Supplementary Information

Ferrocene-functionalized polyheteroacenes for the use as cathode active material in rechargeable batteries

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Experimental methods

Instrument and measurement

NMR spectra were recorded on a Bruker Avance 400 (1H NMR: 400 MHz, 13C NMR: 125 MHz) at 25 °C. Chemical shift values (δ) are expressed in parts per million using residual solvent protons (1H NMR, δH = 7.26 for CDCl3; δH = 3.31 for CD3OD; 13C NMR: δC = 77.16 for CDCl3; δC = 49.00 for CD3OD) as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), m (multiplet). Coupling constants (J) relate to proton-proton couplings. GC/EI-MS (70 eV) measurements were performed on a Shimadzu GC-MS-QP2010 SE. Chemical ionisation (CI) mass spectra were measured on a Finnigan MAT SSQ-7000. Melting points were determined using a Büchi B-565 and a Mettler Toledo DSC 823e. Thermogravimetric analyses (TGA) were carried out with a TGA/SDTA 851e from Mettler Toledo. Elemental analyses were performed on an Elementar Vario EL. FT-IR spectra were measured with a Perkim Elmer Spectrum 2000.

The diffraction data of a brownish crystal of M1 were collected in a stream of nitrogen at 180 K on a Agilent SuperNova, Cu at zero, Atlas CCD using graphite-monochromated Cu Kα radiation. Data collection strategy was performed with the APEX2 software, data reduction,
absorption correction and cell refinement with CrysAlisPro171. The structure was solved by
direct methods with SHELXL-2016/6, revealing all atoms of M1. H atoms were discernible
from difference Fourier maps during refinement on F2 with SHELXL-97. For the final model,
all atoms were refined anisotropically.

Cyclic voltammetry experiments were performed with a computer-controlled Autolab
PGSTAT30 potentiostat in a three-electrode single-compartment cell with a platinum work-
ing electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. All po-
tentials were internally referenced to the ferricenium/ferrocene (Fc+/Fc) redox couple. Spec-
troelectrochemical measurements of the polymer films were carried out in a 0.1 M solution
of tetrabutylammonium hexafluorophosphate in dry acetonitrile. The applied setup has been
described in the literature. A platinum working electrode, a Ag/AgCl reference electrode,
and a platinum sheet as the counter electrode were used. During the recording of the UV-
Vis-NIR spectra the applied potential was kept constant. Instrumental artefacts were re-
moved and marked in the spectra. Moreover, the absorption in the UV-Vis-NIR region below
860 nm was adjusted to the absorption at higher wavelengths to obtain continuous spectra.
The UV-Vis-NIR spectra were recorded on a Perkin Elmer Lambda 19 spectrometer.

Materials
Copper(II) tetrafluoroborate was provided from Aldrich. N,N'-dicyclohexylcarbodiimide
(DCC), 4-dimethylaminopyridine (DMAP) and ferrocenecarboxylic acid 3 were provided from
Alfa Aesar. Solvents were purchased from Merck and Aldrich, purified, and dried by standard
methods prior to use. 4H-cyclopenta[2,1-b:3,4-b']dithiophene-4-one2 and 4H-dithieno[3,2-b:
2',3'-d]pyrrole 3 were prepared according to literature procedures.

Syntheses

4H-cyclopenta[2,1-b:3,4-b']dithiophene-4-one (1). 4H-cyclopenta[2,1-b:3,4-b']dithiophe-
ne-4-one (230 mg, 1.2 mmol), dry THF (7 mL) and anhydrous NiCl2 (0.5 g, 3.6 mmol) were pla-
ced in a Schlenk tube under argon. NaBH4 (0.4 g, 10.8 mmol) was added and the formation
of a black precipitate of nickel boride was observed immediately. The reaction mixture was
stirred at room temperature and its progress was monitored by TLC for disappearance of
starting material. The reaction mixture was diluted with dichloromethane and filtered
through a celite pad. The filtrate was diluted with water and extracted with CH2Cl2 (3×). The
combined organic layers were dried over Na$_2$SO$_4$, concentrated, and purified by column chromatography (n-hexane:EtOAc 1:9). The desired compound was obtained as a white solid (210 mg, 1.08 mmol, 90%). Mp 165.7-167.1°C. $^1$H NMR (CD$_3$OD, ppm): δ = 7.25 (d, 2H, $J = 4.9$ Hz), 7.13 (d, 2H, $J = 4.9$ Hz), 5.26 (s, 1H). $^{13}$C NMR (CD$_3$OD, ppm): δ = 154.7, 139.1, 126.5, 123.9, 70.4. FT-IR (KBr, 25 °C, cm$^{-1}$): ν = 3370, 3303, 3076, 1322, 1299, 1241, 1210, 1104, 1050, 921, 801, 712, 690. Elemental analysis: calc. (%) for C$_9$H$_6$OS$_2$: C 55.64, H 3.11, S 33.01; found: C 56.03, H 2.95, S: 32.19.

4-Ferrocene-4H-cyclopenta[2,1-b:3,4-b']dithiophene (CPDT-Fc, M1). In a closed Schlenk tube 4H-cyclopenta[2,1-b:3,4-b']dithiophene-4-ol 1 (140 mg, 0.7 mmol) and ferrocene carboxylic acid 3 (232 mg, 1 mmol) were dissolved in dry CH$_2$Cl$_2$ (15 mL). The solution was stirred at room temperature and a mixture of N,N'-dicyclohexylcarbodiimide (205 mg, 1 mmol) and 4-dimethylaminopyridine (150 mg, 0.8 mmol) were added in one portion. The solution was stirred at room temperature for two days, filtrated through a pad of celite, and concentrated. The crude product was purified by column chromatography (petroleum ether:EtOAc 5:1), followed by recrystallization from n-hexane. The desired monomer M1 was provided as orange needles (270 mg, 0.66 mmol, 92%). Mp 140.4°C (DSC). $^1$H NMR (CDCl$_3$, ppm): δ = 7.20 (d, $J = 4.9$ Hz, 2H), 7.16 (d, $J = 4.9$ Hz, 2H), 6.38 (s, 1H), 4.85 (t, $J = 1.9$ Hz, 2H), 4.42 (t, $J = 1.9$ Hz, 2H), 4.19 (s, 5H). $^{13}$C NMR (CDCl$_3$, ppm): δ = 127.3, 149.2, 139.7, 125.6, 123.7, 71.6, 70.4, 69.9, 69.5. FT-IR (KBr, 25 °C, cm$^{-1}$): ν = 3096, 2920, 1707, 1653, 1636, 1561, 1459, 1370, 1265, 1134, 1039, 933, 819, 702, 699, 503, 498, 479, 432, 412. Elemental analysis: calc. (%) for C$_{20}$H$_{14}$FeO$_2$S$_2$: C 59.10, H 3.47, S 15.78; found: C 59.09, H 3.52, S 15.21. GC/EI-MS: m/z = 406 [M + H]$^+$, 177 [M–OCOFc + H]$^+$.

Poly(4-ferrocene-4H-cyclopenta[2,1-b:3,4-b']dithiophene) (pCPDT-Fc, P1). A mixture of CPDT-Fc M1 (250 mg, 0.6 mmol) and Cu(BF$_4$)$_2$ (583 mg, 2.2 mmol) in acetonitrile (20 mL) was heated at 60 °C for 2 days. At the end of the reaction, a black precipitate was obtained, isolated via centrifugation, and dried in vacuo. Then, the black polymer was successively washed with acetonitrile, water, methanol, and chloroform. The desired pCPDT-Fc P1 was isolated as a black powder (180 mg, 0.44 mmol, 73%). FT-IR (KBr, 25 °C, cm$^{-1}$): ν = 3085, 2925, 1715, 1454, 1374, 1264, 1128, 1056, 946, 916, 820, 764, 504, 499, 483, 468.

4-Ferrocene-4H-dithieno[3,2-b:2',3'-d]pyrrole (DTP-Fc, M2). A suspension of the unsubstituted DTP 2 (430 mg, 2.4 mmol), ferrocene carboxylic acid 3 (732 mg, 3.1 mmol), N,N'-dicyclohexylcarbodiimide (644 mg, 3.1 mmol), and 4-dimethylaminopyridine (323 mg,
2.6 mmol) in dichloromethane (20 mL) was stirred at room temperature for two days. The reaction mixture was filtrated and concentrated under reduced pressure. The obtained residue was purified by column chromatography on silica gel (petroleum ether:CH₂Cl₂ 3:1) to afford the desired monomer **M2** as an orange solid (907 mg, 2.32 mmol, 97%). Mp 122-124 °C. **¹H NMR** (CDCl₃, ppm): δ = 7.21-7.15 (m, 4H), 4.95-4.93 (m, 2H), 4.55-4.54 (m, 2H), 4.28 (s, 4H). **¹³C NMR** (CDCl₃, ppm): δ = 168.9, 143.4, 124.1, 120.7, 116.8, 76.6, 72.4, 71.2, 71.1. **FT-IR** (KBr, 25 °C, cm⁻¹): ν = 2976, 2934, 2837, 1727, 1614, 1556, 1461, 1372, 1333, 1291, 1255, 1233, 1209, 1176, 1107, 1048, 1027, 856, 836, 779, 754, 671, 581, 567, 503.

Elemental analysis: calc. (%) for C₁₉H₁₃FeNOS₂: C 58.32, H 3.35, N 3.58, S 16.39; found: C 58.12, H 3.53, N 3.81, S 16.32. CI-MS: m/z (%) = 391 (81) [M + H]⁺.

**Poly(4-ferrocene-4H-dithieno[3,2-b:2',3'-d]pyrrole)** (pDTP-Fc, **P2**). Copper(II) tetrafluoroborate (1.61 g, 6.8 mmol) was added to a solution of DTP-Fc **M2** (665 mg, 1.7 mmol) in dichloromethane (15 mL) and acetonitrile (15 mL). The reaction mixture was heated at 50 °C for two days. Afterwards, the black suspension was filtrated and the filter residue was washed with several solvents (methanol, water, petroleum ether, THF, CH₂Cl₂, and ether) to afford the desired polymer **P2** as a dark blue solid (442 mg, 1.14 mmol, 67%). **FT-IR** (KBr, 25 °C, cm⁻¹): ν = 2922, 1637, 1444, 1375, 1296, 1106, 815, 745, 654, 488, 424, 406.

**X-Ray single crystal structure analysis of CPDT-Fc (M1)**

![Crystal structure of M1](image)

**Figure S1**: Crystal structure of M1 with atomic labels. Displacement ellipsoids are drawn at the 50% probability level.
| **Table S1:** X-ray crystallographic data for M1 |
|------------------------------------------------|
| **Empirical formula** | $C_{20}H_{14}FeO_2S_2$ |
| **Formula weight** | 406.28 |
| **Temperature/K** | 149.95(10) |
| **Crystal system** | orthorhombic |
| **Space group** | $P2_12_12_1$ |
| **a/Å** | 5.86404(10) |
| **b/Å** | 10.14209(16) |
| **c/Å** | 27.2116(4) |
| $\alpha$, $\beta$, $\gamma$/° | 90 |
| **Volume/Å$^3$** | 1618.37(4) |
| **Z** | 4 |
| **$\rho_{calc}$ g/cm$^3$** | 1.667 |
| **$\mu$/mm$^{-1}$** | 1.201 |
| **F(000)** | 832.0 |
| **Crystal size/mm$^3$** | $0.2371 \times 0.2102 \times 0.1142$ |
| **Radiation** | MoKα ($\lambda = 0.71073$) |
| **2θ range for data collection/°** | 5.988 to 58.976 |
| **Index ranges** | $-7 \leq h \leq 7$, $-12 \leq k \leq 13$, $-34 \leq l \leq 34$ |
| **Reflections collected** | 15457 |
| **Independent reflections** | 3954 [$R_{int} = 0.0332$, $R_{Isigma} = 0.0330$] |
| **Data/restraints/parameters** | 3954/0/283 |
| **Goodness-of-fit on $F^2$** | 1.083 |
| **Final R indexes [I>=2σ (I)]** | $R_1 = 0.0255$, $wR_2 = 0.0513$ |
| **Final R indexes [all data]** | $R_1 = 0.0287$, $wR_2 = 0.0528$ |
Table S2: Selected bond distances, angles, and torsion angles from the crystal structure analysis of M1. Atom labels correspond to those on Figure S1.

| Atom1 | Atom2 | Distance (Å) |
|-------|-------|--------------|
| C19   | C17   | 1.367(3)     |
| C17   | C12   | 1.410(4)     |
| C12   | C15   | 1.372(3)     |
| C19   | S1    | 1.724(3)     |
| S1    | C15   | 1.709(2)     |
| C15   | C18   | 1.447(3)     |
| C12   | C13   | 1.518(3)     |
| C18   | C14   | 1.380(3)     |
| C14   | C13   | 1.511(3)     |
| C14   | C16   | 1.415(3)     |
| C16   | C20   | 1.359(4)     |
| C20   | S2    | 1.730(3)     |
| S2    | C18   | 1.705(2)     |
| C13   | O3    | 1.454(3)     |
| O3    | C11   | 1.348(3)     |
| C11   | O1    | 1.212(3)     |
| C11   | C5    | 1.472(3)     |
| C5    | C2    | 1.430(4)     |
| C2    | C1    | 1.411(4)     |
| C9    | C10   | 1.423(4)     |
| C10   | C3    | 1.416(4)     |
| C3    | C5    | 1.430(3)     |
| C5    | Fe1   | 2.034(2)     |
| Fe1   | C4    | 2.033(3)     |
| C4    | GR    | 1.415(4)     |
| GR    | C7    | 1.414(4)     |
| C7    | C6    | 1.414(4)     |
| C6    | C2    | 1.420(4)     |

| Atom1 | Atom2 | Atom3 | Atom4 | Torsion [°] |
|-------|-------|-------|-------|-------------|
| S1    | C15   | C18   | S2    | 2.8(4)      |
| C17   | C12   | C13   | O3    | 5.7(4)      |
| C16   | C14   | C13   | O3    | -58.9(3)    |
| C12   | C13   | O3    | C11   | -83.7(2)    |
| C13   | O3    | C11   | O1    | 1.4(3)      |
| C13   | O3    | C11   | C5    | 180.0(2)    |
| O3    | C11   | C5    | C1    | -3.7(4)     |

Table S3: Intermolecular short contact lengths (below van der Waals distances). Atom labels correspond to those on Figure S1.

| Atom in molecule 1 | Atom in molecule 2 | Length (Å) | Symmetry operation1 | Symmetry operation2 |
|--------------------|--------------------|------------|---------------------|---------------------|
| S2                 | C19                | 3.486      | x,y,z               | -1+x,y,z            |
| C20                | C3                 | 3.349      | x,y,z               | -1+x,y,z            |
| H5                 | H18                | 2.386      | x,y,z               | -1+x,y,z            |
| S1                 | H19                | 2.98       | x,y,z               | -1/2+x,1.5-y,1-z    |
| C12                | H19                | 2.891      | x,y,z               | -1/2+x,1.5-y,1-z    |
| C19                | H19                | 2.804      | x,y,z               | -1/2+x,1.5-y,1-z    |
| H4                 | C8                 | 2.843      | x,y,z               | -x,1/2+y,1/2-z      |

6
Infrared spectra of CPDT-Fc (M1), pCPDT-Fc (P1), DTP-Fc (M2), and pDTP-Fc (P2)

Figure S2: Infrared spectra (KBr pellets, 25 °C) of CPDT-Fc M1 (left, black) and pCPDT-Fc P1 (left, red), respectively DTP-Fc M2 (right, black) and pDTP-Fc P2 (right, red).

TGA and DSC measurements of pCPDT-Fc (P1) and pDTP-Fc (P2)

Figure S3: TGA measurements of pCPDT-Fc P1 (left) and pDTP-Fc P2 (right).

Figure S4: DSC measurements of pCPDT-Fc P1 (left) and pDTP-Fc P2 (right).
Cyclic voltammetry of monomers M1 and M2

Figure S5: Cyclic voltammograms of CPDT-Fc M1 (left) and DTP-Fc M2 (right) with a scan rate of 100 mV/s in 0.1 M TBAPF₆ in acetonitrile.

Cyclic voltammetry of polymers P1 and P2

Figure S6: Cyclic voltammograms of pCPDT-Fc P1 in 0.1 M TBAPF₆ in CH₂Cl₂ conducting 30 scans with a scan rate of 100 mV/s.

Figure S7: Cyclic voltammograms of pDTP-Fc P2 in 0.1 M TBAPF₆ in CH₂Cl₂ conducting 30 scans with a scan rate of 100 mV/s.
Electrode preparation and battery tests

Composite electrodes with a composition of 56.6 wt.% active material (PCPDT-Fc or PDTP-Fc), 33.0 % carbon black, and 10.4 wt.% poly(tetrafluoroethylene) (PTFE) were prepared as follows: Approx. 100 mg active material and 60 mg carbon black (Imerys, Super P Li) were pre-mixed by grinding in an agate mortar. Then, the appropriate amount of PTFE powder (Dyneon, TF 2025Z) was added under further grinding, to obtain a plastic mass, which was then calendered into a free-standing film by roll pressing. Electrodes with 12 mm diameter and mass loadings between 6.5 and 7.5 g/cm$^2$ were punched out and pressed onto Al expanded metal grid as current collector, and finally dried at 80 °C under dynamic vacuum (~1 mbar) overnight.

T-type 3-electrode cells were built from these electrodes and Li metal as counter and reference electrodes using 1 M LiPF$_6$ / ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1 by wt.) (Ube Industries) as electrolyte and 3 layers of borosilicate glass microfibre non-wovens (Whatman, GF/A) as separator.

Cyclic voltammograms were recorded with a VMP3 potentiostat from Biologic, using a scan rate of 0.1 mV/s. Galvanostatic cycling tests were performed with a CTS-Lab cycler from Basytec, using a current rate of 0.1C and cut-off potentials of 2.5 / 2.7 and 3.9 V vs. Li$^+$/Li. (A current rate of 1C corresponds to the current which is needed to charge or discharge the theoretical capacity of the material in 1 h. For instance, the theoretical capacity of PCPDT-Fc is 66.3 mAh/g, therefore the 1C rate is 66.3 mA/g, and the 0.1C rate is 6.63 mA/g.) The specific capacities mentioned in the text refer to the mass of active material only.

References

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