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Self-assembly of Thioether Functionalized Fullerenes on Gold and Their Activity in Electropolymerization of Styrene

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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A series of new fulleropyrrolidine alkylaromatic sulphides with different substituents on sulphur atom were synthesized. The redox properties of the C₆₀ derivatives in solution and self-assembled on gold electrode surfaces were characterized by cyclic and differential pulse voltammetry. All fullerene derivatives were found to be bound to the gold surface by the thioether sulphur anchoring group and not through fullerene sphere – Au surface interactions. The unique electrochemical properties of the synthesized fullerene derivatives allowed to show for the first time initiating activity of fullerene molecules in the anionic polymerization of styrene under electrochemical conditions.

Introduction

The unique structure and electron properties of C₆₀ fullerene have been subject of extensive studies since its discovery in 1985.¹ Due to its reversible electron accepting properties, it has found, among others, numerous applications in photovoltaics,² electrocatalysis³ and polymer science.⁴ However, its effective and durable integration into new materials requires suitable functionalization of fullerene core, thus, introduction of desired functional groups. Only appropriate C₆₀ fullerene derivatives, including fulleropyrrolidines, while gaining new features originating from introduced substituents, retain favourable electronic properties of fullerene core, crucial for their later application. For example, thiol^{5,6} or disulphide⁷ functionalities introduced into fullerenes have been used for modification of gold surfaces from the very beginning. Studies in this field showed however that the -SH group, due to its reactivity towards fullerene cage^{8,9} and relative instability, needs to be protected or replaced with other sulphur derivatives¹⁰ or sulphur-free anchoring groups.¹¹

One of the alternatives is the use of sulphides instead of free thiols or less soluble disulphides. Thioethers are generally easier to handle, convenient in synthesis, more soluble and reveal lower tendency to oxidation than thiols and disulphides, being reduction-resistant at the same time.^{12,13} These compounds show also an advantageous feature of the easy monolayer reorganization due to their weaker bonding to the gold surface.^{14,15} On the other hand, for stronger bonding with

gold substrates appropriate molecules bearing multiple thioether groups can be applied, including derivatives with three,^{15,16} four,¹⁷ five¹⁸ or even more –SR moieties.¹⁹

It is well known that not only the anchoring-group but also the head-group, especially built of C₆₀ fullerene, has strong impact on the self-assembly process.^{10,20} Multilayer formation may occur when the deposited compound shows low solubility and/or high tendency to aggregate, as in the case of C₆₀ sphere. Additionally, as a result of anchoring group low affinity to the gold substrate head-to-tail assembly may take place.¹⁰

In the present study, we succeeded to avoid all those handicaps by synthesizing fulleropyrrolidines that are stable, reveal high solubility in organic solvents and, additionally, self-assembly predominantly as monolayers (SAMs) on the gold surface. These goals may be achieved by functionalization of fullerenes with thioether groups.

For this purpose, a series of new fullerene alkylaromatic sulphides with different substituents **I-IV** as well as methoxy analogue of thioether **I-O** were synthesized (Fig. 1). The nature of fullerene sulphides–Au interaction was studied in details as results reported to date are ambiguous and sometimes in opposition with general findings for thioethers, *i.e.* suggesting that fullerene derivatives C₆₀–Au interactions may get the upper hand from those between sulphur and gold.¹⁴ All synthesized compounds were subsequently investigated on their ability to self-assemble on the gold surface.

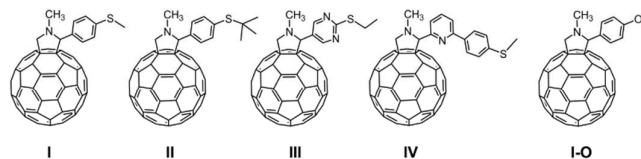


Fig. 1. Structures of synthesized C₆₀ fullerene sulphides **I-IV** and methoxy derivative **I-O**.

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The redox properties of the C₆₀ derivatives in solution and on gold surfaces are characterized by cyclic and differential pulse voltammetry. In addition, the unique electrochemical properties of the synthesized fullerene derivatives allowed us to show for the first time the possibility of applying fullerene molecules as an initiator in the electrochemical anionic polymerization of styrene.

Experimental section

Reagents

4-(Methylthio)benzaldehyde, 2-(ethylthio)pyrimidine-5-carbaldehyde, 4-methoxybenzaldehyde, 6-[4-(methylthio)phenyl]-2-pyridinecarboxaldehyde, *N*-methylglycine (sarcosine), potassium hydroxide, tetrabutylammoniumhexafluorophosphate (TBAHFP), acetonitrile, toluene and styrene were bought from Sigma-Aldrich. 4-(*tert*-butylthio)benzaldehyde and 1,2-dichlorobenzene were obtained from Alfa Aesar. Chloroform, methanol, methylene chloride, *n*-hexane and *n*-pentane were purchased from POCh (Poland). Fullerene C₆₀, 99.9%, was obtained from MER Corp. Toluene, styrene and 1,2-dichlorobenzene were dried and purified before use according to standard procedures, other solvents were analytical grade reagents and were used as received. Ultra pure water was obtained from the Millipore purification system (nominal resistivity: 18MΩ cm at 25°C).

Characterization methods and instrumentation

ESI-MS spectra were acquired on a Micromass LCT ESI-TOF mass spectrometer equipped with an orthogonal electrospray ionization source. Fullerene derivatives were detected by reduction to corresponding radical anions using NaK amalgam in toluene/dimethoxyethane 6:1 as a solvent.²¹ Samples of desorbed monolayers were examined in both positive and negative ion mode using mixture of chlorobenzene/methanol 1:1.

¹H and ¹³C NMR spectra were recorded on Varian Unity Plus 300 MHz spectrometer using CDCl₃ as a solvent.

The infrared experiments for fullerene sulphides were carried out using the Shimadzu FTIR-8400S.

UV-Vis spectrum of polystyrene in CH₂Cl₂ was recorded using Varian Cary 50 UV-VIS spectrophotometer.

XPS measurements were carried out using a VG ESCALAB 210 electron spectrometer equipped with an Al Kα source (1486.6 eV). XPS data were calibrated using the binding energy of C1s = 284.6 eV as the internal standard.

AFM (Atomic Force Microscopy) measurements were carried out with 5500 AFM (Agilent Technologies, Santa Clara, CA, USA). The AFM data was recorded in air using PPP-NCSTR (Nanosensors) silicon probes for soft-tapping AFM mode. As substrates for AFM measurements were used gold beads prepared according to Clavilier method. The atomically flat (111) surfaces at the bead were used for image acquisition.

The molecular weight of polymers was measured by Gel permeation chromatography (GPC) method using Jordi Gel DVB columns operated at 30°C. Methylene chloride was used as mobile phase and calibration was made with polystyrene standards.

Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) experiments were carried out using the Autolab (ECO Chemie, Netherlands) potentiostat. All experiments were performed at room temperature in solvents specified in the text, always containing 0.1M TBAHFP as supporting electrolyte, with a silver/silver chloride (Ag/AgCl) as the reference electrode, platinum foil as the counter electrode and the glassy carbon (GC, BAS, 3 mm diameter) or the modified gold substrates (200 nm) evaporated on glass with a pre-layer of 2-4 nm composed of chromium (Gold Arrandee, GmbH) as the working electrodes. In electrochemical polymerization of styrene as a working electrode glassy carbon with high surface area and two platinum foils as the counter and reference electrodes were used.

Potentials were calibrated using the ferrocene (Fc⁺/Fc, Fc=ferrocene) redox process. Argon was used to deaerate solution and an argon blanket was maintained over the solution during all the experiments.

Synthesis of fullerene sulphides

C₆₀ fullerene sulphides **I-IV** were obtained using the modified synthetic procedure reported by Prato et al.²² In general, to a stirred solution of C₆₀ fullerene (144 mg, 0.2 mmol) in dry toluene (130 mL), corresponding aldehyde (0.2 mmol) and sarcosine (89 mg, 1mmol) were added. The resulting mixture was heated at reflux under argon atmosphere for 6-8 h. The reaction mixture was then cooled, filtered to remove insoluble residue and the solvent was evaporated under reduced pressure. The obtained solid was dissolved in a small amount of toluene and chromatographed on silica gel using mixture 2:1 of *n*-hexane and toluene. Fractions containing the desired products were concentrated under vacuum, precipitated with methanol, centrifuged (10000 RPM, 5 min.), washed twice with *n*-pentane and dried *in vacuo* to give pure C₆₀ fullerene sulphides **I-IV** as dark brown powders.

N-methyl-2-[4-(methylthio)phenyl]-3,4-[60]fulleropyrrolidine **I**

Yield: 33%, the mass spectrum (ESI-MS) showed a [M]⁻ peak at 900.1 (Fig. S1, ESI[†]); IR (KBr disk) ν_{\max} (cm⁻¹) 2963.7, 2912.1, 2835.0, 2776.6, 1558.5, 1490.1, 1461.6, 1424.0, 1331.1, 1267.8, 1179.1, 1125.0, 826.5, 786.0, 667.3, 525.2, see (Fig. S2, ESI[†]); $\delta^1\text{H}$ (300 MHz; CDCl₃; TMS) 2.48 (3H, s), 2.79 (3H, s), 4.22-4.27 (1H, d), 4.88 (1H, s), 4.94-4.99 (1H, d), 7.23-7.27 (2H, d), 7.68-7.71 (2H, d) ppm (Fig. S3, ESI[†]); $\delta^{13}\text{C}$ (125 MHz; CDCl₃) ¹³C NMR (126 MHz, CDCl₃) 14.06, 15.47, 40.02, 69.05, 70.03, 83.26, 126.30, 127.73, 129.72, 130.56, 133.67, 135.73, 136.36, 136.52, 136.68, 138.78, 139.64, 140.17, 140.20, 141.57, 141.71, 141.88, 141.96, 142.06, 142.15, 142.27, 142.62, 142.71, 143.12, 144.43, 144.63, 144.73, 145.19, 145.26, 145.30, 145.37, 145.47, 145.52, 145.56, 145.79, 145.98, 146.17, 146.26, 146.31, 146.34, 146.49, 146.74, 147.34, 147.41, 153.31, 153.45, 154.05, 156.27, ppm (Fig. S4, ESI[†]).

N-methyl-2-[2-(tert-butylthio)phenyl]-3,4-[60]fulleropyrrolidine II

Yield: 41%, the mass spectrum (ESI-MS) showed a [M]⁺ peak at 942.2 (Fig. S5, ESI[†]); IR (KBr disk) $\nu_{\max}(\text{cm}^{-1})$ 2946.4, 2835.0, 2777.6, 1451.5, 1429.8, 1359.9, 1330.9, 1176.1, 1124.6, 764.0, 753.7, 573.8, 552.6, 526.6 see (Fig. S6, ESI[†]); $\delta^1\text{H}$ (300 MHz; CDCl₃; TMS) 1.44 (9H, s), 2.84 (3H, s), 4.37-4.40 (1H, d), 4.97-5.00 (1H, d), 6.11 (1H, s), 7.47-7.62 (3H, m), 8.21-8.24 (1H, d) ppm (Fig. S7, ESI[†]); $\delta^{13}\text{C}$ (125 MHz; CDCl₃) 15.58, 28.55, 29.72, 30.92, 34.14, 40.25, 65.60, 70.18, 84.22, 119.51, 121.86, 126.43, 127.28, 127.72, 130.55, 135.86, 136.55, 136.83, 137.68, 139.44, 139.67, 139.96, 140.23, 141.65, 141.72, 141.76, 141.91, 142.01, 142.14, 142.18, 142.25, 142.32, 142.59, 142.69, 143.04, 143.12, 143.15, 144.44, 144.59, 144.69, 145.15, 145.23, 145.34, 145.39, 145.52, 145.58, 145.67, 145.77, 145.99, 146.10, 146.27, 146.49, 147.03, 147.33, 153.21, 153.82, 153.96, 156.12, 156.23, 157.34 ppm (Fig. S8, ESI[†]).

N-methyl-2-[5-[2-(ethylthio)pyrimidinyl]]-3,4-[60]fulleropyrrolidine III

Yield: 41%, the mass spectrum (ESI-MS) showed a [M]⁺ peak at 915.5 (Fig. S9, ESI[†]); IR (KBr disk) $\nu_{\max}(\text{cm}^{-1})$ 2948.8, 2924.7, 2844.6, 2778.6, 1580.2, 1521.5, 1396.5, 1333.8, 1222.9, 1177.6, 771.0, 572.9, 552.1, 524.7 see (Fig. S10, ESI[†]); $\delta^1\text{H}$ (300 MHz; CDCl₃; TMS) 1.38-1.43 (3H, t), 2.80 (3H, s), 3.15-3.23 (2H, q), 4.25-4.28 (1H, d), 4.88 (1H, s), 4.99-5.02 (1H, d), 8.94 (2H, s) ppm (Fig. S11, ESI[†]); $\delta^{13}\text{C}$ (125 MHz; CDCl₃) 14.28, 25.45, 39.93, 68.92, 70.02, 78.81, 125.53, 135.61, 136.17, 136.26, 137.75, 139.93, 140.27, 140.34, 141.70, 141.75, 141.92, 141.99, 142.11, 142.12, 142.15, 142.22, 142.28, 142.59, 142.66, 142.71, 142.79, 143.09, 143.19, 144.38, 144.47, 144.56, 144.77, 145.27, 145.30, 145.36, 145.41, 145.48, 145.50, 145.57, 145.62, 145.68, 145.70, 145.72, 145.88, 146.03, 146.05, 146.21, 146.26, 146.28, 146.39, 146.41, 147.40, 147.42, 151.37, 152.24, 153.35, 157.96, 155.71, 173.09 ppm (Fig. S12, ESI[†]).

N-methyl-2-[6-[4-(methylthio)phenyl]2-pyridinyl]-3,4-[60]fulleropyrrolidine IV

Yield: 32%, the mass spectrum (ESI-MS) showed a [M]⁺ peak at 977.1 (Fig. S13, Supporting Information); IR (KBr disk) $\nu_{\max}(\text{cm}^{-1})$ 2947.8, 2913.1, 2832.6, 2775.7, 2326.2, 1554.3, 1448.6, 1427.4, 1328.9, 1243.6, 1179.1, 1096.1, 940.1, 812.5, 784.1, 768.1, 597.9, 573.4, 552.1, 524.7 see (Fig. S14, ESI[†]); $\delta^1\text{H}$ (300 MHz; CDCl₃; TMS) 2.47 (3H, s), 2.90 (3H, s), 4.32-4.37 (1H, d), 4.98-5.03 (1H, d), 5.28 (1H, s), 7.18-7.21 (2H, d), 7.60-7.64 (1H, d), 7.81-7.89 (4H, m) ppm (Fig. S15, ESI[†]); $\delta^{13}\text{C}$ (125 MHz; CDCl₃) 15.45, 29.81, 30.53, 40.09, 43.78, 69.89, 83.97, 119.09, 121.65, 123.72, 126.14, 127.12, 127.76, 137.43, 139.34, 139.47, 139.56, 139.62, 140.08, 140.11, 141.50, 141.71, 141.88, 142.03, 142.14, 142.46, 142.54, 142.90, 142.97, 142.99, 144.27, 144.43, 144.52, 144.55, 145.01, 145.07, 145.17, 145.32, 145.39, 145.48, 145.59, 145.84, 145.94, 146.02, 146.11, 146.16, 147.15 ppm (Fig. S16, ESI[†]).

N-methyl-2-[4-methoxyphenyl]-3,4-[60]fulleropyrrolidine I-O

Yield: 25%, the mass spectrum (ESI-MS) showed a [M]⁺ peak at 884.3 (Fig. S17, ESI[†]); IR (KBr disk) $\nu_{\max}(\text{cm}^{-1})$ 2945.4, 2828.7, 2772.8, 2357.1, 2321.9, 1510.3, 1459.7, 1423.0, 1331.0, 1298.1, 1251.4, 1179.1, 1032.9, 829.9, 763.8, 726.7, 668.4, 572.9, 526.2, see (Fig. S18, ESI[†]); $\delta^1\text{H}$ (300 MHz; CDCl₃; TMS) 2.79 (3H, s), 3.82 (3H, s), 4.23-4.26 (1H, d), 4.89 (1H, s), 4.96-4.99 (1H, d), 6.94-6.97 (2H, d), 7.16-7.19 (2H, d) ppm (Fig. S19, ESI[†]); $\delta^{13}\text{C}$ (125 MHz; CDCl₃) 14.01, 21.42, 40.00, 55.24, 68.98, 70.03, 83.21, 114.05, 125.31, 126.91, 128.24, 128.96, 129.05, 130.49, 135.77, 135.81, 136.56, 136.80, 139.59, 139.92, 140.14, 141.56, 141.71, 141.86, 141.99, 142.03, 142.06, 142.11, 142.15, 142.28, 142.31, 142.58, 142.70, 143.00, 143.17, 144.42, 144.64, 144.72, 145.17, 145.25, 145.30, 145.34, 145.48, 145.51, 145.56, 145.81, 145.95, 145.97, 146.12, 146.16, 146.23, 146.33, 146.39, 146.54, 146.83, 147.32, 153.66, 153.69, 154.16, 156.42, 159.61 ppm (Fig. S20, ESI[†]).

Self-assembly of thioether derivatives on gold electrodes

Samples of self-assembled fullerene derivatives were prepared from their 5·10⁻⁵M solutions in freshly distilled 1,2-dichlorobenzene into which the gold substrate was immersed at room temperature under nitrogen atmosphere. All manipulations were carried out inside the glove box to avoid contamination. After 16h gold plates covered with functionalized fullerenes were rinsed with toluene, dried under stream of nitrogen and investigated using XPS, AFM and CV.

Fulleropyrrolidine initiated electrochemical polymerization of styrene

For the electrochemically triggered polymerization of styrene fullerene sulphide **III** was employed as the initiator. 1,2-dichlorobenzene solution containing 5·10⁻⁴M **III** and 0.1M TBAHFP as the supporting electrolyte was prepared and 10% of styrene was added to it. Electrolysis at -1.2V was carried out for 15 hours, then the solution was evaporated to dryness by nitrogen stream, and the resulting solid was washed with methanol. The polymer obtained was dissolved in a small amount of acetone. Compound **III** is insoluble in acetone. The solvent was next removed *in vacuo* from the sample to give polystyrene **F-PS** as a white-beige solid.

Results and discussion**Atomic force microscopy**

The thioether functionalized fullerenes were self-assembled on gold surface and topographically characterized by AFM. AFM images (Fig. 2) show that fullerene sulphides **I-IV** readily self-assemble onto gold substrates forming thin, homogenous and densely packed layers, which completely cover the gold surface.

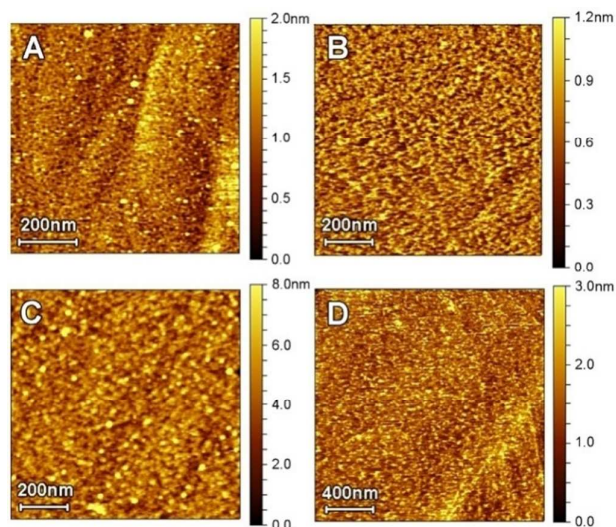


Fig. 2. AFM images of fullerene thioethers I-IV self-assembled on the gold surface.

These observations reveal that the relatively long time of self-assembly (16 h) allows to obtain uniform coating. The height of the layer varies from < 2 nm for flat regions of monolayers obtained for compounds I, II and IV (Fig 2: A, B and D respectively) to few nanometers high for compound III (Fig 2C). This difference suggests that molecules of compound III have higher affinity to each other and assemble as aggregates with larger diameters rather than uniform films. Type of substituent has also an influence on the homogeneity of obtained layers, i.e. derivatives I and IV form more homogenous layers comparing to thioethers II and III. Films of I and IV are similar probably because terminal alkyl chain is the same for both compounds. However, taking into account similar AFM results obtained for the synthesized group of fullerene sulphides I-IV no other significant structure dependent features were observed despite different substituents on the thioether sulphur atom. The nature of fullerene sulphides chemisorption on the gold surface from 1,2-dichlorobenzene solutions was also investigated using X-ray photoelectron spectroscopy.

XPS spectroscopy results

XPS technique was chosen to investigate the nature of the bond between thioether functionalized fullerenes and gold surface. The spectra were recorded for both, pure fullerene sulphide I and its film chemisorbed on Au. X-ray photoelectron spectra of the

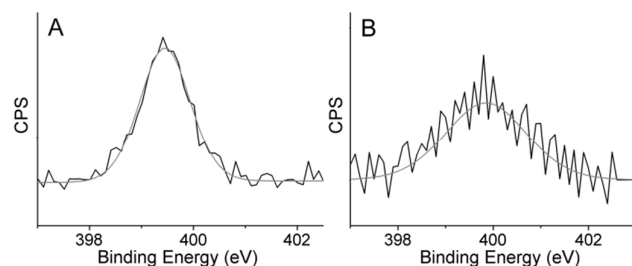


Fig. 3. X-ray photoelectron spectra of the N1s core level region for A) pure fullerene sulphide I B) compound I deposited gold surface.

samples showed the presence of carbon, sulphur and nitrogen atoms. For sample of I deposited on Au surface gold signals were also seen and in the spectrum obtained for sample of pure I on a silicon plate the signals from silicon atoms could be also resolved.

The XPS results confirmed successful functionalization of fullerene core including formation of pyrrolidine ring, by the appearance of N1s signals at 399.4 and 399.6 eV,²³ for the sample of I (Fig 3A) and its layer deposited on gold surface, respectively (Fig 3B).

The spectra in the S2p region for both investigated samples, i.e. pure fullerene sulphide I and its monolayer deposited on gold surface, show one broad peak. Those signals were fitted with good correlation as doublets with area ratios of 2:1 and expected splitting of 1.2 eV. According to the literature data,¹⁸ the doublet observed for pure I at 163.3 and 164.5 eV, assigned to S2p_{3/2} and S2p_{1/2} respectively, is as expected the XPS signal characteristic for the thioether sulphur (Fig 4A).

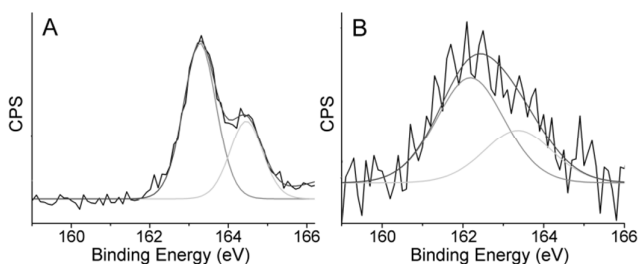


Fig. 4. X-ray photoelectron spectra of the S2p core level region for A) sample of fullerene sulphide I B) sulphide I self-assembled on gold surface.

Self-assembly of sulphide I on the surface of gold leads to a significant change in the S2p region of XPS spectra (Fig. 4B). The doublet has two peaks centered at 162.2 and 163.4 eV, hence shifted by 1.2 eV towards lower binding energies, implying notable S-Au interactions. Similar findings have been reported in numerous papers, i.e. for dialkyl sulphide,²⁴ substituted corannulene¹⁸ and thiomethyl fullerene derivative assembled on gold surface.²⁵ These results are contrary to those presented by del Carmen Gimenez-Lopez et al.¹⁴ who after max. 22min did not observe signals for S different from that of thioether sulphur. The most possible reasons of these discrepancies are the differences in the deposition times and the solvents applied. Indeed, following immersion of the electrode in the solution for only a couple of minutes we did not observe any signs of interactions between thioether sulphur and gold as well. However, elongation of the immersion time from minutes to 16 hours, similarly to experimental conditions reported by Dong²⁵ (48h self-assembly time), the signals described above could be easily recognized. It can be also not excluded that longer immersion time is necessary for reorientation of the molecules from the initial one with fullerene cage directed towards the Au surface to that involving formation of the stronger fullerene sulphide S-Au bond, which has similar binding energy value to thiolate species,¹⁰ as it can be concluded from XPS results. Thus, we can assume that in our work all fullerene derivatives are bound to the gold surface by the sulphur anchoring group and we definitely do not observe adsorption by engaging of C₆₀-Au interactions. Considering the results from XPS studies, it is important to underline that we used 1,2-dichlorobenzene instead of 1,2,4-trichlorobenzene or tetrahydrofuran solvent as it was suggested in

literature,^{14,25} which may also have an impact on the final layout of the resulting film composition.

As the additional proof for S-Au binding of fullerene sulphides to gold, we compared results for thioethers **I-IV** with those obtained for methoxy analogue **I-O** of the thioether **I**, which was synthesized and reported earlier.^{26,27} After series of experiments under the same conditions as for thioethers **I-IV** we can conclude that methoxylated fullerene neither form stable monolayers nor self-assembles on the gold surface, in contrast to all investigated thioethers. Thus, the presence of sulphide sulphur atom in the synthesized fullerene derivatives is crucial for successful chemisorption on the gold surface. Moreover, it is noteworthy to mention here that in our previous work we synthesized S-acetyl analogue of **I**,²⁸ which does not self-assemble on gold without previous deprotection to its free thiol form, implying that methylthio substituted sulphides have higher affinity to gold than the corresponding thioacetates.

We tried also to dispel doubts about the possibility of destructive chemisorption of fullerene sulphides as literature reveals both, cleavage^{24,29} and stability of S-C bond while depositing thioethers on gold surface.^{14,18} For this purpose, samples of self-assembled on gold surface thioethers **I-IV** were desorbed both, thermally by refluxing in chlorobenzene, and electrochemically by reduction in 0.5M KOH (desorption curves are shown in Fig. S21, ESI[†]). Afterwards mass spectrometry experiments were performed, since such measurements have been reported to be reliable for this type of studies.^{30,31} As the result no thiolate anions were detected for all eight examined samples. Thus, no evidences for either dissociative chemisorption, S-C bond cleavage, or any other surface reactions were found. Sulphide bonds remained intact, independently whether the substituent was methyl, ethyl, *tert*-butyl or aromatic ring.

Electrochemical properties of thioether functionalized fullerenes

Cyclic and differential pulse voltammetry were employed to characterize the electrochemical behaviour of the thioether functionalized fullerenes in solution. Results obtained for compound **I** are shown in Fig. 5, other molecules revealed similar electrochemical behavior and their characteristics can be found in ESI (Fig S22-24, ESI[†]).

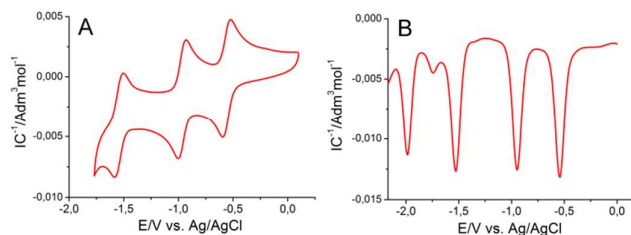


Fig. 5. Cyclic and differential pulse voltammograms of compound **I** in 0.1M TBAHFP solution in toluene/acetonitrile (4:1), (A) CV, $v = 100$ mV/s; (B) DPV, $tp = 3$ ms, $\Delta E = 50$ mV.

The CV results reveal similarity of the electrochemical properties of the synthesized fulleropyrrolidines to that of C_{60} .^{32,33} The sequence of one-electron redox processes (Fig.5A), shows that favorable

“electron-sink” properties of the fullerene core are retained, including the reversibility of each of the reduction steps. In the differential pulse voltammograms for fullerene sulphide **I** (Fig. 5B), as well as for other thioethers **II-IV** (see Fig. S16-18, ESI[†]) four reduction peaks can be also resolved, confirming electron acceptor properties of the synthesized fulleropyrrolidines.

The electron transfer processes are shifted towards more negative potentials, when compared to those of unmodified C_{60} (Tab. S1, ESI[†]). Such shifts are caused by the electron donating properties of the aromatic rings present in compounds **I-IV**. These results show the slightly lower electron affinity of fullerene sulphides compared to unsubstituted C_{60} molecule.

Cyclic voltammetry was also used to follow the chemisorption of thioether functionalized fullerenes at the Au surface. The cyclic voltammogram recorded for gold electrode modified with self-assembled monolayer of C_{60} derivative **I** is shown in Fig. 6. Observed redox peaks correspond to the first and second steps of reduction of deposited fullerene derivative, confirming the attachment of the compound to the surface of the gold electrode.

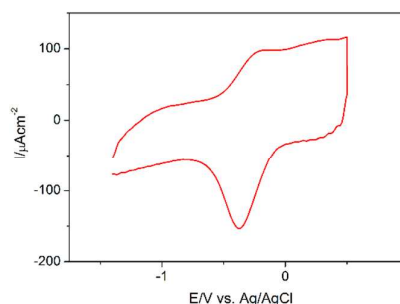


Fig. 6. Cyclic voltammogram of fullerene sulphide **I** self-assembled monolayer recorded in 0.1 M TBAHFP solution in acetonitrile, $v = 2V/s$.

The oxidation and reduction peak potentials are shifted to more positive and more negative values, respectively. The standard rate constants of the electrode process for fullerene derivative **I** immobilized on gold electrode were calculated using the Laviron treatment³⁴: $k_s = \alpha n F v / RT$ or $(1-\alpha) n F v / RT$, for reduction or oxidation, respectively, where n is the number of exchanged electrons, F is the Faraday constant, R is the gas constant, T is the temperature, the v_{ox} and v_{red} are values of scan rates. The values of rate constants obtained for the reduction and oxidation process are $k_{red} = 52 s^{-1}$ and $k_{ox} = 85 s^{-1}$, respectively. The transfer coefficient (α) was obtained by measuring the dependence of the peak potential on the scan rate. A plot of E_p versus $\log v$ yields to two straight lines with slopes equal to $-2.3RT/\alpha n F$ and $-2.3RT/(1-\alpha) n F$ for the cathodic and anodic peaks, respectively, to give values $\alpha = 0.44$ and $\alpha = 0.27$.

The surface concentration of adsorbed molecules and the monolayer packing were evaluated based on the reduction peak of adsorbed **I**. Assuming that all molecules on the Au electrode are electrochemically active, we estimated the surface concentration of derivative **I** using equations for a Nernstian reaction at the adsorbate monolayer (eq. 1):

$$\Gamma = Q/nFA \quad (1)$$

where Γ is the coverage in mol/cm^2 , Q is the integration of the charge under the peak in C. The average value of $(5.9 \pm 1.3) \cdot 10^{-11}$ mol/cm^2 was obtained from the reduction peak of fullerene

derivative and therefore the footprint of compound **I** is $281 \pm 15 \text{ \AA}^2/\text{molecule}$. This value is slightly larger than those obtained for previously investigated fullerene derivatives.³⁵

In case of simple alkanethiols it is also possible to estimate the surface concentration from the integration of the charge under the reductive desorption of the monolayer. Unfortunately, in our case the reductive desorption peak is not developed, hence it is overlapped by the final rise of current even in the ac voltammetry regime. Binding at these negative potentials is additionally weakened by the negative charge of the fullerene anion.

Electropolymerization of styrene

Polymerization of styrene under electrochemical conditions was intensively studied many years ago. Electroreduction of styrene in acetonitrile solutions containing tetra-*n*-butylammoniumtetrafluoroborate on platinum electrodes lead to polystyrene polymer of high 10^6 molecular weight. The process was reported to be highly dependent on the conditions of electrolysis³⁶ *i.e.* electrolyte composition, solvent, temperature and current densities.³⁷

Taking advantage from the multi-electron redox properties of C_{60} fullerene derivatives and increased solubility of the functionalized fullerenes in organic solvents we attempted to polymerize styrene using the synthesized fullerene sulphide. We assumed that electron transfer from the *in situ* reduced C_{60} derivative to the styrene monomer may initiate anionic polymerization and, therefore, improve the electropolymerization efficiency. The living anionic polymerization of vinyl monomers is known to be extremely sensitive to impurities, however in the absence of protons it results in strictly linear polymers with very low polydispersities, due to the absence of side reactions.³⁸ Therefore, the monomer purchased, solvent and remaining chemicals were carefully purified and dried according to conventional methods using inert gas atmosphere. Solutions preparation as well as all syntheses were carried out using the glove-box, hence precautions were taken to work under inert atmosphere and in the absence of moisture.

Using the procedure described in the experimental section and employing fullerene sulphide **III**, we have obtained polystyrene **F-PS** as white-beige solid with conversion 4.3wt%. We have also made a parallel experiment under the same conditions but without addition of fullerene derivative, which resulted in formation of traces only of polystyrene (conversion 0.2 wt%). Molecular weight of the obtained samples of polystyrenes was determined by means of GPC (Fig. 7).

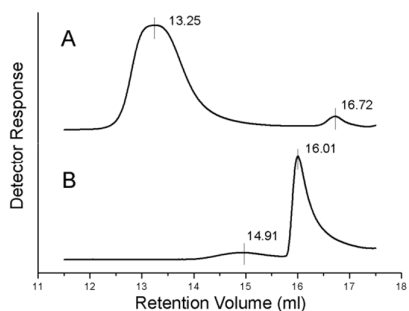


Fig. 7. GPC analyses of A) polystyrene obtained using fullerene thioether **III**, B) products of electropolymerization without addition of fullerene derivative.

GPC chromatogram with retention volume acquired for polystyrene obtained in electropolymerization initiated by fullerene derivative **III** (Fig. 7A) showed strong peak at 13.25ml, corresponding to polymer of $M_w = 16036$ and the polydispersity of 1.65. Small peak appeared at higher retention volume of 16.72ml was considered as impurity and neglected. Lack of signal coming from fullerene sulphide **III** suggests that the obtained polystyrene is not contaminated with initiator. Traces of polystyrene obtained by electrochemical polymerization without **III** were also investigated by means of GPC (Fig. 7B). However, signals at 14.91 and 16.01 correspond to $M_w = 2668$ and 448, respectively, thus, they might be considered as traces of low molecular weight oligomers and remains of supporting electrolyte.

Derivative **III** was chosen for the experiment because of its highest acceptor properties described by lowest potential of second reduction and higher solubility compared to other synthesized derivatives and pure C_{60} . For electropolymerization we decided to use potential of -1.2V, which is slightly below the second reduction step of derivative **III** and should allow to form primary radical-anion of styrene $M^{\cdot-}$ by transferring an electron from the reduced derivative **III** to the styrene molecule that subsequently was able to initiate anionic polymerization.^{37,39}

We believe that that primary radical ion $M^{\cdot-}$, which undergoes dimerization to corresponding dianion, can be created according to the following scheme (Fig.8):

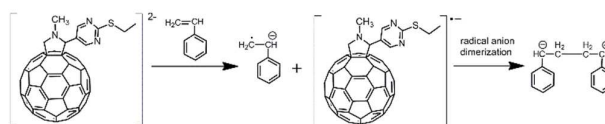


Fig. 8. Initiation mechanism of anionic electropolymerization of styrene using fullerene sulphide **III** as intermediate.

Electrolysis of styrene solutions in tetrahydrofuran with addition of typical polycyclic aromatic hydrocarbon, naphthalene, produced living polymers, however, the role of added naphthalene on the course of the reaction was not elucidated.⁴⁰ Another mechanism involving protonation by THF hydrogens was proposed for styrene/THF/K⁺ system.⁴¹

The obtained polymer was investigated by FT-IR and UV-Vis measurements to determine whether fullerene derivative is present in its structure. UV-Vis spectrum (Fig. S25, ESI[†]), showed a band at 430nm, which can be assigned to fulleropyrrolidine moiety.²² Signals attributed to the fullerene core were also present in the IR spectra (Fig. S26, ESI[†]), where bands at 526 and 1179 were observed.⁴² These findings together with the lack of fullerene derivative elution peak in GPC analysis suggest that the obtained polystyrene contains small amount of chemically bound functionalized fullerenes.

These preliminary results show that anionic electropolymerization of styrene can be greatly enhanced by addition of C_{60} derivatives. The use of functionalized fullerene as an initiator of electropolymerization of styrene allows to obtain higher conversion, higher molecular weight and lower polydispersity.

Importantly, significantly less negative potentials were sufficient to perform the electrolysis than previously reported in the literature.³⁷ Detailed studies of the mechanism of C₆₀ compounds initiation of the styrene electropolymerization are continued in our laboratory.

Conclusions

A series of new thioether functionalized fullerenes was synthesized according to modified Prato method and the compounds were studied in solution and self-assembled on gold surfaces. The proposed deposition procedure allows to obtain densely packed films/monolayers of fullerene thioethers without cleavage of the S-C bonds. Sulphide bonds remained intact, irrespectively of the type of the substituent attached to sulphur atom, including, primary, tertiary alkyls and aromatic rings. Fullerene sulphide **III** was successfully employed in the electropolymerization of styrene, implying that fullerene anions can initiate anionic polymerization under electrochemical conditions. The use of functionalized fullerene as an initiator in electropolymerization of styrene lead to higher conversion, higher molecular weight, and lower polydispersity. Moreover, potentials sufficient to perform the electrolysis in the presence of fullerenes are less negative than required in other procedures for styrene electropolymerization described in the literature. Application of fullerenes as initiator in the synthesis of polymers is subject of our ongoing studies and the results will be presented elsewhere.

Acknowledgements

We gratefully acknowledge the financial support from the National Science Centre Project 2012/07/N/ST5/01966 and from the University of Warsaw, Faculty of Chemistry DSM-107500 Grant.

Notes and references

† Electronic Supplementary Information (ESI) available: Additional characterization data including ESI-MS, FT-IR, ¹H and ¹³C NMR spectra for synthesized compounds, as well as cyclic voltammetry and differential pulse voltammetry results.

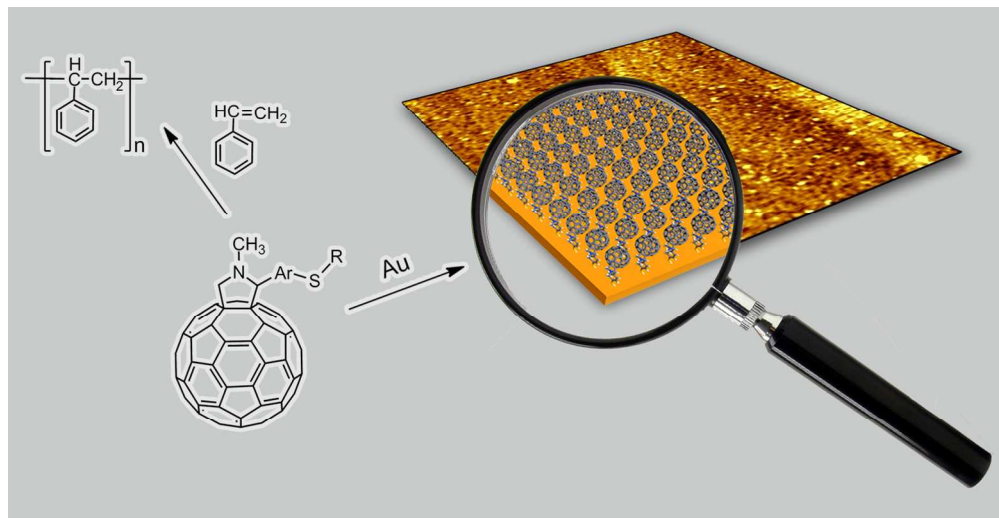
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Fulleropyrrolidine alkylaromatic sulphides were found to form uniform coating on the gold surface through the thioether sulphur anchoring group and can initiate the anionic polymerization of styrene under electrochemical conditions.
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