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3 **Electrocatalytic Reduction of Bromothiophenes vs Bromobenzenes**  
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6 **on Gold and Silver Electrodes:**  
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8 **enhancement from S specific adsorption and modulation from substituent effects**  
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19 *Dedicated to Professor Sergio Trasatti*  
20

21 **Abstract**

22 A voltammetric comparative investigation on the electrochemical activity of substituted bromothiophenes vs  
23 bromobenzenes highlights the combined effects of the aromatic or heteroaromatic ring substituents and the  
24 sulphur atom on both the intrinsic reactivity (accounted for by experiments on a glassy carbon electrode, assumed  
25 to have negligible specific interactions) and the reactivity in the presence of electrocatalytic effects, working on  
26 Au or Ag electrodes. The two series of compounds share similarities concerning the dissociative electron transfer  
27 mechanism for the reductive cleavage of the C-Br bond, including substituent effects. However, the presence of  
28 the sulphur atom in the heteroaromatic series significantly promotes the process both in non-catalytic conditions,  
29 on account of electronic effects, and on catalytic electrodes, performing as adsorption auxiliary. The effect is  
30 particularly remarkable on Au, partially compensating for the effect of the very negative surface charge, and with  
31 significant modulation from the S position with respect to the Br leaving group. The nitrile group might act as an  
32 additional adsorption auxiliary besides the S atom. In dibromobithiophene systems Au and Ag catalytic surfaces  
33 can also induce a remarkable modification in molecular conformation in order to optimize Br and S interactions  
34 with the catalytic surface for both conjugated thiophene rings.  
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48 **Keywords**

49 Molecular electrocatalysis; silver and gold electrodes; bromothiophenes; cyclic voltammetry; dissociative  
50 electron transfer.  
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56 **1. Introduction**

57 The electroreduction of the C-X bond is an important and widely investigated reaction in molecular  
58 electrochemistry, being of high fundamental as well as applicative interest, the latter concerning the synthetic,  
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1 analytical, and environmental fields [1-5]. It proceeds via a dissociative electron transfer (DET) along two  
2 possible mechanisms [6-9]:

- 3 • a *concerted* mechanism (C), with concurrent electron transfer (ET) and bond breaking, directly resulting  
4 in formation of R• radical and X<sup>-</sup> anion. On a non-catalytic electrode, it is typically featured by aliphatic  
5 halides although few cases of aromatic halides have been reported [10];
- 6 • a *stepwise* one (SW), consisting of a first rather fast ET resulting in a stable radical anion, followed by  
7 cleavage of the C-X bond to give R• radical and X<sup>-</sup> anion. On a non-catalytic electrode, it is featured by  
8 many aryl halides.

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10 Concerted DET has always a high activation energy, mainly arising from the bond energy of the breaking C-X  
11 bond. The process occurs with a high overpotential so that an irreversible reduction peak with  $E_p \ll E^\circ$  is observed  
12 in cyclic voltammetry. A reduction peak without anodic partner is often observed also when the reduction process  
13 follows a stepwise DET mechanism. In this case, the rate-determining step of the process could be either the ET  
14 or the bond rupture and the relative importance of the two barriers associated with these steps can be  
15 experimentally evaluated through the diagnostic parameter  $\kappa$  [11], varying between 0 and 1, obtained either as

$$\kappa = \frac{-1.15 \frac{RT}{F}}{\frac{\partial E_p}{\partial \log v}} \quad (1)$$

16 or as

$$\kappa = \frac{1.857RT}{F(E_{p/2} - E_p)} \quad (2)$$

17 with

18  $\kappa = 1$  corresponding to a stepwise mechanism controlled by the bond cleavage step;

19  $0.5 < \kappa < 1$  corresponding to a stepwise mechanism with mixed control, bond cleavage prevailing;

20  $0.3 < \kappa < 0.5$  representing a stepwise mechanism with mixed control, electron transfer prevailing;

21  $\kappa < 0.3$  corresponding to a concerted mechanism: concurrent electron transfer and bond cleavage is more  
22 favorable than formation of a short-lived radical anion undergoing fast bond rupture.

23 In the last two cases,  $\kappa$  coincides with the  $\alpha$  symmetry parameter of the activation energy barrier in the classical  
24 Butler and Volmer theory [11].

25 The reductive cleavage of the R-X bond also provides a good model for mechanistic studies in molecular  
26 electrocatalysis, when performed on electrode surfaces with specific affinity for halide anions, such as silver,  
27 gold, mercury, palladium and copper [2,12-16]. Silver can be regarded as a benchmark material on account of a  
28 substantial and systematic pool of mechanistic studies [2,11,17-21]. Its catalytic activity for C-X reduction,  
29 evaluated as  $E_{p,Ag} - E_{p,GC}$  by comparison with glassy carbon (GC) assumed to have negligible catalytic effects for  
30 the same process, can reach values of the order of 1 V and even more. They regularly increase with decreasing  $\kappa$ ,

1 *i.e.* with increasing significance of the heterogeneous electron transfer ET barrier in the overall DET kinetics.

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3 [11,18]

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5 In particular, in systematic aryl bromide series in aprotic solvents, such effects regularly decrease with  
6 increasingly electron-withdrawing substituents on the aryl ring implying increasing localization of the negative  
7 charge away from the halide leaving group, which has been well rationalized in terms of Hammett plots [11,22].

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10 From the mechanistic point of view, Ag promotes the concerted mechanism through surface interactions leading  
11 to a three-centered intermediate involving the metal, R• and X<sup>-</sup> [11].

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14 The reduction potential of the radical R• produced by DET of RX is often higher than that of the starting organic  
15 halide. Therefore, reductive cleavage of RX on non-catalytic electrodes often triggers a carbanion chemistry [2].

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18 Some exceptions to this general rule have been reported for Ag, which favors radical and intermolecular pathways  
19 such as radical-radical coupling to give dimers or radical addition to coadsorbed acceptors [23-26]; this is a  
20 consequence of both the less extreme potentials of RX reduction and the involvement of the electrode surface in  
21 the chemistry of the radical intermediate.

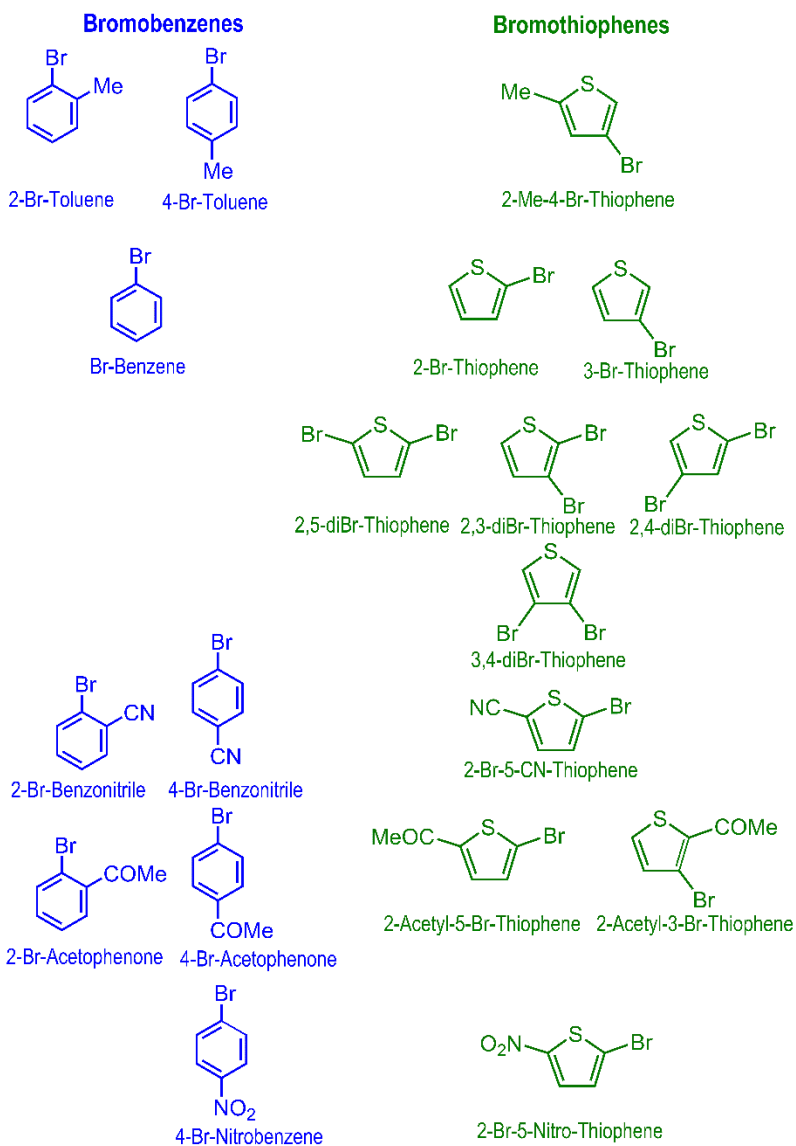
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25 A peculiar, attractive case study is provided by the electrocatalytic reduction of *heteroaromatic* halides [26,27],  
26 in which the heteroatom on one hand makes the aromatic ring asymmetric from the perspective of the electron  
27 density and, on the other hand, can itself have specific interactions with the electrode surface, in addition to that  
28 of the halide ion. For example, thiophenes adsorb on a gold electrode by specific interaction of the sulphur site  
29 [26,28], forming self-assembled monolayers, although without follow-up chemical reactions as with other sulphur  
30 compounds [28,29].

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36 A proof-of-concept comparative study was carried out by us on the electroreduction of a systematic family of  
37 mono-, di-, tri- and tetra- bromothiophenes [26] on Au as well as on non-catalytic reference GC and highly  
38 catalytic Ag. Actually, Au showed lower catalytic effects than Ag for organohalides undergoing concerted DET  
39 [12,20], and practically no catalytic effect for aryl halides undergoing stepwise DET [20]. This can be justified,  
40 as discussed in [20], considering that, although theoretically Au has higher halide affinity than Ag [30-33], its  
41 much more positive potential of zero charge (pzc) (pzc ≈ -0.05 V vs SCE in aqueous solution [34] in comparison  
42 with -0.96 V for Ag [35]), implies a much more negative surface charge in the working potential range for RX  
43 reduction, which hampers halide-surface specific interactions.

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51 However, Au has a very strong affinity for the sulphur atom in the thiophene ring, which can partially  
52 compensate for the repulsive charge effect. A previous study [26] clearly highlighted the important role of the S  
53 atom and of its relative position to the bromide group to be cleaved. In fact, high catalytic effects, even  
54 approaching those of Ag and significantly higher for α-bromothiophenes than β-bromothiophenes, were observed  
55 for the reduction of bromothiophenes on the Au electrode. The process was assumed to involve an intermediate  
56 in which Au strictly coordinates the S heteroatom of the thiophene ring (as in self-assembled thiol monolayers):

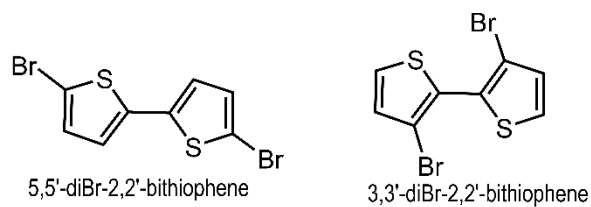
1 as a consequence, when the C-Br to be cleaved is in  $\alpha$  position, *i.e.* adjacent to the sulfur atom, it can benefit from  
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3 a stronger interaction with the catalytic surface with respect to the  $\beta$  case. In other words, thanks to the sulphur  
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5 atom acting as “adsorption auxiliary” or anchoring group, the Au surface can recover most of its intrinsically very  
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7 high catalytic activity, which is hampered by the very negative surface charge in the working potential range.

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9 In the Ag case, specific affinity of the surface for the sulphur atom results in stronger coordination of the  
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11 halothiophene molecule and therefore in increased catalytic effects for its C-Br bond cleavage [26,27], but in this  
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13 case only small differences were observed between  $\alpha$ - and  $\beta$ -bromothiophenes [26], pointing to the surface  
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15 interaction with the halide atom being more determining than the surface interaction with the sulphur atom. Such  
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17 proof-of-concept studies [26,27] however considered only halide atoms (single or multiple groups) as thiophene  
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19 substituents, while the role of additional substituents can be very important on the extent of electrocatalytic  
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21 effects, as was previously shown for substituted aryl halide [11]. In this frame, the study has been extended to a  
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23 series of bromothiophenes bearing additional substituents with different electronic effects (Scheme 1, left), to be  
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25 compared with the homologous series of substituted bromobenzenes (Scheme 1, right).  
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Scheme 1. The investigated bromothiophene and bromobenzene series.

The study is also complemented by a couple of symmetrical dibromo- $\alpha,\alpha'$ -bithiophene dimers with either  $\alpha,\alpha'$  or  $\beta,\beta'$  connectivity of the two bromide substituents. (Scheme 2).



Scheme 2. The investigated dibromo- $\alpha,\alpha'$ -bithiophenes.

## 2. Experimental section

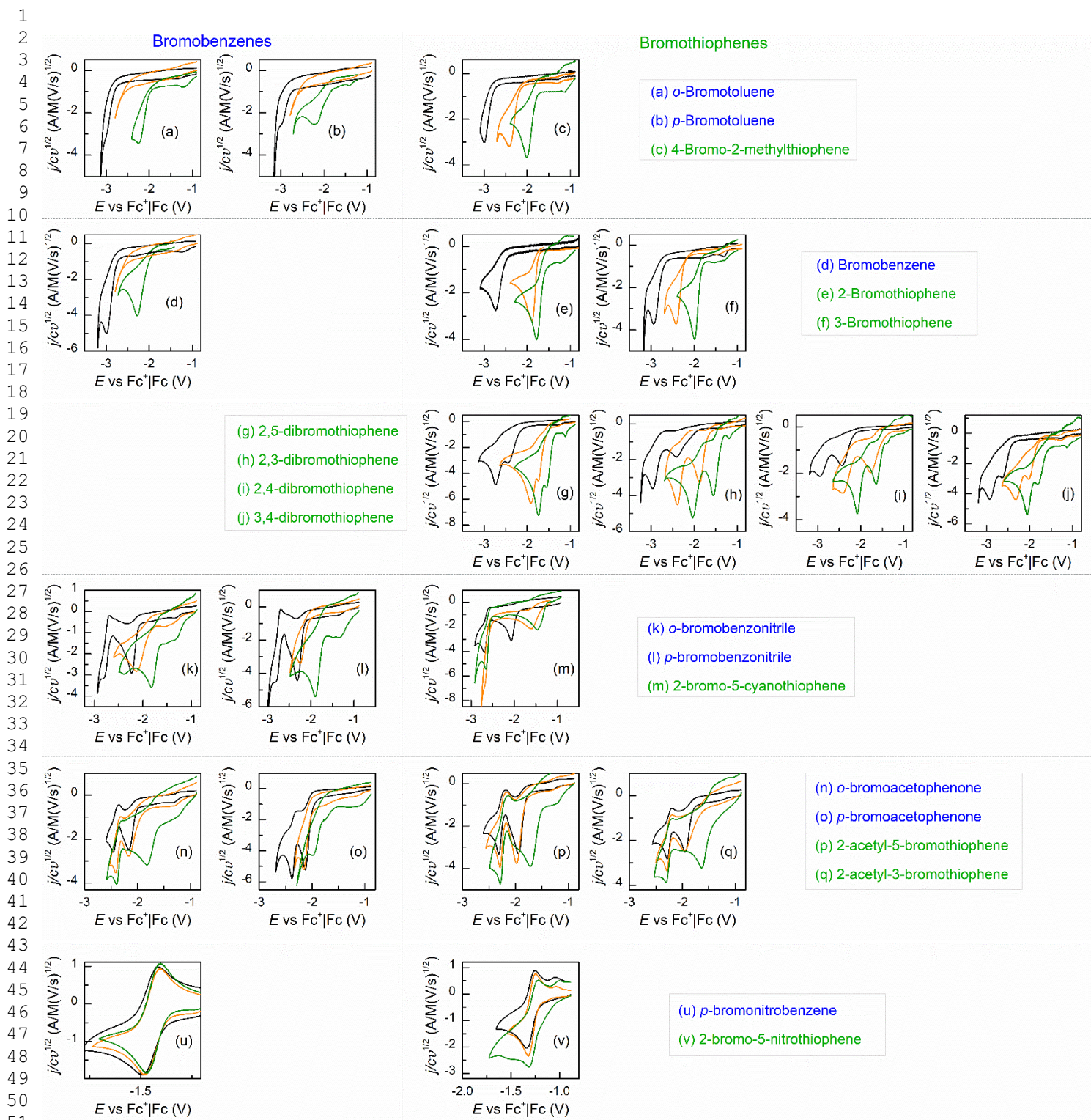
CV patterns for the investigated substrates (Sigma-Aldrich, Merck or TCI) were recorded in acetonitrile (Sigma Aldrich) with 0.1 M Et<sub>4</sub>NBF<sub>4</sub> (Fluka) as supporting electrolyte, in a range of potential scan rates from 0.05 V/s to 2 V/s. All CVs were run on an Autolab PGSTAT potentiostat/galvanostat with a positive feedback (EcoChemie, the Netherlands), run by a PC with GPES software.

Three kinds of Teflon<sup>®</sup>-embedded disks (Amel) were comparatively employed as working electrodes, consisting of GC (Sigradur, grade G, diameter = 0.3 cm), Au (diameter = 0.2 cm) and Ag (diameter = 0.3 cm). The electrodes were always polished with 1 μm diamond powder (Sigma Aldrich) on a wet cloth (DP Nap, Struers). The counter electrode was a Pt wire, while the reference electrode was an aqueous saturated calomel electrode (SCE) inserted into a compartment filled with the working medium CH<sub>3</sub>CN + 0.1 M Et<sub>4</sub>NBF<sub>4</sub> and ending with a porous frit to prevent leakage of water and KCl from the SCE internal solution into the working one. To make easier comparison of the results of this study with literature data, all potentials are referred to the ferricinium/ferrocene (Fc<sup>+</sup>|Fc) couple for which a formal potential of 0.384–0.390 V vs SCE was measured in the same conditions, in accordance with the literature [36].

## 3. Results and discussion

Figure 1 provides a synopsis of normalized CV features of the investigated series of bromothiophene and bromobenzene analogues on GC, Au and Ag working electrodes. All investigated systems, except the nitro derivatives, exhibited a first irreversible cathodic peak attributed to the reductive cleavage of the C-Br bond, followed by the voltammetric pattern of the hydrodehalogenated aromatic or heteroaromatic compounds formed at the first reduction peak. As these additional processes are not of interest for this study, we focused on the first reduction peak of each compound. Regardless of the electrode material, CVs at increasing scan rates ( $\nu$ ) did not show any reversibility for the first peak, which shifted to more negative potentials and increased in current intensity. Plots of peak current  $I_p$  versus  $\nu^{1/2}$  were linear on both catalytic and non-catalytic electrodes, indicating diffusion-controlled reduction processes [37]. The process at the catalytic electrodes certainly involves interaction of the organic halide and/or its reduction products with the metal surface, but the observed dependence of  $I_p$  on  $\nu^{1/2}$  suggests that these interactions are so fast that the overall reduction process occurs under diffusion control. Equations (1) and (2) have been derived for electrode processes without adsorption [37]. They can be used however also in the presence of adsorption provided that the overall electrode process is under diffusion control [38, 39]. Key CV parameters obtained on all electrodes are summarized in Table 1. The reported values of  $\kappa$  were calculated as the average of the values obtained from the dependence of  $E_p$  on scan rate and from the peak width, according to (1) and (2). The catalytic activity of Au and Ag was evaluated as the anodic shift of  $E_p$  measured on the catalytic electrode with respect to the value measured on GC, assumed to present a non-catalytic surface [40].





**Figure 1** Normalized CV features for substituted bromobenzene (left) and bromothiophene (right) analogues, recorded at 0.2 V/s in CH<sub>3</sub>CN + 0.1 M Et<sub>4</sub>NBF<sub>4</sub> on GC (black), Au (orange) and Ag (green) electrodes.

**Table 1** Key CV parameters in CH<sub>3</sub>CN + 0.1 M Et<sub>4</sub>NBF<sub>4</sub> for substituted bromobenzene (top) and bromothiophene (bottom) analogues on GC, Au and Ag electrodes.

Substituents	$E_{p, GC}^a$ vs Fc <sup>+</sup> /Fc / V	$\kappa^b$	$E_{p, Au}^a$ vs Fc <sup>+</sup> /Fc / V	$\kappa^b$	$(E_{p, Au} - E_{p, GC})^c$ / V	$E_{p, Ag}^a$ vs Fc <sup>+</sup> /Fc / V	$\kappa^b$	$(E_{p, Ag} - E_{p, GC})^c$ / V	$\sigma_p^{-d}$
<b>Br-Benzenes</b>									
<i>o</i> -Me	-3.06	0.33	n.d.	n.d.	n.d.	-2.23	0.31	0.83	-0.17
<i>p</i> -Me	-3.01	0.34	n.d.	n.d.	n.d.	-2.22	0.34	0.79	-0.17
H	-2.99	0.34	n.d.	n.d.	n.d.	-2.28	0.30	0.71	0
<i>o</i> -CN	-2.22	0.54	-2.12	0.26	0.10	-1.83	0.52	0.40	1.00
<i>p</i> -CN	-2.30	0.52	-2.25	0.42	0.05	-1.90	0.45	0.40	1.00
<i>o</i> -CH <sub>3</sub> CO	-2.17	0.67	-2.15	0.38	0.02	-1.82	0.36	0.35	0.84
<i>p</i> -CH <sub>3</sub> CO	-2.13	0.58	-2.14	0.64	-0.01	-1.98	0.40	0.15	0.84
<i>p</i> -NO <sub>2</sub>	-1.49 <sup>f</sup>		-1.49 <sup>f</sup>		0.00	-1.47 <sup>f</sup>		0.04	0.02
<b>Thiophenes</b>									
2-Me, 4-Br	-3.00	0.37	-2.42	0.32	0.58	-2.02	0.38	0.98	-0.17
2-Br <sup>e</sup>	-2.74	0.35	-1.89	0.54	0.85	-1.78	0.45	0.96	0
3-Br <sup>e</sup>	-2.93	0.41	-2.42	0.35	0.51	-1.98	0.46	0.94	0
2-Br, 5-Br <sup>e</sup>	-2.44	0.33	-1.76	0.41	0.68	-1.54	0.47	0.99	0.25
2-Br, 3-Br <sup>e</sup>	-2.40	0.35	-1.87	0.40	0.53	-1.56	0.46	0.84	0.25
2-Br, 4-Br <sup>e</sup>	-2.43	0.32	-1.77	0.36	0.66	-1.64	0.49	0.79	0.25
3-Br, 4-Br <sup>e</sup>	-2.64	0.41	-2.02	0.48	0.62	-1.80	0.43	0.84	0.25
2-Br, 5-CN	-2.06	0.47	-1.59	n.d.	0.47	-1.46	0.42	0.60	1.00
2-Br, 5-CH <sub>3</sub> CO	-1.95	0.68	-1.98	0.48	-0.03	-1.72	0.38	0.23	0.84
3-Br, 2-CH <sub>3</sub> CO	-1.96	0.50	-1.95	0.34	-0.01	-1.65	0.42	0.31	0.84
2-Br, 5-NO <sub>2</sub>	-1.34 <sup>f</sup>		-1.33 <sup>f</sup>		0.01	-1.32 <sup>f</sup>		0.01	1.27
<b>2,2'-Bithiophenes</b>									
5,5'-diBr-	-2.12,-2.23	0.34	-2.00	0.24	0.12, 0.23	-1.68	0.27	0.44, 0.55	
3,3'-diBr-	-2.34	0.42	-2.14	0.31	0.20	-1.69	n.d.	0.65	

<sup>a</sup>Peak potentials at 0.2 V/s.

<sup>b</sup>Diagnostic parameter  $\kappa$  obtained as the average of the values calculated with equations (1) and (2).

<sup>c</sup>Catalytic effect calculated as the positive shift of peak potential on Au or Ag with respect to GC.

<sup>d</sup>Hammett substituent constants from reference [22].

<sup>e</sup>Taken from reference [11].

<sup>f</sup>Formal potential  $E^{\circ}$  (for reversible ET systems).

### 3.1. Reactivity on non-catalytic GC electrode

Working on a non-catalytic GC electrode, which accounts for the intrinsic reactivity of the tested molecules in both molecule series, as already observed for bromobenzenes [11], reduction of the C-X bond becomes easier with decreasing electron density on the aromatic ring. The observed substituent order for  $E_p$  in both series is

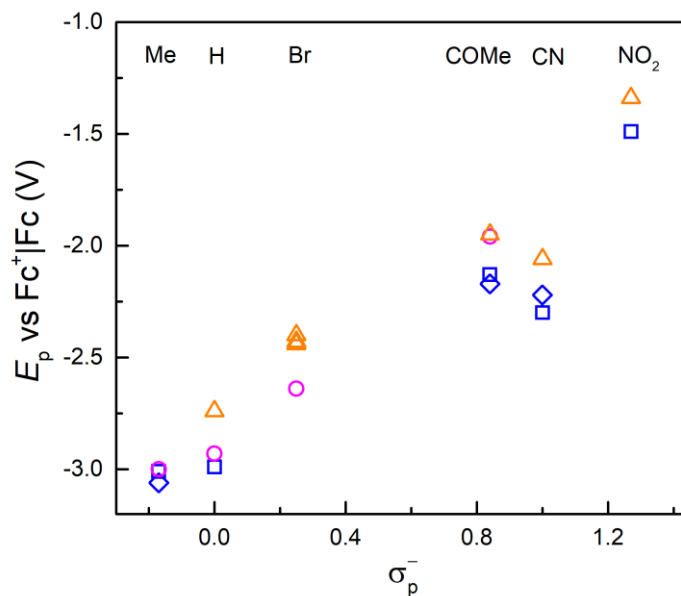


which, as shown in Figure 2, is well rationalized in terms of increasing  $\sigma_p^-$  Hammett parameters [11,22], excepting for the inversion observed for the CN and COCH<sub>3</sub> substituents. Analysis of the CV data provides  $\kappa$  values in the 0.32–0.68 range, with  $\kappa > 0.5$  in several cases. This finding is in line with the large body of literature data showing



1 that DET to aromatic and heteroaromatic halides occurs according to a stepwise mechanism [11,15,18,19,41-44].  
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3 The incoming electron is accommodated in a  $\pi^*$  orbital of the whole aromatic system, including conjugated  
4 substituents if present [45], followed by expulsion of a halide ion in a second step. The electron density is  
5 gradually localized towards the substituent with increasing electron attracting power of the latter; thus, it is  
6 partially localized on the COCH<sub>3</sub> group and fully localized on the NO<sub>2</sub> one, so that in the last case the first  
7 reduction peak becomes monoelectronic and chemically reversible. For this reason, the COCH<sub>3</sub> and NO<sub>2</sub> cases  
8  
9 reduction peak becomes monoelectronic and chemically reversible. For this reason, the COCH<sub>3</sub> and NO<sub>2</sub> cases  
10 should be considered peculiar with respect to the other substituents, which can also explain the above anomaly.  
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12 Also, the diagnostic  $\kappa$  parameter gradually increases with increasing electron withdrawing ability of the  
13 substituent, pointing to the bond cleavage barrier gradually overcoming that of the electron transfer step.  
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18 Importantly, the bromothiophene series has the reduction potentials shifted to more positive potentials with  
19 respect to the bromobenzene analogues, even in the nitro case, where the first reduction is localized on the NO<sub>2</sub>  
20 group. This effect could be justified in terms of electron attracting effect of the S atom as well as of more efficient  
21 radical anion stabilization in thiophene systems with respect to benzene ones. It looks more conspicuous when  
22 the C-Br bond to be cleaved is located in  $\alpha$  position to the S atom, generally resulting in larger positive shifts with  
23 respect to  $\beta$  cases. Moreover, the reactivity of the C-Br group appears more influenced by its position relative to  
24 the S atom than to the additional substituent.  
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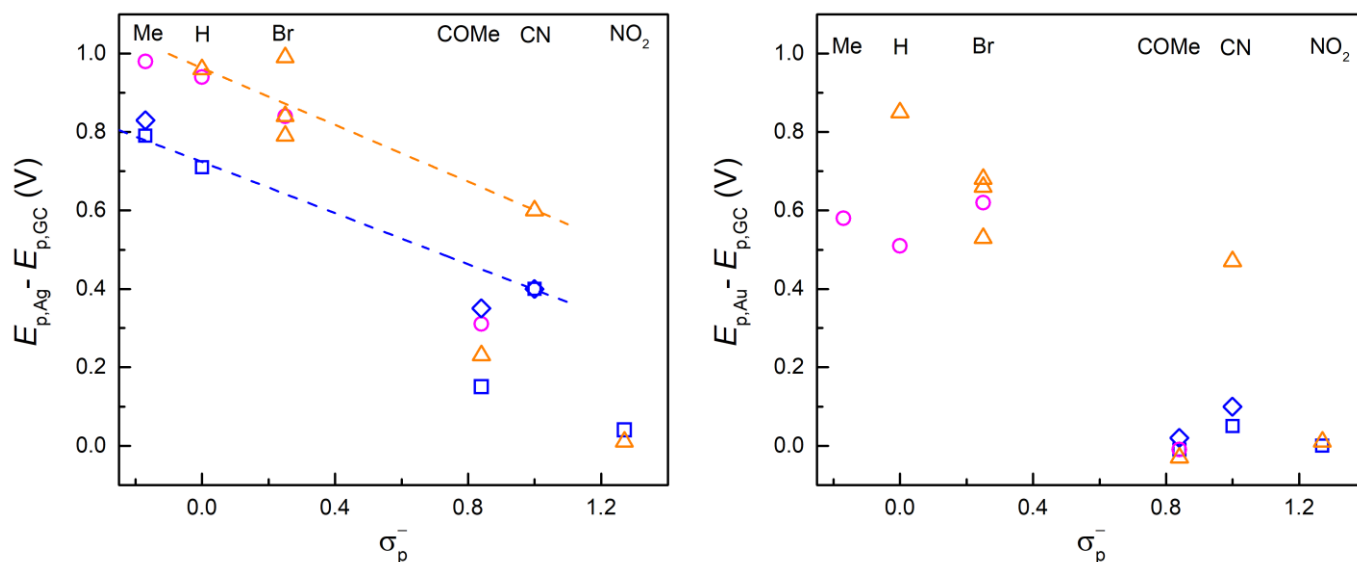


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54 **Figure 2** First reduction peak potentials on GC at 0.2 V/s in CH<sub>3</sub>CN + 0.1 M Et<sub>4</sub>NBF<sub>4</sub> for substituted bromobenzenes (blue;  
55 *p*- position: squares, *o*- position: diamonds) and bromothiophenes ( $\alpha$ -Br: orange triangles,  $\beta$ -Br: magenta circles), as a  
56 function of Hammett's  $\sigma_p^-$  parameters.  
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### 3.2. Reactivity on catalytic Ag and Au

Catalytic effects, estimated as peak potential differences with respect to GC as a non-catalytic benchmark, are observed on Ag for both bromobenzenes and bromothiophenes. As already reported for bromobenzenes [11], also for bromothiophenes they decrease with increasing electron withdrawing power of the substituents and increasing conjugation, *i.e.* with increasing electron density localization away from the C-Br bond to be cleaved (Figure 3, left). The trends of Ag catalytic effects with  $\sigma_p^-$  are approximately linear for both the bromobenzene and the bromothiophene series if Me, H, Br and CN are considered as substituents, whereas systems bearing COCH<sub>3</sub> and NO<sub>2</sub> show a peculiarly negative deviation with the catalytic effect being completely lost in the case of NO<sub>2</sub> substitution, which is consistent with the redox site being localized mostly or totally away from the Br atom.  $\kappa$  values are in both series are generally  $\leq 0.5$  (with the obvious exception of the nitro case), pointing to the electron transfer barrier being the determining one in the stepwise mechanism, or even to a transition to concerted mechanism [11].

The relative positions between substituents can significantly affect Ag catalytic effects. For example, in both the acetyl bromobenzene and acetyl bromothiophene pairs the catalytic effect is higher when the CH<sub>3</sub>CO group is adjacent to the C-Br moiety: 0.35 V vs 0.15 V for *o*-bromoacetophenone vs *p*-bromoacetophenone in the bromobenzene pair, and similarly 0.31 V vs 0.23 V for 2-acetyl-3-bromothiophene vs 2-acetyl-5-bromothiophene in the bromothiophene pair (in spite of the first thiophene compound having the C-Br bond in  $\beta$  position with respect to S and the second one in  $\alpha$  position).



**Figure 3** Catalytic effects of Ag (left) and Au (right) at 0.2 V/s in CH<sub>3</sub>CN + 0.1 M Et<sub>4</sub>NBF<sub>4</sub> for bromobenzenes (blue; *p*-position: squares, *o*-position: diamonds) and bromothiophenes ( $\alpha$ -Br: orange triangles,  $\beta$ -Br: magenta circles), as a function

1 of Hammett's  $\sigma_p^-$  parameters for the additional substituent besides the bromide cleaving at the first reduction peak. The  
2 dashed lines are regression lines for *p*-substituted bromobenzenes (blue) and  $\alpha$ -bromothiophenes (orange).  
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7 The catalytic effects of Au for the bromobenzene series (when observable before the Au background) are much  
8 smaller than in the case of Ag (0.05 – 0.1 V for Au versus 0.4 V for Ag in the carbonitrile case and ~0 V for Au  
9 versus 0.15 – 0.35 V for Ag in the acetyl case). This is consistent with the highly negative charge at the Au surface  
10 in the potential range concerned, on account of the Au pzc being located at much more positive potentials than  
11 that of Ag [34,35]; this condition greatly hampers the potentially very high catalytic activity of the Au electrode  
12 for the process.  
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18 Instead, considering the bromothiophene series, Au shows remarkable catalytic effects, although not reaching  
19 Ag ones, decreasing with  $\sigma_p^-$  (Figure 3, right) as in the Ag case. Such improved catalytic performance can be  
20 justified in terms of the sulphur atom acting as an adsorption auxiliary, partially overcoming the above effect  
21 [26]; actually, such effects are significantly modulated by the reciprocal positions of the group to be cleaved with  
22 respect to the S atom acting as an adsorption auxiliary, promoting reduction of Br groups in  $\alpha$  more effectively  
23 than those in  $\beta$ .  
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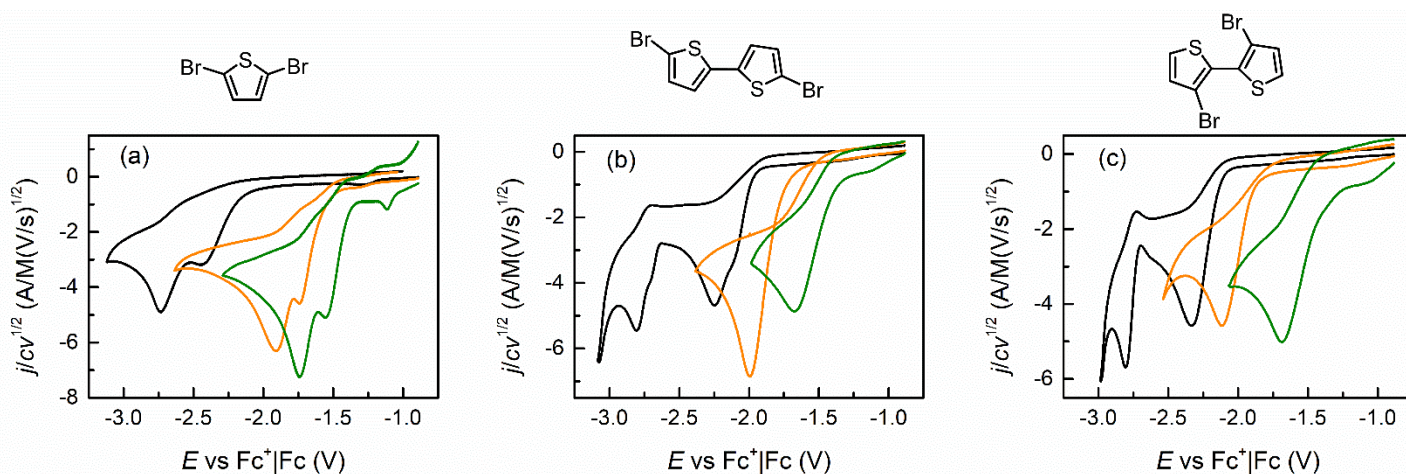
29 The huge catalytic effect of the Au electrode for 2-bromo-5-cyanothiophene (0.47 V) as well as the  
30 significantly higher catalytic effect of the same electrode for *o*-bromobenzonitrile than for *p*-bromobenzonitrile  
31 (0.10 V vs 0.05 V) might point out that also the CN group is specifically interacting with the Au electrode, thus  
32 providing an additional anchoring group. Actually, N atoms can act as adsorption auxiliaries, particularly on Au.  
33 A striking example is provided in a recent paper [46] concerning triimidazole halide electrochemistry, with the  
34 iodide derivatives being reduced on Au at even less negative potentials than on Ag.  
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### 43 3.3 $\alpha, \alpha'$ -Dibromothiophene vs Dibromo- $\alpha, \alpha'$ -bithiophenes

44 As previously discussed [26], 2,5-dibromothiophene features a twin first reduction peak system, consistent with  
45 a couple of equivalent interacting redox centres, and huge catalytic effects are observed on Ag and Au for the  
46 cleavage of both C-Br bonds, both of them being advantageously adjacent to the “auxiliary” S atom. It is  
47 interesting to compare dibromothiophene with dibromobithiophenes (Scheme 2):  
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- 53 • 5,5'-dibromo-2,2'-bithiophene, having both Br leaving groups in  $\alpha$  position with respect to S atoms, but  
54 on different rings, although  $\alpha, \alpha'$  reciprocally linked (a connectivity granting more effective conjugation  
55 than the  $\beta, \beta'$  one)  
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- 57 • 3,3'-dibromo-2,2'-bithiophene, having both Br leaving groups in  $\beta$  position with respect to S atoms on the  
58 same  $\alpha, \alpha'$ -bithiophene scaffold.  
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CV features obtained for the three molecules on GC, Au, and Ag are compared in Figure 4. On non-catalytic GC, a nearly merging first reduction twin peak system is observed for 5,5'-dibromo-2,2'-bithiophene at significantly less negative potentials than in the 2,5-dibromothiophene case (by about 0.3 V) (Figure 4a,b), which is consistent with the more efficient stabilization of the radical anion product in an  $\alpha,\alpha'$ -bithiophene system than in a single thiophene ring. A third peak follows, corresponding to the reduction of the  $\alpha,\alpha'$ -bithiophene scaffold to its radical anion, which can be observed before the background, unlike reduction of single thiophene in the former case.



**Figure 4.** Normalized CV features for 2,5-dibromothiophene (left), 5,5'-dibromo-2,2'-bithiophene (middle) and 3,3'-dibromo-2,2'-bithiophene (right), recorded at 0.2 V/s in  $\text{CH}_3\text{CN} + 0.1 \text{ M Et}_4\text{NBF}_4$  on GC (black), Au (orange) and Ag (green) electrodes.

The merging twin peak system, with a much smaller splitting than in the 2,5-dibromothiophene case, but still significant (Figure 4b) can be explained with the support of a former literature work [47], in terms of 5,5'-dibromo-2,2'-bithiophene consisting of two homotopic redox centres reciprocally interacting through the  $\alpha$ -bithiophene backbone (although less than the two bromide sites in 2,5-dibromothiophene, resulting in a larger splitting on GC).

On the contrary, no peak splitting is observed on GC for 3,3'-dibromo-2,2'-bithiophene (Figure 4c); this is consistent with the higher sterical hindrance between the two moieties [47] on account of the bulky Br atoms in  $\alpha$  to the interannular bond, which can result in a high torsional energy barrier and angle between the two moieties/homotopic redox sites, so that they undergo reduction at the same potential, as if they were reciprocally independent. It would be interesting to calculate such energy barrier, since in case it would result higher than about 25 kcal/mol, the molecule would be atropisomeric and exist in two stable enantiomers at room temperature; if not, it would be a *tropos* system [48]. It can also be noticed that also in this case, a third peak is observed at the

1 same potential of the third peak for the former compound. This is reasonable, since cleavage of both Br  
2 substituents results in the same  $\alpha,\alpha'$ -bithiophene scaffold in both dibromobithiophenes.

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4 Interestingly, the peak splitting of 5,5'-dibromo-2,2'-bithiophene completely disappears on Au and Ag  
5 catalytic electrodes. A rotation around the bond connecting the two rings is probable in this case, affording both  
6 the sulphur atoms to be in convenient positions with respect to the catalytic surface. In this case optimal substrate-  
7 surface interaction would be assured, but the conjugation would be lost; then the two rings would become  
8 independent, and the two homotopic C-Br bonds could be reduced at the same potential (in the Au case the peak  
9 shape could point to some nucleation effects, too). Actually this assumption looks confirmed not only by the  
10 absence of peak splitting, but also by the first reduction potentials being even more negative than those of 2,5-  
11 dibromothiophene, consisting of a single thiophene ring (-1.68 V on Ag and -2.00 V on Au for the bithiophene  
12 system *vs* -1.54 V on Ag, -1.76 V on Au for the thiophene one).  
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15 Also, in the 3,3'-dibromo-2,2'-bithiophene case the reduction potentials on the two catalytic electrodes are  
16 close to, or even more negative than, those of the 3,4-dibromothiophene as a  $\beta,\beta$  benchmark (-1.69 V on Ag and  
17 -2.14 V on Au for the bithiophene cases *vs* -1.80 on Ag and -2.02 V on Au for the thiophene ones). It is worthwhile  
18 noticing that this is quite unlike the GC case, in which both dibromobithiophene molecules result in significantly  
19 more positive reduction potentials with respect to the corresponding dibromothiophene case. In this light, the  
20 smaller observed catalytic effects for the dibromobithiophene systems with respect to 3,4-dibromothiophene  
21 should be justified in terms of comparatively higher reactivity of bithiophene systems on the non-catalytic  
22 electrode (allowing the conjugated biheteroaromatic system to keep its optimal conformation) rather than of really  
23 lower catalytic surface effects.  
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#### 39 **4. Conclusions**

40 Bromothiophenes share with bromobenzenes many similarities concerning the C-Br reductive cleavage in non-  
41 catalytic conditions: the dissociative transfer mechanism and the substituent effects are similar and can be  
42 interpreted with the same rationale. However, in the heteroaromatic series reduction potentials are shifted to  
43 significantly less negative values on account of electronic effects related to the presence of the S atom. The two  
44 series also share, when working on Ag or Au, a similar trend of the surface catalytic effects with substituent  
45 nature, decreasing with increasing electron attracting character of the latter. However, in the bromothiophene  
46 cases the heteroatom also acts as an adsorption auxiliary, enhancing the surface catalytic effects. This effect is  
47 particularly remarkable for Au, partially overcoming in the bromothiophene cases the effect of the very negative  
48 surface charge of the metal in the working potential range, which otherwise would greatly hamper its intrinsically  
49 high catalytic effect, as evident with the bromobenzene series. The position of the substituent with respect to the  
50 Br group to be cleaved appears less relevant than that of the S atom, particularly in the Au case, but the nitrile  
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1 group might act as an additional adsorption auxiliary besides the S atom.

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3 Finally, an even more striking evidence of the importance of concurrent interaction of the catalytic surfaces  
4 with both the Br leaving groups and the S atoms comes from the dibromodithiophene systems. In fact, comparison  
5 of their CV features on non-catalytic GC and catalytic Au and Ag points to the molecule undergoing a remarkable  
6 modification in its conformation in order to optimize S and Br coordination for both conjugated thiophene rings.  
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