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The serendipitous discovery of a readily available redox-bistable molecule derived from cyclic(alkyl)(amino)carbenes†

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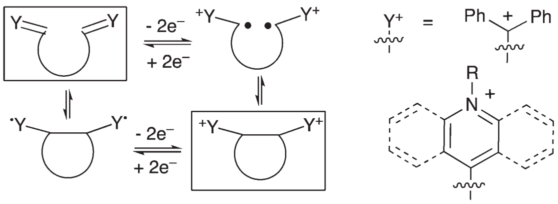
Bis(azoliums) are readily available in one step from cyclic (alkyl)(amino)carbenes and bis(acyl chlorides). A two-electron reduction of the bis(azolium), featuring a *gem*-(dimethyl)malonoyl spacer, leads to the corresponding transient diradical, which undergoes an intramolecular cyclization. The latter can be re-oxidized at a higher potential to yield back the bis(azolium). The redox bistability of this simple organic molecular system is linked to the formation of a weak C–O bond (27 kcal mol^{-1}). Both redox forms can be isolated and stored for months without evidence of decay.

Redox bistable molecules (RBMs) have two oxidation states that can co-exist within a certain range of electrochemical potentials. They are designed based on the so-called square scheme,[1] in which the reduction (or oxidation) of the molecule triggers a reversible chemical transformation such as a conformational change, isomerism, or intramolecular bond formation. RBMs have attracted considerable attention due to their potential applications in molecular electronics.[2] For example, bistability prevents entropy-driven mutual electron exchanges between neighbors and therefore is critical for redox-based data storage at a molecular scale.[3] Redox bistable molecules have also been used in the context of bottom-up approaches for the design of nano-sized devices.[4]

The vast majority of reported RBMs feature coordinated metals[5] and/or complex supramolecular structures, such as rotaxanes and catenanes.[6] In contrast, only a handful of simple organic patterns are known.[7] They generally[8,9] undergo a reversible intramolecular σ-bond formation upon electron transfer. The corresponding square scheme involves a diradical, which is formed upon a 2-electron oxidation of an activated diene (Scheme 1).

The coupling of the two radical units has to be exothermic enough to induce significant stability of the s-bond, but not too much in order to preserve the chemical reversibility of the process. A rough qualitative analysis of square schemes indicates that the corresponding bond dissociation energies should ideally be in the 10–40 kcal mol^{-1} range. Such low values are rarely encountered in standard organic species, which explains the scarcity of simple organic RBM representatives. Note that accessing such a non-standard σ-bond often requires a complex synthesis, which represents a serious drawback for further tuning and applications. Herein we report that the reversible formation of a carbon–oxygen σ-bond between two radical units led to the serendipitous discovery of readily available redox-bistable organic systems.

The combination of an electron-donating and an electron withdrawing substituent stabilizes C-centered radicals through capto-dative substitution,[10] but usually not to such an extent that allows for the isolation of monomeric species. For example, only the corresponding C–C homodimer could be isolated in the case of the 2-oxomorpholin-3-yl radical **A** (Scheme 2).[11,12] However, we recently demonstrated that



Scheme 1 Some organic patterns featuring redox bistability and the associated square scheme.

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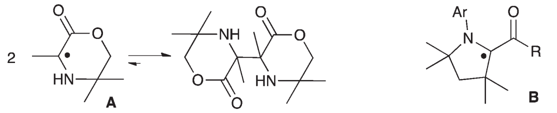
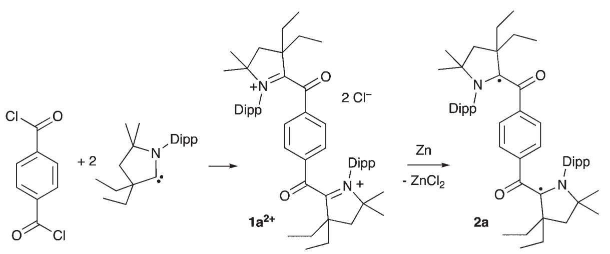
† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of all new compounds, X-ray crystallographic data, VT-EPR plots, electrochemical study of **1c**$^{2+}$ and computational details. CCDC 1825142, 1820818 and 1820817. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8qo00447a



Scheme 2 Dimerization of capto-dative radical **A** and isolated CAAC-based radicals **B**.

(amino)(carboxy)carbon radicals **B**, derived from cyclic (alkyl)(amino)carbenes (CAACs),[13,14] can be isolated.[15,16]

Since paramagnetic species of type **B** are readily available in two steps from the reaction of a stable CAAC with acyl chlorides, followed by a one-electron reduction, we extrapolated this synthetic methodology to the preparation of diradicals[17] such as **2a** (Scheme 3). The latter is stable at room temperature and has been characterized by an X-ray diffraction study.[15a] The two radical units are not conjugated, as they correspond to π-systems that are orthogonal to the phenyl spacer. In addition, they are separated by about 700 pm, which limits through-space interactions. Therefore, it can be predicted that the first triplet and singlet states are nearly degenerate. In order to obtain a precise picture, low temperature EPR experiments were carried out. A frozen acetonitrile solution at 4 K displayed a weak half-field signal, which decreased when increasing the temperature, thus indicating the triplet nature of the ground state (Fig. 1). The half-field band could hardly be detected above 10 K. Fitting our data with the Bleaney–Bowers equation[18] showed that the triplet-singlet gap is less than 0.05 kcal mol^{-1} (see ESI†).



Scheme 3 Synthesis of **1a**$^{2+}$ and **2a**.

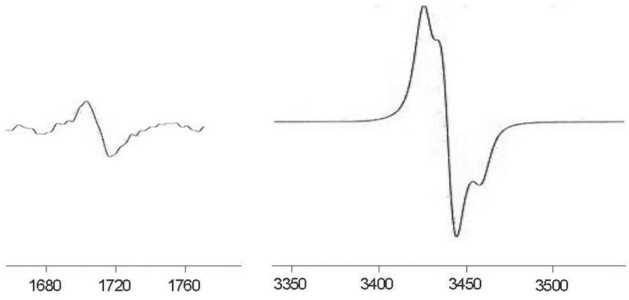
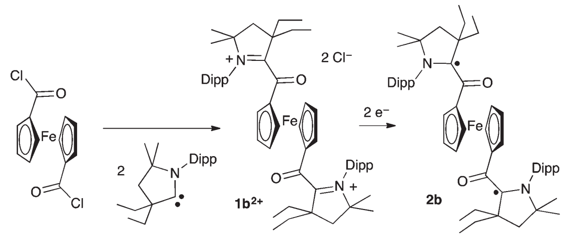


Fig. 1 X-band EPR spectra of diradical **2a** in frozen acetonitrile with zoom on the half-field absorption signals ($\Delta m = \pm 2$) at 5 K (left) and main transition ($\Delta m = \pm 1$) at 20 K (right).

To study the influence of the spacer on the singlet–triplet gap, we prepared the dication **1b**$^{2+}$ from 1,1′-ferrocene dicarbonyl chloride in 93% yield (Scheme 4). Cyclic voltammetry of **1b**$^{2+}$ indicated two reversible reductions at $E_{1/2} = -0.73$ and -0.93 V (Fig. 2), which were attributed to the successive formation of the two radical centers. Further reversible reductions below −1.5 V were attributed to the formation of the corresponding bis(enolate). We performed the quantitative electrolysis of a solution of **1b**$^{2+}$ in acetonitrile at $E_{\text{app}} = -1.35$ V. The stoichiometry (two coulombs per mole of reagent) was consistent with two successive one-electron processes. Cyclic voltammograms of the resulting solution were similar to those of **1b**$^{2+}$ indicating that, indeed, diradical **2b** was formed. The presence of a half-field band in the EPR spectra of frozen samples indicated the triplet nature of the ground state. However, in marked contrast with **2a**, this signal could be easily detected from 4 K up to 80 K. On this broad range of temperature (T), the integrated signal (I), which is proportionate to the magnetization of the sample, followed the Curie law (IT = constant), thus indicating a more significant ferromagnetic coupling of the two spins than in **2a**, with a triplet–singlet gap of at least 0.5–1 kcal mol^{-1}. In addition, the main band features a zero-field splitting parameter $D \sim 42$ G. This value corresponds to an average distance of more than 8.5 Å between the two interacting $\frac{1}{2}$ spins,[17] suggesting that the two radical centers are rather on opposite sides of the ferrocene linker, as depicted on Scheme 4. At higher temperatures, we observed the irreversible formation of a $\frac{1}{2}$ spin radical, likely



Scheme 4 Synthesis of **1b**$^{2+}$ and **2b**.

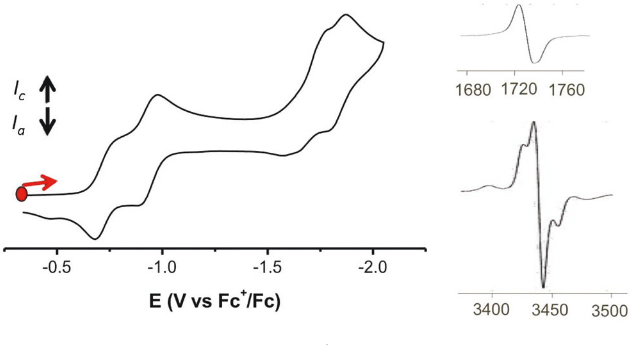


Fig. 2 Cyclic voltammograms of **1b**$^{2+}$ in acetonitrile + 0.1 M $[Bu_4N]PF_6$, scan rate: 100 mV s^{-1} (left); X-band EPR spectra of **2b** in frozen acetonitrile (right) with zoom on the half-field absorption signals ($\Delta m = \pm 2$) at 5 K (top) and main transition ($\Delta m = \pm 1$) at 20 K (bottom).

due to the reaction of **2b** with oxygen, which was inevitably condensed when cooling the EPR tube.

Next, we synthesized dication $\mathbf{1c}^{2+}$ featuring an even shorter spacer (Scheme 5). This compound is perfectly stable as a solid, although slightly moisture sensitive in solution. An X-ray diffraction study of the tetrafluoroborate salt of $\mathbf{1c}^{2+}$ confirmed its structure (Fig. 3).

The cyclic voltammogram of $\mathbf{1c}^{2+}$ is characterized by an irreversible reduction wave at $E_{\mathrm{pc}} = -0.77$ V, with the corresponding re-oxidation wave at $E_{\mathrm{pa}} = -0.16$ V (Fig. 3). A quantitative electrolysis at $E_{\mathrm{app}} = -1.1$ V showed that this reduction corresponds to a two-electron process. The resulting compound **3c** featured a similar cyclic voltammetry and, in turn, yielded back $\mathbf{1c}^{2+}$ upon quantitative oxidation at $E_{\mathrm{app}} = +0.2$ V. We then performed the chemical reduction of $\mathbf{1c}^{2+}$ with zinc powder, which allowed for the isolation of **3c** in 92% yield. Both $\mathbf{1c}^{2+}$ and **3c** are EPR silent. An X-ray diffraction study revealed the spirocyclic structure of **3c**. Note that we also reacted **3c** with two equivalents of silver triflate and isolated the triflate salt of $\mathbf{1c}^{2+}$ in 87% yield.

It is important to note that the C–O cyclization is an extremely fast process. Indeed, even at wide sweep rate range (up to 12.8 V s^{-1}), no reversibility of either electrochemical wave could be evidenced (see ESI†). Similarly, even at −40 °C, the cyclic voltammograms still showed irreversible waves at $E_{\mathrm{pa}} = 0.03$ V (oxidation) and $E_{\mathrm{pc}} = -0.65$ V (reduction).

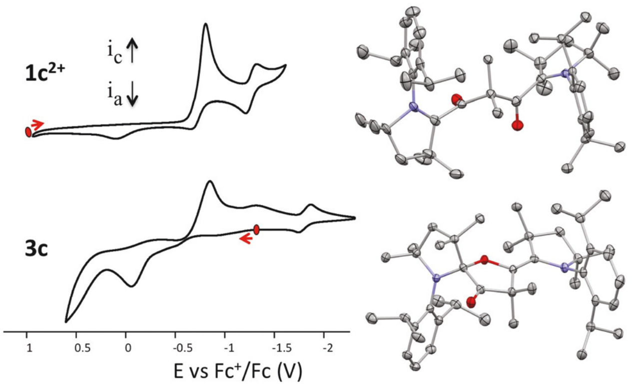
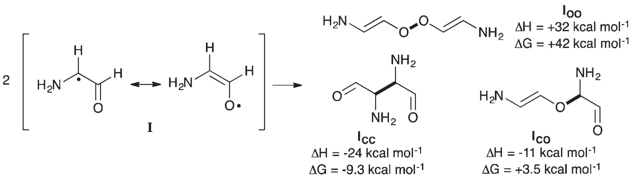


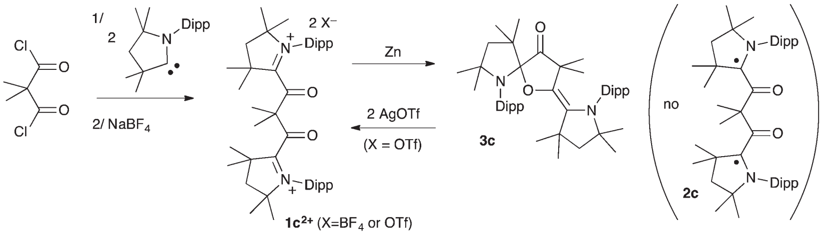
Fig. 3 Cyclic voltammogram of dication $\mathbf{1c}^{2+}$ in acetonitrile + 0.1 M $[Bu_4N]PF_6$, scan rate: 100 mV s^{-1} (top, left) and of its reduced form **3c** (bottom, left), and solid-state structures of $\mathbf{1c}^{2+}$ (top, right) and **3c** (bottom, right) with 50% ellipsoid probability. Hydrogen atoms, anions and solvent molecules were omitted for clarity.



Scheme 6 Energetics for intermolecular dimerization of model radical **I**.

Interestingly, capto-dative carbon radicals are traditionally depicted as C-centered radicals, which afford C–C homodimers as exemplified by the 2-oxomorpholin-3-yl radical **A** (Scheme 1). Although C–O homodimers have never been reported so far, their formation should not be surprising as (amino)(carboxy)carbon radicals also bear significant spin density on the oxygen atom. We considered the three possible dimerization products for model radical **I** at the B3LYP/6-311g** level of theory (Scheme 6).[19,20] As expected, we found that the formation of the O–O dimer $\mathbf{I_{OO}}$ is highly exothermic in enthalpy and endergonic in Gibbs energy, and that the C–C dimerization affording $\mathbf{I_{CC}}$ is the most favorable process. Importantly, the formation of the C–O dimer $\mathbf{I_{CO}}$ was found to be exothermic (−11 kcal mol^{-1}) but slightly endergonic (+3.5 kcal mol^{-1}). In the case of a diradical such as **2c**, the C–O bond formation corresponds to an intramolecular process, in which most of the entropic contribution favoring dissociation is suppressed. Indeed, the ring opening of **3c** to afford diradical **2c** was found to be endergonic by +27 kcal mol^{-1}. This preliminary value corresponds to the homolytic cleavage of a weak C–O bond, perfectly in line with the observed redox-bistability of the system. Note that cyclization through the formation of a C–C bond would require the interpenetration of bulky substituents and no minimum on the hypersurface of energy could be found for the corresponding product.

In conclusion, $\mathbf{1c}^{2+}$ was synthesized in one simple step from a cyclic (alkyl)(amino)carbene, which is itself readily available on large scales.[14] The two-electron reduction triggers a cyclization, which accounts for the redox bistability of the system. Both redox forms could be isolated and stored for months without evidence of decay. We are currently combining in-depth DFT studies, as well as experimental evaluation of a variety of spacers and stable carbenes to determine the scope



Scheme 5 Synthesis of $\mathbf{1c}^{2+}$ and **3c**.

of this new approach towards simple organic redox-bistable molecules.

Experimental section

General considerations

All manipulations were performed under an inert atmosphere of dry argon, using standard Schlenk and drybox techniques. Dry and oxygen-free solvents were employed. Stable carbenes were prepared as previously reported.[14] 1,10-Ferrocene-di(carbonylchloride) was prepared freshly in a two step sequence from 1,10-diacetylferrocene as previously reported.[21] Commercially available dimethylmalonyl chloride was purified by distillation before use. ^{1}H, ^{13}C NMR spectra were recorded on Bruker Advance 300, Varian VX 500 and Jeol ECA 500 spectrometers. Chemical shifts are given relative to $SiMe_4$ and referenced to the residual solvent signal (^{1}H, ^{13}C). Melting points were measured with Büchi Melting Point B-545 apparatus. Electrochemical experiments were carried out in CH_3CN + 0.1 M $[Bu_4N]PF_6$ using a Bio-logic SP-300 potentiostat. Potentials were first referred to an Ag/0.01 M $AgNO_3$ reference electrode in CH_3CN + 0.1 M $[Bu_4N]PF_6$, and all redox potentials in the text are reported with respect to the $E_{1/2}$ of the ferrocene/ferrocenium (Fc^+/Fc) redox couple (Ferrocene was used as a standard, the Fc^+/Fc potential is 0.07 V under our experimental conditions). The working electrode was a vitreous carbon disk (3 mm in diameter; polished with 1 µm diamond paste before each record) and the auxiliary electrode was a platinum wire. Bulk electrolysis were performed using reticulated vitreous carbon electrode as working electrode ($A = 2$ cm^2). EPR spectra were recorded on a Bruker EMX + spectrometer.

Synthesis of bis(tetrafluoroborate) salt of di(iminium) 1b^{2+}

(NB: The following manipulations were performed in the absence of light as the compound was found to be light sensitive.) To a mixture of 1,10-ferrocene-di(carbonylchloride) (0.300 mg, 0.95 mmol) and cyclic (alkyl)(amino)carbene (0.750 mg, 2.41 mmol) was added 5 ml of THF. The solution was stirred for 30 minutes and then filtered. After evaporation of the solvent, the remaining solid was washed with THF (5 mL), Et_2O (5 mL) and pentane (5 mL) to yield the bis(chloride) salt of **1b^{2+}** as a purple powder (841 mg; 93% yield). The anion exchange from chlorine to BF_4 was achieved by stirring **1b^{2+}Cl^{2-}** with excess $NaBF_4$ (4 eq.) at room temperature in CH_3CN for 12 h (*NB: to avoid decomposition during the anion exchange the $NaBF_4$ salt was melted twice under vacuum to remove adventitious water).* After removal of the solvent, the BF_4 salt was extracted with dichloromethane affording, after filtration and evaporation, the tittle compound as a purple solid in nearly quantitative yield. mp: 228–234 °C (dec.) HRMS (*m*/*z*): calc. for $C_{56}H_{78}FeN_2O_2^{\ +}$: 866.5413; found [M$^+$], 866.5412. ^{1}H NMR ($CD_3CN$, 500 MHz): δ 0.77 (d, J = 6.00 Hz, 12H), 1.24–1.28 (m, 24H), 1.52 (s, 12H), 2.16–2.23 (m, 4H), 2.30–2.37 (m, 4H), 2.49 (sept, J = 7.00 Hz, 12H), 2.54 (s, 4H), 4.98 (br s, 4H), 5.02 (br s, 4H), 7.29 (d, J = 8.00 Hz, 4H), 7.47 (t, J = 8.00 Hz, 2H). ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz): δ 9.8, 25.2, 26.9, 29.6, 30.2, 31.4, 41.1, 59.6, 76.0, 76.1, 78.1, 78.2, 79.1, 87.0, 127.5 (br), 128.3, 132.9 (br), 145.8, 192.1, 194.9.

Synthesis of bis(tetrafluoroborate) salt of di(iminium) 1c^{2+}

Dimethylmalonyl dichloride (99 µL, 0.75 mmol) was added to the cyclic (alkyl)(amino)carbene (0.45 g, 1.58 mmol) in solution in THF (10 mL). After stirring for twenty minutes, the solvent was removed by filtration and the precipitate washed with diethyl ether (2 × 10 mL). The solid was then dissolved in water, and an aqueous solution of sodium tetrafluoroborate (0.69 g, 6.31 mmol) was added to the flask. After stirring for one hour, the product was extracted in dichloromethane. The organics were washed with brine and dried over $MgSO_4$ before removing the solvent under vacuum (272 mg; 43% yield). Single crystals were grown by slowly diffusing diethyl ether into a concentrated acetonitrile solution of the product. mp: 146–148 °C. HRMS (*m*/*z*): calc. for $C_{45}H_{68}N_2O_2^{\ 2+}$, 334.2635; found [M^{2+}], 334.2637. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.01–1.04 (br, mult, 16H), 1.12–1.27 (br, mult, 22H), 1.47–1.50 (br, mult, 5H), 1.63–1.72 (br, 8H), 1.86 (br, 11H), 2.26–2.35 (br, 4H), 3.67 (br, 4H), 7.26–7.29 (br, mult, 4H), 7.52 (t, J = 8.00 Hz, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 125 MHz): δ 19.7, 25.5, 25.6, 25.8, 26.3, 26.7, 26.8, 27.0, 28.9, 29.3, 30.6, 47.6, 62.1, 89.0, 127.4 (br), 128.0 (br), 128.8, 133.5, 144.6 (br), 146.5 (br), 194.8, 200.1.

Synthesis of compound 3c

Zinc (20 mg, 0.3 mmol) and **1c^{2+}** (126 mg, 0.15 mmol) were combined under argon, and acetonitrile was added to the flask. After 10 minutes, the solvent was removed *in vacuo*. Subsequent extraction with hexanes (5.0 mL) led to the isolation of a white powder (93 mg; 92% yield). Single crystals for X-ray crystallography were isolated through slow evaporation of a dichloromethane solution of the product. Only the *E* isomer could be evidenced. mp: 217–221 °C. HRMS (*m*/*z*): calc. for $C_{54}H_{68}N_2O_2$, 669.0336; found, [M + Na]$^+$ = 691.5172. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.18–7.11 (m, 3H), 7.08–6.99 (m, 3H), 4.05 (sept, J = 6 Hz, 1H), 3.59 (sept, J = 6 Hz, 1H), 3.53 (m, 2H), 2.14 (d, J = 12 Hz, 1H), 1.79 (s, 3H), 1.73 (s, 3H), 1.55 (s, 3H), 1.48 (s, 3H), 1.46 (d, J = 7 Hz, 1H), 1.32–1.29 (m, 10H), 1.19–1.10 (m, 23H), 0.81 (s, 3H), 0.27 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 213.6 (C), 154.1 (C), 151.6 (C), 148.4 (C), 147.8 (C), 144.3 (C), 142.2 (C), 136.3 (C), 133.6 (C), 127.5 (CH), 125.9 (CH), 125.1 (CH), 124.5 (CH), 107.3 (C), 64.2 (C), 63.6 (C), 58.8 (CH_2), 55.7 (CH_2), 49.7 (C), 45.7 (C), 43.0 (C), 32.9 (CH_3), 30.6 (CH_3), 29.6 (CH_3), 29.4 (CH_3), 28.6 (CH), 28.5 (CH_3), 28.2 (CH), 27.9 (CH), 27.1 (CH_3), 26.9 (CH_3), 26.7 (CH_3), 26.7 (CH_3), 26.6, 26.4, 26.1, 25.9, 25.7, 25.0, 24.0, 21.9.

Synthesis of bis(trifalte salt) of 1c^{2+} from compound 3c

Silver triflate (69 mg, 0.3 mmol) and **3c** (100 mg, 0.15 mmol) were combined under argon. Acetonitrile (5 mL) was added to the flask and the mixture was stirred for 20 minutes. The supernatant was then removed *via* filtration. The solvent was removed *in vacuo* and the solid washed with hexanes to yield **1c**$^{2+}$ (121 mg; 83% yield).

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

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