

**Supporting Information (SI) concerning the manuscript:**

$[\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{LS}}]_2 \Leftrightarrow [\text{Fe}^{\text{III}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{HS}}]_2$  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  $\text{PPh}_4[\text{Fe}^{\text{III}}\{\text{B}(\text{pz})_4\}(\text{CN})_3]$  ( $2 \cdot 10^{-4} \text{ mol.L}^{-1}$ ) (a),  $[\text{Co}^{\text{II}}(\text{bik})_2(\text{S})_2](\text{ClO}_4)_2$  ( $1 \cdot 10^{-2} \text{ mol.L}^{-1}$ ) (b), and a mixture of  $\text{PPh}_4[\text{Fe}^{\text{III}}\{\text{B}(\text{pz})_4\}(\text{CN})_3]$  and  $[\text{Co}^{\text{II}}(\text{bik})_2(\text{S})_2](\text{ClO}_4)_2$  ( $1 \cdot 10^{-4} \text{ mol.L}^{-1}$ ) (c) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (95/5).

**Figure S3.** Evolution curve of the magnetization of **1** under white light irradiation.

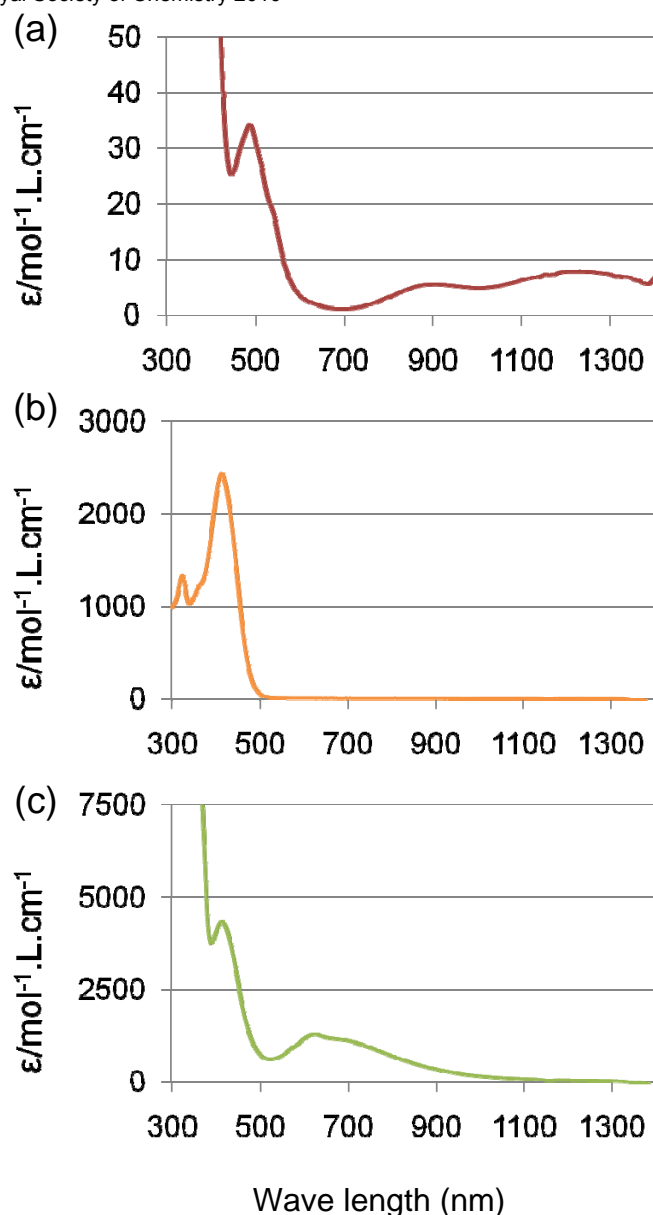
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**N3**

**O3**

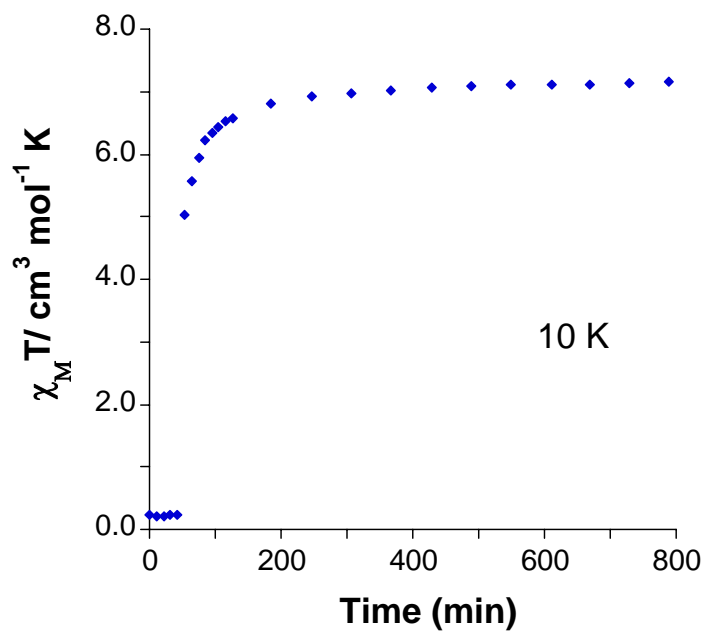
**O7**

***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  $\text{PPh}_4[\text{Fe}^{\text{III}}\{\text{B}(\text{pz})_4\}(\text{CN})_3]$  ( $2 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ) (a),  $[\text{Co}^{\text{II}}(\text{bik})_2(\text{S})_2](\text{ClO}_4)_2$  ( $1 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ ) (b), and a mixture of  $\text{PPh}_4[\text{Fe}^{\text{III}}\{\text{B}(\text{pz})_4\}(\text{CN})_3]$  and  $[\text{Co}^{\text{II}}(\text{bik})_2(\text{S})_2](\text{ClO}_4)_2$  ( $1 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ) (c) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (95/5).

The building block  $[\text{Co}^{\text{II}}(\text{bik})_2(\text{S})_2]$  has been prepared in situ by reaction of  $\text{Co}(\text{ClO}_4)_2$  and BIK.  $\text{PPh}_4[\text{Fe}^{\text{III}}\{\text{B}(\text{pz})_4\}(\text{CN})_3]$  exhibits a sharp peak around 410 nm which can be attributed to the ligand-to-metal charge transfer (LMCT) band.  $[\text{Co}^{\text{II}}(\text{bik})_2(\text{S})_2]$  displays broad absorption peaks at 1200 and 485 nm due to the d-d transitions of  $\text{Co}^{\text{II}}_{\text{HS}}$  ion (a shoulder appears around 950 nm assigned to the absorption of  $[\text{Co}(\text{bik})_3]$  in equilibrium with  $[\text{Co}(\text{bik})_2(\text{S})_2]$ ).



**Figure S3.** Evolution curve of the magnetisation of **1** under white light irradiation.