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PAPER

Organic surface modification using stable conducting materials

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Efficient immobilization methods of amino acids and organic molecules on conducting surfaces were achieved using stable conducting materials such as OBT-functionalized polyterthiophene that allows readily the incorporation of specific motifs on conducting and semi-conducting surfaces. The synthesis of the electropolymerizable monomer has been performed through the protection of the carboxylic acid, followed by a Stille cross coupling reaction, deprotection of the acid and esterification using HOBT (hydroxybenzotriazole) and EDC. The corresponding polymer of **5** (poly(**5**)–Pt) exhibits excellent stability on a platinum electrode as shown by cyclic voltammetry, which allows the introduction of several amino acids and organic molecules on the surface of the functionalized polymer. The modified surface (poly(**6**)–Pt) has been characterized by ATR-Infrared showing a carbonyl stretch corresponding to an amide of the amino acids.

Introduction

Due to their great importance in biological recognition, the immobilization of biological and bioorganic molecules on conducting solid surfaces has attracted much attention in the last few decades.[1,2] The methods commonly used for surface modification purposes are based on the covalent binding of sulfur (S) with a variety of metals, namely the attachment of alkane thiols to Au(111) electrodes carrying target molecules to form self-assembled monolayers (SAMs).[3] Other electrode surfaces such as Pt(111),[4] Ag(111)[5] and glassy carbon (GC)[6] have also been derivatized. Another alternative has been developed through derivatization of semi-conducting surfaces such as Si(111) *via* alkyl chains substituted by electro-polymerizable π-aromatic compounds such as thiophene.[7] The presence of the polythiophene layers at the Si(111) surface prevents the penetration of metals and organic solvents that can potentially damage the Si surface. The key requirement for achieving successful adsorption of a designated organic or bioorganic molecule onto the surface of the electrode relies upon the control of the surface preparation and the nature of the adsorbate.

The introduction of π-conjugated polymers with functionalities such as polythiophenes on the surface of the electrode offers several advantages such as the ability to be regenerated by controlling the thickness of the deposited film layers, to recognize specific motifs and to carry functionalities that can be readily replaced by target molecules.[8] Moreover, cationic poly(fluorene-*co*-phenylene) has been employed to discriminate DNA strands *via* amplification of the optical signal resulting from the electrostatic interactions between DNA strands and the charged polymer.[9]

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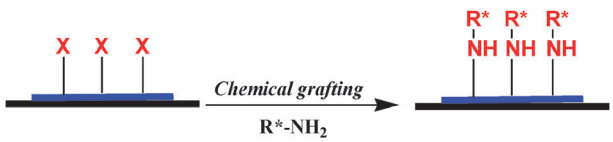


Chart 1

Cationic polythiophenes have also been used in the same way to detect nucleic acids and proteins *via* fluorescence and electrochemical responses, respectively.[10]

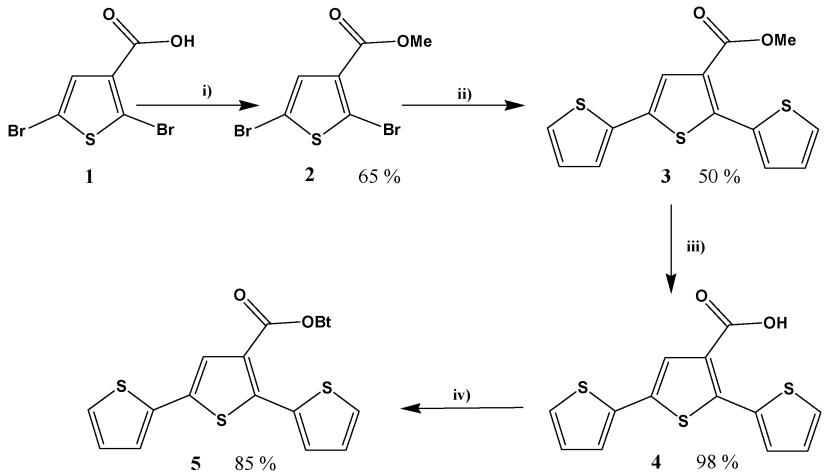
We recently prepared several polythiophenes bearing chiral centers such as leucine and alanine, which exhibit excellent stability and adhesive properties on platinum, gold and glassy carbon electrodes. Moreover, these chiral conducting surfaces present potential recognition toward amino acids and peptides *via* formation of hydrogen bonds on the electroactive chiral surfaces.[11]

Our approach for surface modification is based on the deposition of a stable conducting material on the surface of the electrode that can be readily functionalized with various organic/bioorganic molecules as shown in Chart 1.

Herein, we report (i) the synthesis and deposition of a poly(terthiophene–OBT) on Pt electrodes, (ii) immobilization of the amino acids by substitution of the OBT at the surfaces and (iii) characterization of the modified conducting surfaces.

Result and discussion

Our modification strategy requires the synthesis of terthiophene–OBT (**5**) monomer that has been carried out through a few steps as described in Scheme 1. Since the cross coupling reaction on dibrominated thiophene acetic acid (**1**) was not successful, the protection of the acid was necessary to produce the ester (**2**), which after the Stille cross coupling reaction[12] affords



Scheme 1 Synthetic pathway for terthiophene bearing OBT: (i) $MeOH/H_2SO_4$, (ii) 2-$ThSnBu_3/Pd(PPh_3)_4$, (iii) NaOH/HCl and (iv) HOBT/EDC.

terthiophene (**3**). The hydrolysis of the latter yields the corresponding carboxylic acid (**4**)[13] that reacts with hydroxybenzotriazole (HOBT) in the presence of *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (EDC) to produce terthiophene (**5**) in an excellent yield. Terthiophene–OBT (**5**) exhibits excellent stability in the presence of organic solvents and moisture. The optical properties of the monomers were examined. The absorption maximum of the terthiophenes is red shifted in comparison to the monothiophenes, which is due to the increase in conjugation length in terthiophenes.[14]

Table 1 Electrochemical and optical properties of prepared thiophene monomers in ACN. *First scan using 0.1 V s^{-1} scan rate

Compound	λ_{max} (nm)	E_p (V *vs.* Fc^+/Fc) ± 0.02 V
1	241[a]	—
2	260	—
3	344	0.770
4	346	0.730
5	356	0.710

[a] See ref. 11.

The redox properties of new oligothiophenes were studied using cyclic voltammetry (CV) or linear sweep voltammetry (LSV). Table 1 summarizes the oxidation peak potentials (irreversible systems) of the prepared monomers.

Terthiophene–OBT (**5**) was successfully electropolymerized in a 1 M *n*-Bu_4NPF_6/ACN solution through repeated CV cycling beyond the oxidation peak potential of the terthiophene moiety (irreversible oxidation wave at 0.710 V *vs.* Fc^+/Fc). The 10 scan electropolymerization CVs are presented in Fig. 1A.

An increase in the peak current with each successive scan was observed during the oxidation process, which is due to the deposition of a poly(**5**)–Pt film on the surface of the platinum electrode. The stability and electrochemical properties of poly(**5**)–Pt were examined in a fresh solution of the monomer free ACN/supporting electrolyte. The peak current varies linearly with the scan rate (0.05–0.40 V s^{-1}) indicating a surface bound species.[15]

Terthiophene–OMe (**3**) and terthiophene-OH (**4**) have been electropolymerized under the same conditions as described for the electrochemical oxidation of terthiophene–OBT (**5**).

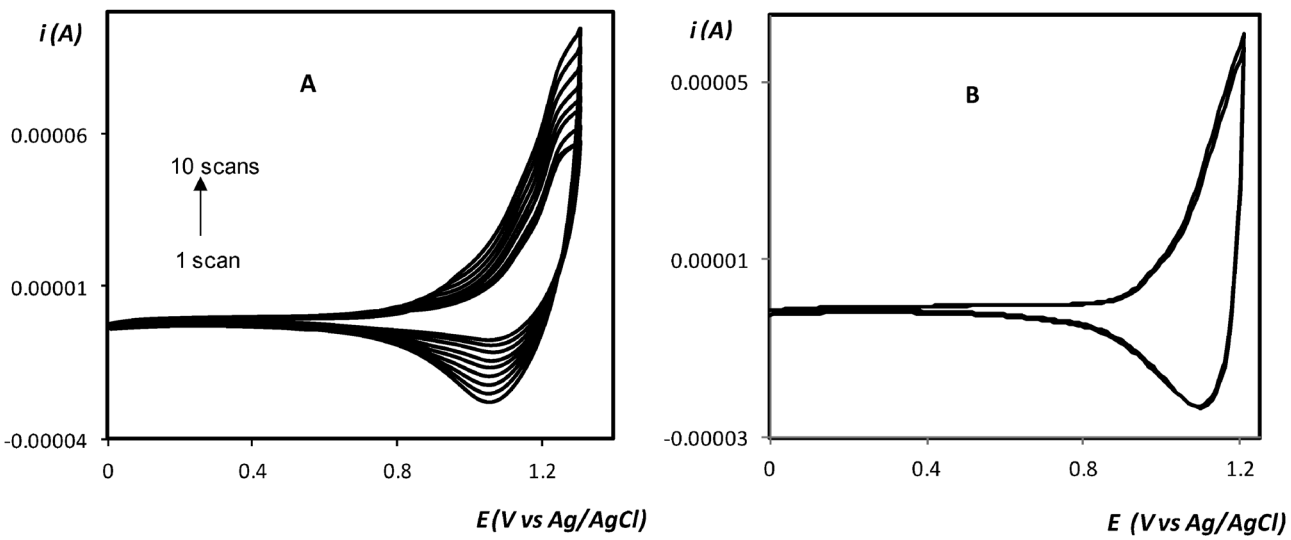


Fig. 1 (A): Electropolymerization of terthiophene–OBT (**5**) using cyclic voltammetry in ACN. Scan rate: 0.1 V s^{-1}; WE: Pt; CE: Pt wire and RE: Ag wire. (B): Stability of poly(**5**)–Pt over 100 CV cycles in ACN at a scan rate of 0.1 V s^{-1}.

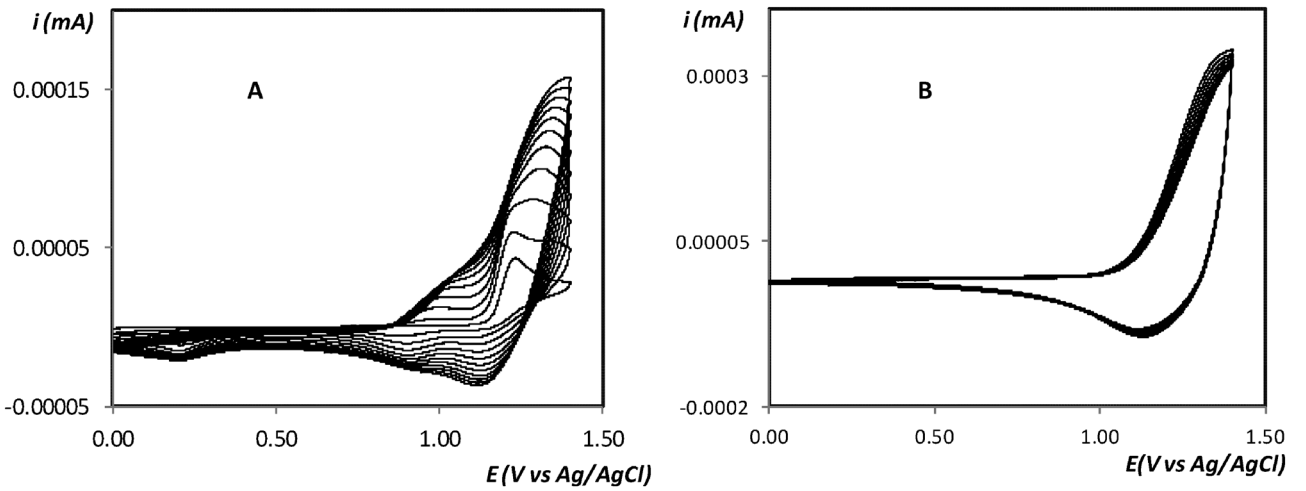


Fig. 2 (A): Electropolymerization of terthiophene-OMe (**3**) using cyclic voltammetry in ACN. Scan rate: 0.1 V s^{-1}; WE: Pt; CE: Pt wire and RE: Ag wire. (B): Stability of poly(**3**)–Pt (20 CV cycles) in ACN at a scan rate of 0.1 V s^{-1}.

Although monomer **3** can be deposited onto the surface of a platinum electrode to give poly(**3**)–Pt (Fig. 2A), the resulting polymer is not stable as shown by a significant decrease in the peak current of the polymer when cycled over 20 CV scans (Fig. 2B) in a fresh monomer free solution. The polymer does not exhibit the same stability and adhesive properties as poly(**5**)–Pt, which is indicated by the fact that the polymer was completely desorbed from the Pt electrode after several scans.

Similar behaviors have been observed for poly(**4**)–Pt. The degradation of the electroactive polymers and their instability (poly(**3**)–Pt and poly(**4**)–Pt) on the surface of the platinum electrode will limit their use as a protective layer for a successful surface modification.

On the other hand, poly(**5**)–Pt displays excellent stability in both doped and undoped states, and is fully reversible. The peak current of poly(**5**)–Pt remains constant and no significant change or degradation of its electrochemical behavior was observed over 100 CV scans (Fig. 1B).

The poly(**5**)–Pt conducting surface exhibits other advantages such as the presence of an OBT group that can be easily replaced by organic or bioorganic molecules, and the ability to be regenerated if an alteration occurs. The surface of poly(**5**)–Pt has been characterized using UV-Vis, IR and ATR-IR techniques.

As shown in Fig. 3b, a characteristic stretch at 1780 cm^{-1} corresponds to the CO (ester), which is also present in the IR-spectrum (KBr) of the terthiophene–OBT monomer (Fig. 3a). The reaction of the pendant ester on the surface of the deposited materials with amino acids (L-alanine methyl ester, L-leucine methyl ester) and a dipeptide (Ala-Leu) affords chiral centers, which were attached to the conducting surfaces with an amide group as depicted in Scheme 2. The carbonyl of the ester in poly(**5**)–Pt is replaced by the carbonyl of the amide group (1646 cm^{-1}) once a substitution reaction occurs at the surface of the conducting materials (poly(**6**)–Pt) (Fig. 3c,d and e).

Moreover, the carbonyl of the ester in the amino acids appears at 1724 cm^{-1}. These results are in agreement with spectra of polymers resulting from electropolymerization of terthiophene bearing either alanine methyl ester or leucine methyl ester.[16]

For poly(**6**)–Pt/*p*-nitro-aniline, in addition to the carbonyl of the amide, two characteristic stretches of the nitro group can be distinguished in Fig. 3f (1540 cm^{-1} and 1383 cm^{-1}).[17]

Poly(**6**)–Pt surfaces are very stable in the presence of air and organic solvents. Moreover, polyterthiophenes bearing amino acids such as L-leucine and D/L alanine have been prepared. They are highly stable to electrochemical oxidation, and can be electrochemically cycled over hundreds of times with no detectable decomposition[11,16]

Summary

In summary, a versatile strategy for the immobilization of organic/bioorganic molecules through the deposition of functionalized stable conducting materials is described. Taking advantage of polythiophene properties, the introduction of amino acids and other molecules onto electrode surfaces was possible. A synthetic approach for the synthesis of terthiophene benzotriazole ester (**5**) has been established. The resulting terthiophene benzotriazole ester can be electrochemically oxidized to give a stable polymer on the surface of a platinum or an ITO electrode. On the other hand, the polymer resulting from the electropolymerization of terthiophene-OMe (**3**) exhibits low stability and weak adhesive properties on Pt electrodes. The resulting polymer from the oxidation of terthiophene benzotriazole ester (**5**) will be promising material for surface modification and recognition of biomolecules. Characterization of the interaction of the immobilized amino acids (peptides) with specific enzymes and the immobilization of oligonucleotide molecules on the surface of poly(**6**)–Pt are currently underway.

Experimental section

Generalities

Unless stated otherwise, all reactions and manipulations were carried out under an oxygenated atmosphere using the standard Schlenk technique. Glassware was oven-dried at 100 °C for 24 h prior to use. Solvents were dried using activated (24 hours at

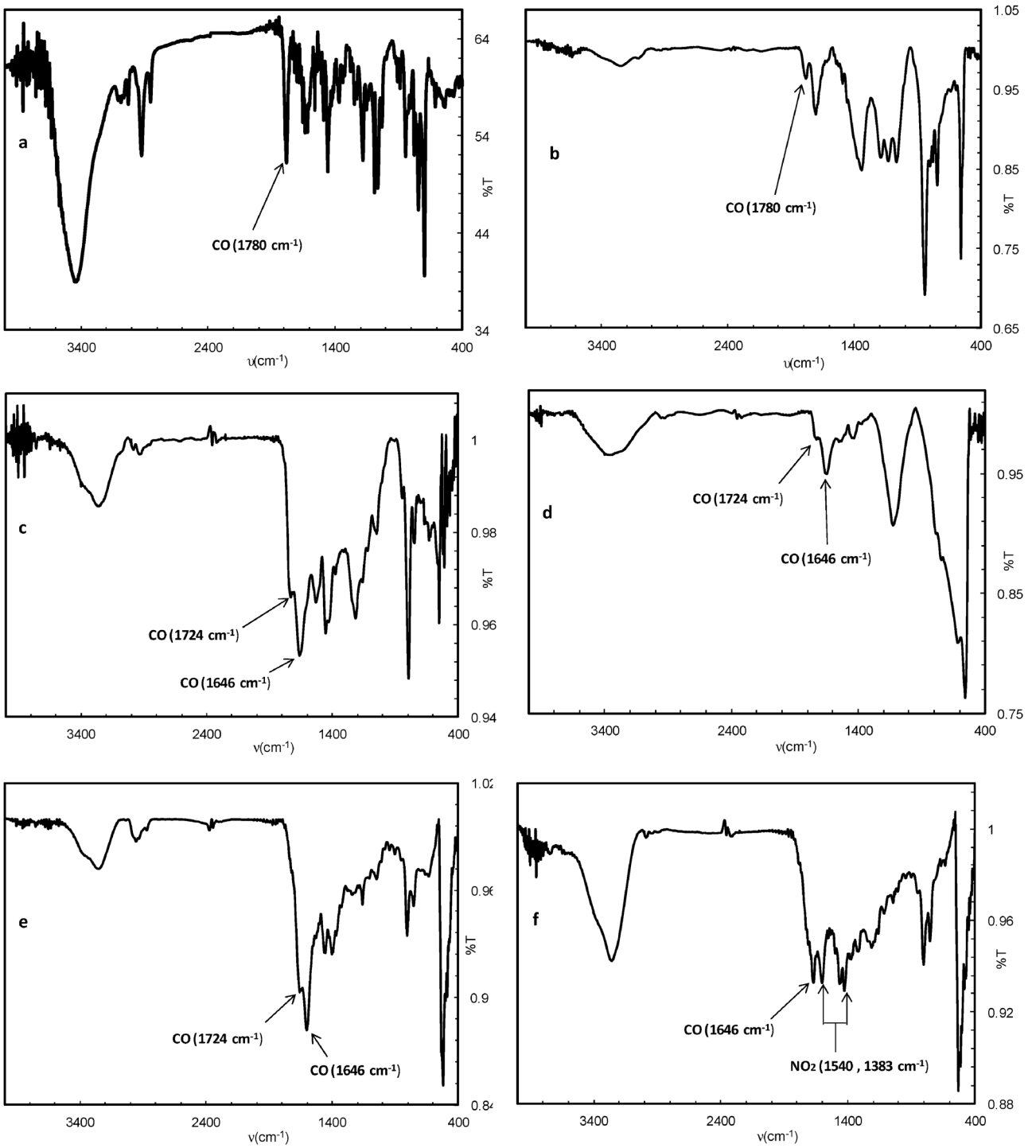
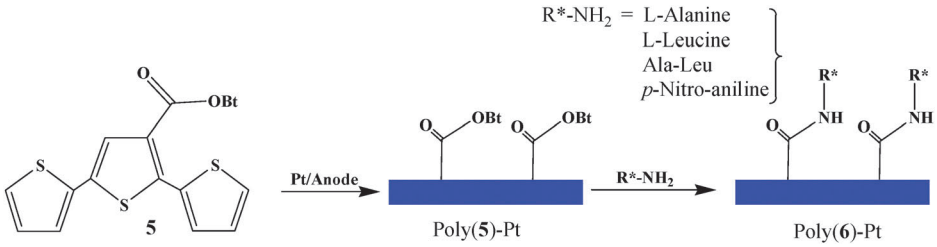


Fig. 3 (a) IR spectrum of **5** and ATR-IR spectra of (b) poly(**5**)–Pt, (c) poly(**6**)–Pt/L-alanine methyl ester and (d) poly(**6**)–Pt/L-leucine methyl ester, (e) poly(**6**)–Pt/Ala-Leu and (f) poly(**6**)–Pt/*p*-nitro-aniline.

100 °C) molecular sieve (4 Å). All reagents were purchased from commercial sources and used as received except where stated otherwise. ^{1}H-proton (^{13}C-carbon) NMR spectra were recorded on a 200 (50) MHz Varian NMR spectrometer. The NMR samples were prepared by using ~20 mg of product dissolved in 1 mL of deuterated solvent (DMSO-d_6 or $CDCl_3$). Melting points are uncorrected. IR spectra were recorded on a Michelson BOMEM Fourier-transform infrared spectrophotometer. The KBr pellet method was utilized to obtain all spectra with a ratio of (Product/KBr) = 1/100. UV-Vis spectra were recorded on an Ultrospec 2100 pro spectrophotometer.

Electrochemistry

The electrochemical experiments were performed using a μAutolab type III (Ecochemie) potentiostat at room temperature (22 ± 2 °C).



Scheme 2 Conducting surface modification using organic/amino acid motifs.

Voltammetric measurements were performed in acetonitrile (ACN) containing 1 M of *n*-Bu_4NPF_6. The platinum electrode (diameter 1.6 mm) was used as the working electrode. Platinum wire was used as an auxiliary electrode and silver wire was used as a reference electrode. All oxidation peak potentials/oxidation potentials were reported *versus* an internal reference ferrocene/ferrocenium redox (E^0 = 0.390 V *vs.* AgCl/Ag, E^0 = 0.350 V *vs.* SCE). The working electrode was polished on alumina before use. iR compensations were applied for all experiments. The bulk electrolyses were performed using a controlled potential in a cell with one compartment using a platinum plate (1.5 cm^2) and an ITO electrode as the cathode and the anode respectively.

General synthesis

Synthesis of 2,5-dibromo-thiophene-3-carboxylic acid methyl ester (2). 2,5-Dibromo-thiophene carboxylic acid (1.50 g, 5.25 mmol) and concentrated H_2SO_4 were added to 50 mL of methanol. After refluxing for 24 hours, the methanol was removed under vacuum and the remaining solid was dissolved in 25 mL of ethyl acetate. The organic phase was then washed with a saturated solution of $NaHCO_3$ (3 × 25 mL), a saturated solution of NaCl (3 × 25 mL), and distilled water (3 × 25 mL). The organic phase was dried over $MgSO_4$ and evaporated to dryness. After cooling in an ice bath, the product was obtained as a white solid. Yield: 65%. Mp: 53 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) = 3.17 (s, 3H, –COC*H*$_3$), 6.64 (s, 1H, Th-*H*). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) = 52.2, 111.5, 119.3, 131.8, 161.2. IR υ/cm^{-1} = 1706 (CO ester). UV-Vis (ACN), $\lambda_{max}(\varepsilon)$ = 260 nm, (1.94 × 10^4 M^{-1} cm^{-1}).

Synthesis of [2,2′;5′,2′′]terthiophene-3′-carboxylic acid methyl ester (3). A 25-mL toluene solution containing 2,5-dibromo-thiophene carboxylic acid methyl ester (0.92 g, 3.07 mmol), 2-tributyl-stannyl-thiophene (3.36 g, 9 mmol) and $Pd(Ph_3)_4$ (0.40 g, 3.46 mmol) was stirred at 90 °C for 48 hours. The reaction was monitored by TLC. After cooling at room temperature the reaction mixture was filtered through celite and diluted with 100 mL of dichloromethane (CH_2Cl_2). The mixture was washed with a cesium fluoride solution (5 × 100 mL) and distilled water (5 × 100 mL). The organic phase was dried over $MgSO_4$ and evaporated to dryness. The residue was then purified *via* column chromatography utilizing CH_2Cl_2 (R_F = 0.70). The product is viscous and yellow. Yield: 50%. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) = 3.58 (s, 3H, –COC*H*$_3$), 6.79 (m, 2H, Th-*H*), 6.92 (m, 1H, Th-*H*), 6.99 (m, 1H, Th-*H*), 7.18 (m, 1H, Th-*H*), 7.22 (m, 1H, Th-*H*), 7.27 (m, 1H, Th-*H*). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) = 50.0, 121.8, 122.8, 124.1, 124.6, 125.3, 127.5, 128.2, 130.6, 142.3, 142.6, 143.3, 149.3, 161.0. IR υ/cm^{-1} = 1708 (CO ester). UV-Vis (ACN), $\lambda_{max}(\varepsilon)$ = 344 nm, (1.21 × 10^4 M^{-1} cm^{-1}).

Synthesis of [2,2′;5′,2′′]terthiophene-3′-carboxylic acid (4). Terthiophene-3-carboxylic acid methyl ester (0.20 g, 0.68 mmol) and 1 N NaOH (2.2 mL) were added to 2 mL of methanol. The reaction mixture was stirred at room temperature for 3.5 hours, after which 1 N HCl (1 mL) was added. The MeOH was then removed *in vacuo* and the remaining solution was cooled in an ice bath. 1 N HCl (2 mL) was then added dropwise to the solution and cooled in the ice bath for 1 hour. The precipitate was filtered and dried under reduced pressure. The product was obtained as a yellow solid. Yield: 98%. Mp: 195 °C. ^{1}H NMR (200 MHz, DMSO-d_6) δ (ppm) = 7.21 (m, 2H, Th-*H*), 7.41 (m, 1H, Th-*H*), 7.53 (m, 2H, Th-*H*), 7.58 (m, 1H, Th-*H*), 7.72 (m, 1H, Th-*H*). ^{13}C NMR (50 MHz, DMSO-d_6) δ (ppm) = 125.0, 125.9, 126.9, 127.8, 128.4, 128.6, 130.2, 133.6, 135.9, 136.1, 143.8, 166.7. IR υ/cm^{-1} = 1679 (CO carboxylic acid). UV-Vis (ACN), $\lambda_{max}(\varepsilon)$ = 336 nm, (6.86 × 10^3 M^{-1} cm^{-1}).

Synthesis of [2,2′;5′,2′′]terthiophene-3′-carboxylic acid benzotriazol-1-yl ester (5). Terthiophene-3-carboxylic acid (0.11 g, 0.38 mmol), *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (0.08 g, 0.40 mmol) and anhydrous hydroxybenzotriaxole (0.05 g, 0.40 mmol) were added to CH_2Cl_2 (25 mL). The reaction mixture was stirred at room temperature for 4 hours. The mixture was then washed with distilled water (10 × 100 mL). The organic phase was then dried over $MgSO_4$ and evaporated to dryness. The product was obtained as a yellow solid. Yield: 85%. Mp: 154 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) = 6.98 (m, 2H, Bz-*H*), 7.12–7.58 (m, 7H, Th-*H*), 7.78 (m, 1H, Bz-*H*), 8.02, (m, 1H, Bz-*H*). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) = 108.7, 120.8, 125.0, 125.3, 125.5, 126.4, 128.2, 128.4, 128.9, 129.1, 129.3, 132.4, 135.1, 136.9, 143.8, 147.5, 158.7. IR υ/cm^{-1} = 1782 (CO ester). UV-Vis (ACN), $\lambda_{max}(\varepsilon)$ = 358 nm, (2.05 × 10^4 M^{-1} cm^{-1}). HRMS (EI) for $C_{19}H_{11}N_3O_2S_3$ [M^+]: calcd. 409.0015; found. 409.0017.

Surface modification (poly(6)–Pt). Poly(**5**)–Pt was prepared *via* controlled potential electrolysis beyond the oxidation peak potential of compound **5** (0.710 V *vs.* Fc^+/Fc) using a platinum electrode (1.5 cm^2) as an anode. The modified electrode (poly(**5**)–Pt) was rinsed and incubated for 15 minutes in a 10 mL CH_2Cl_2 solution containing 20 mg of the amino acid (or organic molecule) and 0.5 mL of Et_3N. The electrode was exhaustively washed with CH_2Cl_2 to ensure the complete removal of the free amino acid (or organic molecule). The electrode was then dried and the ATR-IR spectra of poly(**6**)–Pt were recorded.

Acknowledgements

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