Inorganic Chemistry © Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Phenanthroline-Based Molecular Switches for Prospective Chemical Grafting: A Synthetic Strategy and Its Application to Spin-Crossover Complexes

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Supporting Information

ABSTRACT: 1,10-Phenanthroline represents a well-known versatile ligand system finding many applications in chemistry, biology, and material science. The properties and thus the use of these molecules are determined by coordinating metal ions and ligand substituents. Advanced ligand systems that, for instance, feature simultaneously an integrated photochrome and a surface anchoring group require the introduction of several differing substituents and the synthesis of asymmetric derivatives. In spite of a long history of the ligand system—and to our great surprise—a general synthetic approach allowing the introduction of differing substituents at positions (3,8) and (5,6) of 1,10-phenanthroline is



not known. Here, we present a general approach for the synthesis of such phenanthrolines. The approach is used to integrate a diarylethene photochrome into a functionalized phenanthroline and thus to synthesize a novel photoswitchable phenanthroline and a corresponding spin-crossover molecular photoswitch. The functionality of both the ligand and its iron(II) complex at room temperature has been demonstrated. The importance of this work for chemical grafting of molecular switches based on phenanthrolines is emphasized.

INTRODUCTION

1,10-Phenanthroline (phen) is a classical chelating ligand in coordination chemistry. Its physicochemical properties, relative easy access to derivatives, and the ability to form complexes with most metal ions resulted in its appearance in many branches of science. Molecular recognition and sensing, luminescent and magnetic materials, photosensitizers, DNA/ RNA cleaving reagents, catalysis, and self-assembly are some representative research areas with a strong contribution of phen and its metal complexes.^{1–3}

Introduction of photochromic units into phen renders the latter photoisomerizable,⁴⁻⁶ which provides access to versatile molecular switches.⁷ Thus, spirooxazine^{8,9} and diarylethene¹⁰ photochromes have been successfully integrated¹¹⁻¹³ into phen ligands, and spectacular photoswitching of luminescent¹³ and magnetic^{16–20} properties of corresponding metal complexes, as well as light-controlled binding of metal-free ligands to DNA,²¹ have been demonstrated in recent years.

In our previous work,^{19,20} a photoisomerizable *phen-DAE* ligand, which comprises phen and an electronically coupled diarylethene (DAE) photochrome (Scheme 1), was used to achieve an unprecedented remote control of magnetism in spin-crossover^{22,23} (SCO) metal complexes. Thus, an iron(II) complex with a phen-DAE ligand was successfully switched between paramagnetic high-spin (HS) and diamagnetic low-

Scheme 1. Photoisomerizable phen-DAE Ligand Featuring a **Diarylethene Photochrome**



spin (LS) states with light at room temperature (RT) via the photoisomerization of the diarylethene unit. Unique reversible photoswitching was demonstrated in solution and in the solid state. For many practical applications,^{24–30} thin films of functional molecules are required.³¹⁻³³ Thus, using a physical vapor deposition technique, corresponding thin films were prepared, which, however, showed relatively poor photoswitchability.¹⁷ This is presumably due to unfavorable interactions between molecules and the surface, which is a

Received: May 15, 2019

known phenomenon in SCO research.^{34,35} A possible alternative to physisorption—chemisorption—might provide a great opportunity to diminish or even eliminate such destructive interactions by decoupling the absorbed molecules from the substrate.

For successful chemisorption, the parent SCO molecular switch should be modified: an appropriate anchoring group should be introduced at a proper position of the molecule without functionality loss. Very recently, we showed that positions 3,8 of *phen* (Scheme 1) should be suitable for introducing anchors.¹⁸ However, and to our great surprise, a general synthetic scheme allowing introduction of substituents at positions 3,8 (prospective anchors) with simultaneous functionalization at positions 5,6 (photoactive site) of *phen* is not known.

Here, we present a general approach for the synthesis of *phen* derivatives with *unequal* substituents at positions (5,6) and 3 (Scheme 2). Note that the preparation of some *phen* derivatives with *equal* substituents was mentioned in old literature.^{36,37} We have successfully used this approach to introduce a pro-anchoring³⁸ phenyl group into *phen-DAE*. A novel *Ph-phen-DAE* ligand (Scheme 3) and a corresponding SCO molecular switch [Fe^{II}(*Ph-phen-DAE*)(H₂Bpz₂)₂] (H₂Bpz₂ = bis(1-pyrazolyl)dihydroborate(1–)) have been synthesized, and their switchability at RT has been demonstrated. The developed synthetic strategy opens the route toward novel asymmetric *phen* derivatives including *phen-DAE*-based molecular switches capable of chemisorption.

Scheme 2. A Successful Synthetic Approach toward 3,5,6-Trisubstituted *phen*'s with Differing Substituents ¹R and ²R



EXPERIMENTAL SECTION

Materials. All starting materials and solvents were utilized as received without further purification unless otherwise noted. Pure anhydrous solvents were collected from a solid-state solvent purification system, Glass Contour (Irvine, CA). (2,5-Dimethylth-iophen-3-yl)boronic acid,^{39,40} bis(1-pyrazolyl)borohydride,⁴¹ and 5,6-dibromo-1,10-phenanthroline⁴² were prepared according to literature methods with minor modifications.

Instrumentation. Elemental analyses were carried out with a EURO EA analyzer from EuroVector. Magnetic susceptibility data on solid samples were collected with a Quantum Design MPMS 3 Magnetometer. DC susceptibility data were collected on powder samples restrained within a polycarbonate gel capsule in the applied magnetic field of 1 T at 1 K min⁻¹ heating/cooling rate and 2 K intervals. The magnetic susceptibility data were corrected for diamagnetism using an estimation $\chi_{m,diamag} = 1/2 M_w \cdot 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ with M_w being the molar mass of the compound.⁴³ The χT product was fitted using the van't Hoff equation (eq 1) to give the enthalpy and entropy changes ΔH and ΔS for the LS \rightarrow HS conversion with χ_{LT} and χ_{HT} being low- and high-temperature limits for molar magnetic susceptibility, respectively.

$$\chi T = \frac{\chi_{LT} T + \chi_{HT} T e^{(-\Delta H + T\Delta S)/RT}}{1 + e^{(-\Delta H + T\Delta S)/RT}}$$
(1)

⁵⁷Fe Mössbauer spectra were recorded on a WissEl Mössbauer spectrometer (MRG-500) in constant-acceleration mode. ⁵⁷Co/Rh was used as the radiation source. The temperature of the samples was controlled by an MBBC-HE0106 Mössbauer He/N₂ cryostat within an accuracy of ± 0.3 K. Isomer shifts were determined relative to α iron at 298 K. The program *MFIT* was used for the quantitative analysis of spectra.⁴⁴ NMR spectra were recorded with JEOL ECX400, JEOL ECZ400S, JEOL EX270, and Bruker Avance III HD 600 in rotating 5 mm o.d. tubes and processed with *Delta V4.0* software provided by JEOL Ltd. Electronic absorption spectra were recorded with a Shimadzu UV 3600 spectrophotometer.

Photochemisty. All solutions for photoexperiments were prepared under inert conditions and sealed in custom-made Quartz SUPRASIL cells (QS). An L.O.T.-Oriel Xe(OF) 150 W arc lamp equipped with appropriate filters was used as a light source. Water and bandpass ($\lambda = 282 \pm 5$ nm) filters were used for cyclization with UV, while a set of water, heat absorbing (KG-5), and long-pass ($\lambda \ge 400$ nm) filters was used for cycloreversion with visible. Further cyclization experiments were also conducted with the sample positioned between two opposing UV analytical lamps (Herolab GmBh, 15W, $\lambda = 254$ nm).

Crystallographic Data. The material consisted exclusively of very thin and weakly diffracting crystals (see Figure S12). A suitable single crystal was embedded in protective perfluoropolyalkyether oil on a microscope slide, and a single specimen was selected and subsequently transferred to the cold nitrogen gas stream of the diffractometer. Intensity data were collected using Mo K α radiation (λ = 0.71073 Å) on a Bruker Kappa PHOTON II $I\mu S$ Duo diffractometer equipped with QUAZAR focusing Montel optics at temperatures of 100 and 273 K. Data were corrected for Lorentz and polarization effects, and semiempirical absorption corrections were performed on the basis of multiple scans using SADABS.⁴⁵ The structures were solved by direct methods (SHELX XT)⁴⁶ and refined by full-matrix least-squares procedures on F² using SHELXL 2016/ 6.47 All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in positions of optimized geometry, and their isotropic displacement parameters were tied to those of the corresponding carrier atoms by a factor of either 1.2 or 1.5. *Olex2* was used to prepare material for publication.⁴⁸ Crystallographic data, data collection, and structure refinement details are given in Table S1. At both temperatures the thiophene ring C25, C26, C27, S2, and C28 seemed to be slightly disordered with a change in positions of S2 and C27 (and consequently C29). However, attempts to refine corresponding split positions remained unsuccessful, probably due to the fact that the alternative orientation was occupied by only a small percentage. The compound crystallized with a total of 1.5 molecules of toluene per formula unit with half a toluene molecule being situated disordered on the crystallographic inversion center (C201-C204). The other toluene molecule was also disordered. Two alternative orientations were refined and resulted at 100 K in site occupancies of 47.4(9) and 52.6(9)% and at 273 in site occupancies of 49(2) and 51(2)% for the atoms C101–C107 and C111-C117, respectively. Similarity and pseudoisotropic restraints (with esd's of 0.01 and 0.02) were applied to the anisotropic displacement parameters of the disordered atoms. Fixed distance restraints (with esd's of 0.01) were applied to some of the distances in the disordered toluene molecules.

Synthesis. 5,6-Dibromo-3-iodo-1,10-phenanthroline (5). 5,6-Dibromo-1,10-phenanthroline (1.338 g, 4.1 mmol) and iodine (3.642 g, 14.35 mmol) were dissolved in 32 mL of 1,2-dichloroethane. The reaction mixture was stirred vigorously and heated to reflux before *tert*-butyl hydroperoxide (TBHP) (70% in H₂O, 36.0 mL, 262.8 mmol) was added. After 7 h more TBHP (18.0 mL, 131.4 mmol) was added. After 24 h, the reaction mixture was cooled down to RT and poured into a saturated $Na_2S_2O_3$ solution. The solution turned yellow after stirring for 15 min and was extracted with CHCl₃ (1 × 150 mL, 4 × 50 mL). The combined organic phases were dried

Scheme 3. Explored Synthetic Routes and the Final Synthesis of a Photoisomerizable Ph-phen-DAE Ligand 7



in vacuo. The remaining solid was purified via SiO₂ column chromatography using CHCl₃:EtOAc (1:1) with 5% triethylamine as an eluent. Pure **5** was obtained as a white powder after recrystallization from boiling toluene. Yield: 381 mg, 20%. Elemental analysis calcd. for $C_{12}H_5Br_2N_2$: C 31.07, H 1.09, N 6.04; found: C 30.80, H 1.04, N 5.98. ¹H NMR (269.71 MHz, CDCl₃, 22.9 °C) δ : 9.31 (d, ⁴*J* = 1.9 Hz, 1 H, 1), 9.19 (dd, ³*J* = 4.3, ⁴*J* = 1.6 Hz, 1 H, 5), 9.06 (d, ⁴*J* = 1.9 Hz, 1 H, 2), 8.73 (dd, ³*J* = 8.4, ⁴*J* = 1.6 Hz, 1 H, 3), 7.74 (dd, ³*J* = 8.4, ³*J* = 4.3 Hz, 1H, 4) ppm. ¹³C NMR (67.8 MHz, CDCl₃, 22.7 °C) δ : 156.6 (C_p 1), 151.1 (C_p 10), 145.1 (C_q, 12), 144.8 (C_p 3), 143.9 (C_q, 11), 137.5 (C_p 8), 129.8 (C_q, 4), 128.8 (C_q, 7), 126.1 (C_q, 5), 124.8, (C_p 9), 123.7 (C_q, 6), 94.9 (C_q, 2) ppm.

5,6-Dibromo-3-phenyl-1,10-phenanthroline (6). A Schlenk flask was charged with 5 (552 mg, 1.19 mmol), phenylboronic acid (170 mg, 1.31 mmol), anhydrous Na2CO3 (378 mg, 3.57 mmol), and [Pd(dppf)]Cl₂·DCM (147 mg, 0.18 mmol, dppf = 1,1'-bis-(diphenylphosphino)ferrocene) before it was cycled with nitrogen. Then 14 mL of degassed THF, 14 mL of degassed toluene, and 6.5 mL of degassed H₂O were added. While stirring, the reaction was heated to 95 °C. After 26 h the reaction mixture was extracted with $CHCl_3$ (1 × 50 mL, 3 × 25 mL) and washed with water and brine (2 \times 50 mL). The combined organic phases were dried over Na₂SO₄. All volatiles were removed and the dark red powder was dried in vacuo before it was purified via SiO₂ column chromatography using CHCl₃:EtOAc 1:1 with 5% added triethylamine as an eluent. Recrystallization from the eluent mixture yields 6 as colorless needles. Yield: 390 mg, 79%. Elemental analysis calcd. for $C_{18}H_{10}Br_2N_2\cdot 0.45$ CHCl₃: C 47.37, H 2.25, N 5.99; found: C 47.44, H 2.17, N 5.87. ¹H NMR (270 MHz, CDCl₃, 22.9 °C) δ 9.45 (d, ⁴J = 2.1 Hz, 1H, 8), 9.24 (dd, ${}^{3}J$ = 4.3 Hz, ${}^{4}J$ = 1.5 Hz, 1H, 1), 8.89 (d, ${}^{4}J$ = 2.2 Hz, 1H, 4), 8.77 (dd, ${}^{3}J$ = 8.4 Hz, ${}^{4}J$ = 1.6 Hz, 1H, 3), 7.81 (d, ${}^{3}J$ = 6.9 Hz, 2H, 5), 7.74 (dd, ${}^{3}J = 8.4$, ${}^{3}J = 4.3$ Hz, 1H, 3), 7.59 (t, ${}^{3}J = 7.2$ Hz, 2H, 6), 7.51 (t, ${}^{3}J$ = 7.3 Hz, 1H, 7). ${}^{13}C$ NMR (100.53 MHz, CDCl₃,22.8 °C) δ: 151.3 (C_b 1), 150.2 (C_b 14), 145.6 (C_q, 15/16), 145.5 (C_q, 15/ **16**), 137.6 (C_q , **9**), 137.5 (C_q , **3**), 136.9 (C_q , **10**), 134.8 (C_v , **8**), 129.5 $(C_{\nu} 12)$, 129.0 $(C_{\nu} 13)$, 128.73 $(C_{a}, 4/7)$, 128.70 $(C_{a}, 4/7)$, 128.7 (C_q) , 127.9 $(C_v$ 11), 125.7 $(C_q$, 6/5), 125.5 $(C_q$, 6/5), 124.5 $(C_v$ 2) ppm.

5,6-Bis(2,5-dimethylthiophen-3-yl)-3-phenyl-1,10-phenanthroline (7). A Schlenk flask with inert atmosphere was charged with 6 (640 mg, 1.54 mmol), 2,5-dimethylthiophenyl-3-boronic acid (1.441 g, 9.24 mmol), Na₂CO₃ (1.71 g, 9.24 mmol), and [Pd(tpp)₄] (356 mg, 0.308 mmol). Degassed 1,4-dioxane (24 mL) and degassed water (12 mL) were added, and the reaction mixture was heated to 100 °C under vigorous stirring for 36 h. The biphasic solution was extracted with $CHCl_3$ (5 × 50 mL), and the organic extract was washed with brine $(2 \times 100 \text{ mL})$ before it was dried over Na₂SO₄. The solvent was removed in vacuo, and the crude product was purified via column chromatography on silica using EtOAc/CHCl₃ 1:1 with 5% triethylamine as eluent. The resulting oil was suspended in hexanes and sonicated for 5 min in an ultrasonic bath. The final compound was obtained after extensive drying in vacuo as a beige powder. Yield: 357 mg, 49%. Elemental analysis calcd. for C₃₀H₂₄N₂S₂: C 75.60, H 5.08, N 5.88, S 13.45 found: C 74.71, H 5.05, N 5.79, S 13.31. $^1\mathrm{H}$ NMR (600.13 MHz, CDCl₃, 24.9 °C, contains signals of parallel/ antiparallel conformers with an indiscernible 0.8:1.0 ratio. The minor isomeric species is labeled with a star (*)) δ 9.43 (m, ⁴J = 2.3 Hz, 2H. $12/12^*$), 9.20 (d, ${}^{3}J$ = 4.1 Hz, 2H, 1, 1*), 8.17 (d, ${}^{4}J$ = 2.3 Hz, 1H, 8), 8.11 (d, ${}^{4}J$ = 2.2 Hz, 1H, 8*), 8.03 (dd, ${}^{3}J$ = 8.3 Hz, 1.6 Hz, 1H, **3**), 7.98 (dd, ${}^{3}J$ = 8.3, 1.6 Hz, 1H, **3***), 7.66 (t, ${}^{3}J$ = 7.5 Hz, 4H, **9**, **9***), 7.57 (m, ${}^{3}J$ = 8.3 Hz, ${}^{4}J$ = 4.1 Hz, 2H, 2, 2*), 7.50 (t, ${}^{3}J$ = 7.6 Hz, 4H, **10**, **10***), 7.42 (t, ${}^{3}J$ = 7.4 Hz, 2H, **11**, **11***), 6.37 (m, 4 H, 4/4*, 7/ 7*) 2.40 (m, 12H, 5'/5'*, 6/6*), 2.05 (s, 3H, 5), 2.02 (s, 3H, 6'), 2.01 (s, 3H, 5*), 1.98 (s, 3H, 6'*). ¹³C NMR (100.53 MHz, CDCl₃, 24.7 °C) δ : 149.98 (C_t), 149.97 (C_t), 149.01 (C_t), 148.99 (C_t), 145.54 (C_q), 145.49 (C_q), 144.57 (C_q), 144.52 (C_q), 137.84 (C_q), 137.82 (C_q), 135.97 (C_q), 136.00 (C_q), 135.74 (C_q), 135.66 (C_q), 135.6 (C_q), 135.5 (C_q), 135.26 (C_t), 135.12 (C_t), 134.28 (C_q), 134.22 (C_q) , 133.97 (C_q) , 133.94 (C_q) , 133.91 (C_q) , 133.87 (C_q) , 133.75 (C_q) , 133.66 (C_q) , 133.61 (C_q) , 133.59 (C_q) , 133.5 (C_q) , 132.5 (C_t) , 132.4 (C_t), 129.19 (C_t), 128.7 (C_q), 128.67 (C_q), 128.64 (C_q), 128.5 (C_a) , 128.3 (C_t) , 128.24 (C_t) , 128.21 (C_t) , 127.65 (C_t) , 127.63 (C_t) ,

127.15 (C_t), 127.10 (C_t), 123.12 (C_t), 123.07 (C_t), 15.23 (CH₃), 15.21 (CH₃), 15.18 (CH₃), 14.14 (CH₃), 14.05 (CH₃), 13.97 (CH₃).

[(Ph-phen-DAE)Fe[#](H₂Bpz₂)₂)] (8). A solution of potassium bis(1pyrazolyl)borohydride (0.156 g, 0.84 mmol) in dry MeOH (5 mL) was added dropwise to a stirred dry MeOH solution (3 mL) of FeSO₄·7H₂O (0.116 g, 0.42 mmol) at RT, whereupon a very fine white solid precipitated. The fine powder was removed by centrifugation followed by a decantation of the colorless solution of the *in situ* formed "[Fe^{II}(H₂B(pz)₂)₂]". To this solution, 7 (0.2 g, 0.42 mmol) dissolved in dry MeOH (15 mL) was added, and the resulting violet suspension was stirred for 1.5 h at RT. The suspension was concentrated to ~1/4 volume and stored at -35 °C for 3 days. The violet precipitate was filtered off (glass filter G4) and dried *in vacuo* to give 8 as a fine blue powder. Yield: 238 mg, 69%. Elemental analysis calcd. for C₄₂H₄₀B₂FeN₁₀S₂: C 61.04, H 4.88, N 16.95, S 7.76; found: C 61.02, H 4.90, N 16.86, S 7.68.

RESULTS AND DISCUSSION

We pursued three synthetic routes toward the desired *Ph-phen-DAE* ligand (Scheme 3). 1,10-Phenanthroline was regioselectively brominated according to Yamamoto et al. to yield 3,8-dibromo-1,10-phenanthroline 1,⁴⁹ which was successfully converted into 3,8-diphenyl derivative 2 via a Suzuki cross-coupling with 2 equiv of phenylboronic acid.⁵⁰ The subsequent bromination at positions 5 and 6 of *phen*, which requires harsh conditions (oleum), was unsuccessful, leading to polymers insoluble in common organic solvents. Alternatively, 3,5,6,8-tetrabromo-1,10-phenanthroline 3 can be easily prepared according to Rau et al.⁵¹ The attempted regioselective cross-coupling with 2 equiv of phenylboronic acid was not successful in our hands. Moreover, 3 is poorly soluble in common organic solvents, which hinders the search for optimal conditions for the anticipated regioselective coupling.

Finally, 1,10-phenanthroline was regioselectively brominated to yield 5,6-dibromo-1,10-phenanthroline 4.42 Adopting the procedure of Jain et al.⁵² and using *tert*-butyl hydroperoxide as a radical source, we successfully iodinated 4 to obtain a novel 5,6-dibromo-3-iodo-1,10-phenanthroline 5. A common byproduct-poorly soluble 5,6-dibromo-3,8-diiodo-1,10-phenanthroline-and unreacted 4 can be removed via column chromatography followed by recrystallization. The raw yield before the column was 30-35% as determined by NMR spectroscopy, and the pure product was isolated with the yield of 20%. The relatively low yields are mainly due to the formation of intractable polymers in the free-radical reaction and due to the product loss upon purification. It is very important to note that the novel phen derivative 5 possesses two different types of halogens (Br and I), which provides an exciting opportunity to accomplish two subsequent C-C coupling reactions regioselectively, thus leading to a new library of asymmetric phen ligands.

Thus, a cross-coupling of **5** with 1 equiv of phenylboronic acid yielded exclusively 5,6-dibromo-3-phenyl-1,10-phenanthroline **6** with yields up to 79%. A subsequent C–C coupling with 2 equiv of 2,5-dimethylthiophenyl-3-boronic acid gave the target *Ph-phen-DAE* ligand 7 as a light-beige powder. Due to its asymmetry and the presence of two conformers (parallel and antiparallel),¹⁰ 7 reveals sophisticated NMR spectra (Supporting Information). For instance, seven different methyl groups and four thiophene-protons are observed within 1.21–1.40 and 6.34–6.37 ppm range, respectively.

The ligand was obtained as an open-ring isomer (ground state), and its photochemical properties were tested. Thus, upon irradiation with UV ($\lambda = 282 \text{ nm}$), a colorless solution of

7 becomes red due to photocyclization. The photoreaction is accompanied by decreasing intense absorption bands at 247 and 278 nm and appearance of two novel bands at 363 and \sim 515 (broad) nm, which is characteristic for a closed-ring isomer (Figure 1). The photostationary state was reached



Figure 1. Photocyclization of *Ph-phen-DAE* ligand 7 with UV at RT ($\lambda = 282$ nm, MeCN, $c = 6.0 \times 10^{-5}$ M).

within 180 s under our conditions (MeCN solution, $c = 6.0 \times 10^{-5}$ M, RT, see Supporting Information for details). The reverse reaction, photocycloreversion, is accomplished by irradiation with visible light ($\lambda > 400$ nm), which leads to a nearly complete restoration of the original spectrum of the open-ring form within 1 min (Supporting Information). The photocyclization-cycloreversion cycle can be repeated at least 3 times revealing a very good resistance to fatigue (Supporting Information). The closed-ring isomer shows moderate thermal stability with a half-life of 29.8(8) h at RT in solution. Thus, the closed-ring 7 is less stable than the parent nonsubstituted *phen-DAE* (137 h)²⁰ but much more stable than a derivative with phenyl-substituted thiophenes (12 min).¹⁸

Once the photoswitchability of *Ph-phen-DAE* was confirmed, we used this ligand to control magnetic properties with light at RT. Thus, a SCO complex $[(Ph-phen-DAE)Fe^{II}(H_2Bpz_2)_2]$ 8 was synthesized: A straightforward reaction of *Ph-phen-DAE* with *in situ* formed " $[Fe^{II}(H_2Bpz_2)_2]$ " in absolute MeOH under anaerobic conditions gave 8 as a blue powder with yields up to 69%.

Single-crystal structure determination performed on a rather small crystal of **8** obtained from a toluene/*n*-hexane mixture reveals exclusively a parallel conformer⁵³ (Figure 2). The complex crystallizes in the triclinic PI group and contains 1.5 toluene molecules per molecular unit. At 100 K, all Fe–N bond distances are short (1.990–2.013 Å), suggesting a LS iron(II) center. Upon increasing the temperature to 273 K,⁵⁴ these bond distances become significantly larger (2.150–2.171 Å), which confirms a thermal switching to a HS state. The π system of *phen* is essentially electronically uncoupled from the thiophene π systems as confirmed by dihedral angles between the corresponding unit planes at 64.8 and 70.8°.⁵⁵ The phenyl group is rotated from the *phen* plane by 38.9° due to repulsion between α -hydrogen atoms of phen.

The complex reveals thermally induced SCO both in solid state and solution, which was investigated by SQUID magnetometry, ⁵⁷Fe Mössbauer spectroscopy, and Evans



Figure 2. Molecular structure of open-ring **8** in crystals of 8.1.5 toluene at 100 K showing a parallel conformer. The H atoms and solvent molecules are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level.



Figure 3. Variable temperature χT product of 8 measured on a powder sample at an external magnetic field of 1 T in the heating mode (2 K steps, 1 K min⁻¹). Fitting parameters: $\Delta H = 13.2(1)$ kJ mol⁻¹, $\Delta S = 45.3(5)$ J K⁻¹ mol⁻¹.

NMR method. In the solid state, χT product (χ is molar magnetic susceptibility) of 2.66 cm³ mol⁻¹ K at RT is consistent with the majority of 8 being in a HS state (Figure 3). Upon heating to 360 K, γT increases until 3.09 cm³ mol⁻¹K due to increasing HS fraction. Upon lowering the temperature, χT decreases very gradually reaching a plateau at ~0.27 cm³ mol⁻¹ K due to the thermal switching to a LS state. The nonzero χT at low temperatures is likely due to a residual HS fraction (\sim 7%); however, the contribution of the temperature independent paramagnetism of the LS state cannot be excluded. A van't Hoff fit reveals thermodynamic parameters $\Delta H = 13.2(1) \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S = 45.3(5) \text{ J} \text{ K}^{-1} \text{ mol}^{-1}$ for thermal SCO. The transition temperature $T_{1/2}$ is 244 or 236 K as determined by the maximum of the first derivative $d(\chi T)/d$ dT or from the average $\chi T = (\chi_{\rm HT}T - \chi_{\rm LT}T)/2 = 1.622 \text{ cm}^3$ mol^{-1} K, respectively. Notice that the transition temperature derived through the fitted thermodynamic parameter as $T_{1/2}$ = $\Delta H/\Delta S$ is artificially too high due to the limited applicability of van't Hoff fits to solid samples having intermolecular interactions. The HS fraction is estimated to amount 75 and 86% at RT and 360 K, respectively.

The shape of the transition curve points to substantially weak intermolecular interactions in the solid. Interestingly, although very gradual SCO transitions for ferrous complexes in the solid state are not uncommon, $^{56-58}$ the transition in **8**

seems to be even smoother in the solid state than in a toluene solution (*vide infra*). Similar anticooperative behavior was previously observed for a closely related complex.¹⁸ Finally, magnetic data obtained in the heating and cooling modes are nearly identical, pointing to the absence of thermal hysteresis in the solid 8.

Thermal SCO is further confirmed by Mössbauer spectroscopy (Supporting Information), revealing one quadrupole doublet ($\delta = 0.54 \text{ mm} \cdot \text{s}^{-1}$, $|\Delta E_Q| = 0.49 \text{ mm} \cdot \text{s}^{-1}$) due to a LS state at 77 K. A new doublet ($\delta = 1.50 \text{ mm} \cdot \text{s}^{-1}$, $|\Delta E_Q| = 1.00 \text{ mm} \cdot \text{s}^{-1}$) appears at RT due to a HS state. In toluene solution, 8 adopts a pure HS state at RT. Upon lowering the temperature, the χT decreases gradually, reaching 2.07 cm³ mol⁻¹ K at 188 K, which points to incomplete thermal switching to a LS state at this temperature (Figure 4). The



Figure 4. Temperature dependent χT product of 8 measured with the Evans NMR method in toluene:toluene- d_8 :TMS = 10:2:1 solution. Referenced on TMS. Fitting parameters: $\Delta H = 22.4(8)$ kJ mol⁻¹, $\Delta S = 111(4)$ J K⁻¹ mol⁻¹.

transition temperature $T_{1/2}$ determined using the average $\chi T = (\chi_{\rm HT}T - \chi_{\rm LT}T)/2 = 1.914 \ {\rm cm}^3 \ {\rm mol}^{-1}$ K is 186 K, which is lower than in the solid state. The van't Hoff fit yields thermodynamic parameters for the thermal SCO transition, and the corresponding $T_{1/2} = \Delta H/\Delta S = 200.8(4)$ K.

Photoswitching of 8 was investigated at RT in acetonitrile solution. Upon UV irradiation the intense bands in the UV region decrease, while two new distinct bands at 381 and ~550 (broad) nm emerge (Figure 5). The new bands resemble those of the closed-ring metal-free ligand 7 but appear bathochromically shifted, which points to a successful photocyclization of a coordinated ligand. Photocycloreversion is accomplished by irradiation with visible light, where the parent spectrum of the



Figure 5. Photocyclization of spin-crossover complex 8 with UV at RT ($\lambda = 282$ nm, MeCN, $c = 1.3 \times 10^{-5}$ M).

open-ring 8 is nearly completely restored (Supporting Information). Reversible photocyclization of 8 can be repeated several times (Figure 6 and Supporting Information). The



Figure 6. Multiple photoswitching of **8** at RT (MeCN, $c = 1.3 \times 10^{-5}$ M). The evolution of absorption at 380 nm upon alternating irradiation with UV ($\lambda = 282$ nm, blue, photocyclization) and visible light ($\lambda > 400$ nm, red, photocycloreversion) is shown. The data were fitted according to first-order kinetics.

exceptionally long half-life of the closed-ring 8 of 533(19) h (22 days) at RT in solution exceeds that of the metal-free ligand 7 and all analogues' SCO photoswitches reported before.^{18,20}

The photomagnetic effect was investigated in MeCN/MeCN- d_3 solution at RT using the NMR Evans method. The χT product of 3.21 cm³ mol⁻¹ K, dropped to 2.93 cm³ mol⁻¹ K upon UV irradiation. This corresponds to a HS-to-LS photoconversion of about 9% at RT. Upon irradiation with visible, χT increases to 3.03 cm³ mol⁻¹ K. Albeit small, the detected photomagnetic effect was reproducible. Although variable-temperature Evans measurements on a UV irradiated MeCN/MeCN- d_3 solution showed decreased magnetic moment at all temperatures compared to a nonirradiated solution, confirming a partial HS-to-LS photoconversion, the low quality of those low-temperature data precluded us from a proper analysis.

CONCLUSIONS

In summary, a general approach for the synthesis of 1,10phenanthrolines with unequal substituents at positions (5,6) and 3 has been presented. The approach has been used to synthesize a novel photoswitchable *Ph-DAE-phen* ligand and its spin-crossover iron(II) complex. The photoswitchability of both compounds has been demonstrated at room temperature. The presented synthetic strategy opens the route toward numerous asymmetric derivatives of 1,10-phenanthroline, including photoswitchable systems capable of chemisorption. Further work in this direction is currently under way in our group.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01424.

The details of crystallographic, spectroscopic, and photophysical studies (PDF)

Accession Codes

CCDC 1897471–1897472 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.

ACKNOWLEDGMENTS

This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG Research Grant KH 279/3). Dr. Jörg Sutter is acknowledged for measuring Mössbauer spectra. We thank Jochen Schmidt for acquiring some of the NMR data. MMK is grateful to Prof. Karsten Meyer for providing access to spectroscopic facilities and his continuous support. Maria Mateusch is acknowledged for the assistance with the cover art. AS thanks Prof. Karsten Meyer and German Federal Ministry of Education and Research (BMBF Grant 03SF0502).

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