Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supporting Information

Materials and characterization techniques

Synthesis

Scheme S1 Schematic representation of $[Fe(R\text{-}trz)_3]a_2.n$ 1D chains. {a = anion, n = solvent, R = NH_2}.

Table S1 ^{57}Fe Mössbauer parameters of $[Fe(NH_2trz)_3]$(***tos***)$_2\cdot H_2O$ before and after irradiation. $\Gamma/2$ = half width of the lines.

Fig. S1 PXRD patterns of **CP-1** and **CP-2**.

Fig. S2 ^1H NMR spectra of NH_2trz before and after UV irradiation.

Fig. S3 Diffuse reflectance spectra of ***psca*** and ***dsta***.

Fig. S4 Comparison of $\chi_M T$ *vs.* T plots of **CP-1** and **CP-2** during the first cooling cycles from 300 K to 200 K.

Fig. S5 $\chi_M T$ *vs.* T plots of dehydrated forms of **CP-1** and **CP-2** with ΔT_{80} calculations.

Fig. S6. Photographs of $[Fe(NH_2trz)_3]$(***tos***)$_2\cdot H_2O$ taken before and after UV irradiation, at room temperature.

Fig. S7. TGA curves of $[Fe(NH_2trz)_3]$(***tos***)$_2\cdot H_2O$ before and after UV irradiation. The same amount of mass was (ca. 2.6%) corresponding to one water molecules was observed. Thus, UV irradiation has no effect on the molecular formula.

Fig. S8 ^{57}Fe Mössbauer spectra of $[Fe(NH_2trz)_3]$(***tos***)$_2\cdot H_2O$ before (left) and after irradiation (right), at room temperature.

Materials and characterization techniques

All chemicals were bought from usual chemical companies and used as received without further purification. $[Fe(H_2O)_6)](\textbf{\textit{psca}})_2 \cdot 2H_2O$ and $[Fe(H_2O)_6)](\textbf{\textit{tos}})_2 \cdot 2H_2O$ were prepared by following the reported procedures.[1,2] Elemental analysis for C, H, and N analysis were performed at MEDAC Ltd, UK. Infrared spectra were recorded on a Shimadzu FTIR-8400S instrument using KBr pellets. Powder XRD analysis was done on a D8 Advanced diffractometer from Bruker. The diffractogram was recorded using CuKα radiation (0.15406 nm) and a linkeye XE-T detector (Bruker) in the 2-50° (2θ) range with an increment of 0.0015° and an integration time of 0.15s. Diffuse reflectance spectra (DRS) were recorded at 295 K with a PerkinElmer Lambda9 UV/vis/NIR spectrophotometer equipped with a 60 mm integrating sphere and converted into absorption spectra by using the Kubelka−Munk function, using $BaSO_4$ as a reference. TGA were performed in air (100 mL/min) at the heating rate of 5 °C/min from 298 to 408 K using a Mettler Toledo TGA/SDTA 851e analyzer. Magnetic susceptibility measurements for all the complexes were carried out on a MPMS3 SQUID magnetometer (Quantum Design Inc.) in DC mode, under a DC magnetic field of 1000 Oe, with a temperature rate of 2 K/min. Magnetic data were corrected for the sample holder and diamagnetic contributions. ^{57}Fe Mössbauer spectra were recorded at room temperature in transmission geometry mode with a constant acceleration mode conventional Wissel Mössbauer spectrometer equipped with a $^{57}Co(Rh)$ radioactive source, a Reuter Stokes proportional counter detector and a CMCA-550 multichannel analyzer. All isomer shifts are given respective to α-Fe. Spectra were fitted to the sum of Lorentzian lines by a least-squares refinement using Recoil 1.05 Mössbauer Analysis Software.[3]

Synthesis

$[Fe(H_2O)_6)](\textit{psca})_2 \cdot 2H_2O$:

Single crystals were obtained upon recrystallization from distilled H_2O.[4] Yield: 57% (6.25 g). FTIR (KBr, cm^{-1}): 1695 cm^{-1} (C═O), 1631 (C═C), 1314 (asym S═O), 1126 (sym S═O), 807 (S–O). Elemental analysis calculated for $FeC_{18}O_{18}H_{30}S_2$: C, 33.04; H, 4.62; S, 9.80. Found: C, 33.04; H, 4.60; S, 9.79.

$[Fe(NH_2trz)_3](\textit{psca})_2 \cdot 2H_2O$ (CP-1):

0.126 g (1.5 mmol) of 4-amino-1,2,4-triazole (NH_2trz) was dissolved in methanol (5 mL). To this solution was slowly added a solution of 0.327 g (0.5 mmol) of freshly synthesized $[Fe(H_2O)_6]$(*psca*)$_2$·$2H_2O$ along with a pinch of ascorbic acid in hot methanol (15 mL). A white precipitate appeared immediately. The reaction mixture was stirred for 20 min to ensure the completion of the reaction. The precipitate was then filtered, washed with methanol (10 mL) and dried at ambient conditions. The precipitate changed colour from white to pink during the drying process. Yield: 72% (0.29 g). FTIR (KBr, cm^{-1}): 3280, 3212 (N-H), 3103, 3062 (C-H), 1689 (C=O), 1639 (C=C and C=N), 1307 (asymmetric S=O), 1118 (symmetric S=O), 831 (S-O). *Anal. Calc.* for $FeC_{24}O_{12}N_{12}H_{30}S_2$: C, 36.10; H, 3.79; N, 21.04; S, 8.03. Found: C, 36.05; H, 3.85; N, 21.05; S, 8.10.

$[Fe(NH_2trz)_3]$(*dsta*)·$2.5H_2O$ (CP-2):

The solid state *[2+2]* photodimerization of **CP-1** was performed with a broad UV wavelength 15W fluorescent lamp. **CP-1** was finely ground and spread over a watch glass, thereafter it was irradiated for 18 hours. The sample was mixed throughout the reaction at regular intervals to have maximum exposure of UV light on to the sample. During the course of the reaction the colour of the compound changed gradually from pink to brown as shown in Fig. 2. The colour started to change after c.a. 12 h. of irradiation, however irradiation was continued to 18 h. until ensuring no further colour change was observed. FTIR (KBr, cm^{-1}): 3292, 3220 (N-H), 3107, 3056 (C-H), 1701 (C=O), 1638 (C=C and C=N), 1124 (symmetric S=O), 833 (S-O). *Anal. Calc.* for $FeC_{24}O_{12.5}N_{12}H_{31}S_2$: C, 35.70; H, 3.87; N, 20.81; S, 7.94. Found: C, 35.55; H, 3.92; N, 20.84; S, 7.95.

$[Fe(NH_2trz)_3](tos)_2$·H_2O:

0.126 g (1.5 mmol) of 4-amino-1,2,4-triazole (NH_2trz) was dissolved in methanol (5 mL). To this solution was added a solution of 0.271 g (0.5 mmol) of $[Fe(H_2O)_6]$(*tos*)$_2$·$2H_2O$ along with a pinch of ascorbic acid in hot methanol (15 mL). A white precipitate appeared as soon as the two reactants were mixed. The reaction mixture was stirred for 20 min to ensure the completion of the reaction. The precipitate was then filtered, washed with methanol (10 mL) and dried at ambient conditions. The precipitate changed colour from white to pink during the drying process. Yield: 78% (0.26 g). TGA: 2.61% (1 H_2O molecule).^{57}Fe Mössbauer (α-Fe, mm/s): δ = 1.05, 0.44; ΔE_Q = 2.79, 0.21.

UV irradiation on $[Fe(NH_2trz)_3](tos)_2$·H_2O

$[Fe(NH_2trz)_3](\textit{\textbf{tos}})_2 \cdot H_2O$ was irradiated in solid state with a broad UV wavelength 15W fluorescent lamp. The material was finely ground and spread over a watch glass, thereafter it was irradiated for 20 h with regular mixing and grinding to expose maximum sample to UV light.

UV irradiation on NH_2trz

The irradiation experiment on solid state NH_2trz was done with a broad UV wavelength 15W fluorescent lamp in a closed transparent glass vial for 20 h. No change in colour was observed after irradiation.

References

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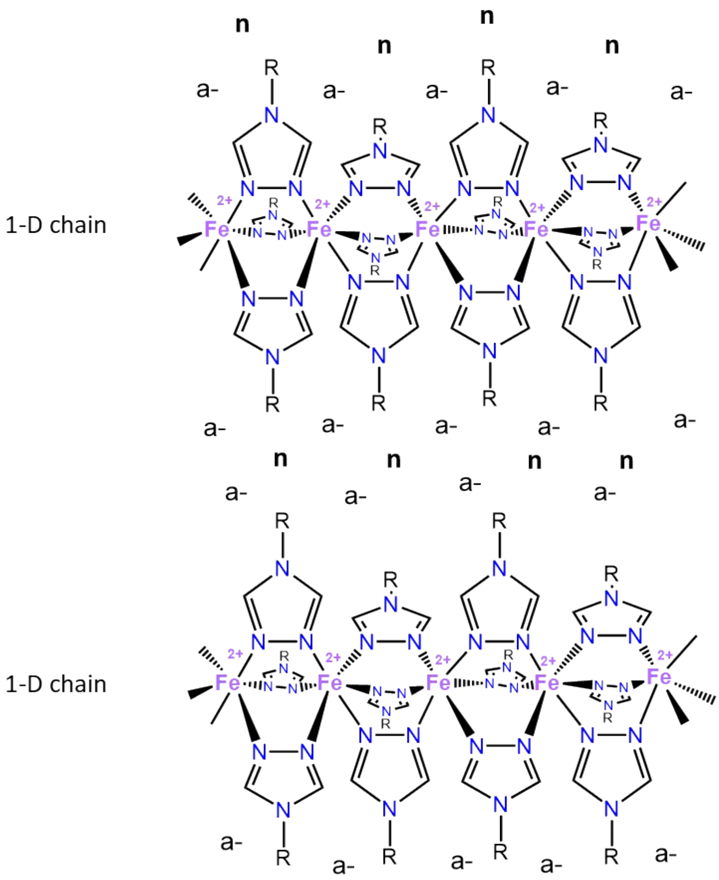
2. F. Ephraim and A. Pfister, *Helv. Chim. Acta*, 1925, **8**, 229–241
3. K. Lagarec and D. G. Rancourt, *Recoil,* Mössbauer Spectral Analysis Software for Windows 1.0, Department of Physics, University of Ottawa, Canada, **1998**.
4. V. Kumar, L. Fusaro, C. Aprile, K. Robeyns and Y. Garcia, *Cryst. Growth Des*., 2020, **20**, 7850-7861.



Scheme S1 Schematic representation of $[Fe(R\text{-}trz)_3]a_2.n$ 1D chains. {a = anion, n = solvent, R = NH_2}.

	Sites	δ (mm/s)	ΔE_Q(mm/s)	$\Gamma/2$(mm/s)	A/A_{tot} (%)
Before UV	HS Fe(II)	1.05(6)	2.79(1)	0.26(1)	11
	LS Fe(II)	0.44(5)	0.21(1)	0.16(8)	89
After UV	HS Fe(II)	1.07(3)	2.68(5)	0.26(4)	10
	LS Fe(II)	0.43(1)	0.18(3)	0.15(3)	90

Table S1 ^{57}Fe Mössbauer parameters of $[Fe(NH_2trz)_3](\boldsymbol{tos})_2\cdot H_2O$ before and after irradiation. $\Gamma/2$ = half width of the lines.

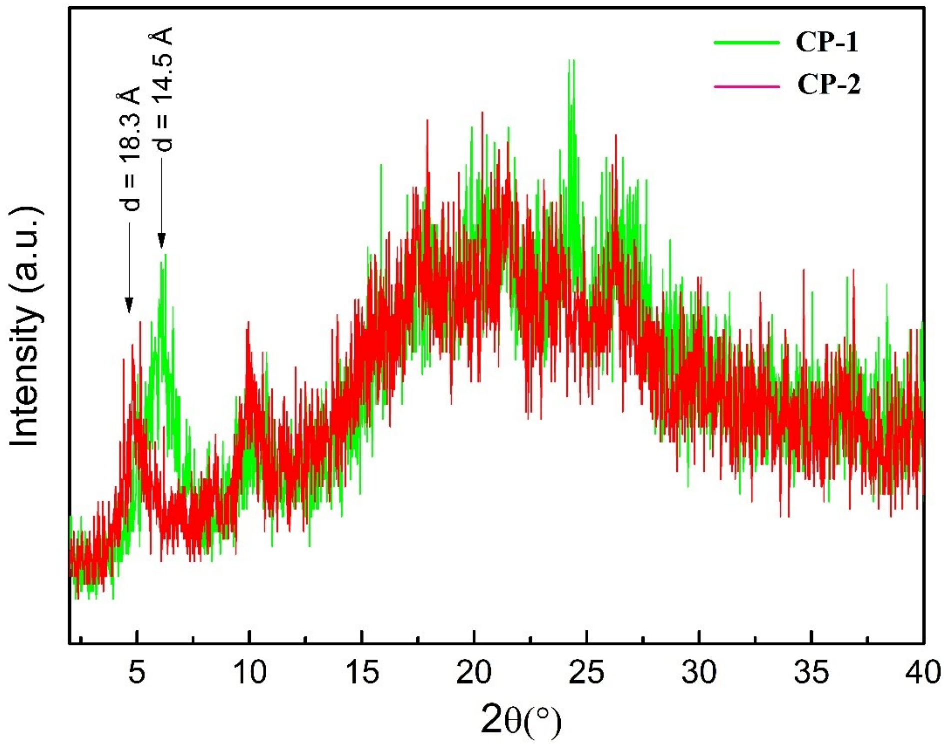


Fig. S1 PXRD patterns of **CP-1** and **CP-2**.

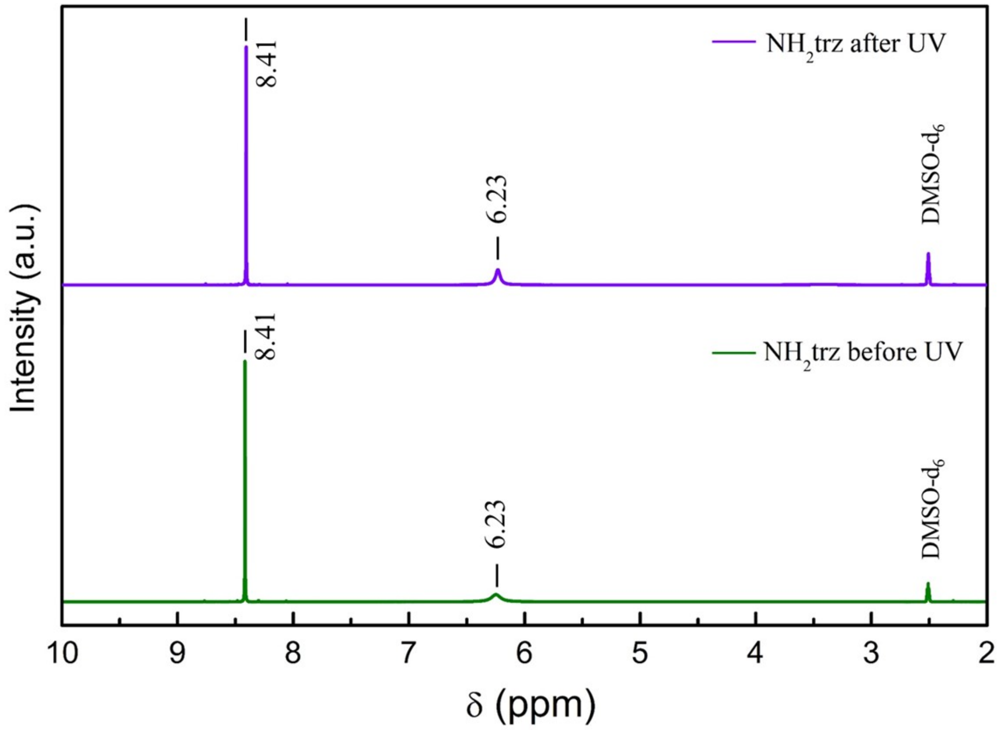


Fig. S2 ^{1}H NMR spectra of NH_2trz before and after irradiation.

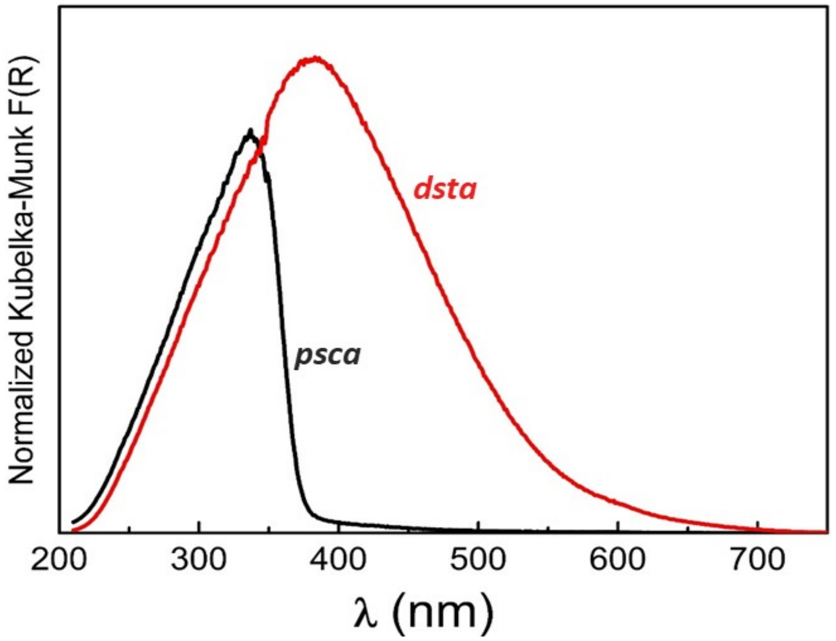


Fig. S3 Diffuse reflectance spectra of ***psca*** and ***dsta***.

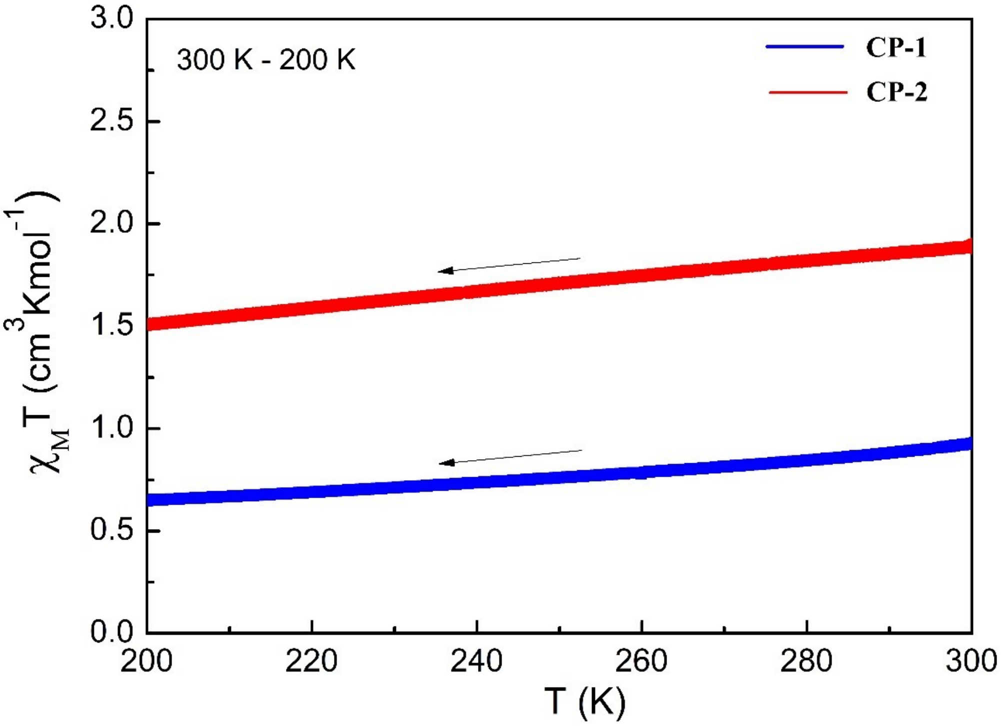


Fig. S4 Comparison of $\chi_M T$ *vs. T* plots of **CP-1** and **CP-2** during the first cooling cycles from 300 K to 200 K.

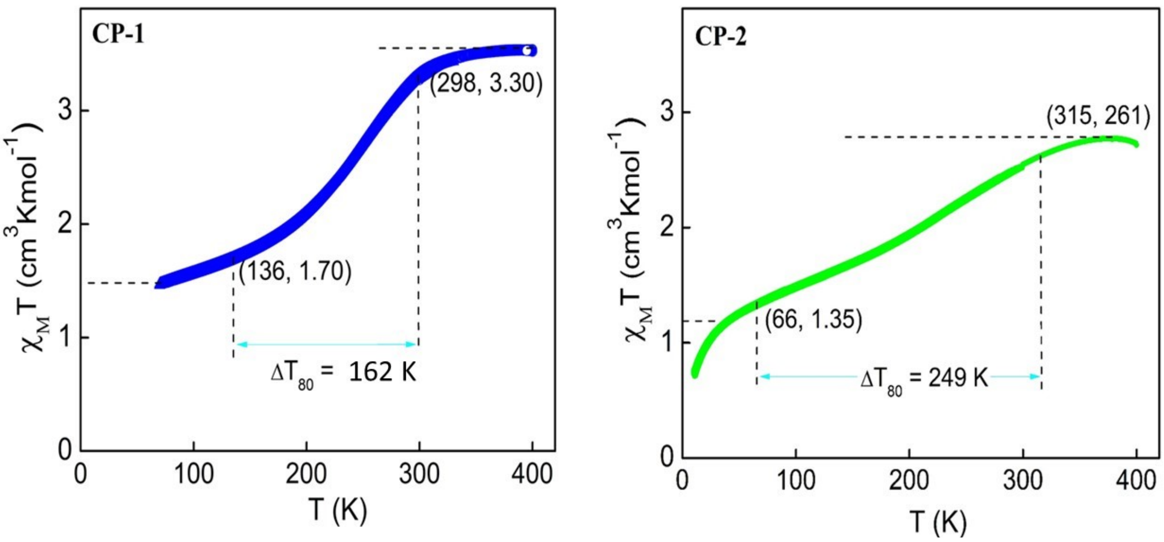


Fig. S5 $\chi_M T$ *vs.* T plots of dehydrated forms of **CP-1** and **CP-2** with ΔT_{80} calculations.

Before UV

After UV

Fig. S6 Photographs of [Fe(NH_2trz)$_3$](***tos***)$_2$·H_2O taken before and after UV irradiation, at room temperature.

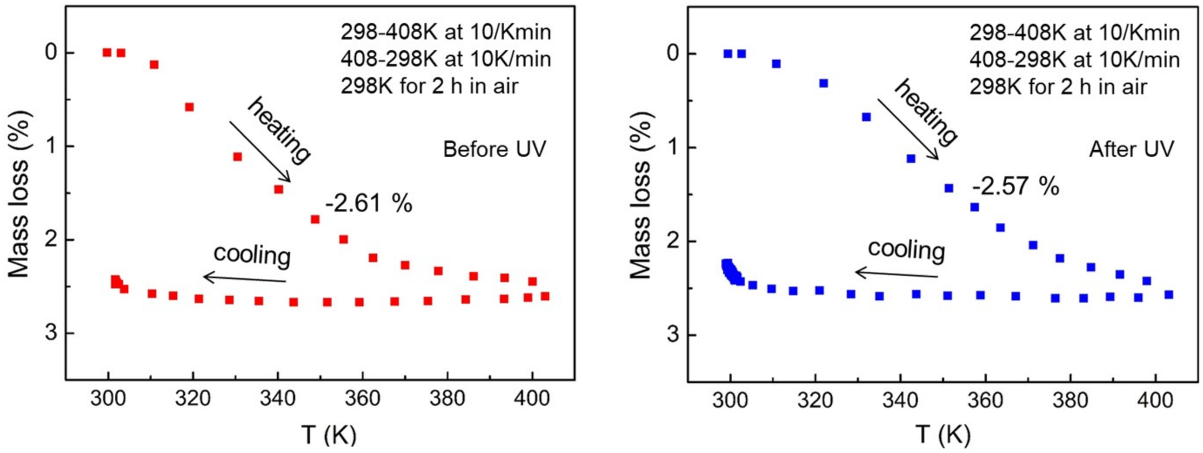


Fig. S7 TGA curves of $[\mathrm{Fe(NH_2trz)_3}](\boldsymbol{tos})_2\cdot\mathrm{H_2O}$ before and after UV irradiation. The same amount of mass was (ca. 2.6%) corresponding to one water molecules was observed. Thus, UV irradiation has no effect on the molecular formula.

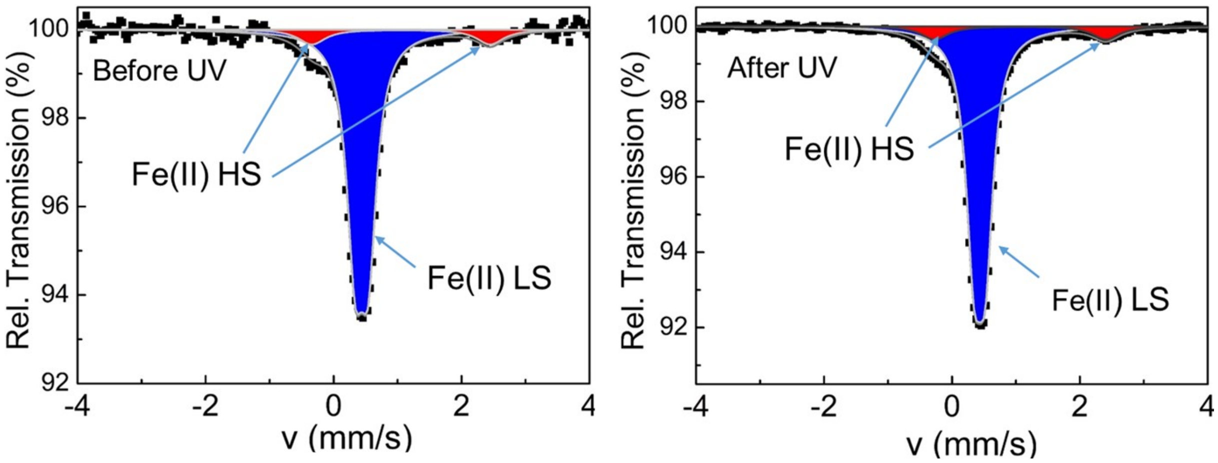


Fig. S8 ^{57}Fe Mössbauer spectra of $[\mathrm{Fe(NH_2trz)_3}](\boldsymbol{tos})_2\cdot\mathrm{H_2O}$ before (left) and after irradiation (right), at room temperature.