

Supplementary Information

Oscillation in the stability of consecutive chemical bonds at the molecule-metal interface – the case of ionic bonding

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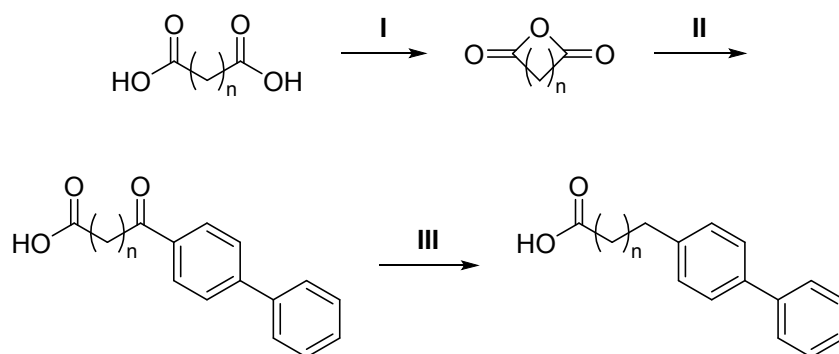
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Synthesis

The BP_nCOOH compounds with $n = 5$ and $n = 6$ were synthesized from adipic and pimelic acid respectively, according to the following scheme:



Conditions:

I Ac₂O (10 eq.), reflux 2 h

II Biphenyl (1 eq.), AlCl₃, PhNO₂, RT, 20 h

III N₂H₄, KOH, triethylene glycol, 210 °C, 4 h

Procedures

The reactions were performed using modified literature procedures.^{1,2}

I Appropriate dicarboxylic acid was refluxed in acetic anhydride (10 eq.) for 2 hours. The excess of anhydride was removed on rotary evaporator. The resulting brown, dense, viscous liquid was subjected to vacuum distillation, yielding clear, colorless viscous oil (Yield: 70 % for $n = 5$ and 64 % for $n = 6$). The anhydrides were immediately subjected to the next step.

II To a round bottom flask, containing 2.5 eq. of anhydrous aluminium chloride, nitrobenzene (1 mL/mmol of substrate) and biphenyl (1 eq.) were added. The resulting mixture was cooled in an ice bath. Appropriate anhydride, dissolved in nitrobenzene, was added dropwise. After the addition, the reaction mixture was allowed to warm to room temperature and stirred for additional 20 hours. The reaction was quenched by careful addition of concentrated HCl. Reaction mixture was diluted with water. The brown precipitate was filtered, dried under vacuum and purified by flash chromatography (SiO₂, DCM:acetone = 2:1), yielding both ketoacids in 20 % yield as off-white powders.

III Reductions were performed, using Huang Minlon modification of Wolff-Kishner reaction, using 1 eq of ketoacid, 3.5 eq of KOH and 3 eq of 85 % hydrazine hydrate in triethylene glycol (1.5 mL/mmol of ketoacid). The reaction mixture was heated in an oil bath at 210 °C under air-cooled reflux condenser. After 4 hours the excess hydrazine was distilled off. The reaction mixture was allowed to cool to room temperature, then poured onto ice-cold water. Aqueous layer was acidified to pH=2 using concentrated HCl and extracted 3 times with chloroform. Organic extracts were combined, washed two times with water and dried over anhydrous MgSO₄. The solvent was evaporated under reduced pressure, yielding beige, crude product, which was purified using flash chromatography (SiO₂, Hexanes:Ethyl acetate = 4:1). The yields for $n = 5$ and $n = 6$ were 75 % and 80 % respectively. The spectroscopic data for the products are in agreement with previously reported ones.¹

SAM Preparation

Ethanol (99,8%) was obtained from POCH (Poland) and used without further purification. The BP n COOH molecules (C₆H₅-C₆H₄-(CH₂) _{n} -COOH) were purchased from Alfa Aesar ($n = 1,2$) and Wako ($n = 3,4$) and used without further purification.

For all used techniques, substrates were prepared by evaporating c.a 35 Å of chromium, then c.a. 1000 Å silver (rate ~1,0 Å/s, room temperature) onto polished silicon wafers (ITME, Warsaw). Chromium was used to improve the adhesion between silver layer and silicon.

Monolayers were obtained by immersing aforementioned substrates in 1 mM ethanol solutions of BP n COOH molecules for 5 min. After incubations, samples were removed from the solutions, rinsed with pure ethanol and dried under nitrogen.

IRRAS

Infrared reflection-absorption spectroscopy (IRRAS) measurements were performed with a dry-air-purged Thermo Scientific Nicolet 6700 FTIR spectrometer model equipped with a liquid nitrogen-cooled MCT detector. All spectra were taken using p-polarized light incident at a fixed angle of 80° with respect to the surface normal. Spectra were measured at a resolution of 2 cm⁻¹ and are reported in absorbance units $A = -\log R/R_0$, where R is the reflectivity of the substrate with a monolayer and R_0 is the reflectivity of the reference. Substrates covered with perdeuterated hexadecanethiolate SAMs were used as the reference samples.

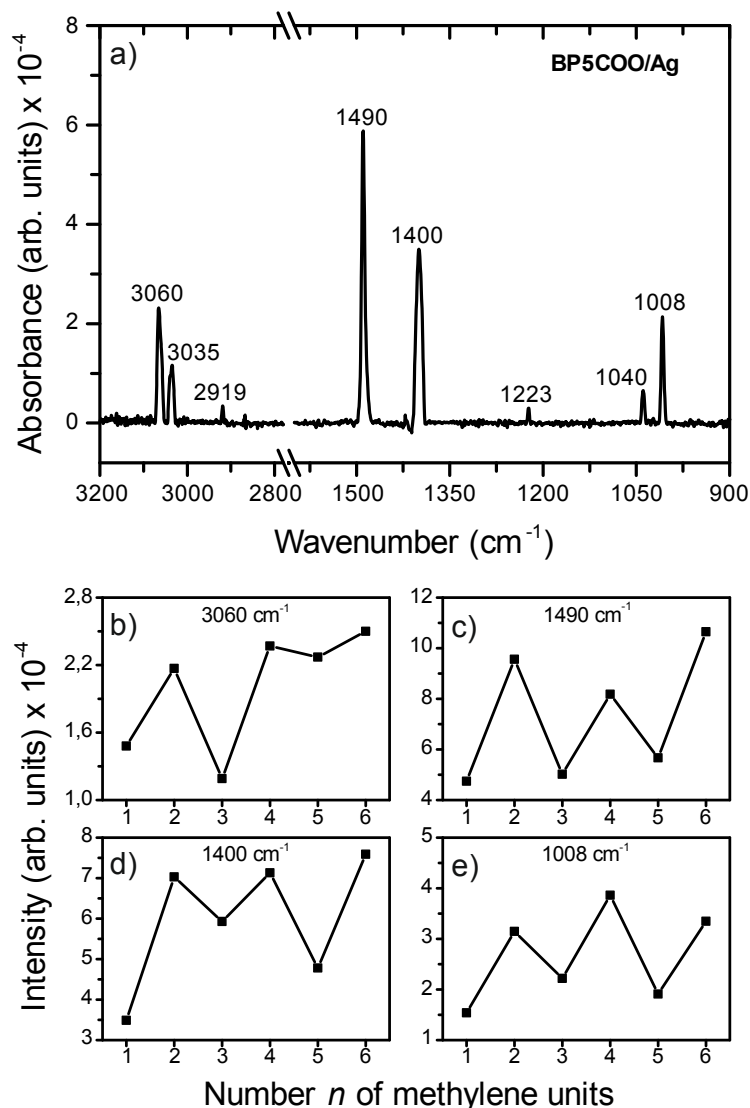


Figure S1. (a) IRRAS spectrum for BP5COO/Ag. Characteristic absorption bands are indicated. (b-e) Intensities of bands at ~ 3060 , ~ 1490 , ~ 1400 , and ~ 1008 cm^{-1} presented as a function of increasing length of the aliphatic spacer (number n of methylene units) in BP n COO/Ag SAMs. Bands at ~ 3060 , ~ 1490 , and ~ 1008 cm^{-1} are related to the biphenyl unit whereas the band at ~ 1400 cm^{-1} corresponds to symmetrical carboxylate stretching. All bands exhibit the odd-even intensity modification correlated with the odd-even reorientation of the biphenyl unit and the plane of the carboxylic bond - see ref. 5 for more detailed description.

XPS

X-ray photoelectron spectroscopy (XPS) measurements were performed with a photoelectron spectrometer equipped with a hemispherical analyzer VG SCIENTA R3000. The spectra were taken using a monochromatized aluminum source Al K α ($E = 1486.6$ eV), MX-650 VG Scienta. The base pressure in the analytical chamber was 5×10^{-9} mbar. The spectral acquisition was

carried out in normal emission geometry with an analyzer energy step of 0.15 eV. The Au 4f_{7/2} peak analysis allowed to reference the binding energy (BE) scale and to define the overall resolution of the spectra – ca. 1,15 eV. All spectra were fitted by the symmetric Voigt functions, and a Shirley-type background was subtracted.

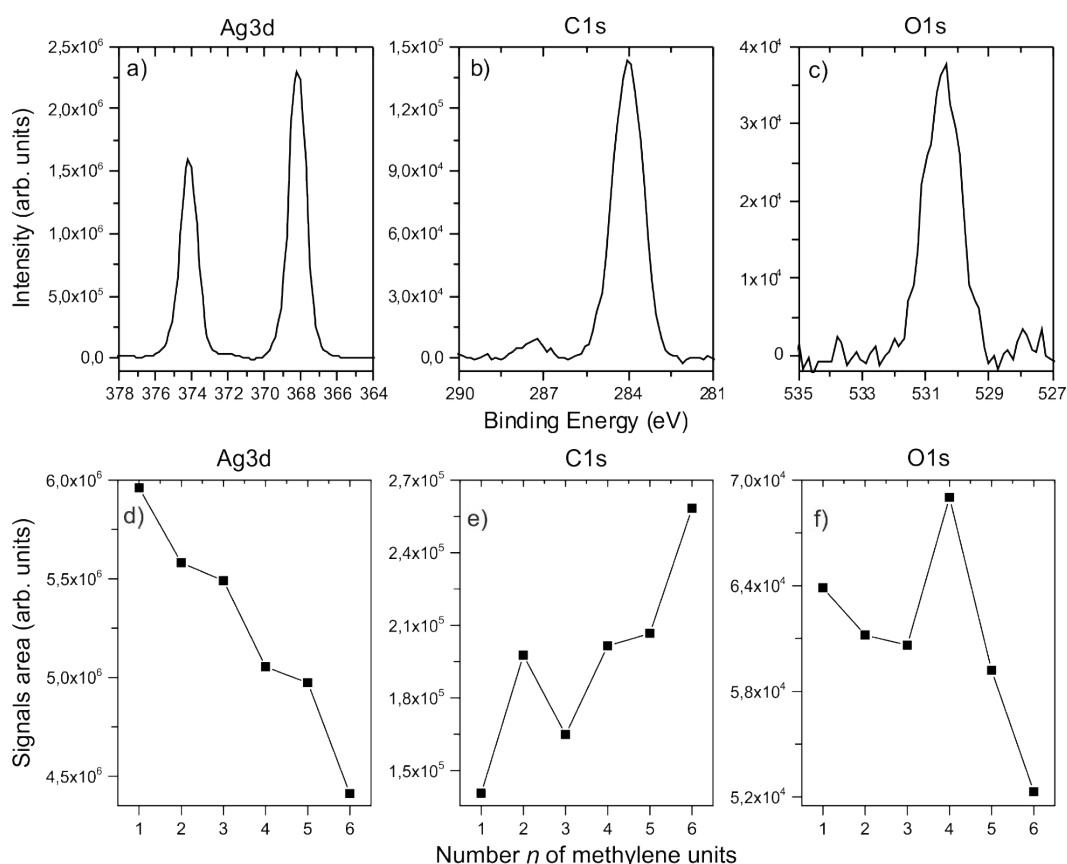


Figure S2. Overview of XPS spectra of (a) Ag3d, (b) C1s, and (c) O1s for BP5COO/Ag, (d-f) together with intensities of above signals presented as a function of increasing length of the aliphatic spacer (number n of methylene units).

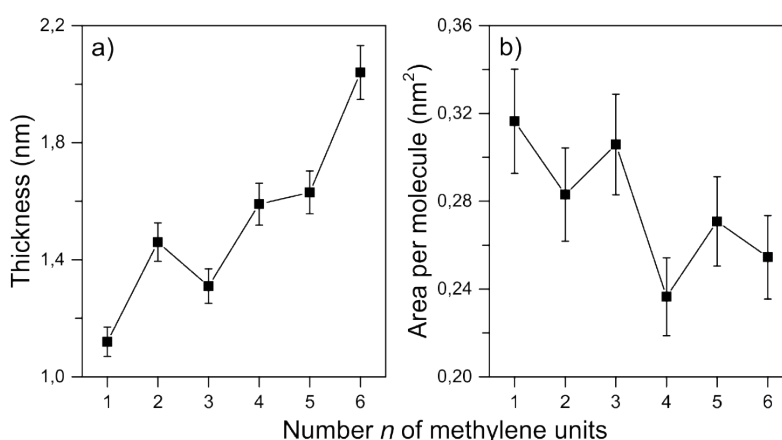


Figure S3. Film thickness (a) and area per molecule (b) calculated from XPS data presented as a function of increasing length of the aliphatic spacer (number n of methylene units). The calculations of the effective film thickness were based on the C1s/Ag3d intensity ratios, assuming the exponential attenuation of the photoelectron signal³ and using attenuation lengths reported earlier.⁴ The method of calculation of the area per molecule was described elsewhere.⁵

S-SIMS

The SIMS experiments were performed using a time-of-flight SIMS (TOF SIMS V system, ION TOF GmbH, Germany). The instrument was operated at a base pressure of 5×10^{-10} mbar. The primary 30 keV Bi^+ ion beam was scanned over a $500 \mu\text{m} \times 500 \mu\text{m}$ area during data acquisition. Both positive and negative secondary ions were extracted into a reflectron TOF mass spectrometer before reaching a multichannel plate (MCP) detector. The total ion doses during measurements were up to 5×10^{10} ions/cm², ensuring the static SIMS regime and that no ion-induced damage was done to samples. Before the analysis, all spectra were normalized to the respective total number of counts.

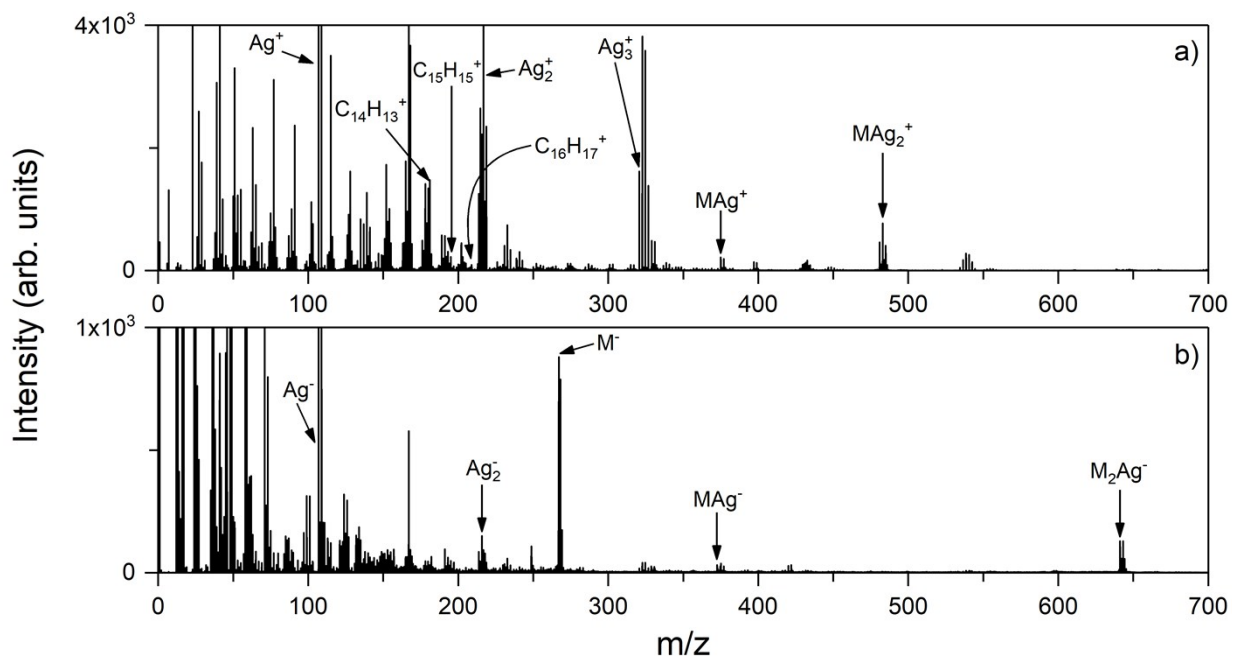


Figure S4. Examples of S-SIMS data: (a) positive and (b) negative spectra for BP5COO/Ag. Characteristic secondary ions are indicated by arrows.

DFT

First-principles calculations were performed using spin-polarized density functional theory (DFT) with the projector augmented waves (PAW)^{6,7} and van der Waals corrected exchange-correlation functional (vdW-DF) available in VASP (Vienna ab-initio simulation package).^{8,9} The optPBE-vdW implementation of the vdW-DF method was used in all the calculations.¹⁰⁻¹¹ The plane wave basis set was restricted by an energy cutoff of 700 eV. Only the Γ point was used in the Brillouin zone sampling. The total energy convergence criterion was chosen to be

10^{-6} eV. The atomic positions were fully relaxed by a conjugate gradient method until the maximum force in any direction was less than 0.01 eV/Å. The Ag(111) substrate has been modeled by a cluster of 18 Ag atoms frozen in Ag(111) atomic positions.

References

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