



**HAL**  
open science

# Tetrathiafulvalene-Tetracyanoquinodimethane Charge-Transfer Complexes Wired to Carbon Surfaces: Tuning of the Degree of Charge Transfer

Joanna Jalkh, Yann Leroux, Antoine Vacher, Dominique Lorcy, Philippe Hapiot, Corinne Lagrost

► **To cite this version:**

Joanna Jalkh, Yann Leroux, Antoine Vacher, Dominique Lorcy, Philippe Hapiot, et al.. Tetrathiafulvalene-Tetracyanoquinodimethane Charge-Transfer Complexes Wired to Carbon Surfaces: Tuning of the Degree of Charge Transfer. *Journal of Physical Chemistry C*, 2016, 120 (49), pp.28021–28030. 10.1021/acs.jpcc.6b09459 . hal-01438122

**HAL Id: hal-01438122**

**<https://hal-univ-rennes1.archives-ouvertes.fr/hal-01438122>**

Submitted on 10 Apr 2017

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Joanna Jalkh, Yann R Leroux, Antoine Vacher, Dominique Marie Lorcy, Philippe Hapiot, and Corinne Lagrost

*J. Phys. Chem. C*, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcc.6b09459 • Publication Date (Web): 14 Nov 2016

Downloaded from <http://pubs.acs.org> on November 15, 2016

### Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

1  
2  
3  
4 **Tetrathiafluvalene-Tetracyanoquinodimethane Charge-Transfer**  
5  
6 **Complexes Wired to Carbon Surfaces: Tuning of the Degree of Charge**  
7  
8 **Transfer**  
9

10  
11 Joanna Jalkh, Yann R. Leroux, Antoine Vacher, Dominique Lorcy, Philippe Hapiot, and  
12  
13 Corinne Lagrost\*

14  
15 *Institut des Sciences Chimiques de Rennes, Equipe MaCSE, CNRS and Université de Rennes*  
16  
17 *1, UMR n°6226, Campus de Beaulieu, 35042 Rennes Cedex, France.*  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

**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, TCNQF<sub>2</sub> (2,5 difluoro-TCNQ) and TCNQF<sub>4</sub> (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 TCNQF<sub>4</sub>, while a neutral complex is obtained after exposure to the less oxidizing TCNQ. Exposition of the TTF monolayers to the intermediate TCNQF<sub>2</sub> 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.<sup>1,2,3,4,5,6,7</sup> The charge-transfer behavior between an electron donor and an electron acceptor is generally investigated in 3D solid-phase systems, either organic crystals<sup>1,3,4,5</sup> or more recently at the interface between two crystals<sup>8,9</sup> or between a powder in contact with a single crystal.<sup>10</sup> 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.<sup>11</sup> 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.<sup>12</sup> More rarely, these systems have been engineered as self-assembled monolayers (SAMs),<sup>13,14,15,16,17,18,19,20</sup> 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.<sup>1</sup> The electron rich TTF molecules (and derivatives) could efficiently associate to electron-deficient acceptors like TCNQ derivatives to form charge transfer complexes.<sup>1</sup> These complexes have remarkable electronic properties that can serve to build high electrically conductive system<sup>21</sup> or molecular rectifier.<sup>22,23</sup>

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.<sup>24</sup> 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.<sup>13,15,16</sup> However, cyclic

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

voltammetry analyses have revealed a puzzling behavior of these SAMs since the immobilized TTFs lost their electroactivity after exposure to TCNQ.<sup>16</sup> 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 TCNQF<sub>4</sub>, 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.<sup>25</sup> 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.<sup>26</sup>

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.<sup>27</sup> Carbon substrates present also interests for preparing materials with new properties as recently exemplified with the modification of graphene layers by TTF derivatives.<sup>28</sup> 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.<sup>27</sup> 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-ArN<sub>2</sub><sup>+</sup>).<sup>29</sup> After removal of the TIPS group, a dense reactive ethynyl-terminated monolayer is obtained and

1  
2  
3 could be post-functionalized by using the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition  
4 with a variety of organic molecules containing an azido group. Interestingly, the distance  
5 between functional groups is controlled by the size of the leaving protecting group.<sup>30</sup> In this  
6 work, we took benefit of this strategy for preparing well-organized, covalently attached TTF  
7 monolayers bridged with alkyl chain of different length (propyl, pentyl and decyl, i.e. C<sub>3</sub>, C<sub>5</sub>  
8 and C<sub>10</sub>, respectively) on a carbon surface. Their charge transfer properties were carefully  
9 investigated upon exposure to a family of acceptors of increasing strength, TCNQ, TCNQF<sub>2</sub>  
10 and TCNQF<sub>4</sub>, by combining cyclic voltammetry, measurements with cavity  
11 ultramicroelectrode (UMEC) and X-ray photoelectron spectroscopy (XPS). Remarkably, our  
12 results evidence the formation of charge transfer complexes of different nature at the interface  
13 as function of the acceptors strength.  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31

## 32 1. EXPERIMENTAL SECTION

33  
34  
35 **Chemicals.** Unless specified, all compounds were commercially available reagents and  
36 were used as received. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) of  
37 electrochemical grade was purchased from Aldrich. 4-((triisopropylsilyl)ethynyl)  
38 benzenediazonium tetrafluoroborate (TIPS-Eth-ArN<sub>2</sub><sup>+</sup>) was prepared according to a  
39 previously described procedure.<sup>31</sup> TCNQF<sub>4</sub> (2,5-difluoro-TCNQ) was prepared according to a  
40 published procedure.<sup>32</sup> The synthesis of the azido TTFs with different alkyl chains was  
41 realized starting from the corresponding iodo-alkyl-TTF according to published procedures  
42 (see supporting information).<sup>33</sup>  
43  
44  
45  
46  
47  
48  
49  
50  
51

52 **Electrochemical Measurements.** Electrochemical modification and characterization  
53 were performed with an Autolab PGSTAT N302 potentiostat/galvanostat (EcoChemie B.V.)  
54 equipped with the GPES software. A conventional three-electrode system, comprising a 3 mm  
55  
56  
57  
58  
59  
60

1  
2  
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.  
9

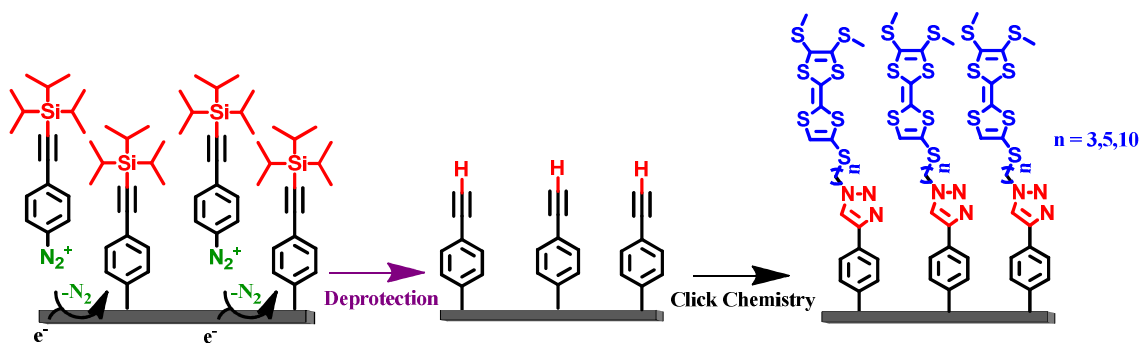
10  
11 For UMEC analyses,<sup>34</sup> the ultramicroelectrode was provided through the “UMEC  
12 Network of CNRS”.<sup>35</sup> The microcavity of the ultra-microelectrode (approximately 17  $\mu\text{m}$   
13 diameter cavity) was filled with a homogeneous mixture of the crystal under study and  
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<sup>-1</sup> KPF<sub>6</sub> as electrolyte at a scan rate of 10 mV s<sup>-1</sup>.  
16

17  
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-ArN<sub>2</sub><sup>+</sup> onto the carbon electrode from  
22 an acetonitrile solution containing 10<sup>-2</sup> mol L<sup>-1</sup> TIPS-Eth-ArN<sub>2</sub><sup>+</sup> and 10<sup>-1</sup> mol L<sup>-1</sup> TBAPF<sub>6</sub> and  
23 using 5 cycles between 0.6 and -0.75 V (vs SCE) at a scan rate of 50 mV s<sup>-1</sup>. 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<sup>-1</sup> mol L<sup>-1</sup> TBAF  
26 (tetrabutylammonium fluoride) in THF for 20 min. N<sub>3</sub>-C<sub>n</sub>-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 (CH<sub>2</sub>)<sub>n</sub>-N<sub>3</sub> (n = 3, 5, 10) (1 mg) in THF and CuSO<sub>4</sub> (2.5 mL, 10<sup>-2</sup> mol L<sup>-1</sup>) was added. After  
30 degassing the solution for 15 min under argon, L(+)-ascorbic acid (10<sup>-2</sup> mol L<sup>-1</sup> in 2.5 mL  
31 water containing 80 mg of NaHCO<sub>3</sub>) was added dropwise to the solution. The reaction  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



1  
2  
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.  
5  
6

7  
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 $\alpha$  X-ray  
10 source working at 1486.6 eV and using a spot size of 0.7 x 0.3 mm<sup>2</sup>. 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).  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28



43 **Scheme 1.** Functionalization of carbon surfaces by TTF-terminated monolayers  
44  
45  
46  
47

## 48 2. RESULTS AND DISCUSSION

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

50  
51  
52 Three TTF derivatives with different alkyl-chain linkers (propyl (C<sub>3</sub>), pentyl (C<sub>5</sub>) and decyl  
53 (C<sub>10</sub>)) were immobilized on the carbon surface following a previously published procedure as  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 depicted in Scheme 1.<sup>29</sup> The C<sub>n</sub>-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<sup>-1</sup> TBAPF<sub>6</sub> 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).<sup>1</sup> 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.<sup>36</sup> 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<sup>-2</sup>  
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),<sup>30</sup> 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  $3.6 \times 10^{-10}$  mol cm<sup>-2</sup>.<sup>13</sup> 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  $2.3 \times 10^{-10}$  mol cm<sup>-2</sup>  
20 for an ideal hexagonal compact arrangement.<sup>30</sup> 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).<sup>26,38,24</sup> While the chemical stability and redox activity of the TTF are generally kept  
24 after immobilization in SAMs,<sup>26,37</sup> 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.<sup>26,38</sup>  
27 These effects were ascribed to the interactions between the TTF moieties, and could be easily  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

identified by cyclic voltammetry.<sup>26</sup> 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).<sup>26,38,24</sup> These observations were explained by strong intermolecular interaction taking place within the monolayers upon the charging process.<sup>26,39</sup> 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 TTF<sup>2+</sup> centers.<sup>26,39</sup>

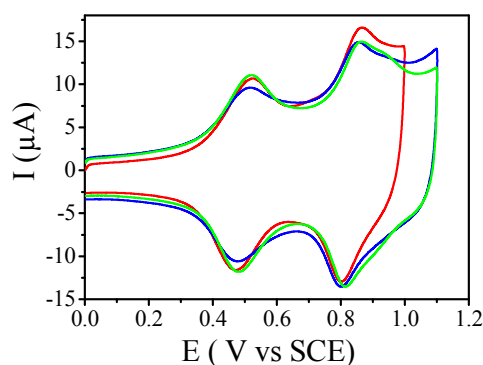
**Table 1. Electrochemical Data from Cyclic Voltammetry for the Oxidation of Monolayers of TTF-C<sub>n</sub> (n= 3, 5, 10)<sup>a</sup> in CH<sub>2</sub>Cl<sub>2</sub> Containing 0.2 mol L<sup>-1</sup> TBAPF<sub>6</sub>.**

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

<sup>a</sup>All 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.<sup>30</sup> 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.<sup>30</sup> This would allow an easier solvation process/counter-ion penetration in the monolayers, decreasing the strength of attraction between the TTF<sup>2+</sup> units. Additionally, a shoulder-like system is observed at the second oxidation peak (located at the more positive potentials side) for the TTF linked

through the longest alkyl chains (TTF-C<sub>5</sub> and TTF-C<sub>10</sub>) (Figure 1). This “extra” peak is even more visible for the TTF with the longest alkyl chain linker (C<sub>10</sub>). The splitting of the oxidation/reduction peaks suggests the co-existence of “isolated” (lower potential) and “clustered” (higher potential) TTF<sup>2+</sup> species, the formation of “clustered” species being facilitated by the flexibility introduced by longer alkyl chains as observed for alkyl-ferrocene layer.<sup>40</sup>

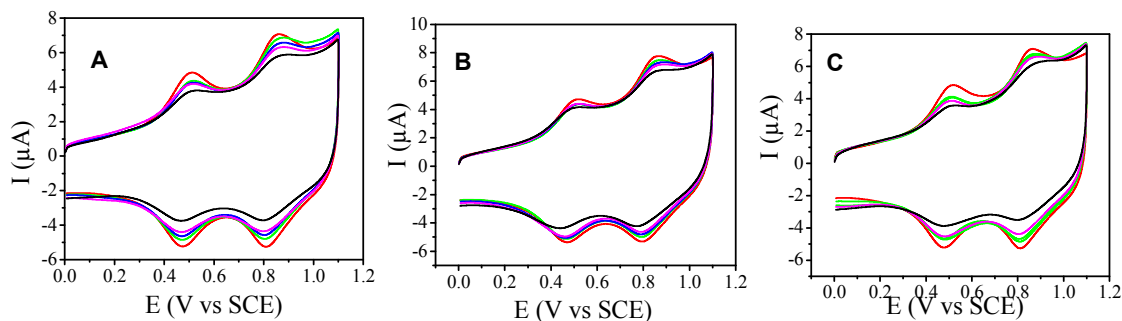


**Figure 1.** Cyclic voltammograms recorded in dichloromethane (+ 0.2 mol L<sup>-1</sup> TBAPF<sub>6</sub>) of TTF-terminated monolayers having bridging units of different chain lengths (C<sub>3</sub> (red) C<sub>5</sub> (blue) and C<sub>10</sub> (green)) at a glassy carbon electrode. Scan rate = 200 mV s<sup>-1</sup>.

#### Acceptor-donor Complexes between TTF-C<sub>n</sub> Monolayers and TCNQ Derivatives.

To examine the properties of charge-transfer complexes with the TTF layer on carbon, cyclic voltammograms of the TTF layers were recorded before and after immersion of the modified electrode in CH<sub>2</sub>Cl<sub>2</sub> solutions of TCNQ, TCNQF<sub>2</sub> and TCNQF<sub>4</sub> with increasing concentrations and after extensive rinsing with clean CH<sub>2</sub>Cl<sub>2</sub>. For the three layers, a considerable decrease of the oxidation peak currents is observed after exposure to the TCNQ derivatives solutions. Figure 2 shows some typical voltammograms obtained for the TTF-C<sub>10</sub> layer. Under our experimental conditions, the current intensities decrease monotonically with the increase of acceptors concentration to reach a constant value when the TCNQs

1  
2  
3 concentrations are above  $2 - 4 \times 10^{-3} \text{ mol L}^{-1}$ . From the maximum current decrease, we could  
4  
5 estimate that roughly 40 to 60 % of the immobilized TTF units become electrochemically  
6  
7 silent after exposure to the TCNQ derivatives solutions. The observation of the current drop is  
8  
9 the least intense for the layer with the short linker, indicating that a more flexible layer favors  
10  
11 the phenomenon. For example, using TCNQF<sub>4</sub> as an acceptor, 40 % of TTF units become  
12  
13 electro-inactive for the TTF-C<sub>3</sub> layer after immersion in the acceptor solution while more than  
14  
15 55 % for TTF-C<sub>5</sub> and TTF-C<sub>10</sub> are silent under the same conditions. In all cases, it was not  
16  
17 possible to recover the initial electro-activity of the layer even after repeated cycling in a  
18  
19 blank CH<sub>2</sub>Cl<sub>2</sub> solution; the cyclic voltammograms of the TTF layer remain unchanged.  
20  
21 Finally, as a test experiment, a comparable monolayer, but functionalized with undecyl-  
22  
23 ferrocene units, was exposed to the same TCNQF<sub>4</sub> solutions. No modifications of the  
24  
25 voltammograms were observed after exposure of the modified surface to TCNQF<sub>4</sub> (Figure  
26  
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  
30  
31 on the strength of the acceptor which can be quantified through its formal reduction potential.  
32  
33 The di- and tetra-fluoro analogues of TCNQ exhibit more positive formal potentials than  
34  
35 TCNQ, i.e.  $E^\circ = 0.53 \text{ V vs SCE}$ ,  $0.39 \text{ V vs SCE}$  and  $+0.17 \text{ V vs SCE}$  for TCNQF<sub>4</sub>, TCNQF<sub>2</sub>  
36  
37 and TCNQ, respectively.  
38  
39  
40  
41  
42 and TCNQ, respectively.



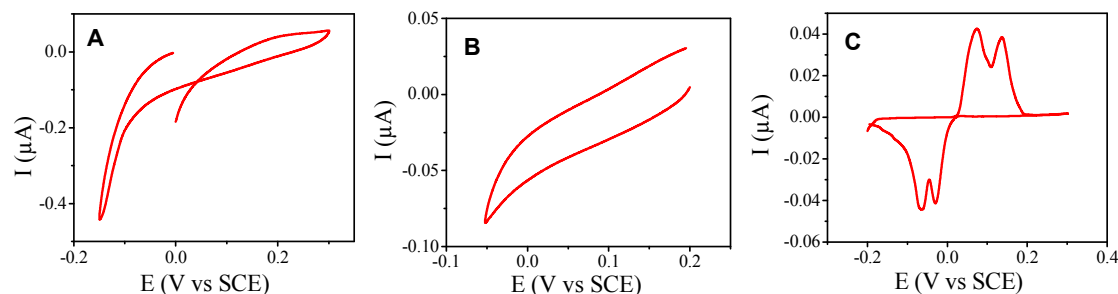
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
**Figure 2.** Cyclic voltammograms in dichloromethane (+ 0.2 mol L<sup>-1</sup> TBAPF<sub>6</sub>) of a glassy carbon electrode modified with the TTF-C<sub>10</sub> monolayer, before (red curves) and after

1  
2  
3 exposure to a solution with increasing concentrations of TCNQ derivatives (A) TCNQ, (B)  
4 TCNQF<sub>2</sub>, (C) TCNQF<sub>4</sub>). S1 = 10<sup>-4</sup> mol L<sup>-1</sup> (green), S2 = 5 10<sup>-4</sup> mol L<sup>-1</sup> (blue), S3 = 10<sup>-3</sup> mol  
5  
6 L<sup>-1</sup> (magenta) and S4 = 8 10<sup>-3</sup> mol L<sup>-1</sup> (black).  
7  
8  
9

10  
11  
12  
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.<sup>16</sup> Authors  
15 suggested that this current drop results from a donor-acceptor interaction between the TTF  
16 and the TCNQ.  
17  
18  
19  
20

21  
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,<sup>1,5</sup> 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 TCNQF<sub>2</sub> (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<sub>n</sub> and  
30 TCNQF<sub>4</sub>. The electrochemical activity of these crystals was investigated by means of the  
31 ultramicroelectrode cavity (UMEC) technique.<sup>34,35</sup> 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-TCNQF<sub>2</sub> 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 TCNQF<sub>2</sub> crystals).  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

The electrochemical measurement was performed in 1:1 (v/v) ethanol/water mixture containing (+0.1 mol L<sup>-1</sup>) KPF<sub>6</sub> 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 TCNQF<sub>2</sub> reduction) that are clearly detected in the pure TTF crystals, disappear in the TTF-TCNQF<sub>2</sub> charge-transfer crystal (Figure 3).



**Figure 3.** Cyclic voltammetry with an UMEC recorded in a 1:1 ethanol/water solution (+ 0.1 mol L<sup>-1</sup> KPF<sub>6</sub>). Scan rate = 10 mV s<sup>-1</sup>. (A) TTF-TCNQF<sub>2</sub> crystal observed in oxidation, (B) TTF-TCNQF<sub>2</sub> 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-TCNQF<sub>2</sub> 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

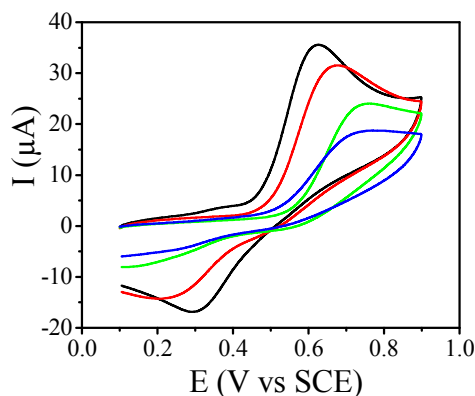
1  
2  
3 compacted pellets.<sup>41</sup> Large overpotentials were required to observe the electrochemical  
4 signature of TTF and TCNQ. Therefore, the remaining electrochemical activity observed with  
5 the TTF monolayers, after exposure to TCNQ derivatives solution, is probably due to the TTF  
6 units, which are not involved in the donor/acceptor interactions.  
7  
8  
9

10  
11  
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<sub>n</sub> 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,  $E^\circ_{TCNQ}$  and on linker length (Figure S9). For the shortest and less  
18 flexible layer (TTF-C<sub>3</sub>), 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-C<sub>10</sub> layer,  
20  $i_p/i_{pTTF}$  varies considerably with the acceptor as the following trend: TCNQF<sub>4</sub> (0.38) < TCNQ  
21 (0.5) < TCNQF<sub>2</sub> (0.7). If the most efficient complexation is indeed observed with TCNQF<sub>4</sub> as  
22 acceptor, having the larger reduction potential, an inversion exists between TCNQ and  
23 TCNQF<sub>2</sub> suggesting that the redox potential is probably not the only relevant parameter to  
24 quantify the strength of such interaction(*vide infra*).  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40

41 To further confirm this puzzling behavior, the blocking properties towards electronic  
42 transfer of the TTF-C<sub>10</sub> 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.<sup>42,43,44</sup> Thus,  
48 observation of electrochemical activity implies that dopamine is able to reach the electrode  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



1  
2  
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-C<sub>10</sub> monolayer before and after  
7 exposure to the TCNQ derivatives.  
8  
9  
10  
11  
12  
13



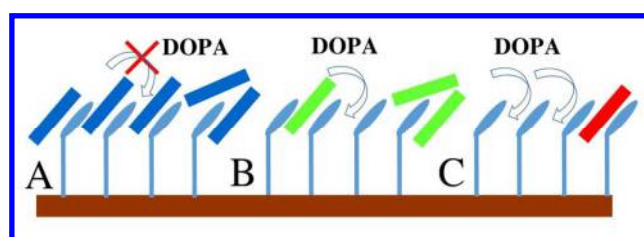
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40

**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 electrode modified with TTF-C<sub>10</sub> monolayers before (black) and after exposure to TCNQ derivatives, TTF-TCNQF<sub>2</sub> (red), TTF-TCNQ (green), and TTF-TCNQF<sub>4</sub> (blue). Scan rate =  $0.1 \text{ V s}^{-1}$ .

41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

A well-defined voltammogram is observed on carbon surfaces modified with TTF-C<sub>10</sub> (before exposure to acceptors), indicating the presence of pathways allowing the passage of dopamine through the TTF layer. After exposure to TCNQ derivatives, the oxidation of dopamine remains visible, but the peak-to-peak potential separations increase, the peak currents display a larger plateau-shape and their intensity are lowered. These observations show that the passage of dopamine through the TTF layer becomes more difficult, corresponding to a more blocking character of the layer after exposure to a TCNQ derivative.<sup>45, 46</sup> However, the magnitude of the variations in the dopamine oxidation signal are

different according to the different acceptors (Figure 4). It is especially remarkable that the same trend is deduced from the ratios  $i_p/i_{pTTF}$  that characterize the strength of the acceptor-donor complexes and from the variations of the blocking character of the layer after exposure to the acceptor, i.e.  $TTF-TCNQF_4 > TTF-TCNQ > TTF-TCNQF_2$ . These results support the idea that intermolecular spaces between the TTF units exist within the monolayer (Figure 4, black line) and can be filled by the acceptors (Figure 4, green/red/blue lines). Indeed, considering that the molecular size of dopamine and TCNQ are comparable, the intermolecular space is large enough to permit the passage of TCNQ derivatives within the layer, promoting the formation of the charge transfer complexes. The TCNQ compounds that interact with the TTF layer literally close the intermolecular spaces and add rigidity in the structure of the monolayer, preventing dopamine from reaching the carbon surface. Depending on the strength of the donor-acceptor interactions, these spaces are more or less well blocked (Figure 5). Thus,  $TCNQF_4$  undergoes the most efficient charge transfer complexation and its interaction with the TTF- $C_{10}$  monolayer leads to the largest blocking of the carbon surface towards dopamine (Figure 4, blue line).



**Figure 5.** Schematic representation of the blocking properties towards dopamine (DOPA) of the TTF- $C_{10}$  monolayer associated with A)  $TCNQF_4$ , B)  $TCNQ$  and C)  $TCNQF_2$

**XPS Analyses of Donor-Acceptor Complex At TTF- $C_{10}$  Monolayers.** PPF (Pyrolyzed Photoresist Film) substrates functionalized with TTF- $C_{10}$  monolayers were analyzed by X-ray

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-C<sub>10</sub> 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 TCNQF<sub>2</sub> and TCNQF<sub>4</sub>. Accordingly, the fluorine atomic percentage is larger with TCNQF<sub>4</sub> than with TCNQF<sub>2</sub>. Trace levels of fluorine (< 1%) are also detected in the survey scans of TTF-C<sub>10</sub> monolayers and TTF-C<sub>10</sub> monolayers exposed to TCNQ (Table 2) probably due to a contamination at the samples during the deprotection step in the monolayer preparation.

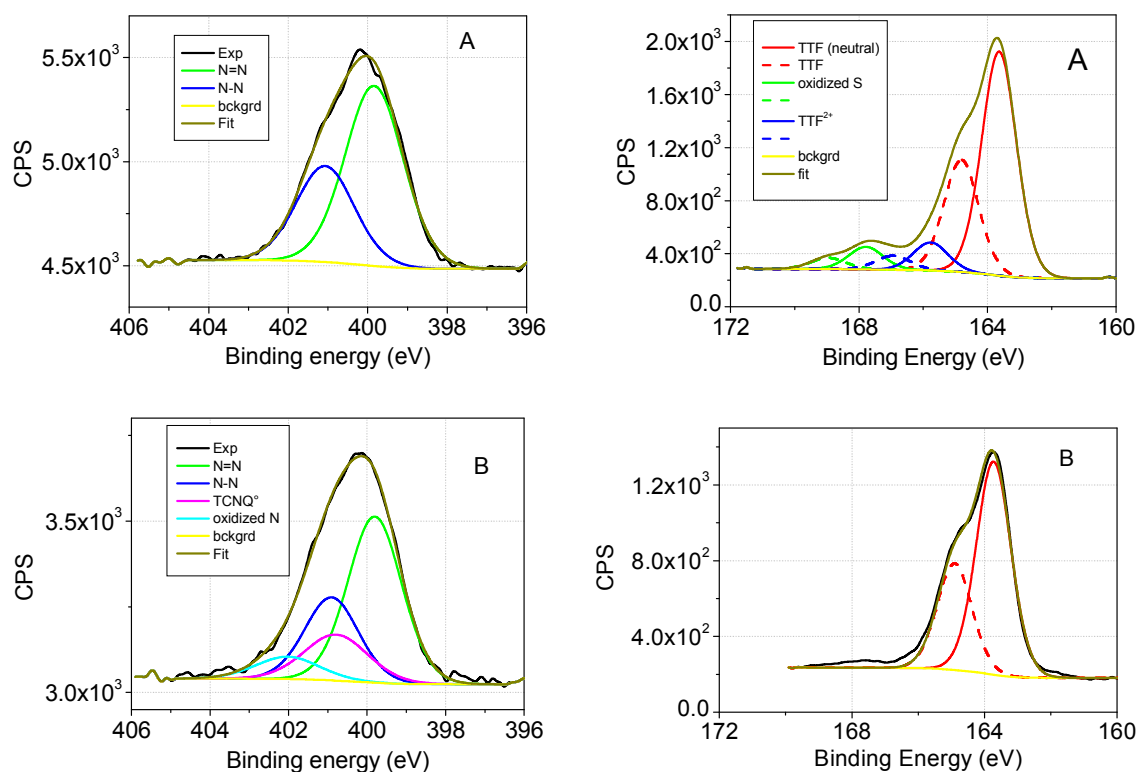
**Table 2. Surface Composition (% atom,  $\pm 20\%$ ) of TTF-C<sub>10</sub> Monolayers before and after Exposure to TCNQ, TCNQF<sub>2</sub> or TCNQF<sub>4</sub> Solutions**

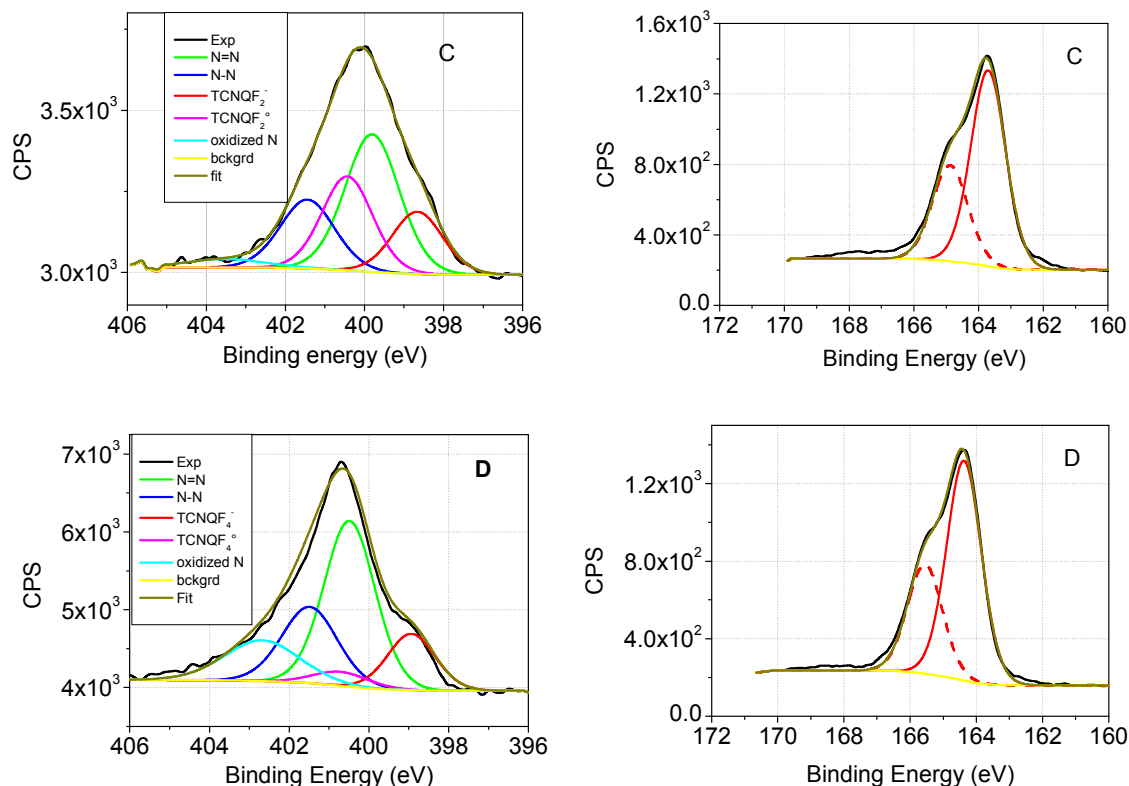
% atom	TTF	TTF-TCNQ	TTF-TCNQF <sub>2</sub>	TTF-TCNQF <sub>4</sub>
%C	79.7	86.8	82.8	82.3
%N	1.7	1.9	1.7	3.6
%F	0.9	0.6	2.9	3.5
% S	4.5	2.9	3.2	3.0
% O	13.2	7.8	9.4	7.6

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 ( $\pm 0.5$ ) (N-N=N) and at 401.1 ( $\pm 0.5$ ) eV (N-N=N), with a ratio of 1:2)<sup>47</sup> for the TTF-C<sub>10</sub> 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 ( $\pm 0.5$ ) eV) for the monolayers exposed to TCNQF<sub>2</sub> and TCNQF<sub>4</sub> (Figure 6). This could be ascribed to the presence of negatively

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

charged TCNQF<sub>2</sub> or TCNQF<sub>4</sub> molecules.<sup>48</sup> The low binding energy contribution is more pronounced for the monolayers exposed to TCNQF<sub>4</sub>, indicating that the monolayers are complexed with larger amount of negatively charged species. In sharp contrast, the TTF-C<sub>10</sub> 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).<sup>48</sup> This component also contributes to the N1s signal of TTF-C<sub>10</sub> monolayer exposed to TCNQF<sub>2</sub> while being only a minor component for TTF-C<sub>10</sub> monolayer exposed to TCNQF<sub>4</sub>.





**Figure 6.** Peak-fitted high resolution core level spectra of N1s (left) and S2p (right) for PPF modified by TTF-C<sub>10</sub> monolayer, before (A) and after exposure to TCNQ (B), TCNQF<sub>2</sub> (C) and TCNQF<sub>4</sub> (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<sub>3/2</sub> and S2p<sub>1/2</sub> peaks (Figure 6). For the TTF-C<sub>10</sub> monolayers unexposed and exposed to TCNQ and TCNQF<sub>2</sub>, the main doublet at 163.6 (± 0.5) eV (S2p<sub>3/2</sub>) and 164.8 (± 0.5) eV (S2p<sub>1/2</sub>) could be ascribed to the neutral TTF units (Figure 6).<sup>49</sup> Interestingly, the TTF-C<sub>10</sub> monolayers exposed to TCNQF<sub>4</sub>, lead to a S2p doublet signal at 164.4 (± 0.5) eV (S2p<sub>3/2</sub>) and at 165.6 (± 0.5) eV (S2p<sub>1/2</sub>), hence significantly shifted to higher binding energy (Figure 6). This result agrees well with the reported position of

1  
2  
3 positively charged TTF molecules ( $\text{TTF}^+$ ),<sup>49,50</sup> indicating that the TTF units are oxidized  
4  
5 when exposed to  $\text{TCNQF}_4$ . The presence of negatively charged  $\text{TCNQF}_4$  as evidenced in the  
6  
7 N1s signal establishes that  $\text{TCNQF}_4$  molecules symmetrically act as electron acceptor,  
8  
9 showing the full charge transfer process between the immobilized TTF units and  $\text{TCNQF}_4$ .  
10  
11 Contrariwise, the XPS analyses indicate that the immobilized TTF units form neutral donor–  
12  
13 acceptor complexes with TCNQ. A less clear-cut phenomenon could be deduced from the  
14  
15 XPS studies in the case of  $\text{TCNQF}_2$ , because of the presence of a mixture of neutral and fully  
16  
17 ionic charge-transfer complexes at the PPF surfaces. Remarkably, these behaviors are fully  
18  
19 similar to those described in the solid-state. In the solid-state, depending on the oxidation  
20  
21 potential value of the donor relatively to the reduction potential of the acceptor, complexes of  
22  
23 different natures could be isolated: for instance, neutral charge-transfer complex if the  
24  
25 potentials difference between acceptor and donor is less than -350 mV, while neutral-ionic  
26  
27 transitions could be observed for potentials difference between 0 and -350 mV.<sup>51,52</sup> A fully  
28  
29 ionic charge-transfer complex could form if the reduction potential of the acceptor is higher  
30  
31 than the oxidation potential of the donor, leading to the formation of a salt with a ionicity  
32  
33 degree equal to 1.<sup>53,54</sup> In our work, the formation of a fully ionic charge-transfer complex  
34  
35 could happen only with the  $\text{TCNQF}_4$  acceptor, by considering the oxidation potential of the  
36  
37 immobilized TTF units relatively to the reduction potential of  $\text{TCNQF}_4$ . Likewise, exposure  
38  
39 of the TTF- $\text{C}_{10}$  monolayers to TCNQ could yield to neutral donor-acceptor complexes, while  
40  
41 the potentials difference between  $\text{TCNQF}_2$  and the immobilized TTF units falls in line with  
42  
43 the coexistence of neutral and ionic charge-transfer complexes. The XPS measurements  
44  
45 strongly support the formation of charge-transfer complexes organized as a 2D arrangement  
46  
47 with variable degree of charge transfer. In the TTF- $\text{C}_{10}$  monolayer exposed to  $\text{TCNQF}_4$ , the  
48  
49 S2p signal clearly shows that all the TTF moieties are under the radical cation form,  
50  
51 interacting with negatively charged  $\text{TCNQF}_4$  as identified in the corresponding N1s spectrum.  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 These latter anionic species account for 80 % of the detected TCNQF<sub>4</sub>, showing that an  
4 excess of neutral TCNQF<sub>4</sub> 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-C<sub>10</sub>  
6 monolayer exposed to TCNQF<sub>2</sub>, 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 TCNQF<sub>2</sub> species co-exist in the layer, supporting  
10 the formation of mixed neutral and ionic complexes.  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20

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-C<sub>10</sub> 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 TCNQF<sub>2</sub> with a  
28 stoichiometry corresponding to one or two TTF for one TCNQ/TCNQF<sub>2</sub> while the charge-  
29 transfer complex TTF-TCNQF<sub>4</sub> involves one TTF for one or two TCNQF<sub>4</sub>. Obviously, some  
30 immobilized TTF units could be free of acceptor neighbors, especially in the case of TCNQ  
31 and TCNQF<sub>2</sub>, 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 TCNQF<sub>2</sub> than that for complexes with TCNQ suggest that there are less TCNQF<sub>2</sub>  
34 molecules interacting with the TTF units.  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

**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-C<sub>10</sub>**

N/S	TTF-C <sub>10</sub>	TCNQ/ TTF-C <sub>10</sub>	TCNQF <sub>2</sub> / TTF-C <sub>10</sub>	TCNQF <sub>4</sub> / TTF-C <sub>10</sub>
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-C<sub>10</sub> 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-C<sub>10</sub> exposed to TCNQF<sub>4</sub>. If there is more than one TCNQF<sub>4</sub> 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<sub>n</sub>) could be immobilized as highly robust monolayers on carbon surfaces through an electrografting method combined to a click chemistry coupling of TTF-C<sub>n</sub>-azide precursors. When the TTF monolayer is exposed to an acceptor like TCNQ, TCNQF<sub>2</sub> or TCNQF<sub>4</sub>, 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



1  
2  
3  
4 complexation could be modulated by varying the alkyl chain lengths of the bridge or by  
5  
6 varying the strength of the acceptor, and the peak current decrease constitutes a convenient  
7  
8 tool to monitor this modulation. The TTF units attached to the surface with the shortest and  
9  
10 less flexible bridge (TTF-C<sub>3</sub>) are hardly sensitive to the variation of the acceptor strength in  
11  
12 sharp contrast to TTF-C<sub>10</sub> that also allow a more efficient complexation with a given acceptor.  
13  
14 XPS measurements point to the formation of donor-acceptor complexes of different nature,  
15  
16 according to the strength of the acceptor. Fully ionic charge-transfer complex is formed upon  
17  
18 exposure of immobilized TTF to the more oxidizing TCNQF<sub>4</sub>, while a neutral complex is  
19  
20 obtained from exposure to the less oxidizing TCNQ. The TTF monolayers exposed to the  
21  
22 intermediate TCNQF<sub>2</sub> yield neutral-ionic systems. Noticeably, these donor-acceptor  
23  
24 interactions evidenced at the carbon surfaces fully mimic those described in the solid-state.  
25  
26 This work gives a rare example of a system directly connected to an electrode surface  
27  
28 incorporating donor-acceptor complexes with a fine control of the degree of charge transfer.  
29  
30 The modulation of the acceptor' strength offers the possibility of crystal-like engineering at a  
31  
32 conductive surface to afford integrated molecular conductors.  
33  
34  
35

### 36 37 38 **ACKNOWLEDGMENTS**

39  
40 J.J. thanks the Région Bretagne for financial support (461-ARED). The authors are grateful to  
41  
42 Dr. D. Hauchard (Institut des Sciences Chimiques de Rennes) for his help in the UMEC  
43  
44 experiments. Dr. O. Jeannin (Institut des Sciences Chimiques de Rennes) is thanked for the  
45  
46 gift of TCNQF<sub>4</sub> compound. J. Hamon (Institut des Matériaux de Nantes, Nantes, France) is  
47  
48 thanked for his help in the X-ray photoelectron spectra experiments. Dr M. Fourmigué  
49  
50 (Institut des Sciences Chimiques de Rennes) is warmly acknowledged for fruitful discussions.  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

## 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.

## AUTHOR INFORMATION

\*E-mail: [corinne.lagrost@univ-rennes1.fr](mailto:corinne.lagrost@univ-rennes1.fr). Phone +33 2 23 23 5940

## REFERENCES

---

(1) Bendikov, M.; Wudl, F.; Perepichka, D. F. Tetrathiafulvalenes, Oligoacenes, and Their Buckminsterfullerene Derivatives: The Brick and Mortar of Organic Electronics, *Chem. Rev.* **2004**, *104*, 4891–4946.

(2) Yamada, J.-i.; Akutsu, H.; Nishikawa, H.; Kikuchi, K. New Trends in the Synthesis of  $\pi$ -Electron Donors for Molecular Conductors and Superconductors, *Chem. Rev.* **2004**, *104*, 5057–5084.

(3) Geiser, U.; Schlueter, J. A. Conducting Organic Radical Cation Salts with Organic and Organometallic Anions, *Chem. Rev.* **2004**, *104*, 5203–5242.

(4) Fourmigué, M.; Batail, P. Activation of Hydrogen- and Halogen-Bonding Interactions in Tetrathiafulvalene-Based Crystalline Molecular Conductors, *Chem. Rev.* **2004**, *104*, 5379–5418.

1  
2  
3  
4  
5  
6 (5) Enoki, T.; Miyazaki, A. Magnetic TTF-Based Charge-Transfer Complexes. *Chem. Rev.*  
7  
8 **2004**, *104*, 5449–5478.

9  
10 (6) Coronado, E.; Day, P. Magnetic Molecular Conductors. *Chem. Rev.* **2004**, *104*, 5419–  
11  
12 5448.

13  
14 (7) Jérôme, D. Organic Conductors: From Charge Density Wave TTF–TCNQ to  
15  
16 Superconducting (TMTSF)<sub>2</sub>PF<sub>6</sub>. *Chem. Rev.* **2004**, *104*, 5565–5592.

17  
18 (8) Alves, H; Molinari, A. S.; Xie, H.; Mopurgo, A. F. Metallic Conduction at Organic  
19  
20 Charge-Transfer Interfaces. *Nat. Mat.* **2008**, *7*, 574-580.

21  
22 (9)Takahashi, Y.; Hayakawa, K.; Takayama, K.; Yokokura, S.; Harada, J.; Hasegawa, H.;  
23  
24 Inabe, T. Charge Conduction Properties at the Contact Interface between  
25  
26 (Phtalocyaninato)nickel (II) and Electron Acceptor Single Crystal, *Chem. Mater.* **2014**, *26*,  
27  
28 993-998.

29  
30 (10) Takahashi, Y.; Hayakawa, K.; Naito, T.; Inabe, T. What Happens at the Interface  
31  
32 between TTF and TCNQ Crystals (TTF = Tetrathiafulvalene and TCNQ = 7,7,8,8-  
33  
34 Tetracyanoquinodimethane)? *J. Phys. Chem. C* **2012**, *116*, 700-703.

35  
36 (11) Talham, D. R. Conducting and Magnetic Langmuir–Blodgett Films. *Chem. Rev.* **2004**,  
37  
38 *104*, 5479-5502.

39  
40 (12) Perepichka, D. F.; Bryce, M. R.; Pearson, C.; Petty, M.C.; McInnes, E. J. L.; Zhao, J.  
41  
42 P. A Covalent Tetrathiafulvalene–Tetracyanoquinodimethane Diad: Extremely Low HOMO–  
43  
44 LUMO Gap, Thermoexcited Electron Transfer, and High-Quality Langmuir–Blodgett Films.  
45  
46 *Angew. Chem. Int. Ed.* **2003**, *42*, 4636-4639.  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

---

(13) Yip, C. M.; Ward, M. D. Self-Assembled Monolayers with Charge-Transfer Groups: n-Mercaptoalkyl Tetrathiafulvalenecarboxylate on Gold. *Langmuir* **1994**, *10*, 549-556.

(14) Skulason, H.; Frisbie, C. D. Self-Assembled Monolayers with Charge-Transfer Functional Groups: Immobilization of the Electron Donor TMPD and the Electron Acceptor TCNQ, *Langmuir* **1998**, *14*, 5834-5840.

(15) Yuge, R.; Miyazaki, A.; Enoki, T.; Tamada, K.; Nakamura, F.; Hara, M. Fabrication of TTF-TCNQ Charge-Transfer Complex Self-Assembled Monolayers: Comparison between the Coadsorption Method and the Layer-by-Layer Adsorption Method. *J. Phys. Chem. B* **2002**, *106*, 6894-6901.

(16) Pacsial, E. J.; Alexander, D.; Alvarado, R. J.; Tomasulo, M.; Raymo, F. M. Donor/Acceptor Interactions in Self-Assembled Monolayers and Their Consequences on Interfacial Electron Transfer. *J. Phys. Chem. B* **2004**, *108*, 19307-19313.

(17) Howell, S.; Kuila, D.; Kasibhatla, B.; Kubiak, C. P.; Janes, D.; Reifenger, R. Molecular Electrostatics of Conjugated Self-assembled Monolayers on Au(111) Using Electrostatic Force Microscopy. *Langmuir* **2002**, *18*, 5120-5125.

(18) Skulason, H.; Frisbie, C. D. Direct Detection by Atomic Force Microscopy of Single Bond Forces Associated with the Rupture of Discrete Charge-Transfer Complexes. *J. Am. Chem. Soc.* **2002**, *124*, 15125-15133.

(19) Kasibhatla, B. S. T.; Labonté, A. P.; Zahid, F.; Reifenger, R. G.; Datta, S.; Kubiak, C. P. Reversibly Altering Electronic Conduction through a Single Molecule by a Chemical Binding Event. *J. Phys. Chem. B* **2003**, *107*, 12378-12383.

(20) Goeltz, J. C.; Kubiak, C. P. Mixed Valence Self-assembled Monolayers: Electrostatic Polarizabilities of the Mixed Valence States. *J. Phys. Chem. C* **2008**, *112*, 8114-8116.

(21) Ferraris, J.; Cowan, D. O.; Walatka, V.; Perlstein, J. H. Electron Transfer in a New Highly Conducting Donor-Acceptor Complex. *J. Am. Chem. Soc.* **1973**, *95*, 948-949.

(22) Aviram, A.; Ratner, M. A. Molecular Rectifier. *Chem. Phys. Lett.* **1974**, *29*, 277-283.

(23) Metzger, R. Unimolecular Electrical Rectifiers. *Chem Rev* **2003**, *103*, 3803-3834

(24) Yokota, Y.; Miyazaki, A.; Fukui, K. I.; Enoki, T.; Tamada, K.; Hara, M. Dynamic and Collective Electrochemical Responses of Tetrathiafulvalene Derivative Self-Assembled Monolayers. *J. Phys. Chem. B* **2006**, *110*, 20401-20408.

(25) Kim, J.-S.; Lee, S.-K.; Lee, H.-J.; Noh, D.-Y. A Charge-transfer Phenomenon between 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F<sub>4</sub>TCNQ) and a Tetrathiafulvalene-based Self-assembled Monolayer Using an Indium-Tin Oxide Electrode. *Bull. Korean Chem. Soc.* **2010**, *31*, 1415-1418.

(26) Blanchard, P. Y.; Alévêque, O.; Boisard, S.; Gautier, C.; El-Ghayoury, A.; Le Derf, F.; Breton, T.; Levillain, E. Intermolecular Interactions in Self-assembled Monolayers of Tetrathiafulvalene Derivatives. *Phys. Chem. Chem. Phys.* **2011**, *13*, 2118-2120.

(27) Pinson, J.; Podvorica, F. Attachment of Organic Layers to Conductive or Semiconductive Surfaces by Reduction of Diazonium Salts. *Chem. Soc. Rev.* **2005**, *34*, 429-439.

(28) Kaminska, I.; Barras, A.; Coffinier, Y.; Lisowski, W.; Roy, S.; Niedziolka-Jonsson, J.; Woisel, P.; Lyskawa, J.; Opallo, M.; Siriwardena, A.; et al. Preparation of a Responsive

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

---

Carbohydrate-Coated Biointerface Based on Graphene/Azido-Terminated Tetrathiafulvalene Nanohybrid Material. *Appl. Mater. Interfaces* **2012**, *4*, 5386-5393.

(29) Leroux, Y. R.; Fei, H.; Noël, J.-M.; Roux, C.; Hapiot, P. Efficient Covalent Modification of a Carbon Surface: Use of a Silyl Protecting Group To Form an Active Monolayer. *J. Am. Chem. Soc.* **2010**, *132*, 14039-14041.

(30) Leroux Y. R.; Hapiot, P. Nanostructured Monolayers on Carbon Substrates Prepared by Electrografting of Protected Aryldiazonium Salts. *Chem. Mater.* **2013**, *25*, 489-495.

(31) Anderson, S. Phenylene Ethynylene Pentamers for Organic Electroluminescence. *Chem. Eur. J.* **2001**, *7*, 4706-4714.

(32) Wheland, R. C. and Martin, E. L. Synthesis of Substituted 7,7,8,8-Tetracyanoquinodimethanes. *J. Org. Chem.* **1975**, *40*, No.21, 3101-3109.

(33) Lorcy, D.; Shin, K.-S.; Guerro, M.; Simonet, J.  $\pi$ -Donor Layer Coverage onto Glassy Carbon by Electrochemical Means. Reduction of  $\omega$ -Iodoalkyl-Tetrathiafulvalenes *Electrochimica Acta*, **2013**, *89*, 784-791.

(34) Cachet-Vivier, C.; Keddam, M.; Vivier, V.; Yu, L T. Development of Cavity Mmicroelectrode Devices and their Uses in Various Research Fields. *J. Electroanal. Chem.* **2013**, *688*, 12-19.

(35) *Microélectrode à cavité - Principe, Développement et Applications pour l'Etude de la Réactivité de Matériaux Insoluble*; V. Vivier (Ed.), Publications de l'Université de Saint-Etienne: Saint-Etienne, 2009.

1  
2  
3  
4  
5 (36) Savéant, J.-M. *Elements of Molecular and Biomolecular Electrochemistry*; Wiley-  
6 Interscience, Hoboken, 2006.

7  
8  
9  
10 (37) Yzambart, G.; Fabre, B.; Lorcy, D. Multiredox Tetrathiafulvalene - Modified Oxide-  
11 Free Hydrogen-Terminated Si(100) Surfaces. *Langmuir* **2012**, *28*, 3453-3459.

12  
13  
14 (38) Paxton, W. F.; Kleinman, S. L.; Basuray, A. N.; Stoddart, J. F.; Van Duyne, R. P.  
15 Surface-Enhanced Raman Spectroelectrochemistry of TTF-Modified Self-Assembled  
16 Monolayers *J. Phys. Chem. Lett.* **2011**, *2*, 1145-1149.

17  
18 (39) Honeychurch, M. J.; Rechnitz, G. A. Voltammetry of Adsorbed Molecules. Part 1:  
19 Reversible Redox Systems. *Electroanalysis* **1998**, *10*, 285-293.

20  
21 (40) Lee, L. Y. S.; Sutherland, T. C.; Rucareanu, S.; Lennox, R. B. Ferrocenylalkylthiolates  
22 as a Probe of Heterogeneity in Binary Self-Assembled Monolayers on Gold. *Langmuir* **2006**,  
23 *22*, 4438-4444.

24  
25 (41) Jaeger, C. D.; Bard, A. J. Electrochemical Behavior of Tetrathiafulvalene-  
26 Tetracyanoquinodimethane Electrodes in Aqueous Media, *J. Am. Chem. Soc.* **1979**, *101*,  
27 1690-1699

28  
29 (42) DuVall, S. H.; McCreery, R. L. Control of Catechol and Hydroquinone Electron-  
30 Transfer Kinetics on Native and Modified Glassy Carbon Electrodes. *Anal. Chem.* **1999**, *71*,  
31 4594-4602.

32  
33 (43) DuVall, S. H.; McCreery, R. L. Self-catalysis by Catechols and Quinones during  
34 Heterogeneous Electron Transfer at Carbon Electrodes. *J. Am. Chem. Soc.* **2000**, *122*, 6759-  
35 6764.

(44) Lhenry, S.; Leroux, Y.R.; Hapiot, P. Use of Catechol As Selective Redox Mediator in Scanning Electrochemical Microscopy Investigations. *Anal. Chem.* **2012**, *84*, 7518-7524.

(45) Amatore, C.; Savéant, J.-M.; Tessier, D. Charge transfer at partially blocked surfaces: A model for the case of microscopic active and inactive sites. *J. Electroanal. Chem.* **1983**, *147*, 39-51.

(46) Compton, R.G.; Menshykau, D. Electrodes Modified with Electroinactive Layers: Distinguishing Through-Film Transport from Pinhole (Pore) Diffusion. *Langmuir* **2009**, *25*, 2519-2529.

(47) Qin, G.; Santos, C.; Zhang, W.; Li, Y.; Kumar, A.; Erasquin, U. J.; Liu, K.; Muradov, P.; Trautner, B. W.; Cai, C. Biofunctionalization on Alkylated Silicon Substrate Surfaces via "Click" Chemistry. *J. Am. Chem. Soc.* **2010**, *132*, 16432-16441.

(48) Tengstedt, C.; Unge, M.; de Jong, M. P.; Stafström, S.; Salaneck, W. R.; Fahlman, M. Coulomb Interactions in Rubidium-Doped Tetracyanoethylene: A Model System for Organometallic Magnets. *Phys. Rev. B* **2004**, *69*, 165208.

(49) Bellitto, C.; Bonamico, M.; Fares, V.; Imperatori, P.; Patrizio, S. Tetrathiafulvalenium salts of planar Pt, Pd, and Cu 1,2-dithio-oxalato-S,S[','] anions. Synthesis, Chemistry and Molecular Structures of bis(tetrathiafulvalenium) bis(1,2-dithio-oxalato-S,S[','])palladate(II), [tff]<sub>2</sub>[Pd(S<sub>2</sub>C<sub>2</sub>O<sub>2</sub>)<sub>2</sub>], and of bis(tetrathiafulvalenium)tetrathiafulvalene bis(1,2-dithio-oxalato-S,S[','])platinate(II), [tff]<sub>3</sub>[Pt(S<sub>2</sub>C<sub>2</sub>O<sub>2</sub>)<sub>2</sub>]. *J. Chem. Soc., Dalton Trans.* **1989**, *4*, 719-727.

(50) Choudhury, D.; Das, B.; Sarma, D. D.; Rao, C. N. R. XPS Evidence for Molecular Charge-Transfer Doping of Graphene. *Chem. Phys. Lett.* **2010**, *497*, 66-69.



1  
2  
3  
4  
5 (51) Lieffrig, J.; Jeannin, O.; Frąckowiak, A.; Olejniczak, I.; Świetlik, R.; Dahaoui, S.;  
6 Aubert, E.; Espinosa, E.; Auban-Senzier, P.; Fourmigué, M. Charge-Assisted Halogen  
7 Bonding: Donor–Acceptor Complexes with Variable Ionicity *Chem. Eur. J.* **2013**, *19*, 14804-  
8 14813.

9  
10  
11  
12  
13  
14 (52) Torrance, J. B.; Vazquez, J. E.; Mayerle, J. J.; Lee, V. Y. Discovery of a Neutral-to-  
15 Ionic Phase Transition in Organic Materials. *Phys. Rev. Lett.* **1981**, *46*, 253-257.

16  
17  
18  
19 (53) Lieffrig, J.; Jeannin, O.; Guizouarn, T.; Auban-Senzier, P.; Fourmigué, M. Competition  
20 between the C–H···N Hydrogen Bond and C–I···N Halogen Bond in TCNQFn (n = 0, 2, 4)  
21 Salts with Variable Charge Transfer. *Crystal Growth & Design* **2012**, *12*, 4248-4257.

22  
23  
24 (54) Iyoda, M.; Suzuki, H.; Sasaki, S.; Yoshino, H.; Kikuchi, K.; Saito, K.; Ikemoto, I.;  
25 Matsuyama, H.; Mori, T. Charge-Transfer Complex and Radical Cation salt of a New Donor  
26 EDT-TTFCl<sub>2</sub>: Unique Conductivities and Crystal Structures *J. Mater. Chem.* **1996**, *6*, 501-  
27 503.  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50

51  
52 **GRAPHICAL ABSTRACT**  
53  
54  
55  
56  
57  
58  
59  
60

