

Mono-cyclopropanated Fullerene Dimer C₁₂₀O and Its Application in a Bulk Heterojunction Solar Cell

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Mono-cyclopropanated C₁₂₀O was prepared to obtain soluble, longish electron acceptor opening the possibility to make organic photoactive layers of supra-molecular and anisotropic order. The C₁₂₀O derivative was characterized by UV-vis spectroscopy, cyclic voltammetry, and thermogravimetric analyses, and applied as electron acceptor in a bulk-heterojunction polymer solar cell. The C₁₂₀O derivative is appraised to be a valuable electron acceptor.

In recent years, a rapid development of bulk-heterojunction (BHJ) polymer solar cells initiated. The power conversion efficiencies of BHJ solar cells continuously increased, but are still low compared to inorganic semiconductor devices.¹ At present, the typical device structure of BHJ solar cells consists of two randomly orientated, disordered interpenetrating networks consisting of a semiconducting polymeric donor and a fullerene-based acceptor making the photoactive layer sandwiched between two asymmetrical work function metal electrodes.¹

Here, the preparation, characteristics, and application of a mono-cyclopropanated C₁₂₀O derivative **1** (Figure 1) are reported. The longish shape of **1** opens the possibility to make photoactive layers of supra-molecular and anisotropic order, which are regarded to significantly improve the performance of BHJ solar cells. Firstly, such structured layers should improve the transport properties of the interpenetrating networks and consequently increase the efficiency of BHJ solar cells. Secondly, such layers should lower the percolation threshold of the fullerene component, which does not significantly contribute to the absorption of light by the photovoltaic devices. In addition, oligomeric fullerenes should stabilize the original blend morphologies—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 cells.¹

The fullerene oxide C₁₂₀O was chosen as skeletal backbone for **1** because it features inter-cage electronic action and is stable upon illumination, chemical, photochemical, and electrochemical reduction, as well as upon heating.² To functionalize

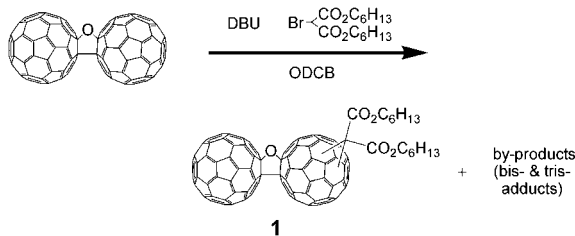


Figure 1. Bingel reaction on C₁₂₀O.

C₁₂₀O, a Bingel cyclopropanation reaction was chosen because of its mild reaction conditions providing high yields and the exclusive formation of [6,6]-bridged adducts.³

C₁₂₀O was prepared by literature methods.⁴ The Bingel reaction was carried out by adding dihexyl bromomalonate [BrCH(CO₂C₆H₁₃)₂, 0.1 mM, 1.5 equiv] and 1,8-diazabicyclo-[5.4.0]-7-undecene (DBU, 0.13 mM, 2 equiv) to a stirred solution of C₁₂₀O (0.07 mM) in 1,2-dichlorobenzene (ODCB) (200 mL) and thereafter stirring the reaction mixture at room temperature for five hours (Figure 1).

As determined by high pressure liquid chromatography (HPLC) analysis (250 × 4.6-mm² Buckprep column, 1-mL/min toluene elution) and mass spectrometry, the product mixture of the reaction contained 40% mono-adduct, 35% bis- and tris-adducts, and 25% unreacted C₁₂₀O (Figure 2). Highly pure mono-adduct **1** was separated from the product mixture by preparative HPLC (20 × 250-mm² Buckyprep column 18-mL/min toluene elution). The structure of **1** was verified by MS, IR, and ¹HNMR spectroscopies.^{5,6} A number of at least four mono-adduct isomers was verified by analytical HPLC (250 × 4.6-mm² Buckprep column, 0.1-mL/min toluene/cyclohexane (1:1, v/v) elution).^{5,6}

1 is a brown solid and readily soluble in toluene, chlorobenzene, or ODCB. A solution of **1** in these solvents is wine red and after evaporation of the solvent of such a solution, **1** remains as a homogeneous film. This is essential for the fabrication of photoactive layers. Under ambient atmosphere and room temperature, dissolved and solid **1** is stable in darkness while under the influence of ambient light in particular dissolved **1** slowly oxidizes just as C₆₀.⁷

Figure 3 shows thermogravimetric analyses (TGA) of **1** measured in synthetic air and in nitrogen atmosphere. Knowledge about the thermal and oxidative stability of **1** is important for the post-processing heat treatment of photoactive blends containing **1**. In synthetic air, **1** is stable up to 200 °C. At higher temperatures, partial and total oxidation occur.⁸ In nitrogen atmosphere, **1** is stable up to 225 °C. At higher temperatures, thermal decomposition and formation of larger fullerene clusters occurs.⁸

Figure 4 shows the absorption spectra of **1** and [60]PCBM,⁹

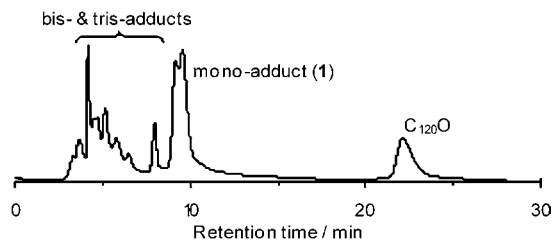


Figure 2. HPLC chart of the product mixture of the Bingel reaction.

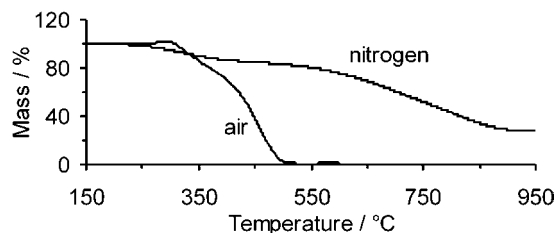


Figure 3. TGA of **1**, measured in synthetic air and in nitrogen (scan rates: 1 °C/min, flow rates: 30-mL/min, sample weights: 1 mg).

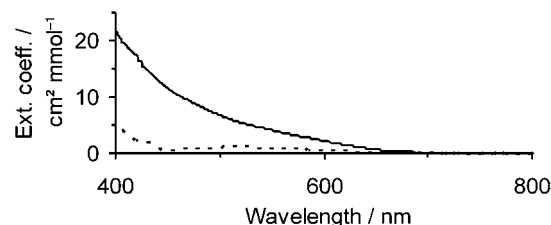


Figure 4. UV-vis absorption spectra of **1** (solid line) and [60]PCBM (dotted line) in 0.01-mg/mL toluene solutions.

Table 1. Redox potentials (V vs. Fc/Fc⁺) of **1** and [60]PCBM¹¹

E_{red}^1 (1)	E_{red}^2 (1)	E_{red}^1 ([60]PCBM)	E_{red}^2 ([60]PCBM)
-1.16	-1.75	-1.14	-1.56

which is a most efficient acceptor for BHJ solar cell applications.¹ Compared to the spectrum of [60]PCBM, that of **1** is featureless and clearly enhanced throughout the visible region. Therewith, **1** shows an improved match with the AM1.5 solar spectrum. The absorption characteristics of **1** can be attributed to the reduced molecular symmetry of **1** and to the interaction of the two fullerene-moieties with regard to electronic transitions.¹⁰

Table 1 shows the first (E_{red}^1) and second (E_{red}^2) half-wave reduction potentials of **1** and [60]PCBM as determined by cyclic voltammetry.¹¹ The E_{red}^1 potentials, being indicative of the acceptor strength of a compound, show only a minor difference. This implies that the obtainable maximum open circuit voltage of solar cells using **1** as acceptor should be similar to that reachable with similar [60]PCBM-based solar cells.¹²

Figure 5 shows the current density–voltage curve of P3HT:**1** BHJ solar cells under illumination.¹³ The maximum photovoltaic power conversion efficiency of such devices of 0.81% was comparatively low¹ but verified the applicability of soluble oligomeric fullerene derivatives to BHJ solar cells. Optimizing

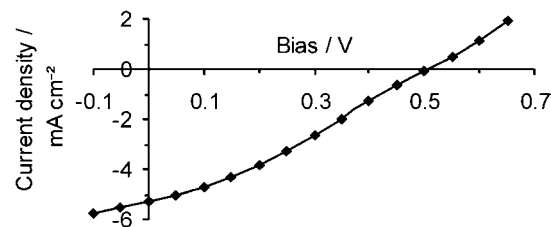


Figure 5. Current density–voltage characteristic of P3HT:**1** (1:0.8, w/w) devices under illumination.¹³

of production parameters to obtain optimal device parameters¹ and studying of the impact of **1** on the morphology of photoactive layers are tasks of future work.

Summing up, the results indicate that **1** is a promising electron acceptor for various photosensitive applications (photovoltaics, -diodes, or -detectors) and that fullerene oxide structures are promising candidates for the skeletal backbone of soluble, well-defined oligomeric fullerene derivatives.

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- HPLC (250 × 4.6-mm² Buckyprep) retention times (min): 9.3, 9.6 (1-mL/min toluene); 243, 246, 255, 266 (0.1-mL/min toluene/cyclohexane (1:1, v/v)). MALDI-TOFMS (DCTB matrix) m/z : 1726.876 (M⁻). IR (KBr) ν (cm⁻¹): 1743 (s), 1456 (m), 1452 (m), 1427 (m), 1373 (w), 1267 (m), 1240 (s), 1182 (m), 1099 (m), 1065 (w), 1034 (s), 964 (w), 849 (m), 744 (m), 577 (w), 550 (w), 526 (s). ¹HNMR: (CDCl₃/TMS, 400 MHz): δ 4.4, 3.54, 1.54, 1.27, 0.88. UV-vis (toluene) λ_{max} (nm): 285, 326, 416 (sh).
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- Cell-design: ITO-Glass/PEDOT:PSS/P3HT:**1**/Al; illumination: 100 mW/cm² AM1.5 from the ITO side; cell area: 25 mm²; P3HT:**1** (1:0.8, w/w) layer spin-coated from chlorobenzene and tempered for 3 min at 150 °C. Device parameters: I_{SC} (mA/cm²) = 5.31; V_{OC} (mV) = 506; $FF(-)$ = 0.3; $\eta_{\text{AM1.5}}$ (%) = 0.81.