Light-Induced Bistability in the 2D Coordination Network \([\text{[Fe(bbtr)}_3][\text{BF}_4]_2\): Wavelength-Selective Addressing of Molecular Spin States**


Dedicated to Hartmut Spiering on the occasion of his 70th birthday

Abstract: Whereas the neat polymeric Fe\(^{II}\) compound \([\text{[Fe(bbtr)}_3][\text{ClO}_4]_2\)]\(_\infty\) (bbtr = 1,4-di(1,2,3-triazol-1-yl)butane) shows an abrupt spin transition centered at 107 K facilitated by a crystallographic symmetry breaking, in the covalently linked 2D coordination network of \([\text{[Fe(bbtr)}_3][\text{BF}_4]_2\)]\(_\infty\), Fe\(^{II}\) stays in the high-spin state down to 10 K. However, strong cooperative effects of elastic origin result in reversible, persistent, and wavelength-selective photo-switching between the low-spin and high-spin manifolds. This compound thus shows true light-induced bistability below 100 K. The persistent bidirectional optical switching behavior is discussed as a function of temperature, irradiation time, and intensity. Crystallographic studies reveal a photoinduced symmetry breaking and serve to establish the correlation between structure and cooperative effects. The static and kinetic behavior is explicated within the framework of the mean-field approximation.

Introduction

The electronic bistability of spin-crossover compounds,[1–3] that is, compounds of transition metal ions with d\(^4\)-d\(^n\) configurations, is governed by the zero-point energy difference, relative electronic degeneracies, and vibrational densities of states of the high-spin (HS) and the low-spin (LS) manifolds. External perturbations such as pressure,[4,5] magnetic fields,[6,7] chemical variation,[8] temperature,[9,10] and electromagnetic radiation[11,12] influence the zero-point energy difference and thus the spin-crossover behavior. In concentrated or neat crystals, the difference in metal–ligand bond length, \(\Delta r_{\text{HL}} = r_{\text{HS}} - r_{\text{LS}}\) between the two spin states of typically 0.2 Å for iron(II) systems[11,12] generates elastic stresses within the lattice, leading to cooperative phenomena of elastic origin. Cooperative effects transform the gradual thermal spin transition, with a Boltzmann distribution between the two spin manifolds, into an abrupt one, often accompanied by a hysteresis in presence or absence of a crystallographic phase transition.[13–16] Cooperative effects have been modeled by the superposition of both short- and long-range interactions. The short-range component is statistically distributed and depends on the shape and distance between neighboring molecules. The long-range component is proportional to the average number of HS molecules per unit volume and is mediated by the crystal lattice.[13,17–23] Thus even though the basic spin-crossover phenomenon is a consequence of the metal–ligand distance dependence of the ligand field strength,[24,25] in the solid-state cooperative effects play an important role. Conformational changes in the ligand sphere[26,27] and the presence of solvent molecules and different counterions can modify the spin-crossover properties and thus cooperativity drastically.[27–31]

The potential use of optical switching in data storage[32] and display devices[32,33] has raised major interest in the light-induced excited-spin-state trapping (LIESST) effect,[9] in which a metastable HS state, albeit with a very long lifetime, is created by optical excitation into spin-allowed as well as spin-forbidden ligand–field transitions or metal–ligand charge-transfer transition of the LS species at temperatures below the thermal spin transition. The reverse transi-
tion (reverse-LIESST) is also observed by light irradiation in the near infrared, that is, into the spin-allowed ligand–field transition of the HS species (inset of Figure 1a). [9,34] If the HS state is the quantum mechanical ground state, that is, for negative values of the zero-point energy difference between two spin manifolds,

\[ \Delta E_0^{HL} = \frac{E_0^{HS}}{C_0} - \frac{E_0^{LS}}{C_2} < 0, \]

either the thermal spin transition does not take place. As the zero-point energy difference between the two spin states is negative, the entropic contribution to the Gibbs free energy ensures that the HS state is the thermodynamically stable state at all temperatures. In such cases it is sometimes possible to induce the spin transition by stabilizing the LS state under external pressure[35] or light[17,36] as physical perturbations. An external pressure results in an effective increase of the internal pressure, leading to the stabilization of the LS state due to the lower molecular volume favored under pressure, such that it may become the molecular ground state and thus the thermodynamically stable state at lower temperatures. Alternatively, the LS state can also be populated at low temperatures by irradiating into the spin-allowed d5dd band of the HS state through an intersystem crossing process. Initially, this photoinduced LS state is just a long-lived metastable state with respect to the individual molecule, but as the light-induced HS → LS conversion proceeds, the cooperative effects destabilize the HS state and the zero-point energy difference between the two spin states may become positive.

True bistability, that is, infinite lifetime in either of two spin states at a given temperature and pressure, is a macroscopic phenomenon that requires strong cooperative interactions. [37] True light-induced bistability is defined by a specific photodynamic situation in which the HS state is initially the thermodynamically stable state seemingly at all temperatures, but with the potential for self-stabilization of the LS state by means of a light-induced HS → LS conversion. [36,38–42] Only a few examples showing a partial light-induced bistability and a short communication on the 2D coordinative network of \([\text{Fe(bbttr)}]_3[\text{BF}_4]_{\infty}\), \(\text{bbtr} = 1,4-di(1,2,3-triazol-1-yl)butane\) have been reported so far. [38] \([\text{Fe(bbttr)}]_3[\text{BF}_4]_{\infty}\) exhibits a layered structure, in which each iron is linked to six neighboring iron centers through bridging bbtr ligands in a common plane, thus forming 2D polymeric net-

![Figure 1. Single crystal absorption spectra of \([\text{Fe}(\text{bbtr})]_3[\text{BF}_4]_{\infty}\), \(d=60\ \mu m\), a) at 295 K, b) at 10 K on cooling from room temperature, and c) upon irradiation at \(\nu_{ex} = 12000 \text{ cm}^{-1}\) (\(\lambda_{ex} = 830\), 10 mW mm\(^{-2}\) for 10 min, d) on subsequent warming to 80 K, e) cooling back to 10 K, and f) warming to 120 K. The broken lines in d) and e) show the spectrum of c) for direct comparison. Recooling to 10 from 120 K results in a spectrum identical to spectrum b) on cooling from 295 K; warming to 295 K from 120 K results in spectrum a). Irradiation at 10 K with \(\nu_{ex} = 21200 \text{ cm}^{-1}\) (\(\lambda_{ex} = 472\) nm), 10 mW mm\(^{-2}\) for 2 min subsequent to irradiation at 12000 cm\(^{-1}\) results in a 100% re-population of the HS state. Inset a): schematic representation of the potential wells of the low-spin and the high-spin potential energy surfaces along the totally symmetric breathing mode of an octahedral iron(II) complex with a zero-point energy difference \(\Delta E_0^{HL} = E_0^{HS} - E_0^{LS} < 0\). Arrows indicate absorption (full lines) and non-radiative relaxation (broken lines) for LIESST and reverse-LIESST.
work perpendicular to the crystallographic c axis. The BF$_4^-$ ions, located in the cavities of the 2D layers, are engaged in intermolecular interactions establishing the crystal packing $^{[15,43]}$. Unlike the isostructural ClO$_4^-$ analogue, which exhibits a thermal spin transition with a 13 K wide hysteresis centered at 107 K $^{[14,15]}$, in [Fe(bbtr)]$_2$[BF$_4$]$_2$ no thermal spin transition has been observed, and the compound stays in the HS state down to 5 K. $^{[38]}$ However, it shows persistent, bidirectional, spin-state switching below 100 K. Herein we present and discuss the wavelength-dependent photoexcitation and relaxation dynamics as a function of temperature and laser power. The results are analyzed within the framework of a dynamic mean-field theory. Further discussions include a photocrystallographic study, in which in contrast to previous studies on the metastable light-induced HS structure $^{[44,45]}$, the light-induced LS structure is reported. The detailed investigation of the bidirectional photoswitching dynamics presented here will thus help to design highly cooperative systems for efficient optical switching and memory devices at higher temperatures $^{[46,47]}$.

**Results and Discussion**

**Optical investigation:** Figure 1 shows high quality single-crystal optical absorption spectra of [Fe(bbtr)]$_2$[BF$_4$]$_2$ at 295 (Figure 1a) and at 10 K (Figure 1b) on cooling at a rate of 0.2 K min$^{-1}$ below 120 K. Both spectra show the characteristic $^3T_2 \rightarrow ^1E$ ligand–field band at 12000 cm$^{-1}$ of the HS species indicating that there is no thermal spin transition. Figure 1c shows the 10 K absorption spectrum upon irradiation at 830 nm. The ligand–field band of the HS species has almost disappeared. Instead the characteristic $^1A_1 \rightarrow ^3T_1$ ligand–field transition and the rise to the intense metal–ligand charge-transfer ($^1$MLCT) band of the LS species are observed. Prolonged irradiation at 12 000 cm$^{-1}$ (830 nm) thus populates the LS state through reverse-LIESST to 85% (see below for a quantitative estimation), corresponding to the steady-state value due to the spectral overlap between the spin-allowed ligand–field transition of the HS species and the spin-forbidden ligand–field transitions of the LS species $^{[34]}$. The corresponding excitation curve leading to the steady-state LS value of 85% is shown in Figure 2. With an irradiation intensity of 10 mW mm$^{-2}$ at 830 nm, it takes about 200 s and therefore 2 J mm$^{-2}$ to achieve saturation. Warming up to 80 K results in 100% population of the LS state borne out by the total disappearance of the HS band and a further increase in the intensity of the LS band by around 15% (Figure 1d). Upon recooling to 10 K, the 100% LS population is maintained (Figure 1e). Upon warming, relaxation to the HS state sets in at 100 K such that the spectrum above that temperature again only shows the HS band at 12 000 cm$^{-1}$ (Figure 1f). Figure 3 summarizes these findings by plotting the HS fraction, $\gamma_{\text{HS}}$, derived from the relative intensity of the $^1A_1 \rightarrow ^3T_1$ transition as a function of temperature along the pathways sketched above. The return from the light-induced LS state to the HS state occurs very abruptly at $T^*=395$ K.

For short irradiation times only a partial LS population is obtained. For instance, irradiating at 10 K with 830 nm light using 10 mW mm$^{-2}$ for 10 s results in a LS population of 15%. With 15% in the LS state, upon warming up at a rate of 0.2 K min$^{-1}$, the system returns directly to the HS state at around 60 K, as also shown in Figure 3. This gives a first indication of the light-induced, macroscopic, and persistent bistability, that is, at 60 K the system remains fully in the prepared spin state indefinitely. This signifies that a critical light-induced LS fraction must exist, above which the system does not return to the HS state on switching off the
irradiation and warming, but continues to increase the LS fraction, whereas below that the critical LS fraction does return fully to the HS state.

From the steady-state LS fraction of 85% after prolonged irradiation at 830 nm at 10 K, the system can also be restored fully to the HS state at that temperature with irradiation at 21 200 cm$^{-1}$ (472 nm). The corresponding excitation curve is included in Figure 2. With an irradiation intensity of only 1.2 mW mm$^{-2}$ at that wavelength, the efficiency of the light-induced LS → HS conversion is much higher, and is actually known to be close to unity. Figures 2 and 3 demonstrate full wavelength-selective and persistent switching between the two spin states below 100 K.

Figure 4 shows relaxation curves at given temperatures between 50 and 70 K following different partial light-induced populations of the LS state upon irradiation at 830 nm (10 mW mm$^{-2}$). The procedure was to always start from the pure HS state at the given temperature and to achieve the partial LS populations with different irradiation times. Because of the small extinction coefficient and the crystal thickness of only 60 μm, the optical density (OD) at that wavelength is <0.1, and therefore concentration gradients in the light-induced LS fraction are negligible. The relaxation curves demonstrate three points:

1) There is indeed a temperature-dependent critical value of the light-induced LS fraction, above which the system relaxes fully to the LS state after switching off the irradiation. For instance at $T=65$ K, $γ_{c,LS}$ is around 0.35, since a generated partial LS population of 0.3 relaxes to the HS state, while a generated partial LS population of 0.4 relaxes to the LS state. The corresponding critical HS fractions, $γ_{c,HS}=1-γ_{c,LS}$, interpolated from the curves in Figure 4, are included in Figure 3.

2) The relaxation time increases with decreasing temperature. Below 50 K it becomes so long that corresponding experiments would take up too much time. Conversely, above 70 K, the relaxation becomes fast enough so that with the chosen laser power of 10 mW mm$^{-2}$ the critical LS fraction is not reached anymore (see below).

3) The relaxation curves both starting below and above the critical values are sigmoidal in shape, which is indicative of strong cooperative effects.

Thus [Fe(bbrt)$_3$][BF$_4$]$\cdot$ can be regarded as a spin-cross-over compound with a very large thermal hysteresis, the abrupt crossover from the full LS state to the HS state at 100 K corresponding to $T_c^{\uparrow}$ of the heating branch of the system, while the cooling branch is not accessible in a simple temperature cycle either because $T_c^{\downarrow}$ is at such a low temperature, that is, below 40 K, that the HS → LS relaxation is too slow, or even at or below zero. Persistent wavelength-selective bidirectional switching can thus be achieved within the hysteresis, that is, at temperatures below 100 K. The behavior during irradiation and the subsequent relaxation for temperatures between 50 and 70 K suggests that a mean-field approach is adequate (for a quantitative discussion see below).

Figure 5 depicts two of the curves from Figure 3 obtained by first irradiating to create the steady-state LS fraction of 85% and a partial LS population of 15% and subsequent warming to 120 K at a scan-rate of 0.2 K min$^{-1}$. In addition it shows curves obtained following partial light-induced population of the LS state at values in between these two. As the temperature is scanned from 10 K, initially nothing much happens, that is, $γ_{LS}$ is constant. At around 50 K the relaxation...
processes become faster. The direction of the relaxation depends on the initial light-induced LS fraction, and thus corroborates the bistability of the system with a critical value of the light-induced LS fraction of around 0.3 at 60 K. The experimental curves first follow a comparatively simple behavior, again reminiscent of mean-field behavior. However, for light-induced LS fractions between 40 and 70% the relaxation behavior above around 60 K becomes more complex. Steps and only partial relaxation during the temperature scan suggested a more complex structural evolution involving a crystallographic phase transition from \( P\bar{3} \) to \( P\bar{1} \) (see section on crystallography below) and the possible formation of a superstructure.

The above results are further borne out by the photoexcitation curves recorded at different temperatures between 10 and 80 K shown in Figure 6a upon irradiation at 830 nm with a laser power density of 10 mW mm\(^{-2}\), and for different laser power densities at 75 K shown in Figure 6b. As before, the evolution of the \( ^1A_1 \rightarrow ^1T_1 \) ligand–field transition was monitored in order to extract the HS fraction during photoexcitation. For the irradiation intensity of 10 mW mm\(^{-2}\) (Figure 6a) and at low temperatures, that is, below 50 K, the excitation curves are superimposable, and the aforementioned steady state with a LS fraction of 85% is established within approximately 300 s. This is in agreement with previous reports.\(^{[9]}\) They are superimposable because at the chosen laser power all relaxation processes between the HS and the LS states are substantially slower than the photoexcitation up to 50 K. At 60 K this is still the case initially, but above the critical light-induced LS fraction the thermal relaxation self-accelerates towards 100% population of the LS state. At still higher temperatures, the LS → HS relaxation already at the beginning of the irradiation is in direct competition with the light-induced HS → LS transformation. As the LS population slowly increases, the LS → HS relaxation becomes slower and above the critical LS fraction HS → LS relaxation takes over. This results in the sigmoidal excitation curves with an incubation period\(^{[48]}\) observed for 70 and 75 K. At 80 K, the initial LS → HS relaxation is too fast and the light-induced HS → LS conversion with 10 mW mm\(^{-2}\) laser power cannot compete against it.

Figure 6b illustrates the photoexcitation dynamics at 75 K as a function of laser power at 830 nm. At this temperature, the relaxation processes are in direct competition with the photoexcitation. The above-mentioned incubation period as the laser is switched on and the sigmoidal shape of the excitation curve in the initial phase are a direct consequence of the cooperative effects and the self-acceleration of the thermal relaxation,\(^{[48]}\) and can be explained on the basis of a mean-field approach. The stepwise increase in the LS fraction at later on, however, indicates that at that temperature the relaxation behavior is more complex. The plateau at around \( \gamma_{LS} = 0.5 \) suggests a superstructure due to the doubling of the unit cell along the \( c \) axis (see section on crystallography below) and the creation of two crystallographically non-equivalent iron(II) sites\(^{[30,45]}\) with different relaxation rate constants, or possibly nucleation and growth phenomena\(^{[14,49,50]}\).

A quantitative analysis based on a mean-field approach: Even though the above results indicate certain deviations from mean-field behavior with the possible formation of a
superstructure in the light-induced phase, the following analysis will be performed using the classic mean-field approximation. The rational behind this is, that the light-induced LS populations are randomly distributed with negligible concentration gradients across the crystal. Therefore, at least at early times in any relaxation process, the conditions of the mean-field approximation are fulfilled. Furthermore, experimentally, steps in the relaxation and excitation curves only occur above 70 K.

In order to reproduce the quasi-static or spinodal points and $T_{c,H} = 100$ K in Figure 3, the following mean-field expression of the equilibrium constant for non-diluted spin crossover compounds is used [Eq. (1)], in which $\Delta H^p$ and $\Delta S^p$ are the standard enthalpy and entropy variations and $\Gamma$ is the interaction parameter.

$$K = \frac{\gamma_{HS}}{1 - \gamma_{HS}} = \exp\left(-\frac{\Delta H^p - T \Delta S^p - 2\Gamma(\gamma_{HS} - 1/2)}{k_B T}\right)$$

As the number of experimental points is limited, it is not possible to realize an unambiguous fit with a unique parameter set $\Delta H^p$, $\Delta S^p$, and $\Gamma$ using only the above-mentioned data. However, by iteratively also considering the kinetic data in Figure 4 and using the classical master equation in mean-field approximation, including both HS-LS and LS-HS relaxation processes according to Equation (2) in which $\dot{\gamma}_{HL}$ is the HS-LS relaxation rate constant at $\gamma_{HS} = 1$ and at a given temperature, a unique parameter set can be found that leads to the best fit of all experimental data, namely $\Gamma = 5$, $\Delta H^p = 395$ K and $\Gamma = 380$. 

$$\frac{d\gamma_{HS}}{dt} = -k_{HL}^0(T)\exp\left(\frac{\Gamma(1 - \gamma_{HS})}{k_B T}\right)\gamma_{HS} + k_{HL}^0(T)\exp\left(\frac{\Gamma(1 - \gamma_{HS})}{k_B T}\right)\times$$

$$\exp\left(-\frac{\Delta H^p - T \Delta S^p - 2\Gamma(\gamma_{HS} - 1/2)}{k_B T}\right)(1 - \gamma_{HS})$$

The values found for $\Delta H^p$ and $\Delta S^p$ are considerably smaller than the values previously obtained for the mixed crystal series of the closely related perchlorate salt of [(Fe(bbtr)3)]_[roll] [BF4]2 which $\Delta H^p = 650$ K and $\Delta S^p = 6.5$. The smaller value of the $\Delta S^p$ for [(Fe(bbtr)3)]_[roll] [BF4]2 can be correlated with its smaller spinodal transition temperature $T_s = \Delta H^p/\Delta S^p = 80$ K instead of 100 K, as at low temperatures $\Delta H^p$ and $\Delta S^p$ are quite strongly dependent on temperature. In Figure 3, the corresponding calculated spinodal curve is shown as dotted line. As $\Gamma < \Delta H^p$, the best fit parameters predict that $T_{c,H}$ is about 25 K. Thus below 25 K, the LS state would be the thermodynamically stable state, but again by comparison with the analogous perchlorate salt, the rate constant for the HS-LS relaxation $k_{HL}$ at that temperature is $< 10^{-7}$ s$^{-1}$ and the HS state is therefore kinetically trapped.

Values of $\dot{\gamma}_{HL}$ as a function of $T$ can be easily obtained extracted from the experimental relaxation data at the same time and can be used for the corresponding calculated relaxation curves included in Figure 4. Taking into account the fact that the same set of parameters $\Delta H^p$, $\Delta S^p$, and $\Gamma$ are used for all simulated relaxation curve, the simulated curves are most satisfactory. In particular the acceleration at short times for the different initial light-induced LS fractions are very well reproduced for 60, 65, and 70 K. This indicates that the light-induced LS fraction is indeed randomly distributed. The simple approach also predicts the very sluggish relaxation behavior at 50 K. Systematic deviations of the experimental curves from the ones calculated in the mean-field approximation manifest themselves in the form of a slow tail towards the end of some relaxation curves. This has been found before in highly cooperative systems and has been attributed to a progressive onset of correlations.

The values of $\dot{\gamma}_{HL}$ in the range of 50 to 70 K are plotted on a logarithmic scale against $T^{-1}$ in Figure 7, together with the data obtained previously for the dilute mixed crystal system of the perchlorate analogue [(Zn1-xFe1-x(bbtr)3-x)(ClO4)x] which $\dot{\gamma}_{HL}$ (bbtr)3] is 0.02 together with those of the dilute mixed crystal system of the analogous perchlorate salt.

![Figure 7](image-url)
and the deviations from the mean-field behavior are observed.

Structure determination: The analysis of the structural aspects and their evolution as a function of temperature and light irradiation are of prime interest to understand the phenomenon of spin crossover in the thermal- and light-induced regimes. In particular the large difference in metal–ligand bond lengths drives the thermal spin transition, and is responsible for the light-induced trapping at low temperatures. In the present work, the crystal structure of ([Fe(bbtr)]$_3$)-[BF$_4$]$\text{$_2$}$ has been determined at selected temperatures and following relevant light irradiation conditions according to the optical investigation detailed above. The HS crystal structure of ([Fe(bbtr)]$_3$-[BF$_4$]$\text{$_2$}$ has been described previously at 295 K in the hexagonal space group $P$3; it is isostructural with the ([Fe(bbtr)]$_3$)[ClO$_4$]$\text{$_2$}$, and with the corresponding spin crossover inactive Zn analogues.[15] As mentioned in the introduction, each iron center is coordinated by six nitrogen atoms from bbtr ligands, each bbtr ligand bridges two iron centers, thus forming a hexagonal 2D layer (Figure 8, top). The layers are stacked along the crystallographic c axis, and held together by a network of hydrogen bonds through the BF$_4$$^-$ counterions located on a threefold axis in the interlayer spacing (Figure 8, bottom). With $Z=1$, the iron centers are all crystallographically equivalent and have $S_5$ site symmetry. The ([Fe(bbtr)]$_3$)[ClO$_4$]$\text{$_2$}$ compound undergoes a structural phase transition from space group $P$3 to space group $P1$, associated with a symmetry breaking and non-merohedral twinning. It has been shown that the structural transition does not trigger the spin transition directly, rather a temperature decoupling between the two has been found and shown to depend on the Zn content for mixed compounds ([Zn$_{1-x}$Fe$_x$(bbtr)]$_3$)[ClO$_4$]$\text{$_2$}$.[16,15] The twinning process associated with the structural transition produces a domain structure in the single crystal evidenced in the crystallographic investigation by a splitting of the diffraction peaks. The domain orientations are related by the threefold axis, which is lost during the symmetry breaking. In contrast to the perchlorate analogues, the space group $P$3 is maintained for ([Fe(bbtr)]$_3$-[BF$_4$]$\text{$_2$}$ down to 10 K; no structural phase transition occurs in the HS state on the whole temperature range. At 10 K, the structural parameters are very similar to those already reported at 90 K. The Fe–N bond length is 2.188(1) Å (Table 1), typical for the HS state in FeN$_6$ coordination. The cis angles N-Fe-N$'$ are all very close to 90° as indicated by the very small value of 1.44° of the sum of all deviations from 90°. The shortest distance between the iron(II) ions of neighboring layers is 7.5217(4) Å. Relative to the reported structure at 90 K, all C–H–F intermolecular distances are systematically reduced at 10 K owing to thermal contraction effects (see Table S1 in the Supporting Information). During the population of the LS state upon irradiation with 830 nm light at 10 K, a crystallographic phase transition with symmetry lowering occurs. The most probable lower symmetry space group is $P1$ with a doubling of the unit cell along the c axis, at variance with the structural transition reported for the perchlorate analogue for which a symmetry lowering to $P1$ without cell doubling occurs. In the present situation, the asymmetric unit in the photoduced state contains one iron(II) ion, three bbtr ligands, and two BF$_4$$^-$ counterions. The site symmetry of the iron centers is reduced to $C_1$. However, with $Z=2$, the two iron centers in the unit cell are still crystallographically equivalent, being connected via the retained inversion center. In the lower symmetry space group, neighboring layers are slightly shifted with respect to each other in comparison to the hexagonal structure. At 10 K after irradiation to the steady-state light-induced LS fraction of 85%, the average Fe–N bond length is reduced to 2.009(5) Å. Upon heating to 60 K and recoiling to 10 K a further small reduction to 1.993(5) Å is observed, in line with the relaxation of FeN$_6$ coordination.

Table 1. Selected structural parameters: Fe–N bond lengths [Å] and angular distortion parameter $\Sigma$ [°] for ([Fe(bbtr)]$_3$-[BF$_4$]$\text{$_2$}$, before and after irradiation at 830 nm.

| $T$ [$\text{K}$] | Before irradiation | After irradiation | Warmed to 60 K | Recooled to 10 K |
|----------------|-------------------|------------------|--------------|----------------|}
| 10             | 1.0               | 0.15             | 0.9          | 0.0            |}
| 2.188(1)       | 1.979(5)          | 1.978(6)         | 1.979(5)     | 1.981(5)       |}
| 2.002(5)       | 1.980(6)          | 1.993(6)         | 1.998(5)     | 2.007(5)       |}
| 2.004(5)       | 1.989(5)          | 1.994(6)         | 2.007(5)     | 2.023(5)       |}
| 2.037(5)       | 2.000(6)          | 1.989(6)         | 1.998(5)     | 2.023(5)       |}
| 2.188(1)       | 2.009(5)          | 1.989(6)         | 1.998(5)     | 2.023(5)       |}
| 1.44           | 9.6               | 9.9              | 10.2         | 10.2           |}

[a] The value of $\gamma_{\text{int}}$ is given as an indication, and is estimated from the optical results. [b] The sum of all deviation from 90° of the 12 cis N-Fe-N$'$ angles of the FeN$_6$ octahedron.
the LS fraction to 100%. Therefore, the total reduction of the Fe–N bond length, \( \Delta r_{\text{II}} = r_{\text{II}} - r_{\text{LS}} = 0.195 \, \text{Å}, \) that is, a value in the typical range for iron(II) spin-crossover systems. The change in unit-cell volume upon full HS → LS conversion in the \( P1 \) setting is 53 Å\(^3\). With \( Z = 2 \), this translates to a molecular volume change of \( \Delta V_{\text{mL}} = 27 \, \text{Å}^3 \) per complex, a typical value for iron(II) spin-crossover systems, which is furthermore very close to the value of 25.4 Å\(^3\) reported for the perchlorate analogue.\(^{[15]}\) The change in unit cell involves a decrease of the \( a \) and \( b \) lattice parameters by 0.301 and 0.269 Å, respectively, while \( c \) increases by 0.280 Å. This evolution is systematically larger than reported for the perchlorate analogue upon the spin transition at 100 K. In addition, the changes in lattice angles (−0.09, +1.52, and −0.12° for \( \alpha, \beta, \) and \( \gamma \) respectively) are reduced by comparison with the perchlorate analogue (+4.93, −3.27, and +0.08° for \( \alpha, \beta, \) and \( \gamma \) respectively). Together with the occurrence of a unit-cell doubling for \( \{[\text{Fe(bbr)}_3]_2][\text{BF}_4]\}_3 \), we can conclude that the overall structural distortion related to the \( P3 \to P1 \) structural transition combined with the HS → LS full conversion follows a different process although the space group change is identical. Owing to this structural distortion, the separation distance between neighboring layers along the \( c \) direction increases from 7.52117(4) to 7.652(2) Å, while adjoining layers are shifted related to each other by nearly 0.72 Å. Interestingly, this value is very close to the shift characterized for the perchlorate analogue. Upon the HS → LS transition and \( P3 \to P1 \) structural transition, and related interlayer shift, the overall network of C–H···F hydrogen bonds is preserved, with a modification of some distances (given in Table S1 and shown in Figure S1 in the Supporting Information). Similar to the perchlorate analogue, the intermolecular contacts between tetrafluoroborate anions and hydrogen atoms may be divided into three groups. The first group comprises \( \text{H}1_1 \cdots \text{F}1 \) contacts formed between the \( \text{F}1 \) atom located on the threefold axis in the \( P3 \) space group and symmetry related \( \text{H}1 \) atoms. In the \( P1 \) space group, only one hydrogen bond is preserved for each \( \text{BF}_4^- \) anion, with a longer bond length. The second group involves intralayer contacts (two kinds of \( \text{C}5 \cdots \text{H}5 \cdots \text{F}2 \), and \( \text{C}2 \cdots \text{H}2 \cdots \text{F}2 \)), which vary in a non-systematic way; some are shorter, while others are longer after the structural transition. The same observation holds for the third group, which involves the interlayer \( \text{C}1 \cdots \text{H}1 \cdots \text{F}2 \) hydrogen bonds.

A more detailed examination of the diffraction pattern during irradiation at 830 nm can provide further information on the interplay between the light-induced HS → LS transition and the structural \( P3 \to P1 \) transition coupled to a twinning process. As shown in Figure 9a, owing to the unit-cell doubling in the \( c \) direction, superstructure reflections with miller indices \( (hkl, l = 2n + 1) \) progressively appear on the diffraction pattern, reflecting the change of periodicity of the crystal. It is worth noting that the sharpness of the diffraction peaks decreases with photoexcitation duration, which is indicative of a progressive decrease in crystalline quality of the sample. This is attributed to the formation of twin domains with three different orientations related by the threefold axis of the parent HS structure with hexagonal \( P3 \) symmetry; this is depicted in Figure S2 (see Supporting Information). The increase in intensity of several selected superstructure reflections has been monitored in parallel to the change in unit-cell volume as a function of photoexcitation duration at 830 nm, with a reduced laser power (1 mW mm\(^{-2}\)), as shown in Figure 9. The unit-cell volume evolves exponentially with a decrease of 40 Å\(^3\) in the \( P1 \) setting over 60 min photoexcitation, in accordance with the value from the structure determination at both ends. The evolution of the unit-cell volume, which is proportional to the light-induced LS fraction, has been fitted with an
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Experimental Section

Optical spectroscopy: High-quality [(Fe(btr))3][BF4]2 single-crystals, hexagonal in shape and having well developed faces were synthesized and grown as previously reported.[60] They cleave easily perpendicular to the c axis and they are colorless at room temperature as well as at low temperature. The thickness of the crystals used for optical spectroscopy varied between 100 and 150 μm. For optical and thermal investigations, all the crystals are mounted on copper plates with a hole of approximately 0.2 mm or less in diameter. For this silver paste was used so as to ensure good thermal contact with the metal plate in order to minimize temperature gradients. The sample holder was placed inside a closed cycle cryostat capable of achieving temperatures down to 4 K (Janis-St mutilo) and equipped with a programmable temperature controller (LakeShore Model No. 331). High-quality single-crystal absorption spectra were recorded by a double-beam spectrometer (Agilent, Cary 5000) as a function of time and temperature. The cooling and heating rate in the experiment has been adjusted from the temperature controller. For reverse-LIESST experiments from 10–55 K, the light from a continuous laser diode at 830 nm (ILEE Model Z40 KV1) was used. However, high-temperature photoexcitation and laser power-dependent studies were performed using a Ti-Sapphire laser (Spectra-Physics 3900). Quantitative light-induced LS—HS transformation was performed using light from a continuous Ar/Kr mixed gas laser at 472 nm. This wavelength was chosen due to the fact that it falls into the high-energy tail of 1A1 H transition. Both at 830 and 473 nm the extinction coefficients are sufficiently small so that the optical density of the crystal is less than 0.1 and therefore concentration gradients during the photoinduced transformation are negligible. In the time-resolved with and without irradiation as well as in temperature-dependent experiments, the spectral evolution of the band corresponding to the 1A1 — 1T1 transition was monitored. Its relative intensity served to extract the LS fraction. For higher temperature experiments, the sample was placed in a He-exchange closed cycle cryostat (Janis-Sulf motovo) capable of achieving temperatures down to 3 K. Variable-temperature kinetic experiments were performed by using a home-built system consisting of 0.28 m monochromator (Spxx 280 m, holographic grating with 150 grooves per mm) equipped with a CCD camera (Jobin–Yvon Spxx CCD 3500) and polychromatic light from a 50 W tungsten halogen lamp as probe. In order to reduce the amount of light from the probe beam onto the sample, natural density filters were used. The probe beam was further gated with a shutter in parallel to the CCD camera. By using this setup, we could effectively minimize the possibility of probe-beam-induced spin transition. Moreover, for precise time-resolved experiments, a home-build computer-controlled electronic shutter-control box was used which controls the electronic shutters both in front of the laser and probe beam simultaneously. With this control setup, it is possible to perform experiments down to millisecond precision, which was sufficient for the present experiments.

Single-crystal X-ray diffraction: A selected single crystal was mounted on a cryoloop using vacuum grease. The diffraction data were collected at given temperatures between 10 and 60 K in a helium open flow cryosys-
Table 2. X-ray data collection and refinement details for \([\text{Fe(bbtr)}]_2[\text{BF}_4]_2\)...

<table>
<thead>
<tr>
<th>Before irradiation</th>
<th>After irradiation</th>
<th>Warmed to 60 K</th>
<th>Recooled to 10 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T [\text{K}])</td>
<td>10</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>crystal system</td>
<td>hexagonal</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>space group</td>
<td>(P3)</td>
<td>(P)</td>
<td>(P)</td>
</tr>
<tr>
<td>(\alpha [\text{\AA}])</td>
<td>11.5943(4)</td>
<td>11.310(2)</td>
<td>11.288(1)</td>
</tr>
<tr>
<td>(b [\text{\AA}])</td>
<td>11.5943(4)</td>
<td>11.349(2)</td>
<td>11.230(2)</td>
</tr>
<tr>
<td>(c [\text{\AA}])</td>
<td>7.5217(4)</td>
<td>15.271(2)</td>
<td>15.327(2)</td>
</tr>
<tr>
<td>(\alpha^* [^\circ])</td>
<td>90.00</td>
<td>89.89(1)</td>
<td>88.68(1)</td>
</tr>
<tr>
<td>(\beta^* [^\circ])</td>
<td>90.00</td>
<td>91.57(1)</td>
<td>91.52(1)</td>
</tr>
<tr>
<td>(\gamma^* [^\circ])</td>
<td>120.00</td>
<td>119.85(2)</td>
<td>119.90(2)</td>
</tr>
<tr>
<td>(V [\text{\AA}^3])</td>
<td>875.66(6)</td>
<td>1699.3(5)</td>
<td>1697.1(4)</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>measured data</td>
<td>7.484</td>
<td>13442</td>
<td>14025</td>
</tr>
<tr>
<td>(\theta_{\text{max}})</td>
<td>31.46</td>
<td>28.28</td>
<td>28.28</td>
</tr>
<tr>
<td>(R_{\text{wp}})</td>
<td>0.0312</td>
<td>0.1300</td>
<td>0.1369</td>
</tr>
<tr>
<td>(R_{\text{wp}})</td>
<td>0.521</td>
<td>0.537</td>
<td>0.538</td>
</tr>
<tr>
<td>(\mu [\text{mm}^{-1}])</td>
<td>0.9330/0.977</td>
<td>0.9330/0.977</td>
<td>0.933/0.977</td>
</tr>
<tr>
<td>independent data</td>
<td>1929</td>
<td>6826</td>
<td>7116</td>
</tr>
<tr>
<td>(\text{fw} [F^2 &gt; 2\sigma(F^2)])</td>
<td>0.0424 [0.0328]</td>
<td>0.1688 [0.0900]</td>
<td>0.1822 [0.0979]</td>
</tr>
<tr>
<td>(\text{fw} [F^2 &gt; 2\sigma(F^2)])</td>
<td>0.0705 [0.0658]</td>
<td>0.2702 [0.2327]</td>
<td>0.3219 [0.2760]</td>
</tr>
<tr>
<td>GOF</td>
<td>1.051</td>
<td>1.005</td>
<td>0.999</td>
</tr>
<tr>
<td>(\Delta \rho_{\text{iso}}/\rho_{\text{max}})</td>
<td>0.431/–0.378</td>
<td>1.367/–1.213</td>
<td>1.410/–1.193</td>
</tr>
</tbody>
</table>

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