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Synthesis, self-assembly and characterization of a novel push-pull thiophene-based chromophore on gold surface

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Push-pull chromophores are widely used and investigated due to their intrinsic electro-optical and non-linear optical properties that are suitable for a variety of applications. However, the grafting and the control of self-organization of such derivatives onto surfaces have been less considered although this may enhance the pre-cited properties and/or enlarge the scope of their use. In this work we present the stepwise synthesis of a novel non-charged push-pull chromophore modified with a fleeting thioacetate group and studied its self-assembling abilities onto a gold surface. Self-assembled dense monolayers formation is clearly demonstrated by electrochemical, XPS and STM measurements. Besides, associated to good film quality a conducting behavior consistent with the structure of the SAM-organized push-pull is also highlighted.

Introduction.

During the last decades the design and synthesis of push-pull chromophores became the spotlight of scientific interest owing to their intrinsic properties useful in numerous optoelectronic applications. From chronological point of view, push-pull molecules have been firstly envisioned as active components in the field of nonlinear optics before finding their interest in other fields such as ambipolar field effect transistors, light emitting diodes, photovoltaic cells, and sensors. Although substantial theoretical and experimental work has been done for a better understanding and control of the intrinsic optoelectronic properties, notably by tuning the molecular structures (donor/acceptor strength, optimization of the conjugated link (rigid structures, introduction of more stable aromatic rings), introduction of groups promoting non-centrosymmetric packing, and so on...), it is still of crucial interest to better control their organization in the solid-state in order to enhance and optimize their properties in the bulk. Analogously well-organized structures can be found in many biological systems for instance in the retina with the photoreceptors responsible of the color vision mechanism or those found in the light-harvesting complex of the photosynthesis process. Among the bottom-up approaches commonly used for such purpose (organic molecular beam epitaxy, CVD, Langmuir-Blodgett films, ionic interactions, solution processing, and so on), self-assembled monolayers (SAMs) appeared to be a method of choice to achieve highly dense and ordered thin film, robustly anchored to large surface areas and that does not require either expensive and sophisticated instrumentation, or intricate sample preparations and expert manpower. To date molecular self-assembling constitutes one of the main promising strategies to obtain easily functionalized surfaces and has found applications in the fabrication of nano-scale materials and in molecular electronic engineering. The classical approach consists in the immersion of a clean metallic (e.g. Au, Ag), oxidized (e.g. SiO₂, ITO) or semiconducting (e.g. Si, Ge) substrates into a dilute solution (typically 1 mM) of functionalized derivatives with thiol, silane, acid or amine end-groups. The molecules are chemisorbed via the formation of anionic, dative, or covalent bonds. Although the majority of the early studies have been performed on alkyl derivatives, the incorporation of bulky polar groups, in particular push-pull chromophores, is of great interest for a variety of applications. To the best of our knowledge, a rapid literature survey shows that only a few examples of SAMs based on dipolar-conjugated chromophores have been described. For instance, G. J. Ashwell et al have reported a series of charged push-pull molecules (named hemicyanines) comprising a dialkylamino group connected to a quinolinium or pyridinium acceptor and self-assembled onto a gold surface via either the acceptor or the donor part. Electrical characterization of the formed SAMs demonstrated a current rectification ascribed to the dipolar character of the monolayer. Interestingly, the diode-type behavior can be reversibly commutated upon acidic treatment while the dipole inversion leads to a change of the current rectification direction. More recently, hemicyanines self-assembled monolayers onto gold substrates have been proven to be useful and efficient for the generation of photocurrent. In addition, the work on SAMs of zwitterionic dyes by A. Facchetti et al has led to impressive dielectric performances (Self-Assembled NanoDielectrics, i.e., SANDs) compared to those of silicon dioxide that are valuable for their implementation in thin film field-effect transistors. However, despite interesting outcomes with pyridinium or zwitterionic dyes, these structures can be considered as charged species that could be problematic, in certain cases, for the foreseen applications because for instance the presence of intercoulombic interactions may hinder proper intermolecular self-organization leading to less dense monolayer packing (increase of the number of defects) or may localize the charges at the surface. Taking into consideration this criterion we envisioned to turn out our attention to the synthesis of SAMs with non-charged push-pull chromophores.

Herein we report the stepwise fragment coupling synthesis of a novel push-pull thiophene-based chromophore bearing a thioacetate anchoring group, linked to the donor side, as well as its self-assembling properties and electrochemical, spectroscopic and microscopic structural and electrical characterizations.

Experimental methods.

All chemicals were purchased from Sigma-Aldrich, TCI-Europe or Acros Organic and used as received from the
commercial sources, unless otherwise stated, without further purification. Infrared spectra were recorded on an Agilent Cary 630 FTIR spectrometer. UV-visible absorption spectra were obtained on a Varian Cary 1E spectrophotometer. The electronic absorption maxima ($\lambda_{\text{max}}$) are directly extracted from absorption spectra of the chromophore-based solution. $^1$H and $^{13}$C NMR spectra were recorded on Bruker AC 250 at 250 MHz and 62.5 MHz, respectively. $^1$H NMR data are reported as follows: chemical shift in parts per million relative to CHCl$_3$ (7.26 ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broadened), coupling constant (Hz), and integration.

High-resolution mass spectroscopy was performed on a Qstar Elite spectrometer (Applied Biosystems SCIEX) with ionization electrospray source (ESI) through the Spectropôle facility of Aix-Marseille University. The titled compound was obtained using standard conditions and procedures and will be discussed in the next section and ESI. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and from Macherey-Nagel EURL. The SAMs were obtained by dipping into a 1 M solution of the titled chromophore in dichloromethane a plane surface of freshly cleaned (by an UV-ozone treatment (15 min) and ethanol/dichloromethane rinsing)

Au/mica (obtained from Scientec) or Au/glass (obtained by the sequential vacuum ($\approx 10^{-5}$ mbar) Joule evaporation of chrome ($v \approx 0.5$ A/s, 6 nm) and gold ($v \approx 1$ A/s, 200 nm) samples. Cyclic voltammetry (CV) data were acquired using a BAS 100 Potentiostat (Bioanalytical Systems) and a PC computer containing BAS100W software (v2.3). A three-electrodes system based on screen-printed gold electrode SPE (DS250AT) obtained from DropSens® (Llanera Spain) consisting of a working electrode (gold Au, 4 mm diameter), a counter electrode (platinum Pt) and a reference electrode (silver, Ag) was used. A cable connector (CAC DropSens®) ensures the interface between the SPE and the potentiostat. The kinetics of chemisorption were performed using a 1M potassium ferricyanide aqueous solution (K$_3$Fe(CN)$_6$) in a 1M KCl solution as supporting electrolyte at a scan rate of 50 mV.s$^{-1}$. Contact angles of water were measured by the sessile drop method using a conventional goniometer Krüss DSA10-Mk2. Mechanically sharpened Pt−Ir (95/5) wires were used as STM. The STM images of Au/mica samples were made by using a Multimode Nanoscope IIIa microscope from Bruker Corp. at ambient conditions. Different tips and samples were used to ensure that the images were reproducible and free from artifacts. STM images presented in this paper were flattened by second-order least-squares fitting using the WSxM 5.0 software.

Results and discussion.

Synthesis

The synthesis of the titled push-pull thiophene-based chromophore 10 is outlined in scheme 1 similar to a methodology described previously. Chromophore 10 was readily obtained from chromophore 9 in two consecutive steps consisting of the introduction of the thioacetate-anchor grouping. Beforehand, chromophore 9 was synthesized in 95% yield from the aldehyde 8 in two steps under basic conditions via a Knoevenagel-type condensation reaction in presence of malononitrile. The aldehyde 8 was for its part readily obtained from the cross coupling reaction of the 5′-(1,3-dioxolan-2-yl)-[2,2′-bithiophen]-5-carbaldehyde 7 core with the phosphonium salt 5. According to the $^1$H NMR a cis/trans mixture at ratio 3:7 was obtained and subsequent isomerization in CHCl$_3$ in presence of traces of I$_2$ affords the pure trans isomer 8 in 93% yield after purification by column chromatography over silica gel. Compounds 1 to 4 were prepared according to reported procedures from $\text{N}$-methylaniline in four steps affording the corresponding compound 4 in 57% overall yield. The reaction of 4 and $\text{HPbBr}_3$ in CH$_3$CN under reflux afforded the phosphonium salt 5 in 82% yield after purification by recrystallization in diethyl ether. 7 was also prepared similarly to reported procedure in 88% yield from 2-((2,2′-bithiophen)-5-yl)-1,3-dioxanol 6.

Scheme 1. Stepwise synthesis of the titled chromophore 10. Synthesis of 5: i) 6-bromohexan-1-ol, THF NaOH TBABr reflux 1h (95%); ii) Ac$_2$O reflux 2.5h (75%); iii) POCI/DMF 1:2-dichloroethane reflux 3h (89%); iv) NaBH$_4$, MeOH 0°C 1h (89%); v) HPPbBr$_3$, CH-CN reflux 3h (82%); synthesis of 7: vi) ethanol,1,2-diol, Phl PTSA, reflux 2d. (92%); vii) BuLi 2.5M (-78°C to r.t) then DMF, THF overnight (88%); synthesis of 8: viii) (Bu)ONa, THF/CH-CN 0°C 2.5h; ix) 2N HCl, r.t. 1h; x) L, CH-CN reflux 1h (93%); synthesis of 9: xi) NaOH, MeOH/CH-CN: TBABr r.t. 3h; xii) CH-CN, Et,N EOH r.t. 3h (95%); synthesis of 10: xiii) PBr$_3$, CH-CN, 2 d., r.t.; xiv) KSAc, DMF/CH-CN, overnight, r.t. (31% yield).

Spectro-electrochemical characterizations

The optical properties, absorption and fluorescence emission, of chromophores 8 and 10 were studied in CH$_2$Cl$_2$ solution (Figure 1). UV-visible absorption spectrum of 10 exhibits two bands centered at 392 nm and 552 nm (with molar absorptivity $\varepsilon = 5.1 \cdot 10^4$ L.mol$^{-1}$cm$^{-1}$). The optical properties of the corresponding chromophore 8 (Figure S1 in ESI) reflecting a better stabilization of the molecule in the first excited state relative to that in the ground state when the solvent polarity increases (i.e. the dipole moment of the chromophore increases upon excitation). A broad band at 712 nm highlighting a large Stokes shift of 160 nm characterizes the emission spectrum of 10 obtained by excitation at 550 nm. It was also anticipated that replacing the CHO group by a stronger acceptor could contribute to improving the optical properties of the corresponding chromophore. Hence, compound 8 presents similar optical behavior to 10 (two bands centered at 342 nm and 460 nm (as...
molar absorptivity $\epsilon = 1.7 \times 10^4 \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, $\epsilon = 3.3 \times 10^4 \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ respectively) but those are blue shifted.

Figure 1. Normalized absorption (8 (-----) and 10 (------)) and emission (8 (.....) and 10 (……..)) spectra of 8 and 10 in CH$_2$Cl$_2$.

Electrochemical behaviors of 8 and 10 were investigated by cyclic voltammetry in CH$_3$CN with n-Bu$_4$NPF$_6$ (0.1M) as the supporting electrolyte. The cyclic voltammograms versus Ag/AgCl are depicted in Figure 2. During the anodic scan, whatever 10 or 8 exhibits two quasi-reversible oxidation peaks at 0.62 - 0.61 V and 0.96 - 0.97 V ascribed accordingly to the radical cation formation on the bithiophene system and on the aniline core respectively. The similar oxidation potentials are relied on the analogous donor part.

Table 1. Redox potentials for compounds 8 and 10 vs Ag/AgCl (+207 mV vs standard hydrogen electrode (SHE)) and their spectroscopic characteristics

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}$ (ox1)</th>
<th>$E_{1/2}$ (ox2)</th>
<th>$E_{1/2}$ (red)</th>
<th>HOMO$^a$</th>
<th>LUMO$^a$</th>
<th>$E_g$</th>
<th>$\lambda_{\text{max}}$ absorption$^c$</th>
<th>$\lambda_{\text{max}}$ emission$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.61 V</td>
<td>0.96 V</td>
<td>-1.39 V</td>
<td>-5.0 eV</td>
<td>-3.0 eV</td>
<td>2.0 V</td>
<td>460 nm</td>
<td>640 nm</td>
</tr>
<tr>
<td>10</td>
<td>0.62 V</td>
<td>0.97 V</td>
<td>-0.88 V</td>
<td>-5.0 eV</td>
<td>-3.5 eV</td>
<td>1.5 V</td>
<td>552 nm</td>
<td>712 nm</td>
</tr>
</tbody>
</table>

$^a$ Cyclic voltammograms were performed in CH$_3$CN. $^b$ The HOMO and LUMO levels were estimated from the first oxidation and the reduction potentials calibrated with the ferrocene/ferrocenium (Fc/Fc$^+$) couple ($E_{1/2}(\text{Fc}) = 0.45$ V). Under the assumption that the energy level of Fc/Fc$^+$ is -4.8 eV, the MO levels were determined from the equation: - (4.8 eV + $e(E_{1/2} - 0.45$ V)). The energy gap ($E_g$) was estimated by subtracting the LUMO energy level from the HOMO energy level. $^c$ Spectra recorded in CH$_3$Cl$_2$.

This observation is also supported by the infrared vibrational spectrum (Figure S2 in ES1). Indeed, the cyano-vibration wavelength serves as an internal probe in determining the efficiency of the donor-acceptor charge transfer as previously reported.44 The predicted theoretical vibration at 2280 cm$^{-1}$ differs from the experimental one observed at 2220 cm$^{-1}$, that highlights an effective charge-transfer for compound 10 resulting of a significant increases of the electron density on the nitrogen atom of the cyano group accompanied with a diminution of the strength of this bond.

Formation and characterization of the self-assembled monolayers

The self-assembled monolayers can be analyzed and characterized by various methods comprising physical measurements like electrochemical methods, contact angle and wettability, optical spectroscopic techniques and scanning probe microscopies. Among them, cyclic voltammetry (CV) is worthy helpful in monitoring the monolayer formation and in the assessment of its quality. Indeed, although the monolayer covers the entire metal surface some pinholes and defects remain allowing the possible diffusion of redox active species at electrode surface. Moreover, homogeneity, compacticity and stability of the monolayer is also under the control of several structural parameters including the nature of the head groups, the nature of the docking group, the chain length, the surface properties, and so on.

Even though disulfides and thiols are the most used anchoring end groups during SAM formation on gold surfaces and electrochemical studies, their access and synthesis as well as their storage are often somewhat difficult and intricate.9 To circumvent such obstacle thiocyanates20 and especially thioacetates26 have been used as a possible alternative guaranteeing notably better stability.28 However, in the most cases the self-assembling process of thioacetate-containing chromophores requires an in situ deprotection step under basic conditions.29 First attempts to self-assemble 10 under basic conditions0 using NaOH, Et$_3$N in CH$_2$Cl$_2$ or TBACN have conducted to a degradation of the chromophore due to the acidic character of the dicyanomethylene proton. Fortunately, successful direct grafting of 10, without any deprotection step, has been proved and clearly demonstrated (see below Figures 3 and 4) as previously speculated.32

Moreover, as aforementioned and exemplified by several literature reports the chain length, bridging the head group to the
surface, plays a crucial role to achieve dense, compact and stable self-assembled monolayers. With this aim we have selected an intermediate chain length of six carbons, which has been proven to be enough to afford well-organized SAMs. Qualitative and quantitative analyses of coverage have been followed by cyclic voltammetric experiments. For instance, Figure 3 shows a comparison of voltammograms, at scan rate 50 mV.s⁻¹, of bare (Figure 3a, 0 min.) and SAM modified DropSens® SPE gold surfaces after a period of immersion ranging from 0 to 120 min. (Figure 3a) into a 1 mM CH₂Cl₂ solution of 10 using potassium ferriyanide (K₃Fe(CN)₆, 1 mM) in 1 M aqueous KCl solution as internal probe. As the monolayer becomes denser and more compact along the time, the current intensity of the redox signal of K₃Fe(CN)₆ diminishes gradually. Hence, the comparison between the bare and the 10-covered gold substrate after 2 h. immersion gives evidence a clear blocking effect of the self assembled monolayer. Furthermore, Figure 3b reflects the isotherm of absorption of 10 onto the gold surface. The latter is based on the variation of the maximum current intensity rooted out from the deconvoluted oxidation peaks, giving consequently substantial information on the kinetics of absorption. The plot of the current intensity decay exhibits two parts: (i) a fast recovery rate described by simple first-order kinetics (ii) followed by a slower phase indicating a reorganization and a densification process within the plane of the monolayer.

Figure 3. (a) A comparison of voltammograms for bare and SAM modified (10) gold surfaces from 0 to 120 min. immersion using the K₃Fe(CN)₆ in 1 M aqueous KCl as internal probe; (b) current intensity decay vs time

The chemisorption behavior of 10 and intensity current decay are in fully agreement with a two-step Langmuir-type mechanism, which can be expressed following the Equation 1:

\[ I_{\text{deaconv}} = I_1 \exp\left(-t/\tau_1\right) + I_2 \exp\left(-t/\tau_2\right) + I_r \]

with, \( I_r \) is the remaining observed current, \( I_1 \) and \( I_2 \) - current constants, \( \tau_1 \) and \( \tau_2 \) - characteristics time constants.

The calculation of the characteristics time constants leads to values nearly 80 seconds and 17 minutes, for \( \tau_1 \) and \( \tau_2 \) respectively. The latter are of same order of magnitude of those reported by Lau et al. for adsorption of thioacetate alkane on gold from a millimolar solution: 60 seconds and 12 minutes. The differences might be ascribed to the higher molecular weight and size for 10 restricting its diffusion to the surface. The obtained values \( I_1 \) and \( I_2 \) of -0.41 µA and -0.13 µA respectively show evidence that the major current decay (~70%) is assigned to the chemisorption step and the minor to the auto-organization leading to a densification of the monolayer 1.3 times greater.

SAMs of 10 formed on Au/mica samples possess slightly hydrophilic surface with water contact angle of ~79°, slightly more than values of ~69-75° reported for single cyano surface group, due to the polar character of terminating dicyanovinyl group. As a comparison, bare Au substrate UV ozone cleaned and immersed into methylene chloride solvent for 24 h exhibits a lower water contact angle of 57.5° ± 1.4°. XPS spectroscopy of obtained SAM on gold samples demonstrated low signals corresponding to an organic layer, but the region of the S2p electron energy could still be resolved. (Figure S3 in ESI) It was found two pairs of bands with binding energy values for the major ones (S2pₓₓ) located at 164.1 eV and 161.9 eV, which corresponds well with presence of two types of sulfur atoms in the layer – the aromatic ones in thiophene moiety and the surface-connected. Obtained values are in a good correspondence with previously reported binding energy values of 164 eV and 162 eV respectively for these two different types of atomic species. No S oxidation peaks (near 168 eV) were observed revealing a good monolayer stability upon several days of air exposure at room conditions.

Scanning tunneling microscopy (STM) observation of SAM of 10 formed on Au/mica samples after 24h in 1 mM dichloromethane solution revealed uniform layer with “etch-pits” typical of the thiol to gold bonding process, and an average roughness around 0.16 nm (Figure 3a). Additional thermal annealing during 2h at 85 °C permitted to decrease the roughness about twice (Figure 3b). As can be seen, thermal treatment reduces the number of etch pits (~six times) with larger flat domains; However, in spite of the presence of the short alkyl chain, none organization could be observed in STM images before and after thermal annealing, whatever the imaging parameters of tunneling bias and current. Even slight solvent polarity variations by adding ethanol did not help to promote visible molecular organization in the SAM.

Figure 4. STM images of obtained SAM of 10.

In parallel, electrical current-voltage characteristics of the SAM were also studied by STM. The tip-SAM distance being fixed by respective tunneling current and voltage of 2 pA and -0.7
Conclusions

In summary, we reported herein the synthesis and characterization of a novel organic push-pull chromophore possessing a fleeting thioacetate anchoring group. Self-assembled monolayers on a gold surface of a non-charged chromophore are for the first time clearly demonstrated by electrochemical, XPS and STM measurements. In addition, good film quality is highlighted and I-V characteristics are consistent with SAMs of molecules standing upright at the surface. This unique combination of properties makes this SAM a system of choice for the foreseen applications as an active or interfacial layer useful for light harvesting in organic photovoltaics or non linear optical devices either as dielectric effective in field effect transistors or sensor applications. Further work and improvements are now under progress.

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Notes and references.

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‡ Electronic Supplementary Information (ESI) available: Detailed experimental section, Us-Vis and infrared spectra, XPS analyses, and transition voltage spectroscopy analyses of I-V characteristics. For ESI or other electronic format see DOI: 10.1039/b000000x
‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Notes

The authors declare no competing financial interest.


Figure 5. Typical STM current-voltage characteristic of SAM of 10 measured at the following tunneling parameters: 2 pA and ~0.7 V.

V, several I – V curves were recorded at different positions of the images.

A typical I-V curve is presented in Figure 5. As shown, current response is nearly symmetrical at negative and positive bias. This indicates that the voltage drop within the Au-SAM-Tip junction should be about symmetrical regarding the bias polarity. In this case, air interface between the STM tip and the topmost part of the SAM (i.e. the dicyano groups) should be compensated by the presence of the insulating six-carbon alkyl chain at the interface between the conjugated part of the molecule and the gold substrate. Such a hypothesis is reasonable considering both that the values of the tip-SAM distance (typically ~1-10 Å) and the six-carbon alkyl chain length (6 x 1.26 Å ~ 7.6 Å) are in the same range, and that alkyl chains and air usually exhibit a similar tunneling damping factor (within ~1.2-2.3 Å) . Compared to more insulating SAM of shorter molecules of dodecanethiol on gold investigated using similar tunneling parameters, STM tip-Au junction exhibits higher current due to the π-conjugated nature of the molecule. In the former case, current is tunneling through the alkyl chain whereas for 10 the sharp current increase beyond ±0.5 V should correspond to resonance with the molecular orbital closer to the Fermi level, as observed by STM on other π-conjugated SAMs on Au (e.g. terthiophene-based moieties) . Similar I-V characteristics were measured by Che and co-workers from push-pull SAM thiol-terminated on gold within the following junction: alkyl chain-donor-π spacer-acceptor. However they observe a clear rectification for the bias polarity that makes the donor extremity more positive than the acceptor end, i.e., at positive bias in our junction. Analyzing deeper our I-V curves (Figure 5), we indeed observe a slight rectification at positive bias (we calculate a rectification ratio of 1.9 at ±0.75 V in Figure 5). In our case the weakening of the rectification could issue from the lower range of the probed voltage and/or a stronger dipole moment in compound 10 (with a positive charge on the donor and a negative one on the acceptor) that may hinder the current flow at positive bias.

Assuming the vacuum levels are aligned, with HOMO being at ~−5 eV from the molecule vacuum level and gold work function being ~−5.2±0.1 eV, HOMO should be ~+0.2±0.1 eV from the Fermi level. This is in good agreement with the transition voltage of ~−0.5 V (see Figure S4 in ESI) determined from the Fowler-Nordheim plots of the I(V) curves (see Figure S5 in ESI) and that is usually assimilated to the voltage needed to match the molecular orbital with the Fermi level . In the case of a symmetric junction where the voltage drop is equally divided on the two electrodes, such a voltage should be twice the energy interval between the molecular orbital and the Fermi level .

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