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Tetrathiafluvalene-Tetracyanoquinodimethane Charge-Transfer Complexes Wired to Carbon Surfaces: Tuning of the Degree of Charge Transfer.

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4 **Tetrathiafluvalene-Tetracyanoquinodimethane Charge-Transfer**
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6 **Complexes Wired to Carbon Surfaces: Tuning of the Degree of Charge**
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8 **Transfer**
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13 Corinne Lagrost*

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Abstract

Charge-transfer complexes involving TTF (tetrathiafulvalene) and TCNQ (tetracyanoquinodimethane) derivatives are engineered in a 2D arrangement onto a carbon surface through the exposure of immobilized TTF units to TCNQ compounds. TTF molecules were immobilized as robust monolayers on carbon surfaces using the electrografting method followed by a click chemistry coupling. When the TTF monolayer is exposed to TCNQ, TCNQF₂ (2,5 difluoro-TCNQ) and TCNQF₄ (2,3,5,6 tetrafluoro-TCNQ), strong donor-acceptor complexes are formed onto the surface. A considerable decrease of the electrochemical response accompanies the formation of the charge transfer complex. This observation is rationalized by the analysis of original crystal samples using an ultramicroelectrode cavity, confirming that charge-transfer complexes are electrochemically silent. A fine control of the degree of charge transfer with the judicious choice of different acceptors is evidenced through electrochemical and XPS measurements. Thus, donor-acceptor complexes of different nature are formed. A fully ionic charge-transfer complex is formed upon exposure of the TTF monolayer to the more oxidizing TCNQF₄, while a neutral complex is obtained after exposure to the less oxidizing TCNQ. Exposition of the TTF monolayers to the intermediate TCNQF₂ yields a mixture of neutral-ionic systems. These donor-acceptor interactions that fully mimic those described in the solid-state are rarely described in such a 2D arrangement, with systems being directly wired to an electrode.

1. INTRODUCTION

Organic charge transfer complexes are a class of molecular conductors that have been widely studied for their conducting and magnetic properties.^{1,2,3,4,5,6,7} The charge-transfer behavior between an electron donor and an electron acceptor is generally investigated in 3D solid-phase systems, either organic crystals^{1,3,4,5} or more recently at the interface between two crystals^{8,9} or between a powder in contact with a single crystal.¹⁰ Charge-transfer complexes could be also processed as Langmuir-Blodgett films, where the donor-acceptor organization allows the formation of high quality monolayers films with appealing conducting and magnetic properties.¹¹ As illustrative example, a covalent TTF(tetrathiafulvalene)-TCNQ(tetracyanoquinodimethane) diad exhibits an extremely low HOMO-LUMO gap, leading to facile electron transfer with five stable redox states.¹² More rarely, these systems have been engineered as self-assembled monolayers (SAMs),^{13,14,15,16,17,18,19,20} despite the great interest of the strategy for realizing integrated devices. Indeed, SAMs would permit to organize charge-transfer complexes in an optimized 2D film structure, hence promoting cooperative properties. As donor molecules, TTF and its derivatives are almost ubiquitous in the field because of a good chemical stability, an accessible synthesis of the building blocks and their remarkable donor properties.¹ The electron rich TTF molecules (and derivatives) could efficiently associate to electron-deficient acceptors like TCNQ derivatives to form charge transfer complexes.¹ These complexes have remarkable electronic properties that can serve to build high electrically conductive system²¹ or molecular rectifier.^{22,23}

Yet, a key question is to know how the special properties of TTF in solution or of TTF-based crystal solids are transferred to surface-confined species.²⁴ In this context, the formation of a donor-acceptor complex was examined for SAMs of TTF alkylthiols chemisorbed on gold surfaces in presence of different acceptors like TCNQ.^{13,15,16} However, cyclic

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voltammetry analyses have revealed a puzzling behavior of these SAMs since the immobilized TTFs lost their electroactivity after exposure to TCNQ.¹⁶ A clear decrease of the oxidation current upon addition of TCNQ was reported. Authors concluded that only “free” TTFs, *i.e.* TTFs that were not involved in the donor-acceptor interactions, could contribute to a detectable electrochemical response but the origin of the phenomenon remained unclear. Note that the formation of a charge-transfer complex between TTF derivatives and TCNQF₄, evidenced by micro-Raman spectroscopy, has led to a comparable decrease of the current response in presence of the acceptor but by using an ITO substrate.²⁵ The main difficulties for understanding these observations are the relative fragility of SAMs on gold and the dynamic nature of the layer that could easily reorganize when a functional group or other bulky constraints are introduced on the layer. For example, it is common to substitute an alkyl-functionality in a prepared SAM by simply soaking the modified surface in a solution containing a different alkyl-thiol.²⁶

Among possible surfaces for immobilizing a redox molecule, carbon materials are substrates of choice because they could be functionalized through a covalent link between the molecule and the substrate, allowing a particularly robust immobilization of the molecule.²⁷ Carbon substrates present also interests for preparing materials with new properties as recently exemplified with the modification of graphene layers by TTF derivatives.²⁸ The electrografting of aryldiazonium salts is a convenient approach for modifying carbon surfaces. The modification is based on the electrochemical production of transient reactive phenyl radicals at the vicinity of the carbon electrode surface that are able to attach on the carbon materials.²⁷ To control the structure and the vertical extension of the layer, we have recently proposed a two-step method based on a bulky protected precursor, 4-((triisopropylsilyl)ethynyl) benzenediazonium tetrafluoroborate (TIPS-Eth-ArN₂⁺).²⁹ After removal of the TIPS group, a dense reactive ethynyl-terminated monolayer is obtained and

could be post-functionalized by using the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition with a variety of organic molecules containing an azido group. Interestingly, the distance between functional groups is controlled by the size of the leaving protecting group.³⁰ In this work, we took benefit of this strategy for preparing well-organized, covalently attached TTF monolayers bridged with alkyl chain of different length (propyl, pentyl and decyl, i.e. C₃, C₅ and C₁₀, respectively) on a carbon surface. Their charge transfer properties were carefully investigated upon exposure to a family of acceptors of increasing strength, TCNQ, TCNQF₂ and TCNQF₄, by combining cyclic voltammetry, measurements with cavity ultramicroelectrode (UMEC) and X-ray photoelectron spectroscopy (XPS). Remarkably, our results evidence the formation of charge transfer complexes of different nature at the interface as function of the acceptors strength.

1. EXPERIMENTAL SECTION

Chemicals. Unless specified, all compounds were commercially available reagents and were used as received. Tetrabutylammonium hexafluorophosphate (TBAPF₆) of electrochemical grade was purchased from Aldrich. 4-((triisopropylsilyl)ethynyl) benzenediazonium tetrafluoroborate (TIPS-Eth-ArN₂⁺) was prepared according to a previously described procedure.³¹ TCNQF₄ (2,5-difluoro-TCNQ) was prepared according to a published procedure.³² The synthesis of the azido TTFs with different alkyl chains was realized starting from the corresponding iodo-alkyl-TTF according to published procedures (see supporting information).³³

Electrochemical Measurements. Electrochemical modification and characterization were performed with an Autolab PGSTAT N302 potentiostat/galvanostat (EcoChemie B.V.) equipped with the GPES software. A conventional three-electrode system, comprising a 3 mm

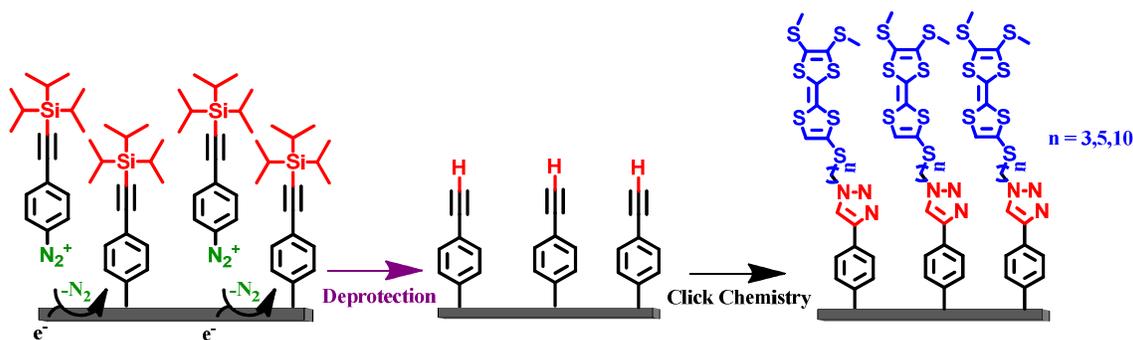
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3 diameter glassy carbon electrode as a working electrode, a platinum wire as the auxiliary
4 electrode, and a SCE electrode as reference, was used. The surface concentration of active
5 TTF centers were derived from the faradaic charge of the first monoelectronic oxidation
6 according to the following equation $\Gamma = Q / FA$, where F is the Faraday constant, A is the
7 surface of the glassy carbon electrode, Q the charge obtained from the integration of the area
8 under the voltammetric peak.
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11 For UMEC analyses,³⁴ the ultramicroelectrode was provided through the “UMEC
12 Network of CNRS”.³⁵ The microcavity of the ultra-microelectrode (approximately 17 μm
13 diameter cavity) was filled with a homogeneous mixture of the crystal under study and
14 graphite powder in a 4:1 ratio. The voltammograms were recorded using a 1:1 v/v
15 ethanol/water solution containing 0.1 mol L⁻¹ KPF₆ as electrolyte at a scan rate of 10 mV s⁻¹.
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18 **Electrode Modification.** The electrochemical procedure used for the modification of the
19 carbon electrodes (glassy carbon disk or pyrolyzed photoresist films (PPF) substrates) is
20 presented in Scheme 1 and is based on the method described in reference 29. Briefly, the first
21 step was the electrografting of the protected TIPS-Eth-ArN₂⁺ onto the carbon electrode from
22 an acetonitrile solution containing 10⁻² mol L⁻¹ TIPS-Eth-ArN₂⁺ and 10⁻¹ mol L⁻¹ TBAPF₆ and
23 using 5 cycles between 0.6 and -0.75 V (vs SCE) at a scan rate of 50 mV s⁻¹. The modified
24 surfaces were then rinsed with acetone and stirred in THF for 20 min. TIPS deprotection was
25 performed by immersing the modified electrodes in a stirred solution of 10⁻¹ mol L⁻¹ TBAF
26 (tetrabutylammonium fluoride) in THF for 20 min. N₃-C_n-TTF molecules were then coupled
27 to the resulting H-Eth monolayers by a Huisgen 1,3-dipolar cycloaddition (click chemistry).
28 For that, the H-Eth modified electrodes were immersed in a stirred 5 mL solution of TTF-
29 (CH₂)_n-N₃ (n = 3, 5, 10) (1 mg) in THF and CuSO₄ (2.5 mL, 10⁻² mol L⁻¹) was added. After
30 degassing the solution for 15 min under argon, L(+)-ascorbic acid (10⁻² mol L⁻¹ in 2.5 mL
31 water containing 80 mg of NaHCO₃) was added dropwise to the solution. The reaction
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3 mixture was left stirring under argon for 1 hr. The resulting electrodes were then stirred in a
4 saturated EDTA solution for 10 min to remove any residual copper.
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8 **X-Ray Photoelectron Spectroscopy Measurements.** X-ray photoelectron spectroscopy
9 data have been collected using a Kratos Axis Nova spectrometer using the Al K α X-ray
10 source working at 1486.6 eV and using a spot size of 0.7 x 0.3 mm². Survey spectra (0-1000
11 eV) were acquired with an analyzer pass energy of 80 eV (0.5 eV/step); high-resolution
12 spectra used a pass energy of 20 eV (0.1 eV/step). Binding energies were referenced to C1s
13 peak at 285 eV. The atomic percentage for surface composition was estimated using the
14 integrated peak areas in the survey spectra; the peak areas were normalized by the
15 manufacturer-supplied sensitivity factor. The core level spectra were peak-fitted using the
16 CasaXPS software, Ltd., version 2.3.17).
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43 **Scheme 1.** Functionalization of carbon surfaces by TTF-terminated monolayers
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48 2. RESULTS AND DISCUSSION

49 **Redox Behavior of a Glassy Carbon Electrode Modified with the alkyl-TTF layers.**

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51 Three TTF derivatives with different alkyl-chain linkers (propyl (C₃), pentyl (C₅) and decyl
52 (C₁₀)) were immobilized on the carbon surface following a previously published procedure as
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3 depicted in Scheme 1.²⁹ The C_n-TTFs functionalized with azide groups were coupled to the
4 reactive ethynyl monolayer by “click chemistry”. Figure 1 shows the cyclic voltammetry in
5 dichloromethane containing 0.2 mol L⁻¹ TBAPF₆ recorded after copious rinsing of the
6 modified electrodes. For the three layers, two successive well-defined redox processes are
7 observed and are characteristic to the reversible oxidation of the TTFs to their cations and to
8 their dications, respectively (Table 1).¹ For the three modified surfaces, the intensity of the
9 peak currents varies linearly as a function of the scan rates as expected for a surface-confined
10 redox couple.³⁶ Moreover, the TTF layers present good electrochemical stability upon
11 cycling, the cyclic voltammetry experiments could be repeated more than 10 times without
12 any significant variation (See Figure S1 in the supplementary section). By integration of the
13 faradaic oxidation current, surface concentrations were estimated to $5 (\pm 2) \times 10^{-10}$ mol.cm⁻²
14 based on repeated measurements. Considering the roughness of a glassy carbon electrode
15 (typically the roughness factor is 2-2.5 for a carefully polished electrode),³⁰ this value
16 confirms that relatively dense monolayers of TTF are obtained. The surface concentration of
17 an ideal close-packed monolayer of TTF was reported to be 3.6×10^{-10} mol cm⁻².¹³ However
18 in our case, the maximum packing of the TTF units is imposed by the steric hindrance of the
19 TIPS protective group, hence leading to a surface concentration equal to 2.3×10^{-10} mol cm⁻²
20 for an ideal hexagonal compact arrangement.³⁰ The experimental value found is in a fairly
21 good agreement with this theoretical value. The overall shape of the cyclic voltammetry
22 differs from those previously reported for the oxidation of alkylthiol-TTF monolayers on gold
23 (SAM).^{26,38,24} While the chemical stability and redox activity of the TTF are generally kept
24 after immobilization in SAMs,^{26,37} their electrochemical characteristics are considerably
25 modified. Notably, the peak shapes and widths are affected, depending on the oxidation states
26 of TTF, on the organization of the TTF units in the layer and on the electrolyte media.^{26,38}
27 These effects were ascribed to the interactions between the TTF moieties, and could be easily
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identified by cyclic voltammetry.²⁶ Published studies have reported voltammograms with a first dissymmetric wide peak (full width at half maximum, FWHM, around 160-170 mV) and a much narrower second one (FWHM of 50-60 mV).^{26,38,24} These observations were explained by strong intermolecular interaction taking place within the monolayers upon the charging process.^{26,39} The small FWHM values for the second process (much narrower than the ideal 90 mV expected for non-interacting redox centers) have been ascribed to strong attractive interactions between the TTF²⁺ centers.^{26,39}

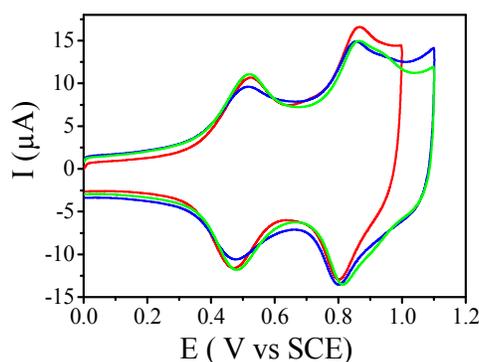
Table 1. Electrochemical Data from Cyclic Voltammetry for the Oxidation of Monolayers of TTF-C_n (n= 3, 5, 10)^a in CH₂Cl₂ Containing 0.2 mol L⁻¹ TBAPF₆.

Monolayers	At 0.2 Vs ⁻¹	Redox process #1	Redox process #2
TTF-C ₃	E ^o (V vs SCE)	0.50	0.83
	FWHM (mV)	178	126
TTF-C ₅	E ^o (V vs SCE)	0.49	0.82
	FWHM (mV)	176	124
TTF-C ₁₀	E ^o (V vs SCE)	0.50	0.84
	FWHM (mV)	186	122

^aAll the monolayers exhibit close surface concentrations

In our experiments, the second redox peak is also narrower than the first one, but shapes of the two processes are more comparable, with FWHM larger than those reported for the TTF SAMs on gold. All these observations correspond to weaker interactions between the TTF moieties. It is likely that the covalent grafting of our arylethynyl platform limits the reorganization and packing in the TTF monolayers.³⁰ The steric hindrance of the bulky protective TIPS group controls the distance between the anchorage sites of the TTF units and leaves space between them resulting in a sort of frozen arrangement.³⁰ This would allow an easier solvation process/counter-ion penetration in the monolayers, decreasing the strength of attraction between the TTF²⁺ units. Additionally, a shoulder-like system is observed at the second oxidation peak (located at the more positive potentials side) for the TTF linked

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3 through the longest alkyl chains (TTF-C₅ and TTF-C₁₀) (Figure 1). This “extra” peak is even
4 more visible for the TTF with the longest alkyl chain linker (C₁₀). The splitting of the
5 oxidation/reduction peaks suggests the co-existence of “isolated” (lower potential) and
6 “clustered” (higher potential) TTF²⁺ species, the formation of “clustered” species being
7 facilitated by the flexibility introduced by longer alkyl chains as observed for alkyl-ferrocene
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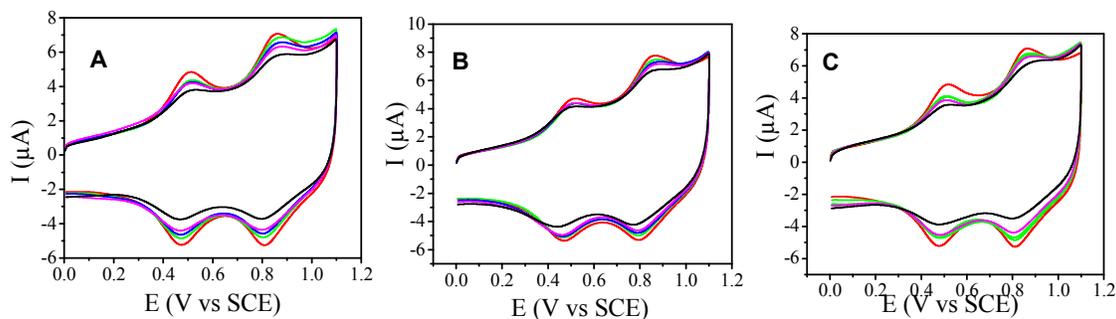


30 **Figure 1.** Cyclic voltammograms recorded in dichloromethane (+ 0.2 mol L⁻¹ TBAPF₆) of
31 TTF-terminated monolayers having bridging units of different chain lengths (C₃ (red) C₅
32 (blue) and C₁₀ (green)) at a glassy carbon electrode. Scan rate = 200 mV s⁻¹.
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39 **Acceptor-donor Complexes between TTF-C_n Monolayers and TCNQ Derivatives.**

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41 To examine the properties of charge-transfer complexes with the TTF layer on carbon, cyclic
42 voltammograms of the TTF layers were recorded before and after immersion of the modified
43 electrode in CH₂Cl₂ solutions of TCNQ, TCNQF₂ and TCNQF₄ with increasing
44 concentrations and after extensive rinsing with clean CH₂Cl₂. For the three layers, a
45 considerable decrease of the oxidation peak currents is observed after exposure to the TCNQ
46 derivatives solutions. Figure 2 shows some typical voltammograms obtained for the TTF-C₁₀
47 layer. Under our experimental conditions, the current intensities decrease monotonically with
48 the increase of acceptors concentration to reach a constant value when the TCNQs
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3 concentrations are above $2 - 4 \times 10^{-3} \text{ mol L}^{-1}$. From the maximum current decrease, we could
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5 estimate that roughly 40 to 60 % of the immobilized TTF units become electrochemically
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7 silent after exposure to the TCNQ derivatives solutions. The observation of the current drop is
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9 the least intense for the layer with the short linker, indicating that a more flexible layer favors
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11 the phenomenon. For example, using TCNQF₄ as an acceptor, 40 % of TTF units become
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13 electro-inactive for the TTF-C₃ layer after immersion in the acceptor solution while more than
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15 55 % for TTF-C₅ and TTF-C₁₀ are silent under the same conditions. In all cases, it was not
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17 possible to recover the initial electro-activity of the layer even after repeated cycling in a
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19 blank CH₂Cl₂ solution; the cyclic voltammograms of the TTF layer remain unchanged.
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21 Finally, as a test experiment, a comparable monolayer, but functionalized with undecyl-
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23 ferrocene units, was exposed to the same TCNQF₄ solutions. No modifications of the
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25 voltammograms were observed after exposure of the modified surface to TCNQF₄ (Figure
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27 S2). All these observations indicate that the interactions between TTF and the TCNQ
28
29 derivatives are strong and specific of the TTF layers. Importantly, this effect does not depend
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31 on the strength of the acceptor which can be quantified through its formal reduction potential.
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33 The di- and tetra-fluoro analogues of TCNQ exhibit more positive formal potentials than
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35 TCNQ, i.e. $E^\circ = 0.53 \text{ V vs SCE}$, 0.39 V vs SCE and $+0.17 \text{ V vs SCE}$ for TCNQF₄, TCNQF₂
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37 and TCNQ, respectively.
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55 **Figure 2.** Cyclic voltammograms in dichloromethane (+ $0.2 \text{ mol L}^{-1} \text{ TBAPF}_6$) of a glassy
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57 carbon electrode modified with the TTF-C₁₀ monolayer, before (red curves) and after
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3 exposure to a solution with increasing concentrations of TCNQ derivatives (A) TCNQ, (B)
4 TCNQF₂, (C) TCNQF₄). S1 = 10⁻⁴ mol L⁻¹ (green), S2 = 5 10⁻⁴ mol L⁻¹ (blue), S3 = 10⁻³ mol
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6 L⁻¹ (magenta) and S4 = 8 10⁻³ mol L⁻¹ (black).
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13 Similar current decreases were previously reported for self-assembled layer of
14 thioalkyl TTFs onto a gold electrode surfaces in presence of acceptor molecules.¹⁶ Authors
15 suggested that this current drop results from a donor-acceptor interaction between the TTF
16 and the TCNQ.
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22 To further support this hypothesis, a key question is about the expected
23 electrochemical response of a charge transfer complex involving TTF and TCNQ derivatives.
24 If these associations are commonly considered and described in the literature,^{1,5} there was no
25 specific examinations about their electrochemical responses, particularly under a crystallized
26 form that could be compared to a TTF layer. In that purpose, we prepared crystals of a charge
27 transfer complex with TTF (E° = 0.33 V vs SCE) and TCNQF₂ (E° = 0.39 V vs SCE). Note
28 that, in this case, the reduction potential of the acceptor is larger than the oxidation potential
29 of the donor, which could lead to a fully ionic charge transfer as in the case of the TTF-C_n and
30 TCNQF₄. The electrochemical activity of these crystals was investigated by means of the
31 ultramicroelectrode cavity (UMEC) technique.^{34,35} The UMEC technique allows the
32 electrochemical analysis of a very small amount of powder materials and is particularly
33 relevant for electrochemical analysis of crystals. The cavity of the ultramicroelectrode was
34 filled with crystals of TTF-TCNQF₂ charge transfer complex. As comparative experiments,
35 the electrochemical signals of the oxidation of TTF crystals filling the same cavity were also
36 recorded (See Figure S4 for experiments with pure TCNQF₂ crystals).
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The electrochemical measurement was performed in 1:1 (v/v) ethanol/water mixture containing (+0.1 mol L⁻¹) KPF₆ as supporting salt to limit the dissolution of the crystal in the solution. As a remarkable feature, the electrochemical signals of the TTF oxidation (or of the TCNQF₂ reduction) that are clearly detected in the pure TTF crystals, disappear in the TTF-TCNQF₂ charge-transfer crystal (Figure 3).

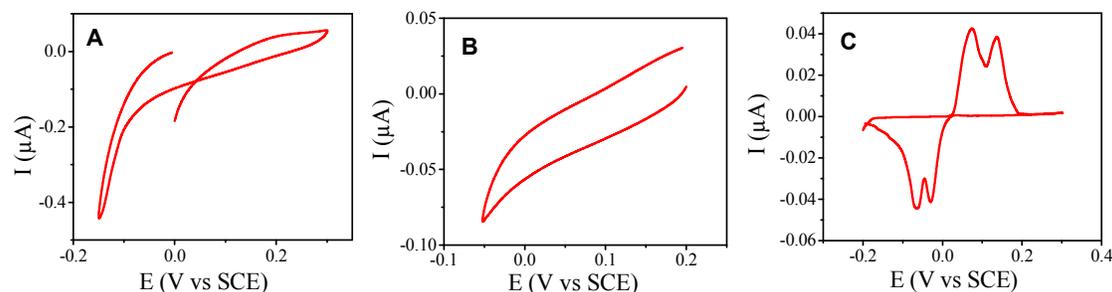


Figure 3. Cyclic voltammetry with an UMEC recorded in a 1:1 ethanol/water solution (+ 0.1 mol L⁻¹ KPF₆). Scan rate = 10 mV s⁻¹. (A) TTF-TCNQF₂ crystal observed in oxidation, (B) TTF-TCNQF₂ crystal observed in reduction. (C) For comparison, oxidation of a TTF crystal with same conditions showing the two successive reversible oxidation steps.

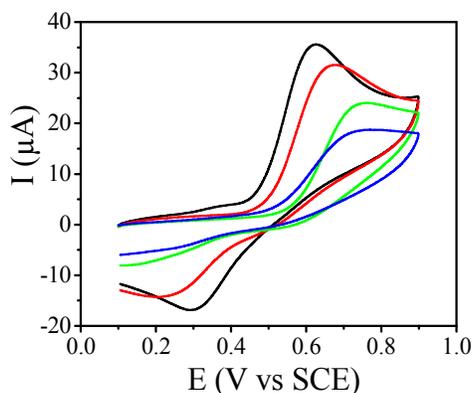
These observations confirm that the charge transfer complex displays no electroactivity in the potentials range where the oxidation of TTF is observed, clearly supporting the assumption that charge transfer between the immobilized TTF and the TCNQ derivatives suppress their electrochemical activity as described above. This absence of electroactivity of the complex could be due to the strong activation energy that would be required to break the TTF-TCNQF₂ association, making the oxidation of TTF more difficult. Indeed, a small signal around 0.2 V that could be ascribed to the TTF oxidation appears after scanning the potential scan with an expanded window (notably towards a more negative potentials excursion). Similar observations have been reported for TTF-TCNQ complexes as

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3 compacted pellets.⁴¹ Large overpotentials were required to observe the electrochemical
4 signature of TTF and TCNQ. Therefore, the remaining electrochemical activity observed with
5 the TTF monolayers, after exposure to TCNQ derivatives solution, is probably due to the TTF
6 units, which are not involved in the donor/acceptor interactions.
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12 The ratio i_p/i_{pTTF} (where i_p and i_{pTTF} are the first oxidation peak currents recorded by
13 cyclic voltammetry measured after and before immersion of the TTF-C_n layer in the TCNQ
14 derivative solution, respectively) could be considered to quantify the efficiency of the
15 formation of the donor-acceptor complexes in the layer. The smallest i_p/i_{pTTF} corresponds to
16 the strongest donor/acceptor interactions. It is noticeable that i_p/i_{pTTF} depends both on the
17 acceptor redox potential, E°_{TCNQ} and on linker length (Figure S9). For the shortest and less
18 flexible layer (TTF-C₃), comparable i_p/i_{pTTF} variations are observed for the three different
19 acceptors with i_p/i_{pTTF} around 0.6 (Figure S9). In contrast, for the more flexible TTF-C₁₀ layer,
20 i_p/i_{pTTF} varies considerably with the acceptor as the following trend: TCNQF₄ (0.38) < TCNQ
21 (0.5) < TCNQF₂ (0.7). If the most efficient complexation is indeed observed with TCNQF₄ as
22 acceptor, having the larger reduction potential, an inversion exists between TCNQ and
23 TCNQF₂ suggesting that the redox potential is probably not the only relevant parameter to
24 quantify the strength of such interaction(*vide infra*).
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41 To further confirm this puzzling behavior, the blocking properties towards electronic
42 transfer of the TTF-C₁₀ monolayers, before and after exposure to the different acceptors, were
43 studied. In that purpose, we used a classical electrochemical probe, dopamine that was
44 originally proposed by R. McCreery *et al.* Oxidation of dopamine to the corresponding *ortho*-
45 quinone requires the adsorption of dopamine onto the carbon electrode substrate for a fast
46 charge transfer kinetics and the coating of the carbon electrode surface with a dense and
47 compact monolayer was demonstrated to inhibit the oxidation of dopamine.^{42,43,44} Thus,
48 observation of electrochemical activity implies that dopamine is able to reach the electrode
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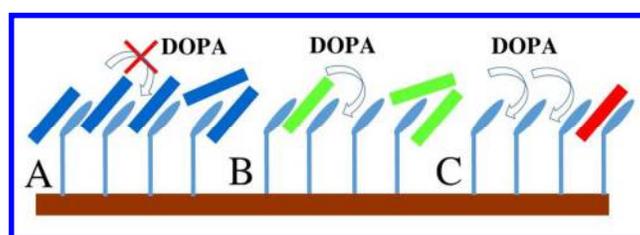
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3 surface. Examination of the electrochemical response of dopamine oxidation provides
4 evidence about the presence of pinholes in a monolayer and, consequently about its
5 compactness on a carbon substrate. Figure 4 displays the voltammograms of the dopamine
6 oxidation on a glassy carbon electrode modified with the TTF-C₁₀ monolayer before and after
7 exposure to the TCNQ derivatives.
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29 **Figure 4.** Cyclic voltammetry of 10^{-3} M dopamine in $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution on a GC
30 electrode modified with TTF-C₁₀ monolayers before (black) and after exposure to TCNQ
31 derivatives, TTF-TCNQF₂ (red), TTF-TCNQ (green), and TTF-TCNQF₄ (blue). Scan rate =
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41 A well-defined voltammogram is observed on carbon surfaces modified with TTF-C₁₀
42 (before exposure to acceptors), indicating the presence of pathways allowing the passage of
43 dopamine through the TTF layer. After exposure to TCNQ derivatives, the oxidation of
44 dopamine remains visible, but the peak-to-peak potential separations increase, the peak
45 currents display a larger plateau-shape and their intensity are lowered. These observations
46 show that the passage of dopamine through the TTF layer becomes more difficult,
47 corresponding to a more blocking character of the layer after exposure to a TCNQ
48 derivative.^{45, 46} However, the magnitude of the variations in the dopamine oxidation signal are
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3 different according to the different acceptors (Figure 4). It is especially remarkable that the
4 same trend is deduced from the ratios i_p/i_{pTTF} that characterize the strength of the acceptor-
5 donor complexes and from the variations of the blocking character of the layer after exposure
6 to the acceptor, i.e. $TTF-TCNQF_4 > TTF-TCNQ > TTF-TCNQF_2$. These results support the
7 idea that intermolecular spaces between the TTF units exist within the monolayer (Figure 4,
8 black line) and can be filled by the acceptors (Figure 4, green/red/blue lines). Indeed,
9 considering that the molecular size of dopamine and TCNQ are comparable, the
10 intermolecular space is large enough to permit the passage of TCNQ derivatives within the
11 layer, promoting the formation of the charge transfer complexes. The TCNQ compounds that
12 interact with the TTF layer literally close the intermolecular spaces and add rigidity in the
13 structure of the monolayer, preventing dopamine from reaching the carbon surface.
14 Depending on the strength of the donor-acceptor interactions, these spaces are more or less
15 well blocked (Figure 5). Thus, $TCNQF_4$ undergoes the most efficient charge transfer
16 complexation and its interaction with the TTF- C_{10} monolayer leads to the largest blocking of
17 the carbon surface towards dopamine (Figure 4, blue line).
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47 **Figure 5.** Schematic representation of the blocking properties towards dopamine (DOPA) of
48 the TTF- C_{10} monolayer associated with A) $TCNQF_4$, B) $TCNQ$ and C) $TCNQF_2$
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55 **XPS Analyses of Donor-Acceptor Complex At TTF- C_{10} Monolayers.** PPF (Pyrolyzed
56 Photoresist Film) substrates functionalized with TTF- C_{10} monolayers were analyzed by X-ray
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Photoelectron spectroscopy (XPS), before and after exposure to the TCNQ derivatives, to gain a deeper understanding of the nature of the donor-acceptor complexation. The survey spectra exhibit substantial changes after the exposure of the TTF-C₁₀ monolayers to the TCNQ derivatives, indicating modifications in surface compositions (Figure S6). Intense C1s peaks are detected at 285 eV due to the PPF substrate and to the TTF monolayers, whether complexed with TCNQ derivatives or not. N1s (at 400 eV) and S2p (at 164 eV) peaks that are fully characteristic to the organic monolayers are also observed. F1s peaks (at 688 eV) with significant atomic percentage could be identified for the TTF monolayers exposed to TCNQF₂ and TCNQF₄. Accordingly, the fluorine atomic percentage is larger with TCNQF₄ than with TCNQF₂. Trace levels of fluorine (< 1%) are also detected in the survey scans of TTF-C₁₀ monolayers and TTF-C₁₀ monolayers exposed to TCNQ (Table 2) probably due to a contamination at the samples during the deprotection step in the monolayer preparation.

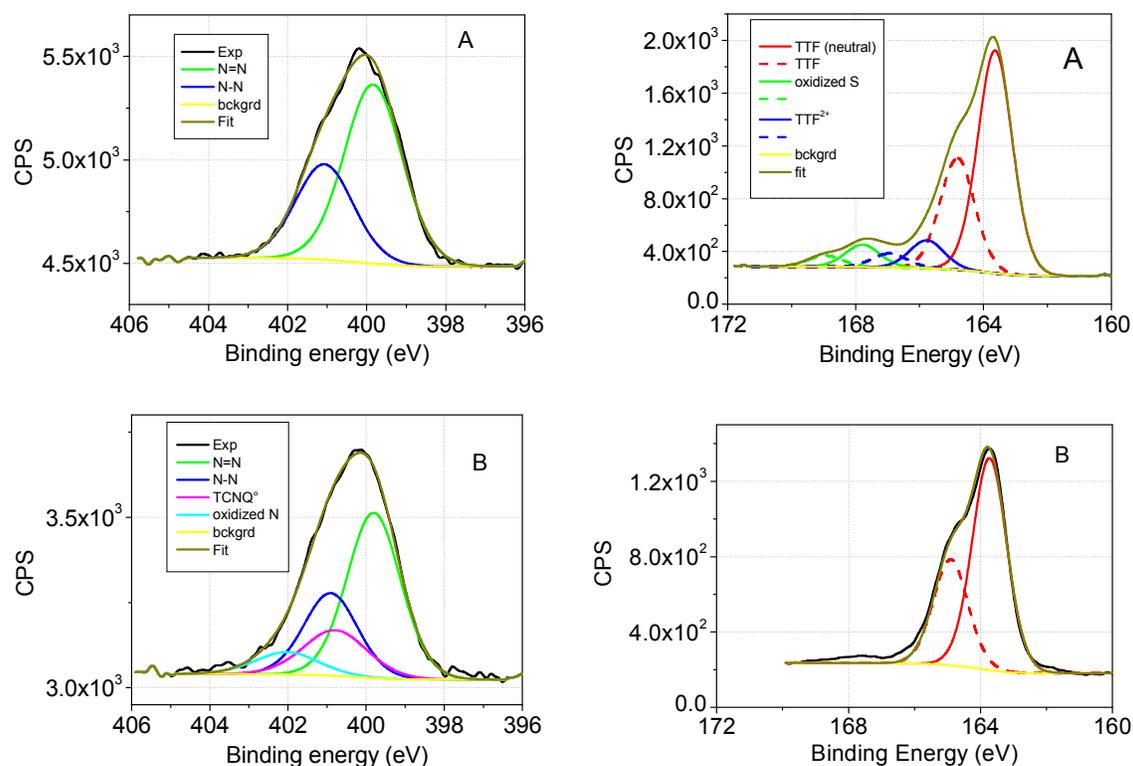
Table 2. Surface Composition (% atom, ± 20%) of TTF-C₁₀ Monolayers before and after Exposure to TCNQ, TCNQF₂ or TCNQF₄ Solutions

% atom	TTF	TTF-TCNQ	TTF-TCNQF ₂	TTF-TCNQF ₄
%C	79.7	86.8	82.8	82.3
%N	1.7	1.9	1.7	3.6
%F	0.9	0.6	2.9	3.5
% S	4.5	2.9	3.2	3.0
% O	13.2	7.8	9.4	7.6

The N1s core level spectra could be decomposed into several components that take into account the triazole groups (i.e. two peaks at 399.9 eV (± 0.5) (N-N=N) and at 401.1 (± 0.5) eV (N-N=N), with a ratio of 1:2)⁴⁷ for the TTF-C₁₀ monolayers and the TCNQ derivatives for the exposed monolayers (Figure 6). An important feature is the appearance of a shoulder-like peak at lower binding energy (398.5 (± 0.5) eV) for the monolayers exposed to TCNQF₂ and TCNQF₄ (Figure 6). This could be ascribed to the presence of negatively

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charged TCNQF₂ or TCNQF₄ molecules.⁴⁸ The low binding energy contribution is more pronounced for the monolayers exposed to TCNQF₄, indicating that the monolayers are complexed with larger amount of negatively charged species. In sharp contrast, the TTF-C₁₀ monolayers exposed to TCNQ do not show this contribution and the decomposition gives a component at 400.4 (± 0.5) eV that is attributed to neutral TCNQ species (Figure 6).⁴⁸ This component also contributes to the N1s signal of TTF-C₁₀ monolayer exposed to TCNQF₂ while being only a minor component for TTF-C₁₀ monolayer exposed to TCNQF₄.



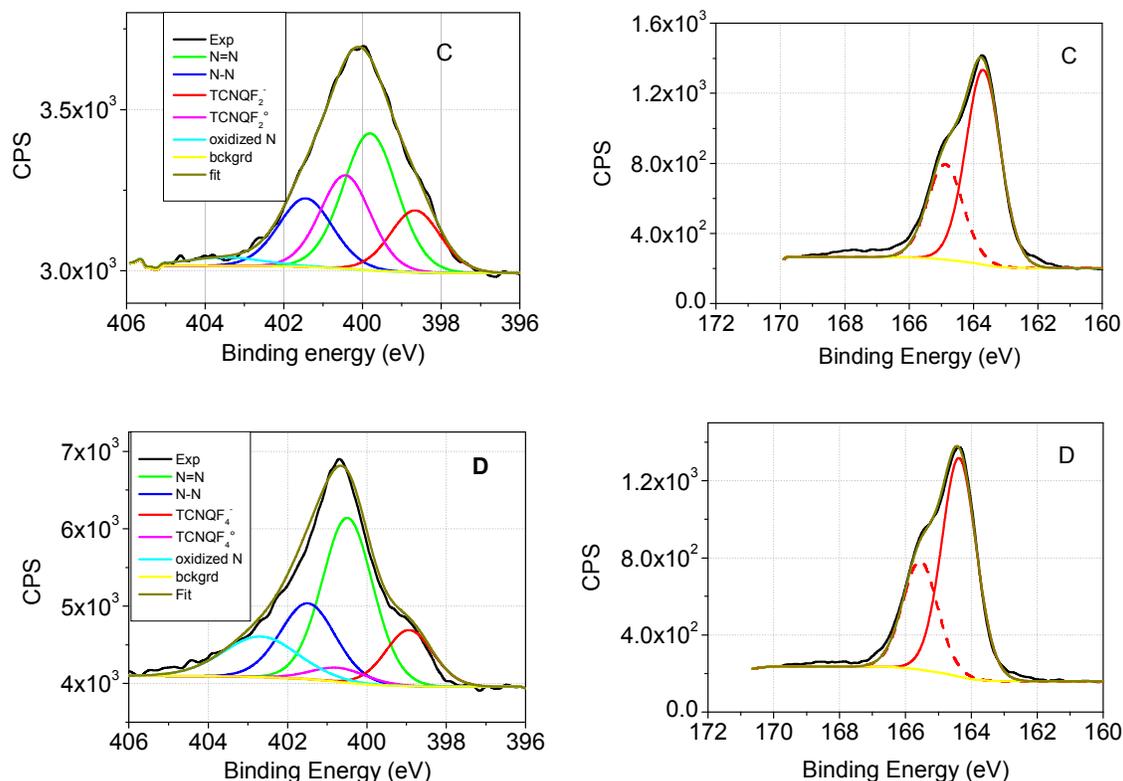


Figure 6. Peak-fitted high resolution core level spectra of N1s (left) and S2p (right) for PPF modified by TTF-C₁₀ monolayer, before (A) and after exposure to TCNQ (B), TCNQF₂ (C) and TCNQF₄ (D), respectively.

It is further interesting to focus on the signal corresponding to S2p for the four different samples. In all cases, the experimental signal exhibits the expected doublet structure due to spin orbit splitting that leads to S2p_{3/2} and S2p_{1/2} peaks (Figure 6). For the TTF-C₁₀ monolayers unexposed and exposed to TCNQ and TCNQF₂, the main doublet at 163.6 (± 0.5) eV (S2p_{3/2}) and 164.8 (± 0.5) eV (S2p_{1/2}) could be ascribed to the neutral TTF units (Figure 6).⁴⁹ Interestingly, the TTF-C₁₀ monolayers exposed to TCNQF₄, lead to a S2p doublet signal at 164.4 (± 0.5) eV (S2p_{3/2}) and at 165.6 (± 0.5) eV (S2p_{1/2}), hence significantly shifted to higher binding energy (Figure 6). This result agrees well with the reported position of

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3 positively charged TTF molecules (TTF^+),^{49,50} indicating that the TTF units are oxidized
4 when exposed to TCNQF_4 . The presence of negatively charged TCNQF_4 as evidenced in the
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positively charged TTF molecules (TTF^+),^{49,50} indicating that the TTF units are oxidized when exposed to TCNQF_4 . The presence of negatively charged TCNQF_4 as evidenced in the N1s signal establishes that TCNQF_4 molecules symmetrically act as electron acceptor, showing the full charge transfer process between the immobilized TTF units and TCNQF_4 . Contrariwise, the XPS analyses indicate that the immobilized TTF units form neutral donor-acceptor complexes with TCNQ. A less clear-cut phenomenon could be deduced from the XPS studies in the case of TCNQF_2 , because of the presence of a mixture of neutral and fully ionic charge-transfer complexes at the PPF surfaces. Remarkably, these behaviors are fully similar to those described in the solid-state. In the solid-state, depending on the oxidation potential value of the donor relatively to the reduction potential of the acceptor, complexes of different natures could be isolated: for instance, neutral charge-transfer complex if the potentials difference between acceptor and donor is less than -350 mV, while neutral-ionic transitions could be observed for potentials difference between 0 and -350 mV.^{51,52} A fully ionic charge-transfer complex could form if the reduction potential of the acceptor is higher than the oxidation potential of the donor, leading to the formation of a salt with a ionicity degree equal to 1.^{53,54} In our work, the formation of a fully ionic charge-transfer complex could happen only with the TCNQF_4 acceptor, by considering the oxidation potential of the immobilized TTF units relatively to the reduction potential of TCNQF_4 . Likewise, exposure of the TTF- C_{10} monolayers to TCNQ could yield to neutral donor-acceptor complexes, while the potentials difference between TCNQF_2 and the immobilized TTF units falls in line with the coexistence of neutral and ionic charge-transfer complexes. The XPS measurements strongly support the formation of charge-transfer complexes organized as a 2D arrangement with variable degree of charge transfer. In the TTF- C_{10} monolayer exposed to TCNQF_4 , the S2p signal clearly shows that all the TTF moieties are under the radical cation form, interacting with negatively charged TCNQF_4 as identified in the corresponding N1s spectrum.

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3 These latter anionic species account for 80 % of the detected TCNQF₄, showing that an
4 excess of neutral TCNQF₄ that are not strongly interacting with the immobilized TTF radical
5 cations are also present in the layer (see table 3 and discussion below). In the TTF-C₁₀
6 monolayer exposed to TCNQF₂, S2p signal does not allow to quantify confidently the two
7 kind of TTF species (neutral and radical cation species) because the XPS resolution cannot
8 mitigate the strong overlapping of these two signals. However, analysis of the N1s signal
9 shows that 40 % anionic and 60% neutral TCNQF₂ species co-exist in the layer, supporting
10 the formation of mixed neutral and ionic complexes.
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21 Because of the fluorine contamination of the samples, only the N/S ratio was further
22 considered to study more quantitatively the surface composition of the immobilized
23 complexes. It is noticeable that the experimental ratio agrees well the theoretical expected
24 ones for the TTF-C₁₀ monolayers before exposure to any of the TCNQ compounds. Different
25 theoretical ratios were calculated in Table 3 depending on the stoichiometry of the donor-
26 acceptor complex. From comparison with the experimentally estimated ratio, it could be
27 proposed that the immobilized TTF units form a complex with TCNQ or TCNQF₂ with a
28 stoichiometry corresponding to one or two TTF for one TCNQ/TCNQF₂ while the charge-
29 transfer complex TTF-TCNQF₄ involves one TTF for one or two TCNQF₄. Obviously, some
30 immobilized TTF units could be free of acceptor neighbors, especially in the case of TCNQ
31 and TCNQF₂, as reflect the experimental N/S ratios which are lower than the theoretical ones,
32 whatever the proposed stoichiometries. Similarly, the lower N/S ratio obtained for complexes
33 with TCNQF₂ than that for complexes with TCNQ suggest that there are less TCNQF₂
34 molecules interacting with the TTF units.
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Table 3. Experimental N/S Ratios Evaluated from XPS Data and Comparison with the Theoretical Ratios Calculated for Different Complex Stoichiometries TCNQ Derivatives over TTF-C₁₀

N/S	TTF-C ₁₀	TCNQ/ TTF-C ₁₀	TCNQF ₂ / TTF-C ₁₀	TCNQF ₄ / TTF-C ₁₀
Experimental	0.38 (<i>theor.</i> 0.43)	0.66	0.53	1.20
1:1	-	1	1	1
1:2	-	0.71	0.71	0.71
2:1	-	1.57	1.57	1.57

It is worth outlining that these results fall in line with the different blocking behaviors toward dopamine of the TTF-C₁₀ monolayers exposed to the acceptors and with the decrease of the electrochemical activity of the layer. Thus, the strongest blocking behavior is observed for the TTF-C₁₀ exposed to TCNQF₄. If there is more than one TCNQF₄ compounds around the TTF units, the resulting steric hindrance prevents the dopamine from accessing the carbon surface. The decrease of electroactivity of the layer through the ratio $i_p/i_{p_{TTF}}$ could be considered as a quantification of the strength of the association between the immobilized TTF and the different acceptors in relation with the 2D organization probably driven by the ionic, neutral or mixed nature of the charge-transfer complexes.

CONCLUSION

Alkyl-TTF molecules (TTF-C_n) could be immobilized as highly robust monolayers on carbon surfaces through an electrografting method combined to a click chemistry coupling of TTF-C_n-azide precursors. When the TTF monolayer is exposed to an acceptor like TCNQ, TCNQF₂ or TCNQF₄, donor-acceptor complexes are formed on the surface. The formation of the complexes lead to a considerable decrease of the voltammetric peak currents. UMEC measurements with original crystal samples unambiguously confirm that a strong reduction of electro-activity accompanies the formation of charge-transfer complexes. Interestingly, the

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4 complexation could be modulated by varying the alkyl chain lengths of the bridge or by
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6 varying the strength of the acceptor, and the peak current decrease constitutes a convenient
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8 tool to monitor this modulation. The TTF units attached to the surface with the shortest and
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10 less flexible bridge (TTF-C₃) are hardly sensitive to the variation of the acceptor strength in
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12 sharp contrast to TTF-C₁₀ that also allow a more efficient complexation with a given acceptor.
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14 XPS measurements point to the formation of donor-acceptor complexes of different nature,
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16 according to the strength of the acceptor. Fully ionic charge-transfer complex is formed upon
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18 exposure of immobilized TTF to the more oxidizing TCNQF₄, while a neutral complex is
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20 obtained from exposure to the less oxidizing TCNQ. The TTF monolayers exposed to the
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22 intermediate TCNQF₂ yield neutral-ionic systems. Noticeably, these donor-acceptor
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24 interactions evidenced at the carbon surfaces fully mimic those described in the solid-state.
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26 This work gives a rare example of a system directly connected to an electrode surface
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28 incorporating donor-acceptor complexes with a fine control of the degree of charge transfer.
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30 The modulation of the acceptor' strength offers the possibility of crystal-like engineering at a
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32 conductive surface to afford integrated molecular conductors.
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ASSOCIATED CONTENT

Supporting Information .Synthetic procedures and compounds characterization, additional electrochemical experiments for TTF layers and ferrocenyl layers, details about UMEC preparation and additional CVs of crystals, XPS survey spectra and high resolution core level fitted spectra.

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52 **GRAPHICAL ABSTRACT**
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