Raman and surface enhanced Raman scattering study of the orientation of cruciform 9,10-anthracene thiophene and furan derivatives deposited on a gold colloidal surface

J. Muñoz-Pérez [a], P. Leyton [a, *], C. Paipa [a], J.P. Soto [a], J. Brunet [a], J.S. Gómez-Jeria [b], M.M. Campos-Vallette [b]

[a] Instituto de Química, Pontificia Universidad Católica de Valparaíso, Valparaíso, Chile
[b] Laboratorio de Espectroscopía Vibracional, Departamento de Química, Facultad de Ciencias, Universidad de Chile, P.O. Box 653, Santiago, Chile

ARTICLE INFO

ABSTRACT

The 9,10-di(thiophen-2-yl)anthracene (TAT), 9,10-di(furan-2-yl)anthracene (FAF) and 2-[(10-(thiophen-2-yl)anthracen-9-yl)]furan (TAF) cruciform molecular systems were synthesized using one-step coupling reactions and structurally characterized via Raman, infrared, ^{1}H NMR, ^{13}C NMR and mass spectroscopies. The orientation of the analytes on a gold colloidal surface was inferred from a surface-enhanced Raman scattering (SERS) study. The metal surface interaction was driven by the S and O atoms of the thiophene and furan α-substituents, and the plane of the anthracene fragment remained parallel to the surface. Theoretical calculations based on a simplified molecular model for the analyte-surface interaction provide a good representation of the experimental data.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Recently, metallic or semiconductor nanoparticle fabrication and modification techniques have been developed to produce surfaces with suitable properties for use in electronic, optical and spectroscopic devices [1–3]. The design of these devices often requires the immobilization of a molecular system on the surface of a nanostructure or continuous metallic surfaces via specific chemical adsorption [4,5] or self-aggregation mechanisms [6]. Therefore, the rational design of this type of molecular device has been focused on molecular electronics applications, such as molecular wires, rectifiers, switches, transistors and sensors that have the ability to selectively recognize a certain type of substrate. Self-assembled monolayers consisting of conjugated organic molecules have generated much interest due to their electronic conduction controlled by the functional groups at the ends of the structure [7].

In comparison to the extensively developed chemistry of self-assembled monolayers (SAM) of aliphatic organic molecules on a surface, relatively few studies on homologous aromatic building blocks have been performed. Studies on bi-dimensional aromatic conjugated compounds of a considerable size adsorbed on metallic surfaces are also scarce. A significant issue for applications involving simple aromatic molecules, especially for aromatic thiols and dithiols, involves the assumption that the formed films have a specific orientation on the surface. The orientation is dependent on thermodynamic and kinetic factors, which directly influence the vertical growth of the monolayer and limit the potential applications of these systems [8–12].

Currently, surface-enhanced Raman spectroscopy (SERS) has become a powerful technique for use in various areas (e.g., biology, cultural heritage, and environmental pollution). The characteristics of this technique include its high sensitivity. This behavior is primarily due to the substantial electromagnetic enhancement from the nanostructured metal surfaces, and the resonance effect associated with adsorbate-metal charge transfer.

However, one of the most attractive results obtained from the technique involves the ability to gain insight into the orientation of molecules that are adsorbed onto metallic nanostructured surfaces. Intensity changes due to surface effects are interpreted based on the SERS selection rules [13,14]; modes with a Raman polarizability z-component that is perpendicular to the surface are most likely to be more enhanced than the parallel ones. Therefore, the orientation and organization of the analytes on the metal surface can be

inferred. The spectral shifting observed due to surface effects for some bands is related to a probable electronic charge transfer resulting from the ligand-metal surface interaction.

It is important to note that polycyclic aromatic hydrocarbons, such as anthracene, do not exhibit a SERS spectrum except when molecular assemblers are used [15,16]. Both furan and thiophene compounds exhibit SERS effect when deposited on various nanostructured metal surfaces [17–19]. Therefore, the furan and thiophene substituents in positions 9 and 10 in anthracene may drive or allow the approximation of the whole molecular system relative to the metal surface. In addition, SERS possesses unique features that make it a suitable tool for the study the basic aspects of molecular devices involving metal contacts, such as substrate-adsorbate interactions and molecular orientations on nanostructured metal surfaces.

Here, we performed a systematic study of the molecular structure, orientation and organization on gold colloidal nanoparticles of a family of cruciform molecular derivatives of 9,10-dibromoanthracene: 9,10-di(thiophen-2-yl)anthracene (TAT), 9,10-di(furan-2-yl)anthracene (FAF) and 2-[(10-(thiophen-2-yl)anthracen-9-yl)]furan (TAF) (Fig. 1). The main goal was to clarify the molecular origin of the self-aggregation process in order to control the supramolecular organization of organic molecules. Gaining an understanding of these factors is a pre-requisite for the development of new methodologies to fabricate molecular aggregates on surfaces with a definite structure. The present contribution could give insights on the fabrication of molecular electronics devices or specific sensors.

2. Experimental section

2.1. Synthesis of gold nanoparticles

All of the solutions were prepared using water obtained from a Milli-Q Simplicity system (Millipore), which produced water with a resistivity in the 10–15 MΩ × cm range. Gold nanoparticles (Au-NP) were obtained by citrate reduction of $HAuCl_4$ using the Frens method [20].
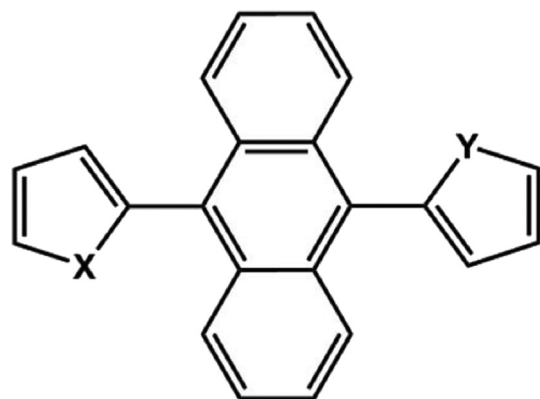
	X	Y
TAT	S	S
FAF	O	O
TAF	S	O

Fig. 1. Family of cruciform molecular derivatives from 9,10-dibromoanthracene: 9,10-di(thiophen-2-yl)anthracene (TAT), 9,10-di(furan-2-yl)anthracene (FAF) and 2-[(10-(thiophen-2-yl)anthracen-9-yl)]furan (TAF).

2.2. Synthesis of symmetrical and unsymmetrical 9,10-diarylanthracene derivatives

9,10-Di(thiophen-2-yl)anthracene (TAT), 9,10-di(furan-2-yl)anthracene (FAF) and 2-[(10-(thiophen-2-yl)anthracen-9-yl)]furan (TAF) were synthesized using a previously published protocol by Durso et al. [21] and Kotha et al. [22] with modifications via Grignard reagent (supplementary material S1). The characterization of the obtained products is in agreement with that reported by the authors.

2.3. Instrumentation

The IR spectra were recorded on a JASCO FTIR-4600 spectrometer equipped with a DLA-TGS detector (deuterated L-alanine doped triglycine sulfate) with Peltier temperature control. The spectral resolution was 4 cm⁻¹ and 32 scans were performed. IR spectral data along with the assignment of the most intense bands are available as supplementary material S1.

The Raman and SERS spectra were obtained using a Witec Alpha 300 confocal Raman microscope system equipped using an excitation laser wavelength of 785 nm and an electrically cooled CCD camera. The signal was calibrated using the 520 cm⁻¹ line of a Si wafer and a 20× objective. The laser power on the samples was 2 mW. The resolution was set to 4 cm⁻¹ and 20 scans with an integration time of 1 s were performed. The spectra were recorded over the 200–1800 cm⁻¹ region. All of the samples were photostable when probed at 785 nm.

2.4. Computational details

Similar to our previous studies, we simulated the gold surface by constructing a large Au cluster with a face centered-cubic structure using the Hyperchem software [23]. Briefly, a large face centered-cubic structure with a = 0.4786 nm was built and trimmed to get a planar double layer composed of 512 gold atoms. The geometry optimization was carried out at the OPLS level by keeping constant the bilayer geometry and by letting evolve the probe molecules over the rigid Au surface. TAT (TAF) were placed at different distances and orientations from the center of the Au bilayer. No solvent was included in the optimization procedure because the direct molecule-surface interaction was modeled, which is required to obtain the SERS spectrum (the other condition involves the molecule-metal interaction occurring on a hot spot). Extended Hückel theory (EHT) was employed to calculate the wave function of the molecules as isolated systems as well as interacting with the metal surface. EHT was chosen because within the Hartree–Fock–Rüdenberg representation, EHT is compatible with the nonempirical Hartree–Fock method in Roothaan's form.

On the other hand, the electronic structure of the molecules was calculated at the B3LYP/6-31G(d,p) level with the Gaussian suite of programs with full geometry optimization [24]. This last calculation provided the HOMO and LUMO structures and energies together with the IR and Raman spectra. This approach provided qualitative explanations of our previous SERS results for several different molecular systems interacting with Ag or Au surfaces [25–31]. Further information is available as Supplementary material S2.

3. Results and discussion

3.1. Raman spectral analysis

3.1.1. Bands assignment

The Raman band assignment for TAT, FAF and TAF was performed using general spectral information [32–34] and analysis of