

Photochemistry of the $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ –thiolate system

Konrad Szaciłowski, Janusz Oszajca, Grażyna Stochel and Zofia Stasicka*

Department of Inorganic Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland. E-mail: stasicka@trurl.ch.uj.edu.pl

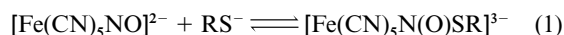
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The studied system consists of $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ **1**, mercaptosuccinate or another thiolate (RS^-) and $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{SR}]^{3-}$ **2** in equilibrium. The photochemical study has shown that both complexes **1** and **2** undergo either photooxidation or photoreduction, depending on the excited state energy. The present study is focused on the low energy effects, which consist of an inner-sphere photooxidation mode followed by a substitution pathway yielding pentacyanoferrate(III) complexes and NO or NOSR $^-$ radicals for **1** and **2**, respectively. In the presence of mercaptosuccinate the $[\text{Fe}^{\text{III}}(\text{CN})_5\text{SR}]^{3-}$ complex **3** and nitrosomercaptosuccinate were identified as the most stable products. The photochemical reactivity of the $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{SR}]^{3-}$ complex thus resembles the photooxidation-substitution mode characteristic of $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ but produces nitrosothiol instead of NO and needs considerably lower energy to be induced (MLCT band at λ_{max} 526 nm). Consequently, the photoreactivity of **2** creates the possibility of using the **1**– RS^- system to photogenerate a nitrosothiol *in situ* using non-hazardous radiation.

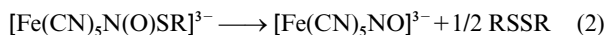
Introduction

Thermal reactivity of the title system was studied repeatedly, especially because of its well known analytical^{1–5} and prospective physiological importance.^{6–16} Thiols are considered as one of the critical sites of the NO-donor interactions in biological systems, perhaps explaining why proteins, peptides and other species containing thiol groups that undergo nitrosation might modulate cellular functions.^{17–28}

Reaction of $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ **1** with a thiolate (RS^-) proceeds in two successive steps: the very fast¹⁵ reversible formation of the red intermediate $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{SR}]^{3-}$, **2** [eqn. (1)] and its



subsequent reduction [eqn. (2)] followed by secondary processes



yielding different (dependent on conditions), iron complexes and NO species.^{7–16,29}

For a long time all the red products (**2**) were considered as more or less unstable compounds; recent investigations, however, have shown that the stability of **2** depends strongly on the thiolate composition and structure and by judicious selection of the R group complexes of different lifetimes can be produced.²⁹ This enabled us to investigate the photochemical behaviour of the red products (**2**).

The most important stimulus for this study was recent interest in photochemical delivery of nitric oxide to biological targets using different NO-donors as the sources.^{30,31} This work focused on checking the possibility of using the $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{SR}]^{3-}$ complexes (**2**) for *in situ* generation of the pharmacologically active NO species *via* irradiation by non-hazardous low energy light.

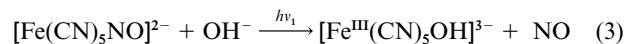
Results and discussion

The photochemical study of the $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ –thiolate systems was carried out mostly for $\text{RS}^- =$ mercaptosuccinate because its respective $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{SR}]^{3-}$ complex **2** is relatively stable ($\tau_{1/2} \geq 36$ h at 295 K) and its absorption spec-

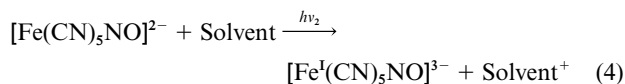
trum²⁹ (λ_{max} 526 and 318 nm, ϵ 6000 and 1320 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$, respectively) is well suited for the study of low energy irradiation effects.

The equilibrium leading to the formation of **2** [eqn. (1)] is highly sensitive to different factors, and moreover its shift to the right is accompanied by an increased rate of decay of **2** [eqn. (2)].^{11,15,29} In consequence, the photochemical study was carried out for a mixture of the two complexes **1** and **2**, maintaining a moderately alkaline medium (pH = 10) and keeping temperature and ionic strength constant.

Fortunately, the photochemical behaviour of **1** has been studied repeatedly^{32–39} and two main modes were recognised: (i) intramolecular photooxidation resulting from the metal-centred and ligand-centred transition,^{32–38} accompanied by NO ligand substitution [eqn. (3)] yielding aqua- or pentacyano-



hydroxoferrate(III) (the latter form dominates at pH ≥ 10) and (ii) outer-sphere photoreduction to an Fe(I) complex [eqn. (4)]



induced by the more energetic LMCT + LLCT transition ($\lambda_{\text{irr}} < \approx 310$ nm).^{34,35} Prolonged irradiation at $\lambda < 500$ nm induces photosubstitution and photoreduction of the $[\text{Fe}^{\text{III}}(\text{CN})_5\text{OH}]^{3-}$ complex yielding CN^- , $(\text{CN})_2$ and $\text{Fe}(\text{OH})_3$.³⁸

As the present study was limited to irradiation over a short timeframe within a moderately low energy region ($578 \text{ nm} \geq \lambda_{\text{irr}} \geq 313 \text{ nm}$), the photooxidation-substitution reaction [eqn. (3)] was the only, or at least major, effect expected. Its product, $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$, is characterised by a band at λ_{max} 392 nm (ϵ 1800 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$, $\text{p}K_{\text{a}} = 8.4$).⁴⁰ The absorption changes accompanying the photooxidation reaction of **1** [(eqn. (3))] are illustrated in Fig. 1(a). However, when mercaptosuccinate or another thiol generating stable **2** is present in the system quite different spectral changes result from irradiation [Fig. 1(b)]: the decrease in the initial absorption, characteristic of both **1** and **2**, is accompanied by a major increase in absorption at $\lambda > 600$ nm ($\lambda_{\text{max}} \approx 700$ nm) and a minor growth at $\lambda < 450$ nm.

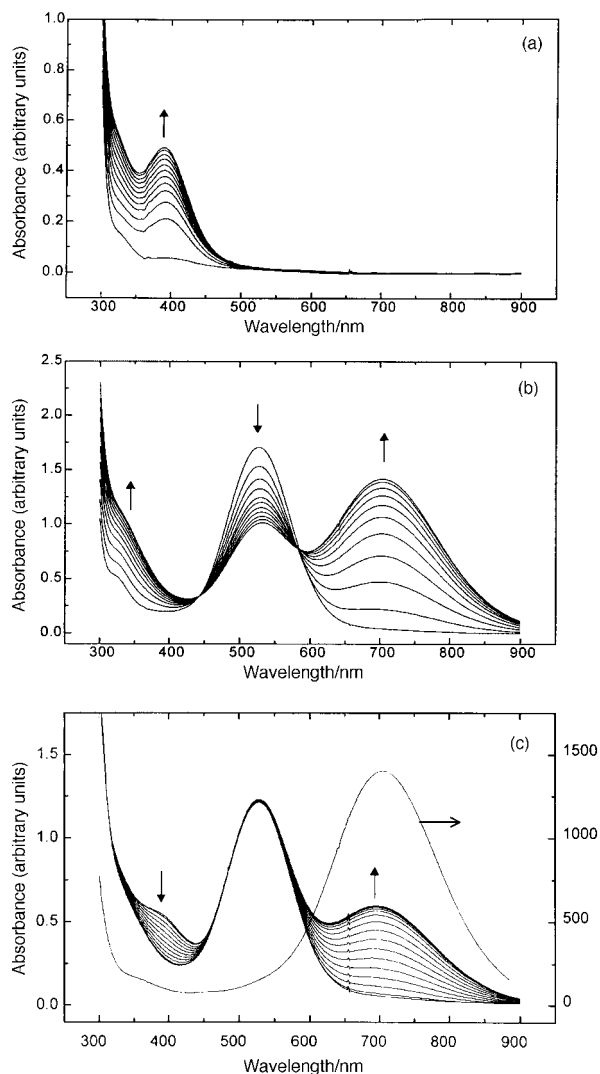


Fig. 1 Spectral changes observed during irradiation of $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ solution in carbonate–borate buffer (2.5×10^{-3} M, pH 10, λ_{irr} 365 nm) without (a) or with (b) 12.5×10^{-2} M mercaptosuccinate; spectra recorded every 60 s. (c) Illustrates thermal changes in the spectra of irradiated solutions of **1** [the highest curve in (a)] upon addition of mercaptosuccinate up to the same reagent concentrations as in (b); spectra recorded every 5 s; the single line represents the absorption spectrum of $[\text{Fe}(\text{CN})_5\text{SR}]^{3-}$ ($\text{SR}^- = \text{mercaptosuccinate}$).

To identify the photoproduct(s) the thiol was added to the previously irradiated $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ solution [Fig. 1(c)]: the absorption with λ_{max} at 526 nm appeared immediately which was consistent with the expected shift of the equilibrium [eqn. (1)] towards the formation of **2**. Then, within seconds, an increase in absorption at 700 nm at the expense of that at ≈ 400 nm $\{[\text{Fe}(\text{CN})_5\text{OH}]^{3-}\}$ was recorded. This behaviour was compared with the reaction between pentacyanohydroxoferrate(III) and different thiolates: in all cases within minutes a green product (**3**) absorbing significantly around 600–785 nm was generated (Fig. 2). Such reactivity is consistent with the tendency of the $[\text{Fe}^{\text{III}}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ and $[\text{Fe}^{\text{III}}(\text{CN})_5\text{OH}]^{3-}$ complexes to substitute the aqua or hydroxo ligand.^{41,42}

Surveying the UV/Vis spectra of the $[\text{Fe}(\text{CN})_5\text{L}]^{n-}$ complexes of Fe(II) or Fe(III) with S-donor ligands one notices a close resemblance between the spectra of the green products (**3**) and those of the pentacyanothiolatoferrate(III) species for which an intense low energy LMCT band is a “finger print” (Table 1). This conclusion is supported by lack of such spectral changes upon mixing the thiolates with the analogous iron(II) complex, $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$, unless an oxidant is present. To recap the thiolates in excess transform the pentacyanohydroxoferrate(III) almost completely into $[\text{Fe}^{\text{III}}(\text{CN})_5\text{SR}]^{3-}$

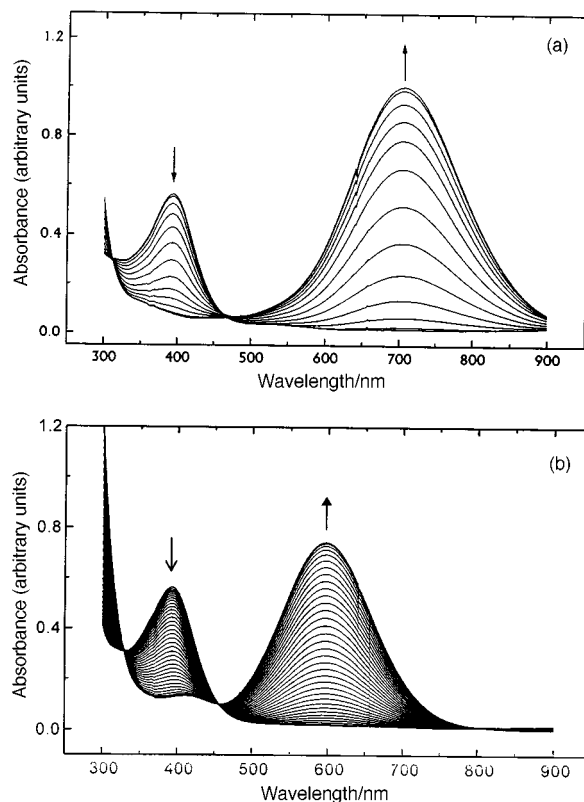
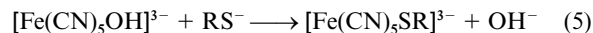


Fig. 2 Spectral changes recorded during reaction between $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ (6.5×10^{-4} M) and thiolate (5.0×10^{-3} M): (a) $\text{RS}^- = \text{mercaptosuccinate}$, spectra recorded every 5 s; and (b) $\text{RS}^- = \text{mercapto-1-methyltetrazolate}$, spectra recorded every 30 s. In both cases pH = 10 (carbonate–borate buffer) and $T = 298$ K.



The thiolato complexes are only moderately stable towards reduction and their lifetime is of the order of minutes (Table 1). The most stable of these have $\text{RS}^- = \text{mercaptosuccinate}$ or 5-mercapto-1-methyltetrazolate (Fig. 2).

Identification of the photoproduct absorbing at $\lambda > 600$ nm as the $[\text{Fe}(\text{CN})_5\text{SR}]^{3-}$ complex (**3**) may be interpreted in terms of (i) the photooxidation-substitution mode of $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ [eqn. (3)] followed by substitution of the RS^- ligand for OH^- [eqn. (5)], or (ii) photochemistry of both the irradiated complexes, *i.e.* $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ **1** and $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{SR}]^{3-}$ **2**. The latter hypothesis is advocated by a difference in the spectra of the photolysed solutions when thiolate is added before or after irradiation [at $\lambda < 450$ nm, *cf.* Figs. 1(b) and 1(c)].

To solve the problem, the **1**– RS^- system was irradiated within (313, 365 nm) or practically out of the absorption region for **1** (546, 578 nm) and the quantum yield for the formation of **3** was compared with that for the photooxidation of **1** (Φ_1). The **1**– RS^- system was found to produce the $[\text{Fe}(\text{CN})_5\text{SR}]^{3-}$ complex within the whole irradiation range studied even when $\Phi_1 \cong 0$ (Table 2).

This leads to the conclusion that not only $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ but also the $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{SR}]^{3-}$ complex undergoes intramolecular photooxidation and substitution yielding pentacyanothiolatoferrate(III) either directly [eqn. (6)] or *via* the hydroxo-complex [eqn. (7)] followed by the substitution [eqn. (5)].

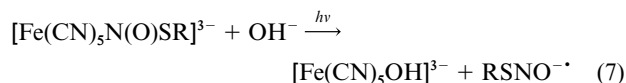
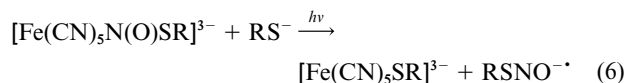


Table 1 Spectral characteristics of selected $[\text{Fe}^{\text{II}}(\text{CN})_5\text{L}]^{n-}$ and $[\text{Fe}^{\text{III}}(\text{CN})_5\text{L}]^{m-}$ complexes with S-donor ligands

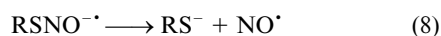
Ligand	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)		$\tau_{1/2}/\text{s}$	Ref.
	$[\text{Fe}^{\text{II}}(\text{CN})_5\text{L}]^{n-}$	$[\text{Fe}^{\text{III}}(\text{CN})_5\text{L}]^{m-}$		
SCN ⁻	390	590 (2680)		42
Thiourea	407 (400)	595 (2500)		43
Thioacetamide	400 (400)	565 (2500)		43
Dithioamide	395 (500)	560 (1990)		43
Methionine	390 (270)	508 (400)		44
Penicillamine	421 (360)			45
		683 (≈ 4000)		^a
Mercaptosuccinate		700 (2700)	650	^a
5-Mercapto-1-methyltetrazolate		601 (3020)	>1800	^a
Thiobenzoate		618 (>2500)	≈ 300	^a
2-Mercapto-4-methylpyrimidinate		650 (>1260)	290	^a
2-Mercaptothiazolate		660 (3040)	210	^a
Ethyl xanthate		680	≈ 120	^a
Diethyldithiocarbamate		785	≈ 120	^a

^a This work.**Table 2** Quantum yields of the **1**-mercaptosuccinate system

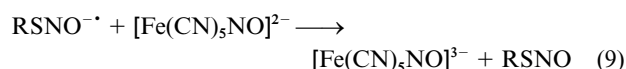
$\lambda_{\text{irr}}/\text{nm}$	A_1^a	Atmosphere	$[\Phi_1]^b$	$[\Phi_2]^c$
313	0.20	Ar	0.302 ± 0.01^d	0.079 ± 0.003
		O ₂	0.332 ± 0.003	0.120 ± 0.004
365	0.06	Ar	0.290 ± 0.001	0.041 ± 0.001
		O ₂	0.293 ± 0.005	0.052 ± 0.001
546	<0.01	Ar	0.006 ± 0.001	0.025 ± 0.002
		O ₂	0.006 ± 0.001	0.022 ± 0.002
578	<0.01	Ar	$\leq 0.0015 \pm 0.001$	0.023 ± 0.002
		O ₂	$\leq 0.0015 \pm 0.001$	0.023 ± 0.001

^a Fraction of light absorbed by **1** in the system containing 5.0×10^{-3} M of **1** + 2.5×10^{-2} M of mercaptosuccinate. ^b Quantum yield of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ formation, measured for 2×10^{-2} M of **1**, pH = 10. ^c Quantum yield for the photolysis of **2**, measured for 5.0×10^{-3} M of **1** + 2.5×10^{-2} M of mercaptosuccinate, pH = 10, calculated for 23% conversion **1** \rightarrow **2**. ^d Standard deviation.

The photooxidation of **2** was expected to be accompanied by formation of the nitrosomercaptosuccinate radical. Support for this hypothesis came from EPR experiments: irradiation of the $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{SR}]^{3-}$ complex at $\lambda \geq 380$ nm generated a radical species characterised by a signal at $g = 2.01$ and $A(^{14}\text{N}) = 32$ G. The nitrosothiol radicals were reported earlier to be generated in the reaction between thiols and NO or S-nitrosothiols^{46,47} and to decay either by reaction with oxygen⁴⁸ or by dissociation.⁴⁹



In the studied system the $\text{RSNO}^{\cdot-}$ radical should also react with the Fe(III) product complexes and with excess complex **1**. The radical signal decayed upon annealing whereas upon re-freezing the signal characteristic of the $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ complex⁵⁰ appeared. The latter could be formed as in eqn. (9),



the products of which absorb in the range 300–450 nm: nitrosomercaptosuccinate λ_{max} 330 nm (ϵ 840 $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ λ_{max} 350 and 430 nm (ϵ 3500 and 550 $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).^{51,52} An additional confusion comes from the absorption of **2** at 318 nm (ϵ 1320 $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

To clear up the origin of the absorption between 300 and 450 nm a numerical analysis of the spectra was performed which showed that four independent spectral components could be found in all the spectra of photolysed **1**- RS^- solutions, three of which were identical to those of **1** (increased absorption start-

ing from $\lambda \approx 350$ nm), **2** (maxima at 320 and 530 nm) and **3** (maximum at 700 nm). The fourth simulated spectrum was diffuse within 300 and 500 nm with two shoulders at about 330 and 430 nm and its shape was strongly affected by experimental conditions. The spectrum is fairly consistent with the absorption of both $\text{RSNO}^{\cdot-}$ and $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$.

A more quantitative analysis was carried out by comparing the photooxidation quantum yields of neat **1** with those of the **1**- RS^- system (Table 2). The quantum yield values obtained for **1** resemble those reported earlier^{32,34,35} and in the visible region they decrease as λ_{irr} is increased up to $\Phi_1 \approx 0$. Φ_1 is independent of the presence of oxygen unless $\lambda_{\text{irr}} = 313$ nm, where the difference may be interpreted in terms of an increasing contribution from the photoreduction of **1** [eqn. (4)] which is upset by oxygen oxidation of its product $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$.

The analysis of the **1**- RS^- system shows that not only the photochemical mode but also the yield depends on the radiation range: (i) in the UV range, $\Phi_1 > \Phi_2$, where Φ_2 is more oxygen sensitive, suggesting an efficient contribution from the photoreduction mode. (ii) In the visible range when the photoreactivity of **1** approaches zero, the quantum yield for the photooxidation of **2** is significant, constant within the 526 nm band ($\Phi_2 \approx 0.023$) and independent of the presence or absence of O₂.

The results of this paper show that the $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{SR}]^{3-}$ complex, similarly to $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, undergoes photooxidation-substitution as well as photoreduction modes but that both processes are induced by much lower energy radiation (Table 2). Irradiation by low energy light ($\lambda > 500$ nm) leads selectively to the photooxidation of **2**. The $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{SR}]^{3-}$ (**2**) complexes can thus be a source of nitrosothiols generated *in situ* by visible light. This also offers a chance to modify the photobiochemical activity of **1** as the NO-donor by adding an appropriate S-nucleophile. Since light transmission of mammalian tissues is more effective at longer wavelengths, the **1**- RS^- systems photosensitive to lower energetic radiation than **1** alone, seem to be even more appropriate for the photochemical delivery of the NO-species. For example, with mercaptosuccinate the photosensitivity limit nearly overlaps the beginning of the "phototherapeutic window" (650–850 nm).

Experimental

UV/Vis spectra were recorded using Shimadzu UV-Vis 2100, Hewlett-Packard HP 8463 and Ocean Optics SD-1000 spectrophotometers in standard 1 cm quartz cells. A high pressure mercury lamp HBO 200 with LPS 250 power supply (PTI) was used as a light source. Interference filters were used to select appropriate wavelengths. Quantum yields were measured on the

homemade computer controlled equipment according to the method described previously.⁵³ The experiments were performed at 298 ± 0.1 K, and solutions were stirred by a slow stream of argon or oxygen.

The reaction progress was followed by monitoring increases in the product absorption at 392 nm and 700 nm, for [Fe(CN)₅OH]³⁻ and [Fe(CN)₅SR]³⁻, respectively. When the latter was the only product of both the photochemical paths the Φ_2 values were calculated as follows: from an increase in concentration of **3** the apparent quantum yield for **3**, ψ_3 , was calculated. As **3** was assumed to be produced by both **1** and **2** with the yields Φ_1 and Φ_2 , respectively, the latter value was calculated from eqn. (10):

$$\Phi_2 = \frac{\psi_3 - \Phi_1 A_1}{A_2} \quad (10)$$

where A_1 and A_2 are fractions of light absorbed by **1** and **2**, respectively. The **1** → **2** conversion in unirradiated solution was calculated from its absorption spectrum. Quantum yield values were extrapolated to $t_{irr} = 0$. Carbonate–borate buffer (0.1 M K₂CO₃ + 0.1 M H₃BO₃, pH 10) was used in all measurements.

Numerical analysis of the spectra was performed applying principal factor analysis (PFA), target testing (TTEST) and spectral isolation factor analysis (SPEXFA) using Target 96M software (MATLAB version).⁵⁴ For the calculations either matrices containing 11 spectra from a single photochemical experiment or sets of 24–49 spectra randomly chosen from different experiments were taken as input data.

The EPR spectra were recorded using a Bruker ESP 500 spectrometer operating at the X band, with 100 kHz modulation. The samples in propan-1,3-diol and 0.1 M K₂CO₃ (1:1 v/v) were irradiated at room temperature at $\lambda \geq 380$ nm, cooled immediately and measured at 77 K.

[Fe(CN)₅OH]³⁻ was obtained in solution by the acid hydrolysis of K₃[Fe(CN)₅NO₂] (prepared according to refs. 55 and 56) followed by addition of the buffer. The thiolato complexes, [Fe^{III}(CN)₅SR]^{m-}, were produced in solution from [Fe(CN)₅OH]³⁻ and the thiolate ligand in 5-fold excess. The reaction was monitored by UV/Vis and molar absorption coefficients were calculated from the relation between the decrease in the absorbance of the [Fe(CN)₅OH]³⁻ substrate at 392 nm and the increase in absorbance of the [Fe(CN)₅SR]^{m-} products at their absorption maxima (601–785 nm).

[Fe(CN)₅N(O)SR]³⁻ was prepared in solution; the attempted preparation of the solid potassium salt resulted in impure red solid phases; IR: 2100 and 2075 cm⁻¹ (ν_{CN}) and 1557 and 1410 cm⁻¹ (ν_{CO}).²⁹

All other chemicals were commercially available (Aldrich, Fluka, Merck) and were used without any purification.

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