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RICERCA DI SISTEMA ELETTRICO

Sintesi di derivati fullerenici e nanostrutture di carbonio per celle
fotovoltaiche organiche

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SINTESI DI DERIVATI FULLERENICI E NANOSTRUTTURE DI CARBONIO PER CELLE
FOTOVOLTAICHE ORGANICHE

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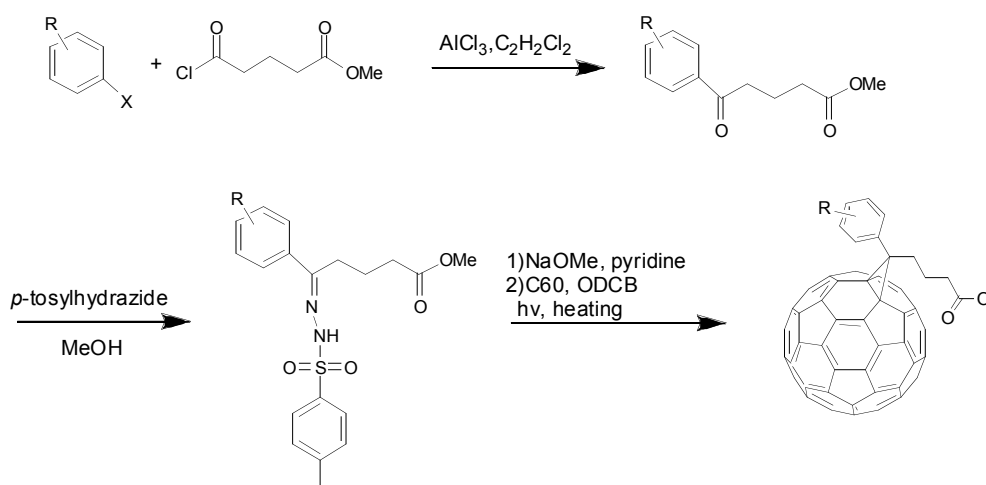
Tema: Ricerca su celle fotovoltaiche innovative

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The need to develop inexpensive renewable energy sources stimulates scientific research for efficient, low-cost photovoltaic devices. The organic, polymer-based photovoltaic elements have introduced at least the potential of obtaining cheap and easy methods to produce energy from light. The possibility of chemically manipulating the material properties of polymers (plastics) combined with a variety of easy and cheap processing techniques has made polymer-based materials present in almost every aspect of modern society. Organic semiconductors have several advantages: (a) low-cost synthesis, and (b) easy manufacture of thin film devices by vacuum evaporation/sublimation or solution cast or printing technologies.^{1,2} Photoinduced electron transfer from donor-type semiconducting polymers onto acceptor-type polymers or molecules, such as C₆₀, is utilized in organic solar cells. Much work has been done in improving organic solar cells; efficiencies of more than 2.5% have been reached by using a MDMO - PPV:[60]PCBM blend (poly[2-methoxy-5-(3,7-dimethyloctyloxy)-p-phenylenevinylene]:phenyl C₆₁ butyric methylester). Several factors are of importance in improving the efficiency of this type of organic solar cell. It is essential that the conjugated polymer has a low band gap (< 1.8 eV) to efficiently absorb light in the visible area of the solar spectrum.³

There is, within certain limits, a linear relationship between the donor-HOMO and acceptor-LUMO energy difference and the V_{oc} of the bulk-heterojunction device. Consequently, the upper limit for the V_{oc} of bulk-heterojunction solar cells is determined by the energy difference of the HOMO of the electron donor and the LUMO of the electron acceptor. In this report, we present on our efforts to influence the LUMO level of PCBM by placing electron-donating (methoxy groups).⁴ Additionally, higher adducts of PCBM were used to further increase the V_{oc} of P3HT-based OPVs by approximately 100 meV per saturated double bond. The synthesis of bis-adducts is yielding to 22 regioisomers which is a drawback to this approach, compared with the synthesis of mono-adducts such as PCBM. Even bis-adducts with two identical, symmetric addends (the functional group that forms a bond to the fullerene cage) can be formed as eight different regioisomers.⁵ The presence of multiple isomers of bis-PCBM decreases electron mobility in OPVs by reducing the p-p interactions between fullerene cages. Different isomers can also have different reduction potentials and isomers with less-negative reduction potentials than the average will act as (shallow) electron traps. Moreover, the overall morphology of OPVs is negatively impacted by the presence of a mixture of isomers. In addition are reported the some attempts in other carbon allotropes which can be used either as donor (Multi Walled Carbon Nanotubes-MWCNT) or as acceptors (Carbon Nanohorns-CN).⁶

1. Synthesis of PCBM bearing electron donating groups



Scheme 1: Synthetic overview of the PCBM derivatives.

5-(2,5-dimethoxyphenyl)-5-oxo-pentanoic acid methyl ester : Aluminum trichloride (9.04 g, 67.8 mmol) was suspended in dichloroethane (50 ml), placed under nitrogen and cooled to 0°C while stirred. To the suspension p-dimethoxybenzene (6.29 g, 45.5 mmol) was added at once. Subsequently, methyl 5-chloro-5-oxopentanoate (5.05 g, 30.7mmol) was added dropwise. The resulting mixture turned from green to brown and HCl gas formation was observed. The solution was allowed to warm up to RT and stirred for 20 h. The reaction mixture was poured out on ice (100 g). To the obtained yellow mixture 50 ml of dichloromethane was added and the mixture was stirred until all the ice had molten. The obtained mixture was then separated. The aqueous layer was extracted with dichloromethane (3x 50 ml). The organic layers were combined, washed with water (1x 75ml) and brine (2x75ml) and dried over Na₂SO₄. Evaporation of the solvents afforded a yellow oil. The oil was redissolved in ether (200 ml) and washed with a NaOH solution (0.5 M, 4x 50 ml). The ethereal layer was then washed with water (1x 100 ml) and dried over Na₂SO₄. Concentration in vacuum afforded a light yellow liquid. The product was collected pure yielding as a whitepowder (5.72 g, 21.5 mmol, 70%). NMR spectroscopy and MS spectrometry are in agreement with the published ones.⁴

cis-2,5-(dimethoxy-benzoyl)-methylbutyrate-p-tosylhydrazone: 5-(2,5-dimethoxy-phenyl)-5-oxo-pentanoic acid methyl ester (3.02 g, 11.35 mmol) was dissolved in methanol (25 ml). p-Tosylhydrazide (2.57 g, 13.8 mmol) was added at once. The remaining yellow solution was heated to reflux for 12 h. The mixture was concentrated to ~10 ml and cooled to 0°C resulting in crystallization. The obtained crystals were filtered by suction and a white powder remained (0.78 g, 1.73 mmol) with a cis:trans ratio of 1:13.5 (by ¹H NMR). The filtrate was left in the freezer overnight and filtered by suction. A white powder remained (2.76 g, 6.13 mmol) with a cis:trans ratio of 9.7:1. Combined yield 3.54 g (7.85 mmol), 69.2%. The cis product (2.76 g, 6.13 mmol) was recrystallized from a mixture of ethylether (50 ml) and t-butylmethyl-ether (3 ml). The obtained crystals were filtered by suction and dried in vacuo at 50°C. White crystals were obtained (1.78 g, 3.95 mmol, 34.8%). Spectroscopic characterization is in agreement with the published results.⁴

5-(2,4,6-trimethoxyphenyl)-5-oxo-pentanoic acid methyl ester: A dried 250 ml flask was charged with AlCl₃ (9.2g, 69 mmol) under Ar. Dichloroethane (50 ml) was added and the suspension was cooled on ice while stirred. 1,3,5-Trimethoxybenzene (7.57g, 45mmol) was added at once resulting in a homogeneous solution. After stirring for a few minutes methyl 5-chloro-5-oxopentanoate (4.94g, 30mmol) was added at once. The solution quickly turned dark brown. The cooling bath was removed and the mixture was stirred at RT for ~22 h. The reaction mixture was poured onto crushed ice and dichloromethane (50ml) was added. The resulting mixture was separated. The aqueous layer was extracted with dichloromethane (3 x 50 ml). The combined organic layers were washed with H₂O (1x75ml) and brine (2x75ml), dried over Na₂SO₄ and concentrated in vacuum obtaining a purple oil. An SiO₂ column (5x11cm) was prepared. Mixture was dissolved in toluene (50ml) and brought on. Elution was started with toluene removing side products. Product was eluted with toluene:ether (9:1). Evaporation yielded a yellow viscous oil (7.58 g, 25.6 mmol, 85 %). Spectroscopic characterization is in agreement with the published results.⁴

2,4,6-(Trimethoxy-benzoyl)-methylbutyrate-p-tosylhydrazone: 5-(2,4,6-trimethoxyphenyl)-5-oxo-pentanoic acid methyl ester (4.45 g, 15 mmol) was dissolved in methanol (25 ml) and p-tosylhydrazide (3.36 g, 18 mmol, 1.2 eq.) was added at once. The resulting mixture was refluxed for 12 h. After cooling to RT no crystallization took place. Mixture was concentrated in vacuo. During concentration crystallization started. Mixture was left in the fridge (4°C) overnight. The obtained crystals were filtered off yielding a white microcrystalline powder which was washed with cold methanol (2 x 2 ml). The obtained powder was dried in air. A second batch was obtained from the motherliquor. Combined yield: 5.81 g (12.5 mmol, 83 %). Spectroscopic characterization is in agreement with the published results.⁴

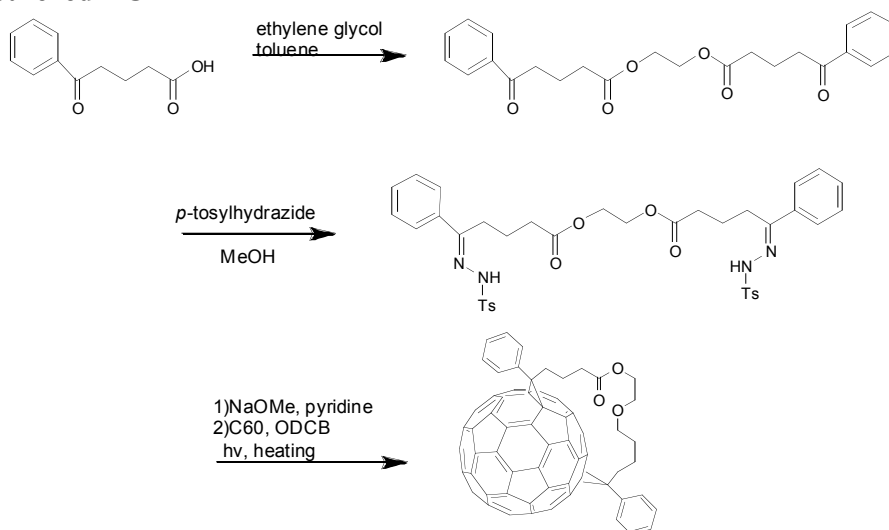
General method for a diazomethane addition to C₆₀ : A mixture of methoxy-substituted benzoyl-methylbutyrate-p-tosylhydrazone (449 mg, 1.11 mmol), sodium methoxide (60 mg,

1.07 mmol) and dry pyridine (15ml) was placed under nitrogen and stirred at RT for 30 min. To the mixture a solution of C₆₀ (735mg, 1.02mmol) in 1,2-dichlorobenzene (75ml) was added. The mixture was deoxygenated using ultrasound and three vacuum/N₂ purge cycles. Irradiation was started using a 400 W Hg-lamp, no cooling was applied. The mixture was stirred and allowed to reach thermal equilibrium (T~86°C). The reaction was allowed to continue for 12 h during which the color turned from purple to brown. The obtained mixture was concentrated in vacuo to 25 ml. An SiO₂ column was prepared (2.5x 20 cm) with 1,2-dichlorobenzene. The mixture was admitted and eluted with 1,2-dichlorobenzene. The fraction containing mono-adduct was collected and concentrated in vacuo, redissolved in a minimal amount of 1,2-dichlorobenzene and transferred to a centrifugal tube (100 ml). The product was precipitated with MeOH, centrifuged and decanted. The remaining pellet was washed twice with methanol. The obtained pellet was dried under vacuo at 40°C for 24 h. From this procedure we collect a mixture of 2 isomers (5,6 and 6,6). For this reason the same reaction took place under heating procedure. Thus, after the addition of the C₆₀ in the starting mixture, the solution boiled at 160°C for an overnight. Following the same cleaning procedures we yielded to the final product, the (6,6) isomer.

2,5-dimethoxy-[6,6]-PCBM: Spectroscopic characterization is in agreement with the published results.⁴

2,4,6-trimethoxy-[6,6]-PCBM: Spectroscopic characterization is in agreement with the published results.⁴

Synthesis of tethered PCBM



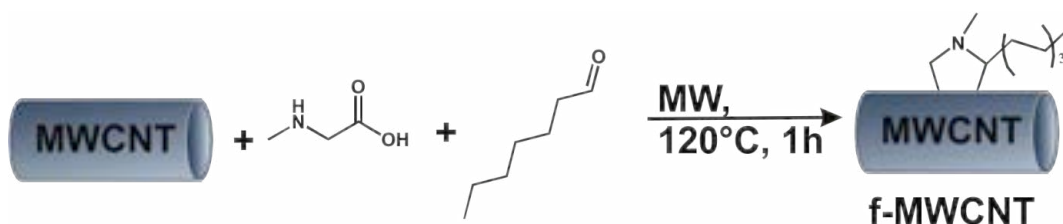
Scheme 2: Synthesis of the ethylene-tethered bis-(4-benzoylbutyric acid tosylhydrazone) 3 and the addition to the fullerene moiety.

Tethered Keto ester: A flame dried 250 ml three-neck flask, equipped with stirring bar and Dean Stark setup, was charged with 10.0 g 4-benzoylbutyric acid (52.0 mmol), 1.4 ml ethylene glycol (0.5 eq.), and 100ml toluene. A few drops of concentrated sulphuric acid were added. The resulting suspension was heated to reflux temperature and stirred overnight. Upon heating a clear solution was formed. The solution was cooled to room temperature and the solvent was removed in vacuo. Pure product was obtained after column chromatography (SiO₂, petroleum ether 40-60/ethyl acetate 2:1), followed by recrystallisation from diethyl ether. Tethered Keto ester (9.0 g) was obtained as a white solid. Spectroscopic characterization is in agreement with the published results.⁵

Bis-tosylhydrazone: A flame dried 250 ml three-neck flask, equipped with stirring bar and Dean Stark apparatus, was loaded with 7.0 g keto ester 2 (17.1 mmol), and 7.0 g tosylhydrazide (2.2 eq.) in 100 ml toluene. The resulting mixture was heated to reflux temperature and stirred overnight. Upon heating a clear solution was formed. The solution was cooled to room temperature. White solids precipitated from the solution upon cooling. The solids were filtered off and placed in a vacuum oven overnight for drying (11.2 g, 88%).⁵

Tethered C 60 bis-adduct: Bis-tosylhydrazide 3 (0.5g, 0.69 mmol) was dissolved in 50 ml pyridine in a flame dried 2L flask under inert atmosphere. 0.22 ml 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added (1.47 mmol, 2.1 eq) and the resulting mixture was stirred for 30 minutes. A solution of 0.5 g C 60 (0.69 mmol) in 500 ml ortho-dichlorobenzene (ODCB) was added together with an additional 500 ml ODCB. The resulting solution was heated with aid of a heat-gun in 15 minutes to 82°C and overnight illumination with a 400W mercury lamp was started. The mixture was concentrated in vacuo and purified by column chromatography (SiO₂, toluene). After removal of the eluent in vacuo a dark solid remains. The solid was precipitated from ortho-dichlorobenzene in pentane and subsequently centrifuged. The remaining red pellet was washed twice with pentane and dried in a vacuum oven at 40°C overnight. We did not receive the final product. Further tries are under procedure.

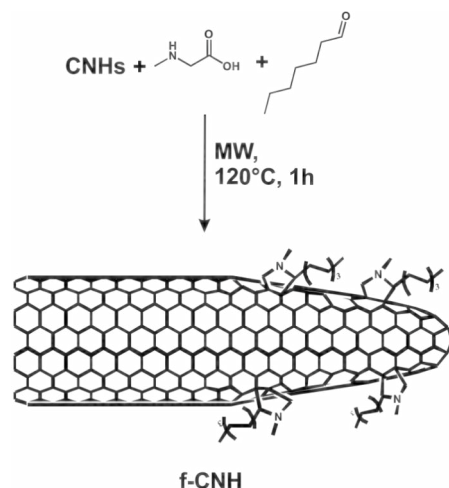
2. Synthesis of Functionalized MWCNT



Scheme 3: Synthesis of functionalized MWCNT through 2+3 cycloaddition.

Synthesis of f-MWCNTs: 100mg of MWCNTs were dispersed in 5ml of ODCB, afterwards equimolar amounts (0.73 mmol) of sarcosine and heptanal were added to the solution. The mixture sonicated again for 15min. The reactions were carried out under MW irradiation at 20-50 watt for 1 hour (T bulk =160°C), with stirring. The mixture was then cooled down at room temperature, suspended in DMF, and ultimately filtrated through a Millipore filter (JH 0.45 μm). The resulting material was extensively washed with DMF and diethylether, and then it was recovered and re-suspended in DMF, upon sonication, for 20 minutes. The resulting mixture was filtered, washed on the filter with DMF and diethylether and at this point the collected black material was suspended in acetone and sonicated for 20 minutes in order to remove all the solvents. Finally, it was filtered and washed with acetone and diethylether. The products were analyzed by TGA, TEM, Raman spectroscopy. Results: TGA: Weight loss= 7%, functionalization loading= 0.23mmol/g, Raman: I_D/G_{norm.} = 1.8.

3. Synthesis of f-CNHs



Scheme 4: Synthesis of functionalized CNHs through 2+3 cycloaddition.

Synthesis of f-CNHs: 100mg of CNHs were dispersed in 5ml of ODCB, afterwards equimolar amounts (0.73 mmol) of sarcosine and heptanal were added to the solution. The mixture sonicated again for 15min. The reactions were carried out under MW irradiation at 20-50 watt for 1 hour (T bulk =160°C), with stirring. The mixture was then cooled down at room temperature, suspended in DMF, and ultimately filtrated through a Millipore filter (JH 0.45 µm). The resulting material was extensively washed with DMF and diethylether, and then it was recovered and re-suspended in DMF, upon sonication, for 20 minutes. The resulting mixture was filtered, washed on the filter with DMF and diethylether and at this point the collected black material was suspended in acetone and sonicated for 20 minutes in order to remove all the solvents. Finally, it was filtered and washed with acetone and diethylether. The products were analyzed by TGA, TEM, Raman spectroscopy. Results:TGA: Weight loss= 10%, functionalization loading= 0.34mmol/g, Raman: $I_{D/Gnorm.} = 2.1$.

4. Conclusion

Finally 4 products were synthesized and characterized. The bis-tethered PCBM is under preparation checking the conditions of the reaction. Additionally the reactions with MWCNT and CNH yielded to successful functionalized materials which are ready for use. Additionally tries will be held with different tethered PCBM materials and also we try to attach the same adducts onto C₇₀. In addition aretaking place different functionalization procedures on Carbon Nanotubes and Nanohorns for more effective properties.

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