Electronic Supplementary Information

Study of the electrochemical and optical properties of fullerene and methano[60]fullerenediphosphonate derivatives in solution and as self-assembled structures

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Synthesis of fullerene derivatives (1-4)

(Fullerene derivatives (1-4) were synthesized similar to the procedure described elsewhere.[1] Structures 1,2,3 and 4 shown in Scheme 1)

Synthesis of tetraethylmethano[60]fullerenediphosphonate (1)

[60]Fullerene (120 mg, 0,168 mmol) and Bis(diethoxyphosphoryl)bromomethane (50 mg, 0,35 mmol) were dissolved in toluene (50 ml). NaH suspension (140 mg) was added and the mixture was stirred in RT. The reaction was followed by HPLC until all the starting material was consumed. The mixture was filtered and passed through a layer of silica gel and the unreacted fullerene was collected with toluene, then the product was collected with $CHCl_3$ and solvent was evaporated to dryness *in vacuo* to give 100 mg of the product as 60% yield. ^{1}H NMR (600.13 MHz, $CDCl_3$): δ 4.47 (m, 8H), 1.52 (t, 12H, J_{HH} = 7.1 Hz). ^{13}C NMR (150.90 MHz, $CDCl_3$): δ 146.0 (t, 4C, J_{PC} = 5.2 Hz), 145.3 (4C), 145.2 (4C), 145.1 (4C), 145.0 (2C), 144.9 (2C), 144.7 (4C), 144.6 (4C), 144.1 (4C), 143.1 (2C), 143.0 (4C), 142.9 (4C), 142.4 (4C), 142.3 (4C), 141.0 (4C), 140.4 (4C), 68.2 (t, 2C, J_{PC} = 4.2 Hz), 64.0 (m, 4C) 39.8 (t, 1C, J_{PC} = 153.8 Hz), 16.7 (t, 4C, J_{PC} = 3.0 Hz). The number and intensities of distinct ^{13}C NMR peaks are consistent with a [6,6]-closed product, showing that the methano carbon reacted mainly at the double bond between two six membered rings. The fourfold (4C) and twofold (2C) carbon chemical shift equivalencies observed in the ^{13}C NMR spectrum are a result from the two orthogonal planes of symmetry present in the [6,6]-closed structure (C_{2v} point group); the former equivalency takes place for carbons which are out of either plane of symmetry whereas the latter happens for carbons lying in one of these planes. The single carbon (1C) signal at 39.8 ppm belongs to the methano carbon, which lies in both of the planes of symmetry. Some traces of impurities were seen but we could not determine whether these were *bis*-adducts or if the carbon had reacted between five membered ring and six membered ring.

Synthesis of methano[60]fullerenediphosphate (2)

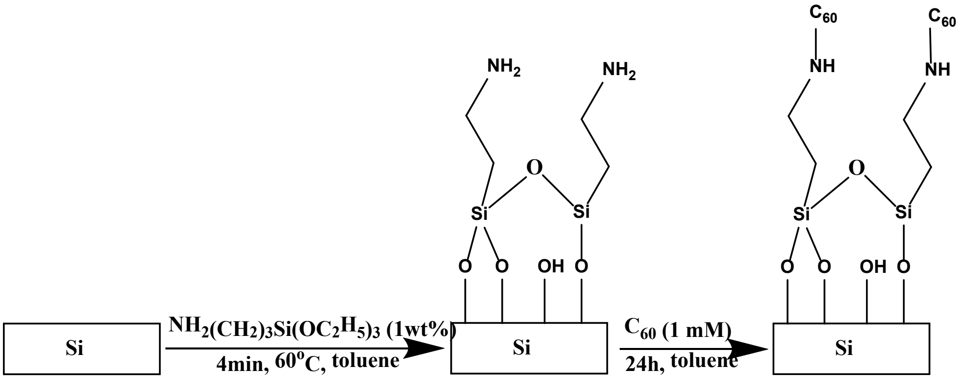
Tetraethylmethano[60]fullerenediphosphonate (85 mg, 0,085 mmol) was dissolved in tetrachloromethane (50 µl) under nitrogen atmosphere. Bromotrimethyl silane (0,21 ml, 0,5 mmol) was added and the solution was stirred at 50˚C for one hour. Water (50 µl) was added and the product was collected and dried under vacuum. Derivative 2 was not soluble in organic solvents or DMSO and showed low solubility in D_2O. Hydrolysis was confirmed by FTIR spectroscopy showing the characteristic broad OH stretch at 2700-1600 cm^{-1}.

Synthesis of octaisopropylmethano[60]fullerenetetraphosphonate (3)

[60]Fullerene (1 g, 1,39 mmol) and Bis(diisopropoxyphosphoryl)bromomethane (50 mg, 3,5 mmol) were dissolved in toluene (800 ml). NaH suspension (2 g, 83 mmol) was added and the mixture was stirred in RT. The reaction was followed by HPLC until the reaction stopped. The monoadduct shows in HPLC one peak, followed by the second fraction containing the bisadduct showing many peaks due to the different isomers formed. The mixture was then filtered and passed through a layer of silica gel and quickly washed with toluene to remove any unreacted fullerene, the product was then collected with $CHCl_3$ and solvent was evaporated to dryness *in vacuo* to give 900 mg of the product as 46% yield. As the bisadduct, compared to derivative 1, shows in HPLC several isomers (eight possible) the ^{13}C-NMR spectrum will contain a lot of overlapping peaks.

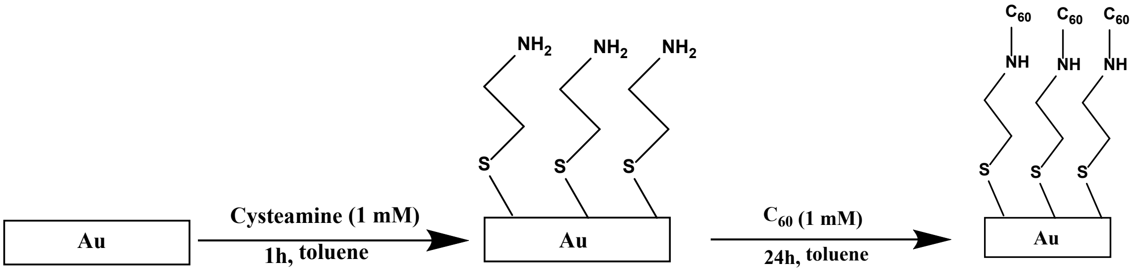
Synthesis of methano[60]fullerenetetraphosphate (4)

Octaisopropylmethano[60]fullerenetetraphosphonate (220 mg, 0,157 mmol) was dissolved in tetrachloromethane (80 ml) under nitrogen atmosphere. Bromotrimethyl silane (1,2 ml, 9,1 mmol) was added and the solution was stirred at 40˚C for 2 days. Water (1,6 ml) was added and the product was purified by first collecting it to 1M KOH aqueous phase. The filtered aqueous phase was then made acidic with concentrated hydrochloric acid. The precipitation was collected with centrifugation and washed once with 1M HCl(aq). Drying with reduced pressure gave 50 mg of the product as 30% yield. Derivative 4 showed good solubility in water. Due to the high amount of isomers formed in the previous reaction step the ^{13}C-NMR spectrum will contain a lot of overlapping peaks. Hydrolysis was confirmed by FTIR spectroscopy showing the characteristic broad OH stretch at 2700-1600 cm^{-1}.



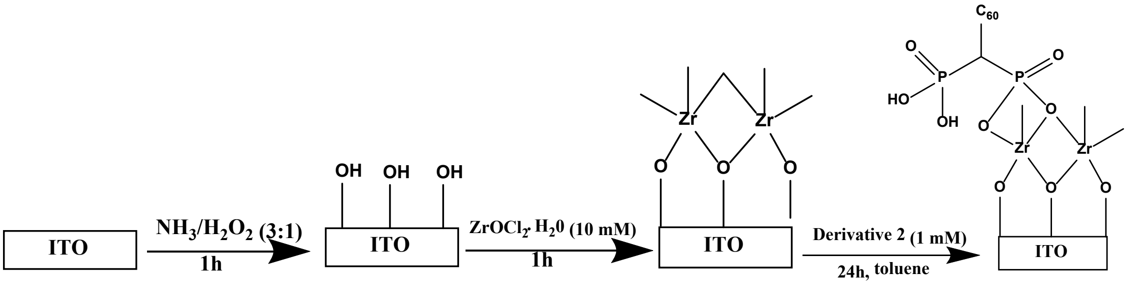
Scheme S1. Preparation steps for the fullerene-terminated SAMs on silanized Si surface.

Si(100) wafers (Okmetic, Finland) 12 mm x 12 mm were cleaned in a fresh piranha solution (concentrated H_2SO_4/30% H_2O_2 in proportion 3:1), rinsed thoroughly with quartz distilled water and dried. Double quartz distilled water was used in all aqueous experiments. (*Warning!* piranha solution is extremely corrosive and must be treated with extreme caution. It should not be stored in tightly closed vessels). The piranha cleaned silicon substrates were silanized with (3-aminopropyl)triethoxysilane in toluene solution (1% v/v) for 4 min at 60 ^{0}C. After silanization the wafers were rinsed thoroughly with toluene solution. The silanized silicon wafers were thereafter placed in a 1 mM toluene solution of C_{60} for 24 h (preparation steps shown in Scheme S1). The used fullerene solution was filtered through a 0,45 μm PTFE filter. Then the surface was rinsed thoroughly with toluene to remove physisorbed C_{60} and thereafter dried before characterization. The thickness of the natural oxide layer on Si wafers was measured by ellipsometry to be around 3 nm. In the text these Si oxide covered substrates are marked as Si.



Scheme S2. Preparation steps for the fullerene-terminated SAMs on gold surface functionalized by cysteamine.

On some of the piranha cleaned Si wafers a thin gold layer (ca. 150 nm) was evaporated using the Edwards E306A coating system. Before use these substrates were additionally cleaned with O_2 plasma using the Harrick PDC-3XG plasma cleaner. The plasma cleaned Au surface was immediately soaked in a 10 mM toluene solution of cysteamine for 1 h. After that the surface was rinsed with toluene, ethanol and water for 30 min each and dried. The cysteamine covered Au surface was then immediately placed in a 1 mM toluene solution of C_{60} for 24 h (preparation steps shown in Scheme S2). Then the surface was rinsed with toluene and dried.



Scheme S3. Preparation steps for the fullerene-terminated SAMs on functionalized ITO surface.

ITO electrodes (Delta Technologies) were cleaned for 10 min in successive ultrasonic baths in acetone, ethanol and water. Some of the cleaned ITO electrodes were further treated in the solution mixture of NH_3/H_2O_2 (3:1) for one hour, rinsed thoroughly with water and dried. Before use these substrates were additionally cleaned with O_2 plasma using a Harrick PDC-3XG plasma cleaner. Some of the OH-treated ITO wafers were further placed in a 10 mM solution of $ZrOCl_2 \cdot 8H_2O$ for one hour and thoroughly rinsed and dried. Treated wafers were then immersed in a toluene solution of fullerene derivatives 2 and 4 (1 mM) for 24 h (preparation steps shown in Scheme S3). The substrates were taken from the solution and rinsed with toluene to remove excess molecules from the surface and finally dried. For the ITO electrodes also another OH-treatment was used. In this case the cleaned wafers were placed in an $H_2O_2/NH_4OH/H_2O$ (1:1:5) solution and heated to $80^{o}C$. After 30 min the wafers were rinsed with water. The zirconium phosphonate chemistry has been used and well characterized in a previous work by the group in order to form mechanically and chemically stable and well-ordered LB films.[2]

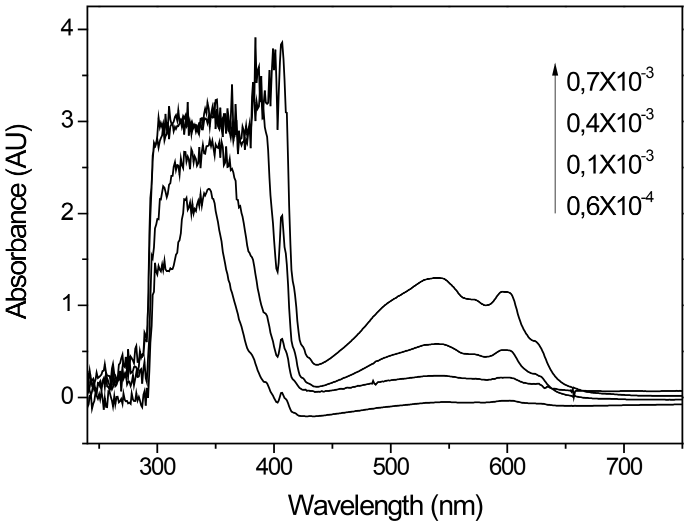


Figure S1. UV-Vis spectra for C_{60} at different concentrations (in the 1,2-dichlorobenzene-DMF solvent mixture).

Room temperature electronic absorption spectra recorded between 380 and 750 nm for C_{60} at different concentrations in the solvent mixture 1,2-dichlorobenzene-DMF (3:1) are shown in Figure S1. C_{60} itself gives a purple solution thus exhibiting a broad absorption between 435 and 665 nm, which exhibits maxima at 500, 540, 570, 600 and 625 nm.

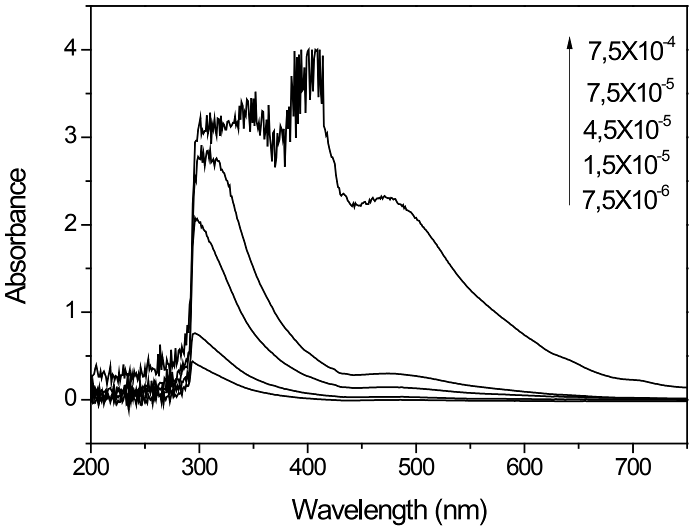
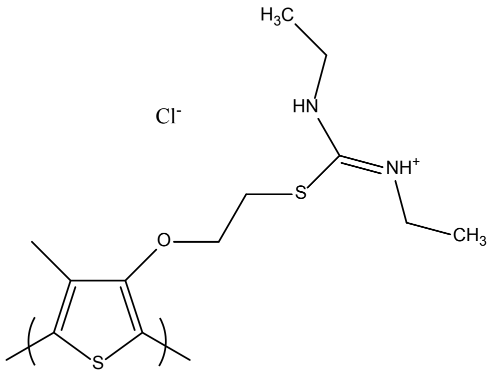


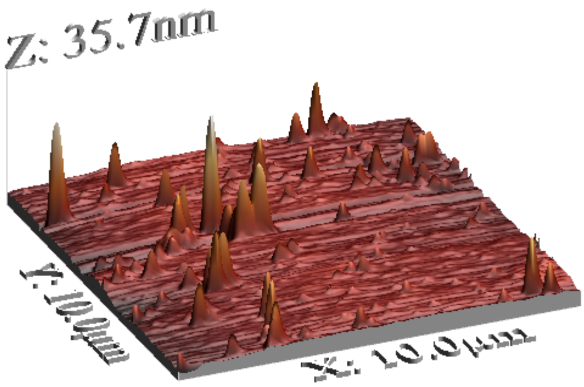
Figure S2. UV-Vis spectra for fullerene derivative 4 at different concentrations (in the 1,2-dichlorobenzene-DMF solvent mixture).

The spectrum of bis-adducts 3 and 4, which gives orange-brown solutions, resembles in its general shape the spectrum of a mono-adduct, although the broad Vis absorption band displays a shift from 500 nm to 470 nm. The UV-Vis spectra recorded at different concentrations of bis-adduct 4 are shown in Figure S2. In Figure S2 no shift is observed for the position of the peak maxima with concentration showing the absence of aggregation. In a characteristic manner, the diagnostic mono-adduct peak around 427 nm is no longer observed in the spectrum for the bis-adducts.



Scheme S4. Structure for the water soluble polythiophene

Scheme S4 shows the structure of a water soluble polythiophene (PT) based polymer synthesized in the group.[3] This thiophene polymer was used both for the SAMs with fullerene derivatives and blended with fullerene derivative 4 in order to obtain photoluminescence (PL) spectra.



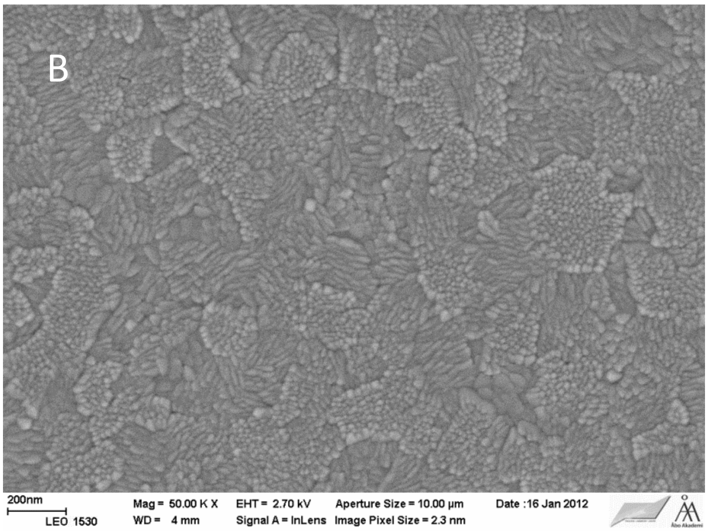


Figure S3. AFM (A) and SEM (B) images of SAMs of derivative 4 on ITO.

The assembled layers of derivative 4 on ITO that had been hydrolysed and treated with Zr are shown in Supplementary Information, Figure S3A. Treatment with Zr resulted in SAMs with more sample particles on the surface than if the ITO plate had been just hydrolyzed. As seen from Figure S3A the SAMs of derivative 4 showed an rms of 0.6 nm with particles at maximum 20 nm in height with a diameter of 0.4 µm. The surface image of derivative 4 on ITO obtained by SEM (Figure S3B) shows the typical surface structure of ITO with a coherent, but not fully covering SAM layer.

1. A.L. Mirakyan and L.J. Wilson, *J. Chem. Soc., Perkin Trans*. 2, 2002, **6**, 1173.
2. A. Viinikanoja, J. Lukkari, T. Ääritalo, T. Laiho and J. Kankare, *Langmuir*, 2003, **19**, 2768.
3. A. Viinikanoja, S. Areva, N. Kocharova. T. Aeaeritalo, M. Vuorinen, A. Savunen, J. Kankare and J. Lukkari, *Langmuir*, 2006, **22**, 6078.