Considerable progress has been made in the past decade on the synthesis, purification and functionalization of perfluoroalkyl-fullerenes (PFAFs); their potential applications span the fields of organic electronics, imaging of biological objects, and energy conversion devices.1 Incorporation of PFAFs in organic optoelectronic devices may be carried out using solution processing, or vapor deposition, enabled by improved solubility and thermal stability compared to commonly used organofullerenes. In this work, the formation of self-assembled monolayers (SAMs) of PFAF functionalized alkylphosphonic acids on aluminum oxide surfaces has been probed for the first time.

Use of SAMs for modification of electrical properties of various inorganic substrates has been proven as an effective method that may lead to improved conductivity and overall performance of organic optoelectronic devices.2 For example, one-dimensional metal oxide nanorods, such as AlOx nanostructures show promise as new components in high-tech electronics.3 However, MoOx nanostructures suffer from substandard charge transfer across the particle/particle interfaces, so mainstream electronics cannot be tested to discover the optimal electron-withdrawing strength and degree of fluorine insulation.

In this work, we have explored Bingel-Hirsch cycloaddition reactions with several trifluoromethylfullerenes (TMFs) C60(CF3)n that differ by composition (n = 2, 4, and 10) and by the isomeric structures in the case of C60(CF3)10. The Schlegel diagrams of the TMFs used in this study are shown in Figure 2. Formation of SAMs on AlOx surface was studied using one of the TMFs that demonstrated higher selectivity.

Experimental

Synthesis of 11-(tetrahydropranyloxy)-1-bromoundecane.—PPTS (0.230 g, 0.907 mmol) and DHP (0.52 mL, 5.7 mmol) were

Figure 1. Schematic representation of aluminum oxide surfaces coated with SAMs using different PFAFs. Reduction potentials of PFAFs without phosphonic acid linkages are shown.
added to 11-bromo-1-undecanole (1.14 g, 4.54 mmol) in DCM (100 mL). After 16 h the reaction mixture was washed with a saturated NaHCO₃ solution (300 mL) and separated. The aqueous layer was washed with additional DCM (100 mL). The two organic solutions were combined and washed with a saturated NaCl solution (200 mL) then dried over Na₂SO₄. The solvent was removed by rotovap and the product was obtained as a colorless oily liquid. Yield: 1.55 g, 100%.

**Synthesis of diethyl [18-(tetrahydropyranyloxoy)undecyl] phosphonate.—** A yellow mixture of 11-(tetrahydropyranyloxoy)1-bromoundecane (1.07 g, 3.19 mmol) and triethylphosphite (5.46 mL, 31.9 mmol, 10 equiv.) was refluxed for 6 hours (oil bath temperature = 170 °C). The excess triethylphosphite was removed by vacuo at reduced pressure and the crude product was used in the next step without further purification and isolation.

**Synthesis of (60-10-3)(phosphonic ester).—** Under nitrogen and exclusion of light, 60-10-3 (35.7 mg, 25.3 mmol) was dissolved in degassed toluene (18 mL) at room temperature. Subsequently, 11-(diethoxyphosphoryl)undecyl methyl malonate (0.20 mL, 0.60 equiv.) and I₂ (1.80, 0.76 equiv.) were added. A solution of DBU in toluene (0.79 equiv.) was added dropwise over the course of seven minutes. The reaction was monitored by TLC and was stopped after 20 h when unreacted 60-10-3 was no longer observed. White precipitate was filtered from a dark brown solution and the solution was subjected to flash chromatography on silica with toluene and toluene/methanol mixtures. The fractions containing (60-10-3)(phosphonic ester) monoadducts were further purified by HPLC in toluene. The product was analyzed by ¹H, ³¹P, and ³¹P NMR and MALDI mass spectrometry. Two peaks were present in the mass spectrum; 1830 m/z is 14 more than desired product and unknown, 1748 m/z is C₆₀(CF₃)₉(malonate/phosphonic ester) + 1, which corresponds to the loss of one CF₃ group in the mass spec experiment. Yield: 14.7 mg, 32% yield based on starting 60-10-3.

**Synthesis of (60-10-3)(phosphonic acid).—** A dry dichloromethane solution (5 mL) of (60-10-3)(phosphonic ester) (11.7 mg, 6.44 mmol) was cooled in an ice bath and BrSMe₂ (0.1 mL, 38 mmol, 5.9 equiv.) was slowly added. The ice bath was removed after 2 h and the solution was stirred for an additional 19 hours. Toluene, hexamethydisiloxane and the excess of bromotrimethylsilane were removed under vacuum. To remove any remaining traces of reagents, dry toluene (5.0 mL) was added and subsequently removed under vacuum. The residue was dissolved in CHCl₃ (5 mL) and then MeOH (5 mL) and H₂O (1 mL) were added at room temperature and stirred for 2 hours. The solvents, except for H₂O, were removed under vacuum. Acetone was added and the acetone/H₂O azetrope was removed under vacuum. The solid was dissolved in CHCl₃, dried over Na₂SO₄, and then filtered. This entire reaction scheme was repeated several times. In some cases, HCl(aq) was substituted for H₂O or mixtures of CHCl₃/MeOH were used for final collection. The product was analyzed by ¹H, ³¹P, and ³¹P NMR and MALDI mass spectrometry. The peaks in NMR have the same chemical shifts as starting (60-10-3)(phosphonic ester), but are more broadened. Proton peaks corresponding to the ester moiety were reduced. MALDI mass spectra indicated that there was a mixture of partially converted products, unreacted (60-10-3)(phosphonic ester), and (60-10-3)(phosphonic acid). This mixture was used for SAM formation, since only the completely converted products form strong bonds and the esters and half esters can be washed away from the strongly bound SAM.

**SAM characterization techniques.—** X-Ray reflectivity Spectral X-ray reflectivity (XRR) measurements and Grazing Incidence X-ray Diffraction (GIXD) experiments were carried out at beamline ID10 at the European Synchrotron Radiation Facility in Grenoble using 22 keV X-rays, the details of the measurements were described elsewhere.¹⁵

**Preliminary FET testing.—** FET devices using (60-10-3)(PA)-SAMs were tested (Figure SI-4). Several different transistor setups and layouts (top contact, bottom contact, patterned by photolithography/  E-beam lithography, and shadow masks) were fabricated, but in all cases the drain current across the transistor channel did not exceed the leakage current through the SAM. In case of the shadow mask patterned devices during the gold evaporation for the source/drain electrodes, some gold leached into the transistor channel leading to an ohmic part of the current-voltage curve. Due to this leach, the drain current was lifted above the leakage current level and a current modulation with the gate voltage could be observed. This demonstrates that, in general, the devices worked. However, the charge transport in the SAM layer was so poor that it was hidden behind the leakage current in all other devices. A charge carrier mobility of approximately 10⁻⁷ cm²/Vs (approximately two orders of magnitude lower than in the non-fluorinated C₆₀-SAMs) could be estimated. However, the devices with gold in the channel cannot really be considered FETs and none of the other devices worked. Various experiments to increase the
thickness of the dielectric were attempted in order to reduce the leak-
age current, but did not improve device performance.

Results and Discussion

A limited number of reports on chemical derivatization of PFAFs involved Bingel-Hirsch and Diels-Alder cycloadditions to C_{70}(CF_3)_{n} (n = 8 and 10)\(^{6,8}\) and nucleophilic additions of CN\(^{-}\) to TMFs of C_{60} and C_{70} with varying numbers of trifluoromethyl groups.\(^{10-12}\) Previously, selection of C_{70}(CF_3)_{n} (n = 8 and 10) for cycloaddition chemistry was based on the hypothesis that the presence of a reactive double bond on the C_{70} cage might promote regiospecific adduct for-
mation, as proven to occur for both C_{70} TMFs. However, the C_{70}(CF_3)_{n} (n = 8 and 10) compounds do not have sufficiently different electronic properties from those of parent fullerene, and thus they were excluded from the current study.

In order to covalently link a TMF electron acceptor to the AlO\(_x\) surface, a phosphonic acid moiety has to be attached to a fullerene core. No experimental or theoretical work has been done on the Bingel-Hirsch cycloaddition chemistry with C_{60}(CF_3)_{n} compounds, prior to this study, despite the fact that many C_{60} TMFs can be prepared with reasonable yields and purity. The selected compounds (shown on Figure 2) have a wide range of reduction potentials that allow electronic tuning probing to be tested effectively.

The synthesis of 11-(diethoxyphosphoryl)undecyl methyl malonate and subsequent Bingel-Hirsch reactions were carried out according to modified literature procedures (Scheme 1).\(^{4-6}\)

We found that selectivity of a Bingel-Hirsch reaction with phos-
phonic acid malonatic ester greatly depended on the TMF substrate. Furthermore, the number of phosphonic ester (PE) additions and iso-
mers formed varied significantly, depending on the TMF substrate.

![Scheme 1.](image)

In general, the derivatives with more CF_3 groups, i.e., C_{60}(CF_3)_{10} isomers, were more selective than derivatives with two or four CF_3 groups. In contrast, reactions with 60-2-1 and 60-4-1 resulted in far too many products that were inseparable by combinations of flash chromatography and HPLC. These product mixtures exhibited complex and broad \(^{19}\)F NMR signals which indicated the forma-
tion of many products (Figures SI-1, SI-2). Furthermore, significant amounts of insoluble products were formed during the reactions, which is not common for a typical Bingel-Hirsch reaction. Further work with 60-2-1 and 60-4-1 adducts toward SAMs was therefore not pursued.

On the other hand, Bingel-Hirsch reactions with 60-10-3, 60-10-5, and 60-10-6 were more selective and did not produce as many prod-
ucts and undesirable insoluble materials. It appears that the presence of many CF_3 groups on the fullerene core helps direct the malonate ad-
tions to the unique sterically unhindered unsubstituted cage regions present in C_{60}(CF_3)_{10} isomers, which was not the case for the less sub-
stituted TMFs 60-2-1 and 60-4-1. Monoadducts were separated from bis- and trisadducts by flash chromatography with toluene/methanol mixtures and then the major monoadducts were further purified with HPLC in toluene.

The best result was obtained in the reaction with 60-10-3: a single, predominant isomer of (60-10-3)(PE) (PE is phosphonic ester) was formed and purified by HPLC in toluene using a Buckyprep column; the isolated yield was 32% based on starting 60-10-3. The \(^{19}\)F NMR spectrum of this product exhibited a ten-multiplet spectrum with similar chemical shifts to parent 60-10-3, indicating that the addition pattern of the ten CF_3 groups remained unchanged upon phosphonic ester addition (Figure 3). A peak at 1748 m/z in the MALDI mass spectrum corresponded to C_{60}(CF_3)_{9}(PE)H\(^+\) and confirmed the addition of a single malonate to the fullerene core, in line with the results of analysis of the \(^1H\) and \(^31\)P NMR spectra. A Bingel-Hirsch reaction with 60-10-5 and malonate phosphonic ester produced a yellow solution containing two predominant isomers of (60-10-5)(PE) as determined by \(^31\)P NMR (Figure 4). The two isomers were produced in relatively equal amounts according to \(^1H\) and \(^31\)P NMR analyses and could not be separated by HPLC using a Buckyprep column. The reaction with 60-10-6 was the least selective of the C_{60}(CF_3)_{10} reactions investigated. At least six isomers of (60-10-6)(PE) (see Figure SI-3) were produced that could not be separated by HPLC in 100% toluene using a Buckyprep column, so the product mixture was not used for further reactions.

The phosphonic ester moieties on one isomer of (60-10-3)(PE) and the mixture of two isomers of (60-10-5)(PE) were then converted to phosphonic acids (PA), C_{60}(CF_3)_{10}(PA) (Scheme 1). Phosphonic esters do not bind to MO\(_x\), as strongly as phosphonic acids, so the acid derivatives were desired for SAM formation. The phosphonic acid
TMF derivative was synthesized by performing several steps of the reported literature procedure. Each phosphonic ester TMF derivative was dissolved in dry dichloromethane with excess BrSiMe3 for 1 to 3 days before the solvent was removed and MeOH and HCl were added. This procedure was repeated several times to maximize acid formation. The solubility of the product mixtures were much lower than the starting phosphonic ester derivatives; this was also observed with other C60(PA) derivatives. Solubility of the product mixtures decrease in the series of chloroform/methanol, chloroform, toluene, toluene/methanol, DCM, DCM/methanol, methanol, and CS2. A decrease in the 1H NMR signals of the ester moiety relative to other 1H signals indicated a loss of phosphonic ester. Broadening of the CF3 multiplets in 19F NMR spectra were observed with no shifts in peak positions. Mass spectra (ESI and MALDI in positive and negative mode) showed peaks due to the formation of the phosphonic acid and partially reacted ester products. Complete conversion to the phosphonic acid is not essential, since the partial and full esters will not bind as strongly when forming the SAM and can be washed away to leave a pure monolayer of the C60(CF3)10(phosphonic acid) derivatives.

The successfully synthesized (60-10-3)(PA) sample was then used for preliminary testing its electronic properties in self-assembled monolayer filed-effect transistors (SAMFETs). In brief, SAMs were formed on AlOx substrates (formed by atomic layer deposition (ALD) on Si substrates) by immersion in (60-10-3)(PA) solution. Monolayers of (60-10-3)(PA) bound to the AlOx surface while weakly bound excess layers and (60-10-3)(PE) were washed away with solvent, which left a single monolayer denoted as (60-10-3)(PA)-SAM. In some cases mixed monolayers were formed starting with C10F17(carboxylic acid) SAMFETs that were exchanged with a solution of (60-10-3)(PA)-SAM according to previous reports.

Confirmation of SAM formation was obtained by static contact angle (SCA) and X-ray reflectivity (XRR) measurements. The SCA of (60-10-3)(PA)-SAMs with water were 101.0° ± 0.7° which is indicative of a hydrophobic surface. In comparison, similarly fabricated non-fluorinated C60-SAMs showed contact angle values < 90°. The vertical electron density profile from XRR shows that the (60-10-3)(PA) molecules arrange preferentially with the fullerene moieties on top of the SAM (Figure 5). Grazing incidence X-ray diffraction (GID) measurements of (60-10-3)(PA)-SAMs exhibited no diffraction peaks, which indicated that the SAM was (predominantly) amorphous. In comparison, the non-fluorinated C60-SAMs showed a hexagonal crystalline order.

Preliminary testing of SAMFET devices using (60-10-3)(PA) SAMs was carried out. The measured electrical conductivity in FET devices with TMF-based SAMs was below the leakage current through the dielectric and was thus much lower than in non-fluorinated fullerene SAMs. This decrease in drain current is in accordance with the insulating effects of the fluorous coat on the carbon cage of highly fluorinated fullerene SAMs.
Figure 5. The vertical electron density profile of {eq}(60-10-3)(\text{phosphonic acid})\text{-SAMs on ALD AlO}_x\text{ plotted over a representative cartoon of the layers.}