Zuschriften

TTF–TCNQ-
Diade
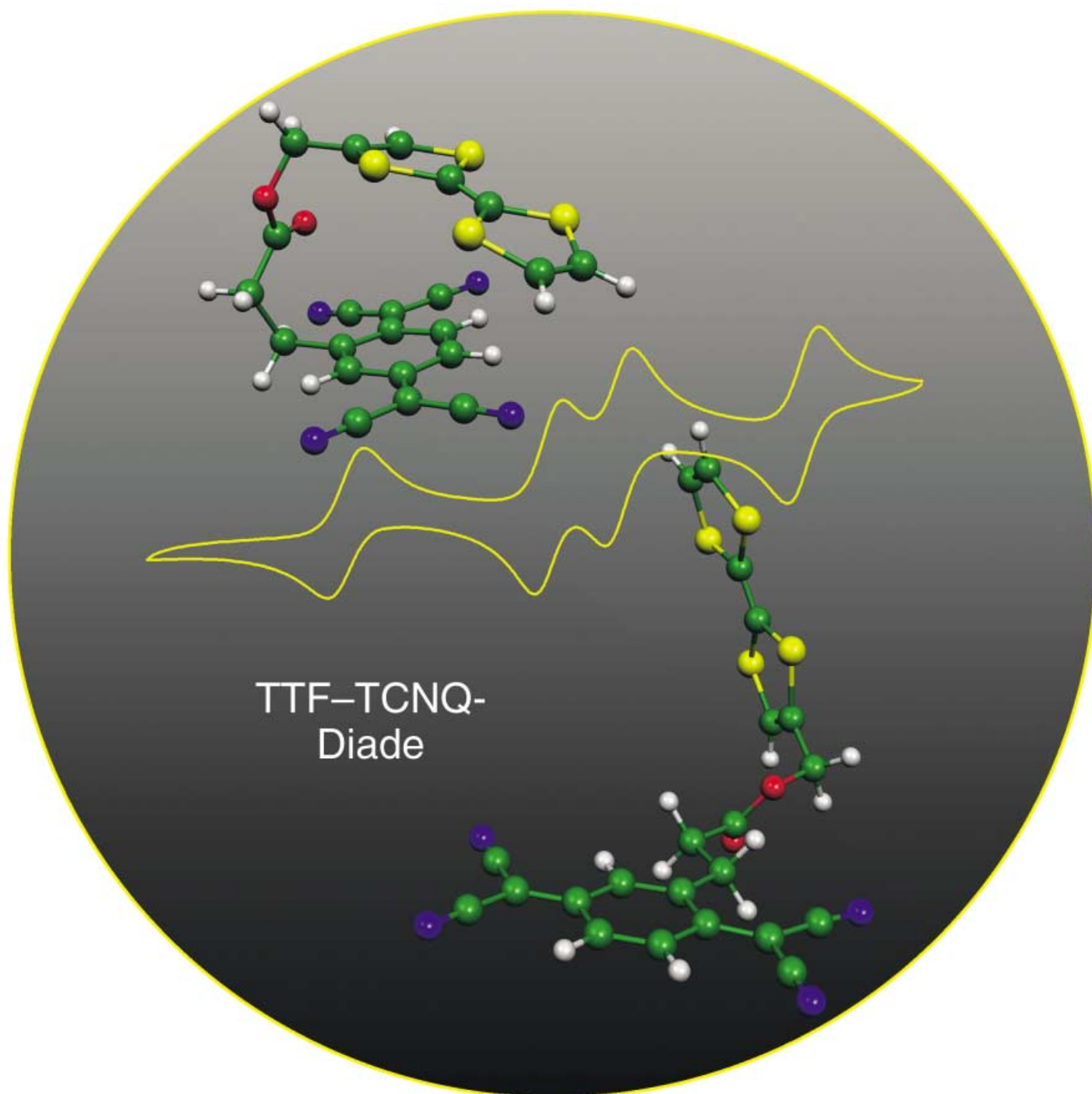
M. R. Bryce et al. beschreiben auf den folgenden Seiten die beiden abgebildeten Konformere einer Verbindung, in der eine Tetrathiafulvalen(TTF)-Donoreinheit kovalent mit einer Tetracyanchinodimethan(TCNQ)-Acceptoreinheit verknüpft ist. Die bemerkenswert kleine HOMO-LUMO-Lücke ermöglicht einen einfachen thermisch angeregten Elektronentransfer.

A Covalent Tetrathiafulvalene–Tetracyanoquinodimethane Diad: Extremely Low HOMO–LUMO Gap, Thermoexcited Electron Transfer, and High-Quality Langmuir–Blodgett Films**

Dmitrii F. Perepichka, Martin R. Bryce,*
Christopher Pearson, Michael C. Petty,
Eric J. L. McInnes, and Jing P. Zhao

The challenge of covalently linking an electron donor tetrathiafulvalene (TTF) moiety to an electron acceptor tetracyano-*p*-quinodimethane (TCNQ) moiety was initiated in a theoretical paper by Aviram and Ratner published in 1974,[1] shortly after the first report[2] of metallic conductivity in the intermolecular 1:1 charge-transfer complex (CTC) formed between TTF and TCNQ. It was proposed that a single donor–acceptor molecule (specifically a TTF-σ-TCNQ diad) when aligned between two electrodes could serve as a rectifier of electric current, because the TTF$^{+\cdot}$-σ-TCNQ$^{-\cdot}$ state (supporting direct electron flow) is highly preferable over TTF$^{-\cdot}$-σ-TCNQ$^{+\cdot}$ (which is required for reverse electron flow).[1] Since then numerous attempts to synthesize TTF–TCNQ hybrid molecules have been undertaken. Such covalent diads have also been sought as a means of controlling the unpredictable stoichiometry of CTCs to obtain organic metals[3] and energy-harvesting materials for solar cells.[4] However, the task of covalently coupling a strong π-electron donor to a strong π-electron acceptor (which is required to achieve the unusual electronic properties in the diad, including rectification behavior[5]) is extremely difficult,[4b, 6] although many different acceptor moieties with moderate electron affinity have been attached to TTF.[4b, 7] For example, TTF has been linked to tetracyanoanthraquinodimethane (TCNAQ)[8], which is not a "true" TCNQ system due to the

much weaker acceptor properties that result from its buckled structure. Several TTF–benzoquinone diads have been identified as potential precursors to TTF–TCNQ, but all attempts at converting the quinone moiety to the corresponding TCNQ derivative have been unsuccessful[7] due to the sensitivity of the TTF nucleus to the acidic conditions ($TiCl_4$) of this reaction.

In the first report in 1976 claiming covalent linkage of TTF and TCNQ, Hertzler described the reaction of a TTF–diisocyanate with a TCNQ–dialcohol which could reasonably form a TTF–TCNQ polyurethane.[9] However, the only characterization data reported for the intractable reaction product were elemental analysis ($\delta > 1\%$) and electrical conductivity ($\sigma_{rt} = 10^{-7}$ S cm^{-1}). In 1984 Panetta et al. reported that the coupling of suitably functionalized TTF and TCNQ units gave EPR-active products, the structures of which were not convincingly established.[10] In particular, the absence of TCNQ reduction waves in cyclic voltammetry (CV) experiments seems inconsistent with the proposed TTF–TCNQ diad structure. No further experimental investigation has been published, although the structures of postulated TTF–TCNQ diads have recurred in several review articles.[4b, 7, 11] We recently reported TTF-σ-polynitrofluorene diads which are highly electrochemically amphoteric systems ($E_{ox}^0 - E_{red}^0 \approx 0.3$ V).[12] We now present the first well-characterized TTF-σ-TCNQ diad, and describe the unusual physical properties of this compound.

The key idea allowing a covalent coupling of TTF and TCNQ moieties was to use highly reactive functionalities (an acid chloride and an alkoxide anion), which can compete with the electron-transfer and following side reactions (Scheme 1).
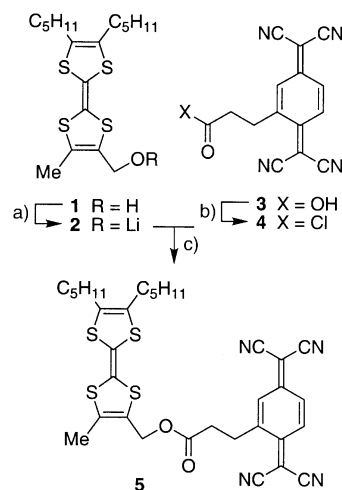
Scheme 1. Synthesis of TTF-σ-TCNQ diad: a) *n*BuLi, THF, −78 °C, 30 min; b) (COCl)$_2$, 20 °C, 72 h; c) **2** + **4**, THF, −100 °C→20 °C, 12 h.

The reagents for our synthesis are TTF derivative **1**[12] (the pentyl chains were chosen for increased processability) and TCNQ derivative **4**, which was obtained from the acid precursor **3**[13] by reaction with oxalyl chloride. The lithium alkoxide salt **2**[12] was generated in situ and reacted with compound **4** to give analytically pure product **5** in 27 % yield

[*] Prof. M. R. Bryce, Dr. D. F. Perepichka
Department of Chemistry and Centre for Molecular and
Nanoscale Electronics
University of Durham, Durham, DH1 3LE (UK)
Fax: (+44) 191-384-4737
E-mail: m.r.bryce@durham.ac.uk

Dr. D. F. Perepichka
INRS-Énergie et Matériaux
Université du Québec
Varennes, Quebec H3H 1X1 (Canada)

Dr. C. Pearson, Prof. M. C. Petty
School of Engineering and
Centre for Molecular and Nanoscale Electronics
University of Durham, Durham, DH1 3LE (UK)

Dr. E. J. L. McInnes, Dr. J. P. Zhao
The EPSRC EPR Service Centre, Department of Chemistry
The University of Manchester, Manchester M13 9PL (UK)

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as a stable dark-brown powder. The purity of the compound was established by HPLC and elemental analysis, and its structure was proved beyond doubt by NMR and HRMS data.

In CV experiments compound **5** shows reversible amphoteric redox behavior consisting of two, single-electron reduction waves (from the TCNQ moiety), and two, single-electron oxidations (from the TTF fragment) thus revealing five stable redox states (Figure 1). The mutual effect of the donor and acceptor moieties on the redox properties of their counter-
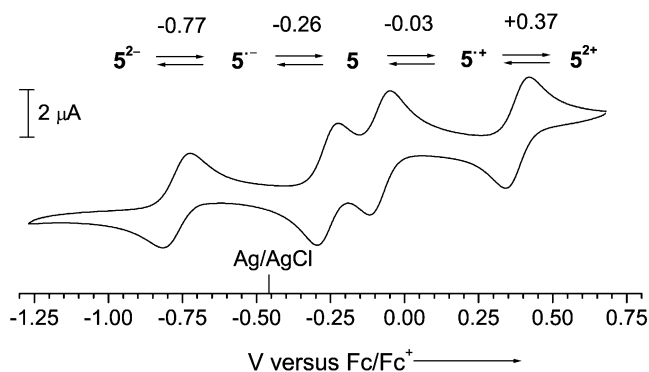
Figure 1. Cyclic voltammetry of compound **5** in MeCN (0.1 M Bu$_4$NPF$_6$), scan rate 100 mV s^{-1}, 20°C.

parts is small due to the isolating nature of the linker; there is a 20 mV shift of the first reduction and oxidation potentials, compared to separate TTF and TCNQ molecules and, in contrast to our expectations based on TTF–fluorene diads,[12] the separation between the first and second redox process increases in the diad **5** (benzoyl-**1**: $E^0_{1ox} = -0.11$ V, $E^0_{2ox} = +0.43$ V; **3**: $E^0_{1red} = -0.24$ V, $E^0_{2red} = -0.72$ V. Remarkably, the difference between the first oxidation and first reduction potentials ($E^0_{1ox} - E^0_{1red}$) of compound **5** is only 170 mV, presenting the lowest known electrochemical HOMO–LUMO gap (0.17 eV) in an organic molecule. Such a small difference for $E^0_{1ox} - E^0_{1red}$ is expected[14] to lead to a high degree (> 0.7) of charge transfer in the solid state. Indeed, the C≡N stretching frequency in the IR spectra (KBr pellet, see Supporting Information) of **5** ($\tilde{\nu}_{CN} = 2187$ cm^{-1}) is between those of neutral and radical anion TCNQ ($\tilde{\nu}_{CN} = 2225$ and 2180 cm^{-1}, respectively),[15] which is consistent with ≈ 85% charge transfer.[14]

In solution, intramolecular charge transfer (ICT) in compound **5** is manifested by a broad absorption band in the near-IR region of its electronic spectra with $\lambda_{max} = 1630$ nm (0.75 eV; $\varepsilon = 3600$ M^{-1} cm^{-1}) and a red edge at ≈ 2700 nm (0.45 eV) (see Supporting Information). Its intramolecular nature was established by a linear concentration dependence in the range 2×10^{-4}–3×10^{-3} M. Taking into account the density functional theory (DFT) calculations (B3LYP/6-31G*) for a homologue **5′**, which suggest the coexistence of linear and intramolecularly complexed head-to-tail conformations[16] we attribute the ICT band to π–π through-space charge transfer (Figure 2). The discrepancy between the electrochemically and spectroscopically deter-
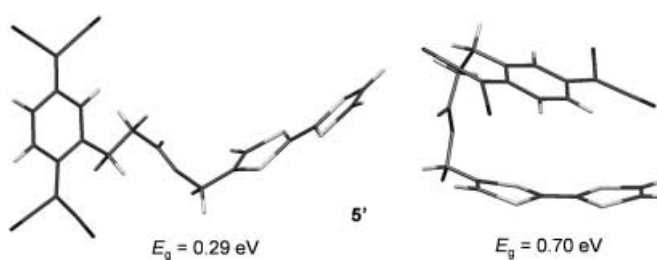

Figure 2. Geometries and HOMO–LUMO gaps (E_g) of an extended (left) and a head-to-tail intramolecularly complexed (right) conformation of a model TTF–TCNQ diad **5′**, and calculated at the B3LYP/6-31G(d) level.

mined HOMO–LUMO gaps (0.17 eV and 0.75 eV, respectively) is due to the fact that the optical HOMO–LUMO transition occurs only in the head-to-tail conformation (where the HOMO and LUMO orbitals are in close proximity), whereas CV experiments characterize an extended, "uncomplexed" state of the compound, which is easier to reduce/oxidize (because the charge-transfer interaction in the head-to-tail conformation decreases HOMO and increases LUMO energies, see Supporting Information). This conclusion is in full agreement with the calculation results, which predict HOMO–LUMO gaps of 0.29 eV and 0.70 eV for two conformations of **5′** (Figure 2). In powdered samples the CT band maximum shifts bathochromically by ≈ 300 nm as a result of intermolecular complexation[17] (see Supporting Information), and its tail is seen in the FTIR spectra down to 2000 cm^{-1}. Such a low energy band is usually indicative of electrical conductivity; accordingly, two-probe measurements on pressed pellets of **5** gave a value of $\sigma_{rt} \approx 10^{-6}$ S cm^{-1}.

Compounds for which color and transparency in the visible and near-IR region can be changed by applying various potentials are of great interest.[18] Although conducting polymers are currently the most studied materials in this respect, the majority of polymer electrochromic devices can operate only in on/off mode. Molecular electrochromic materials[19] bring the advantage of multicolor switching using a single material. Evaluation of the electrochromic properties of **5** revealed that stepwise application of various redox potentials to a brown solution of neutral **5** results in complete disappearance of the near-IR ICT band at 1630 nm, and subsequently turns the solution green (**5**$^{•+}$ at +0.5 V versus Pt wire), orange (**5**$^{2+}$ at +1 V), blue (**5**$^{•-}$ at −0.5 V), and red (**5**$^{2-}$ at −1.4 V; Figure 3 and Supporting Information). All four redox processes are completely reversible, that is, the initial spectrum of **5** returned after resetting the potential to +0.2 V, which demonstrates that this compound is a promising multicolor electrochromic material for the visible/near-IR region.

The EPR spectrum of a solution of **5** in CH$_2$Cl$_2$ at 290 K comprises two signals, which can be well simulated assuming a 1:1 ratio of TTF radical cation ($g = 2.0080$, $\Delta B_{p-p} = 2.5$ G) and TCNQ radical anion ($g = 2.0045$, $\Delta B_{p-p} = 4.5$ G) (Figure 4). Spin-quantification experiments under these conditions show ≈ 1.4 mol% of radical species, that is, approximately 0.7% of the compound exists in solution in a biradical state. The shape of the spectra is essentially unchanged on cooling the solution
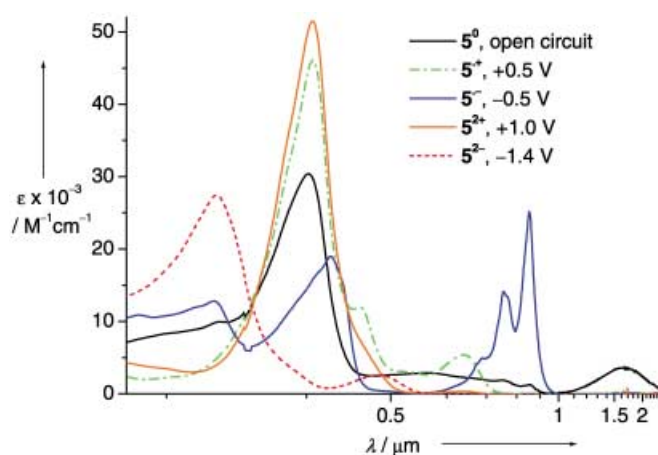
Figure 3. Spectroelectrochemistry of compound **5** in CH$_2$Cl$_2$ (0.1 M Bu$_4$NPF$_6$); potentials are versus a Pt wire quasi-reference electrode.
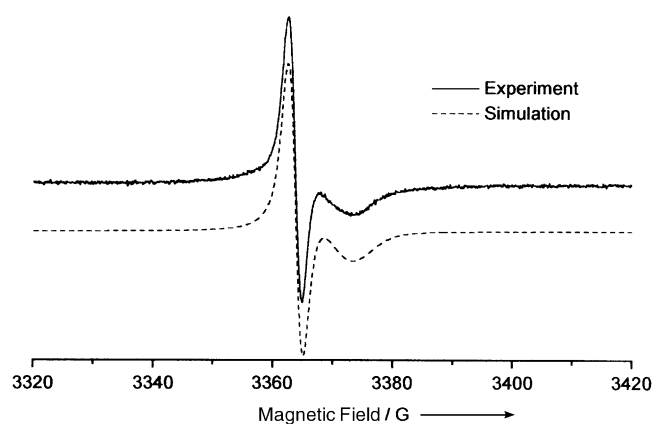
Figure 4. EPR spectrum of compound **5** in CH$_2$Cl$_2$ solution at 290 K and a simulation line.

from 290 to 175 K, but the intensity of the signal drops by a factor of about three (see Supporting Information). This is evidence for the first observation of a thermoexcited electron transfer in a donor–acceptor diad.[20] Calculation of the concentration of the thermoexcited biradical state [D$^{\bullet+}$A$^{\bullet-}$] from the Arrhenius equation ($K = [$D$^{\bullet+}$A$^{\bullet-}]/[$DA$] = e^{-\Delta E/kT}$, where $\Delta E = E^0_{1ox} - E^0_{1red}$) predicts 0.12% of the biradical state at 290 K, which is somewhat lower than the observed value of 0.7%, presumably due to the influence of intramolecular[21] head-to-tail complexation of **5**.

To approach molecular electronics applications, we prepared Langmuir–Blodgett (LB) films of **5**. Surface pressure versus area isotherms for the first, second, and third compressions are almost identical, which indicates the high reversibility of the LB film formation (Figure 5). The initial rise of the surface pressure (at an area of ≈ 0.65 nm^2 molecule^{-1}) is followed by a region of relative stability (with a pressure of 20–25 mN m^{-1}) and then a rapidly increasing pressure below a surface area ≈ 0.3 nm^2 molecule^{-1}. Multilayer LB deposition was attempted at two different surface pressure values, either side of the surface pressure "plateau", 35 and 15 mN m^{-1} (hereafter called high and low pressure,
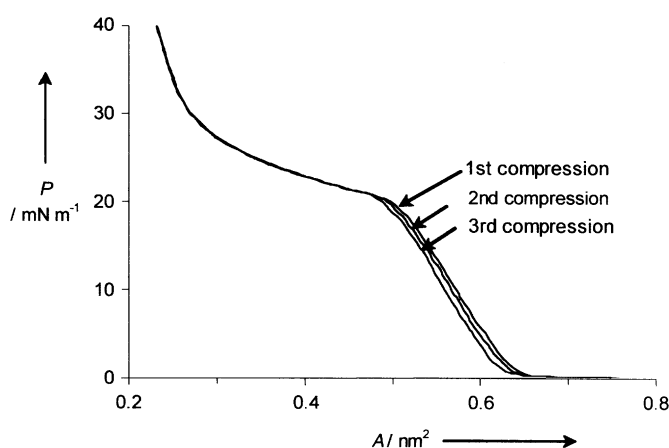
Figure 5. Surface pressure (P) versus area per molecule (A) isotherms for compound **5**.

respectively). At high pressure, only poor-quality patchy films could be deposited, which precluded their further investigation. At low pressure, however, Y-type deposition (that is, film transfer on both the downward and upward movements of the substrate through the air/water interface) was achieved and high-quality uniform films could be transferred onto different substrates with a transfer ratio close to unity (up to 240 layers).

Film-thickness measurements by low-angle X-ray reflection, ellipsometry, and surface profiling over the range of 20 to 240 layers indicate a layer thickness of 1.39 ± 0.08 nm. Absence of a CT band in the optical spectra of **5**-LB films and a shift of the CN stretching peak to 2218 cm^{-1} (close to the value of a noninteracting TCNQ moiety, see Supporting Information) suggest that a specific molecular conformation (and the interlayer architecture, Y-type deposition) prevent a donor–acceptor interaction between TTF and TCNQ fragments. The in-plane conductivity of a 20-layer film on a glass substrate was less than 10^{-7} S cm^{-1}, and very little change was evident after exposure to iodine vapor. The out-of-plane current versus voltage curves for a 240-layer film were symmetrical for different polarities of applied voltage. The dc conductivity was estimated to be very small, less than 2 × 10^{-11} S cm^{-1}, and ac voltage (1 MHz) measurements gave a value of 3.6 ± 0.2 for the relative permittivity of the organic film. These data are consistent with the neutral state of **5** in the film. To date, our attempts to measure the out-of-plane conductivity for a single monolayer of **5** (that is, to investigate molecular rectification) have been unsuccessful due to the difficulty of establishing reliable metallic top contacts. However, we are currently exploring alternative strategies.

The molecular area of **5** on the water surface, the transferred layer thickness, the absence of charge transfer, and the poor conductivity of the multilayer LB film (compared to other amphiphilic charge-transfer LB materials)[22] can be explained by the molecular orientation comprised of the TCNQ moiety lying on the surface and the TTF units making an angle with the surface of $\approx 45°$ (calculated molecular area of ≈ 0.7 nm^2 and the monolayer thickness of ≈ 1.4 nm, see Supporting Information). This molecular

arrangement prevents close face-to-face stacking of either the TCNQ or TTF units, and accounts for the low dc conductivities in both the in-plane and through-plane directions. The region in the isotherm in Figure 5 above the surface pressure plateau could correspond to the formation of a bilayer floating film, with the TTF units interleaved.

In conclusion, we report the first synthesis of a well-characterized TTF–TCNQ diad **5**. The electrochemistry is characteristic of both donor and acceptor moieties, which result in five stable redox states, each with a distinctive color, suggesting the use of **5** as a multichannel electrochromic material. The extremely low HOMO–LUMO gap in **5** leads to facile electron transfer, which may occur in solution at room temperature with thermal excitation. Compound **5** gives high-quality LB films, which are poorly conductive due to the specific film structure.

Experimental Section

5: Compound **3**[13] (32 mg, 0.117 mmol) was stirred in oxalyl chloride (0.8 mL) for 72 h at 20 °C. The mixture was filtered and the filtrate was evaporated in vacuo to give acid chloride **4** as a yellow powder. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.65$ (1 H, d, $J = 9.5$ Hz), 7.49 (1 H, d, $J = 9.5$ Hz), 7.37 (1 H, s), 3.43 (2 H, t, $J = 6$ Hz), 3.36 ppm (2 H, t, $J = 6$ Hz). *n*BuLi (1.6 M solution in hexane; 65 μL, 0.104 mmol) was added to a solution of compound **1**[12b] (39 mg, 0.100 mmol) in anhydrous THF (10 mL) at −78 °C, stirred for 30 min and a solution of **4** in anhydrous MeCN (4 mL) was added dropwise over 10 min at −100 °C. The reaction mixture was stirred at −78 °C for 5 h and left to warm to 20 °C overnight. The solvent was removed in vacuo, the residue was dissolved in ethyl acetate, washed with water, dried over MgSO$_4$ and the solvent was removed in vacuo. The residue was redissolved in ethyl acetate (0.3 mL), diluted with hexane (0.3 mL) and quickly filtered through a 1 cm pad of silica, eluting with ethyl acetate/hexane (1:1 v/v). Flash chromatography of the filtrate (silica; eluent: ethyl acetate/hexane 1:4 v/v) afforded pure compound **5** as a dark-brown powder (18 mg, 27 %), m.p. 152–154 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 2.91$ (2 H, br), 1.61 (4 H, br), 1.37 (8 H, br), 0.89 ppm (6 H, m); three aromatic protons, three CH$_2$ groups, and one CH$_3$ group adjacent to the TTF and TCNQ nuclei are unobservable due to paramagnetic broadening (see Supporting Information). IR (KBr): $\tilde{\nu} = 2187$ (CN), 1734 (CO), 1348, 1279, 1165 cm^{-1}. MS (FAB): *m/z* 646 (M^+, 65 %), 388 (35 %), 371 (100 %). HRMS (EI): 646.1539; calcd for C$_{33}$H$_{34}$N$_4$O$_2$S$_4$: 646.1564. Elemental analysis calcd (%): C 61.27, H 5.30 N 8.66; found: C 61.01, H 5.28, N 8.55.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the authors, comprising experimental details; extended discussion of quantum-mechanical calculations, spectroelectrochemical, EPR, low-angle X-ray reflection and AFM experiments; the ^{1}H NMR spectrum of **5**; UV/Vis/NIR spectra of **5** in solution, powder, and LB film; FTIR spectra of **5** in powder and LB film; EPR spectra of **5** in powder and frozen solution; temperature dependence of the EPR signal of a solution of **5**; AFM images of LB films of **5**; diagram of a proposed structure of **5** in LB films; X-ray reflection data for compound **5**; correlation of the LB film thickness measured by different methods; diagram of HOMO and LUMO orbitals of **5'**.

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[16] Geometry optimization of a model homologue of **5** lacking three alkyl substituents on TTF using DFT suggests that linear and folded "head-to-tail" conformations, where intramolecular π–π interactions can take place are energetically almost equal: $E = -1\,761\,805.8$ and $-1\,761\,807.2$ kcal mol^{-1}, respectively, see Supporting Information.

[17] A similar band (λ_{max} 1585 nm, absorption 0.31 in 1 mm cuvette) is seen in the solution spectrum of the intermolecular complex of CH$_3$(C$_5$H$_{11}$)$_2$TTF and TCNQ (1.0×10^{-2} M of each in MeCN); this band vanishes rapidly on dilution, and is not observable at concentrations $< 10^{-3}$ M due to complex dissociation.[12]

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