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LETTER

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Diazoalkane Addition Reaction on the Fullerene Dimer C₁₂₀O and Characterization of the Resulting Mono-adduct.

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A mono-adduct of the fullerene dimer C₁₂₀O was prepared via a diazoalkane addition reaction to obtain rod-like analogue of [60]PCBM opening the possibility to make photovoltaic and photosensitive layers of supra-molecular and anisotropic order. The mono-adduct was obtained as a mixture containing five isomers. The structure of the mono-adduct was verified by mass-, IR-, and ¹H-NMR-spectroscopies. The mono-adduct is readily soluble in common fullerene solvents and shows a broader and stronger optical absorption than [60]PCBM. The mono-adduct features a similar acceptor strength as [60]PCBM and [70]PCBM, is stable in air below 150 °C and in nitrogen below 500 °C. The mono-adduct is expected to be a valuable material for photovoltaic and photosensitive applications.

Introduction : In recent years, a rapid development of bulk-heterojunction (BHJ) polymer solar cells initiated and the power conversion efficiencies of BHJ solar cells increased continuously. However, the power conversion efficiencies of BHJ polymer solar cells are still a factor four lower compared to inorganic semiconductor devices. At present, the typical device structure of bulk-heterojunction polymer solar cells consists of two randomly orientated, disordered interpenetrating networks consisting of a semiconducting polymeric donor and an organic acceptor making the photovoltaic active layer sandwiched between two asymmetrical work function metal electrodes [1, 2].

Among currently available acceptors, the well known methanofullerene [60]PCBM ([6,6]-phenyl C₆₁-butyric acid methyl ester) [3] has proven to be a most efficient acceptor material for solar cell applications [1, 2]. As an alternative to [60]PCBM, the analogous [70]PCBM [4] and [84]PCBM [5] have been prepared, characterized, and applied.

In this letter, the preparation and characteristics of a dimeric C₆₀ analogue (**1** in Figure 1) of [60]PCBM is presented.

The rod-like structure of (**1**) opens the possibility to make photoactive layers of supra-molecular and anisotropic order, which might improve the performance of BHJ solar cells. Firstly, such structured layers would improve the transport properties of the interpenetrating networks and consequently increase the efficiency of BHJ solar cells. Secondly, such layers would lower the percolation threshold of the fullerene component, which does not significantly contribute to the absorption of light by the photovoltaic

device [2]. In addition, dimeric fullerenes should stabilize the original blend morphology – achieved by post-processing heat treatment – by delaying the aging process of fullerene aggregation leading to a degradation of the interpenetrating network and consequently to a decrease of the power conversion efficiency of the cell [2].

The compound (**1**) is a derivative of the dimeric C₆₀ fullerene oxide C₁₂₀O [6]. The intrinsic properties of C₁₂₀O have been investigated quite extensively. For instance, C₁₂₀O features inter-cage electronic action [7], is stable upon illumination, chemical, photochemical [8], and electrochemical [7] reduction, as well as upon heating [9]. Due to the unique combination of these properties, C₁₂₀O was chosen as the skeletal backbone for the rod-like analogue of [60]PCBM. However, no research has been done with respect to chemical functionalizing of C₁₂₀O.

Preparation : The C₁₂₀O derivative (**1**) was realized via a diazoalkane addition reaction [3] performed on C₁₂₀O (Figure 1). C₁₂₀O was prepared by literature methods [6, 10]. The diazoalkane addition reaction was carried out by heating a stirred solution of C₁₂₀O (100 mg, 0.07 mM) in ortho-dichlorobenzene (ODCB) (200 ml) under a nitrogen atmosphere to 70 °C, and thereafter adding a suspension of 4-benzoyl-methylbutyrate p-tosylhydrazone (52.5 mg, 0.14 mM, 2 eq.) and sodium methoxide (7.6 mg, 0.14 mM, 2 eq.) in pyridine (5 ml) to the stirred solution. The homogeneous reaction mixture was stirred under nitrogen at 70 °C for 24 h. Subsequent, the reaction mixture was concentrated by evaporating the volatile components in vacuum.

As shown in the high pressure liquid chromatography (HPLC) analysis of the reaction product (Figure 2) the product mixture of the reaction contained up to 40 % mono-adduct as main product, bis-, tris-, and tetra-adducts as by-products, as well as un-reacted $C_{120}O$.

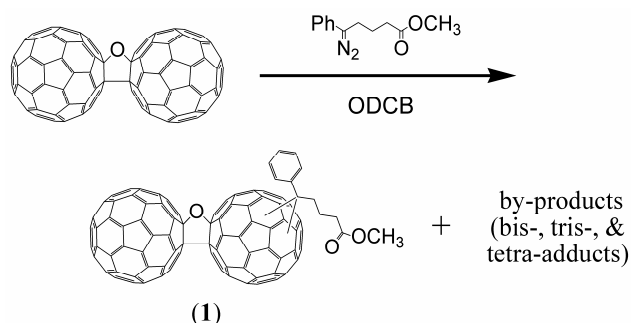


Figure (1) : Reaction scheme of the diazoalkane addition reaction on $C_{120}O$.

High purity mono-adduct (1) was separated from unreacted $C_{120}O$ and multi-adducts by preparative HPLC through the use of a Cosmosil Buckyprep column (20 x 250 mm) eluted with 18 ml/min toluene. The identification of the fractions was based on mass spectrometry (MALDI-TOF). Most important, the reaction product can also be separated by preparative flash chromatography using silica gel. Elution with cyclohexane/toluene (5:1, v/v) yields unreacted $C_{120}O$. Subsequent elution with cyclohexane/toluene (4:1, v/v) yields the mono-adduct fraction with purity of 85 %. The multi-adducts can be obtained by further elution with toluene or ODCB.

Figure (2) shows that the HPLC retention times of the $C_{120}O$ -adducts significantly decrease with the number of side chains. The multi-adducts even feature HPLC retention times similar to those of C_{60} (7.8 min), [60]PCBM (5.1 min), and [70]PCBM (7.1 min). On the Buckyprep column, the retention times of fullerenes decrease with increasing solubility and decreasing size of the fullerenes. Concluding, the solubility of the $C_{120}O$ -adducts increases with the number of side chains, and despite their size, the $C_{120}O$ -adducts are soluble like [60]PCBM and [70]PCBM. This matters for the processing of dimeric fullerenes in solution.

To verify the number of formed mono-adduct (1) isomers, the mono-adduct fraction (1) was additionally studied by analytical HPLC using a Buckyprep column (250 x 4.6 mm) eluted with 0.1 ml/min toluene/ cyclohexane (1:1, v/v). This HPLC analysis revealed five peaks. In conclusion, the mono-adduct fraction (1) contains a minimum of five isomers.

Mono-adduct (1) is a brown solid and readily soluble in common fullerene solvents such as toluene, chlorobenzene, or ODCB. A solution of (1) in these solvents is orange to brown and after evaporation of the solvent of such a solution, (1) remains as a homogeneous film. This is relevant for the fabrication of photoactive layers [1, 2].

Under ambient atmosphere and room temperature, dissolved and solid (1) are stable in the dark while under the influence of ambient light in particular dissolved (1) slowly oxidizes.

Analytical Data : The analytical data presented are that of (1): HPLC (Buckyprep) retention times [min]: 12.3, 13.0 (two peaks using 1 ml/min toluene elution); 352, 364, 380, 409, 446 (five peaks using 0.1 ml/min toluene/ hexane (1:1, v/v) elution). IR (KBr) ν [cm^{-1}]: 1737 (s), 1627 (m), 1598 (w), 1492 (m), 1456 (s), 1444 (s), 1432 (s), 1371 (m), 1330 (w), 1245 (m), 1155 (m), 1101 (m), 1031 (s), 964 (w), 848 (m), 804 (m), 765 (m), 702 (m), 547 (m), 526 (s), 478 (m), 403 (w). MALDI-TOF MS (DCTB matrix) m/z: 1646.836 (M). 1H -NMR: ($CDCl_3/TMS$): δ [ppm] = 7.0-7.52 (phenyl; 5 H), 3.61, 3.68 (OCH_3 ; 3 H), 2.36 (CH_2CO_2Me ; 2 H), 1.56 ($CH_2CH_2CO_2Me$; 2 H), 1.25 ($PhCCH_2$; 2 H). UV-vis (toluene) λ_{max} [nm]: 287, 325, 368 (shoulder), 418 (shoulder).

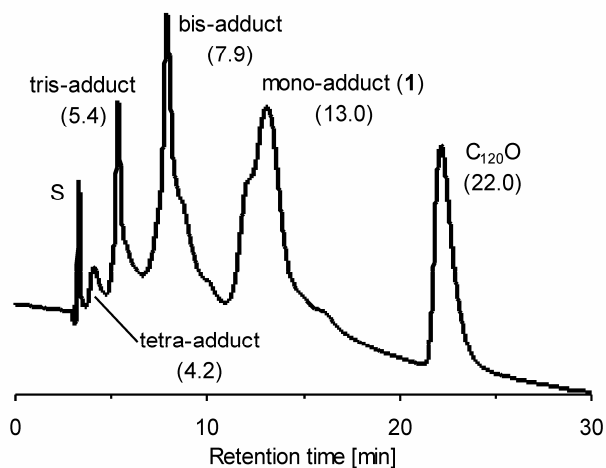


Figure (2) : HPLC chart of the product mixture of the diazoalkane addition reaction on $C_{120}O$. Conditions: 250 x 4.6 mm Buckyprep column eluted with 1 ml/min toluene; UV detection at 330 nm. The numbers in brackets declare the retention times of the fractions in [min].

Electronic Absorption : Figure (3) confronts the absorption spectrum of (1) with those of [60]PCBM and [70]PCBM. Molar absorptivity values were scaled for comparison of the intensities. Because each fullerene cage in (1) can be electronically excited, absorptivities approximately twice those of [60]PCBM could be expected for (1). However, throughout the visible region, the absorptivities of (1) clearly exceed these values. In addition, compared with the absorption spectrum of [60]PCBM, that of (1) is actually featureless throughout the visible region. The absorption characteristics of (1) may be attributed to the interaction of the two fullerene-moieties with regard to electronic transitions and to the reduced molecular symmetry of (1) [11, 12].

However, even though the absorptivities of (1) clearly exceed the values of [60]PCBM, they do not reach the values of [70]PCBM. Therewith, (1) shows a better match with the AM 1.5 solar spectrum than [60]PCBM but not than [70]PCBM. This is not only most relevant for applications in photovoltaics but also for applications in photodiodes and photodetectors.

Electrochemical Characterization : To test the electron accepting properties of (1), cyclic voltammetry (CV) experiments were performed. The measurements

revealed that **(1)** undergoes at least two sequential chemically reversible and electrochemically quasi-reversible reductions (Table 1). To estimate the relative acceptor strength of **(1)**, a comparison was made with [60]PCBM and [70]PCBM. The first half-wave reduction potentials (E_{red}^1) being indicative of the acceptor strength of the compounds show only minor differences (Table 1). This implies that the obtainable maximum open circuit voltage (VOC) of solar cells using **(1)** as acceptor should be equal to the maximum open circuit voltage reachable with similar [60]PCBM based solar cells as the open circuit voltage in fullerene-based plastic solar cells is directly related to the acceptor strength of the fullerenes [13].

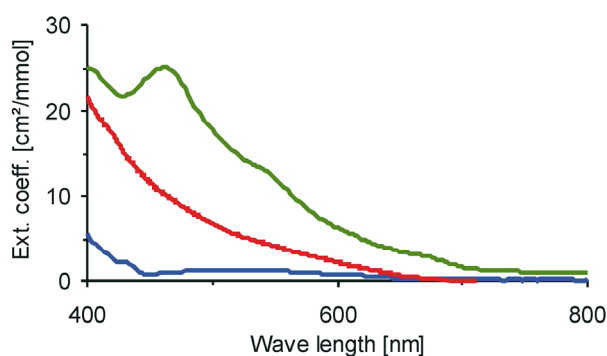


Figure (3) : UV-vis absorption spectra of **(1)** (red line), [60]PCBM (blue line), and [70]PCBM (green line), determined using toluene solutions of concentrations of about 0.01 mg/mL.

Table (1) : Redox potentials^{a)} [V] vs. Fc/Fc⁺ of **(1)**, [60]PCBM, and [70]PCBM determined by CV.

Compound	(1) ^{b)}	[60]PCBM	[70]PCBM ^{b)}
E_{red}^1	-1.12	-1.14	-1.09
E_{red}^2	-1.58	-1.56	-1.48

a) Experimental conditions: glassy carbon as working electrode, Pt-wire as pseudo reference electrode, Pt foil as counter electrode; TBAPF6 (0.1M) as supporting electrolyte; toluene/MeCN (4:1) as solvent; scan rate 100 mV/s; room temperature, 0.2 mM **(1)**, 1 mM [60]PCBM, 0.8 mM [70]PCBM. b) Isomeric mixture.

Oxidative and Thermal Stability : Figure (4) shows the thermogravimetric analysis (TGA) traces of **(1)** in synthetic air and in nitrogen. In order to enhance the steps in the thermo-gravimetric curves, the corresponding derivative thermo-gravimetric (DTGA) trace are also shown in Figure (4).

The TGA trace recorded in synthetic air shows a pronounced weight gain starting at ~ 170 °C and peaking at 300 °C. This weight gain indicates the partial oxidation of **(1)** by oxygen [14]. With further increase of temperature, the weight initially decreases almost linearly up to 400 °C and then still linearly but more rapidly. This weight loss denotes the oxidation of **(1)** to CO and CO₂ [14]. The sample lost 75 % of its initial weight at 500 °C and an amorphous poly-condensate [14] of unknown structure was remaining.

In the TGA trace recorded in nitrogen atmosphere, the sample weight remains constant up to 500 °C. With further increase of temperature, the weight steadily decreases in at

least four distinct stages. The sample lost 60 % of its initial weight at 1000 °C and an amorphous poly-condensate of unknown structure was remaining. Evidently, the sample did not simply undergo a sublimation process, but also some other processes – presumably dissociation and formation of larger fullerene structures by Diels-Alder [15] like reactions – may have occurred.

However, these thermo-gravimetric analyses clearly indicate that **(1)** can be tempered in air below 150 °C and in nitrogen below 500 °C without risking any damages. This is important for the feasibility of growing thin films for devices and/or transport property studies in principle and for post-processing like controlled phase separation and crystallization induced by heat treatment of photoactive blends in particular.

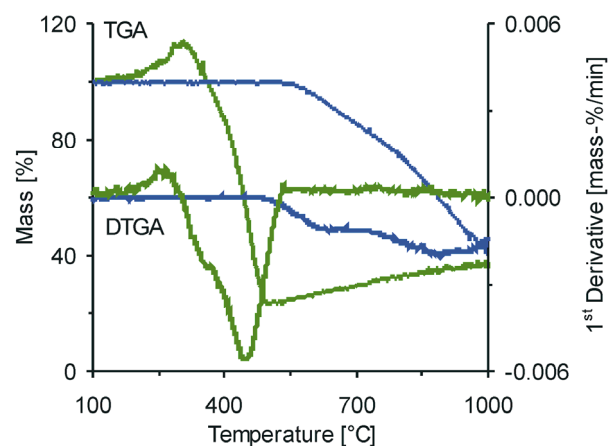


Figure (4) : Thermogravimetric analysis (TGA) and corresponding first derivatives (DTGA) of **(1)**, measured in synthetic air (green lines) and in nitrogen (blue lines) at scan rates of 1 °C/min and flow rates of 30 ml/min, sample weights: approx. 1 mg.

Summary and Conclusions : Summing up, a dimeric analogue **(1)** of [60]PCBM was prepared via a diazoalkane addition reaction performed on the dimeric C₆₀ fullerene oxide C₁₂₀O. **(1)** is readily soluble in common fullerene solvents; shows a significant broader and stronger absorption than [60]PCBM but not than [70]PCBM; features a similar acceptor strength as [60]PCBM and [70]PCBM; and is stable in air below 150 °C and in nitrogen below 500 °C. Most important, the rod-like structure of **(1)** opens the possibility to make photoactive layers of supra-molecular and anisotropic order.

Our appraisal is that **(1)** is not only a promising material for photovoltaics but for various molecular electronic applications for instance photodiodes or photodetectors.

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