

General Design. In this study, we used yet another method to change the coordination number and the spin of the central Ni(II) ion: we employed photodissociable ligands (PDLs). In this approach, the switchable ligands are not covalently attached to the complex but are added to the solvent. They are designed in such a way that they bind to the Ni−porphyrin in only one of their configurations, with the other isomer being unable to coordinate because of steric reasons (Figure 1).

Azopyridines[22] are suitable PDLs for this purpose. Similar to the related azobenzenes, azopyridines isomerize from the more stable trans form to the cis configuration upon irradiation with UV light (~365 nm), and they switch back to the trans form with visible light (~440 nm).[23] According to investigations of Otsuki and co-workers on the complexation of Zn−porphyrins with 4-azopyridine, the steric hindrance increases only slightly upon switching from the trans to the cis configuration.[24] In 2-azopyridine, the cis isomer should bind more strongly than the trans form, but the cis isomer as well suffers from steric problems upon axial coordination.[25] According to our preliminary studies, 3-azopyridines (**2a**−**c**; Scheme 1) are most qualified for our experiments. Otsuki et al.[25,26] used a similar strategy to switch the fluorescence of Zn−porphyrins with 3-phenylazopyridines. An additional advantage of 3-azopyridine is the fact that the electron-withdrawing azo group is meta with respect to the pyridine, and therefore, the donor strength of the pyridine is less strongly reduced than would be the case with the azo group in the ortho or para position. However, the disadvantage of 3-azopyridine (**2a**) is that both configurations (cis and trans) exhibit three different conformations (α, β, and γ; Scheme 2). Whereas all three conformations of the trans configuration are able to bind to the Ni−porphyrin, the coordination of the γ conformation of the cis azopyridine is sterically hindered (Scheme 2). To increase the difference in binding of the cis and trans configurations, therefore, further molecular design would be necessary. Particularly, the α and β binding conformations of the cis form would have to be sterically disfavored by proper substitution to leave the nonbinding γ as the predominant conformation of the cis form in solution.

Theoretical Calculations. According to our DFT calculations (PBE/SVP), this nonbinding γ conformation is more stable than the binding conformers (α and β) and thus should prevail in the conformational equilibrium in solution. However, to prevent binding of the cis isomer efficiently, the energy difference between the binding conformations (α and β) and the nonbinding form (γ) must be larger than the binding energy of α and β to the Ni−porphyrin. To disfavor binding by the α and β conformations of the cis isomer even further, we introduced substituents at the 4- and 4′-positions [R = Me (**2b**), *i*Pr (**2c**)]. According to our

Scheme 2. Conformations α, β, and γ of 4,4′-Disubstituted 3-Azopyridines [R = H (2a), Me (2b), *i*Pr (2c)] in the (top) Trans and (bottom) Cis Configurations[a]



[a] Computed conformational energies (PBE/SVP in kcal mol^{-1}) relative to the γ conformer are given below the structures (for details, see the SI).

calculations, the energy difference between the conformations indeed increases with increasing steric demand of the substituents. For the cis isomer of **2a** (R = H), the relative energies of α, β, and γ are 0.81, 0.31, and 0.00 kcal mol^{-1}, respectively, which can be compared with 6.45, 3.08, and 0.00 kcal mol^{-1} in **2c** (R = *i*Pr). The steric hindrance is due to the fact that in the α conformations the substituents at the 4- and 4′-positions and in the β conformations the substituent at the 4-position and the H atom at the 2′-position are close to each other (Scheme 2). Remarkably, the relative stabilities of the trans isomers of **2a**–**c** are affected by substitution as well. Whereas α is the most stable conformation of the parent system **2a**, the γ conformation is the global minimum of **2b** and **2c**. This is in agreement with an X-ray structure analysis of the complex **1**·**2b** (see below). The structure reveals that **2b** is bound to the Ni–porphyrin in its γ conformation.

To investigate the steric effect of the substituents in the 4- and 4′-positions experimentally, we synthesized the three different azopyridines **2a**–**c** shown in Schemes 1 and 2.

Photochemical and Thermal Isomerization of Azopyridines 2a–c. Initially the properties of the free azopyridines **2a**–**c** were investigated in solution in the absence of Ni–porphyrin **1** [Table 1; for the UV spectra, see the Supporting Information (SI)]. Upon irradiation with UV light (365 nm), the thermodynamically less stable cis isomer is formed with more than 80% yield in the photostationary state (see Table 1). Besides the complete reisomerization to the trans configuration upon heating (half-life of 1–2 weeks at 25 °C), a photochemical isomerization is possible. Upon irradiation with 455 nm light, a photostationary state with 10–18% cis isomer is obtained. The trans/cis ratio was determined by integration of the ^{1}H NMR signals of the 4-H (**2a**), 4-methyl (**2b**), and 4-isopropyl C*H*Me_2 (**2c**) protons (see Figure 2).

Table 1. Switching Properties of 4,4′-Disubstituted 3-Azopyridines 2a–c[a]

	PSS-365 % cis	PSS-455 % cis	thermal half-life (h)
2a	81.0	17.8	337 ± 7
2b	85.0	17.4	178 ± 3
2c[b]	85.5	10.4	262 ± 3

[a] PSS-365 % cis and PSS-455 % cis are the percentages of the cis isomer in the trans/cis photostationary state (PSS) after irradiation at 365 and 455 nm, respectively. The cis ratios and thermal half-lives were determined by ^{1}H NMR spectroscopy (for details, see the text, Figure 2, and the SI). [b] The X-ray analysis data are listed in the SI.

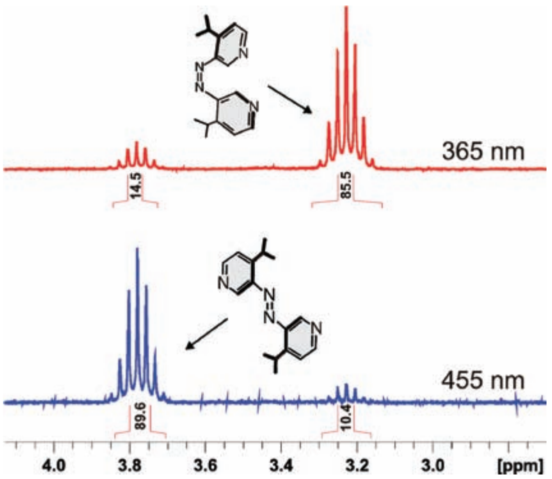


Figure 2. Determination of the trans/cis ratio in the photostationary state (PSS) of **2c** after irradiation at (top) 365 and (bottom) 455 nm. The trans/cis ratio was calculated by integration of the signals of the CH group of the isopropyl substituent.

Light-Driven Coordination-Induced Spin-State Switching (LD-CISSS) of the Ni–Porphyrin·Azopyridine Complexes 1·2a–c. Similar to the parent pyridine, the trans isomers of azopyridines **2a**–**c** form paramagnetic complexes with porphyrin **1**. We previously showed by numerous titration experiments of porphyrin **1** with various pyridines that the chemical shift of the pyrrole protons is a sensitive probe of the formation of paramagnetic Ni–porphyrins.[18] Moreover, the pyrrole proton shift can be used to determine the diamagnetic/paramagnetic ratio of the Ni–porphyrin with high accuracy. Without axial ligands, the chemical shift of the pyrrole protons in **1** is 8.54 ppm -(diamagnetic complex), and in pure pyridine-d_5 (complete complexation), a broad peak at 52.4 ppm is observed (paramagnetic complex). On the NMR time scale, the ligand exchange is very fast. Consequently, a time-averaged signal is observed at different diamagnetic/paramagnetic ratios of the Ni–porphyrin. The ratio of the paramagnetic/diamagnetic Ni–porphyrin complexes can be accurately determined from the chemical shift of the pyrrole protons according to eq 1:[18,20]

$$\frac{\text{para}}{\text{dia}} = \frac{\delta - \delta_0}{\delta_{\max} - \delta} = \frac{\delta - 8.54\text{ppm}}{52.4\text{ppm} - \delta} \tag{1}$$

where "para" denotes the sum of the concentrations of the paramagnetic Ni–porphyrin complexes, "dia" is the concentration of the diamagnetic Ni–porphyrin, δ_0 is the chemical shift (in ppm) of the pyrrole-*H* of the uncomplexed, diamagnetic porphyrin, δ is the measured chemical shift (in ppm), and $\delta_{\max}$ is the maximum chemical shift (in ppm) at complete complexation.

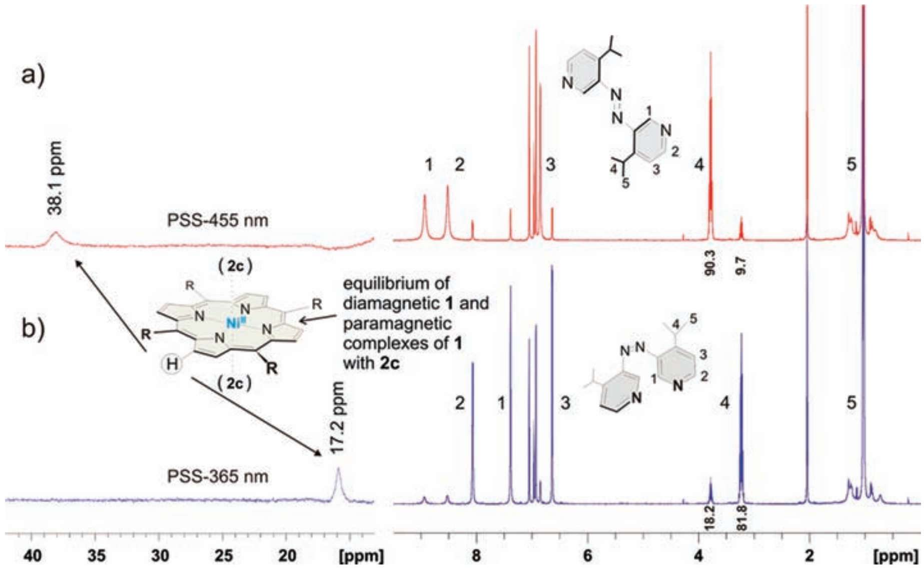


Figure 3. (a) ^{1}H NMR spectrum of Ni−porphyrin **1** in the presence of an excess of azopyridine **2c** as an axial ligand after irradiation at 455 nm in toluene-d_8. (b) ^{1}H NMR spectrum of the same solution after irradiation at 365 nm. Solution composition: 0.106 mM Ni-TPFPP (**1**) and 69.21 mM **2c** in toluene-d_8. The chemical shift of the pyrrole protons is deshielded by the paramagnetic Ni^{2+} ion. A shift from 17.2 ppm in the PSS-365 to 38.1 ppm in the PSS-455 is observed. The scale of the downfield region of the spectra has been increased for better visibility of the pyrrole signals. Since ligand exchange is fast on the NMR time scale, the pyrrole peaks are time-averaged signals of diamagnetic **1** and paramagnetic complexes of **1** with **2c**.

Table 2. Irradiation of Solutions of Ni−Porphyrin 1 and Large Excesses of Azopyridine Ligands 2a−c at 365 and 455 nm[a]

	% cis isomerization of **2a**−**c**[b]		magnetic response of **1** (% paramagnetic Ni^{2+})[c]		
	PSS-365	PSS-455	PSS-365	PSS-455	SE (%)[d]
2a	81.0	17.4	28 (20.9)	38 (25.2)	10
2b	82.4	11.4	38 (25.5)	74 (41.1)	36
2c	81.8	9.7	20 (17.2)	68 (38.1)	48

[a] PSS-365 and PSS-455 are the photostationary states at 365 and 455 nm, respectively. The compositions of the solutions were as follows: 0.106 mM Ni−porphyrin **1** and 60.63 mM **2a** (572 equiv), 75.9 mM **2b** (715 equiv), or 69.21 mM **2c** (653 equiv) in toluene-d_8 at 25 °C. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined from the ^{1}H NMR shifts of the pyrrole protons (in ppm, shown in parentheses) using eq 1. [d] Switching efficiency, defined as the difference between the percentages of paramagnetic porphyrin at PSS-455 and PSS-365.

The association of ligands **2a**−**c** to Ni−porphyrin **1** and the light-driven switching of magnetic properties were investigated by measurement of the chemical shifts of the pyrrole protons and subsequent analysis of the data using eq 1. The results were also confirmed by Evans measurements (see below). The trans/cis ratios of the azopyridine ligands were determined from the same ^{1}H NMR spectra by integration of the 4-H, 4-methyl, and 4-isopropyl group C*H* protons, as described in Figure 2.

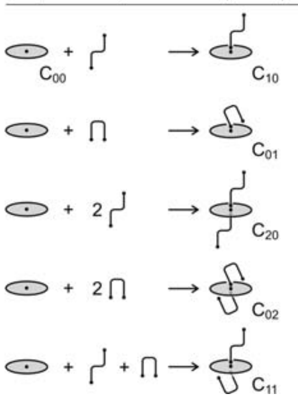
Irradiation experiments confirmed that azopyridines **2a**−**c** also switch between the trans and cis configurations in the presence of Ni−porphyrin **1** with similar photostationary states as in the absence of **1**. Alongside the photochemically induced isomerization of the azopyridines, we observed strong shifts of the ^{1}H NMR signal of the pyrrole protons of porphyrin **1** that, as anticipated, indicate a drastic change in the diamagnetic/paramagnetic ratio of the Ni porphyrins.

Figure 3 presents the ^{1}H NMR spectra of 0.106 mM Ni−porphyrin **1** in toluene-d_8 in the presence of a 653-fold excess of azopyridine **2c** after irradiation at 365 nm (81.8% cis isomer in the PSS-365) and after irradiation at 455 nm (9.7% cis isomer in PSS-455). Also in agreement with our calculations and model considerations is the fact that the switching efficiency (SE, the difference between the percentages of paramagnetic porphyrin at PSS-455 and PSS-365) increased with increasing steric demand of the substituents at the 4- and 4′-positions (Scheme 2 and Table 2). The largest photoinduced change was observed for **2c** (R = *i*Pr). After irradiation of a solution of 0.106 mM **1** and 69.21 mM **2c** (653-fold excess) in toluene-d_8 with 365 nm UV light, 20% of the nickel species in solution were paramagnetic, and after irradiation at 455 nm, this value increased to 68%.

Even though the ^{1}H NMR shift of the pyrrole protons is a very reliable and sensitive measure of the ratio of diamagnetic and paramagnetic Ni−porphyrin species, it does not provide information on the exact composition of the different Ni−porphyrin complexes in the dynamic equilibrium in solution. There are six conceivable Ni−porphyrin complexes $[\mathbf{1}\cdot\mathbf{2}_p^{\mathbf{trans}}\cdot\mathbf{2}_q^{\mathbf{cis}}$, with $(p, q) = (0, 0), (1, 0), (0, 1), (2, 0), (0, 2)$, and $(1, 1)$; Scheme 3]. For the sake of simplicity, we use the denotation C_{pq} to define the complex composition, where p and q are the numbers of ligands in the trans and cis configurations, respectively. Ni−porphyrin **1** without axial ligands (C_{00}) is the only diamagnetic Ni species. All of the complexes with one or two azopyridines in the trans or cis configuration (C_{01}, C_{10}, C_{20}, C_{02}, and C_{11}) are paramagnetic.

To prove our concept of photodissociable ligands and quantify the weaker binding of the cis configuration, we performed ^{1}H NMR titration experiments and determined the association constants β_{pq} for the trans and cis isomers of **2a**−**c** (Scheme 3; also see the SI). For each ligand **2a**−**c**, a 0.106 mM solution of Ni−porphyrin **1** in toluene-d_8 was titrated (**2a**, 0−572 equiv; **2b**, 0−1288 equiv; **2c**, 0−331 equiv). A ^{1}H NMR spectrum was measured at each titration point in the PSS-365 and PSS-455.

Scheme 3. Association Constants of Ni−Porphyrin 1 with Azopyridine Derivatives 2a−c at 298 K in Toluene-d_8



$1 + p\, 2^{trans} + q\, 2^{cis} \rightarrow 1\cdot 2_p^{trans}\cdot 2_q^{cis}$	β_{pq}	2a	2b	2c
C_{10}	β_{10}[a]	4.79 ± 0.10	10.25 ± 0.06	9.99 ± 0.03
C_{01}	β_{01}[a]	1.74 ± 0.11	1.50 ± 0.03	0.30 ± 0.01
C_{20}	β_{20}[b]	215.89 ± 3.70	467.10 ± 2.46	383.41 ± 1.52
C_{02}	β_{02}[b]	124.05 ± 4.32	64.07 ± 1.05	8.59 ± 0.71
C_{11}	β_{11}[b]	159.86 ± 8.83	66.65 ± 6.34	34.17 ± 3.78

[a] Association constant in $L\cdot mol^{-1}$. [b] Association constant in $L^2\cdot mol^{-2}$.

The trans/cis ratio and the ^{1}H NMR shift of the pyrrole protons were both determined from the same spectrum. The association constants for all of the complexes were calculated using nonlinear titration curve fitting.[27,28] The results were confirmed independently using linear curve fitting as described previously.[18] It is highly unlikely at a more than 500-fold excess of the ligand that there are complexes involving more than one Ni−porphyrin. However, to rule out definitively 2:2 or higher complexes or even oligomers (as observed in the solid state; see the crystal structure below), we also checked the curve fitting based on our model (Scheme 3) at higher concentrations and a much lower excess of the ligand. At a **1** concentration of 0.85 mM with a 50-fold excess of **2b**, small deviations (15% deviation between the measured and calculated ^{1}H NMR shifts of the pyrrole protons) from our fitting model were observed, indicating the presence of complexes that were not included in the model. Under the conditions used for the determination of the association constants and in the switching experiments, however, higher complexes can be excluded.

The association constant of Ni−porphyrin **1** with azopyridine *trans*-**2a** (β_{10} = 4.79 $L\cdot mol^{-1}$) is smaller than the corresponding binding constant of parent pyridine (k_1 = 8.20 $L\cdot mol^{-1}$),[18] which is probably due to the electron-withdrawing effect of the azo group.[29] A methyl group at the para position with respect to the pyridine nitrogen atom (as in **2b**) increases the binding (donor) strength (β_{10} = 10.25 $L\cdot mol^{-1}$). The corresponding isopropyl-substituted azopyridine **2c** binds slightly less efficiently (β_{10} = 9.99 $L\cdot mol^{-1}$), probably because of weak steric interactions in the γ conformation of **2c** with the porphyrin ring (see the X-ray structure below). However, as expected and predicted by the calculations, the steric effects are much more pronounced in the cis configurations of azopyridines **2a**−**c**. In *cis*-**2b**, the steric hindrance that disfavors the binding conformations α and β overcompensates for the inductive effect of the methyl group. The bulky isopropyl group reduces the binding constant of **2c** (β_{01} = 0.3 $L\cdot mol^{-1}$) even more efficiently, by a factor of 5.8 with respect to the unsubstituted system **2a** (β_{01} = 1.74 $L\cdot mol^{-1}$). The weak steric effects in the trans configurations and the strong decrease in binding affinities with increasing bulk of the substituents at the 4- and 4′-positions in the cis forms give rise to an increasing difference in binding between the trans and cis forms. The ratios of binding constants β_{10}/β_{01} for the trans and cis configurations of **2a**−**c** are 2.75, 6.83, and 33.30. Similar trends were also observed for the formation of the 1:2 complexes C_{20}, C_{02}, and C_{11}. The ratios of association constants β_{20}/β_{02} for **2a**−**c** are 1.74, 7.29, and 44.63.

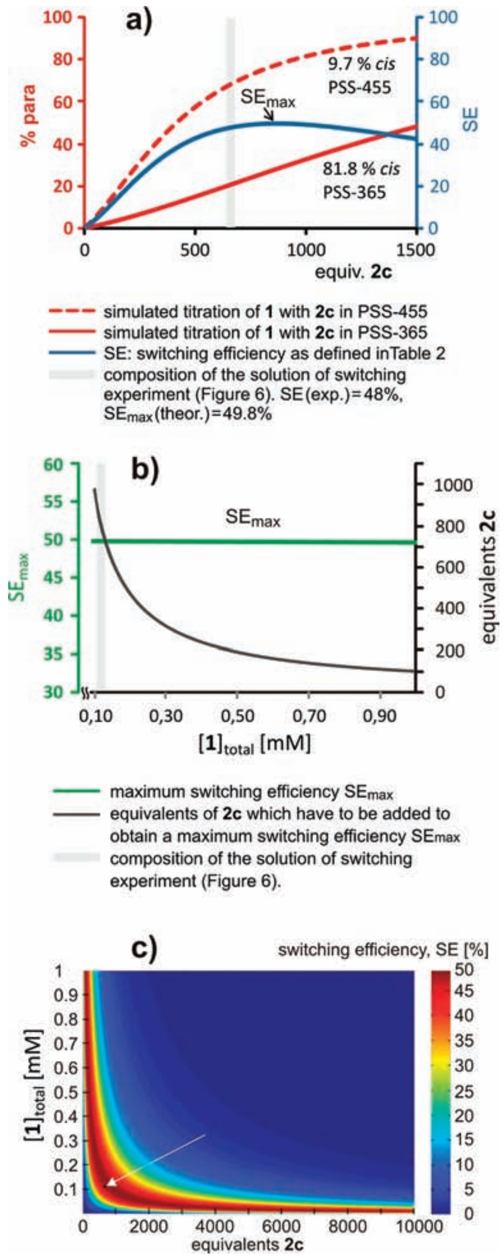


Figure 4. (a) Calculated percentages of paramagnetic Ni−porphyrin complexes in the two PSSs (red curves) and the switching efficiency (blue curve) as functions of the number of equivalents of **2c** added to a 0.106 mM solution of Ni−porphyrin **1**. The data were calculated from the association constants (Scheme 3). (b) Maximum switching efficiency (SE_{max}) as a function of the total concentration of Ni−porphyrin **1** ($[\mathbf{1}]_{total}$). (c) SE as a function of $[\mathbf{1}]_{total}$ and the number of equivalents of **2c**. The composition of the solution in the switching experiments (Figure 6) is indicated with an arrow.

The knowledge of the association constants for all of the complexes involved in the equilibria allows the calculation of the ratios of porphyrin **1** and axial ligands **2a**−**c** that lead to the optimum (i.e., largest) switching efficiencies. In Figure 4, the calculated percentages of paramagnetic Ni species at a concentration of 0.106 mM are plotted as functions of the number of added equivalents of axial ligand **2c** in both PSSs (red curves), and the SE (blue curve) is given as well. The maximum SEs (SE_{max}) were attained when excesses of 679, 645, and 867 equiv of ligands **2a**−**c**, respectively, were added. SE_{max} increases with increasing steric bulk of the substituents in **2a**−**c** (10.6, 36.0, and 49.8%). The experimental SEs listed in Table 2 compare well with the calculated SE_{max} values. (The experimental data listed in Table 2 were determined close to the optimum mixing ratios of **1** and **2a**−**c**, shown for **2c** by the gray bar in Figure 4). The lower the initial concentration of Ni−porphyrin **1** ($[\mathbf{1}]_{total}$), the greater is $eq_{\mathbf{2a-c}}$, defined as number of equivalents of ligands **2a**−**c** that must be added to achieve SE_{max} (i.e., $eq_{\mathbf{2a-c}}$ is inversely proportional to $[\mathbf{1}]_{total}$). However, it is important to note that SE_{max} does not depend on the total concentration of **1** ($[\mathbf{1}]_{total}$)! Hence, the maximum switching efficiency SE_{max} is an unambiguous number that characterizes a chemical system whose properties are changed by changing association constants.

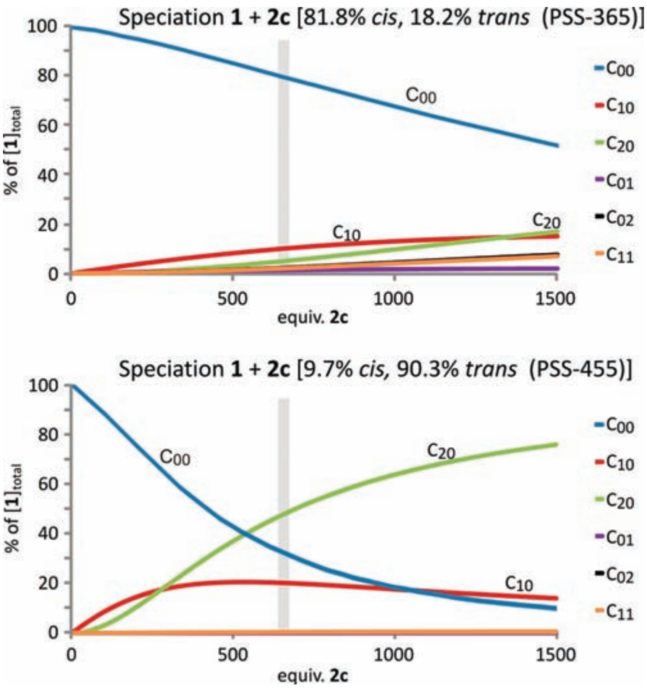


Figure 5. Speciation plot of the six complexes C_{00}, C_{10}, C_{20}, C_{01}, C_{02}, and C_{11} of **1** as a function of the number of equivalents of added **2c** in the PSS-365 (top) and PSS-455 (bottom) for $[\mathbf{1}]_{total}$ = 1.06 mM. The gray bars indicate the composition of the solution that was used for the switching experiments (Figure 6).

A speciation diagram (Figure 5) reveals that the predominant species in the PSS-365 of **2c** (81.8% cis, 18.2% trans) at the mixing ratio of **1** and **2c** that corresponds to SE_{max} is the bare Ni−porphyrin **1** without axial ligands (C_{00}, 79.5%). In the PSS-455 (9.7% cis, 90.3% trans), the complex with two *trans*-**2c** ligands prevails (C_{20}, 47.6%). The concentrations of the 1:1 complexes (C_{10} and C_{01}) and the complexes including the cis configuration of the ligand (C_{01}, C_{02}, and C_{11}) are always below 21%.

Photochemical switching experiments were performed with solutions of **1** ($[\mathbf{1}]_{total}$ = 0.106 mM) containing 679, 650, and 867 equiv of **2a**−**c**, respectively, in toluene-d_8. The solutions were irradiated in an alternate sequence using light-emitting diodes with wavelengths of 365 nm (Nichia NC4U133) and 455 nm (NS6C083AT) in an NMR tube until the PSS was reached. Figure 6 shows that the switching process is fully reversible over a large number of cycles. Side products or fatigue were not observed.

The magnetic properties of a solution of Ni−porphyrin **1** and azopyridine *trans*-**2b** in toluene-d_8 were also investigated using the Evans method with tetramethylsilane as the reference.[19,30−32] A large excess of the axial ligand was employed to ensure that the Ni−porphyrin would be completely converted to the paramagnetic form, which was confirmed by the chemical shift of the pyrrole protons of 52.4 ppm[18] (for details, see the SI). The diamagnetic correction can be neglected when a similar diamagnetic complex is used as a reference.[33] Therefore, we synthesized the porphyrin Zn-TPFPP containing Zn as the central metal ion, and a solution of this complex with same concentration of *trans*-**2b** was used as the reference.

By these means, a molar paramagnetic susceptibility of $\chi_M^P = 3594 \times 10^{-6}\ cm^3 \cdot mol^{-1}$ was determined for Ni−porphyrin **1**, and a magnetic moment of $\mu_{eff} = 2.94\ \mu_B$ was calculated for the paramagnetic Ni^{2+}. This value is in good agreement with the limiting value of the magnetic moment (2.9 μ_B) that was obtained by titration of Ni−porphyrin **1** with pyridine.[18]

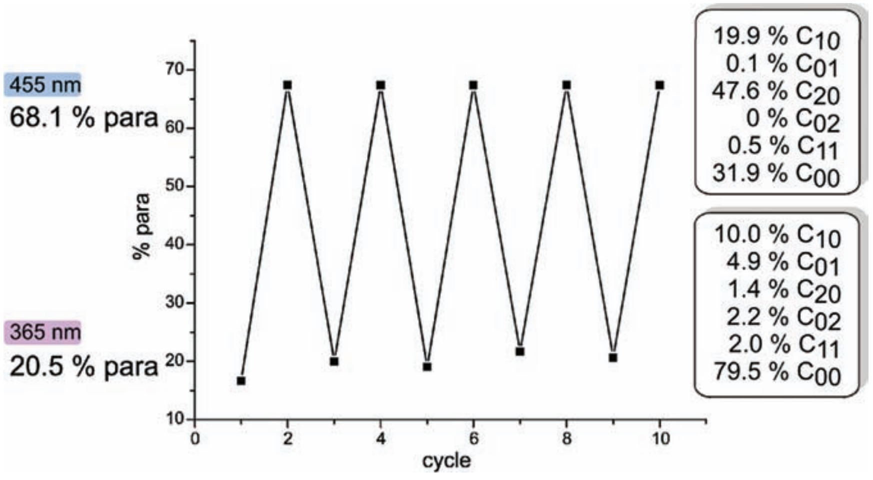


Figure 6. Light-driven coordination-induced spin-state switching (LD-CISSS) of Ni−porphyrin **1** in solution ($[\mathbf{1}]_{total}$ = 0.106 mM in toluene-d_8) in the presence of an excess of azopyridine **2c** (653 equiv) by alternating irradiation at 365 and 455 nm (also see Table 2).

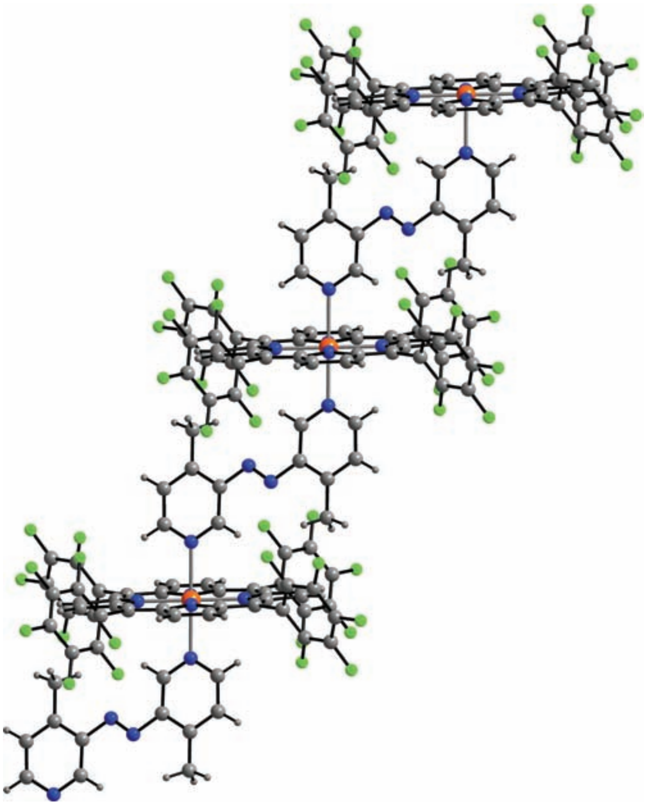


Figure 7. Crystal structure of a coordination polymer of Ni-TPFPP (**1**) and the γ form of azopyridine *trans*-**2b**. The X-ray analysis data are listed in the SI.

We also investigated the complex of Ni−porphyrin **1** with azopyridine **2b** in the solid state. The X-ray analysis revealed that coordination polymers are formed with alternating units of the bidentate γ conformation of *trans*-**2b** and Ni−porphyrin **1** with its two axial coordination sites. (Figure 7). Hence, the Ni ions in these crystals should be paramagnetic. To investigate the magnetic properties in the solid state, the magnetic susceptibility was determined as a function of the temperature over the range from 300 to 2 K in an applied field of 0.1 T (for plots of χ_M vs T, χ_M^{-1} vs T, and $\chi_M T$ vs T, see the SI). A magnetic moment of $\mu_{\text{eff}} = 2.9 \pm 0.1\ \mu_B$ was determined, in good agreement with the solution value of $2.94\ \mu_B$ (see above). Photoswitching obviously is not possible in the solid state. Even after prolonged irradiation of the crystals of **1**·**2b** with 365 nm UV light, no change in the X-ray powder diffractogram was observed. This could be due to the fact that the rigid coordination polymer framework prevents a geometry change or to quenching of the $\pi-\pi^*$ excitation of **2b** by the porphyrin chromophore of **1**.[34] In solution, under the conditions applied for our switching experiments, energy transfer between azopyridines **2a**−**c** and Ni−porphyrin **1** is unlikely, however. At a more than 600-fold excess of **2a**−**c**, and since the ligand exchange at the Ni−porphyrin occurs very rapidly, it is more likely that the vast excess of the uncomplexed azopyridine ligand undergoes photoisomerization and replaces the other isomer within the ligand sphere. Further evidence that there is no energy transfer involved is provided by the fact that the photostationary states of **2a**−**c** (PSS-365 and PSS-455) are similar in the presence and absence of Ni−porphyrin **1**.

■ CONCLUSION

We have proposed a new approach for switching the magnetic properties of homogeneous solutions at room temperature by light-driven ligand-induced spin-state switching (LD-CISSS).[18,21] Azopyridines **2a**−**c** were used as photodissociable axial ligands (PDLs) to control the coordination number and concurrently the spin state of Ni−porphyrin **1**. In the trans configuration, the azopyridines bind to the Ni−porphyrin as axial ligands, forming paramagnetic ($S = 1$) 1:1 and 2:1 complexes. Upon light-induced isomerization to the cis configuration, the binding is drastically reduced because of steric hindrance. By dissociation of the cis azopyridines, the diamagnetic ($S = 0$) square-planar Ni−porphyrin is formed. The difference between the binding constants for the cis and trans configurations was increased and systematically investigated by introducing substituents at the 4- and 4′-positions of the azopyridines [R = H (**2a**), CH_3 (**2b**), *i*Pr (**2c**)]. Association constants for all of the 1:1 and 2:1 complexes involving the cis and trans configurations of **2a**−**c** with Ni−porphyrin **1** were determined by NMR titration. Upon alternating irradiation of a solution of Ni−porphyrin **1** and a large excess of azopyridine **2c** with UV light (365 nm) and violet-blue light (455 nm), the percentage of paramagnetic Ni centers was switched between 20.5 and 68.1%, and the molar paramagnetic susceptibility was reversibly changed between $\chi_M^P = 1006 \times 10^{-6}$ and $2444 \times 10^{-6}\ \text{cm}^3 \cdot \text{mol}^{-1}$. No side products or fatigue was observed over a large number of cycles. Thus, in regard to reversibility and efficiency, the system is superior to previous LD-LISC systems.

The switching efficiency (SE) depends on the mixing ratio of Ni−porphyrin **1** and the axial ligand **2a**−**c**. We define the maximum SE (SE_{max}) as the SE at the optimum mixing ratio of the two components. SE_{max} depends on the photostationary states at the two wavelengths (SE of the ligand) and the association constants. However, it is independent of the absolute concentrations of the components (**1** and **2a**−**c**). Hence, SE_{max} is a characteristic parameter that can be used to define the efficiency of systems whose properties are switched with PDLs.

In contrast to classical spin crossover and the LIESST effect, the LD-CISSS approach thus allows spin-state switching at room temperature without cooperative interactions. This opens new applications such as the switching of isolated molecules on surfaces,[35] switching of the relaxivity of contrast agents for magnetic resonance imaging,[36,37] and switching catalysis.[38,39]

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Syntheses of **1** and **2a**−**c** and the corresponding analytical data. This material is available free of charge via the Internet at http://pubs.acs.org. The crystal structure data for **2c** (CCDC 800914) and $(\mathbf{1}\cdot\mathbf{2b})_n$ (CCDC 800913) are available from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ AUTHOR INFORMATION

Corresponding Author

rherges@oc.uni-kiel.de

■ ACKNOWLEDGMENT

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft via SFB 677.

REFERENCES

(1) Sato, O.; Tao, J.; Zhang, Y.-Z. *Angew. Chem.* **2007**, *119*, 2200–2236. *Angew. Chem., Int. Ed.* **2007**, *46*, 2152–2187.

(2) Murray, K. S.; Kepert, C. J. *Top. Curr. Chem.* **2004**, *233*, 195–228.

(3) Šalitroš, I.; Madhu, N. T.; Boča, R.; Pavlik, J.; Ruben, M. *Monatsh. Chem.* **2009**, *140*, 695–733.

(4) Renz, F.; Oshio, H.; Ksenofontov, V.; Waldeck, M.; Spiering, H.; Gütlich, H. *Angew. Chem.* **2000**, *112*, 3832–3834. *Angew. Chem., Int. Ed.* **2000**, *39*, 3699–3700.

(5) Létard, J.-F. *J. Mater. Chem.* **2006**, *16*, 2550–2559.

(6) Boldog, I.; Gaspar, A. B.; Martínez, V.; Pardo-Ibañez, P.; Ksenofontov, V.; Bhattacharjee, A.; Gütlich, P.; Real, J. A. *Angew. Chem.* **2008**, *120*, 6533–6537. *Angew. Chem., Int. Ed.* **2008**, *47*, 6433–6437.

(7) Roux, C.; Zarembowitch, J.; Gallois, B.; Granier, T.; Claude, R. *Inorg. Chem.* **1994**, *33*, 2273–2279.

(8) Boillot, M.-L.; Roux, C.; Audière, J.-P.; Dausse, A.; Zarembowitch, J. *Inorg. Chem.* **1996**, *35*, 3975–3980.

(9) Boillot, M.-L.; Chantrine, S.; Zarembowitch, J.; Lallemond, J. Y.; Prunet, J. *New J. Chem.* **1999**, *23*, 179–184.

(10) Sour, A.; Boillot, M.-L.; Rivière, E.; Lesot, P. *Eur. J. Inorg. Chem.* **1999**, 2117–2119.

(11) Sénéchal-David, K.; Zaman, N.; Walko, M.; Halza, E.; Rivière, E.; Guillot, R.; Feringa, B. L.; Boillot, M.-L. *Dalton Trans.* **2008**, 1932–1936.

(12) Kolb, J. S.; Thomson, M. D.; Novosel, M.; Sénéchal-David, K.; Rivière, E.; Boillot, M.-L.; Roskos, H. G. *C. R. Chim.* **2007**, *10*, 125–136.

(13) Boillot, M.-L.; Pillet, S.; Tissot, A.; Rivière, E.; Claiser, N.; Lecomte, C. *Inorg. Chem.* **2009**, *48*, 4729–4736.

(14) Hirose, S.; Hayami, S.; Maeda, Y. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2059–2066.

(15) Hasegawa, Y.; Kume, S.; Nishihara, H. *Dalton Trans.* **2009**, 280–284.

(16) Baker, E. W.; Brookhart, M. S.; Corwin, A. H. *J. Am. Chem. Soc.* **1964**, *86*, 4587–4590.

(17) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley-Interscience: New York, 1999.

(18) Thies, S.; Bornholdt, C.; Köhler, F.; Sönnichsen, F. D.; Naether, C.; Tuczek, F.; Herges, R. *Chem.—Eur. J.* **2010**, *16*, 10074–10083.

(19) Crawford, T. H.; Swanson, J. *J. Chem. Educ.* **1971**, *48*, 382–386.

(20) Walker, F. A.; Hui, E.; Walker, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 2390–2397.

(21) Venkataramani, S.; Jana, U.; Dommaschk, M.; Sönnichsen, F. D.; Tuczek, F.; Herges, R. *Science* **2011**, *331*, 445–448.

(22) Campell, N.; Henderson, A. W.; Taylor, D. *J. Chem. Soc.* **1953**, 1281–1285.

(23) Brown, E. V.; Granneman, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 621–627.

(24) The implementation of steric hindrance with respect to the coordination of *cis*-4-phenylazopyridine was successful only with very large substituents (the shuttlecock principle). See: (a) Suwa, K.; Otsuki, J.; Goto, K. *Tetrahedron Lett.* **2009**, *50*, 2106–2108. (b) Suwa, K.; Otsuki, J.; Goto, K. *J. Phys. Chem. A* **2010**, *114*, 884–890. (c) Otsuki, J.; Harada, K.; Araki, K. *Chem. Lett.* **1999**, 269–270.

(25) Otsuki, J.; Narutaki, K. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1537–1544.

(26) Otsuki, J.; Narutaki, K.; Bakke, J. M. *Chem. Lett.* **2004**, *33*, 356–357.

(27) Piero, S. D.; Melchior, A; Polese, P.; Portanova, R.; Tolazzi, M. *Ann. Chim.* **2006**, *96*, 29–49.

(28) Thordarson, P. *Chem. Soc. Rev.* **2011**, *40*, 1305–1323.

(29) Shorter, J. Electronic Effects of Hydrazo, Azo and Azoxy Groups. In *The Chemistry of the Hydrazo, Azo, and Azoxy Groups, Volume 2*; Patai, S., Ed.; Wiley: New York, 1997.

(30) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005.

(31) Piguet, C. *J. Chem. Educ.* **1997**, *74*, 815–816.

(32) Naklicki, M. L.; White, C. A.; Plante, L. L.; Evans, C. E. B.; Crutchley, R. J. *Inorg. Chem.* **1998**, *37*, 1880–1885.

(33) The usual estimation of the contribution of the diamagnetic susceptibility to the total molar magnetic susceptibility by using increments would lead to a large error (underestimation) because the contribution of the strong diatropic ring current in the large [18]annulene perimeter of the porphyrin would thus be neglected.

(34) Whitten, D. G.; Wildes, P. D.; DeRosier, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 7811–7823.

(35) Matino, F.; Schull, G.; Jana, U.; Köhler, F.; Berndt, R.; Herges, R. *Chem. Commun.* **2010**, *46*, 6780–6782.

(36) Lauffer, R. B. *Chem. Rev.* **1987**, *87*, 901–927.

(37) Christian-Albrechts-Universität Kiel, Universitätsklinikum Schleswig-Holstein, DE 10 2010 034 496, Aug 16, 2010, patent pending.

(38) Stoll, R. S.; Peters, M. V.; Kuhn, A.; Heiles, S.; Goddard, R.; Bühl, M.; Thiele, C. M.; Hecht, S. *J. Am. Chem. Soc.* **2009**, *131*, 357–367.

(39) Berkessel, A.; Bats, J. W.; Schwarz, C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 106–108.