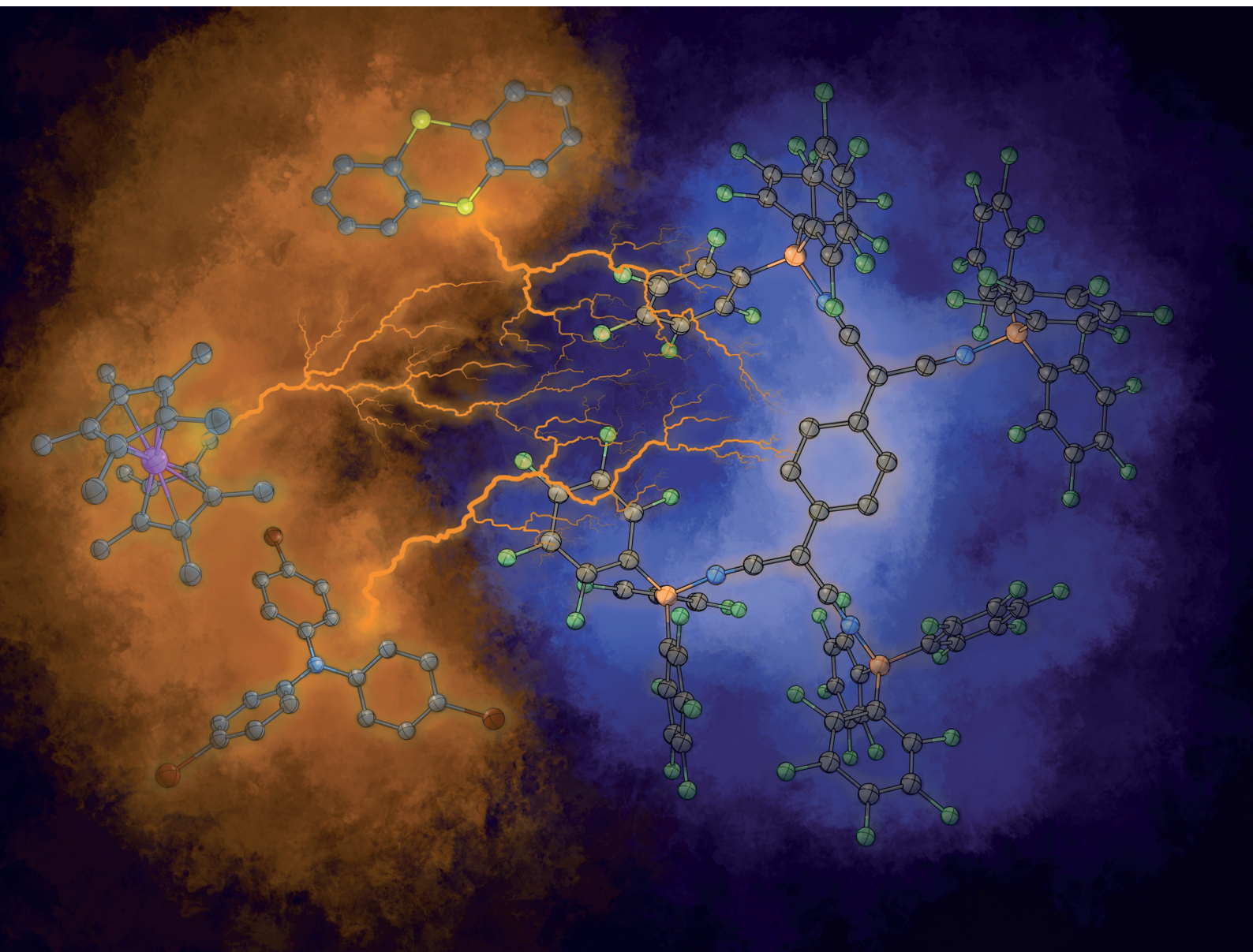


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Increasing the oxidation power of TCNQ by coordination of $B(C_6F_5)_3$ [†]

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The oxidation power of the cyanocarbon TCNQ (tetracyanoquinodimethane) can be significantly increased to approximately $E = +0.9$ V vs. Cp_2Fe by coordination of up to four equivalents of the strong fluorinated Lewis acid $B(C_6F_5)_3$, resulting in a highly reactive but easy-to-use oxidation system. Thianthrene and tris(4-bromophenyl)amine were oxidized to the corresponding radical cations. Dianionic $[TCNQ-4 B(C_6F_5)_3]^{2-}$ was formed upon reduction with two equivalents of ferrocene or decamethylcobaltocene. $[TCNQ-4 B(C_6F_5)_3]^-$ and $[TCNQ-4 B(C_6F_5)_3]^{2-}$ are rare cases of redox-active weakly-coordinating anions.

Strong one-electron oxidizing agents are of great synthetic utility, providing access to highly reactive target molecules. However, it is challenging to find a good balance between oxidation power, absence of side reactions, ease of handling and availability of the reagents. For example, inorganic fluorine compounds like (gaseous) AsF_5 or metal hexafluorides are extremely powerful oxidants *e.g.* in liquid SO_2 , but they can often not be handled in standard laboratories.^{1,2} In their seminal review on chemical redox agents, Connelly and Geiger discussed more popular reagents, *e.g.* Ag^+ and NO^+ , ferrocenium and triarylaminium salts.³ They classified all reagents with redox potentials $E > +0.8$ V vs. Cp_2Fe as very strong oxidants. However, it has to be stated, that especially in combination with transition metal complexes, the use of Ag^+ or NO^+ can lead to side reactions.^{4,5} Interestingly, the oxidation power of Ag^+ can be significantly increased in combination with elemental halogens X_2 ($X = Cl, Br, I$), since the formation of insoluble AgX provides an additional driving force.^{6,7} Another highly useful system was developed by Poleschner. By using XeF_2 in combination with fluoride acceptors ($BF_3 \cdot Et_2O$, Me_3SiOTf , *etc.*)

different weakly-coordinating anions can be introduced.⁸ Jenne demonstrated the very high oxidation power of the boron cluster radical $Me_3NB_{12}Cl_{11}$, however its multi-step synthesis seems to have prevented widespread use by other groups.⁹ The same is true for Michl's $CB_{11}Me_{12}$ or a perfluorinated ammoniumyl cation of the Krossing group.^{10,11} In contrast to this, cyanocarbons, although mild oxidants, are often commercially available and air-stable. Due to the electron-withdrawing character of the cyano groups, neutral cyanocarbons are molecules with high electron affinities.¹² Consequently, they easily form radical anions (or even dianions) of significant stability when treated with a reducing agent. This has led to a plethora of applications, *e.g.* in molecular magnetism^{13,14} and for the doping of organic polymers.¹⁵ Since tetracyanoquinodimethane (TCNQ) is only a mild oxidant (first reduction potential $E = -0.30$ V, second reduction potential $E = -0.88$ V vs. Cp_2Fe),^{3,16,17} we assumed that its electron affinity could be increased and manipulated by coordination of Lewis acids to the terminal nitrogen atoms.¹⁸

Tris(pentafluorophenyl)boron is a commercially available and potent Lewis acid.¹⁹ It has a high affinity for hard donor atoms, *e.g.* nitrogen, but is typically non-oxidizing.^{20,21} Indeed, the reduction to its radical anion is only achieved at redox potentials below $E = -1.7$ V vs. Cp_2Fe .^{22–24} Interestingly, it has been shown by Stephan and Erker that the combination of two equivalents of $B(C_6F_5)_3$ with the electron acceptor *p*-benzoquinone $C_6H_4O_2$ is able to oxidize decamethylferrocene to its cation.^{25,26} Depending on the stoichiometry $[C_6H_4O_2 \cdot 2 B(C_6F_5)_3]^{-/2-}$ mono- or dianions are obtained. By choosing other Lewis acids, the oxidation power of the system can be tuned.²⁷ Another example for cooperative effects between electron acceptors and fluorinated Lewis acids is the combination of dioxygen with two equivalents of $B(C_6F_5)_3$ which is even able to oxidize air-stable ferrocene to ferrocenium under formation of $[(C_6F_5)_3BOOB(C_6F_5)_3]^{2-}$ dianions.²⁸ In the area of coordination chemistry, seminal works by Fukuzumi have shown the importance of Lewis acidic metal centers in dioxygen activation.^{29–31}

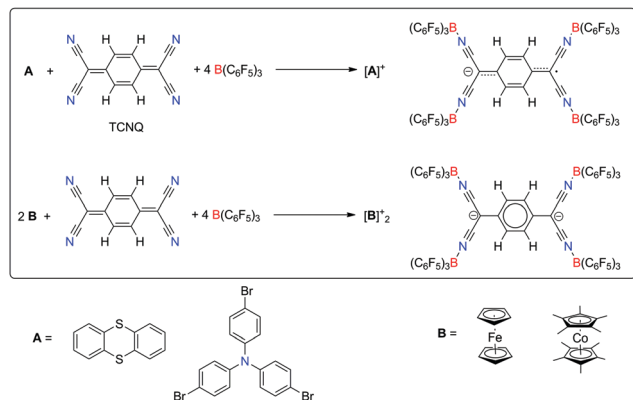
In order to develop a new oxidizing system, we investigated the combination of TCNQ with four equivalents of $B(C_6F_5)_3$

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Scheme 1 Substrate scope of the new oxidation system TCNQ + 4 B(C₆F₅)₃.

(Scheme 1).³² Although we were not able to isolate a neutral 1 : 4 adduct (due to the precipitation of the 1 : 2 adduct), this mixture is strongly oxidizing in weakly-basic solvents like dichloromethane or *o*-dichlorobenzene. Both *tris*(4-bromophenyl)amine ($E = +0.70$ V vs. Cp₂Fe) and thianthrene ($E = +0.86$ V vs. Cp₂Fe) are instantaneously oxidized to their corresponding (blue/violet) radical cations,³ forming monoanionic [TCNQ-4 B(C₆F₅)₃][−] as the counterion. Both [N(C₆H₄Br)₃]⁺ [TCNQ-4 B(C₆F₅)₃][−] · 4 *o*-C₆H₄Cl₂ and [(C₆H₄)₂S₂]⁺ [TCNQ-4 B(C₆F₅)₃][−] were structurally characterized *via* single crystal X-ray diffraction (Fig. 1).³³ Due to the 4 : 1 stoichiometry, all cyano groups are coordinated to the Lewis acidic boron centers. Consequently, no potential nitrogen donor sites are present,³⁴ resulting in a new, large weakly-coordinating monoanion with 60 fluorine atoms involved. To estimate the reduction potential that is needed to reduce the radical monoanions to diamagnetic dianions, we successfully used two equivalents of ferrocene per TCNQ. Their oxidation to ferrocenium showed the significant oxidation power of the radical monoanions. Additionally, this indicates potential stability of the dianion against dioxygen. Nevertheless these adducts are sensitive to water and Lewis bases. Despite its low solubility in dichloromethane, the structure of [Cp₂Fe]⁺₂ [TCNQ-4 B(C₆F₅)₃]^{2−} · 2 CH₂Cl₂ could be determined *via* single-crystal X-ray diffraction.³³ To prepare a

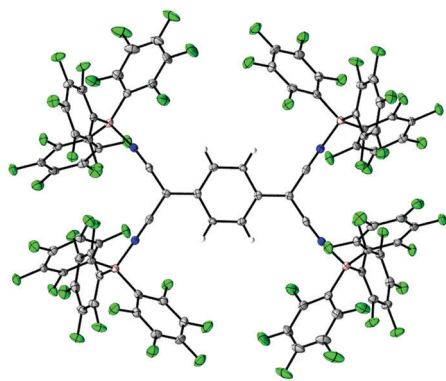


Fig. 1 Molecular structure of the radical anion in [(C₆H₄)₂S₂]⁺ [TCNQ-4 B(C₆F₅)₃][−], thermal ellipsoids shown with 50% probability, colour code: hydrogen white, carbon grey, fluorine green, nitrogen blue, boron rose.

salt with diamagnetic cations and anions (and better solubility), two equivalents of decamethylcobaltocene were successfully used as reducing agent. Correspondingly, the structure of [Cp⁺₂Co]⁺₂ [TCNQ-4 B(C₆F₅)₃]^{2−} · 2 CH₂Cl₂ was also determined.³³ In all four characterized salts, the structures of the cations are in accordance with literature reports and will not be further discussed here. H⋯F contacts between cations and anions are in the range of 2.4–2.7 Å and can therefore be considered as weak hydrogen bond contacts. In general, the mono- and dianions look very similar at first sight since the four cyano groups are slightly tilted out of the plane of the central six-membered ring (angles 4.75°–11.21°). However, several characteristic trends regarding specific bond lengths of the TCNQ core can be noticed. Neutral TCNQ displays significant variations regarding the C–C bond lengths in its six-membered ring due to its quinoidal nature. However, upon reduction to its mono- and (aromatic) dianion, these differences are becoming less pronounced.³⁵ The same trend is observed for the adducts [TCNQ-4 B(C₆F₅)₃]^{0/−2−} (Fig. 2, Table. 1). The six-membered ring in [(C₆H₄)₂S₂]⁺ [TCNQ-4 B(C₆F₅)₃][−] is characterized by two short (1.359(3) Å) and four long bonds (1.414(3)–1.426(3) Å). The C–C(CN)₂ bond has a length of 1.426(3) Å. In [Cp₂Fe]⁺₂ [TCNQ-4 B(C₆F₅)₃]^{2−} · 2 CH₂Cl₂ the C–C bonds of the six-membered ring of TCNQ are all very similar in length (1.383(2)–1.396(2) Å), indicating a more effective electron delocalization. The corresponding C–C bond to the C(CN)₂ group is longer (1.480(2) Å) than in the monoanion. In the ferrocenium salt the average C≡N bond length (1.149(2) Å) is very similar to the corresponding value of the thianthrenium salt (1.145(3) Å). The changes of the B–N bond lengths are more significant: 1.550(2)–1.561(2) Å in the dianions compared to 1.580(3)–1.590(3) Å in the monoanions, indicating a stronger donor–acceptor interaction in the dianions.

Quantum-chemical calculations at the DFT level B3LYP-D3(BJ)/Def2-SVP have been performed to evaluate the structure and the vibrational frequencies of the neutral, mono- and dianionic 4 : 1 adducts between B(C₆F₅)₃ and TCNQ. They confirm that, upon reduction, the C–C bond lengths of the six-membered ring become less variable. Additionally, a slight increase of C≡N bond lengths is predicted upon reduction of the neutral species to the mono- and dianion (1.152 Å → 1.156 Å → 1.165 Å). Principally, one would expect a decrease of the computed $\tilde{\nu}(\text{C}\equiv\text{N})$ frequency for the reduced species. In general, four different $\nu(\text{C}\equiv\text{N})$ vibrations are predicted within the range of

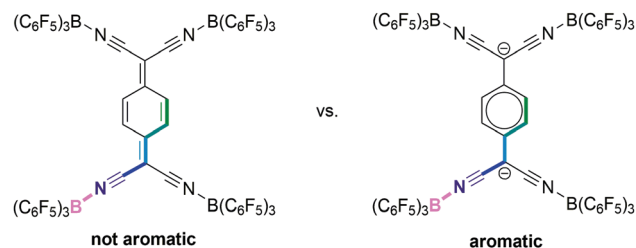


Fig. 2 Lewis formulas of [TCNQ-4 B(C₆F₅)₃] (left) and [TCNQ-4 B(C₆F₅)₃]^{2−} (right) and assignment of the labels for the discussion of bond lengths.



Table 1 Experimental (all four crystal structures) and calculated (B3LYP-D3(BJ)/Def2-SVP) bond lengths in Å for [TCNQ-4 B(C₆F₅)₃]^{0/-2-}, labels a to f according to Fig. 2

| Bond | [TCNQ-4 B(C ₆ F ₅) ₃] calculated | [TCNQ-4 B(C ₆ F ₅) ₃] ⁻ calculated | [TCNQ-4 B(C ₆ F ₅) ₃] ⁻ experimental | [TCNQ-4 B(C ₆ F ₅) ₃] ²⁻ calculated | [TCNQ-4 B(C ₆ F ₅) ₃] ²⁻ experimental |
|------|---|--|--|---|---|
| a | 1.358–1.365 | 1.371–1.378 | 1.359(3)–1.364(6) | 1.391–1.394 | 1.383(2)–1.388(2) |
| b | 1.440–1.444 | 1.425–1.426 | 1.411(6)–1.426(6) | 1.406–1.407 | 1.396(2)–1.399(2) |
| c | 1.401–1.402 | 1.431–1.433 | 1.426(6)–1.431(3) | 1.477–1.480 | 1.470(2)–1.480(2) |
| d | 1.412–1.416 | 1.401–1.405 | 1.397(6)–1.405(6) | 1.383–1.386 | 1.382(2)–1.385(2) |
| e | 1.151–1.154 | 1.154–1.156 | 1.140(6)–1.145(3) | 1.164–1.166 | 1.147(2)–1.151(2) |
| f | 1.574–1.582 | 1.562–1.588 | 1.580(6)–1.589(3) | 1.550–1.561 | 1.550(2)–1.561(2) |

2220–2350 cm⁻¹. Upon reduction, the red-shift of the symmetric $\tilde{\nu}(\text{C}\equiv\text{N})$ vibration (which is highest in energy) is relatively little pronounced in the series (2348 → 2345 → 2317 cm⁻¹). In contrast, the shift of the antisymmetric $\tilde{\nu}(\text{C}\equiv\text{N})$ vibration (which is lowest in energy) is much more pronounced (2311 → 2290 → 2221 cm⁻¹). Indeed, the experimental IR spectra of salts that contain the monoanions have two bands at 2290 and ≈ 2250 cm⁻¹, while two bands at 2284 and ≈ 2205 cm⁻¹ are observed for the dianion (see Fig. S9, ESI†). The widening of the range of $\tilde{\nu}(\text{C}\equiv\text{N})$ frequencies upon reduction is consequently both experimentally and computationally found. Attempts to measure Raman spectra of the products were unsuccessful due to intense fluorescence or decomposition by laser light.

Based on DFT calculations (B3LYP-D3(BJ)/Def2-SVP) the adiabatic electron affinities of the neutral adduct was estimated to be 583 kJ mol⁻¹ (6.04 eV). The reduction of the corresponding monoanion to the dianion is also highly favourable (310 kJ mol⁻¹, 3.21 eV). In comparison, free TCNQ has an experimental electron affinity of 3.38 eV.³⁶ A similar trend can be seen when LUMO energies are taken into account. While the calculated LUMO energy of TCNQ is -4.98 eV, the corresponding value for neutral [TCNQ-4 B(C₆F₅)₃] is -6.80 eV (extension on some C₆F₅ rings). Consequently, the coordination of Lewis acids clearly increases its oxidation power and underlines our cooperativity concept for such systems.

Cyclic voltammetry of [Cp*₂Co]⁺₂ [TCNQ-4 B(C₆F₅)₃]²⁻ in CH₂Cl₂ allowed the determination of the electrochemical properties of the oxidation system (Fig. 3). At a scan rate of 100 mV s⁻¹, a (pseudo)reversible oxidation at $E_{1/2}$ = +0.065 V vs. Cp₂Fe (for the dianion/moanion redox couple) and an irreversible process at E_{pa} = +1.226 V vs. Cp₂Fe (for the irreversible oxidation to the neutral species) were determined. Large peak separations may be caused by slow electron exchange on the electrode. Additionally, [Cp*₂Co]⁺₂ [TCNQ-4 B(C₆F₅)₃]²⁻ had sufficient solubility in CD₂Cl₂ to allow its characterization *via* multi-nuclear NMR spectroscopy. Two signals in the ¹H-NMR can be assigned to the TCNQ protons (δ = 6.82 ppm) as well as the methyl protons of decamethylcobaltocenium (δ = 1.65 ppm). In the ¹¹B NMR spectrum a broad signal at δ = -11.5 ppm is assigned to the tetracoordinate boron atoms in [TCNQ-4 B(C₆F₅)₃]²⁻ which is also in agreement with other nitrogen-containing adducts.³⁷ For example, [CH₃CN·B(C₆F₅)₃] has a ¹¹B NMR shift of -10.3 ppm (in C₆D₆).²¹ In comparison the

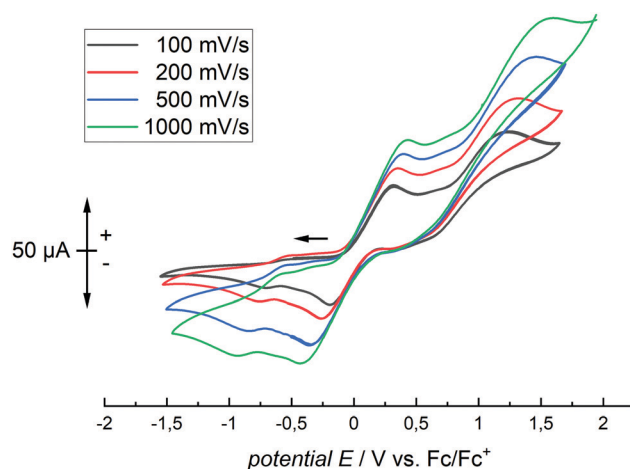


Fig. 3 Cyclic voltammogram of [Cp*₂Co]⁺₂ [TCNQ-4 B(C₆F₅)₃]²⁻ in CH₂Cl₂.

¹¹B NMR shift of uncoordinated B(C₆F₅)₃ is observed at +59.2 ppm.³⁸ In the ¹⁹F NMR three main signals are observed for the meta, para and ortho fluorine atoms in the C₆F₅ rings δ = -165.4, -159.3 and -134.8 ppm). These signals are slightly shifted in comparison to uncoordinated B(C₆F₅)₃ (δ = -161.3, -144.2 and -128.4 ppm). Additionally, it was possible to find and assign almost all signals in the ¹³C NMR spectrum. The decamethylcobaltocenium cation gives two signals at δ = 8.2 and 94.6 ppm which is in agreement with literature values.³⁹ For the central TCNQ moiety in [TCNQ-4 B(C₆F₅)₃]²⁻ as well as for the pentafluorophenyl rings four signals are each expected. However, only seven peaks could be detected. The proton-decoupled ¹³C NMR spectrum displays three doublets for the fluorine-bound carbon atoms of the pentafluorophenyl rings (δ = 148.6; 140.4 and 137.6 ppm). Additionally, one broad signal at δ = 118.3 ppm was observed. These signals are slightly shifted in comparison to free B(C₆F₅)₃ (δ = 149.1 (*ortho*), 145.8 (*para*), 138.3 (*meta*) and 113.8 (*ipso*) ppm).³⁸ Two additional signals at δ = 126.0 and 123.1 ppm belong clearly to the aromatic TCNQ core of the dianion. In the uncomplexed neutral TCNQ the chemical shifts differ more significantly: δ = 132.6 and 151.7 ppm. For uncomplexed TCNQ the chemical shift of the cyano group is δ = 112.6 ppm.⁴⁰ However, no corresponding signal was found. Interestingly, one signal of the [TCNQ-4 B(C₆F₅)₃]²⁻ dianion is strongly high-field shifted:



the carbon atom of the TCNQ moiety that is bound to the two cyano groups. Due to some carbanion character, the signal is located at $\delta = 30.5$ ppm. In comparison, the same carbon resonates at $\delta = 90.8$ ppm in free TCNQ.

EPR spectroscopy at room temperature in dichloromethane was used to prove that electron transfer between the diamagnetic starting materials has taken place. Three experiments were performed: TCNQ with 4 equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ was reacted with either tris(4-bromophenylamine), thianthrene or a small amount of ferrocene to generate $[\text{Cp}_2\text{Fe}]^+ [\text{TCNQ} \cdot 4 \text{B}(\text{C}_6\text{F}_5)_3]^-$. In the first two cases EPR spectra showed the presence of two radical species each: the corresponding, well-known radical cations as well as the desired radical anion. In the last case only the spectrum of $[\text{TCNQ} \cdot 4 \text{B}(\text{C}_6\text{F}_5)_3]^-$ was observed, since ferrocenium is not EPR-active at room temperature. The EPR spectrum of the radical anion $[\text{TCNQ} \cdot 4 \text{B}(\text{C}_6\text{F}_5)_3]^-$ consists of one broad, isotropic signal at $g_{\text{iso}} \approx 2.002$ which confirms the strong delocalization of the unpaired electron. Hyperfine splitting was not observed due the large number of spin-carrying nuclei as well as the presence of isotopomers (natural abundance of $^{10}\text{B} = 20\%$, $I = 3$, and $^{11}\text{B} = 80\%$, $I = 3/2$).

In summary, we report a potent oxidation system from commercially available chemicals that works in non-coordinating organic solvents and is easy to use. The combination of TCNQ with four equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ is able to quantitatively oxidize substrates up to an oxidation potential of $E \approx +0.9$ V and generates large, previously unknown weakly-coordinating anions that are redox-active. The resulting $[\text{TCNQ} \cdot 4 \text{B}(\text{C}_6\text{F}_5)_3]^-$ mono-anion has still enough oxidation power to oxidize ferrocene to ferrocenium. We are optimistic that similar systems (using cyano-carbons in combination with Lewis acids) could not only be used in molecular chemistry, but will also be of interest for the doping of organic polymers.

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Conflicts of interest

There are no conflicts to declare.

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