Supporting Information (SI) concerning the manuscript:

\[ \text{[Fe}^\text{II}_{\text{LS}}\text{Co}^\text{III}_{\text{LS}}]\text{]}_2 \Leftrightarrow \text{[Fe}^\text{III}_{\text{LS}}\text{Co}^\text{II}_{\text{HS}}]\text{]}_2 \text{ photoinduced conversion in a cyanide-bridged heterobimetallic molecular square} \]

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**Figure S1.** View of the hydrogen bonds (dashed line) in 1.

**Figure S2.** UV-vis absorption spectra of PPh₄[Fe³⁺{B(pz)₄}(CN)₃] (2 × 10⁻⁴ mol.L⁻¹) (a), [Co²⁺(bik)₂(S)₂](ClO₄)₂ (1 × 10⁻² mol.L⁻¹) (b), and a mixture of PPh₄[Fe³⁺{B(pz)₄}(CN)₃] and [Co²⁺(bik)₂(S)₂](ClO₄)₂ (1 × 10⁻⁴ mol.L⁻¹) (c) in CH₃CN/H₂O (95/5).

**Figure S3.** Evolution curve of the magnetization of 1 under white light irradiation.
Figure S1. View of the hydrogen bonds (dashed line) in 1. O red, Cl green, Fe yellow, Co blue-violet.
Figure S2. UV-vis absorption spectra of PPh₄[Fe^{III}{B(pz)₄}(CN)₃] (2 \times 10^{-4} \text{ mol.L}^{-1}) (a), [Co^{II}(bik)₂(S)₂][ClO₄]₂ (1 \times 10^{-2} \text{ mol.L}^{-1}) (b), and a mixture of PPh₄[Fe^{III}{B(pz)₄}(CN)₃] and [Co^{II}(bik)₂(S)₂][ClO₄]₂ (1 \times 10^{-4} \text{ mol.L}^{-1}) (c) in CH₃CN/H₂O (95/5).

The building block [Co^{II}(bik)₂(S)₂] has been prepared in situ by reaction of Co(ClO₄)₂ and BIK. PPh₄[Fe^{III}{B(pz)₄}(CN)₃] exhibits a sharp peak around 410 nm which can be attributed to the ligand-to-metal charge transfer (LMCT) band. [Co^{II}(bik)₂(S)₂] displays broad absorption peaks at 1200 and 485 nm due to the d-d transitions of Co^{II} HS ion (a shoulder appears around 950 nm assigned to the absorption of [Co(bik)₃] in equilibrium with [Co(bik)₂(S)₂].
Figure S3. Evolution curve of the magnetisation of 1 under white light irradiation.