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Photophysical properties of Co(III) photosensitizers with phenothiazine-based ligands

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The ultrafast decay inherent to metal complexes with a $3d^6$ configuration limits their application as photosensitizers. Despite recent advances in improving the photophysical properties of these complexes, existing ligand designs restrict further modification and are often synthetically challenging. Here, we show how sulfur-bridged ligands can be used to tune the structural and photophysical properties in Co(III) photosensitizers. Two complexes, **CoS** ($[\text{Co}(\text{PTZIm}_2)_2]\text{PF}_6$) and **CoSO₂** ($[\text{Co}(\text{PTZO}_2\text{Im}_2)_2]\text{PF}_6$), adopt facial geometries due to a less rigid ligand backbone compared to other pincer-type ligands. The lowest-lying absorption bands of both **CoS** and **CoSO₂** display metal/ligand-to-ligand charge-transfer (M + L)LCT character with different contributions from the sulfur-bridged ligand. TD-DFT analysis indicates that **CoSO₂** has a lower contribution from the phenothiazine moiety to the band at 400 nm. The sulfur oxidation state also affects the electronic density at the metal center, with **CoS** showing a lower $M^{IV/III}$ oxidation potential. Transient absorption experiments reveal that fast non-radiative decay channels are facilitated in **CoS**. However, a photoactive long-lived component (8.0 ns) is also observed. Oxidation of phenothiazine extends the lifetimes of short-lived components in **CoSO₂**, where both electronic and structural effects may be playing a role. These findings demonstrate that the photophysical properties of Co(III) complexes can be modulated by variation of the sulfur oxidation state to achieve different photophysical properties of the complexes.

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Introduction

The picosecond excited-state lifetimes of $3d^6$ metal complexes are too short for these to be useful as practical photosensitizers.^{1–5} The lifetimes for Fe(II) and Co(III) complexes can be increased with the use of strong σ -donating ligands and highly conjugated groups.^{6–10} However, current ligand designs restrict the electronic density at the metal center, which limits the substrate scope for such complexes in photoredox catalysis.^{2,11} Sulfur-bridged ligands with tunable oxidation states allow modulation of the electronic density at the metal center.¹² The oxidation state of the sulfur atom controls the electronic density without alteration of the metal complex core structure.

Efforts to extend the lifetime of Fe(II) complexes have focused on destabilizing the metal centered (MC) states (Fig. 1A). The fast deactivation path is restricted when MC states are higher in energy than the photoactive states, resulting in long decay lifetimes.^{13–15} N-Heterocyclic carbene (NHC)

and cyclometalated ligands increase the ligand field strength, but these complexes have yet to be widely used in photocatalysis.^{15–17} Co(III) photosensitizers have been explored because the higher oxidation state increases the energy of the deactivating d-d states.^{18–21} Most of these complexes have an extended π ligand system that lowers the energy of the lowest unoccupied molecular orbital (LUMO). The lower LUMO energy allows the photoactive state to be populated using visible light.^{22–24}

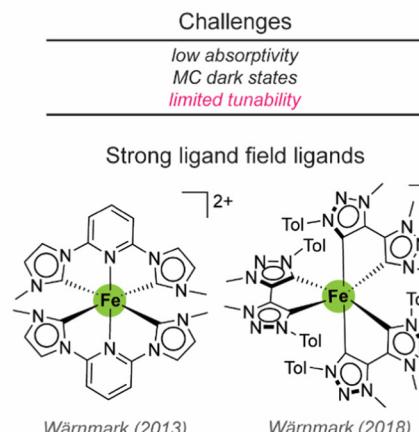
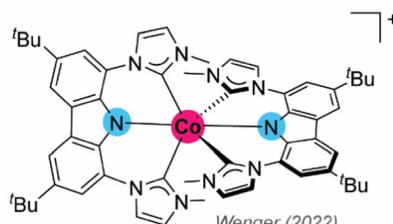
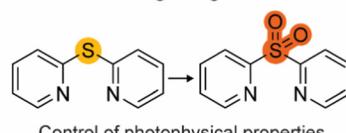
Ligands containing organic chromophores enhance the photoactivity of many coordination complex-based photosensitizers.^{25–29} They can extend the π conjugation in the ligands on first-row metal complexes, thereby shifting the photoactive band to lower energies.^{25,28–32} Conjugated chromophores such as pyrene have also served as long-lived triplet reservoirs or as the lowest-lying excited state in metal complexes with an extended lifetime.^{26,27,29} Wenger and coworkers used a carbazole group to obtain a photoactive Co(III) complex that shows a nanosecond lifetime that is active towards photoinduced electron transfer (PET) (Fig. 1B).³³ These complexes embody interesting properties, however efforts to systematically modify the electronic density at the metal center remain limited.

Our group has previously investigated how sulfur-bridged ligands can alter the photophysical properties of metal com-

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A Earth-Abundant Photosensitizers**B Organic Chromophores****C S-bridged ligands****D This Work**

How does S influence the photophysical properties of Co(III) photosensitizers?

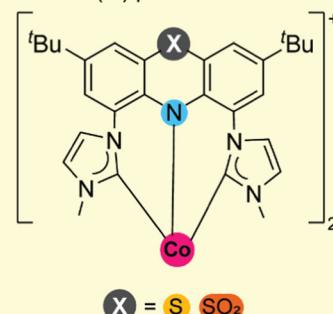


Fig. 1 (A) Challenges and ligand design proposed previously for first-row d⁶ photosensitizers.^{13,14} (B) Co(III) complex containing carbazole-based ligands with MLCT excited state with nanosecond lifetime.³³ (C) Sulfur-bridged ligands tune the photophysical properties of metal complexes.¹² (D) New Co(III) complexes containing phenothiazine-based ligands investigated herein.

plexes, including those based on Cu(I), Re(I), Pt(II), and Ir(III).^{12,34–38} Oxidation of the sulfur bridge alters the energy of the ligand-centered molecular orbitals, thereby modulating the luminescence and ³MLCT state lifetimes (Fig. 1C). Photoreduction of carbon dioxide by bimetallic rhenium(I)-ruthenium(II) dyads is also influenced by the sulfur oxidation state of a bridging ligand.³⁸ Recently, luminescent B(III) complexes containing a sulfur-bridge-containing amido π -donor ligand, phenothiazine, were reported. Further oxidation of sulfur in the phenothiazine altered the photophysical and electrochemical properties of the complexes.³⁹

We now demonstrate use of sulfur-bridged ligands in Co(III) photosensitizers (Fig. 1D). In this work, we disclose a tridentate chelating ligand combining two σ -donating NHC units and a central phenothiazine π -donor. The sulfur bridge creates a more flexible backbone compared to other pincer-type ligands, favoring the formation of the *facial* isomer and affecting the excited-state lifetime.^{33,40} The electron density at the metal center is modulated by the oxidation state of sulfur, thus dictating the excited-state dynamics. Our study also includes iron(III) analogs to better understand the impact of the sulfur-bridge ligand in their structural and electrochemical properties.

Results and discussion

Synthesis and characterization

Cobalt(III) complexes containing phenothiazine [Co(PTZIm₂)₂]PF₆ (**CoS**) and phenothiazine-5,5'-oxide [Co(PTZO₂Im₂)₂]PF₆ (**CoSO₂**) NHC ligands along with iron(III) analogs [Fe(PTZIm₂)₂]PF₆ (**FeS**) and [Fe(PTZO₂Im₂)₂]PF₆ (**FeSO₂**), were synthesized. The sulfur-bridged imidazolium ligands **PTZIm₂H** and **PTZO₂Im₂H** were prepared using previously published procedures with modifications (Scheme S1).^{33,41} The

reaction between 2.0 eq. of the corresponding ligands and 6.6 eq. of lithium bis(trimethylsilyl)amide (LiHMDS) with 1.0 eq. of the cobalt(II) bromide or iron(II) bromide in THF at -78 °C led to the corresponding cobalt(III) and iron(III) complexes after exposure to air, with yields between 29% and 44% (Fig. 2A).

The diamagnetic Co(III) complexes were characterized by ¹H, ¹³C{¹H}, ³¹P{¹H} and ¹⁹F{¹H} NMR spectroscopies, X-ray crystallography, HR-ESI mass spectrometry and infrared spectroscopy (FT-IR). The paramagnetic Fe(III) complexes were characterized by FT-IR, HR-ESI mass spectrometry, EPR spectroscopy, and X-ray crystallography. Symmetric stretching of the sulfone (SO₂) at 1135 and 1129 cm⁻¹ in the FT-IR spectra, is observed in **CoSO₂** and **FeSO₂** respectively, but is absent in **CoS** and **FeS**. Additionally, a stretching peak at 833 cm⁻¹ confirms that PF₆⁻ is the counterion for all complexes (Fig. S1 and S2). HR-ESI mass spectra show peaks corresponding to the molecular ions with characteristic cobalt and iron isotopic patterns (Fig. S6–S9). The protons characteristic of the imidazolium groups in **PTZIm₂H** and **PTZO₂Im₂H**, at 8.53 ppm and 8.69 ppm in the ¹H NMR spectra, respectively, are absent in the spectra of **CoS** and **CoSO₂** (Fig. S12–S23). Two sets of ligand peaks in the ¹H and ¹³C{¹H} NMR spectra of the complexes indicate that they adopt a *facial* arrangement. New peaks in the ¹³C{¹H} NMR spectra between 174.5 and 160.3 ppm are characteristic of the ligating carbon atom of the NHC units. These results are in line with observations in previously reported Co(III)-NHC complexes.^{20,29,33} In addition, ³¹P{¹H} and ¹⁹F{¹H} NMR spectra show the expected PF₆ signal between -143.1 and -142.7 ppm and between -73.5 and -70.3 ppm, respectively, with *J*_{P-F} = 700 Hz.

X-band EPR spectra of the iron(III) complexes in acetonitrile at 298 K show broad signals consistent with low-spin d⁵ Fe(III) centers.^{15,31,33,42} These spectra were simulated as isotropic signals with *g* = 2.0752 for **FeS** (Fig. S24) and *g* = 2.1410 for



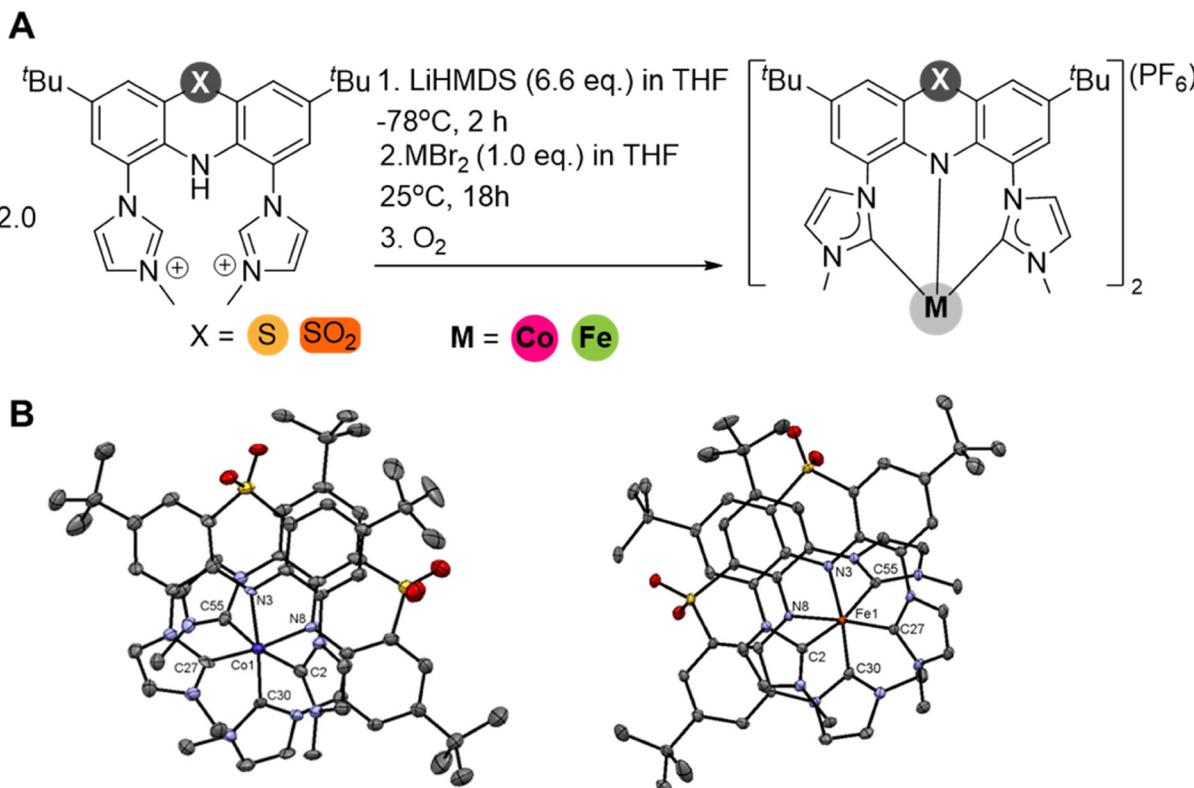


Fig. 2 (A) Synthesis route using LiHMDS as a base and subsequent metalation with corresponding metal bromide salt to obtain Co(III) and Fe(III) complexes. (B) Perspective drawing of CoSO_2 (left) and FeSO_2 (right). Ellipsoids are plotted at the 50% probability level. Solvent molecules and H atoms are removed for clarity.

FeSO_2 (Fig. S25). The higher g value for FeSO_2 is assigned to the greater electron-withdrawing effect of the SO_2 group, which increases delocalization of unpaired electron density onto the ligand, impacting both the ligand field splitting and bond covalency.^{31,43,44} Similar effects have been reported from electron withdrawing groups in other amido-bridged metal complexes.⁴⁴ Small signals (<1%) are tentatively attributed to minor amounts of an additional Fe(III) complex and uncomplexed phenothiazine radicals.^{45,46}

Single crystal X-ray diffraction (XRD) analysis confirmed that CoSO_2 and FeSO_2 crystallized in the *facial* geometry (Fig. 2B and Tables S1–S3). Both complexes adopt a distorted octahedral geometry with $\text{N}_{\text{amido}}\text{–M–C}_{\text{NHC}}$ axial angles in the range of 172.7(2) to 175.5(2)° for CoSO_2 and 173.26(10) and 175.65(11)° for FeSO_2 . The $\text{Co–N}_{\text{amido}}$ bond length is 2.045(5) Å in CoSO_2 and the $\text{Fe–N}_{\text{amido}}$ bond length in FeSO_2 is 2.026(2) Å. These values are longer than in some other amido-bridged complexes, resulting from the electron withdrawing ability of the SO_2 group, which weakens the amido bond and reduces the covalent character.^{31,33,47} The Co–C_{NHC} bond length *trans* to the amido groups averages 1.938(2) Å in CoSO_2 and 1.984(8) Å in FeSO_2 . These are shorter than the axial Co–C_{NHC} bonds in CoSO_2 (1.994(6) Å) and FeSO_2 (2.025(3) Å), attributed to the SO_2 group. The overall values are in line with other iron(III) and cobalt(III) NHC complexes.^{17,29,31,32} Helical twisting in the

coordination environment is associated with *P*- and *M*-chirality.⁴⁸ In both cases, the packing structure indicates the co-crystallization of two different enantiomers as a *P*- and *M*-pair (Fig. S26). Similar complexes containing Co(III), Fe(III) and Cr(III) also show the same behavior.^{32,33,49,50} Intramolecular phenothiazine-5-5'-oxide ring distances between 3.492 and 3.506 Å in both complexes indicate $\pi\cdots\pi$ stacking interactions in the solid state.

Structural analysis of the ground state geometry of CoSO_2 using B3LYP/DEF2-tzvp(-f) with ZORA scalar relativistic corrections is in good agreement with the crystal structure (Table S5). The average error in the bond length is 1.06%, and 1.59% for coordinating bond angles. We also modelled the structure of CoS using DFT, which shows a shorter $\text{Co–N}_{\text{amido}}$ bond length of 2.0110 Å, comparable to other amido-bridged complexes.^{31,33} Complex CoS exhibits a larger distortion from a perfect octahedral geometry, with an average $\text{N}_{\text{amido}}\text{–Co–C}_{\text{NHC}}$ axial angle of 168.47°. The lowest-lying triplet geometry (T_1) of both complexes was optimized with the unrestricted DFT method (Table S6). Overall, the $\text{Co–N}_{\text{amido}}$ and *trans* C–C_{NHC} bond lengths increase, and the axial Co–C_{NHC} bonds shorten relative to the ground state. The complexes show root-mean-square deviations (RMSDs) of 0.333 for CoS and 0.314 for CoSO_2 between the ground state and T_1 geometries, in line with the greater distortion expected in CoS .



Ground-state spectroscopy

We investigated the electronic properties of the Co(III) complexes and ligands in acetonitrile solutions using UV-vis spectroscopy (Fig. 3A, Fig. S27 and Table 1). The absorption spectra of **CoS** and **CoSO₂** show bands between 350 and 450 nm, distinct from the free ligands. **CoS** displays a broad band peaking at 392 nm, assigned as a mixture of metal/ligand-to-ligand charge-transfer [(M + L)LCT] [$d(\text{Co}) + \pi(\text{N}_{\text{amido}}) \rightarrow \pi^*(\text{C}_{\text{NHC}})$] and metal-centered (MC) [$d(\text{Co}) \rightarrow d^*(\text{Co})$] transitions according to the computational studies discussed below. The **CoSO₂** complex shows a band at 402 nm, assigned to a mixture of (M + L)LCT [$d(\text{Co}) + \pi(\text{N}_{\text{amido}}) \rightarrow \sigma^*(\text{C}_{\text{NHC}})$] and MC [$d(\text{Co}) \rightarrow d^*(\text{Co})$] states (Fig. 3D). The Co(III) complexes reported here show similar features as seen in other Co(III) NHC complexes.^{20,33} Complexes of the SO₂ series show a distinct band with high absorptivity ($\sim 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) peaking at 336 nm in **CoSO₂** and 331 nm in **FeSO₂** assigned to predominantly intraligand charge transfer (ILCT) between phenothiazine-5'-oxide ligands and minor MC character (Fig. S34, state S₁₄). Ligand **PTZO₂Im₂H** shows a similar feature at 339 nm, in line with the band assignment as predominantly ligand-based. Complex **FeS** shows a band at 800 nm and **FeSO₂** bands at 789 nm and 903 nm, similar to other iron(III) and iron(II) complexes con-

Table 1 Electronic absorption data of complexes **CoS**, **CoSO₂**, **FeS** and **FeSO₂** and ligands **PTZIm₂H** and **PTZO₂Im₂H** in acetonitrile solution ($2 \times 10^{-5} \text{ mol L}^{-1}$)

Entry	Compound	Absorption/ λ_{abs} [nm] ($\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$)
1	PTZIm₂H	258 (3500), 327 (500)
2	PTZO₂Im₂H	276 (13 000), 339 (6800), 358 (5500), 409 (400), 424 (400)
3	CoS	260 (38 600), 392 (10 000), 488 ^a (1000)
4	CoSO₂	336 (16 900), 402 (10 000), 455 ^a (800)
5	FeS	267 (27 300), 379 (8900), 414 ^a (6800), 800 (2000)
6	FeSO₂	331 (21 200), 719 (2600), 903 (2300)

^a Shoulder.

taining amido bridge ligands (Fig. 3B).^{31,33,51,52} The “HOMO inversion” lowers the bandgap by mixing 3d metal orbitals with $\pi(\text{N}_{\text{amido}})$ orbitals. We also observed an increase in the absorptivity in iron(III), with $\epsilon = 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$, higher than for a typical d-d transition. The oxidation of sulfur causes a blue-shifted absorption in **FeSO₂** compared to **FeS** caused by the electron withdrawing ability of SO₂ which lowers the 3d orbital energies.

Time-dependent density functional theory (TD-DFT) simulated spectra show good agreement with experimental data

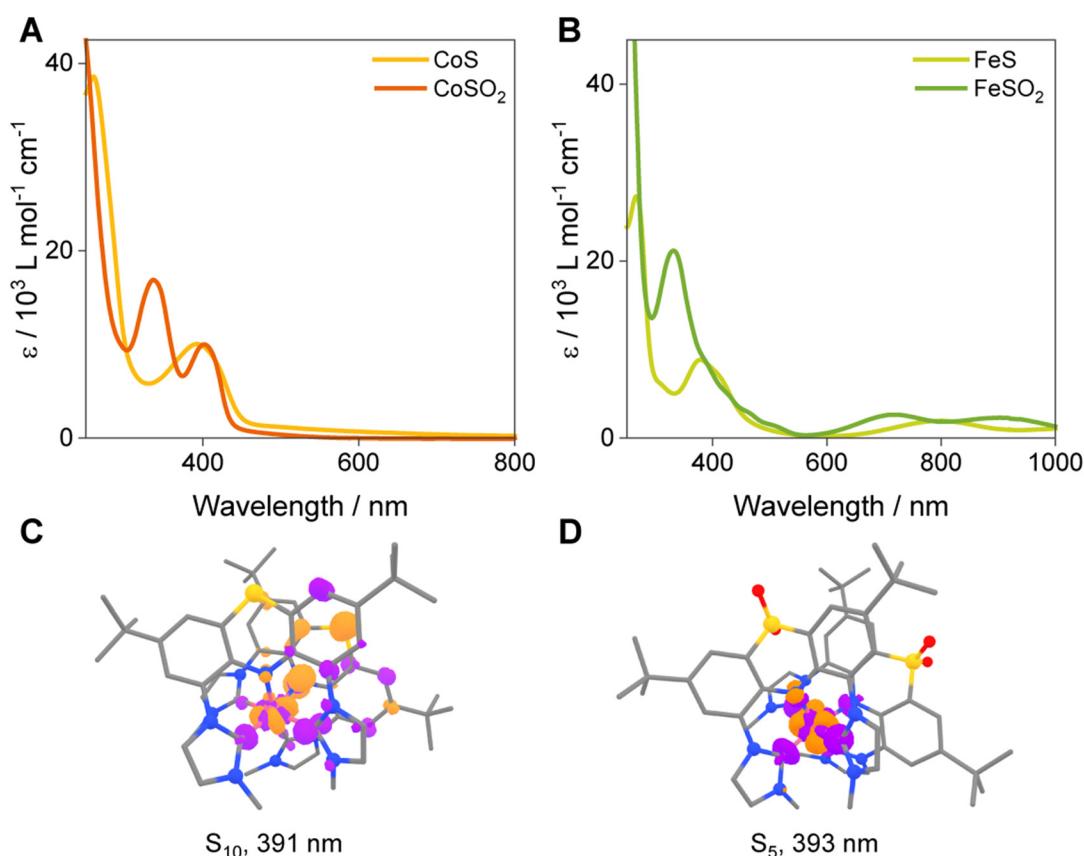


Fig. 3 UV-vis absorption spectra of **CoS** and **CoSO₂** (A), and **FeS** and **FeSO₂** (B) in acetonitrile at 298 K. Electron density difference plot for S₁₀ at 391 nm of **CoS** (C) and S₅ at 393 nm of **CoSO₂** (D), based on TD-DFT calculations. The orange region shows depletion, and the purple region shows a gain in electron density.



(Fig. S29–S35 and Tables S7–S8). For **CoS**, an electron density difference map of state S_{10} at 391 nm shows a (M + L)LCT transition with electron density depletion (orange) localized on the metal center, amido nitrogen and sulfur atoms, and density gain (purple) at the metal center and NHC ligands (Fig. 3C). This state is composed of a mixture of 20% HOMO \rightarrow LUMO+4, 11% HOMO \rightarrow LUMO+3 and 11% HOMO-1 \rightarrow LUMO+3 transitions. Similar character and oscillator strength is found in the S_{11} state at 391 nm and S_{14} at 329 nm. The density map of state S_5 **CoSO₂** at 393 nm shows electron depletion at both the metal center and the amido nitrogen, with increased density at the cobalt d-orbitals and the phenothiazine moiety (Fig. 3D). This state has mixed (M + L)LCT/MC character and is composed of 46% HOMO \rightarrow LUMO+1 and 44% HOMO \rightarrow LUMO transitions. The oxidation also causes a blue shift of the absorption to the S_1 state from 575 nm in **CoS** to 482 nm in **CoSO₂** where both transitions have low oscillator strength (>0.0005). The oxidation of the sulfur atom lowers the energy of the ligand orbitals, caused by the electron-withdrawing ability of the SO₂ moiety compared to sulfide. This is in line with the cyclic voltammetry data shown below. Higher energy transitions show $\pi \rightarrow \pi^*$, MLCT and LLCT character with low oscillator strengths.

Electrochemistry and spectroelectrochemistry

The redox behaviour of the complexes in 0.1 M (⁷Bu₄N)(PF₆) acetonitrile solution was examined with cyclic voltammetry (CV). Redox assignments from the cyclic voltammograms in Fig. 4A are shown in Table 2, based on the spectroelectrochemistry data shown below and comparison with similar compounds and ligands (Fig. S36).^{33,39} **CoSO₂** exhibits a chemically irreversible wave at $E_{pc} = -1.54$ V vs. Fc^{+/-} assigned as ligand reduction. No reduction event associated with the Co^{III/II} couple is observed. This is attributed to the strongly electron-donating nature of the ligand and the complexes possess

Table 2 Electrochemical potentials (in V vs. Fc^{+/-}) of **CoS**, **CoSO₂**, **FeS** and **FeSO₂** and previously reported NHC complexes of cobalt(III) and iron(III)

Entry	Compound	$E_{1/2\text{red}}^a$ (L ^{+/-})	$E_{1/2}^a$ (L ^{*/+/-})	$E_{1/2}^a$ (M ^{IV/III})	$E_{1/2}^a$ (L ^{2+/-})
1	CoS	N/A	-0.32	+0.02	+0.83
2	CoSO₂	-1.54 ^b	+0.51	+0.77 ^b	N/A
3	[Co(L ^{CNC}) ₂] ⁺ ^c	-2.21 ^b	+0.72	+0.42	N/A
4	[Co(PhB(MeIm) ₃) ₂] ⁺ ^d	N/A	+1.55	+0.96	+1.76
5	FeS	-1.40	-0.35	+0.21	+0.78
6	FeSO₂	-0.78	+0.44	+0.95 ^b	N/A
7	[Fe(L ^{CNC}) ₂] ⁺ ^c	-1.38	+0.56	+0.05	N/A

^a Potential referenced to Fc^{+/-} in V. ^b Irreversible wave. ^c L^{CNC} = 3,3'-(3,6-di-*tert*-butylcarbazole-9-id-1,8-diy)bis(1-methyl-1*H*-imidazol-3-ium-2-ide) (Fig. 1B).³³ ^d PhB(MeIm)₃ = tris(3-methylimidazolin-2-ylidene)(phenyl)borate.²⁰

similar values to other NHC-based Co(III) complexes.^{20,29,33} **FeS** and **FeSO₂** display two chemically reversible reduction waves at $E_{1/2} = -1.40$ and -0.78 V vs. Fc^{+/-}, respectively, assigned to the Fe^{III/II} reduction couples. The reduction potential is positively shifted in the SO₂ complexes as the amido σ donation is weakened with greater oxidation of sulfur, stabilizing the d*(Fe) orbitals. Similarly, the Fe^{IV/III} oxidation couple is anodically shifted in **FeSO₂** relative to in **FeS**, resulting from the influence of HOMO inversion on the d orbital energies. This effect is greater than in other Fe(III) complexes containing electron withdrawing/donating groups.^{25,53,54}

Three chemically reversible oxidation waves are observed in **CoS** and **FeS** (Table 2, entries 1 and 5). The first wave at -0.32 V vs. Fc^{+/-} for **CoS** and -0.35 V vs. Fc^{+/-} for **FeS** is absent in the SO₂ complexes and in the carbazole series and is assigned to one-electron oxidation of the phenothiazine.³⁹ The second wave is cathodically shifted from +0.21 in **FeS** to +0.02 V vs. Fc^{+/-} in **CoS**. These are assigned to the Fe^{IV/III} and Co^{IV/III}

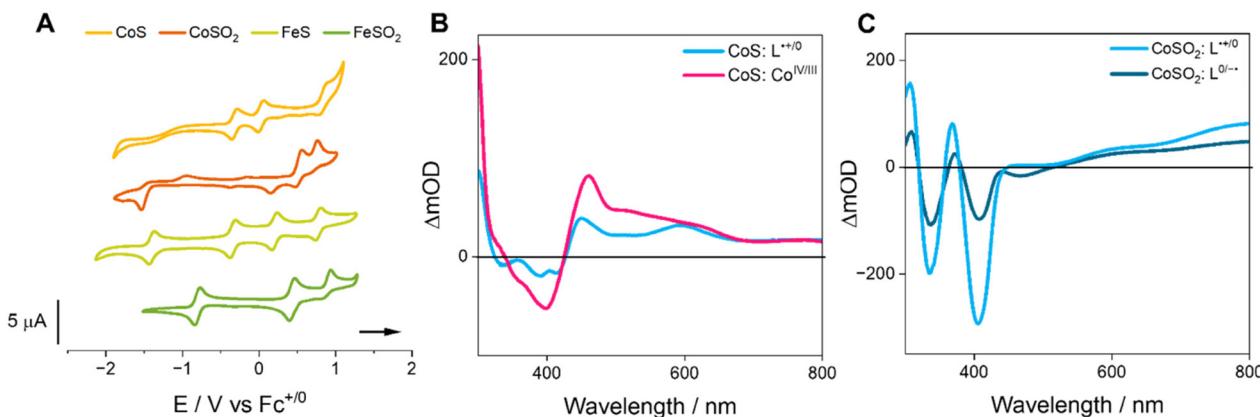


Fig. 4 (A) Cyclic voltammograms in argon-sparged dry acetonitrile in 0.1 M (⁷Bu₄N)(PF₆) at 298 K of **CoS**, **CoSO₂**, **FeS** and **FeSO₂** (1 mM) swept anodically at a scan rate of 100 mV s⁻¹, and initiated at the open circuit potential (**CoS**: -0.6 V vs. Fc^{+/-}, **CoSO₂**: -0.5 V vs. Fc^{+/-}; **FeS**: -1.0 V vs. Fc^{+/-}, **FeSO₂**: -0.6 V vs. Fc^{+/-}). (B) UV-vis changes following ligand-based oxidation (light blue, scanning from -0.02 to +0.40 V vs. Fc^{+/-}) and metal-based oxidation (pink, scanning from -0.6 to -0.02 V vs. Fc^{+/-}) of **CoS** in de-aerated acetonitrile at 298 K. (C) UV-vis changes following ligand-based oxidation (light blue, scanning from 0 to -0.70 V vs. Fc^{+/-}) and ligand-based reduction (dark blue, scanning from 0 to -1.80 V vs. Fc^{+/-}) of **CoSO₂** in de-aerated acetonitrile at 298 K.



couples, respectively. The combination of σ - and π -donor properties with the addition of sulfur results in a higher donating ability of **CoS** in comparison with the carbazole-based Co(m) complex (Table 2, entry 3), lowering the oxidation potential of the Co^{IV/III} oxidation couple.^{33,39} The third wave shows similar values of +0.83 V vs. Fc^{+/-} in **CoS** and +0.78 V vs. Fc^{+/-} in **FeS**, assigned to the second oxidation of the phenothiazine unit.³⁹

Complex **CoSO₂** shows two chemically irreversible oxidation processes at +0.51 and +0.77 V vs. Fc^{+/-}, assigned to ligand and Co^{IV/III} oxidation, respectively (Table 2, entry 2). The reversibility of the ligand oxidation is influenced by the metal oxidation event (Fig. S37). When scanned past +0.77 V vs. Fc^{+/-}, the event at +0.51 V vs. Fc^{+/-} is chemically irreversible. However, this wave becomes more reversible when the potential is limited to +0.65 V vs. Fc^{+/-}. We also observed the disappearance of the wave at +0.15 V vs. Fc^{+/-}, suggesting that a chemical step takes place upon oxidation of Co^{III} to Co^{IV} at +0.77 V vs. Fc^{+/-}. A cathodic shift greater than 0.73 V is observed in the M^{IV/III} oxidation couple between the S and SO₂ series. This result showcases the influence of the oxidation state of the sulfur on the electronic density of the metal, which is greater than in other S-bridged metal complexes.³⁴⁻³⁸

Spectroelectrochemistry experiments support the CV assignments and help rationalize the character of the excited states (Fig. 4B, C and Fig. S38-S46). Upon oxidation of the ligand at -0.35 V vs. Fc^{+/-}, **CoS** shows a decrease in the intensity of the bands at 332, 388 and 413 nm and an increase in the bands at 450 and 596 nm. These spectral changes are attributed to a single-electron transfer to generate a phenothiazine radical, consistent with observations in other phenothiazine-based complexes.^{55,56} **FeS** shows an increase in the band at 596 nm in the same voltage range, supporting the phenothiazine oxidation assignment (Fig. S42). When the potential is scanned past +0.40 V vs. Fc^{+/-}, the band at 392 nm decreases in intensity while the band at 460 nm increases, supporting assignment of the wave as Co^{IV/III}. These results are consistent with the (M + L)LCT nature of the 392 nm band as predicted by TD-DFT. **CoSO₂** shows similar features when scanned to +0.7 V vs. Fc^{+/-} and -1.8 V vs. Fc^{+/-}, supporting the ligand character of the redox events. In both cases, the bands at 335 and 406 nm show depletion and bands at 307, 368, 800 nm increase in intensity. The observed spectral changes align with ligand events observed in spectroelectrochemistry of **FeSO₂**. Upon oxidation of the ligand at +0.44 V vs. Fc^{+/-}, the band at 331 nm decreases in intensity and a broad band spanning from 600 to 900 nm increases in intensity (Fig. S45).

Excited-state dynamics

We used femtosecond transient absorption (fsTA) to investigate the non-radiative decay lifetimes of the complexes **CoS** and **CoSO₂**. Upon excitation at 400 nm, **CoS** shows a ground-state bleach (GSB) at 392 nm and excited-state absorption (ESA) bands at 448 nm and 565 nm (Fig. S47-S48). Global analysis of the transient absorption data yielded four exponential decays: lifetimes of 0.2 ps, 3.3 ps, 35.1 ps and 8.0 ns (Fig. 5A). The 0.2 ps component shows broad spectral features between

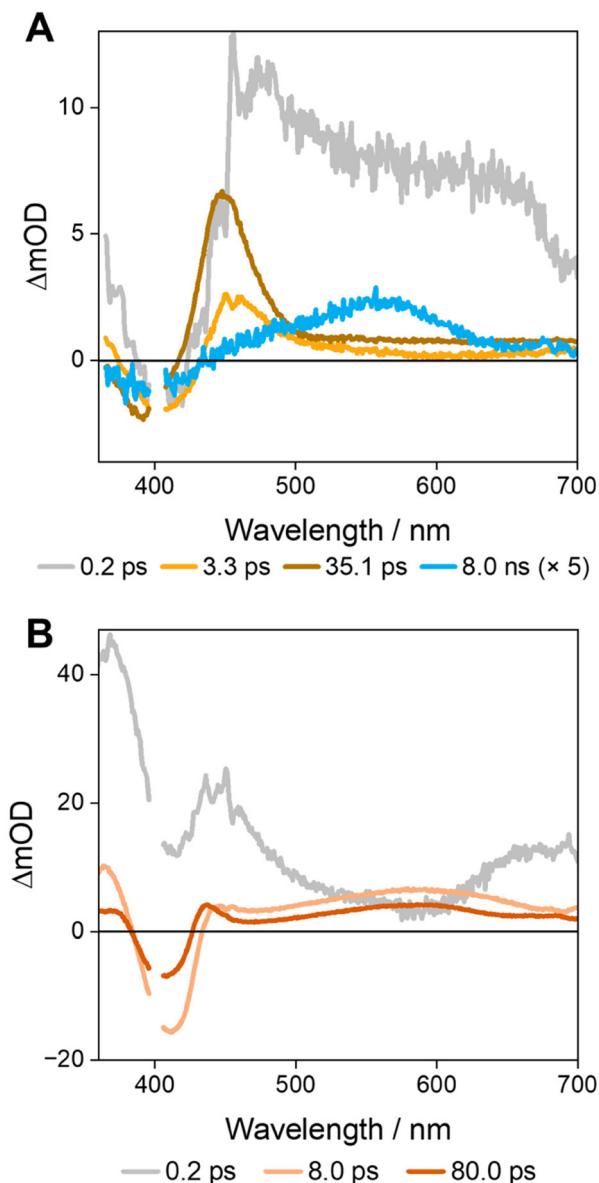


Fig. 5 Decay-associated spectra (DAS) of **CoS** (A) and **CoSO₂** (B) obtained from femtosecond transient absorption in de-aerated acetonitrile at 298 K prompted by a 400 nm excitation source.

440 and 700 nm and between 350 and 380 nm. We propose that this component is associated with vibrational cooling and an intersystem crossing that the ¹(M + L)LCT state undergoes, similar to other d⁶ metal complexes.⁵⁷⁻⁶¹ The 3.3 ps and 35.1 ps components are associated with the 392 and 448 nm bands. Both components are associated with ³MC states as suggested by spectroelectrochemical results and SOC-TD-DFT (Table S9 and Fig. S33).⁶² The long-lived 8.0 ns component exhibits bands at 392 and 565 nm. The 565 nm band corresponds to a one-electron oxidized phenothiazine radical unit, as observed in the spectroelectrochemistry experiments discussed above and other compounds containing phenothiazine.⁶³⁻⁶⁵ We thus tentatively assign the long component as having primarily triplet phenothiazine character, as



also predicted by the SOC-TD-DFT results (Fig. S33 and Table S9).

Complex **CoSO₂** shows a GSB at 402 nm and ESAs at 350 nm, 436 and 590 nm (Fig. S49 and S50). Four decay-associated spectra (DAS) are associated with the excited-state dynamics: 0.002, 0.2, 8.0 and 80.0 ps (Fig. 5B). The shortest component (0.002 ps) accounts for the coherent and solvent effects and is excluded from the excited-state dynamics.^{57,66} The 0.2 ps component shows ESAs at 368, 450 and 693 nm. This component is also tentatively assigned to vibrational relaxation of the singlet excited state followed by intersystem crossing (ISC) to the lowest triplet vibrational state.^{57–61} The 8.0 ps component is associated with signals at 363, 411, and 590 nm, while the longer 80.0 ps component correspond to bands at 371, 408, 437 and 590 nm. These features do not fully match with the spectroelectrochemical spectra following ligand oxidation and reduction, particularly the band at 436 nm. We hypothesize that these decay components are associated with ³MC states based on the SOC-TD-DFT results (Table S9 and Fig. S34). Their lifetimes are longer than the fast decay components observed in **CoS**. Both energetic and structural effects could be playing a role in the extension of the decay lifetimes. The energy of the T₁ state in **CoSO₂** is 0.3 eV higher than in **CoS**. We expected that the lower T₁ energy would increase the non-radiative rate constant, decreasing the decay lifetime.⁶⁷ Oxidation of the sulfur atom could also increase ligand rigidity, thereby extending the ³MC state lifetimes. This is evidenced by the larger RMSD between the T₁ and S₀ states in **CoS** compared to **CoSO₂** in the optimized DFT structures (Table S6), suggesting that the T₁ state is more distorted in **CoS**, facilitating non-radiative decay. The same effect is observed in B(m) complexes containing phenothiazine and other sulfur-bridged complexes reported in our group, where non-radiative decay is slower upon sulfur oxidation.^{12,34–39}

The ²LMCT state is populated in complexes **FeS** and **FeSO₂** when excited at 400 nm. The fsTA spectra of **FeS** display an increase in intensity at 460 and 550 nm and a depletion at 380 and 700 nm. **FeSO₂** shows ESAs at 368 and 585 nm, and a small GSB at 700 nm (Fig. S51–S55). Global analysis of **FeS** yielded three components that are associated with the internal conversion (0.2 ps), ²LMCT decay (0.8 ps) and ³MC (11.5 ps) (Fig. S53). We observed an increase in the decay lifetime upon oxidation of the sulfur, similarly to in the cobalt(m) complexes. In the case of **FeSO₂** the global analysis showed components of 0.3 ps associated with internal conversion and 8.3 ps associated with ²LMCT decay. A long component with a lifetime of 741.9 ps could originate from a high-spin iron(m) complex, as has also been observed in another amido-bridged iron(II) complex (Fig. S54–S56).⁶⁸ Both complexes show decay lifetimes comparable to the Fe(m) carbazole-NHC complex and are two to three orders of magnitude shorter than in other recently reported Fe(m) complexes.^{17,33,42,69,70}

We observed a substantial increase in the lifetime when comparing the Fe(m) and Co(m) complexes. The higher nuclear charge in Co(m) could increase the energy of the MC states, leading to longer lifetimes. On the other hand, the d⁵ Fe(m)

complexes show sub-picosecond lifetimes. “HOMO inversion” achieved with the amido-bridged ligand lowers the energy of the charge transfer band to extend the decay lifetime in Fe(II) complexes. This is not beneficial for the Fe(m) series, as it requires strong ligand field ligands to achieve longer lifetimes.^{14,17,42,70} In the Fe d⁵ system, organic chromophores are effective in extending lifetimes when not directly bonded to the metal center.^{25,28}

Finally, we examined whether radiative decay could occur in any of the complexes or ligands. **PTZIm₂H** and **PTZO₂Im₂H** show a broad blue/green emission in acetonitrile with maxima at 432 and 493 nm, respectively (Fig. S28). Both display decay lifetimes in the nanosecond range with quantum yields (Φ_{em}) of 0.9% for **PTZIm₂H** and 1.3% **PTZO₂Im₂H** (Table S4). These results are similar to other ligands containing phenothiazine units.³⁹ Photoluminescence was not observed in complexes at 298 and 77 K under inert conditions. These results suggest that non-radiative decay is the major decay path in these complexes.

Conclusions

This study presents a method to control the electronic density in Co(m) photosensitizers using sulfur-bridged ligands. Changing the oxidation state of sulfur in the Co(m) complexes led to three key insights. First, the more flexible backbone of the ligands relative to other pincer-type ligands favoured the formation of *facial* isomers. NMR spectroscopies and XRD confirmed the presence of the *facial* isomer in solid and in solution. This structural flexibility likely contributes to the observed fast decay components and alters the excited state character of the complexes. Second, the oxidation state of sulfur modulated the metal electronic density. Cyclic voltammetry experiments showed that the higher donating nature of the **PTZIm₂H** ligand favours the formation of M^{IV/III} for both **CoS** and **FeS**. Oxidation to SO₂ cathodically shifted the oxidation couples. This effect is greater than for other sulfur-bridged ligands previously reported in our group.^{35–37} UV-vis spectra and TD-DFT analysis also revealed that the phenothiazine unit has less contribution to the band at 400 nm after sulfur oxidation in **CoSO₂**. Finally, excited state dynamics depended on the oxidation state of sulfur. Transient absorption experiments showed that the phenothiazine in **CoS** facilitated fast non-radiative channels, however a long component >8.0 ns is observed. Oxidation of the S in **CoSO₂** reduced the non-radiative rate and increased the lifetime of the short components. These results show that sulfur oxidation state can be used to control the photophysics of first-row photosensitizers beyond traditional ligand designs.

Author contributions

J. T., K. M. T. and M. O. W. wrote the manuscript. J. T. carried out the synthesis, characterization, photophysical properties



and DFT calculations. K.-M. T. and B. O. P. collected and refined the XRD structures. S. K. carried out time-resolved measurements and global analysis of the spectroscopic data. C. J. W. collected and simulated the EPR data. M. O. W. supervised the project. All authors discussed the progress of the research and reviewed the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

The data supporting this study can be found in the article or in the supplementary information (SI). Supplementary information: all experimental procedures, FT-IR, EPR and NMR spectra, HR-ESI mass spectra, crystal and structure determination data, additional photophysical, electrochemical and computational data. See DOI: <https://doi.org/10.1039/d5qi02362a>.

CCDC 2480167 and 2480168 contain the supplementary crystallographic data for this paper.^{71a,b}

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