Electronic Supplementary Material for CrystEngComm



# Photo- and Thermally-Enhanced Charge Separation in Supramolecular Viologen-Hexacyanoferrate Complexes

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**Supporting Information**

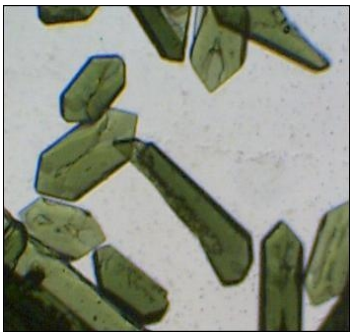


**Fig. S1** Crystals of the viologen/hexacyanoferrate complex under visible-light microscope

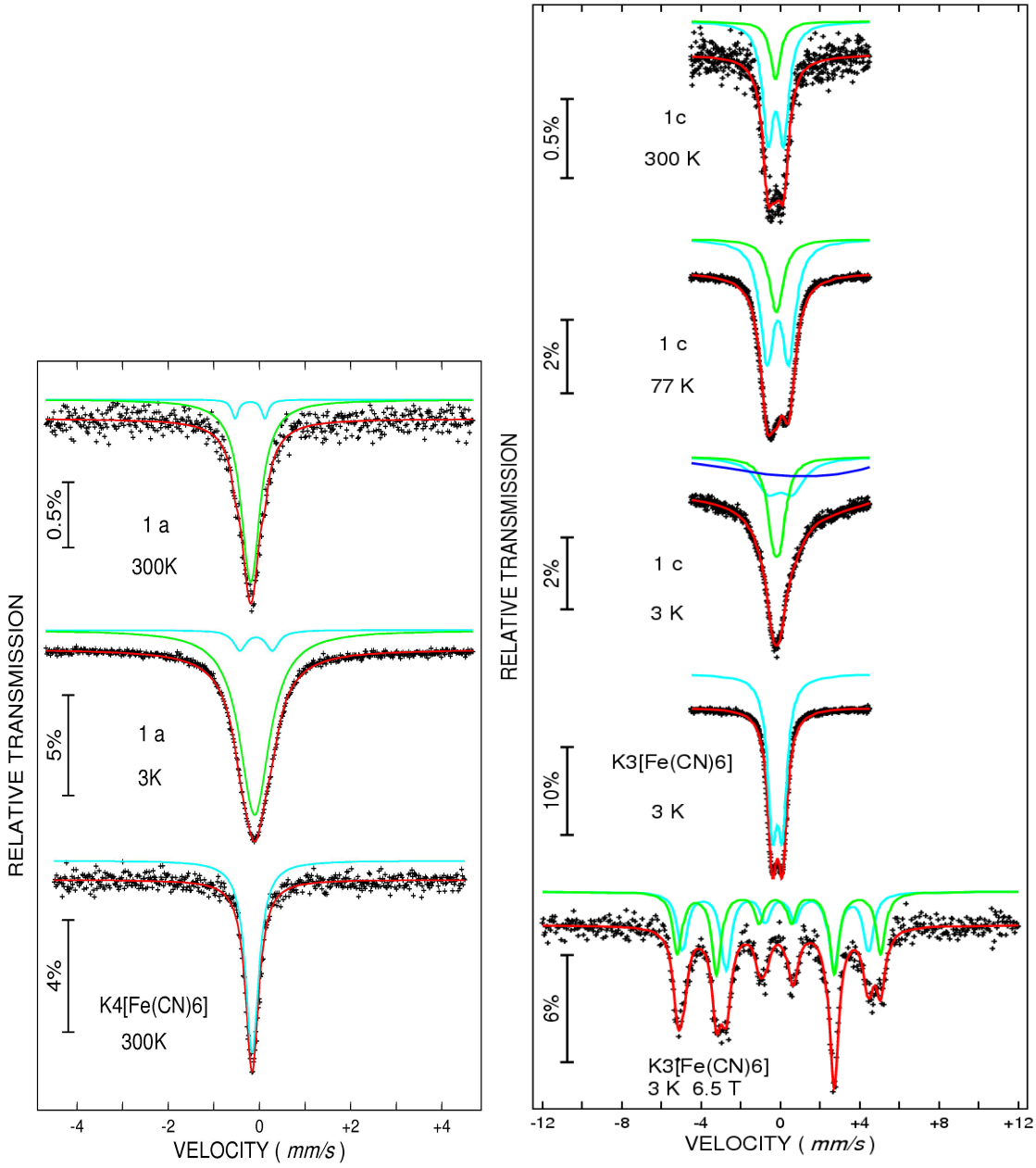



**Fig. S2** Mössbauer spectra of (**1a**) at 300 and 3 K (left), and (**1c**) at 300, 77 and 3 K (right). Mössbauer spectra for $K_4[Fe^{II}(CN)_6]$ and $K_3[Fe^{III}(CN)_6]$ are shown for comparison.

**Table S1**. Mössbauer data for (**1a**).

| T, K | Type of Fe | $\delta$[a], mm/s | $\Delta E_Q$ or $\varepsilon$, mm/s | $\Gamma$, mm/s | $B_{eff}$, T |
|---|---|---|---|---|---|
| 300 | Fe(II) | -0.008(3) | 0 | 0.52(1) | - |
| | Fe(III) | -0.097(8) | 0.66(3) | 0.25(1) | - |
| 3 | Fe(II) | 0.006(1) | 0 | 0.80(3) | - |
| | Fe(III) | -0.036(5) | 0.72(1) | 0.25(1) | - |
| 3K, 6.5T | Fe(II) | 0.009(1) | 0.004(8)[b] | 0.33(1) | 6.76 |
| | Fe(III) | -0.069(8) | 0.46(1)[b] | 0.27(4) | 30.90 |

[a] Relative to $\alpha$-Fe at room temperature.
[b] For magnetically-split spectra $\varepsilon = \frac{1}{2}\Delta E_Q(3\cos^2\theta\text{-}1)$ (quadrupole shift).

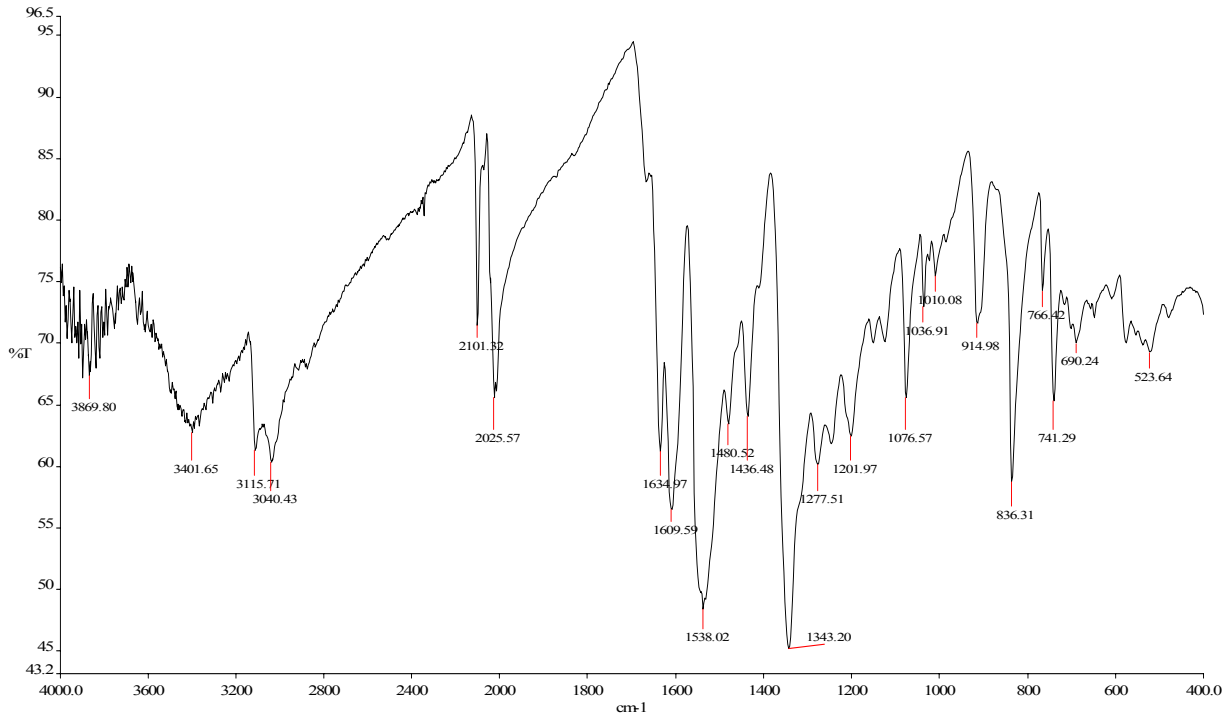
**Table S2**. Mössbauer data for (**1c)**.

| T, K | Type of Fe | $\delta$[a], mm/s | $\Delta E_Q$ or $\varepsilon$, mm/s | $\Gamma$, mm/s | $B_{eff}$, T | Area, % |
|---|---|---|---|---|---|---|
| 300 | Fe(II) | -0.096(8) | 0 | 0.67(6) | - | 20.0 |
| | Fe(III) | -0.116(7) | 0.78(2) | 0.66(2) | - | 80.0 |
| 77 | Fe(II) | -0.067(1) | 0 | 0.82(1) | - | 24.86 |
| | Fe(III) | -0.085(2) | 1.02(3) | 0.80(1) | - | 75.14 |
| 3 | Fe(II) | -0.041(8) | 0 | 0.75(4) | - | 28.4 |
| | Fe(III) | -0.061(4) | 1.12(4) | 0.75(4) | - | 71.6 |
| 3K, 6.5T | Fe(II) | 0.006(9) | 0.004(7)[b] | 0.45(1) | 6.75 | 28.4 |
| | Fe(III) | -0.097(6) | 0.031(8)[b] | 0.83(7) | 30.52 | 71.6 |

[a] Relative to $\alpha$-Fe at room temperature.
[b] For magnetically-split spectra $\varepsilon = \frac{1}{2}\Delta E_Q(3\cos^2\theta\text{-}1)$ (quadrupole shift).

**Table S3.** Microanalyses of the fresh and heated samples at 80 °C, 95 °C and 150 °C.

| **Condition** | **Formula unit** | **Calculated** | **Found** |
|---|---|---|---|
| Fresh sample<br>(dried in vacum) | $C_{50}H_{28}FeN_{18}O_{16}.7.5H_2O$ | C, 45.23<br>H, 3.26<br>N, 18.99 | C, 45.18<br>H, 3.01<br>N, 18.24 |
| Heated at 80 °C | $C_{50}H_{28}FeN_{18}O_{16}.1H_2O$ | C, 49.60<br>H, 2.50<br>N, 20.82 | C, 49.53<br>H, 2.48<br>N, 20.71 |
| Heated at 95 °C | $C_{50}H_{28}FeN_{18}O_{16}.0.5H_2O$ | C, 49.97<br>H, 2.43<br>N, 20.98 | C, 49.93<br>H, 2.22<br>N, 20.51 |



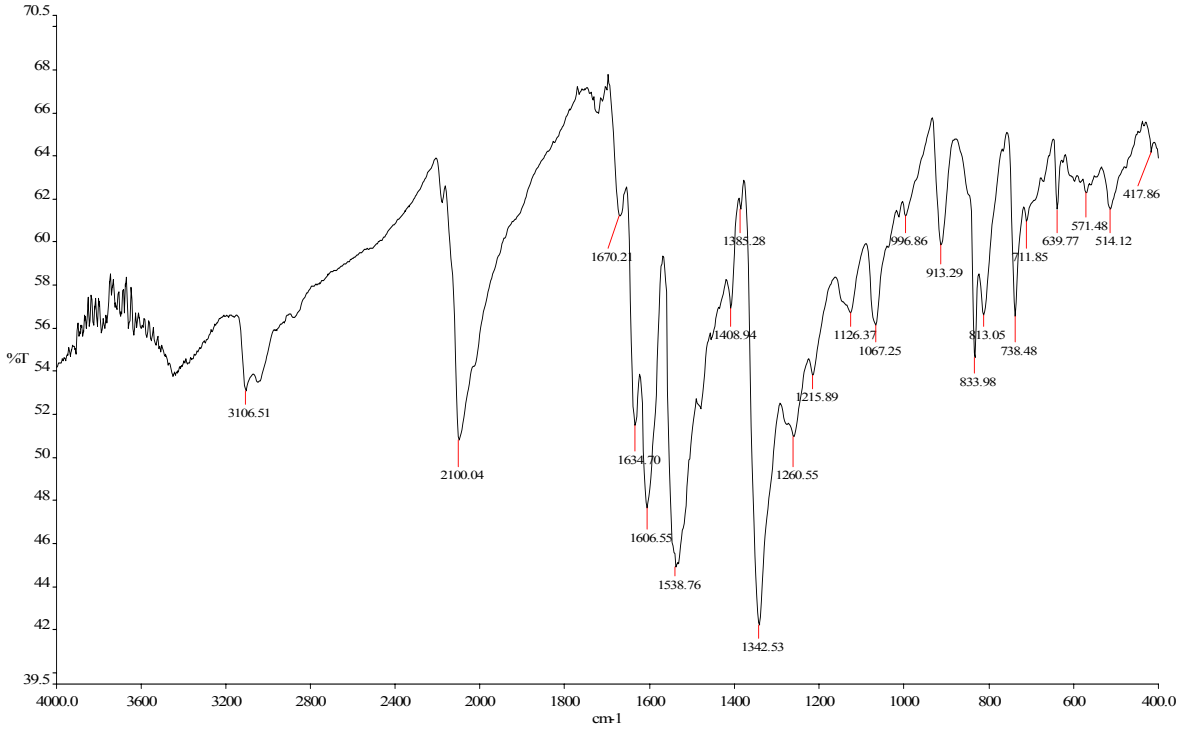



**Fig. S3** IR spectra of the complexes (**1a),** top**;** and (**1c)**, bottom in the range 400 - 4000 $cm^{-1}$.

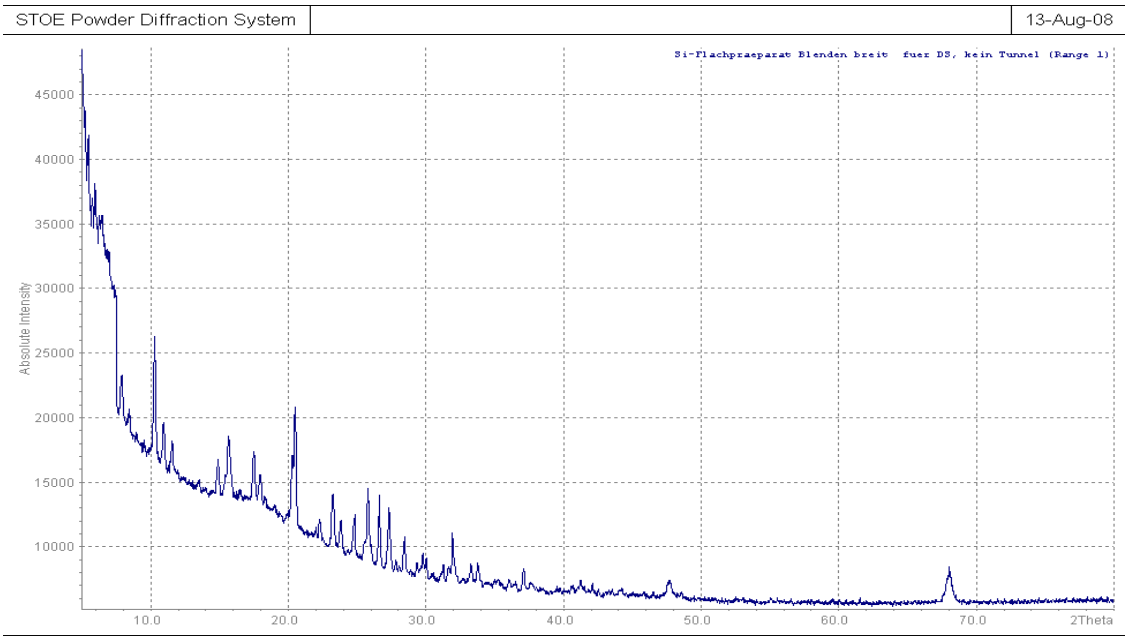



**Fig. S4** X-ray powder pattern for sample (**1a**).

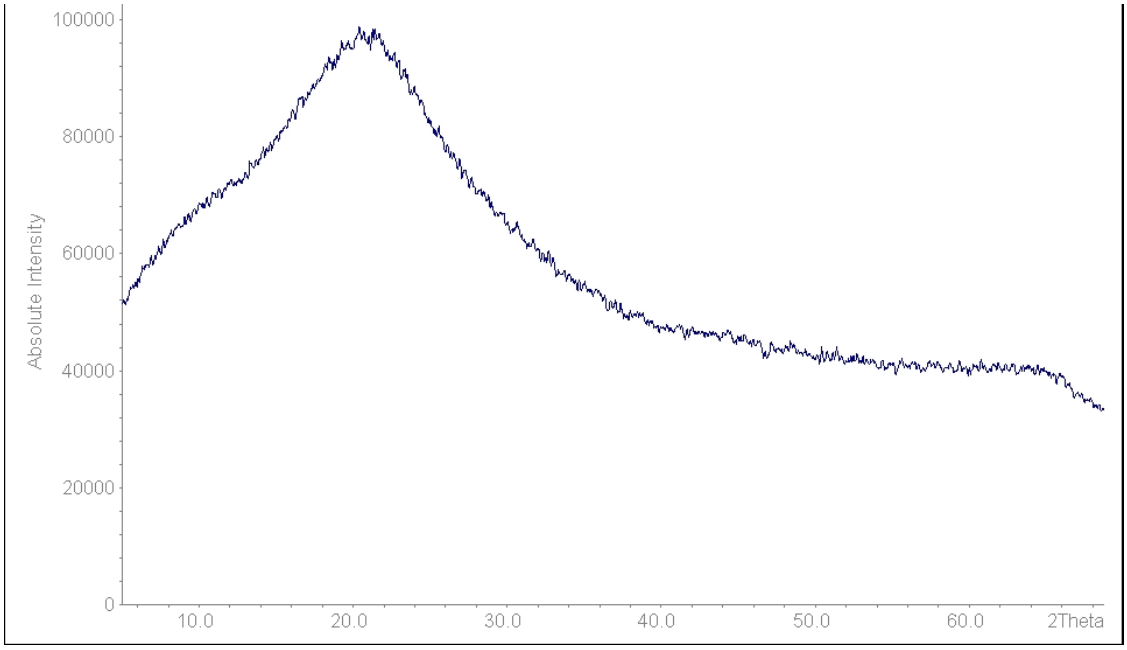



**Fig. S5** X-ray powder pattern for sample (**1c**).