

## RESEARCH ARTICLE

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 Cite this: *Inorg. Chem. Front.*, 2023, **10**, 118

## Towards panchromatic Fe(II) NHC sensitizers via HOMO inversion†

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A combined experimental and theoretical study of iron(II) complexes with pyridyl N-heterocyclic carbene ligands is presented, with a new focus on the effect of extending the ligands with thiophenes of variable number. In agreement with recent theoretical predictions by the Jakubikova group, these ligands induce a substantial mixture of the occupied  $t_{2g}$  and  $\pi$  HOMO orbitals, as manifested by a near 80 nm red-shift of the  $^1\text{MLCT}$  transition and a 2–3 fold increase of the molar extinction coefficient. The thiophene moieties permit delocalisation of the MLCT state on the ligands, which results in excited state lifetimes in the 13–18 ps range, almost twice as much as for the reference compound lacking the thienyl substituents. Relaxation into  $^3\text{MC}$  states remains the main  $^3\text{MLCT}$  quenching mechanism, and the effect of the number of thiophenes in lengthening the  $^3\text{MLCT}$  lifetime is qualitatively consistent with a reduction in the  $^3\text{MLCT}$ – $^3\text{MC}$  energy gap.

 Received 2nd September 2022,  
Accepted 10th November 2022

DOI: 10.1039/d2qi01903e

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## Introduction

The replacement of noble metals by earth-abundant substitutes is at the forefront of current research<sup>1–4</sup> aimed at developing sustainable photoactive materials required for solar energy conversion or photocatalysis. Iron is by far the most abundant metal in Earth's crust and appears a promising candidate to replace the ruthenium gold standard that is in the same column of the periodic table.

Ruthenium polypyridine complexes have been applied extensively for sensitization in Dye-sensitized solar cells (DSSCs).<sup>5–10</sup> Their photophysical and redox properties facilitate efficient light harvesting through long-lived Metal-to-Ligand Charge Transfer (MLCT) states which are responsible for electron transfer into semiconductors and efficient ground state regeneration after excitation.<sup>11–13</sup>

In contrast Fe(II)-polypyridines have short-lived MLCT states due to an ultrafast intersystem crossing populating their low-lying metal centred (MC) states.<sup>14–17</sup> To date increasing the ligand field strength has been the strategy of choice to increase

the energy of the unreactive low-lying ligand field states. Ligands based on  $\sigma$ -donating NHC (N-heterocyclic carbenes). The MLCT lifetime has reached tens of picoseconds for complexes with tridentate  $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$ <sup>18–20</sup> and bidentate  $\text{C}^{\wedge}\text{N}$  ligands,<sup>21–24</sup> and nanoseconds for compounds bearing tridentate  $\text{C}^{\wedge}\text{C}^{\wedge}\text{C}$  ligands,<sup>25</sup> making it possible for iron to be used in photochemical applications such as iron-sensitized DSSCs.<sup>26–31</sup> However, apart from the recently published Fe(II) complex with phenN,N<sup>^</sup>C ligands,<sup>32</sup> this improvement in lifetime was obtained at the sacrifice of achieving the panchromatic absorption required for solar energy conversion applications. Recently, “HOMO inversion” has emerged as a promising concept in the field.<sup>33–35</sup> This approach aims to adjust the filled orbital energetic levels in order to mix metal  $t_{2g}$  and ligand molecular orbitals thus switching the HOMO localization from the metal to the ligand (Fig. 1). This approach was demonstrated experimentally by the Herbert group<sup>35</sup> to design new panchromatic iron(II) complexes using ligands combining amido donors with benzannulated phenanthridine and quinoline. The covalent amido–Fe bond deeply strengthened the

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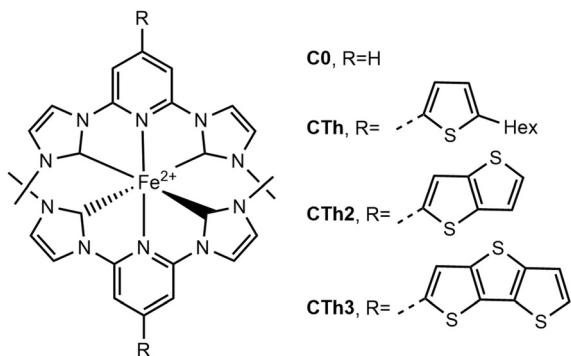
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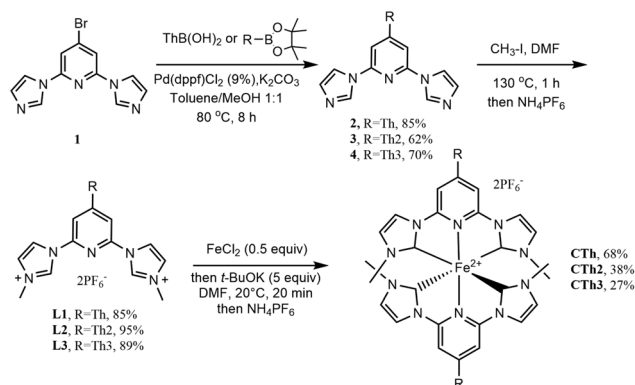
 † Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d2qi01903e>


Fig. 1 Energetic diagrams illustrating the HOMO inversion concept.





**Fig. 2** Complexes studied in this work. The counterion is  $\text{PF}_6^-$  throughout.



**Scheme 1** Synthesis of ligand precursors and thienyl substituted complexes.

ligand field subsequently producing long lived excited states with up to 2.5 ns lifetime.

The group of E. Jakubikova<sup>33</sup> has reported a computational work on a series of iron(II) polypyridine complexes and predicted that the ligand  $\pi$ -delocalization should promote notable changes in absorption features and suggested that the same effect could be expected with pyridylNHC Fe(II) complexes. To our knowledge besides this exclusively computational work, the effect of  $\pi$ -delocalization and the impact of HOMO inversion on the photophysical and electronic properties of pyridylNHC Fe(II) complexes has not been investigated yet.

Herein we report the synthesis of complexes **CTh**, **CTh2** and **CTh3** designed with thiophene and fused polythiophenes conjugated with the central pyridine ring of the pyridylNHC ligand (Fig. 2) and the investigation of their photophysical properties by means of ultra-fast transient absorption. Complex **C0** is the proto-typical  $[\text{Fe}(\text{bmip})_2]^{2+}$ , where  $\text{bmip} = 2,6\text{-bis}(3\text{-methyl-imidazole-1-ylidene})\text{-pyridine}$ , published by the group of Wärnmark.<sup>18,36</sup> We demonstrate that, as compared to **C0**, extending the delocalization promotes an important red-shift of the pyridine-MLCT absorption band and an impressive increase of the molar extinction coefficients. The excited state lifetimes were also increased substantially by comparison with the unsubstituted complexes while they were slightly impacted by the conjugation extent.

## Results and discussion

### Synthesis of ligands and complexes

The imidazolium salts **L1**, **L2** and **L3**, that are the required precursors of the pyridyl-NHC ligands to be coordinated to iron, were first synthesized (Scheme 1, see ESI† for experimental details). **L1** was obtained following our reported procedure.<sup>27</sup> **L2** and **L3** were obtained in good yields respectively by quaternization of pyridylimidazoles **3** and **4** resulting from a Suzuki coupling of the bromo derivative **1**<sup>27</sup> with the appropriate preformed thienyl boron pinacol esters that were obtained by a lithiation-borylation sequence on the parent thienyl compounds (see ESI†).<sup>37,38</sup> The target complexes were finally

obtained in good to moderate yield applying an *in situ* coordination protocol.  $\text{FeCl}_2$  was first reacted with the appropriate ligand precursor, then  $t\text{-BuOK}$  was added to generate the carbene moiety. The coordination yield was found dependent on the number of thiophenes attached to the central pyridine. This agrees with the weakening of the pyridine nitrogen coordination ability by conjugation with the extended  $\pi$ -system.

### Electronic properties of complexes

The UV-Vis absorption spectra of the three complexes in deaerated acetonitrile solution are shown in Fig. 3 and the data concerning the lowest energy bands are collected in Table 1. The complexes display three distinct absorption bands. The band at higher energy (250–350 nm) is assigned to ligand-centered  $\pi-\pi^*$  transitions, while the two other bands at lower energy, correspond to Fe-NHC transitions (340–420 nm) and Fe-pyri-



**Fig. 3** UV-Vis spectra of complexes in acetonitrile. Inset: normalized absorbance for the lowest energy band.



**Table 1** Spectroscopic and electrochemical properties of complexes

Complex	$\lambda_{\max}$ (nm) ( $\epsilon(\text{M}^{-1} \text{cm}^{-1})$ )	$E_{\text{ox}}$ (Fe <sup>II</sup> /Fe <sup>III</sup> ) (V SCE <sup>-1</sup> )	$E_{\text{red}}$ (V SCE <sup>-1</sup> )	$\Delta E$
<b>C0</b> <sup>18,22</sup>	284 (31 433) 390 (9077) 457 (15 955)	0.80 (rev)	-1.95 (irr)	2.75
<b>CTh</b>	319 (51 619) 399 (12 519) 516 (39 330)	0.68 (rev)	-1.69 (qr)	2.37
<b>CTh2</b>	328 (61 027) 401 (18 354) 526 (44 300)	0.71 (rev)	-1.56 (qr)	2.27
<b>CTh3</b>	359 (51 200) 535 (30 240)	0.73 (rev)	-1.52 (irr)	2.25

dine MLCT transitions (410–650 nm). In **CTh3**, the very broad  $\pi$ - $\pi^*$  absorption band of the dithienothiophene moiety masks the Fe-NHC MLCT band.

As a general trend, the substitution of complex **C0** with thiophenes promoted a notable bathochromic effect on both the  $\pi$ - $\pi^*$  and Fe-pyridine MLCT bands and the amplitude of the red-shift was directly related to the number of thiophene units ( $\Delta\lambda = 78$  nm going from **C0** to **CTh3**). In contrast, the thiophenes had no impact on the Fe-carbene MLCT band the transition energy of which remained constant.

Focusing on the lowest-energy portion of the spectrum, the MLCT Fe-pyridine band, **CTh**, **CTh2** and **CTh3** present a broad and intense absorption, ranging from 450 to 620 nm. Among all, **CTh3** showed the broadest and most red shifted absorption (535 nm,  $\epsilon = 30\,240 \text{ M}^{-1} \text{cm}^{-1}$ ) and **CTh2** the highest extinction coefficient (526 nm,  $\epsilon = 44\,300 \text{ M}^{-1} \text{cm}^{-1}$ ).

The cyclic voltammetry data (Table 1) globally confirm the UV-Vis absorption spectroscopy results. The electrochemical gap markedly decreased when comparing **CTh** to **C0** in agreement with the 59 nm redshift of the MLCT band upon addition of one thiophene unit on the central pyridine. Also corroborating the absorption spectra, a decrease of the gap was observed albeit in a lesser extent going from **CTh** to **CTh3**.

Table 2 gathers the computed energy and oscillator strengths for the lowest singlet excited states of **C0**, **CTh**, **CTh2** and **CTh3** that are associated with the lowest band in the absorption spectrum. Consistent with the experimental observations, a red shift of the lowest transitions of **CTh**, **CTh2** and

**Table 2** Computed energies of the HOMO and LUMO energies and lowest singlet excited states of **C0**, **CTh**, **CTh2** and **CTh3** calculated at the ground state optimized geometry using TDDFT(B3LYP\*)

Complex	$\lambda$ (nm) ( $f$ )	$\epsilon_{\text{HOMO}}/\text{eV}$	$\epsilon_{\text{LUMO}}/\text{eV}$	$\Delta E/\text{eV}$
<b>C0</b>	518 (0.00163)	-5.33	-2.02	3.31
	518 (0.00162)			
<b>CTh</b>	615 (0.00340)	-5.29	-2.41	2.88
	614 (0.00370)			
<b>CTh2</b>	628 (0.00290)	-5.32	-2.56	2.76
	627 (0.00260)			
<b>CTh3</b>	637 (0.00430)	-5.33	-2.62	2.71
	637 (0.00340)			

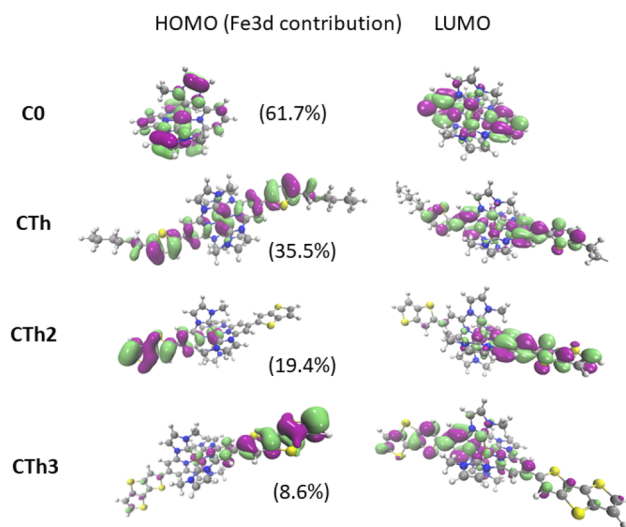
**CTh3** compared to **C0** is observed and this increases with the delocalization of the MLCT state. The HOMO–LUMO gap is slightly larger than experimentally measured, but exhibits the same trend as the cyclic voltammetry data in Table 1.

The HOMO and LUMO have been plotted for all the complexes (Fig. 4 and ESI†). Fig. 4 clearly evidenced a significant enhancement of the mixing between the ligand and metal orbitals in the HOMO as the thiophene units are included. The Fe 3d orbitals contribution to the HOMO decreased with the increase of the number of thienyl units in the substituent.

### Excited state dynamics and relaxation

Temporal evolution of the fs-TAS signal of the **CTh** series of molecules bears a number of common features and therefore will be illustrated on the example of **CTh3** (Fig. 5, see the ESI† for data on the other molecules). In particular, upon optical excitation of the Fe-pyridine MLCT transition by the pump pulse the differential transient spectra in the 360–680 nm spectral range reveal two negative and two positive features. The former ones (<390 nm, 500–580 nm) come from the depletion of the population of the initial state (ground state bleaching, GSB) and peak around the absorption maxima of the Fe-pyridine and Fe-NHC MLCT transitions (Fig. 5B). In turn, the positive features originate from the excited state absorption (ESA) of the states populated by the pump pulse. Notably, the high-energy ESA (400–470 nm) shows twice the intensity of the low energy ESA feature (>580 nm).

The initially observed spectral features exhibit an ultrafast evolution on the sub-200 fs time scale. Namely, the high-energy ESA undergoes a pronounced blue-shift, which is most evident by the zero-crossing point moving from 500 nm at 0 ps to ~475 nm at 200 fs (Fig. 5B and 480 nm trace in Fig. 5C). The low-energy ESA shows similar development. Also, a somewhat delayed rise of the low-energy GSB band suggests that it overlaps with the ultrafast evolving ESA. Further temporal evol-

**Fig. 4** HOMO–LUMO plots for all the complexes including the contribution of Fe 3d orbitals in HOMO.



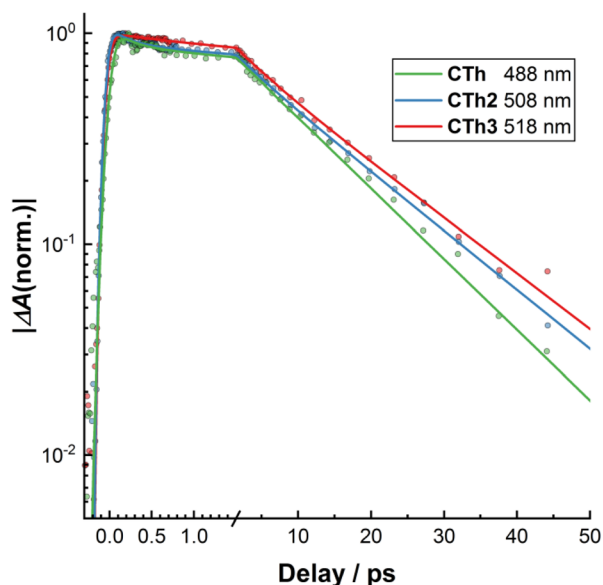


to two different  $^3\text{MLCT}$ - $^3\text{MC}$  relaxation pathways in the multi-dimensional excited state landscape. As a side remark, a parallel population of both  $^3\text{MLCT}$  and  $^3\text{MC}$  on the sub-picosecond time scale<sup>36,43,45</sup> cannot be excluded, since population of the latter states go commonly un-noticed in UV-VIS transient absorption experiments.<sup>42</sup>

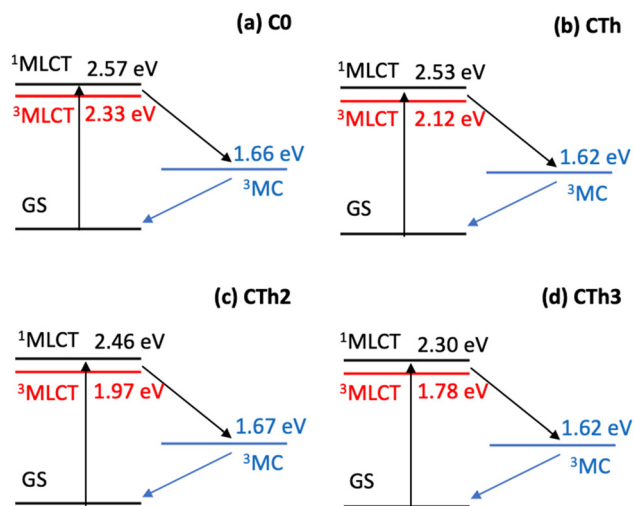
Concerning the influence of the number of fused thiophene rings in the **CTh** series of molecules on the excited state dynamics one can see from the results of the global analysis (Table 3) as well from the bleach recovery kinetics (Fig. 7) that increasing the number of fused thiophene rings and thereby promoting the electron delocalization in the MLCT state leads to a moderate slow-down of all the steps of the excited state relaxation. Nonetheless, this delocalization effect is apparently not enough to alter the overall relaxation cascade mechanism observed for related Fe-NHC complexes.

A Jablonski diagram showing the computed energetics of the key states for the series of complexes is shown in Fig. 8. While the MLCT states show a distinct red shift, the  $^3\text{MC}$  states, which mix very little with the fused thiophene units (see spin density in Fig. S20†) remain largely unchanged among the **CTh**, **CTh2** and **CTh3** series compared to **C0**. The geometry of all the important structures are provided in the ESI.†

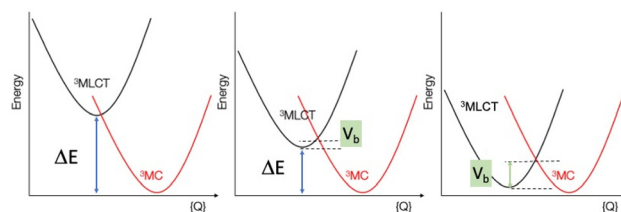
Given the significant structural reorganization between the  $^3\text{MLCT}$  and  $^3\text{MC}$  states, the decreasing energy gap ( $\Delta E$ ) between the two states as the number of thiophene units is increased may introduce a small barrier to the transformation between the two states, responsible for the increase in  $\tau_3$  and  $\tau_4$  observed experimentally. This counterintuitive effect is highlighted in Fig. 9. Indeed, and as in Marcus theory for electron transfer,<sup>46</sup> the energy barrier between the states decreases, and



**Fig. 7** Semi-log plot of normalized kinetics of the bleach recovery of **CTh**, **CTh2** and **CTh3**. Dots are measured datapoints whereas lines are results of the global fit (see text).



**Fig. 8** Computed Jablonski diagrams of the important excited states in (a) **C0**, (b) **CTh**, (c) **CTh2** and (d) **CTh3**. Using TDDFT, the energies of the  $^1,^3\text{MLCT}$  states were computed at the  $^3\text{MLCT}$  optimized geometry and the energies of the  $^3\text{MC}$  was computed at the  $^3\text{MC}$  optimized geometry ( $^1\text{MLCT}$  and  $^3\text{MLCT}$  states have similar geometries). Both geometries were computed using UKS and the relevant geometries are in the ESI.†



**Fig. 9** Schematic representation of the  $^3\text{MLCT}$  and the  $^3\text{MC}$  states approximated as harmonic potentials along an effective structural coordinate  $Q$ . When the energy gap  $\Delta E$  decreases (left to right), the barrier  $V_b$  between  $^3\text{MLCT}$  and  $^3\text{MC}$  increases, leading to a longer  $^3\text{MLCT}$  lifetime.

reaches zero only when  $\Delta E$  is equal to the structural reorganization energy. A similar behavior was recently also put forward in a study on solvent effects of Fe complexes.<sup>47</sup>

## Conclusions

In conclusion, we present here a combined experimental and theoretical study of iron(II) complexes with pyridyl NHC ligands conjugated with thiophene and fused polythiophenes. As predicted theoretically,<sup>33</sup> these ligands induce a substantial mixture of the occupied  $t_{2g}$  and  $\pi$  HOMO orbitals, as manifested by a near 80 nm red-shift of the  $^1\text{MLCT}$  transition and a 2–3-fold increase of the extinction coefficient. The thiophene moieties allow for a delocalisation of the MLCT state on the ligands, which results in excited state lifetimes in the 13–18 ps range, almost twice as much as for the reference compound lacking the thiophene side groups. Relaxation into  $^3\text{MC}$  states remains the main  $^3\text{MLCT}$  quenching mechanism, and the



effect of the number of thiophenes in lengthening the  $^3\text{MLCT}$  lifetime is qualitatively consistent with a stabilisation of the  $^3\text{MLCT}$  energy due to increased charge delocalisation. As a result, the  $^3\text{MLCT}$ – $^3\text{MC}$  energy gap is reduced (Fig. 8), which leads to an increased barrier for the excited state structural relaxation involved in the  $^3\text{MLCT}$ – $^3\text{MC}$  transition (Fig. 9). Works are in progress to further amplify the mixing between metal and ligand orbitals *via* a wider  $\pi$ -extended delocalization in various parts of the ligands.

## Experimental

### General

Solvents and commercially available reagents were used as received. Thin layer chromatography (TLC) was performed by using silica gel 60 F-254 (Merck) plates and visualized under UV light. Chromatographic purification was performed by using silica gel 60 (0.063–0.2 mm per 70–230 mesh).  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were taken on a DRX400 Bruker spectrometer at ambient temperature. The chemical shifts ( $\delta$ ), were calibrated by using either tetramethylsilane (TMS) or signals from the residual protons of the deuterated solvents and are reported in parts per million (ppm) from low to high field, NMR signal assignments for **L2**, **L3**, **CTh**, **CTh2** and **CTh3** are detailed in the ESI.†

High-resolution mass spectrometry (HRMS) data was obtained by using Bruker micrOTOF-Q spectrometer. UV-vis spectra were recorded in a 1 cm path length quartz cell on a LAMBDA 1050 (PerkinElmer), spectrophotometer. Cyclic voltammetry was performed on a Radiometer PST006 potentiostat using a conventional three-electrode cell. The saturated calomel electrode (SCE) was separated from the test compartment using a bridge tube. The solutions of studied complexes (0.2 mM) were purged with argon before each measurement. The test solution was acetonitrile containing 0.1 M  $\text{Bu}_4\text{NPF}_6$  as supporting electrolyte. The working electrode was a vitreous carbon rod (1  $\text{cm}^2$ ) wire and the counter-electrode was a 1  $\text{cm}^2$  Pt disc. After the measurement, ferrocene was added as the internal reference for calibration. All potentials were quoted *versus* SCE. In these conditions the redox potential of the couple  $\text{Fc}^+/\text{Fc}$  was found at 0.39 V. In all the experiments the scan rate was 100  $\text{mV s}^{-1}$ .

### Synthesis of complexes

**CTh**. To an Ar degassed solution of **L1**<sup>27</sup> (88 mg, 0.126 mmol) in 2 mL of anhydrous DMF was added anhydrous  $\text{FeCl}_2$  (8 mg, 0.063 mmol). Then *t*-BuOK (0.071 g, 0.630 mmol) was added to the above mixture and stirred at room temperature for 20 min. A saturated aqueous solution of  $\text{NH}_4\text{PF}_6$  was added (10 ml) and the precipitate was collected by filtration. The crude product was further purified by silica gel column chromatography eluting with an acetone/ $\text{H}_2\text{O}/\text{KNO}_3(\text{sat}) = 10/3/0.5$  mixture. The reddish fraction was collected and after evaporation of acetone, the left solution was treated with a saturated solution of  $\text{NH}_4\text{PF}_6$ . The desired complex precipitate

was then filtered, washed with distilled water followed by ether, and dried under vacuum. **CTh** was obtained as a reddish solid (50 mg, 68% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ,  $\delta$  ppm): 8.12 (d,  $J = 2.19$  Hz, 2H), 7.95 (s, 2H), 7.84 (d,  $J = 3.72$  Hz, 1H), 7.06 (s,  $J = 3.72$  Hz, 1H), 7.04 (d,  $J = 2.19$  Hz, 2H), 2.99 (t,  $J = 7.51$  Hz, 2H), 2.62 (s, 6H), 1.79 (q, 2H), 148–1.35 (m, 6H), 0.95 (t,  $J = 7.09$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ ,  $\delta$  ppm): 201.1, 154.5, 151.4, 144.5, 138.0, 128.7, 127.2, 127.0, 116.1, 101.6, 35.3, 32.0, 31.8, 30.5, 29.0, 22.9, 14.0. ESI-HRMS calcd for  $\text{C}_{46}\text{H}_{54}\text{FeN}_{10}\text{S}_2$   $m/z = 433.1656$ . Found: 433.1653 [ $\text{M} - 2\text{PF}_6$ ].

**CTh2**. The same procedure was repeated using **L2** (80 mg, 0.119 mmol),  $\text{FeCl}_2$  (8 mg, 0.06 mmol) and *t*-BuOK (68 mg, 0.597 mmol). **CTh2** was obtained as a purple solid (50 mg, 38% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ,  $\delta$  ppm): 8.26 (s, 1H), 8.17(d,  $J = 2.10$  Hz, 2H), 8.05(s, 2H), 7.76(d,  $J = 5.30$  Hz, 1H), 7.52(d,  $J = 5.28$  Hz, 1H), 7.05(d,  $J = 2.10$  Hz, 2H), 2.64(s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ ,  $\delta$  ppm): 200.8, 154.6, 144.6, 142.2, 141.7, 141.0, 131.7, 127.1, 120.9, 120.7, 117.1, 101.9, 35.3. ESI-HRMS calcd for  $\text{C}_{38}\text{H}_{30}\text{FeN}_{10}\text{S}_4$   $m/z = 405.0438$ . Found: 405.0493 [ $\text{M} - 2\text{PF}_6$ ].

**CTh3**. The same procedure was repeated using **L3** (57 mg, 0.079 mmol),  $\text{FeCl}_2$  (5 mg, 0.039 mmol) and *t*-BuOK (44 mg, 0.392 mmol). **CTh3** was obtained as a purple solid (13 mg, 27% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ,  $\delta$  ppm): 8.30 (s, 1H), 8.17 (d,  $J = 2.12$  Hz, 2H), 8.06 (s, 2H), 7.71 (d,  $J = 5.29$  Hz, 1H), 7.53 (d,  $J = 5.30$  Hz, 1H), 7.06 (d,  $J = 2.09$  Hz, 2H), 2.65 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ ,  $\delta$  ppm): 200.8, 154.6, 144.5, 144.2, 143.3, 140.8, 133.1, 131.2, 129.7, 127.2, 122.4, 122.0, 117.1, 101.8, 35.3. ESI-HRMS calcd for  $\text{C}_{42}\text{H}_{30}\text{FeN}_{10}\text{S}_6$   $m/z = 461.0159$ . Found: 461.0175 [ $\text{M} - 2\text{PF}_6$ ].

### Computational details

All complexes were optimized in the ground state and  $^3\text{MC}$  and  $^3\text{MLCT}$  states using DFT within the approximation of the B3LYP\* exchange and correlation functional<sup>48</sup> and a def2-SVP basis set<sup>49</sup> as implemented within the ORCA quantum chemistry package.<sup>50</sup> While this is only valid for the lowest state of each multiplicity, both the  $^3\text{MC}$  and  $^3\text{MLCT}$  are the lowest triplets at their respective optimized geometries. Numerical frequencies calculations were carried out on the geometries optimized to ensure no negative frequencies. TDDFT calculations, used to calculate the excited state energies of each complex used the Tamm–Dancoff approximation<sup>51</sup> and were also performed using B3LYP\*. All simulations were performed using a polarisable continuum model with the parameters of acetonitrile.

### Fs-TAS measurements

The home-built transient absorption spectrometer has been described in detail elsewhere<sup>52,53</sup> and only substantial parameters will be given here. The pump pulses were tuned to be in resonance with the absorption maxima of the studied compounds (510 nm for **CTh**, 525 nm for **CTh2** and 535 nm for **CTh3**). The probe light covering 360–700 nm range was generated by focusing 40 fs 800 nm pulses of the primary laser



source in a 2 mm thick CaF<sub>2</sub> plate mounted on a motorized linear stage to reduce thermal effects. Sample solutions (1 mM in dry acetonitrile) were circulated in a flow cell with 200 μm optical pathlength (Starna). The probe beam was focused to ca. 60 μm Gaussian spot diameter (1/e<sup>2</sup>). The pump spot size was ca. 150 μm in diameter (1/e<sup>2</sup>) and typical maximal energy densities were 0.25 mJ cm<sup>-2</sup> (in the center of the Gaussian beam profile) to keep the fraction of excited molecules below 5%. Solvent subtraction and correction for wavelength-dependent time-zero were performed using previously established protocols<sup>52,53</sup> using the neat solvent data acquired under identical conditions.

## Author contributions

A. R. M. performed the synthesis and ground state characterization of ligands and complexes. B. M. performed transient absorption spectroscopy experiments and analysed the results with S. H., T. P. performed DFT computations and analysed the results. P. C. G. conceived the project and wrote the manuscript with B. M., T. P. and S. H.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The Strasbourg team is grateful to Dr O. Crégut for expert help in laser maintenance and development of data acquisition software, and for the funding provided by the ITI 2021–28 program of the University of Strasbourg, CNRS and Inserm, supported by IdEx Unistra (ANR 10 IDEX 0002), by SFRI STRAT'US project (ANR 20 SFRI 0012) and EUR QMAT ANR-17-EURE-0024 under the framework of the French Investments for the Future Program. The L2CM thanks the French Agence Nationale de Recherche (ANR-16-CE07-0013-02), Lorraine Université d'Excellence (IMPACT N4S) and the European Regional Development Funds (Programme opérationnel FEDER-FSE Lorraine et Massif des Vosges 2014-2020/"Fire Light" project: "Photo-bio-active molecules and nanoparticles" for financial support and grants to A. R. M. The L2CM also warmly thanks S. Parant for the electrochemical experiments and F. Dupire from the mass spectrometry MassLor platform of Lorraine. TJP acknowledges the EPSRC through grant EP/V010573/1 for support.

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