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► To cite this version:

V. Gadenne, B. Grenier, C. Praveen, P. Marsal, J. C Valmalette, et al.. Combined SERS/DFT studies of push–pull chromophore self-assembled monolayers: insights into their surface orientation. *Physical Chemistry Chemical Physics*, 2019, 21 (46), pp.25865-25871. 10.1039/C9CP04008K . hal-02396854

HAL Id: hal-02396854

<https://hal.science/hal-02396854>

Submitted on 6 Dec 2019

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Combined SERS/DFT studies of push-pull chromophores self-assembled monolayers: insights of their surface orientation.

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Abstract

Having clear and deep information on the surface/interface of deposited molecules is of crucial importance for the development of efficient optoelectronic devices. This paper reports on a joint experimental/theoretical approach based on Raman spectroscopy in order to provide information on the orientation of deposited push-pull chromophores onto a gold surface. In addition, several parameters can strongly control or impede the orientation of such molecules on the surface such as: the molecular structure, the surface itself, the method of deposition and the solvents used. From this approach, additional information has been highlighted such as perpendicularly depositing the molecule on the surface, the bithiophene compounds displaying more solvent effects compared to terthiophene molecules and so on. According to the results, the joint SERS/DFT study proves to be an effective tool for probing the arrangement of push-pull chromophores and selecting right experimental conditions to tune the surface properties.

1- Introduction

π -conjugated organic semi-conductors¹ are of crucial interest in the development of flexible advanced materials and are largely studied due to their intrinsic properties (optical, electrical, magnetic etc.) that can be useful for the fabrication of optoelectronic devices and could represent a cost-effective and promising alternative to their inorganic counterparts. Among them, push-pull chromophores² represent an extensively studied class of π -conjugated molecules that have found their slot in many optoelectronic applications³ such as nonlinear optics,⁴ field-effect transistors (OFET),⁵ light emitting diodes (OLED),⁶ photovoltaic cells (OPV),⁷ dye sensitizing solar cells (DSSC)⁸ and so on. However, several obstacles have hampered the performance and development of such devices. One of the most critical being the orientation of the molecules at the surface of the electrodes that could drastically affect the charge injection, the charge transport, the optical response etc. Thus, it is of great importance to develop reliable, inexpensive and non-sophisticated methods that can give rise to information and/or can finely probe the modified surfaces with the above mentioned chromophores in order to have access to their locally molecular order, the surface-molecule interactions, their intramolecular or intermolecular interactions, their defects and anticipate their properties.

Solid-state absorption spectroscopy is commonly used to provide information both on the electronic structures of the molecules and to assign their main orientation when deposited onto a surface as a thin film either by

ultra-high vacuum techniques or solution processes. Therefore, based on the red shift or the blue shift of the lowest energy band, information regarding the orientation can be obtained wherein a bathochromic shift corresponds to a parallel orientation while a hypsochromic shift coincides to a comparable perpendicular arrangement. Nevertheless, no additional clue can be obtained from this method concerning the morphology, the order, the intramolecular interactions etc.

Raman spectroscopy is a useful analytical technique, complementary to IR absorption spectroscopy, providing a structural fingerprint from which molecules can be easily identified. Raman spectroscopy⁹ has been widely used to characterize π -conjugated chromophores in their neutral state by determining the degree of π -conjugation as well as the efficiencies of the intramolecular charge transfer in the case of push-pull molecules.⁸ Most of the studies can be carried out on molecules either in solution or in the solid state. From combined Raman theoretical and experimental studies it has been observed that molecular nonlinear optical efficiencies, in solution, depend on several parameters such as molecular π -conjugated skeleton and solvent environment.¹⁰ Moreover, in solid-state their properties, such as intramolecular charge transfer (ICT) and spectroscopic responses, are strongly affected by structural and surface imperfections which need to be avoided and/or known in order to prevent the damage or disappearance of these properties. In addition, even if Raman spectroscopy seems to offer many advantages this approach is rather limited due to a low signal-to-noise ratio and presents small cross sections.¹¹

To overcome these main drawbacks, surface enhanced Raman scattering (SERS)¹² appears to be a better technique as the signals are enhanced by a 2-9 orders of magnitude. Thus, SERS provides superior and accurate information regarding (i) the interactions between the chemisorbed chromophores to metallic surface and (ii) the molecular vibrational changes either induced by their adsorption or rising from intermolecular interactions. This SERS signal enhancement arises from the contribution of two main mechanisms, one chemical and a second electromagnetic.¹³ Moreover, SERS signals can be only observed if both the molecules interact at a short distance with the metal surface and the surface selection rules are satisfied.¹⁴ Electromagnetic mechanism (its contribution exceeds 9 orders of magnitude) comes from the enhancement of the local electric field due to surface plasmon resonance while chemical enhancement (contribution up to two orders of magnitude) is attributed to some changes in the molecular electronic structure arising from (i) the chemical interactions between the molecule and the metal surface, (ii) the ICT (in molecules with π -conjugated systems) and (iii) the molecular HOMO-LUMO transitions affording selectively increases intensity of some vibrational modes.

Although SERS has been extensively used to study *in situ* (in sensing devices) the trace amounts of adsorbed analytes or their reaction products, it is worth mentioning that SERS has been scarcely used as scanning analytical tool of self-assembled monolayers in order to acquire information about the arrangement of the molecules within the plane of the layers.

Herein, we aim at demonstrating that SERS, in combination with DFT calculations, can be an effective tool for probing the arrangement of push-pull chromophores within a SAM and help to highlight the origin of changes from the deposition conditions used. To achieve that, we focused our work on the SERS analysis of the two push-pull chromophores depicted in Figure 1.

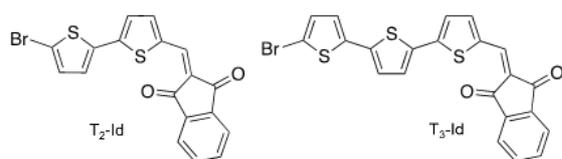


Figure 1: Molecular structures of chromophores **T₂-Id** and **T₃-Id**

The chromophores **T₂-Id** and **T₃-Id** are unsymmetrical molecules possessing one electron-withdrawing group (namely the 1,3-indandione, **Id**) connected, through a methylene bond, to an electron-donating part that can interchangeably be an α -bromo-bithiophene (**T₂**) or an α -bromo-terthiophene (**T₃**). We have studied the modification of the SERS spectra according both to the method of deposition and to the variation of the dielectric constant of the solvents used. In addition, with the help of DFT, vibrational calculations of the main infrared and Raman features of the chromophores have been performed in order to facilitate their assignment. In conjunction with their structures, compounds **T₂-Id** and **T₃-Id** can dimerize in a parallel or antiparallel configuration (ESI, Figure S1 for **T₂-Id**).

Thus, in order to simulate such aggregation modes and to have access to the expected theoretical vibration data in those simple models we have used the Avogadro software.¹⁵ Calculations for both monomers and dimers have been performed according to the protocol described in the computational method section.

2- Results and discussion

a- Assignment of the vibrational bands

Firstly, in order to validate the computational method, the derivatives bithiophene **T₂** and terthiophene **T₃** (Figure 2) have been selected as model compounds. Comparison of their experimental and theoretical Raman vibrational modes has been done after their deposition onto a gold surface as a SAM from a acetonitrile solution at a mass concentration of [C]= 0,5g. L⁻¹.



Figure 2: Model compounds bithiophene **T₂** and terthiophene **T₃**

The experimental Raman spectra of the two model compounds **T₂** and **T₃** deposited using acetonitrile solvent have been found to resemble those obtained by calculations (*vide infra*) (ESI, Figures S2 and S3 respectively) and present some characteristic bands as found in polymeric or oligomeric thiophene species reported on Ag substrate.¹⁶ Moreover, the comparison of the SERS spectrum of compound **T₃** with the one obtained by Fujita *et al*¹⁷ reveals close characteristics. According to experimental SERS spectrum of **T₃** and the literature, the scale factor choices for the calculated Raman frequencies: 0.955 in the 600-1200 spectra area and 0.96 in the 1200-1600 could be justified.

Interestingly we have found some main vibrational features. Certainly, for each chromophore **T₂-Id**, **T₃-Id** (ESI, Table S1 for **T₂-Id** and Table S2 for **T₃-Id**) and model compounds **T₂** and **T₃** (ESI, Table S3 and S4 respectively) the Raman spectra can be divided into seven main parts corresponding to specific vibration modes. The first region, from 600 to 750 cm⁻¹, has found to correspond to the C-S stretching in which all carbon and sulphur movement are recovered for all compounds. In this area, the DFT and experimental vibrational modes have weak intensities (ESI, Figure S2 and S3). In the region 750-960 cm⁻¹ the majority of the bands (9/11 for **T₂**, 11/15 for **T₃**, 4/7 for **T₂-Id**, 6/10 for **T₃-Id**) corresponds to the twisting and wagging motions of the carbon and hydrogen atoms along the π -conjugated system. In all the SERS spectra recorded, these modes are not observed. According to the surface selection rules, the out-of-plane vibrational modes should not appear on the experimental spectra if molecules are oriented perpendicularly to the metal surface. Consequently, we assume that molecules are oriented perpendicularly to the metal surface. The third part of the Raman shift from 960-1050 cm⁻¹ corresponds for all compounds both to the C-C stretching and to the δ (C-H) bending modes. The fourth

region from 1060 to 1160 cm^{-1} is assigned to the electron-withdrawing group for the compounds **T₂-Id** and **T₃-Id**. Whereas such bands for the compounds **T₂** and **T₃** are attributed to vibrational modes of thiophene rings. The fifth spectral Raman region from 1180 to 1400 cm^{-1} consists of a high density of vibrational bands that are stretching and bending modes found in the thiophene part as well as in the electron-withdrawing group. The sixth Raman spectral region from 1430 to 1520 cm^{-1} is referred to as the $\nu(\text{C}=\text{C})$ stretching for all compounds. And finally, the Raman region from 1550 to 1600 cm^{-1} is due to the effective conjugation coordinate mode.

Figures 3 and 4 display the SERS spectra of the thin film deposited by two methods tested (drop casting, self-assembly) and obtained from acetonitrile and CH_2Cl_2 solutions of chromophores **T₂-Id** and **T₃-Id** respectively.

All spectroscopic behaviours described above are in full agreement with the DFT calculations. Thus, the major predicted vibrational modes are well ascribed and labelled for all compounds on the experimental spectra. Importantly, we can assume that vibrations having the same genesis in each monomeric unit are very close in term of frequency and might be individually observed in the self-assembled monolayers. Finally, compounds with large polarizability tensor components, like aromatic compounds and even push-pull chromophores, which are oriented perpendicularly to the metal surface will have more enhanced signals. Furthermore, the out-of-plane vibrational modes do not appear on the experimental spectra. All these findings would suggest a well-organized monolayer on the gold surface.

From the given spectra all observations and results are consistent with a slice deposition of the compounds **T₂-Id** and **T₃-Id** rather than a flat (parallel) orientation on the substrate. The presence of the acceptor groups does not impede the adsorption of the thiophene part on the surface.

b- Solvent effects

It has been previously established that the solvents influence dramatically the dipole moment of push-pull chromophores (as solvatochromism in UV/Vis absorption spectra reflecting the difference in dipole moment between the ground and excited states of the chromophores). Taking this into account, we undertook a study to determine if the dielectric constant of the solvent can influence significantly or not the mode of arrangement of the molecular thin film on the surface. Firstly, DFT calculations have been performed in order to establish the solvent effects both on the electronic structures and on the vibrational properties. Within this study two solvents, possessing different dielectric constants (ϵ), have been used *i.e.* dichloromethane ($\epsilon = 9.1$) and acetonitrile ($\epsilon = 37.5$) respectively. However, the solubility of the chromophores is different in both solvents, as the chromophores have demonstrated higher solubility in CH_2Cl_2 and will have certainly an impact on the SAMs. Based on the theoretical calculations (M06-2X/6-31G(d,p), effect of solvent on the repartition of the electronic density (ESI, Figure

S4)), it appears that the theoretical spectra in both solvents remain unchanged for compounds **T₂-Id** and **T₃-Id** respectively. These behaviours indicate that in these particular cases the solvents will not alter the electronic properties of the chromophores. Regarding the theoretical Raman spectra of **T₂-Id** and **T₃-Id** performed in the same conditions (ESI, Figures S5 and S6) they remain also identical in both solvents and exhibit only slight differences.

SERS spectra of **T₃-Id** remain almost unchanged in both solvents while for compound **T₂-Id** a clear difference was observed. For the latter, the wavenumbers are not shifted but a net enhancement of the relative intensities of the bands at 1430, 1471 and 1516 cm^{-1} in the dichloromethane solution was independently noticed in the deposition method used. From the theoretical spectrum these bands have been assigned to the stretching of $\nu(\text{C}=\text{C})$, $\nu(\text{C}-\text{C})$ in thiophene groups, $\nu(\text{C}-\text{C})$ inter-thiophene ring and to the bending of $\nu(\text{C}=\text{C})$, $\nu(\text{C}-\text{C})$ and $\nu(\text{S}-\text{C})$. Moreover, the aforementioned intensity in Raman spectroscopy is

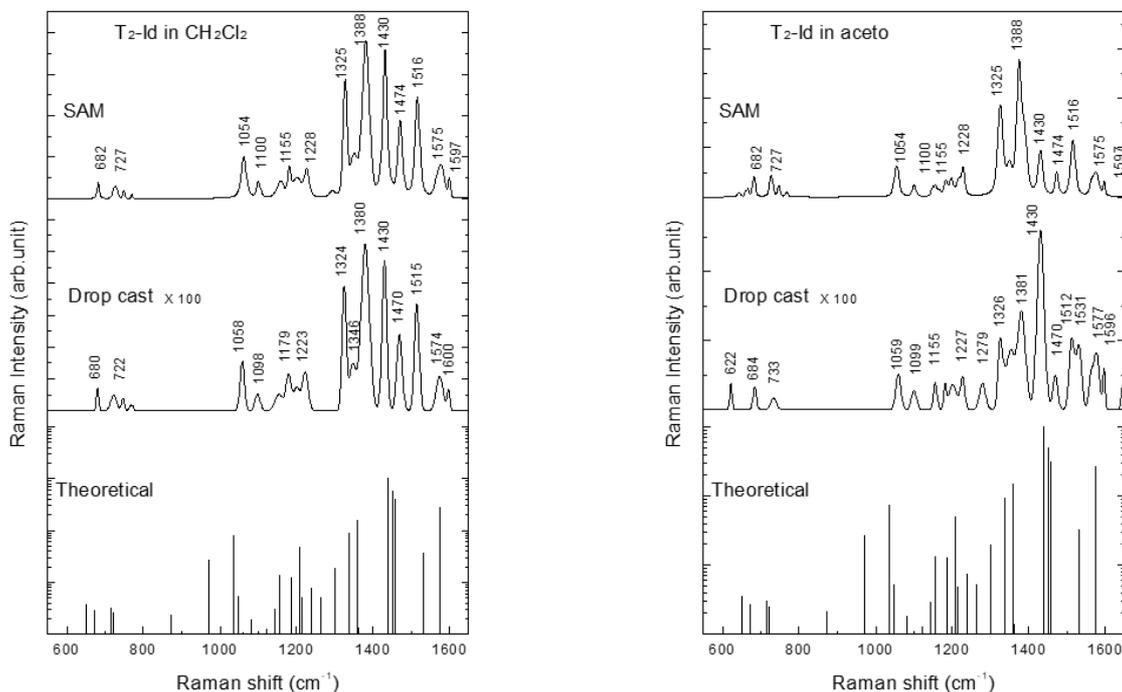


Figure 3: SERS spectra of the **T₂-Id** layer on gold substrate in acetonitrile and in dichloromethane.

directly correlated to the modulation of bond polarizability in the molecule. It can be explained in terms of charge transfer taking place between the metal surface and the adsorbed chromophores. This phenomenon is an additional clue reflecting the geometry and orientation of the adsorbed molecules.

The event of main vibrational modes of thiophene groups being similarly enhanced can be the result of a strong interaction of two thiophene groups with the surface. So **T₂-Id** adsorption in Syn (synperiplanar) conformation on the surface could be promoted from the dichloromethane solution.

Moreover, this solvent effect is also observed in the SERS spectrum of **T₂** (Figure S2) in which the band located at 1472 cm⁻¹ exhibits the highest increase and the band at 1410 cm⁻¹ is shifted to 1420 cm⁻¹. In the literature, the band at 1422 suggests the presence of a quinoid form along the π -conjugated backbone.¹⁸ This also suggests that CH₂Cl₂ seems to favour more efficiently the quinoid form unlike acetonitrile during the adsorption process.

c- Impact of the deposition method.

It was foreseeable to think that the methods of preparation of thin films could also have an impact on the molecular arrangement on surfaces. To this end, we decided to undertake the preparation of thin films by two different deposit solutions processes. The thin films were prepared either by a drop casting or a dip coating technique. Then, the SERS spectra were respectively recorded after evaporation of the solvent

or after careful rinse of the SAM in order to remove either non-absorbed molecules or aggregates. The main differences between the two processes depend on the kinetics of adsorption. The first one usually leads to a less ordered film compared to the second one and a higher thickness.

Importantly, we noticed for the very first time that in the case of self-assembled monolayers the Raman signal is 100-fold magnitude higher than the one obtained in the drop cast films. This phenomenon is also consistent with the so-called “first layer effect”¹⁹ which is correlated to the chemical-enhanced mechanism in SERS when a monolayer is formed on the substrate surface. Indeed, the enhancement maximum is obtained on the SAM deposition because of the film formed is certainly molecular thickness and the molecules may be oriented in order favourable to give rise to the maximum contribution of polarizability in the direction of the surface normal. Whereas by drop casting, the film must be composed of aggregates or/and multilayers having orientation unfavourable for maximum enhancement which results in the decrease in the relative enhancement factor. Furthermore, the comparison of the spectra from the drop casting and dip

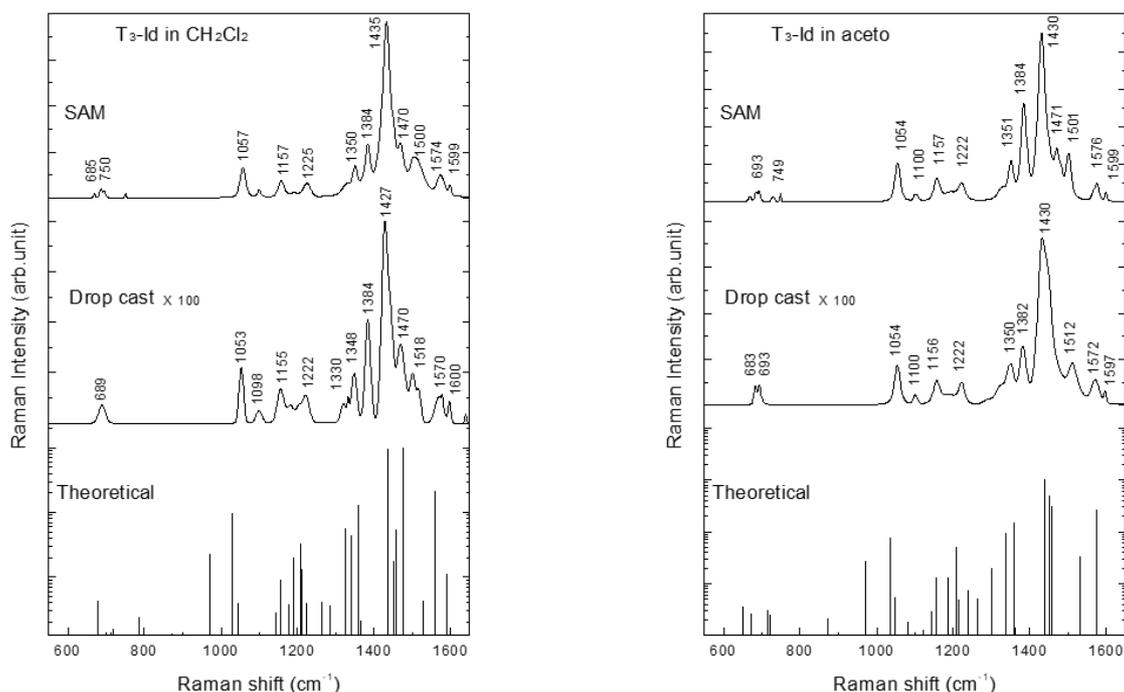


Figure 4: SERS spectra of the T_3 -Id layer on gold substrate in acetonitrile and in dichloromethane.

coating methods for T_2 -Id and T_3 -Id (Figures 3 and 4 respectively) has led to highlight some noticeable differences. The vibrational pattern in both cases is different and some vibrational bands are split in the case of the films obtained by drop casting, for instance, in acetonitrile in the region 1512 - 1531 cm^{-1} for T_2 -Id (Figure 3b) and between 683 - 693 cm^{-1} for T_3 -Id (Figure 4a) or in CH_2Cl_2 between 1320 - 1330 cm^{-1} and 1501 - 1516 cm^{-1} for T_3 -Id (Figure 4b). Interestingly this phenomenon is not perceived in the SERS spectra of the films obtained by dip coating for both T_2 -Id and T_3 -Id because by this method the film order must be better.

These behaviors are corroborated with the DFT calculations performed on the dimeric species of T_2 -Id and T_3 -Id (ESI, Figure S7). Indeed, the comparison of the DFT calculations of the Raman spectra performed on monomeric and dimeric species of T_2 -Id and T_3 -Id suggests a splitting of the bands when aggregation occurs. Therefore, the splitting observed in the experimental SERS spectra can undoubtedly be assigned to the formation of agglomerate, which it seems to be favoured in case of the drop casting deposition method or when the solubility of the molecules reaches its limits.

3- Experimental, theoretical description.

a- Computational methods.

All calculations have been carried out with Gaussian 09 package.²⁰ All structures have been optimized at the Density Functional Theory level (DFT). The Minnesota M06-2X²¹ hybrid Exchange Correlation energy functional has been used for all monomeric and dimeric states geometries optimizations; this method is well known to predict dispersion effects.²² This function was combined with a 6-31G(d,p) basis set. The results acquired from this basis have been compared with those obtained with 311+G(d,p) basis set and only slight differences have been found (ESI, Figure S8 and Table S5) in the reproducibility of the acquired data. Hence, 6-31G(d,p) basis set represents a good compromise between accuracy and computational costs. Calculations have been performed in gas phase, CH_2Cl_2 and acetonitrile using the Conductor-like Polarizable Continuum Model (C-PCM)²³ in order to predict the solvent effects. For all optimizations, no imaginary frequencies have been found. The optimized geometries have been used to calculate the Raman frequencies. As reported in literature,²⁴ we decided to fit the experimental spectra in the ranges 600 - 1200 cm^{-1} and 1200 - 1600 cm^{-1} , using scale factors for the calculated Raman frequencies: 0.955 in the 600 - 1200 spectra area and 0.96 in the 1200 - 1600 . Parallel and antiparallel dimers (ESI, Figure S1) are considered. Thus, these two kinds of dimers illustrate the simplest models of aggregation. Moreover, if molecules aggregate in a perfect crystal lattice we might have either only parallel or antiparallel dimers. Therefore, we have assumed that these two types of dimers represent a good portrayal of the aggregation effects.

b- Synthesis and sample preparation.

Chromophores **T₂** and **T₃** have been purchased from Alfa Aesar while chromophores **T₂-Id** and **T₃-Id** have been synthesized according to a Knoevenagel-type reaction. Commercially available 1*H*-indene-1,3-(2*H*)-dione and 5'-bromo-5-formyl-2,2'-bithiophene or 5''-bromo-5-formyl-2,2':5',2'-terthiophene respectively, both prepared from literature procedures,²⁵ were heated in anhydride acetic at 80°C for 24h. The obtained solids were filtered off, washed with cold ethanol and dried under vacuum prior to use[‡]. The SERS active surfaces were obtained by thermal evaporation, under ultrahigh vacuum conditions (2.10⁻⁶ mbar) as a gold thin film with thickness around 7 nm on a glass substrate.²⁶ Two solution processes have been used to deposit the chromophores on the SERS surfaces. The first has consisted in a drop casting process of a solution of **T₂-Id** or **T₃-Id** at a concentration [C]= 0.5 mg. mL⁻¹ on the gold surface. Raman analysis was done after evaporation of the solvent. The second was done by dipping the substrate into a solution of **T₂-Id** or **T₃-Id** at a concentration [C]= 0.5 mg. mL⁻¹ during 24h at room temperature. The sample was taken out and the surface was rinsed with solvent in order to remove the aggregates and the non-absorbed molecules, dried under N₂ flow prior to record Raman spectrum.

c- Raman spectra.

SERS spectra were recorded on a Labram HR800 spectrophotometer. The excitation wavelength used was 632,8 nm. The laser beam was focused on the sample through a 100x objective. All spectra were calibrated in respect to a silicon wafer at 520,7 cm⁻¹. For each substrate, SERS spectra were performed on three different areas of the surface to ensure the reproducibility of the acquired data.

4- Conclusion.

To summarize, we have found from an elegant joint SERS/DFT study the possibility to probe the arrangement of deposited thin films of push-pull chromophores. We have also highlighted according to this approach that depending on the experimental conditions, *i.e.*, solvents used or the coating methods noticeable differences can be witnessed by SERS allowing us the possibility to select the right conditions to tune the surface properties. In addition, by this mean it is easy to analyse the presence or absence of some defects, in terms of arrangement and/or morphology, and correlate the obtained properties to those

imperfections. Based on the study we have rationalized different hypotheses *i.e.* the molecules deposit perpendicularly rather than a flat orientation, the solvent has a strong impact on the structure of the chromophores promoting, in the case of CH₂Cl₂, the quinoid form or a syn bithiophene conformation and finally drop casting favours the formation of aggregates unlike in self-assembled monolayers. We are confident that the strategy is valuable and worth pursuing because this unique combination of SERS/DFT methods makes this approach very interesting and complementary within the arsenal of surface analysis techniques. Work is in progress exploring this approach on other π -conjugated systems.

5- Acknowledgements.

This work was supported by the Centre National de la Recherche Scientifique (CNRS) and the Ministère de l'Enseignement Supérieur et de la Recherche. The ANR program (SAGE III-V project ANR-11-BS10-012) and "Solutions Communicantes Sécurisées" competitive cluster are also acknowledged for their financial support and for C.P.'s post-doctoral fellowship. B. G. also thanks the Ministère de l'Enseignement Supérieur et de la Recherche for his doctoral financial support.

6- Notes and references.

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[§]Push-pull organic chromophores (or molecules) are molecules consisting of electron donor (D) and electron acceptor (A) moieties typically bridged together by a π -conjugated organic backbone. Due to this particularly special electronic framework, low-lying excited electronic states of D⁺A⁻ character appear as a result of the facilitated D→A intramolecular charge transfer (CT).

[‡] ¹H NMR data for **T₂-Id** and **T₃-Id**. 5-bromo-5'-[(indan-1,3-dione-2-ylidene)methyl]-2,2'-bithiophene **1**. (Orange solid, 16%). ¹H NMR (250 MHz, DMSO-*d*₆, ppm): 8.21 (d, ³J= 4.0 Hz, 1H); 8.07 (s, 1H); 7.98-7.94 (m, 4H), 7.61 (d, ³J= 4.0 Hz, 1H), 7.52 (d, ³J= 4.0 Hz, 1H), 7.38 (d, ³J=4.0 Hz, 1H). 5-Bromo-5''-[(indan-1,3-dione-2-ylidene)methyl]-2,2':5',2'-terthiophene **2**. (Brown solid, 49%). ¹H NMR (250 MHz, DMSO-*d*₆): δ 7.28-7.43 (m, 4H), 7.57-7.66 (m, 3H), 7.94-8.21 (m, 3H), 9.91 (s, 1H).

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