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Isolation and characterization of carbene-supported air stable Co(II)-radical complexes with bidentate redox non-innocent ligands: stability, bonding, ring-opening copolymerization studies and photo-catalytic ring cyclization activity

We report two redox-active Co(II)-radical complexes, featuring a high-spin tetrahedral Co(II) center and redox non-innocent ligands. The complex displays antiferromagnetic coupling between the Co(II) ion and a ligand-centered radical, as magnetometry, EPR, and DFT studies revealed. It exists in a temperature-dependent $S = 1$ and $S = 2$ equilibrium. These air-stable complexes are structurally characterized and electrochemically active notably, complex **3a** functions as a photocatalyst for natural product synthesis and copolymerization under visible light.

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Isolation and characterization of carbene-supported air stable Co(II)-radical complexes with bileptic redox non-innocent ligands: stability, bonding, ring-opening copolymerization studies and photo-catalytic ring cyclization activity†

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Two redox-active Co(II)-radical complexes (**3a** and **3b**), featuring a high-spin tetrahedral Co(II) ion, have been isolated as dark blue needles and remain stable in air for over a week. These complexes contain two redox non-innocent ligands (a carbene and a dithiolene), each with different coordinating atoms (two sulfur atoms and one carbon atom). Cyclic voltammetry (CV) reveals that complex **3a** and **3b** can form their corresponding mono-cation at potentials above -0.61 V. The structure of the complexes has been determined by single-crystal X-ray diffraction, and it has been further characterized by UV-vis, IR, Raman, EPR, and spectroscopy. DC/AC magnetometry measurements of complex **3a** show antiferromagnetic coupling between the high-spin tetrahedral Co(II) ion and the dithiolene-centered radical electron, as concluded from DFT calculations, with support from EPR measurements. Quantum mechanical magnetic model fitting to the experimental data sets suggested that complex **3a** exists in equilibrium between $S = 1$ and $S = 2$ states, depending on temperature, as reflected in the M vs. H plots. The stability, bonding, and electron density distribution of this air-stable complex **3a** have also been studied using various quantum chemical calculations. This dark-colored, photo-redox active complex (**3a**) was found to catalyse the synthesis of the well-known alkaloid natural product, *N*-isopentylcrinasiadine (**5b**), under photocatalytic conditions using a 427 nm Kessil light source. Additionally, complex **3a** also catalyses a copolymerization reaction in the presence of a chloride ion.

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The first organic radical, $[\text{Ph}_3\text{C}^\bullet]$, was isolated by Gomberg in 1900.¹ This synthesis breakthrough also contributed to the development of EPR spectroscopy in 1944. Approximately 2% of $\text{Ph}_3\text{C}^\bullet$ exists in its monomeric radical form in benzene, while the rest undergoes dimerization. Considerable research efforts were required to fully stabilize this class of radicals.² Introduction of a Cl-atom to the 2,6-positions of each benzene ring enhances the stability of the trityl radical, which adopts a

propeller-like conformation due to $\text{Cl}\cdots\text{Cl}$ interaction within the molecule.² Stable radicals have been employed in various fields of chemistry, biology, and material science.³ Recently, an air-stable dinuclear Co(II) complex bridged by a radical ion was reported by Sarkar *et al.*⁴ In the past two decades, several Co(II)-radical complexes have been isolated and characterized.^{5–10} In general, most of the complexes are highly sensitive to air and moisture, limiting their potential applications. However, some Co(II)-radical complexes were reported to be stable in air.^{5–10} C–C bond scission *via* the formation of short-lived Co(II)-radical intermediate, followed by a radical-type migratory insertion reaction, has been proposed, leading to useful catalytic organic transformation.^{11a} Furthermore, an aminyl-radical-Co(II)-superoxide catalysed aerobic deformylation has been reported.^{11b} In 2017, Robinson *et al.* isolated redox non-innocent dithiolene radical anion and its dianion.¹² The former was prepared by reacting *N*-heterocyclic carbenes (NHCs) with BuLi and then treating it with sulfur powder. The

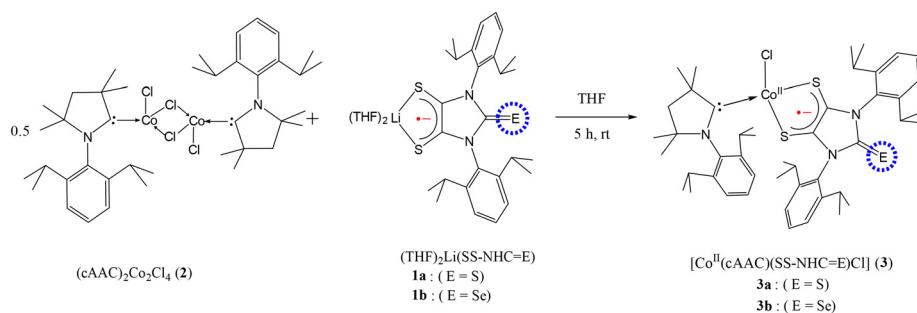
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stable dithiolene radical anion $[(\text{THF})_2\text{Li}(\text{SS-NHC}=\text{S}^{\cdot-})]$ is a highly air-sensitive, dark purple crystalline solid.¹² It was reacted with $\text{BBr}_3/\text{C}_2\text{B}_2\text{Cl}$ and AlI_3 to produce $\text{Br}_2/\text{C}_2\text{B}_2$ ($\text{SS-NHC}=\text{S}^{\cdot-}$) and $\text{Al}(\text{SS-NHC}=\text{S}^{\cdot-})_3$ compounds.¹³ The C_2B_2 ($\text{SS-NHC}=\text{S}^{\cdot-}$) is a mono-radical species with an $S = \frac{1}{2}$ spin state, while triradical $\text{Al}(\text{SS-NHC}=\text{S}^{\cdot-})_3$ is an antiferromagnetically coupled genuine triplet species at low temperatures ($S = 1$). At higher temperatures, the quartet state ($S = 3/2$) was populated, as concluded from temperature-dependent magnetic susceptibility measurements.^{13b} The $\text{Mg}(\text{II})$ centre was coordinated to the dithiolene anion, leading to the isolation of an octahedral $\text{Mg}(\text{II})$ -radical complex $[(\text{THF})_4\text{Mg}(\text{SS-NHC}=\text{S})]^{+}$. However, the redox-active dithiolene radical anion (with C–C 1.40 Å)¹⁵ is unable to keep its radical character when reacted with $\text{Si}(\text{II})/\text{Ge}(\text{II})$ precursors, instead converting to a dianionic state (C–C 1.35 Å) eventually forming hyper-coordinated $\text{Si}(\text{IV})/\text{Ge}(\text{IV})$ compounds.^{16,17}

In the past, cyclic alkyl(amino) carbene (cAAC) has been shown to stabilize unusual molecular fragments, as well as mono-, di-, and tri-atomic elements, unstable radicals, and radical ions through their σ -donation and π -backacceptance properties.^{18a,b} There is no report of a stable metal-dithiolene-radical complex containing a carbene to date.^{18c} Here, we

present a synthetic strategy for stabilization of the dithiolene radical anion by coordinating it with the $[(\text{cAAC})\text{Co}(\text{II})\text{Cl}]^+$ unit. The isolated air-stable and antiferromagnetically coupled cAAC- $\text{Co}(\text{II})$ (Cl)-dithiolene-radical complex was characterized using various analytical techniques. Additionally, the stability, bonding, and electron density distribution of this complex were examined through theoretical calculations.

A 2:1 mixture of dithiolene radical anion $[(\text{THF})_2\text{Li}(\text{SS-NHC}=\text{E})]$ ($\text{E} = \text{S}$, **1a**¹² and Se , **1b**) and $(\text{cAAC})_2\text{Co}_2\text{Cl}_4$ (**2**)^{19a} was reacted in THF for 5 hours, resulting in a dark royal blue solution of $[\text{Co}^{\text{II}}(\text{cAAC})(\text{SS-NHC}=\text{E})\text{Cl}]$ ($\text{E} = \text{S}$, **3a** and Se , **3b**), which was then evaporated, and the dry mass was extracted with *n*-hexane (Scheme 1). Dark blue plates/needles (**3a**) or blocks (**3b**) of complex **3a–3b** (Fig. 1) were isolated with a 50–56% yield from the concentrated *n*-hexane solution. Complex **3** was stable in the solid state under an inert atmosphere for at least three months. The royal blue-coloured THF solution of $\text{Co}(\text{II})$ -radical complex **3a** exhibits two strong UV-vis bands at 350 ($1.559 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 598 nm ($1.67 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$), with a broad feature at 552 nm. The band at 552 nm is nearly identical to one of the bands of the dark purple-coloured dithiolene radical anion $[(\text{THF})_2\text{Li}(\text{SS-NHC}=\text{S})]$ (**1a**) at 554 nm, while the band at 598 nm is red-



Scheme 1 Synthesis of stable $\text{Co}(\text{II})$ -radical complex $[\text{Co}^{\text{II}}(\text{cAAC})(\text{SS-NHC}=\text{E})\text{Cl}]$ ($\text{E} = \text{S}$, **3a** and Se , **3b**).

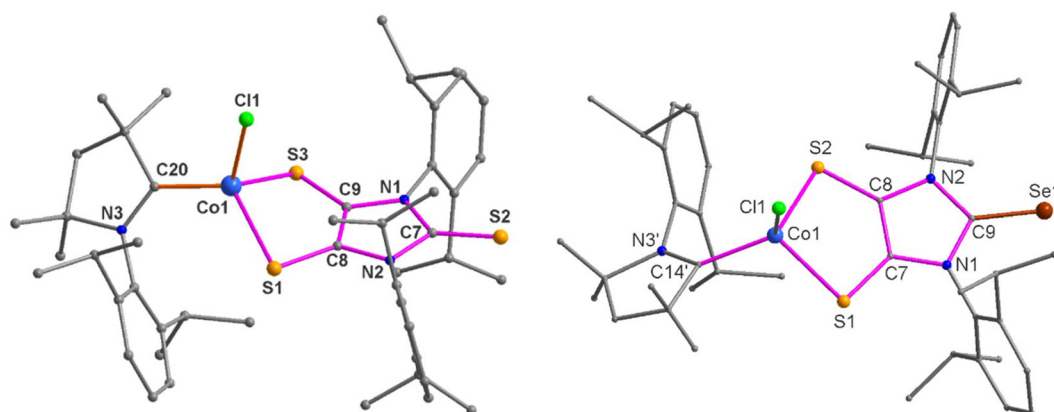


Fig. 1 Molecular structure of complex $[\text{Co}^{\text{II}}(\text{cAAC})(\text{SS-NHC}=\text{E})\text{Cl}]$ [$\text{E} = \text{S}$ (**3a**), left; Se (**3b**), right]. H-atoms are omitted for clarity. Selected bond lengths (Å), and angles ($^\circ$), **3a**: Co1–S1 2.3148(7), Co1–S3 2.3183(7), Co1–C20 2.003(2), Co1–Cl1 2.1909(7), C8–C9 1.414(3), C20–N3 1.307(3), S3–C9 1.682(2), S1–C8 1.675(2), C7–S2 1.644(2); C20–Co1–S1 120.24(7), S1–Co1–S3 94.28(2), S3–Co1–C20 108.42(6), C20–Co1–Cl1 115.51(7), S1–Co1–Cl1 107.67(3), S3–Co1–Cl1 108.19(3), see ESI† for bond parameters of **3b** ($\text{E} = \text{Se}$).

shifted compared to the corresponding band of $[(\text{THF})_2\text{Li}(\text{SS-NHC}=\text{S})]$ (579 nm). It is noteworthy that the precursor $(\text{cAAC})_2\text{Co}_2\text{Cl}_4$ (**2**) was reported to show a strong band at 653 nm, along with a lower intensity band at 576 nm.^{21a-d} The dark blue THF solution of complex **3a** retains its colour for approximately 12–14 hours in air before completely turning colourless after 16 hours. UV-vis measurements indicate that **3a** takes 9 hours to lose 50% of its intensity in solution (Fig. 2). See ESI† for detailed synthesis and characterizations of **3b**.

The strong band at 598 nm gradually decreases over time, while the band at 350 nm increases, accompanied by the appearance of a shoulder at 428 nm when the blue-coloured THF solution of complex **3a** is exposed to air. In comparison, $[(\text{THF})_2\text{Li}(\text{SS-NHC}=\text{S})]$ (**1**) loses its purple colour within 30 seconds in air, resulting in a brown solution. Dark blue

needles of complex **3a** remain stable in air at room temperature for over a week.

The Raman spectra of complexes **3a–3b**, $[\text{Co}(\text{II})(\text{cAAC})(\text{SS-NHC}=\text{E})\text{Cl}]$, display several diagnostic vibrational features corresponding to metal–ligand and ligand-based modes (Fig. 3; see ESI† for analysis of **3b**). Single crystals were utilized for satisfactory, less noisy Raman bands of both the complexes. Raman spectra of dithiolene radical anion (**1a**) have been placed in the ESI (Fig. S54†).

A weak band observed at 97 cm^{-1} , along with additional bands at 205 cm^{-1} and 256 cm^{-1} (weak and medium, respectively), is attributed to Co–Cl stretching vibrations, consistent with related cobalt halide systems.^{24a} A weak shoulder at 293 cm^{-1} is assigned to the Co–S stretching mode, aligning well with previously reported values around $288\text{--}297\text{ cm}^{-1}$.^{24b,c} The medium-intensity band at 389 cm^{-1} is ascribed to S–C–C bending, comparable to the reported 364 cm^{-1} , with the frequency shift likely reflecting the modified coordination environment.^{24a–c} A C–S stretching vibration is observed at 560 cm^{-1} (medium), falling within the expected $570\text{--}750\text{ cm}^{-1}$ range. Ligand-based modes include a weak C–H deformation band at 1152 cm^{-1} , closely matching reported values ($1151\text{--}1163\text{ cm}^{-1}$), and a very strong phenyl ring C–C stretching vibration at 1271 cm^{-1} , consistent with the expected $1280\text{--}1292\text{ cm}^{-1}$ region.^{24a–c} Imidazole ring C–N stretching bands appear as weak features at 1324 , 1352 , and 1377 cm^{-1} , within the reported ranges of $1320\text{--}1328$, $1341\text{--}1348$, and $1387\text{--}1391\text{ cm}^{-1}$, respectively. Finally, a weak band at 1540 cm^{-1} is attributed to the C=C stretching vibration of the imidazole ring, consistent with the $1532\text{--}1540\text{ cm}^{-1}$ range (Fig. 3).^{24d} Thermo-gravimetric analysis (TGA) of complex **3b** showed that it remains stable in air up to $\sim 200^\circ\text{C}$ for nearly nine minutes (see Fig. S17 and S18, ESI†), after which it undergoes decomposition. Complex **3a** is stable for at least 1.5 h at 120°C when it was heated under an argon atmosphere (see ESI†).

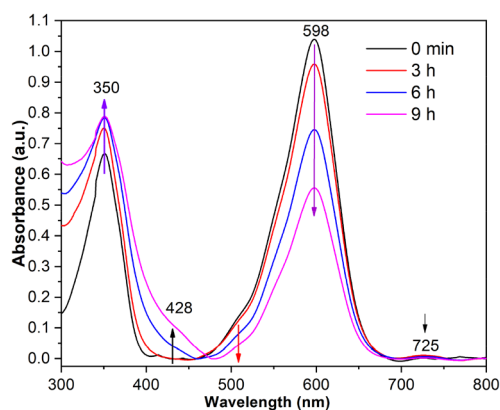


Fig. 2 Time-dependent UV-vis spectra of **3** in THF at the indicated time interval.

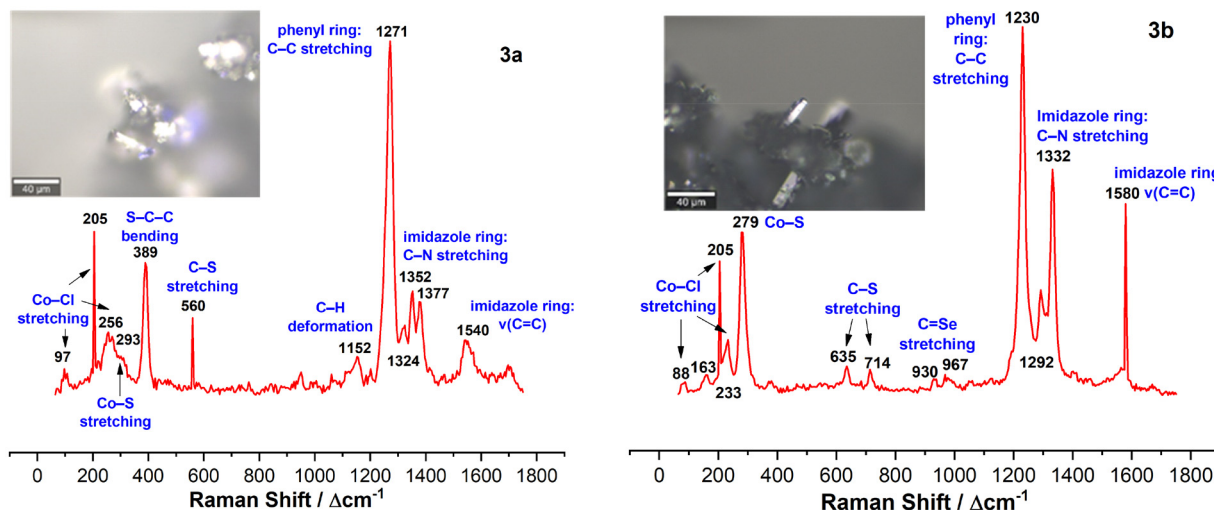


Fig. 3 Solid-state Raman spectra of complexes **3a** (left) and **3b** (right) measured in the alpha300 R Raman Microscope using a 532 nm laser focussing on single crystals (inset).

Complex $[\text{Co}^{\text{II}}(\text{cAAC})(\text{SS-NHC}=\text{S})\text{Cl}]$ (**3a**) crystallizes either in the triclinic $P\bar{1}$ or in orthorhombic $Pbca$ space group as dark plates and needles from *n*-hexane solution, respectively, suggesting polymorphism of **3a**. The bond parameters are slightly different (see ESI†). Complexes **3a** ($\text{E} = \text{S}$) and **3b** ($\text{E} = \text{Se}$) are isostructural (Fig. 1), and only the structural aspects of **3a** will be discussed here in detail. Single-crystal X-ray structure analysis revealed that the complex contains one $\text{Co}(\text{II})$ ion in a pseudo-tetrahedral coordination geometry ($\tau_4 = 0.88$), one dithiolene mono-radical anion ($\text{SS-NHC}=\text{S}^{\cdot-}$), one chloride ion, and one cAAC ligand (Fig. 1). The central $\text{Co}(\text{II})$ ion adopts a distorted tetrahedral geometry with a CS_2Cl donor set. The Co-S distances [2.3148(7), 2.3183(7) Å] are longer than the Co-Cl bond [2.1909(7) Å], but are closer to the previously reported $\text{Co}(\text{II})-\text{S}_{\text{Ph}}$ bond distances.^{19b} The $\text{Co}(\text{II})-\text{C}_{\text{cAAC}}$ bond length (2.003(2) Å) is also very similar to that of its precursor (**2**).^{19a} The S-Co-S chelation angle (94.28(2)°) is more acute than the other two $\text{S-Co-C}_{\text{cAAC}}$ angles (108.42(6), 115.51(7)°). The $\text{C-S}_{\text{SS-NHC}=\text{S}}$ distances [1.682(2), 1.675(2) Å] of the dithiolene radical anion ligand $\text{SS-NHC}=\text{S}^{\cdot-}$ in **3a** are very similar to the corresponding C-S bond lengths of 1.678(4), and 1.687(4) Å for $[\text{Mg}^{\text{II}}(\text{SS-NHC}=\text{S})(\text{THF})_4]^+ \cdot$, and 1.680(3) and 1.694(3) Å for $[(\text{Cy})_2\text{B}(\text{SS-NHC}=\text{S})]^{\cdot+}$.¹³ The $\text{C-C}_{\text{SS-NHC}=\text{S}}$ bond distance in **3a** is 1.414(3) Å, which is very similar to that of the precursor ($\text{SS-NHC}=\text{S}^{\cdot-}$ ligand).^{12–14} Thus, the central cobalt ion is bonded to one neutral cAAC ligand, one monoanionic ligand $\text{SS-NHC}=\text{S}^{\cdot-}$, and a chloride anion (Cl^-), suggesting the oxidation state of cobalt is +2 for charge neutrality.

Direct Current (DC) magnetic susceptibility measurements of plates (space group $P\bar{1}$) of complex **3a** showed a transition between $S = 1$ and $S = 2$ spin states [$S = |3/2 - 1/2|$ to $|3/2 + 1/2|$; high-spin $\text{Co}(\text{II})$, spin-half radical ligand] occurring at $H \sim 3$ T (Fig. 4). A similar situation ($S = 1/2 \leftrightarrow 3/2$) was proposed for the previously reported $\text{Al}(\text{SS-NHC}=\text{S})_3$ complex, based on

temperature-dependent magnetic susceptibility and EPR measurements.^{13b} An interesting feature in the magnetic field scans of complex **3a** was observed, particularly at very low temperatures, where a slight local maximum appeared at around 3 T. The inset in Fig. 4 shows the difference curves between the measured magnetic field scans and a linear curve (m_{linear}), which extends from the origin (0,0) to the maximum value at 7 T (determined for each temperature). The difference curves highlight the presence of local maxima in the field scan data. This feature is also reproduced by the simulated magnetization vs. field curves of the applied **model J1EX** (see black line for 2 K in Fig. 4). The model's Zeeman diagram (Fig. S8†) shows that, with increasing magnetic field, the antiferromagnetic coupling is more easily overcome, as the energy levels of the first excited state approach those of the ground state (with a crossing slightly above 6 T).^{22a–b} As a result, with increasing magnetic field, the excitation energy to the first excited state decreases, and the transition to this excited state is reflected in the local maxima observed in the magnetic field scan curves. The magnetic properties of the cobalt-dithiolene complex have also been found to be unusual in the past.^{22c}

A previously reported octahedral $[\text{Co}(\text{II})(\text{tpyphNO})_2](\text{CF}_3\text{SO}_3)_2$, containing two antiferromagnetically coupled radical ligands, exhibited a high-spin $\text{Co}(\text{II})$ to low-spin $\text{Co}(\text{II})$ spin crossover transition around 140 K [$2J_{\text{Co-rad}}/k_{\text{B}} = -3.63(12)$ K, $g_{\text{avg}} = 2.352(9)$] via spin-orbit coupling (SOC).⁶ The radical centres of this complex are distant from the $\text{Co}(\text{II})$ centre, with coupling occurring only through space.⁶ An octahedral high-spin $\text{Co}(\text{II})$ complex has been shown to exhibit dominant ferromagnetic coupling with a semiquinonate ligand, although the shape of the χT vs. T plot did not indicate this, due to the influence of other parameters of the $\text{Co}(\text{II})$ centre.²³ A redox active, air stable tetrahedral high-spin $\text{Co}(\text{II})$ complex, containing two chelating *o*-iminobenzosemiquinonate radicals, was shown to exhibit dominant antiferromagnetic coupling, leading to an $S = \frac{1}{2}$ spin ground state.⁵ Several high-spin octahedral $\text{Co}(\text{II})$ complexes, each containing two air-stable nitronyl nitroxide radicals, have been reported to exhibit dominant antiferromagnetic coupling with the central $\text{Co}(\text{II})$ ion [$J_{\text{Co-rad}} = -152, -133 \text{ cm}^{-1}$].¹⁰ A tri-anionic $\text{Co}(\text{II})$ complex, containing two high-spin tetrahedral $\text{Co}(\text{II})$ ions bridged by a trianionic-radical ligand, was found to exhibit very strong ferromagnetic coupling with the radical [$J_{\text{Co-rad}} = 440(40) \text{ cm}^{-1}$, $D_{\text{Co}} = -115(15) \text{ cm}^{-1}$, $g_{\text{Co},\parallel} = 2.85(3)$, $g_{\text{Co},\perp} = 2.09(7)$].⁴ A tetrahedral high-spin $\text{Co}(\text{II})$ complex, $[\text{Co}(\text{II})(\alpha\text{-imino-pyridine}^{\cdot-})_2]$, containing two chelating radical anionic ligands, was reported to have an $S = 1/2$ spin ground state with a metal-radical coupling constant of $J_{\text{Co-rad}} = -694 \text{ cm}^{-1}$.⁹

It is quite challenging to model $\text{Co}(\text{II})$ -radical complexes since it is hard to locate the spin densities.^{4–10,23} Strong antiferromagnetic coupling ($J_{\text{Co-rad}} = -533.62 \text{ cm}^{-1}$ with $D = +21.31 \text{ cm}^{-1}$) between the high-spin $\text{Co}(\text{II})$ ion ($S = 3/2$) and the unpaired electron with on $\text{SS-NHC}=\text{S}$ in **3a** inferred from high-level *ab initio* calculations (Tables S7–S18 and Fig. S23–S25†).

The X-band EPR spectrum^{20,23} of complex **3a**, recorded in a THF solution at 77 K, shows broad lines at $g_{\text{isor}} = 2.006731$

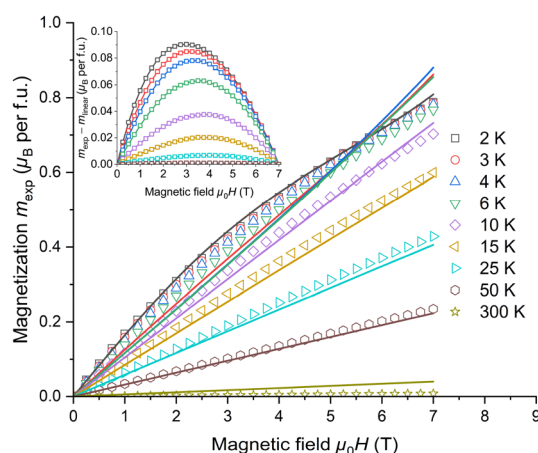


Fig. 4 M vs. H plots of complex **3** at different temperatures. The open symbols represent the experimentally measured values, and the solid lines represent the best fits according to the quantum mechanical **model J1EX**. The inset shows the difference curves between the experimentally measured field scans with linear approximation as outlined in the main text.

(Fig. S16†). The well-resolved hyperfine lines of parent radical¹² (SS-NHC=S)^{•−} have been affected in complex **3a** due to electronic interaction with the Co(II) ion ($I = 7/2$).⁹ The EPR spectra of solid samples of complex **3a**, recorded at room temperature and frozen at 77 K (Fig. S14 and S15; see ESI†), showed multiple EPR lines at $g = 2.0078$. This was due to the interaction between the high-spin Co(II) ion ($S = 3/2$; $I = 7/2$),²³ and radical anion (SS-NHC=S)^{•−} ($S = 1/2$; two ^{14}N , $I = 1$) (Fig. 5). EPR simulations for other possibilities were shown in Fig. S11, ESI.†^{11c} A Broadening of the EPR signal was observed at 77 K, which may be due to spin coupling. Rhombic EPR spectrum was obtained for **3b** (Fig. S51 and S52†). Complex **3a** does not exhibit any slow relaxation of magnetization, even at 2 K under various applied DC fields (Fig. S10†). The spin configuration

of Co(II) was computed to be $S = 3/2$, as concluded from *ab initio* and CASSCF calculations (Tables S11–S17†).

We optimized the Co(II)-radical complex **3a** replacing the Dip (2,6-diisopropylphenyl)-groups with Me-groups, as **3a'** and it's equally stable in both triplet and quintet electronic states ($S_{\text{total}} = 1$ and 2) at B3LYP-D3(BJ)/Def2-TZ2P level of theory (see ESI, Fig. S19†) since $S_{\text{Co(II)}} = 3/2$ due to high-spin Co(II) ion of **3a'** is interacting with the $S_{\text{radical}} = 1/2$ radical electron of (SS-NHC=S)^{•−} to produce two possible spin states $S_{\text{total}} = 1$ and 2. The Mulliken spin densities favour the presence of three unpaired electrons distributed mainly over the Co(II)-centre and one electron on the radical (SS-NHC=S)^{•−} fragment (Fig. 4 and Fig. S19;† $S_{\text{total}} = 1, 2$).

The energy decomposition analyses coupled with natural orbital for chemical valence (EDA-NOCV) (Fig. 6 and Table S6†) were performed to study bonding interactions between them to rationalize the unusual stability of dark needles of **3** in the open air by making the fragment (cAAC) (Cl)Co⁺ and (SS-NHC=S)^{•−} in quartet and doublet electronic state, respectively. The ΔE_{int} gives the total interaction strength for two Co–S bonds, which is $-176.1 \text{ kcal mol}^{-1}$ ($S_{\text{total}} = 2$). The ΔE_{elstat} has the highest contribution in bond formation, at 61.2%, while the covalent character (ΔE_{orb}) is 35.4% of the total attraction energy. The NOCV method gives the pairwise interaction to this covalent character. The (SS-NHC=S)^{•−} fragment is donating from its filled orbitals HOMO–1 and HOMO

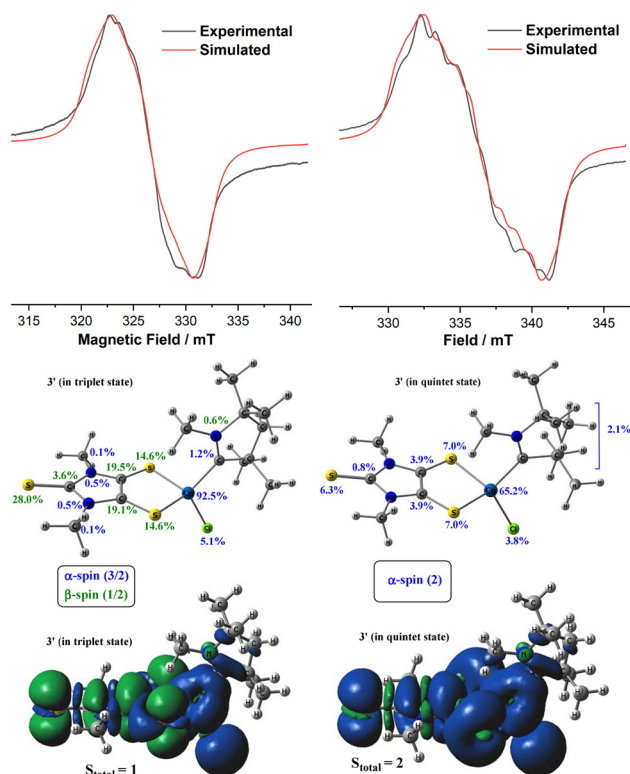


Fig. 5 X-Band solid-state EPR spectrum (black) of complex [(cAAC)Co(II)Cl(SS-NHC-S)] (**3a**) at rt (left). Red and black lines represent the simulated and the experimental (top, left, 77 K and top, right, rt) spectra of **3a** using the EasySpin program. For left-side: [$g_x = 2.02781$, $g_y = 2.00622$, $g_z = 1.98941$, LWPP (Gaussian broadening) = 0.0362627 mT, LWPP (Lorentzian broadening) = 1.14499 mT, $A_x(^{59}\text{Co}) = 23.1943 \text{ MHz}$, $A_y(^{59}\text{Co}) = 27.3576 \text{ MHz}$, $A_z(^{59}\text{Co}) = 21.5656 \text{ MHz}$, $g_{\text{isor}} = 2.0078748$; X-band experimental frequency = 9.177528 GHz]. For right-side: [$g_x = 2.02732$, $g_y = 2.00663$, $g_z = 1.99043$, LWPP (Gaussian broadening) = 0.026615 mT, LWPP (Lorentzian broadening) = 0.809999 mT, $A_x(^{59}\text{Co}) = 21.5404 \text{ MHz}$, $A_y(^{59}\text{Co}) = 29.3571 \text{ MHz}$, $A_z(^{59}\text{Co}) = 20.2722 \text{ MHz}$, $g_{\text{isor}} = 2.0081834$; X-band experimental frequency = 9.452804 GHz]. The spin density percentages (%) (up) and spin density plots (down) for complex **3'** in its triplet (left) as well as quintet (right) electronic state at B3LYP-D3(BJ)/Def2TZVPP level of theory. The blue and green colour represents the α - and β -spin, respectively.

Complex 3a' ($S_{\text{total}} = 2$)	(SS-NHC=S) (D)	CoCl(cAAC) ⁺ (Q)
(a) $\Delta\rho_{(1)}$ $\Delta E_{\text{orb}(1)} = -48.7$; $ v = 0.25/0.78$	(a') HOMO-1 ($\epsilon = -2.23 \text{ eV}$)	(a'') SOMO ($\epsilon = -9.68 \text{ eV}$)
(b) $\Delta\rho_{(2)}$ $\Delta E_{\text{orb}(2)} = -27.3$; $ v = 0.15/0.46$	(b') HOMO ($\epsilon = -1.78 \text{ eV}$)	(b'') SOMO-1 ($\epsilon = -10.36 \text{ eV}$)
(c) $\Delta\rho_{(3)}$ $\Delta E_{\text{orb}(3)} = -5.2$; $ v = 0.18$	(c') HOMO-3 ($\epsilon = -2.81 \text{ eV}$)	(c'') SOMO ($\epsilon = -9.68 \text{ eV}$)

Fig. 6 The shape of the deformation densities $\Delta\rho_{(3)-(4)}$ that correspond to $\Delta E_{\text{orb}(3)-(4)}$ for complex **3a'** in quintet electronic state ($S_{\text{total}} = 2$), and the associated molecular orbitals of (CAAC)(Cl)Co⁺ and (SS-NHC=S)^{•−} in quartet and doublet electronic state at the B3LYP-D3(BJ)/TZ2P level of theory. The isosurface value is 0.001 au for $\Delta\rho_{(1-2)}$ and 0.0002 for $\Delta\rho_{(3)}$. The eigenvalues $|\nu_n|$ give the size of the charge migration in e. The charge flow direction of the deformation densities is from red $\rightarrow$ blue.

to the SOMO and SOMO-1 of (cAAC)(Cl)Co⁺ fragment with 46.2% and 26.0% contribution to the total orbital interaction, respectively (Fig. 6a and b). The third interaction [$\Delta\rho_{(3)}$] is taking place between HOMO-3 of (SS-NHC=S)⁻ fragment and SOMO of (cAAC)(Cl)Co⁺ fragment, with a slight involvement of SOMO of (SS-NHC=S)⁻ fragment. This interaction contributes only 5% to the total orbital interaction, stating the weakness of the interaction (Fig. 6c). The contribution due to favourable dispersion energy is nearly 3.4%. The charge migration from one fragment to the other fragment [(SS-NHC=S)⁻ → [Co(II)(cAAC)Cl]⁺] was shown in deformation densities (red-blue). All three deformation densities showed charge migration from anionic dithiolene radical to cationic cAAC-Co(II)Cl unit. Finally, a significant amount of charge accumulation was observed between Co(II)-carbene. It is worth mentioning that our detailed bonding analyses employing the EDA-NOCV method have rationalized the stability of complex **3a** in the open air when it is compared to that of the precursor [(THF)₂Li(SS-NHC=S)] (**1a**) (Fig. 6 and Fig. S20†).¹²

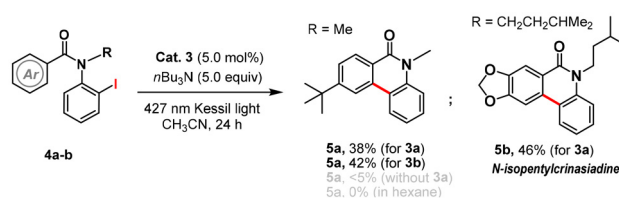
The redox properties of dithiolene radical anion (**1a**) have been previously reported to possess two separate electron transfer processes under electrochemical conditions.^{14,15} CV of complexes **3a–3b** has been studied in THF solution in the presence of an electrolyte. Complexes **3a–3b** were found to be redox active,⁵ displaying one quasi-reversible process at $E_{1/2}$ = -0.50 V, suggesting the formation of **3⁺** above -0.50 V (Fig. 7).

The species (THF)₂Li⁺(SS-NHC=S)⁻ exhibits two electrochemical quasi-reversible reduction processes^{14,15} at -1.47 V and -0.78 V, which were previously assigned to (SS-NHC=S)²⁻ → (SS-NHC=S)⁻ and (SS-NHC=S)⁻ → (SS-NHC=S)⁰,¹⁵ respectively. The energy of SOMO of in (SS-NHC=S)⁻ is significantly higher than that of the [Co(II)(cAAC)Cl]⁺ fragment (Fig. 6(b') and (a'')). As a result, the loss of one electron from (SS-NHC=S)⁻ unit above -0.50 V is more likely to originate from (SS-NHC=S)⁻, leading to the formation of **3⁺** as shown in the bottom right Fig. 7. The reduction from mono-anion (SS-NHC=S)⁻ to the dianion (SS-NHC=S)²⁻ in **3a–3b** was

observed near $E_{1/2}$ = -0.80 V (Fig. 7).^{14a,b} **3a** was reacted with NO⁺BF₄⁻ in THF, which led to the isolation of previously reported ligand oxidized dimeric product (SS-NHC=S)₂.^{12–16}

The dark colored complexes **3a/3b** absorb in the UV-VIS region (strong bands at 300–450/300–400 nm and 490–690/530–830 nm). The characteristic outlined in the previous section (Fig. 2 and 7) suggests that this class of photo-redox active complexes could act as photocatalysts in organic synthesis. To confirm the photocatalytic activity, we carried out a dehalogenative cyclization reaction to produce biologically significant phenanthridinones (Scheme 2). The reaction mechanism is given in ESI (Scheme S1†).^{25b}

When 2-iodo-*N*-methylbenzamide **4a** was treated with complex **3a/3b** (5.0 mol%) in the presence of *n*Bu₃N and irradiated with 427 nm Kessil light in CH₃CN solvent, the desired cyclization product **5a** was obtained in moderate yield (Scheme 2). Interestingly, when the reaction was performed with amide **4b**, the tetracyclic compound **5b** was obtained in synthetically useful yield (Scheme 2). Notably, the product **5b** is a renowned alkaloid natural product (*N*-isopentylcrinasiadine), underscoring the synthetic utility of this class of products.²⁵ It is important to note that the product formation was negligible in the absence of photocatalyst **3a**. No photo-chemical reaction product (**5**) was obtained when the reaction was carried out in *n*-hexane.



Scheme 2 Photocatalysis activity of **3a** towards the synthesis of phenanthridines.

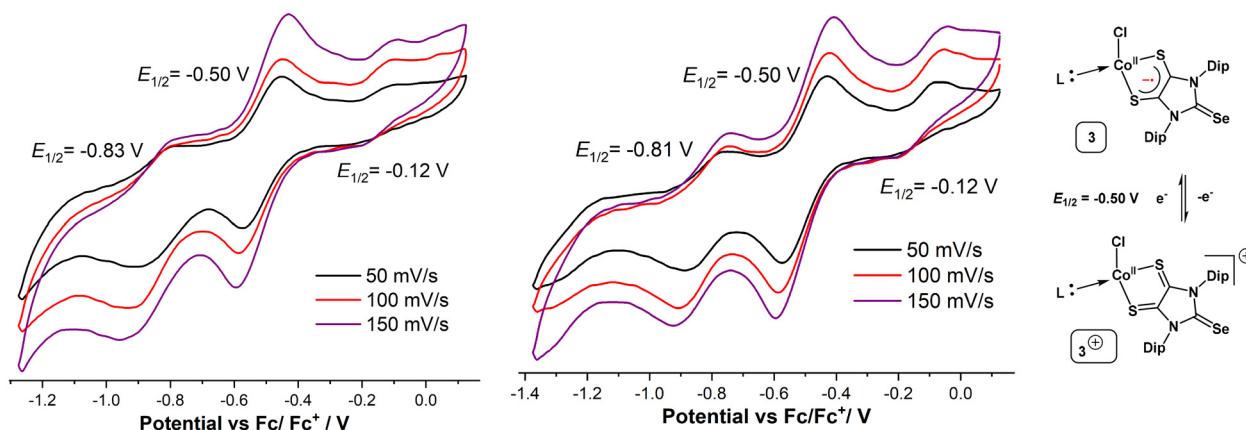


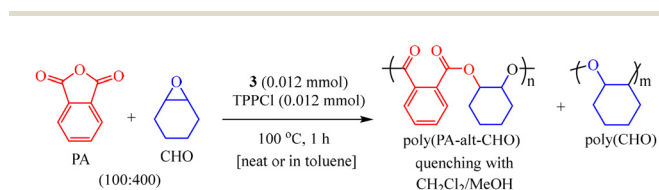
Fig. 7 The cyclic voltammograms of complexes **3a** (left) and **3b** (right) in THF containing 0.1 M [*n*-Bu₄N][PF₆] as the electrolyte at scan rates of 50/100/150 mV s⁻¹. Reduction (left) and oxidation (right). Glassy carbon as WE (working electrode), platinum wire as CE (counter electrode), and Ag wire as RE (reference electrode). L = cAAC.

The Co(II)-radical complex (**3a**) was subsequently used as a catalyst for the ROP (ring-opening polymerization) of *rac*-LA (LA = lactide) and ROCOP (ring-opening copolymerization) of CHO (cyclohexene oxide) with PA (phthalic anhydride) (Scheme 3). However, **3** was found to be sluggish for the ROP of *rac*-LA with only 29% conversion into toluene at 100 °C (Fig. S30†). This could be attributed to the unfavorable coordination of the lactide monomer to the Co(II) center due to the narrow bond angle. We are unable to explore the catalytic activity of short-lived cationic intermediate species (**3**⁺). There is no report of a stable cobalt-radical complex showing photocatalytic^{25b} ring cyclization reaction to date.^{5–11}

The results of the ROCOP are summarized in Table S19.† It was observed that without any cocatalyst, the copolymerization reactions led to substantial PA conversion with less than 50% ester linkage (Table S19,† entry 1), with CHO mainly forming the homopolymer poly(cyclohexene oxide) (PCHO). This demonstrated that the ROCOP of CHO with PA is not viable without a cocatalyst. Subsequently, we conducted a screening of ROCOP reactions with **3a** and various cocatalysts, including PPNCI [bis(triphenylphosphine) iminium chloride], TPPCI (tetraphenylphosphonium chloride), and TBAB (tetrabutylammonium bromide). It was noted that PA conversion was the lowest (16%) when TBAB was employed as a cocatalyst (Table S19,† entry 3). This is due to Br[−], being a larger nucleophile, not readily reacting with CHO (in comparison to Cl[−]) or coordinating effectively with the Co(II) center. Both PA conversion and selectivity were higher when TPPCI was utilized as the cocatalyst. This is because TPPCI can more readily release the Cl[−] ion compared to PPNCI, as TPPCI benefits from better charge delocalization onto the phenyl groups, while PPNCI's electron-withdrawing nitrogen reduces cation stability.^{26,27} Thus, TPPCI emerged as the most effective cocatalyst among those screened, achieving nearly complete PA conversion (>99%) and a remarkably striking ester linkage (Table S19,† entry 4) with just 0.012 mmol of catalyst loading. The catalytic performance of this pair was also promising, exhibiting TOF of 100 and 99 h^{−1} under neat conditions and in toluene, respectively. The **3a** catalyzed polymerization reaction was found to be completed within 1 h. The polymerization reaction exhibited good control (PDI = 1.10) in toluene, yielding a high *M_n* (Table S19,† entry 5). This is likely due to the reduction in chain transfer reactions in toluene compared to the neat condition. The diacids produced by the hydrolysis of anhydrides act as chain transfer agents. The occurrence of chain transfer to the ROCOP of epoxide and anhydride has been previously

reported in the literature.²⁸ The chain transfer reactions in the ROCOP of epoxide and anhydrides may also be induced by the zwitterionic form of the cocatalyst or the anhydride.²⁹ Therefore, it is extremely difficult to eliminate the possibility of chain transfer reactions, even after removing trace amounts of diacid and water. To investigate the effect of temperature on the polymerization, we conducted the reaction at a lower temperature of 80 °C. By lowering the temperature, the PA conversion, selectivity (ester linkage), and molecular mass of the polymer decreased significantly with an increase in the PDI value (Table S19,† entry 6), and the reaction took a longer time, which further diminished the turnover frequency (TOF). We also performed the ROCOP reaction using TPPCI alone at 100 °C in toluene and found the TOF to be significantly lower compared to when the cocatalyst was used in combination with the catalyst. The molecular mass of the polymers decreases drastically through the monomer conversion, and ester linkages were almost comparable (Table S19,† entry 7) with those where the cocatalyst and catalyst were both used together.

The ¹H NMR analysis of the isolated pure polymers revealed nearly exclusive polyester linkages (>99%) with chemical shifts (δ) between 5.05 and 5.20 ppm, and no signal corresponding to polyether linkages (δ = 3.2 – 3.8 ppm) was detected (Fig. S38†). The GPC traces of the polymers were unimodal, with narrow dispersity values (Fig. S40–S42†). Catalytic polymerization reaction of **3a** is much better than that of **3b** (see ESI†). In the proposed mechanism, the epoxide is coordinated to the metal center, and the external nucleophile Cl[−], originating from the cocatalyst TPPCI, initiates the ring-opening to form a metal-alkoxide intermediate. The proposed mechanism is outlined in Fig. 8. Since the Co–Cl bond length



Scheme 3 Synthesis of poly(PA-*alt*-CHO) catalyzed by **3** and co-catalyzed by TPPCI.

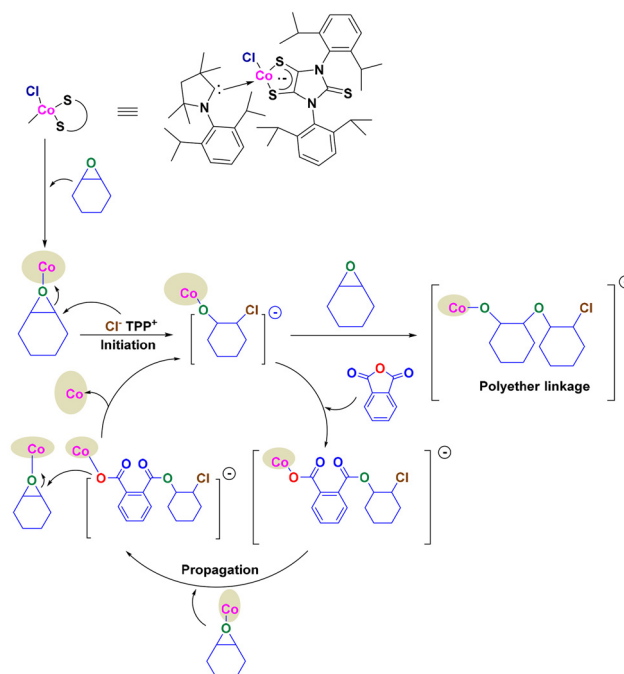


Fig. 8 Proposed mechanism for ROCOP of CHO with PA.

in **3** is slightly lower (2.19 Å) than the conventional Co–Cl bond length, the dissociation of this bond is somewhat difficult, which prevents the Cl[−] attached to Co from initiating the copolymerization reaction. This metal-alkoxide intermediate then undergoes an insertion reaction with the anhydride, leading to the formation of a metal-carboxylate intermediate. The process involves the alternating incorporation of epoxide and anhydride, resulting in the production of the linear polyester chain. Such a type of copolymerization mechanism catalyzed by a metal complex with a cocatalyst was reported previously and optimized through computational studies.^{31,32} EPR spectroscopy is sensitive to the coordination geometry and distribution of spin densities around a metal centre.^{3f} Thus, this co-polymerization reaction has been studied with X-band EPR spectroscopy (Fig. 9) at rt. A comparison between two EPR spectra (Fig. 5 vs. Fig. 9) suggests that the Co-centre of **3a** participates in the binding of epoxide (CHO).²³ A very similar EPR spectrum was reported for five coordinate Co-radical species was previously reported [$A(^{59}\text{Co}) = 20\text{--}26\text{ MHz}$].^{3g} The same co-polymerization reaction was carried out at identical conditions with $[(\text{THF})_2\text{Li}(\text{SS-NHC}=\text{S})]$ ($\text{E} = \text{S}$, **1a**)¹² as a catalyst. The results show that the reaction time is three times higher than that of **3a** with much lower molecular weight of the polymer products (see ESI†).

The DSC trace of the polyester synthesized through the ROCOP of PA and CHO using **3** revealed a glass-transition temperature (T_g) of 94.6 °C, which is by the literature-reported value³⁰ (Fig. S43†). The decomposition temperature found from the TGA trace was 339.75 °C, and the decomposition was completed at 359 °C (Fig. S44†). The catalytic co-polymeriz-

ation reaction (Scheme 3) is expected to be non-redox active (Fig. 8), rather Co(III)-centre is proposed to facilitate the polymerization reaction^{29,32} and hence the role of **3**⁺ in such catalytic reaction was not studied. This is probably the first report of Co(II)-catalyzed ring-opening copolymerization of phthalic anhydride and cyclohexene oxide.^{29–32}

Conclusions

To summarize, we have successfully isolated an air-stable cyclic alkyl(amino) carbene coordinated Co(II)Cl-dithiolene-radical complex (**3**) featuring a tetrahedral Co(II) ion. The dark blue THF solution of **3** remains stable in air for several hours, while the dark blue crystalline needles are stable at least for a week when exposed to open air. Cyclic voltammetry (cv) measurement revealed that complex **3** can be oxidized to **3**⁺ cation at potentials above −0.61 V, while magnetic measurements indicated that the Co(II) ion in **3** is in high-spin state with $S = 3/2$ and is antiferromagnetically coupled to the unpaired π -electron of the dithiolene radical anion ($S = 1/2$). Magnetization *versus* field plots demonstrated that the spin ground state is $S = 1$, while its excited state $S = 2$ is populated at a field strength greater than 3 T.¹² We have carried out EDA–NOCV analysis of **3**. Our in-depth bonding analysis revealed that 35.4% of the overall stabilization originates from covalent interaction between the dithiolene radical anion and the Co(II) Cl(cAAC)⁺ fragments. A significant portion of the total covalent interaction energy comes from the delocalisation of radical electrons onto the Co(II)Cl(cAAC)⁺ fragments through two distinct sets of orbital interactions ($\Delta E_{\text{orb}(3-4)}$). In contrast, the precursor lithium salt of dithiolene radical anion (**1**) rapidly reacts with oxygen and moisture on exposure to open air, resulting in its decomposition and the loss of the radical character. Finally, we demonstrated that the photo-redox active Co(II)-radical complex (**3**) can catalyse photochemical organic transformations, leading to the synthesis of the well-known alkaloid natural product (*N*-isopentylcrinasiadine) (**5b**). Furthermore, we have shown that the Co(II) centre in **3**, which carries a radical-anion, remains active for catalytic copolymerization in the presence of a free chloride anion source. Two types of catalytic reactions, reported here, are unprecedented to the best of our knowledge.^{25–32}

Author contributions

K. C. M. provided the concept, and S. D. did the experimental work and characterization. S. M. and C. M. carried out CV measurements and synthesis of one of the precursors. A. A. R. carried out an EPR simulation. S. A. performed Raman measurements. S. S. carried out the theoretical calculation. B. S. investigated the magnetic properties. K. M. carried out the catalytic reactions and purification. R. K. R. carried out the polymerization reaction, K. C. M., M. B., D. C., and B. S. wrote the manuscript.

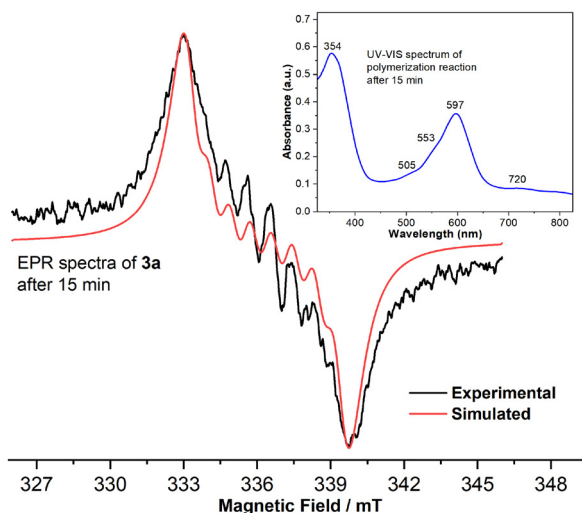


Fig. 9 X-Band EPR spectrum (black) of the polymerization reaction after 15 minutes at rt in THF. Red and black lines represent the simulated and experimental spectra, respectively, and the simulation was performed using the EasySpin program. [$g_{\text{iso}} = 2.00676$, LWPP (Gaussian broadening) = 0.092442 mT, LWPP (Lorentzian broadening) = 0.99954 mT, $A(^{59}\text{Co}) = 24.0456\text{ MHz}$, X-band experimental frequency = 9.447941 GHz]. UV-VIS spectrum of polymerization reaction after 15 min (inset).

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article (NMR, UV-vis, Raman, TGA, CV, EPR, crystallographic table, theoretical analysis and catalysis) have been included as part of the ESI†

CCDC 2374724 (**3a**; at 100 K), 2453737 (**3a**; 298 K), and 2450066 (**3b**; at 100 K) contain the supplementary crystallographic data for this paper.

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