Electronic Supporting Information

Light-induced decarboxylation in a photo-responsive iron-containing complex based on polyoxometalate and oxalato ligands

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1. IR spectra

![Infra-red spectra of 1 (red) and 2 (violet).](image)

Fig. S1. Infra-red spectra of 1 (red) and 2 (violet).

2. Thermogravimetric analysis

The interpretation of the thermogravimetric analysis curves of 1 and 2 (Figs. S2 and S3) are based on previously reported thermal decompositions reactions of the salts $K_3[Fe(C_2O_4)_3] \cdot 3H_2O^1$ and $K_3[Fe(C_3H_2O_4)_3] \cdot H_2O^2$. According to them, the thermal decomposition reactions of 1 and 2 can be established as:

$$K_{16}[(PW_9O_{34})_2Fe_2(C_2O_4)_2] \cdot 29H_2O \rightarrow K_{12}P_2W_{18}O_{68}Fe_2 + K_2O + K_2CO_3 + CO_2 + 2CO + 29H_2O$$

$$K_{16}[(PW_9O_{34})_2Fe_2(C_3H_2O_4)_2] \cdot 27H_2O \rightarrow K_{12}P_2W_{18}O_{68}Fe_2 + K_2O + K_2CO_3 + CO_2 + 2CO + C_2H_4 + 27H_2O$$

which allow to calculate the theoretical percentage values for the total weight loss of 1 and 2 (10.56% and 10.44%, respectively).
**Fig. S2.** Thermogram curve of 1 from room temperature to 500°C (experimental total weight loss: 10.56%).

**Fig. S3.** Thermogram curve of 2 from room temperature to 500°C (experimental total weight loss: 10.44%).

**Fig. S4.** Thermogram curve of an irradiated sample of 1 from room temperature to 500°C (experimental total weight loss: 7.57%).
3. X-ray crystallography

Further details of the crystal structure investigation(s) may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, on quoting the deposition number CSD-430800).

Table S1. Crystallographic data for \( \text{K}_{15}\{\text{K} \subset [\{(A-\alpha-\text{PW}_{9}\text{O}_{34})_{2}\text{Fe}_{2}(\text{C}_{2}\text{O}_{4})_{2}\}] \cdot 29\text{H}_{2}\text{O} \) (1) and \( \text{K}_{15}\{\text{K} \subset [\{(A-\alpha-\text{PW}_{9}\text{O}_{34})_{2}\text{Fe}_{2}(\text{C}_{3}\text{H}_{2}\text{O}_{4})_{2}\}] \cdot 27\text{H}_{2}\text{O} \) (2).

| Compound | 1 | 2 |
|----------|---|---|
| Empirical formula | \( \text{C}_{4}\text{H}_{56}\text{Fe}_{2}\text{K}_{16}\text{O}_{104}\text{P}_{2}\text{W}_{18} \) | \( \text{C}_{6}\text{H}_{58}\text{Fe}_{2}\text{K}_{16}\text{O}_{103}\text{P}_{2}\text{W}_{18} \) |
| Formula weight | 5877.02 | 5887.06 |
| Temperature (K) | 120.05(10) K | 120.00(10) K |
| Wavelength [Å] | 0.71073 Å | 0.71073 Å |
| Crystal system | Triclinic | Monoclinic |
| Space group | \( P-1 \) | \( C2/c \) |
| \( a/Å \) | 12.7825(4) | 16.7363(2) |
| \( b/Å \) | 13.3179(4) | 26.2852(4) |
| \( c/Å \) | 15.8979(3) | 23.9398(4) |
| \( \alpha^\circ \) | 90.6680(18) | 90 |
| \( \beta^\circ \) | 109.604(2) | 101.127(2) |
| \( \gamma^\circ \) | 104.435(3) | 90 |
| \( V/Å^3 \) | 2455.52(12) | 10333.6(3) |
| \( Z \) | 1 | 4 |
| \( \rho_{\text{calc}}/\text{g cm}^{-3} \) | 3.974 | 3.784 |
| \( \mu/\text{mm}^{-1} \) | 22.108 | 21.013 |
| \( R[F_o^2 > 2\sigma(F_o^2)] \) | 0.0770 | 0.0327 |
| \( R_{w}[F_o^2 > 2\sigma(F_o^2)] \) | 0.1800 | 0.0766 |

\( a = \sum (|F_o| - |F_c|)/|F_o|) \sum |F_o| b = w[F_o^2 - F_c^2]^2/w[|F_o^2 - F_c^2|]^2, w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP], where P = (F_o^2 + 2F_c^2)/3. \)
Table S2. Fe-O bond distances (Å) and O-Fe-O angles (°) in 1 and 2.

|                  | 1        | 2        |
|------------------|----------|----------|
| Fe(1)-O(1F)     | 1.947(19)| 2.028(6) |
| Fe(1)-O(9F)'    | 1.957(13)| 1.976(6) |
| Fe(1)-O(6F)     | 1.990(14)| 1.992(6) |
| Fe(1)-O(2F)     | 2.011(18)| 2.022(6) |
| Fe(1)-O(4F)'    | 2.025(15)| 1.977(6) |
| Fe(1)-O(5F)     | 2.037(14)| 1.982(5) |
| O(1F)-Fe(1)-O(9F)' | 91.3(7) | 94.4(2)  |
| O(1F)-Fe(1)-O(6F) | 87.6(7) | 87.7(2)  |
| O(9F)'-Fe(1)-O(6F) | 175.3(7) | 176.6(2) |
| O(1F)-Fe(1)-O(2F) | 82.1(8) | 86.4(2)  |
| O(9F)'-Fe(1)-O(2F) | 91.1(7) | 87.1(2)  |
| O(6F)-Fe(1)-O(2F) | 93.2(7) | 90.3(2)  |
| O(1F)-Fe(1)-O(4F)' | 97.9(7) | 87.5(2)  |
| O(9F)'-Fe(1)-O(4F)' | 87.8(6) | 89.0(2)  |
| O(6F)-Fe(1)-O(4F)' | 87.9(6) | 93.8(2)  |
| O(2F)-Fe(1)-O(4F)' | 178.9(6) | 172.5(2) |
| O(1F)-Fe(1)-O(5F) | 167.8(7) | 175.3(2) |
| O(9F)'-Fe(1)-O(5F) | 93.1(6) | 90.0(2)  |
| O(6F)-Fe(1)-O(5F) | 88.9(6) | 87.9(2)  |
| O(2F)-Fe(1)-O(5F) | 86.5(7) | 92.1(2)  |
| O(4F)'-Fe(1)-O(5F) | 93.6(6) | 94.2(2)  |

Symmetry transformations: (i) −x+1, −y, −z+1 (for 1); −x, −y, −z+1 (for 2).
4. Bond valence sum (BVS) calculations

For determination of the oxidation states of metal centers, bond valence sum (BVS) calculations were carried out using the method of I. D. Brown. The calculation formula is $S_i = \exp[(R_0 - R_i)/B]$, where $S_i$ is the bond valence of bond $i$, $R_0$ is a constant dependent upon the bonded elements, $R_i$ is the bond length of bond $i$, and $B$ equals to 0.37. $R_0$ values were taken from the literature for calculations performed on Fe and O sites [$R_0 (\text{Fe - O}) = 1.745$].

| Iron atoms | BVS$^1$ |
|------------|---------|
| 1          | 2.99    |
| 2          | 3.03    |

**Fig. S5.** Bond valence sum (BVS) calculations for the Fe atom in 1 and 2 (top). Polyhedral and ball-and-stick mixed representations of 1 and 2. The assigned oxidation states are highlighted in bold and shaded.
5. **X-ray powder diffraction**

X-ray Powder Diffraction Measurements were carried out using ground samples of 1, 2 and an irradiated sample of 1, which were packed into 0.7 mm borosilicate capillaries prior to being mounted and aligned on an Empyrean PANalytical powder diffractometer, using Cu Kα radiation (\( \lambda = 1.54056 \) Å). For each sample, three repeated measurements were collected at room temperature (\( 2\theta = 4 - 40^\circ \)) and merged in a single diffractogram.

![Figure S6](image1.png)

**Fig. S6.** Comparison of simulated and experimental powder X-ray diffraction patterns for 1.

![Figure S7](image2.png)

**Fig. S7.** Comparison of simulated and experimental powder X-ray diffraction patterns for 2.

![Figure S8](image3.png)

**Fig. S8.** Comparison of the powder X-ray diffraction patterns of sample 1 before and after irradiation.
6. **UV-vis spectra of 1 and 2 in aqueous solution**

The UV-vis spectra of 1 and 2 in aqueous solution were recorded on an Agilent 8453 UV-vis spectrophotometer from 190 to 400 nm using 1.000-cm-optical-path quartz cuvettes in milli-Q water.

![UV Spectra of 1 (top) and 2 (down) in aqueous solution.](image)

**Fig. S9.** UV Spectra of 1 (top) and 2 (down) in aqueous solution.
7. **Coloration kinetics**

The $R(t)$ vs $t$ relationship for 1 is perfectly fitted by $R^{525}(t) = a/[bt+1] + [R^{525}(0)-a]$. (See reference\textsuperscript{5} for details of the kinetics model used here). $R^{525}(0)$ is the reflectivity value at $t = 0$, i.e., at the time just before UV illumination. The $a$ parameter is the difference between the reflectivity values at $t = 0$ and at $t = \infty$, i.e. at the end of the photocoloration process. The half-life $t_{1/2}$, is defined as the time required for $R(t)$ to reach the $[R(0)+R(\infty)]/2$ value. $t_{1/2}$ is given by $t_{1/2} = b^{-1}$.

**Fig. S10.** Evolution of the photogenerated Reflectivity $R(t)$ of 1 in the $380 – 800$ nm range after 0, 0.17, 0.67, 1.17, 1.67, 2.17, 2.67, 3.17, 3.67, 4.33, 5, 5.67, 6.33, 9, 10, 11, 14, 16, 18, 22, 29 and 34 min of UV irradiation (351 nm). After being irradiated for 34 min, the compound was stored in the dark during 7 days and its absorption spectrum recorded (dotted line).
Fig. S11. Reflectivity $R(t)$ vs. $t$ plot for 1 measured at 525 nm for 0, 0.17, 0.67, 1.17, 1.67, 2.17, 2.67, 3.17, 3.67, 4.33, 5, 5.67, 6.33, 9, 10, 11, 14, 16, 18, 22, 29 and 34 min of UV irradiation (351 nm).

| $R(t)$ | 0.835 |
|--------|-------|
| $a$    | 0.722 |
| $b$    | 0.230 |
| $R^2$  | 0.99174 |
| $t_{1/2}$ (min) | 4.35 |

Table S3. Regression coefficient values of the fitting parameters describing the $R(t)$ vs $t$ relationship for 1.
**Fig. S12.** Comparison of the absorption spectra of 2 at 0 min (black line) and after 30 min (red line) of UV irradiation (351 nm).

**Fig. S13.** (a) Crystals of 1 after 5 min UV irradiation at 351 nm. (b) The same crystals as in (a) cut to observe the colour of the interior. (c-d) Different views of the cut crystals in (b). These photographs show that the interior of transparent crystals exhibit the same colour as their surface, suggesting that the photocoloration process happens in the bulk crystals. For powder samples (with less transparency), the photocoloration effect mostly happens on the surface.
**Fig. S14.** Some crystals of 1 before irradiation (left) and after 5min of UV irradiation at 351 nm (right).
### 8. Mössbauer spectroscopy

**Table S4.** Estimated parameters from the Mössbauer spectra taken at room temperature of sample $^{57}$Fe and $^{57}$Fe.

| $^{57}$Fe | $^{57}$Fe | $^{57}$Fe | $^{57}$Fe |
|----------|----------|----------|----------|
| $t_{UV}$ | IS (mm/s) | QS (mm/s) | I         | Fe state |
| 0.41     | 0.10     | 100%     | Fe(III)  |
| 0.40     | 0.35     | 100%     | Fe(III)  |
| 0.37     | 0.56     | 21%      | Fe(III)  |
| 1.13     | 1.49     | 79%      | Fe(II)   |
| 0.36     | 0.54     | 33%      | Fe(III)  |
| 1.13     | 1.50     | 67%      | Fe(II)   |
| 0.40     | 0.50     | 50%      | Fe(III)  |
| 1.12     | 1.50     | 50%      | Fe(II)   |
| 0.39     | 0.50     | 60%      | Fe(III)  |
| 1.12     | 1.51     | 40%      | Fe(II)   |
| 0.38     | 0.38     | 77%      | Fe(III)  |
| 1.13     | 1.46     | 23%      | Fe(II)   |
| 0.38     | 0.39     | 87%      | Fe(III)  |
| 1.09     | 1.44     | 13%      | Fe(II)   |
| 0.38     | 0.35     | 89%      | Fe(III)  |
| 1.10     | 1.40     | 11%      | Fe(II)   |
| 0.37     | 0.35     | 96%      | Fe(III)  |
| 1.05     | 1.38     | 4%       | Fe(II)   |
| 12 days  | 0.37     | 100%     | Fe(III)  |
| 0.28     | 1.68     | 3%       | Fe(II)   |

IS isomer shift relative to metallic $\alpha$-Fe at 295 K; QS quadrupole splitting; I relative areas. Estimated errors are $\leq 0.02$ mm/s for IS, QS, $\leq 2\%$ for I, $t_{UV}$, elapsed time between mid-spectrum collection and the moment when UV irradiation was switched off, is defined in the text.

**Fig. S15.** Mössbauer spectrum of $^{57}$Fe sample.
Fig. S16. Relative areas of Fe(II), I(Fe$^{3+}$), estimated from Mössbauer spectra of $^{57}$Fe vs. average time after first (closed circles) and second (open squares) UV-irradiation.

Fig. S17. Mössbauer spectra of $^{57}$Fe sample taken after a second 6h UV irradiation for $t_{UV} \sim 0.37$ h (a), 4 h (b), 24 h (c), 7 days (d), and 12 days (e). $t_{UV}$, time after irradiation was switched off, is defined in the text. The lines over the experimental points are the sum of two quadrupole doublets shown slightly shifted for clarity (estimated parameters in Table S4).
9. Magnetic properties

Experimental. Variable-temperature susceptibility measurements were carried out in the temperature range 2-300 K on compacted powder moulded from ground crystalline samples of 1 and 2 on a magnetometer equipped with a SQUID sensor (Quantum Design MPMS-XL-5). The data were corrected for the diamagnetic contributions of the polyanions as deduced by using the Pascal’s constant tables. Isothermal magnetization measurements at low temperature (2 K and 5 K) were performed up to a field of 5 T in the same apparatus.

Results and discussion. The $\chi_m T$ product of 1 has a constant value around 8.4 cm$^3$ mol$^{-1}$ K above 40 K (see Fig. S18) which is consistent with the presence of two Fe(III) ions with spins $S = 5/2$ (8.75 cm$^3$ mol$^{-1}$ K). Below this temperature a sharp drop occurs which suggests the presence of antiferromagnetic exchange coupling between the two metal ions, although the local anisotropy of Fe(III) can also have an influence. Below 1 T, magnetization data at 2 K show a small increase with the magnetic field, in agreement with the presence of antiferromagnetic exchange, and a nonmagnetic ground spin state. Above 1 T, the magnetization increases more rapidly due to the population of excited states having higher spin multiplicities.

The appropriate spin Hamiltonian for this type of dinuclear compound is written as

$$\hat{H} = -2J \hat{S}_1 \hat{S}_2 + D(\hat{S}_{z1}^2 + \hat{S}_{z2}^2).$$

In this equation, $\hat{S}_1$ and $\hat{S}_2$ are the spin operators associated with the Fe(III) ions, and $J$ and $D$ are the exchange and ZFS parameters, respectively. Taking into account both effects and using a simultaneously fit of susceptibility and magnetization curves, we have obtained an excellent fit of the experimental data from the following parameters $D = -1.5$ cm$^{-1}$, $J = -0.24$ cm$^{-1}$, and $g = 2.05$ (solid line in Fig. S18). The dependence of the fit with respect to the parameters is shown in a two-dimensional plot of the error factor R on the values $J$ and $D$ (see inset Fig. S18). A minimum error region can be observed for each sign of $D$, negative
and positive. However, the minimum of the region with negative $D$ has an error two orders of magnitude lower. This difference in quality between the two minimum shows that only a solution with both negative parameters can reproduce the crossing of the magnetization curves.

![Graph showing magnetic properties](image)

**Fig. S18.** Magnetic properties of 1: (up) thermal dependence of the $\chi_m T$ product (inset: surface error plot of $\chi_m$ vs. $T$ as a function of $J$ and $D$ revealing two banana minima); (down) magnetization curves at 2 and 5 K. Solid lines represent the calculated curve from the best simultaneous fit of susceptibility and magnetization curves.

Other combinations of parameters do not lead to a crossing between the M curves at 2 and 5 K, regardless of the field value. Similar results were obtained for 2. The minimum errorless set of parameters is $D = -2.4 \text{ cm}^{-1}$, $J = -0.10 \text{ cm}^{-1}$, and $g = 2.01$ (see Fig. S19). This negative value of $D$ is very unusual for Fe$^{III}$. There is similar magnitude and sign of $D$ in Fe(III)
peroxides.\textsuperscript{6,7} Negative sign can be attributed to low symmetry and spin-orbit coupling of the \(6\text{A}_1\) ground-state with excited quartet-LF and sextet-CT states.\textsuperscript{8} Another model that considers a positive value for the ZFS and replaces the isotropic exchange by anisotropic dipolar interaction has not given satisfactory solutions. Magnetic dipolar interactions between cations of different molecules were not considered because in general distances greater than 10 Å separate them.

![Graph](image)

**Fig. S19.** Magnetic properties of 2: thermal dependence of the \(\chi_m T\) product (inset: surface error plot of \(\chi_m\) vs. \(T\) as a function of \(J\) and \(D\)). Solid line represents the calculated curve from the best simultaneous fit of susceptibility curve.

Magnetic measurements on an irradiated sample have also been performed. Thermal dependence of the \(\chi_m T\) product for this sample shows no significant changes with respect to 1. Still, important differences appear in the isothermal magnetization performed at low temperatures (see Fig. S20). For example, the crossing of the magnetization curves at 2 and 5 K is not observed. This is not surprising since, according with the scenario depicted by DRS, IR, XPS and Mossbauer measurements, only a part of the oxalato ligands have been oxidized, and therefore there is a mixture of different coordination spheres and possible oxidation states for iron ions. Thus, a quantitative data fitting is not possible. Assuming an average effect with
only one $J$ and $D$ parameter in the sample and using the same model used before, a positive $D$ of about 7 cm$^{-1}$ has been obtained and negligible exchange. This large $D$ value may reflect the presence of Fe(II), which is more anisotropic than Fe(III). Still, what is important to notice is that the irradiation leads to a small but detectable modification in the magnetic properties of the solid, which is in agreement with the fact that the decarboxylation process caused by the irradiation takes place mainly in the surface of the sample.

**Fig. S20.** Magnetic properties of irradiated sample 1: thermal dependence of the $\chi_m T$ product (inset: magnetization curves at 2 and 5 K).
10. References

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