Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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

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Experimental Part

Synthesis

All preparations were performed under inert conditions. Solvents were dried and stored over molecular sieves. *Tris*(pentafluorophenyl)borane and *tris*(4-bromophenyl)amine were purchased from ABCR. Tetracyanoquinodimethane (TCNQ), thianthrene and decamethylcobaltocene were purchased from Sigma Aldrich. Ferrocene was purchased from Alfa Aesar.

IR Spectra were recorded on a Bruker ALPHA FTIR spectrometer inside a glovebox equipped with a diamond ATR attachment. ^{19}F and ^{11}B NMR spectra were measured on a JEOL 400 MHz ECZ spectrometer. ^{1}H and ^{13}C spectra were measured on a Bruker AVANCE700 (700 MHz) spectrometer.

EPR spectra were recorded in the X-band at 298 K with a *Magnetech MS 5000* spectrometer. The samples were sealed in Argon atmosphere inside a 4 mm PFA tube. Simulations were performed with *Easyspin*. [1]

$[N(4\text{-}BrC_6H_4)_3]^+$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^-$

In a glovebox 10.2 mg (0.0500 mmol) TCNQ, 24.1 mg (0.0500 mmol) *tris*(4-bromophenyl)amine and 103 mg $B(C_6F_5)_3$ (0.200 mmol) are placed in a Schlenk tube. After addition of 5 mL of CH_2Cl_2, the mixture is stirred at room temperature for a minutes. The mixture turns blue. Evaporation of the solvent in vacuum gives the product in quantitative yield. Single crystals can be obtained by layering an *ortho*-dichlorobenzene solution of the product with pentane in a fridge (4 °C).

$\tilde{\nu}$ (IR, ATR powder) = 2286 (br), 1648 (w), 1548 (w), 1517 (m), 1505 (w), 1464 (s), 1385 (w), 1354 (w), 1287 (w), 1256 (w), 1171 (w), 1103 (m), 1065 (m), 973 (s), 859 (w), 830 (w), 795 (m), 773 (m), 738 (w), 681 (m), 649 (w), 616 (w), 589 (w), 575 (w), 532 (w) cm^{-1}

EPR (X-Band, CH_2Cl_2, RT): two signals: g_{iso}=2.0143 (radical cation) and g_{iso}=2.0026 (radical anion).

$[C_6H_4S_2C_6H_4]^+$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^-$

In a glovebox 10.2 mg (0.0500 mmol) TCNQ, 10.8 mg (0.0500 mmol) of thianthrene and 103 mg $B(C_6F_5)_3$ (0.200 mmol) are placed in a Schlenk tube. After addition of 5 mL of CH_2Cl_2, the mixture is stirred at room temperature for a minutes producing a violet suspension. Evaporation of the solvent in vacuum gives the product in quantitative yield. Recrystallization can be accomplished by vapor diffusion of pentane into a concentrated dichloromethane solution of the product.

$\tilde{\nu}$ (IR, ATR powder) = 2290 (m), 2252 (w), 1646 (w), 1517 (m), 1505 (w), 1458 (s), 1383 (w), 1350 (w), 1287 (w), 1103 (m), 973 (s), 857 (w), 793 (m), 773 (m), 742 (w), 681 (m), 651 (w), 618 (w), 573 (w), 557 (w), 536 (w) cm^{-1}

EPR (X-Band, CH_2Cl_2, RT): two signals, g_{iso}=2.00788 (radical cation) and g_{iso}=2.00266 (radical anion)

$[C_{10}H_{10}Fe]^+_2$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^{2-}$

In a glovebox 10.2 mg (0.0500 mmol) TCNQ, 18.6 mg ferrocene (0.100 mmol) and 103 mg $B(C_6F_5)_3$ (0.200 mmol) are placed in a Schlenk tube. After addition of 5 ml of CH_2Cl_2, the mixture is stirred at room temperature for a minutes, producing a red-blue suspension. Evaporation of the solvent in vacuum gives a green solid in quantitative yield. Single crystals can be obtained by layering dichloromethane solutions with pentane.

$\tilde{\nu}$ (IR, ATR powder) = 2284 (w), 2207 (m), 1646 (w), 1515 (m), 1460 (s), 1422 (w), 1379 (w), 1283 (w), 1089 (m), 973 (s), 875 (w), 855 (w), 824 (w), 800 (m), 765 (m), 744 (w), 710 (w), 673 (m), 647 (w), 624 (w), 598 (w), 575 (w) cm^{-1}

EPR (X-Band, CH_2Cl_2, RT): one signal g_{iso}=2.00238 (radical anion)

$[C_{20}H_{30}Co]^+_2$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^{2-}$

In a glovebox 10.2 mg (0.0500 mmol) TCNQ and 32.9 mg (0.100 mmol) decamethylcobaltocene are added. After addition of 5 ml of CH_2Cl_2, and a few minutes of stirring, 103 mg $B(C_6F_5)_3$ (0.200 mmol) are added and stirring at room temperature is continued for a few minutes. The mixture turns yellow-brown. Evaporation of the solvent in vacuum gives the product in quantitative yield. Single crystals can be obtained by layering dichloromethane solutions with hexane.

$\tilde{\nu}$ (IR, ATR powder) = 2284 (w), 2203 (m), 1644 (w), 1515 (m), 1464 (s), 1381 (w), 1285 (w), 1099 (m), 977 (s), 873 (w), 824 (w), 800 (m), 773 (m), 749 (w), 710 (w), 683 (m), 675 (w) 651 (w), 624 (w), 600 (w), 575 (w) cm^{-1}

^1H NMR (700 MHz, CD_2Cl_2, RT): 6.82 (4H, TCNQ), 1.65 (60 H, $Cp^*_2Co^+$) ppm.

$^{13}C\{^1H\}$ NMR (176 MHz, CD_2Cl_2, RT): 148.6 (d, $^1J(^{13}C\text{-}^{19}F)$ =241.4 Hz, o-C_6F_5), 140.4 (d, $^1J(^{13}C\text{-}^{19}F)$ = 248.9 Hz, *p*-C_6F_5), 137.6 (d, $^1J(^{13}C\text{-}^{19}F)$ = 247.5 Hz, *m*-C_6F_5), 126.0 (s, TCNQ), 123.1 (s, TCNQ, C-H), 113.8 (s (broad), *ipso*-C_6F_5), 94.6 (s, $Cp^*_2Co^+$, Cp-ring), 30.5 (s, TCNQ, C^-), 8.2 (s, $Cp^*_2Co^+$, CH_3) ppm, CN signal not observed.

^{11}B NMR (128 MHz, CD_2Cl_2, RT): −11.5 ppm (broad).

^{19}F NMR (377 MHz, CD_2Cl_2, RT): −134.75 (m, 24 F, *ortho*-C_6F_5), −159.26 (m, 12 F, *para*-C_6F_5), −165.63 (m, 24 F, *meta*-C_6F_5) ppm

Crystallographic Data

X-Ray data was collected on a BRUKER D8 Venture system. Data was collected at 100(2) K using graphite-monochromated Mo K_α radiation (λ_α = 0.71073 Å). The strategy for the data collection was evaluated by using the Smart software. The data were collected by the standard "*ψ*-*ω* scan techniques" and were scaled and reduced using Saint+software. The structures were solved by using Olex2,[2] the structure was solved with the XT[3] structure solution program using Intrinsic Phasing and refined with the XL refinement package [4, 5] using Least Squares minimization. If it is noted, bond lengths and angles were measured with Diamond Crystal and Molecular Structure Visualization Version 4.6.2.[6] Drawings were generated with POV-Ray and Mercury 3.5.1.[7, 8] The crystal structures discussed in the manuscript have been reported as CSD Communications (deposition numbers CCDC 2133128, 2133132, 2133133 and 2133134).[9] These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Table S1: *Crystallographic Data*

Compound	**$[N(p\text{-}BrC_6H_4)_3][TCNQ \cdot 4\ BCF] \cdot 4\ C_6H_4Cl_2$**
Empirical formula	$C_{126}H_{32}B_4Br_3Cl_8F_{60}N_5$
Formula weight	3322.13
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/Å	44.679(3)
b/Å	10.8432(6)
c/Å	26.3729(17)
α/°	90
β/°	107.024(2)
γ/°	90
Volume/Å³	12217.0(13)
Z	4
ρ_{calc}/g·cm³	1.806
μ/mm^{-1}	1.313
F(000)	6496.0
Crystal size/mm³	0.25 × 0.2 × 0.18
Crystal shape	block
Radiation	MoK_α (λ = 0.71073)
2Θ range for data collection/°	3.88 to 50.79
Index ranges	-53 ≤ h ≤ 53, -12 ≤ k ≤ 13, -31 ≤ l ≤ 31
Reflections collected	75310
Independent reflections	11195 [R_{int} = 0.0697, R_{sigma} = 0.0428]
Data/restrains/parameters	11195/0/1102
Goodness-of-fit on F²	1.076
Final R indexes [I>=2σ(I)]	R_1 = 0.0538, wR_2 = 0.1469
Final R indexes [all data]	R_1 = 0.0723, wR_2 = 0.1584

Largest diff. peak/hole / e·Å³	1.36/-0.68

Compound	**$[C_{12}H_8S_2][TCNQ \cdot 4\ BCF] \cdot 4\ C_6H_4Cl_2$**
Empirical formula	$C_{96}H_{12}B_4F_{60}N_4S_2$
Formula weight	2468.46
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	10.9498(7)
b/Å	12.3024(9)
c/Å	17.1179(10)
α/°	85.529(2)
β/°	83.538(2)
γ/°	79.619(2)
Volume/Å³	2249.8(3)
Z	1
ρ_{calc}g/cm³	1.822
μ/mm⁻¹	0.239
F(000)	1208.0
Crystal size/mm³	0.36 × 0.24 × 0.22
Crystal shape	block
Radiation	MoK_α (λ = 0.71073)
2Θ range for data collection/°	4.02 to 50.71
Index ranges	$-13 \le h \le 13, -14 \le k \le 14, -20 \le l \le 20$
Reflections collected	39121
Independent reflections	8243 [R_{int} = 0.0662, R_{sigma} = 0.0472]
Data/restraints/parameters	8243/0/748
Goodness-of-fit on F²	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0391, wR_2 = 0.0800
Final R indexes [all data]	R_1 = 0.0595, wR_2 = 0.0881
Largest diff. peak/hole / e Å⁻³	0.33/-0.32

Compound	**$[FeC_{10}H_{10}]_2[TCNQ \cdot 4\ BCF] \cdot 2\ CH_2Cl_2$**
Empirical formula	$C_{106}H_{28}B_4Cl_4F_{60}Fe_2N_4$
Formula weight	2794.06
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	12.5554(7)
b/Å	13.8172(9)
c/Å	16.2965(11)
α/°	70.236(3)
β/°	73.627(2)
γ/°	75.624(2)
Volume/Å³	2515.8(3)
Z	1
ρ_{calc}g/cm³	1.833
μ/mm⁻¹	0.561
F(000)	1327.0
Crystal size/mm³	0.50 × 0.16 × 0.15
Crystal shape	needle
Radiation	MoK_α (λ = 0.71073)
2Θ range for data collection/°	3.888 to 52.79
Index ranges	$-15 \le h \le 15, -17 \le k \le 17, -20 \le l \le 20$
Reflections collected	89098
Independent reflections	10302 [R_{int} = 0.0474, R_{sigma} = 0.0229]
Data/restraints/parameters	10302/0/856
Goodness-of-fit on F²	0.997
Final R indexes [I>=2σ (I)]	R_1 = 0.0310, wR_2 = 0.0772
Final R indexes [all data]	R_1 = 0.0369, wR_2 = 0.0805
Largest diff. peak/hole / e Å⁻³	0.37/-0.48

Compound	**$[CoC_{20}H_{30}]_2[TCNQ\cdot 4\ BCF]\cdot 2\ CH_2Cl_2$**
Empirical formula	$C_{126}H_{68}B_4Cl_4Co_2F_{60}N_4$
Formula weight	3080.74
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	12.5039(6)
b/Å	15.5207(8)
c/Å	16.4844(9)
α/°	76.137(2)
β/°	78.772(2)
γ/°	76.995(2)
Volume/Å^3	2992.6(3)
Z	1
ρ_{calc}g/cm^3	1.709
μ/mm^{-1}	0.515
F(000)	1534.0
Crystal size/mm^3	0.60 × 0.55 × 0.45
Crystal shape	block
Radiation	MoK_α (λ = 0.71073)
2Θ range for data collection/°	3.932 to 56.606
Index ranges	$-16 \le h \le 16$, $-20 \le k \le 20$, $-21 \le l \le 21$
Reflections collected	126581
Independent reflections	14869 [R_{int} = 0.0377, R_{sigma} = 0.0193]
Data/restraints/parameters	14869/0/911
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0302, wR_2 = 0.0772
Final R indexes [all data]	R_1 = 0.0344, wR_2 = 0.0794
Largest diff. peak/hole / e Å^{-3}	0.39/-0.49

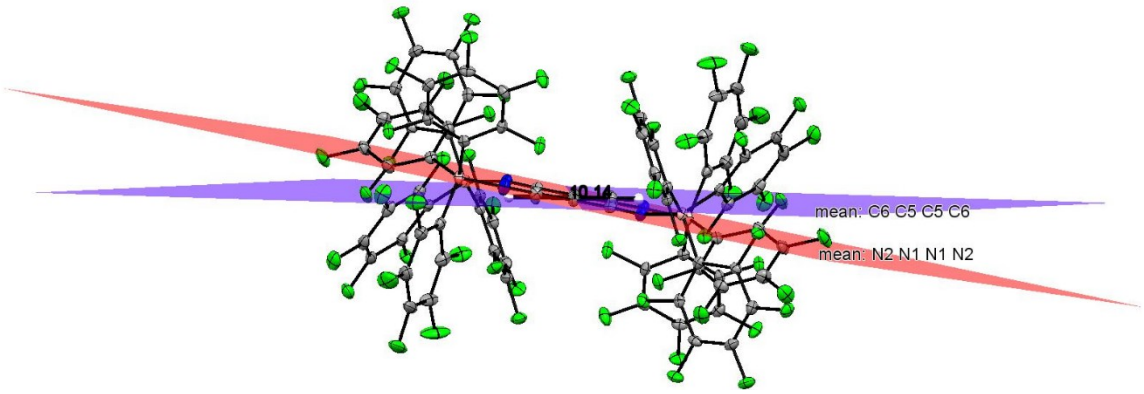


Figure S1. Structure of the dianion in the ferrocenium salt.

Angle between N4 plane (red) and plane of the central four carbon atoms (bound to hydrogen – in blue): 10.14°.

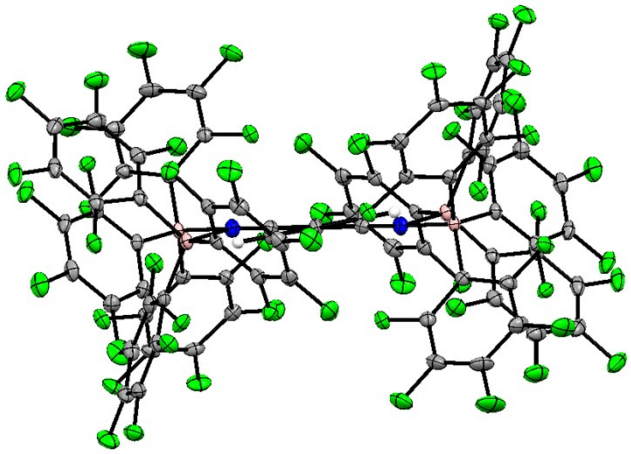


Figure S2. Structure of the dianion in the decamethylcobaltocenium salt. Angle between N4 plane and plane of the central four carbon atoms (bound to hydrogen): 10.22°.

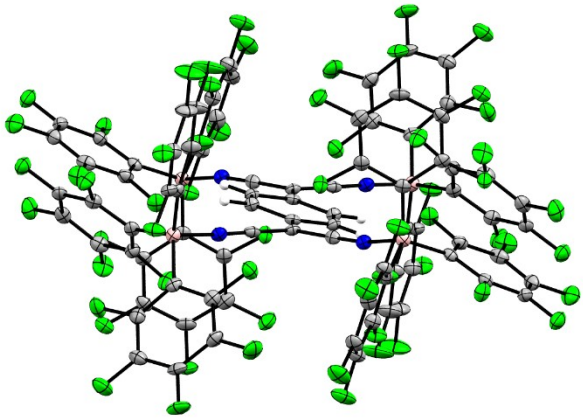


Figure S3. Structure of the anion in the aminium salt.

Angle between N4 plane and plane of the central four carbon atoms (bound to hydrogen): 11.21°.

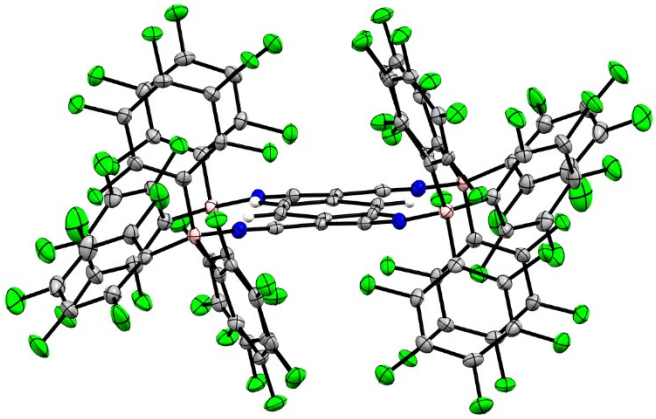


Figure S4. Structure of the anion in the thianthrenium salt.

Angle between N4 plane and plane of the central four carbon atoms (bound to hydrogen): 4.75°.

Vibrational Spectroscopy

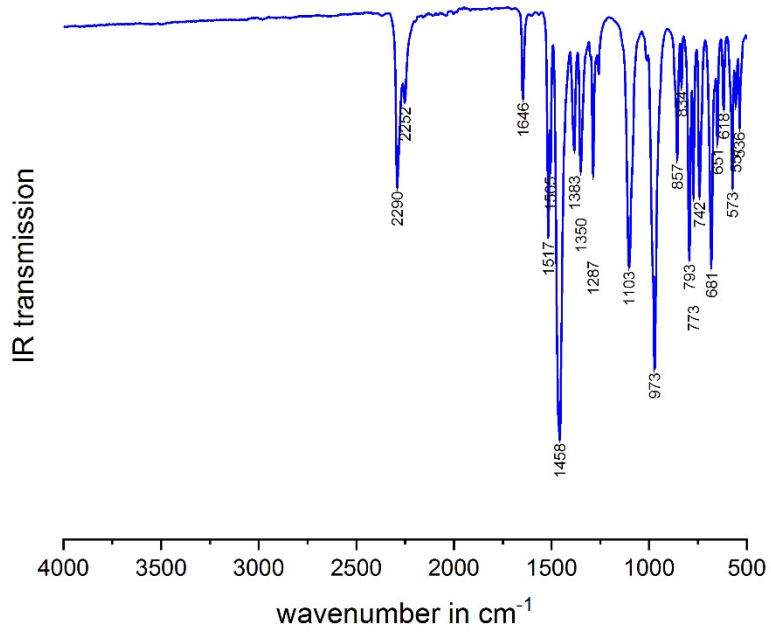


Figure S5. IR Spectrum (ATR, powder) of $[(C_6H_4)_2S_2]^+$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^-$.

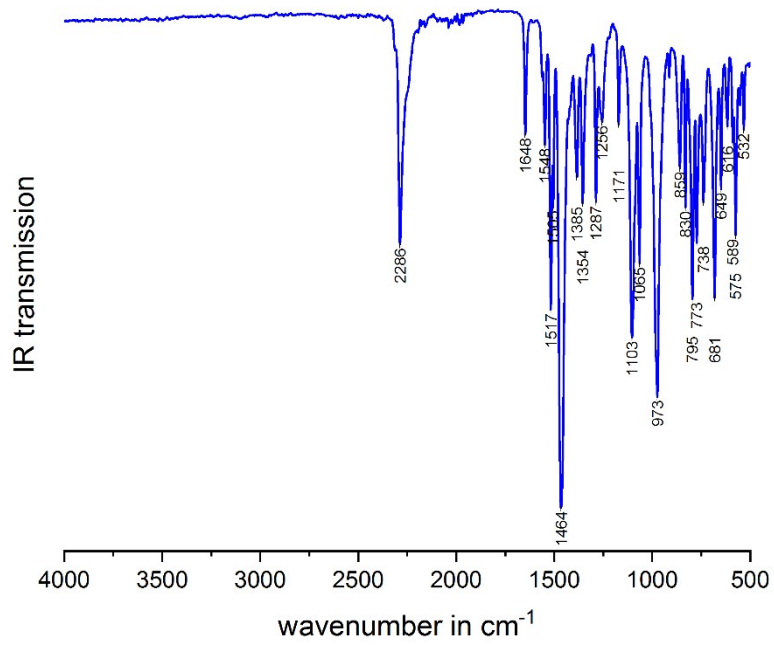


Figure S6. IR Spectrum (ATR, powder) of $[N(C_6H_4Br)_3]^+$ $[TCNQ{\cdot}4B(C_6F_5)_3]^-$.

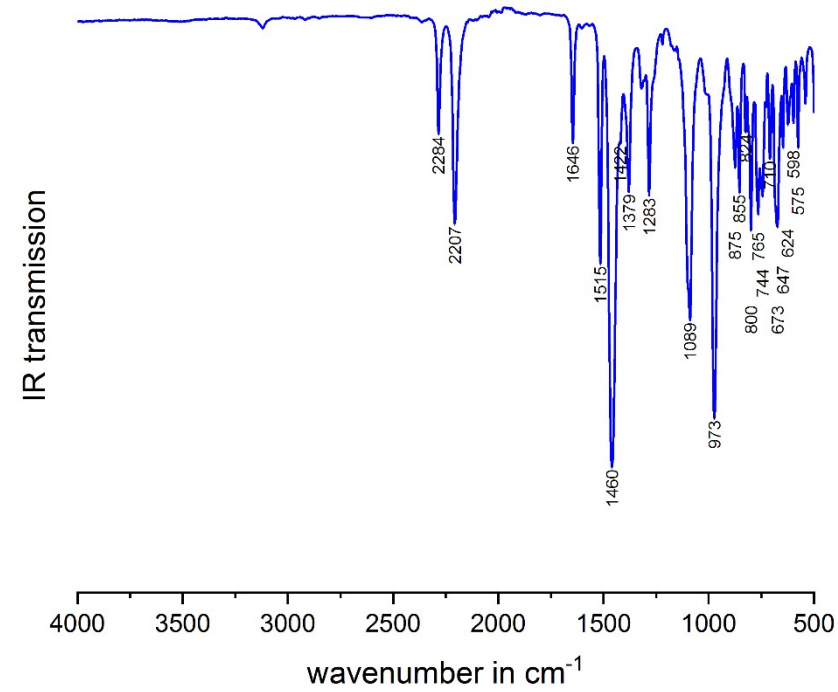


Figure S7. IR Spectrum (ATR, powder) of $[Cp_2Fe]^+_2$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^{2-}$.

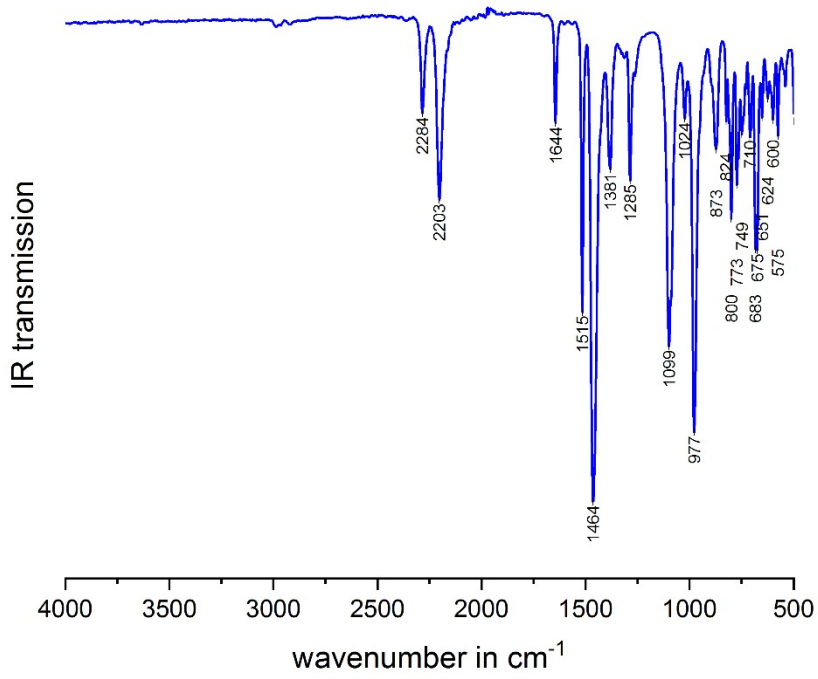


Figure S8. IR Spectrum (ATR, powder) of $[Cp^*_2Co]^+_2$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^{2-}$.

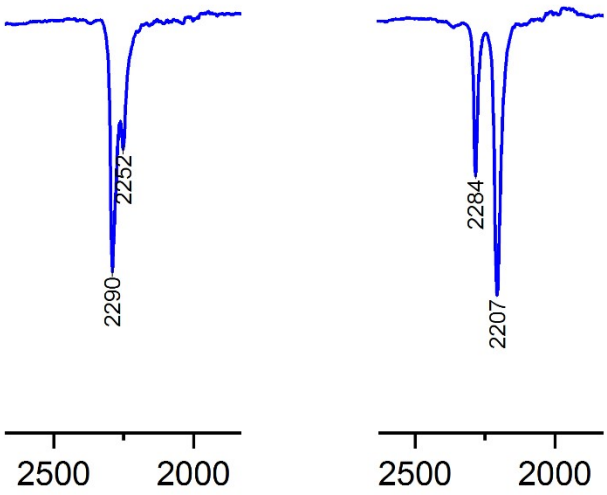


Figure S9. Region of $\tilde{\nu}$(C≡N) vibrations in the IR spectra of $[(C_6H_4)_2S_2]^+$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^-$ (left) and $[Cp_2Fe]^+_2$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^{2-}$ (right).

NMR Spectra

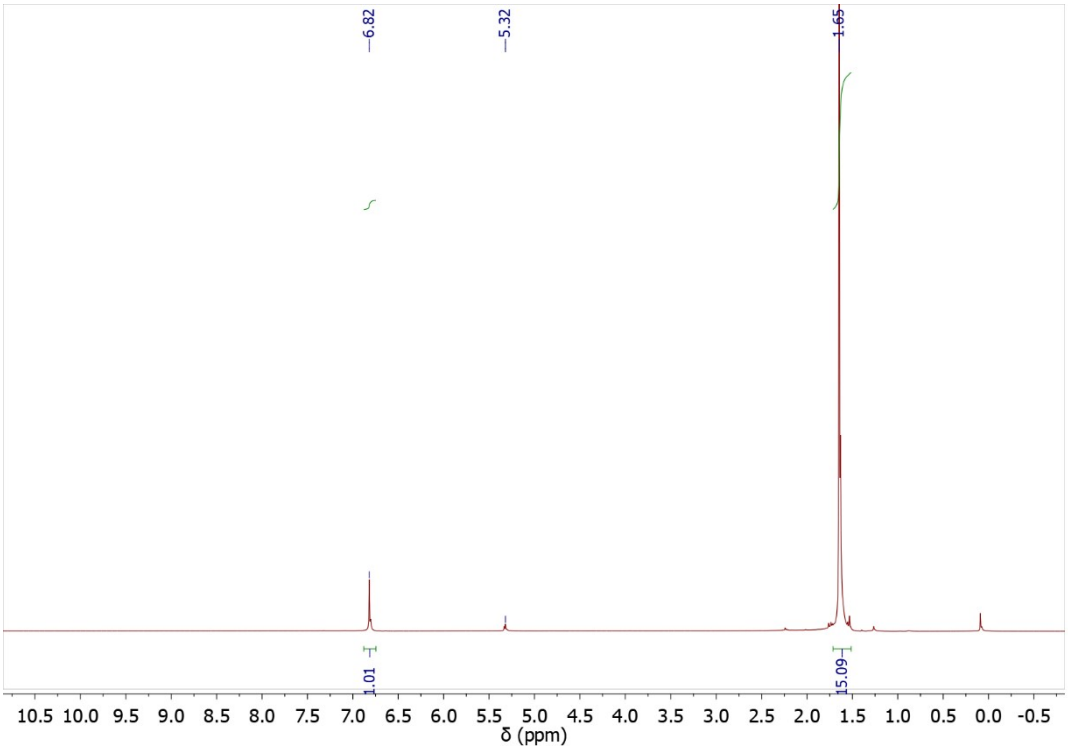


Figure S10. ^{1}H NMR of $[Cp^*_2Co]^+_2$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^{2-}$ in CD_2Cl_2 (700 MHz, RT).

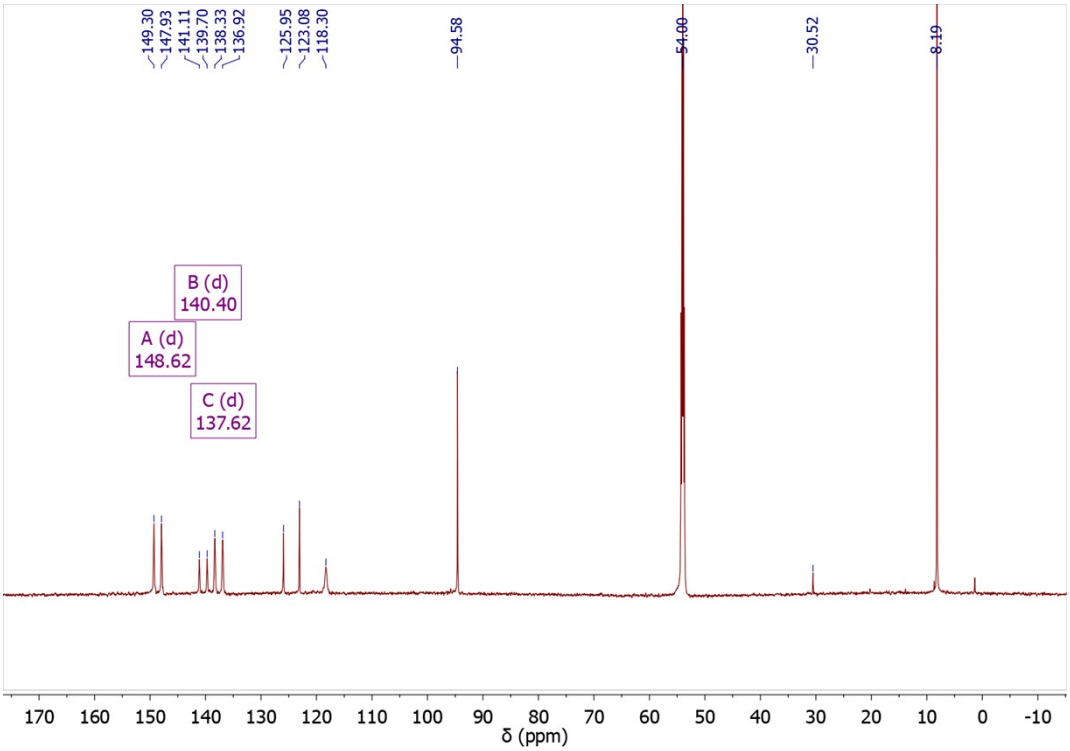


Figure S11. ^{13}C NMR of $[Cp^*_2Co]^+_2$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^{2-}$ in CD_2Cl_2 (176 MHz, RT).

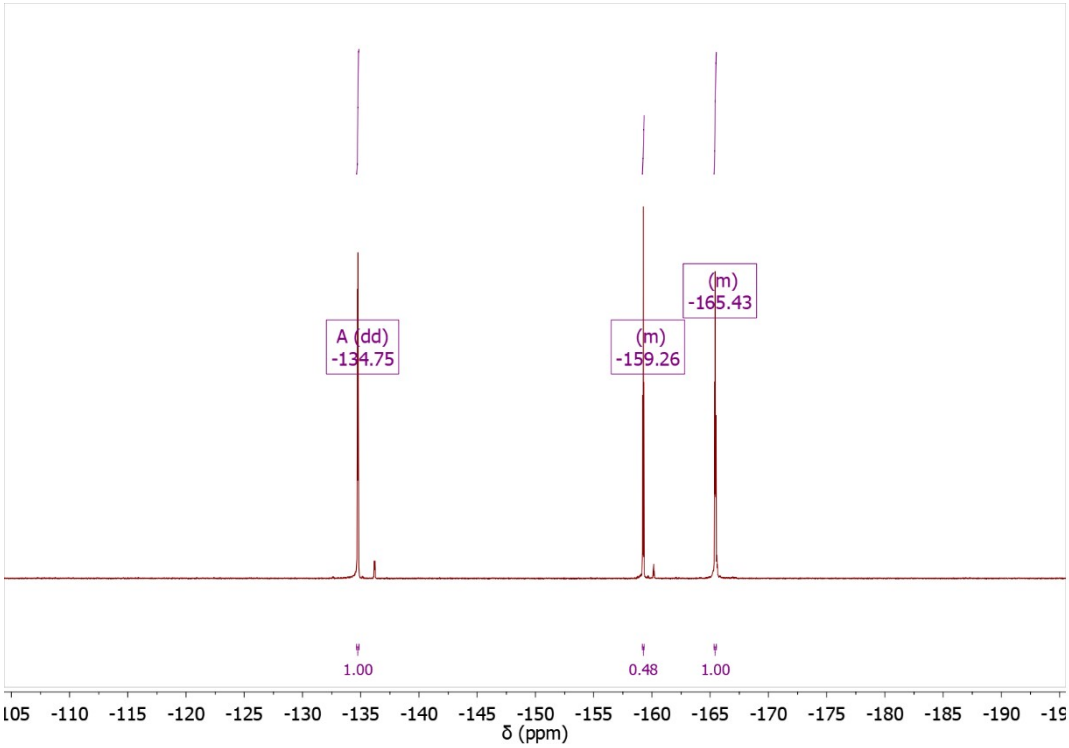


Figure S12. ^{19}F NMR of $[Cp^*_2Co]^+_2$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^{2-}$ in CD_2Cl_2 (377 MHz, RT).

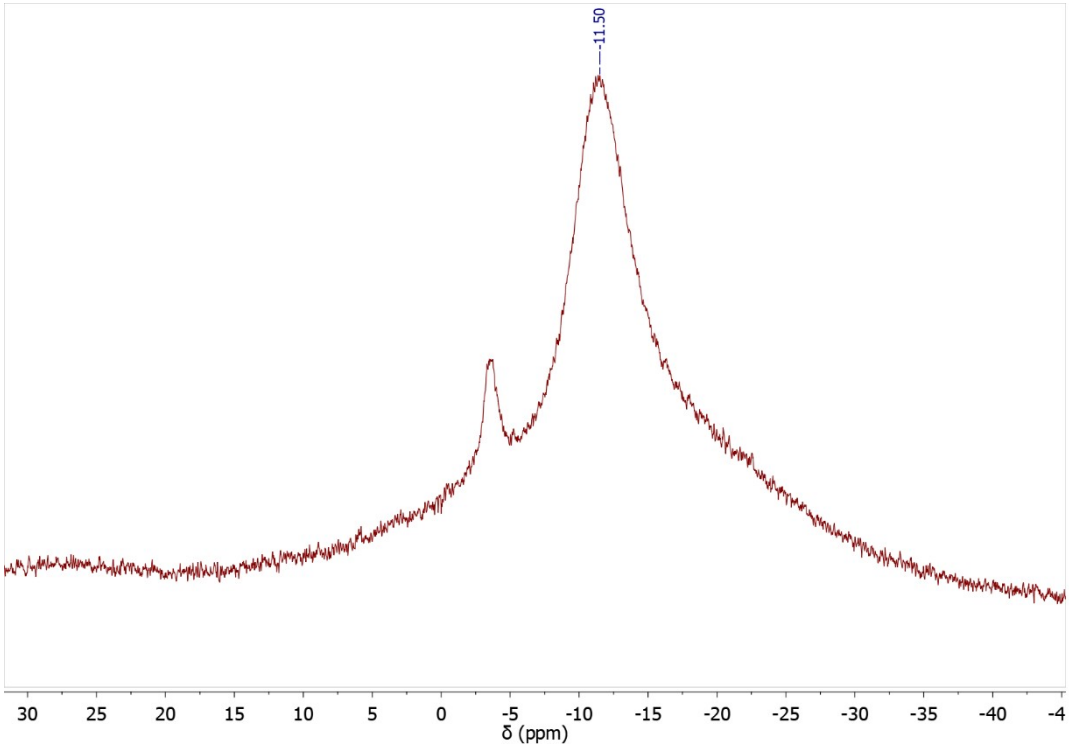


Figure S13. ^{11}B NMR of $[Cp^*_2Co]^+_2$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^{2-}$ in CD_2Cl_2 (128 MHz, RT).

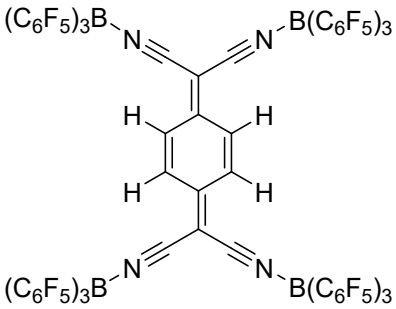
DFT Calculations

Due to the large number of atoms in the 4:1 adducts, B3LYP-D3(BJ)/Def2-SVP was chosen for the structure optimizations and frequency calculations. Adiabatic electron affinities were calculated as energy differences between the optimized structures of the neutral, monoanionic and dianionic adducts. For frequency calculations a scaling factor of 0.9671 was used.[10] Gaussian16 was used for the calculations.[11] Electrostatic surface potentials were generated with the software MultiWFN and visualized with VMD.[12, 13]

TCNQ singlet S=0 HF= -678.0912122 Hartree

7	-4.595594000	-3.837137000	0.000000000
7	-0.312967000	-4.950813000	0.000000000
7	1.786304000	3.121240000	0.000000000
7	-2.496288000	4.235028000	0.000000000
6	-1.127412000	-4.121918000	0.000000000
6	-3.480522000	-3.510021000	0.000000000
6	0.671225000	2.794156000	0.000000000
6	-1.681873000	3.406100000	0.000000000
6	-0.694642000	2.372145000	0.000000000
6	-2.114662000	-3.087983000	0.000000000
6	-1.764288000	-1.740704000	0.000000000
6	-0.375423000	-1.327411000	0.000000000
6	-0.033499000	-0.012711000	0.000000000
6	-1.045018000	1.024867000	0.000000000
6	-2.775803000	-0.703128000	0.000000000
6	-2.433874000	0.611570000	0.000000000
1	-3.828199000	-0.994003000	0.000000000
1	-3.211204000	1.378318000	0.000000000
1	0.401917000	-2.094146000	0.000000000
1	1.018900000	0.278151000	0.000000000

TCNQ·4B(C_6F_5)$_3$ singlet S=0 HF=-9504.8228263 Hartree



9	8.700184000	6.605139000	-2.323233000
9	8.838185000	0.066122000	-2.760582000
9	9.611146000	-1.172138000	-0.462383000
9	-9.226961000	-3.010450000	-3.833384000
9	-4.315949000	-3.254346000	4.857668000
9	-6.681831000	-2.752677000	-4.781300000
9	-5.822348000	-0.998871000	5.120135000
9	-3.714866000	-4.216170000	2.448226000

9	-9.654194000	-3.310911000	-1.157954000
9	-7.602569000	-3.323999000	0.548546000
9	7.029672000	2.057437000	-2.681085000
9	6.570516000	8.011763000	-3.276751000
9	8.521105000	-0.398950000	1.928663000
9	-1.953478000	-8.117501000	-0.698849000
9	-6.768355000	0.270400000	2.887739000
9	1.976223000	3.162512000	3.145815000
9	8.327413000	4.302646000	-1.002779000
9	-4.394763000	-7.929022000	0.512813000
9	3.600624000	4.559785000	4.838729000
9	-0.787728000	-5.862876000	-1.745769000
9	4.033150000	7.073611000	-2.885445000
9	2.801315000	2.453087000	0.734489000
9	-6.174339000	-0.684159000	0.456561000
9	6.767246000	1.574870000	2.035027000
9	-4.595444000	-2.777981000	-3.081579000
9	-5.623278000	-5.535293000	0.712220000
9	6.122226000	5.241442000	4.032911000
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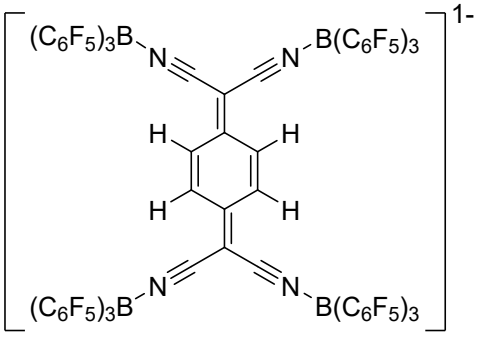

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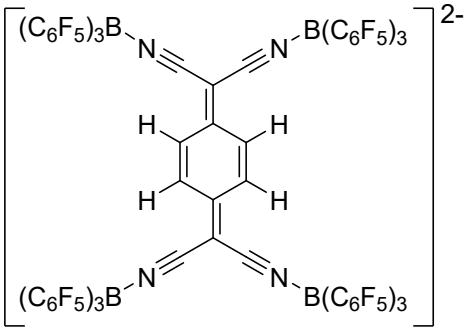

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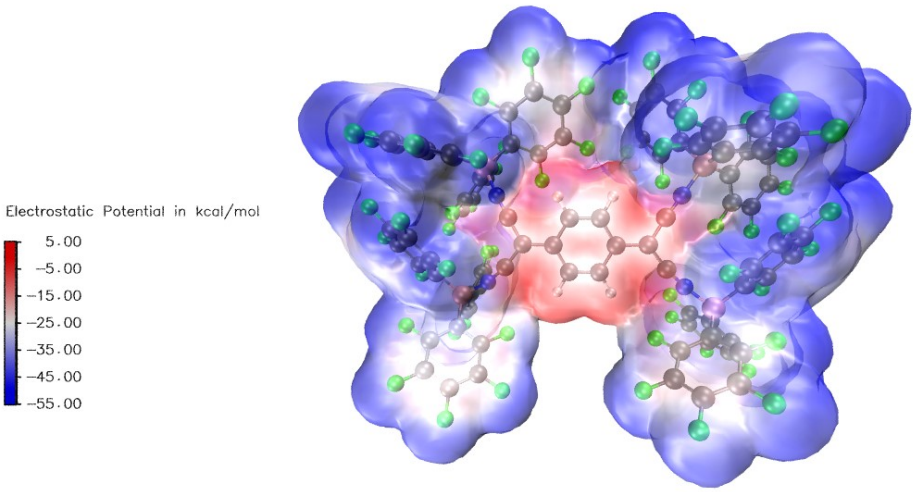

Figure S14. Calculated electrostatic potential of the [TCNQ·4 $B(C_6F_5)_3]^-$ monoanion, maxima in red, minima in blue.

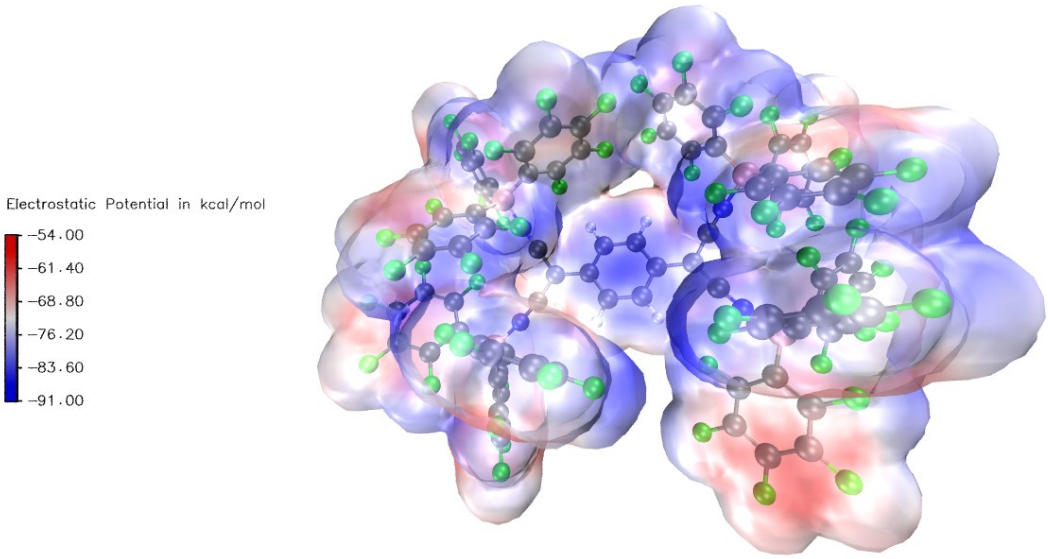

Figure S15. Calculated electrostatic potential of the $[TCNQ{\cdot}4\ B(C_6F_5)_3]^{2-}$ dianion, maxima in red, minima in blue.

EPR

Tris(4-Bromophenyl)aminium radical cation + TCNQ·4 $B(C_6F_5)_3$ radical anion

The isotropic spectrum, recorded in DCM at room temperature, shows two signals. The one with g_{iso}=2.0143 can be assigned to the radical cation. The isotropic g-value corresponding to the radical anion is g_{iso}=2.0026.

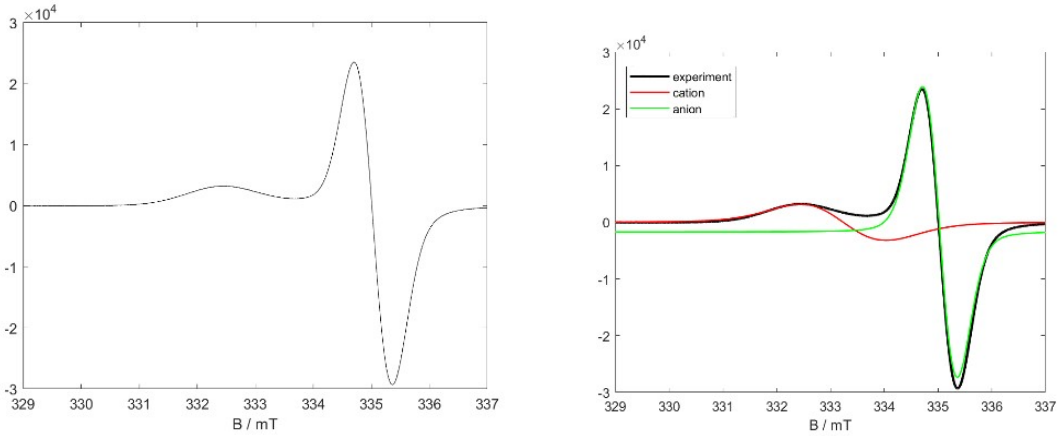

Figure S16. Measured EPR spectrum and simulation of $[N(C_6H_4Br)_3]^+$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^-$.

Thianthrenium radical cation + TCNQ·4 $B(C_6F_5)_3$ radical anion

The isotropic spectrum, recorded in DCM at room temperature, shows two signals. The one with g_{iso}=2.00788 can be assigned to the radical cation. The signal shows some indication of hyperfine structure, yet it is not completely resolved. The isotropic g-value corresponding to the radical anion is g_{iso}=2.00266.

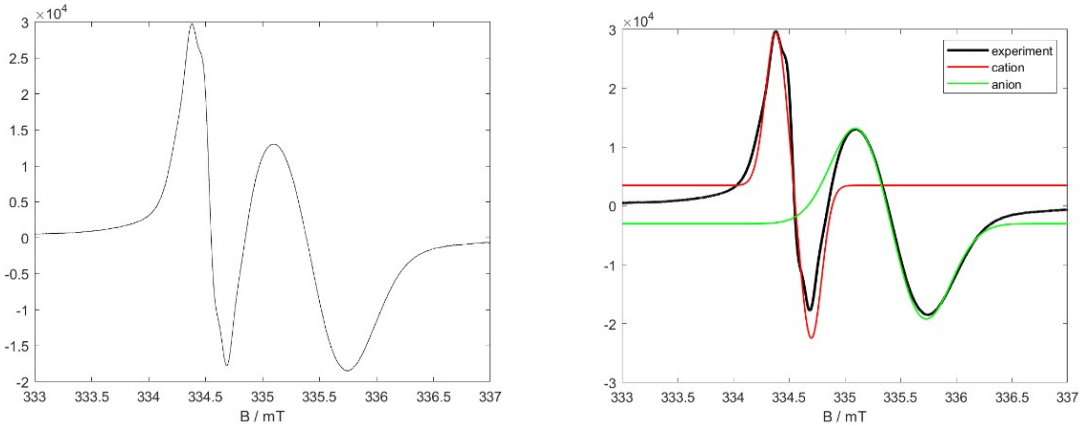

Figure S17. Measured EPR spectrum and simulation of $[(C_6H_4)_2S_2]^+$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^-$.

Ferrocenium radical cation + TCNQ·4 $B(C_6F_5)_3$ radical anion

The isotropic spectrum, recorded in DCM at room temperature, shows only one signal, since the ferrocenium radical cation is EPR silent at room temperature. The corresponding isotropic g-value of the radical anion is g_{iso}=2.00238.

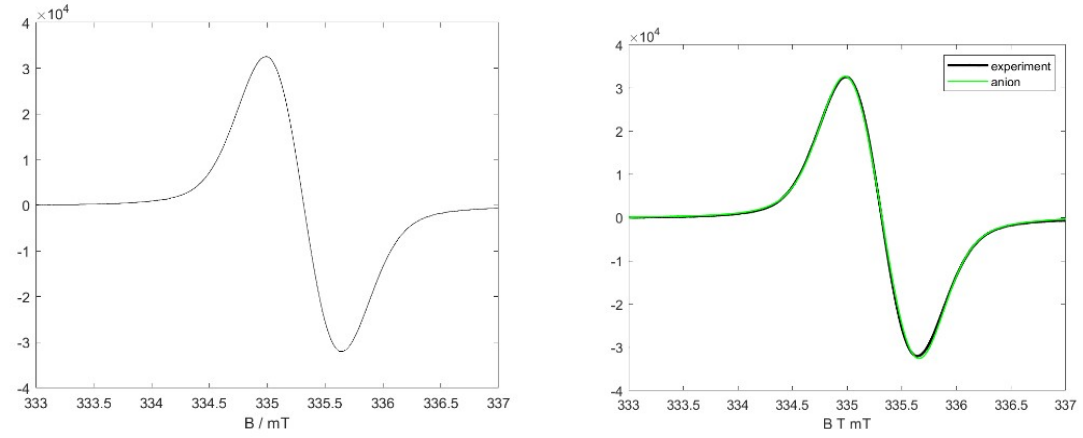

Figure S18. Measured EPR spectrum and simulation of $[Cp_2Fe]^+$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^-$.

Electrochemistry

Cyclic voltammetry was performed on an Interface 1010 B Potentiostat/Galvanostat/ZRA from Gamry Instruments. The investigations were carried out starting from 0 V going to the reduction first and then to the oxidation. The measurements were performed at a scan rate of 100 mV/s in anhydrous solvents under argon atmosphere without extra supporting and platinum wires as working-, counter-, and quasi-reference electrodes. The voltammograms were internally referenced against $Cp_2Fe^{0/+}$ using decamethylferrocene as internal standard. The software OriginPro 2017G was used to plot the data.[14]

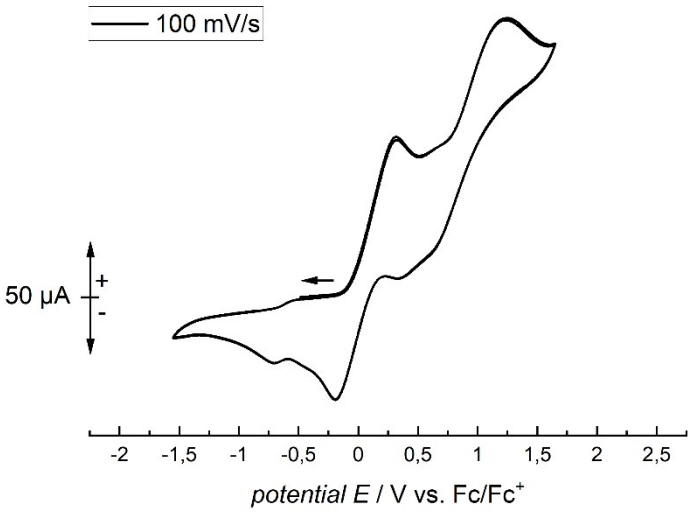

Figure S19. Cyclic voltammogram of $[Cp^*_2Co]^+_2$ $[TCNQ{\cdot}4\ B(C_6F_5)_3]^{2-}$ measured in CH_2Cl_2.

References

1. S. Stoll and A. Schweiger, *J. Magn. Reson.*, 2006, **178**, 42-55.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
3. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.
4. G. M. Sheldrick, SHELXL Version 2014/7, Program for Crystal Structure Solution and Refinement, Göttingen, Germany, 2014.
5. G. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.
6. K. Brandenburg. Diamond: Crystal and Molecular Structure Visualization. http://www.crystalimpact.com/diamond.
7. Persistance of Version Pty. Ltd. Persistance of Vision Raytracer (Version 3.6). Ltd., Persistence of Vision Pty. 2004, Retrieved from http://www.povray.org/download/.
8. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.*, 2006, **39**, 453-457.
9. P. A. Albrecht, S. M. Rupf, M. Sellin, J. Schlögl, S. Riedel and M. Malischewski, *CSD Communications*, 2022.
10. M. K. Kesharwani, B. Brauer and J. M. L. Martin, *J. Phys. Chem. A.*, 2015, **119**, 1701-1714.

11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, J. E. P. Jr., F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
12. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.
13. W. Humphrey, A. Dalke and K. Schulten, *J. Molec. Graphics*, 1996, **14**, 33-38.
14. OriginPro, 2017G. OriginLab Corporation, Northampton, MA, USA.