

Reversible Photoswitching of a Spin-Crossover Molecular Complex in the Solid State at Room Temperature

Benedikt Rösner, Magdalena Milek, Alexander Witt, Benoît Gobaut, Piero Torelli, Rainer H. Fink,* and Marat M. Khusniyarov*

Dedicated to Professor Philipp Gütllich on the occasion of his 80th birthday

Abstract: Spin-crossover metal complexes are highly promising magnetic molecular switches for prospective molecule-based devices. The spin-crossover molecular photoswitches developed so far operate either at very low temperatures or in the liquid phase, which hinders practical applications. Herein, we present a molecular spin-crossover iron(II) complex that can be switched between paramagnetic high-spin and diamagnetic low-spin states with light at room temperature in the solid state. The reversible photoswitching is induced by alternating irradiation with ultraviolet and visible light and proceeds at the molecular level.

Spin-crossover (SCO) metal complexes are a well-known class of molecular switches whose magnetic, conductive, color, and other physicochemical properties can be reversibly switched by external triggers, such as temperature, pressure, or light.^[1] Six-coordinate iron(II) species, which are the most common SCO complexes, offer the opportunity to shift reversibly between diamagnetic low-spin (LS, $S=0$) and paramagnetic high-spin (HS, $S=2$) electronic states. Such SCO metal complexes are considered as promising candidates for future applications in molecular electronics and spintronics, communication networks, ultra-high-density memory systems, displays, and sensors.^[2]

To be integrated into devices, a molecular switch should ideally operate under ambient conditions: at room temperature and atmospheric pressure. Much effort has therefore been devoted to the design of SCO complexes that are switchable at room temperature.^[3] Systems featuring a thermal hysteresis loop near room temperature and thus showing

a thermally induced memory effect under ambient conditions have been highly desired.^[2a,4] However, addressing the spin state with light is more attractive because of short response times, low power dissipation, and high selectivity. Thus, bistable coordination polymers that are switchable by means of a photoinduced phase transition at room temperature were developed.^[5] This type of switching requires strong interaction between monomeric units, as achieved by covalent bonding within the crystal lattice of the polymer. Importantly, switching at the single-molecule level is fundamentally impossible in such systems, thus diminishing the potential advantage of SCO switches over established bistable bulk-phase materials and nanomaterials used in modern technology. Photoswitching genuinely at the single-molecule level has been realized in the light-induced excited spin state trapping (LIESST) effect.^[6] This approach, however, suffers from the drawback that it usually requires temperatures below 50 K, as the light-induced HS state rapidly relaxes to the LS ground state within nanoseconds at room temperature.^[7] Control of the electronic spin state and thus the magnetic properties on a genuine molecular level at room temperature is still the key challenge for the development of functioning SCO devices.

A potential solution to overcome these issues consists of the incorporation of photoisomerizable ligands into bistable molecules to trigger SCO at the metal center remotely.^[8] This approach has been demonstrated in ligand-driven light-induced spin change^[9] and light-driven coordination-induced spin-state switching.^[10] In contrast to the LIESST effect, the light-induced state in the ligand-driven effects is as stable as the resulting photoisomer of the ligand, whose lifetime can amount to years at room temperature.^[11] Importantly, these effects do not require the presence of a macroscopic phase or strong intermolecular interactions, since they are of pure molecular origin. Thus, control of the electronic state and associated magnetic properties at the single-molecule level under ambient conditions becomes feasible. In spite of significant progress in photoswitching through ligand-driven effects in the liquid phase,^[10,12] reversible photoswitching in the solid state, as required for applications, has not yet been described, although strictly unidirectional photoswitching in the solid state has been reported.^[13]

Recently, we^[12] and others^[14] independently synthesized a molecular SCO iron(II) complex featuring a photoisomerizable diarylethene ligand^[15] (Figure 1). Whereas Nihei et al. demonstrated one-way photoswitching of spin states at low

[*] B. Rösner, M. Milek, A. Witt, Prof. Dr. R. H. Fink, Dr. M. M. Khusniyarov
Department of Chemistry and Pharmacy
Friedrich-Alexander University of Erlangen-Nuremberg
Egerlandstrasse 1–3, 91058 Erlangen (Germany)
E-mail: rainer.fink@fau.de
marat.khusniyarov@fau.de
Homepage: <http://chemie.fau.de/khusniyarov>
Dr. B. Gobaut
Sincrotrone Trieste S.C.p.A.
S.S. 14 km 163.5, Area Science Park, 34149 Trieste (Italy)
Dr. P. Torelli
Laboratorio TASC, IOM-CNR
S.S. 14 km 163.5, Basovizza, 34149 Trieste (Italy)

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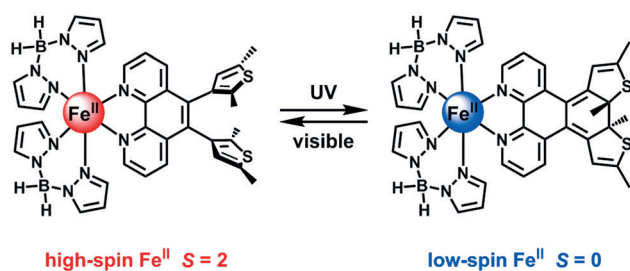


Figure 1. Ligand-driven light-induced spin-crossover in the iron(II) complex at room temperature. The open-ring and closed-ring isomers of the ligand stabilize the HS and LS states of the iron(II) center, respectively.

temperatures only,^[14] we observed an efficient and reversible ligand-driven light-induced SCO at room temperature.^[12] The ligand-driven photoswitching was accomplished by us using alternating UV and visible light irradiation under ambient conditions in solution. The half-life of the photoinduced state at room temperature was about 18 days, which greatly exceeds the half-lives of nanoseconds commonly observed for the LIESST effect. Owing to the unique ability of diarylethenes to undergo reversible photoswitching in a single-crystalline phase,^[16] photoswitching of this complex becomes also possible in the solid state.

In this study, we investigate the photomagnetic properties of the iron(II) complex (Figure 1) in the solid state. By using electronic absorption spectroscopy and element-specific spectroscopic methods, we demonstrate that the electronic state of the molecular SCO complex and the associated magnetic properties can be reversibly switched with light in the solid state at room temperature. Moreover, we show that X-ray photoelectron spectroscopy (XPS) combined with near-edge X-ray absorption fine structure (NEXAFS) spectroscopy represent a useful tool for monitoring ligand-driven SCO quantitatively.

The photochemistry of the complex in the solid state was examined qualitatively by electronic absorption spectroscopy in the UV and visible regions. Upon irradiation of the sample with UV light ($\lambda = 282$ nm) for 50 min at room temperature, the prominent absorption band at 232 nm decreased, whereas the absorption in the near-UV and visible regions increased (Figure 2a). These findings closely resemble the changes observed in solution^[17] and point to the photocyclization of a diarylethene ligand: open-ring isomer $\rightarrow$ closed-ring isomer. The reverse reaction—photocycloreversion—was accomplished within 5 min by irradiating the sample with visible light ($\lambda > 400$ nm), which led to the recovery of the 232 nm band and a decrease in the intensity of the bands in near-UV and visible regions. Irradiation with visible light did not lead to complete recovery of the open-ring isomer. This is common for diarylethene containing metal complexes owing to the non-zero absorption of the open-ring form in the visible region. Importantly, subsequent irradiation with UV light triggered photocyclization again, and thus the whole cycle can be repeated (Figure 2b). Under our conditions, photocycloreversion proceeded one order of magnitude faster than photocyclization. Assuming first-order kinetics, we deter-

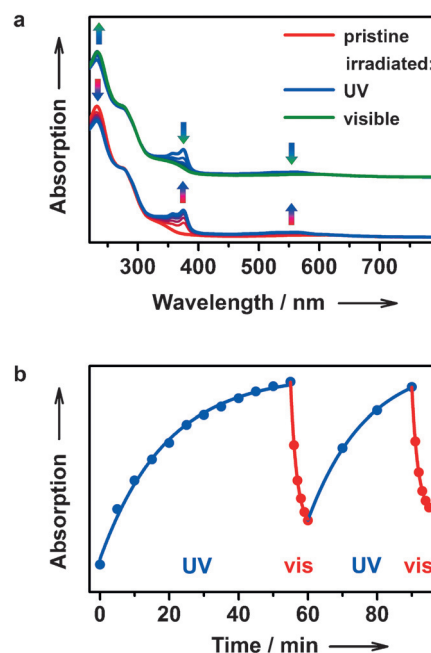


Figure 2. Photocyclization and photocycloreversion of the complex as detected by electronic absorption spectroscopy in the solid state at room temperature. a) UV-induced photocyclization ($\lambda = 282$ nm, total time: 50 min, from red to blue), and subsequent photocycloreversion with visible light ($\lambda > 400$ nm, total time: 5 min, from blue to green). b) Multiple photoswitching as a function of the intensity of the absorption band at 375 nm. Blue circles: photocyclization; red circles: photocycloreversion; blue and red lines: fitted kinetics.

mined time constants of (3.2 ± 0.2) and (3.6 ± 0.2) s⁻¹ for the first and second cyclization photoreaction, respectively, and (33 ± 1) and (32.6 ± 0.4) s⁻¹ for the first and second cycloreversion. The closed-ring isomer demonstrated high thermal stability, with a half-life of about 7 days in the solid state at room temperature. Note that the cyclization reaction could not be accomplished in the dark thermally, thus revealing the exceptional thermal stability of the open-ring isomer, which is the electronic ground state of the molecule.

Photocyclization was quantified by XPS at the S 2p core levels. The pristine complex revealed two major peaks at 164.7 and 165.9 eV (relative intensity $(96.3 \pm 2.8)\%$), which were assigned to the sulfur 2p_{3/2} and 2p_{1/2} levels of aromatic thiophene groups in the open-ring ligand (Figure 3a). The minor features, with binding energies of 162.2 and 163.4 eV $((3.7 \pm 1.6)\%)$, were attributed to the corresponding levels in non-aromatic sulfur atoms of the closed-ring isomer.^[18] The trace amounts of the closed-ring isomer in the pristine sample can be decreased to 1.5% (within the experimental error), but cannot be completely avoided during synthesis, transport, and sample handling. After the specimens were irradiated with UV light for 12 h at room temperature, the XPS spectrum changed significantly:^[19] the high-binding-energy peaks of the open-ring isomer decreased in relative intensity $((67.9 \pm 4.9)\%)$, whereas the low-binding-energy peaks of the closed-ring ligand increased accordingly $((32.1 \pm 4.1)\%)$; Figure 3b). The photoemission spectrum remained unchanged when the sample was subjected to continuous X-ray irradi-

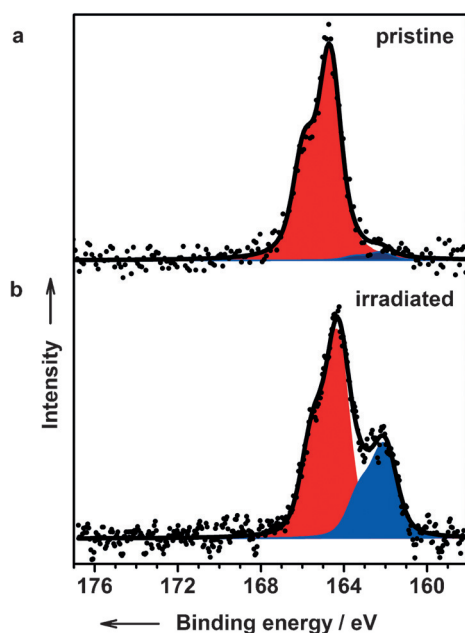


Figure 3. Sulfur 2p XPS spectra at room temperature: a) pristine complex; b) after UV irradiation ($\lambda = 282$ nm) at room temperature. The fit areas in red correspond to the open-ring isomer (96.3% in (a) and 67.9% in (b)); the fit areas in blue correspond to the closed-ring isomer (3.7% in (a) and 32.1% in (b)).

ation (700 eV) for at least 1 h at room temperature, thus indicating that the diarylethene ligand is stable under these conditions (see Figure S9 in the Supporting Information).

The photomagnetic effect in the solid state could not be investigated by magnetic measurements owing to very strong absorption of the complex in the UV region and subsequent severe problems with the penetration depth of UV light into the bulk material. Thus, we used NEXAFS spectroscopy at the Fe L_3 and L_2 absorption edges as a surface-sensitive method to examine the spin state of the iron(II) ion in solid samples. Different occupation of the t_{2g} and e_g orbitals in the HS and LS states can be probed as a function of the intensity of excitation from the Fe 2p core levels into the unoccupied d orbitals, allowing the determination of the spin state.^[20] Importantly, the spin state of the complex can be switched thermally in the solid state: the complex revealed a pure HS state at room temperature, whereas it was converted into a LS state at low temperatures. Thus, we acquired variable-temperature NEXAFS spectra on solid samples to obtain spectroscopic references for both spin states. In the following, we concentrate on the Fe L_3 edge, which is most sensitive to the spin state (see Figure S6 for full spectra).

The NEXAFS spectrum recorded at room temperature shows two main electronic excitations: a main resonance at 708.7 eV (Fe $2p_{3/2} \rightarrow t_{2g}$) and a shoulder at 709.7 eV (Fe $2p_{3/2} \rightarrow e_g$) with an energy splitting typical for a HS state (Figure 4a).^[20] The spectrum recorded at 82 K shows the Fe $2p_{3/2} \rightarrow e_g$ transition as the main feature shifted towards the higher energy of 710.2 eV due to the larger d-orbital splitting in the LS state. The spectra at intermediate temperatures show a gradual interconversion between the HS and LS states, thus confirming the temperature-induced SCO. A

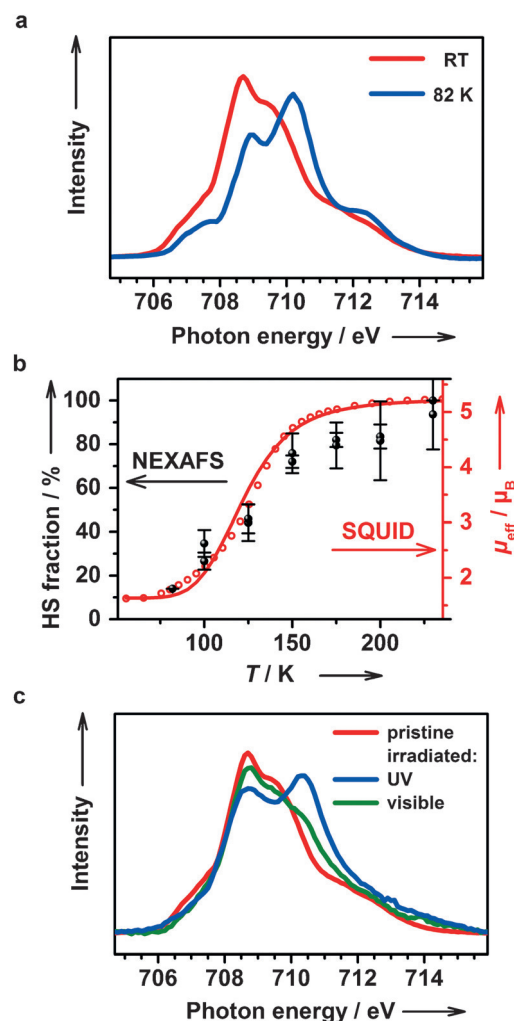


Figure 4. Quantification of spin states on the basis of NEXAFS spectra at the Fe L_3 edge and photoswitching of spin states at room temperature. a) NEXAFS spectra recorded at room temperature (red, a pure HS state) and at 82 K (blue, a mixture of LS (86%) and HS (14%) states). b) Quantification of the HS fraction from temperature-dependent NEXAFS data (black circles), as compared with magnetic susceptibility measurements performed with a SQUID magnetometer (red circles; van 't Hoff fit: red line; fit parameters: $\Delta H = 10.2(4)$ kJ mol⁻¹, $\Delta S = 76(3)$ J K⁻¹ mol⁻¹, $T_{1/2} = 135(5)$ K; see Ref. [12]). c) NEXAFS spectra acquired at room temperature on a pristine sample (red, a pure HS state (100%)), after UV irradiation ($\lambda = 282$ nm, blue, 68% HS and 32% LS), and after subsequent irradiation with visible light ($\lambda > 400$ nm, green, 84% HS and 16% LS).

correlation between the variable-temperature NEXAFS spectra and magnetic susceptibility measurements^[12] enabled us to quantify the NEXAFS data taking into account a residual HS fraction (14%) at 82 K (Figure 4b). Subsequently, a linear combination of the room-temperature spectrum and the reference spectrum recorded at 82 K allowed reliable determination of the HS and LS fractions in each spectrum.^[20,21]

After exposure of the pristine complex to UV light ($\lambda = 282$ nm) for 12 h at room temperature, the main resonance at 708.7 eV decreased and the excitation at 709.7 eV (Fe $2p_{3/2} \rightarrow e_g$) increased in intensity and shifted to a higher energy of

710.2 eV (Figure 4c). Since these spectral changes closely resemble those of the thermally induced SCO, the light-induced HS→LS transition at room temperature in the solid state has been unambiguously confirmed. The UV-induced HS→LS transition is due to stabilization of the LS state by the closed-ring isomer that exhibits a stronger ligand field.^[12] Analysis of the spectrum after UV irradiation yielded a spin-state conversion of $(32.0 \pm 5.8)\%$ (32% LS and 68% HS). This value is in perfect agreement with the photocyclization conversion determined by XPS ($(32.1 \pm 4.1)\%$, see above). Hence, the photocyclization of each ligand triggers the spin transition at one coordinated iron(II) ion. Owing to intrinsic molecular origin of the photocyclization reaction and the true molecular origin of ligand-driven effects, the observed photoswitching of the spin states is likely to proceed at the molecular level. This is confirmed by the results obtained in solution, where all molecules are isolated: each photocyclization event at the ligand was accompanied by a spin transition at one iron center in solution.^[12] The UV-induced SCO in the solid state is not complete, most likely because of the presence of two conformers featuring antiparallel and parallel orientations of the thiophene rings at the photoactive ligand. According to the Woodward–Hoffman rules, only the antiparallel form is photoactive, whereas the parallel isomer is photoinactive.^[22] Both isomers are present in the solid sample, and their ratio can vary on sample preparation. Thus, the yield of UV-induced SCO, when corrected for a photoactive fraction, should exceed the reported 32% by far.

Photocycloreversion with visible light was expected to induce the reverse LS→HS transition at the metal center. Indeed, after illumination for 8 h with visible light ($\lambda > 400$ nm) at room temperature,^[19] a sample that had been partially switched to the LS state with UV light (32% LS and 68% HS) showed an increased HS fraction of $(83.6 \pm 3.2)\%$ (Figure 4c). This is the first clear indication for reversible SCO at the molecular level in the solid state at room temperature.

To further demonstrate the potential of our system, we followed multiple photoswitching upon in situ irradiation with alternating UV and visible light by NEXAFS spectroscopy. The X-ray absorption was continuously recorded at regular time intervals of 30 s with a minimized X-ray dose to avoid potential X-ray damage. The intensity of the Fe $2p_{3/2} \rightarrow e_g$ transition (710.2 eV) thereby served as a probe for the LS content (Figure 5). Upon UV irradiation, the LS content increased considerably (0–15 min and 25–40 min), whereas the LS content decreased upon irradiation with visible light (15–25 min and 40–55 min). Thus, two light-induced HS→LS→HS cycles were examined, in agreement with the opening→closed-ring→open-ring cycles determined by electronic absorption spectroscopy. The NEXAFS data were fitted by assuming first-order kinetics to give time constants of $(3.19 \pm 0.03) \times 10^{-3}$ and $(1.24 \pm 0.04) \times 10^{-3} \text{ s}^{-1}$ for the first and second photocyclization reactions, and $(7 \pm 3) \times 10^{-4}$ and $(2.5 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ for the first and second photocycloreversion events.^[23] Note that different absorption cross-sections and/or flux densities in the NEXAFS experiment result in much smaller time constants as compared to those obtained

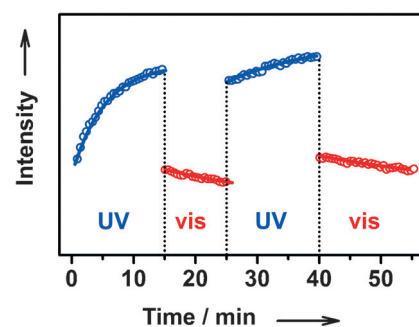


Figure 5. Multiple photoswitching of spin states at room temperature. Evolution of the LS content as the intensity of the peak at 710.2 eV (Fe $2p_{3/2} \rightarrow e_g$ in the LS state) in the NEXAFS spectra at the Fe L_3 edge upon in situ alternating irradiation with UV ($\lambda = 282$ nm, blue circles) and visible light ($\lambda > 400$ nm, red circles). The offsets in the observed intensity upon changing between UV- and visible-light irradiation are due to secondary electrons emitted by UV light, which are detected in the total electron yield as part of the constant background. Blue and red solid lines: fitted kinetics.

from electronic absorption spectroscopy. Therefore, the values will not directly correlate.

The herein presented iron(II) complex with a photoisomerizable diarylethene ligand is the first example of a SCO molecular photoswitch that fulfils the general requirements for implementation in functional molecular devices: reversible switching, operation at room temperature, in the solid state, and at the molecular level. The alternating irradiation with UV and visible light induces reversible isomerization of the photoactive ligand, which in turn triggers reversible SCO at the coordinated magnetic center. Besides modulation of the magnetic properties, switching of the electronic states of SCO complexes results in large modulation of electric conductivity.^[24] The prospective integration of the iron(II) molecular complex into electronic circuits^[25] may open a new area in the construction of photocontrolled molecular devices with variable resistance.

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