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Synthesis and investigation of fullerene-based acceptor materials

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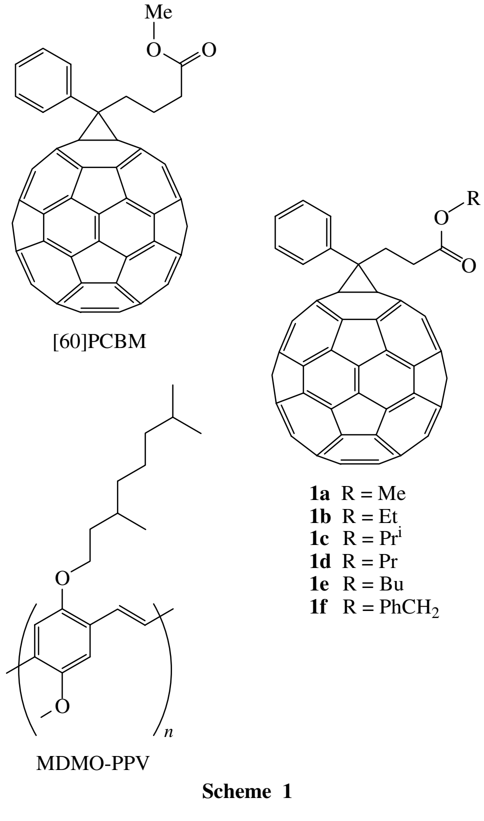
We synthesised a range of new fullerene compounds that showed significantly different photoluminescence quenching abilities in the blends with a polyconjugated polymer; the observed influence of the size and shape of the groups attached to the fullerene cage on the photoinduced charge separation can potentially be used for improvement of power conversion efficiencies in plastic solar cells.

A flexible plastic that converts solar light to electrical power can indeed be considered as the most exciting type of solar cells.[1] It was just a scientific fiction until Tang demonstrated the first organic *p–n* junction solar cell, which showed an outstanding (at that time) efficiency of around 1%.[2] Since that time nobody was able to design much more efficient organic photovoltaic devices until fullerenes were applied as electron acceptors and a concept of bulk *p–n* heterojunction was invented.[3–5]

An extensive investigation of fullerene-based organic solar cells during the last decade resulted in their significant improvement; the power conversion efficiencies approaching 5% were demonstrated.[6] The values of 9–10% are also reachable, as concluded from the theoretical calculations.[7,8]

It was well documented that not pristine fullerenes but their highly soluble derivatives are the most promising acceptor materials for plastic solar cells.[1,4,5] Many fullerene derivatives were investigated in solar cells. Surprisingly, just only one derivative of C_{60} named [60]PCBM (Phenyl-C_{61}-Butyric acid Methyl ester, Scheme 1) and a similar compound of C_{70}, ([70]PCBM) showed acceptable efficiencies in photovoltaic devices.[9,10] The reasons for such a superior performance of PCBM are not understood yet.



[60]PCBM

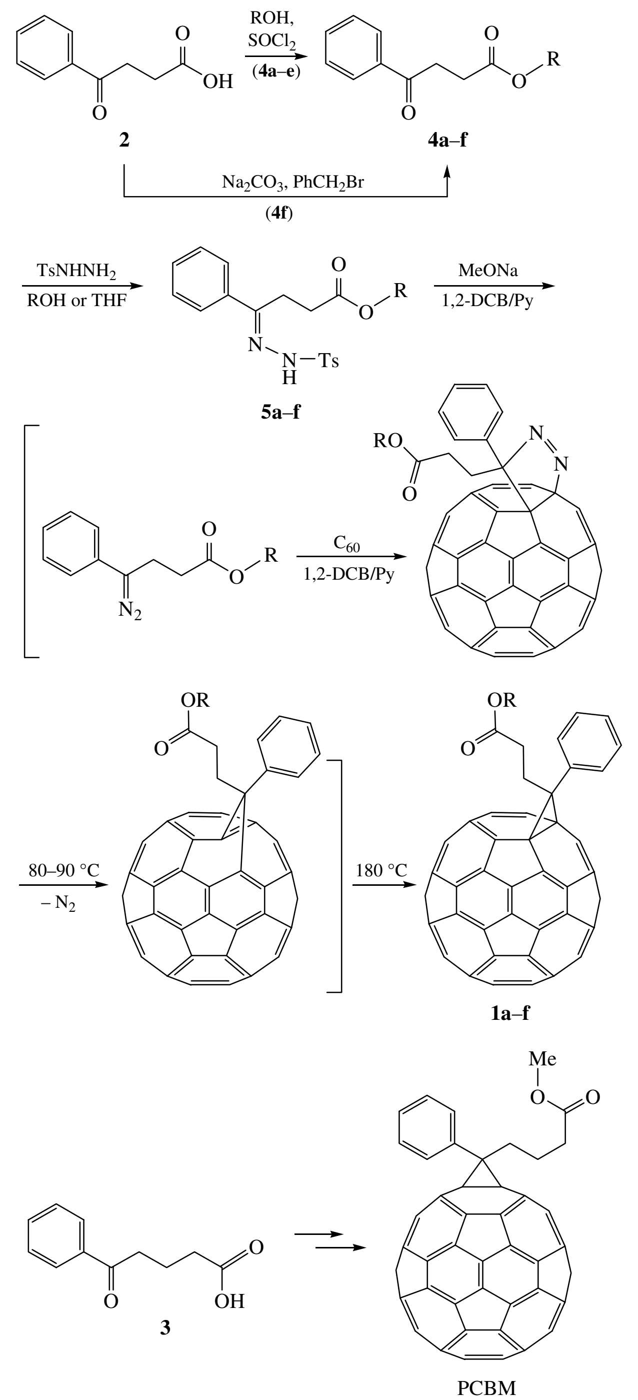
1a R = Me
1b R = Et
1c R = Pr^i
1d R = Pr
1e R = Bu
1f R = $PhCH_2$

MDMO-PPV

Scheme 1

Here we report the preparation of methanofullerenes **1a**–**f**, which are structurally similar to the well-defined PCBM material (Scheme 1). However, even small variations in the size and shape of groups attached to the fullerene cage influence strongly the properties of these materials, including their electron acceptor ability in composites with polyconjugated polymers.

Fullerene compounds **1a**–**f** (Scheme 1) were synthesised according to the method developed by Hummelen *et al.*[9] for preparation of PCBM. The key precursor for the synthesis of these fullerene derivatives was 2-benzoylpropionic acid **2**, a much more available and less expensive compound than 3-benzoylbutyric acid **3** used for the preparation of PCBM. Benzoylpropionic acid esters **4a**–**f** were synthesised using standard procedures (Scheme 2) and easily converted to corresponding tosylhydrazones **5a**–**f**. Finally, **5a**–**f** were introduced into the reaction with [60]fullerene conducted in 1,2-dichlorobenzene as a solvent and using MeONa/pyridine for *in situ* generation of diazo compounds. The addition of the diazo compounds to the fullerene cage at low temperature (80–90 °C) is known to lead initially to the corresponding pyrazolidinofullerenes, which are very unstable and release N_2 to yield open-caged annulene-like compounds called fulleroids (like reported before for the open-caged isomer of [60]PCBM[9]). However, the closed-cage methanofullerenes are known to perform better in organic solar cells than open-caged fulleroids due to a difference in their electronic properties (LUMO level energies).[11] Therefore, the intermediate fulleroids were not isolated in this work and were converted to the closed-shell methanofullerenes by continuous heating at reflux in 1,2-dichlorobenzene (*ca.* 180 °C; 12 h). Finally, the solvent was removed on a rotary evaporator, and the solid residue was redissolved in carbon tetrachloride; the resulting solution was diluted with an equal amount of hexane and poured on a silica gel column. The unreacted fullerene was washed out during the solution deposition with a CCl_4–hexane (1:1) mixture. Further elution with pure CCl_4 afforded the fractions of desired methanofullerenes **1a**–**f**.



Scheme 2

The structural characterization of the prepared methanofullerenes was performed using NMR spectroscopy. The ^{1}H NMR and ^{13}C NMR spectra were obtained for all compounds, while the 2D C–H HSQC NMR spectra were obtained for selected fullerene derivatives (see Online Supplementary Materials). Note that the only admixtures occasionally detected in the prepared samples were isomeric open-caged fullereoids; a prolonged heating at reflux in 1,2-dichlorobenzene allowed us to get rid of these impurities in the methanofullerene samples.

Table 1 Reduction potentials of the methanofullerenes *vs.* SCE.

Compound	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$	$E^4_{1/2}$
1a	0.74	1.12	1.61	2.09
1b	0.74	1.12	1.61	2.09
1c	0.74	1.12	1.61	2.09
1d	0.76	1.16	1.67	2.17
1e	0.76	1.15	1.68	2.19
1f	0.78	1.17	1.67	2.29
PCBM	0.76	1.15	1.68	2.19

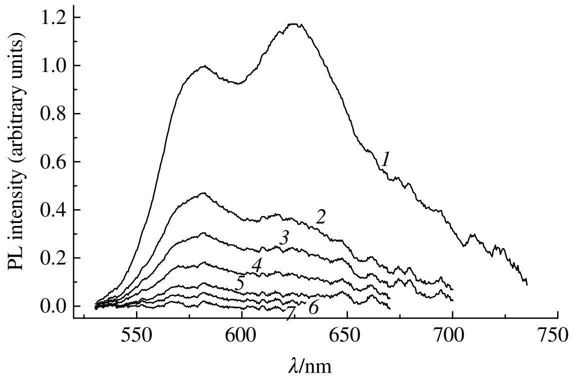


Figure 1 The quenching of MDMO-PPV photoluminescence by **1b**. The concentrations of **1b** in the films were (*1*) 0, (*2*) 0.26, (*3*) 0.5, (*4*) 1, (*5*) 2, (*6*) 4 and (*7*) 7.7 wt%.

All of the prepared methanofullerenes have very similar molecular structures to the commonly used PCBM material; therefore, one can expect that all properties of these compounds should also be similar. Indeed, the first reduction potentials (potentials at which monoanions are formed from the neutral molecules) of **1a**–**f** are virtually equal to that of PCBM (Table 1); therefore, all these fullerene acceptors have more or less the same electron affinities.

However, the side chains appended at the ester groups in **1a**–**f** have a strong influence on the physical properties of these compounds, such as solubility in organic solvents. Particularly, it ranges from *ca.* 5 mg cm^{-3} (R = Et) to > 200 mg cm^{-3} (R = Bu or $PhCH_2$) for chlorobenzene, which is the typically used solvent for active layer deposition in the fabrication of organic solar cells. It is supposed now that the solubility of photoactive materials can strongly affect the nanomorphology of their blend and hence the photovoltaic performance.

At the same time, organic addends attached to the fullerene cage can interact with the side chains of the donor polyconjugated polymer (van der Waals bondings); such non-covalent interactions can facilitate or, in contrast, complicate photoinduced charge separation that is a primary event responsible for the light harvesting in organic solar cells. An efficient photoinduced electron transfer from an excited state of a donor polymer to a fullerene acceptor always results in a strong (or virtually complete) quenching of the polymer photoluminescence (PL) in fullerene/polymer blends.[12]

We investigated the ability of compounds **1a**–**f**, PCBM and pristine C_{60} as a reference to quench the PL of poly(2-methoxy-5-{3′,7′-dimethyloctyloxy}-*p*-phenylene vinylene) (MDMO-PPV, Scheme 1) in thin films. A typical plot that illustrates the PL quenching of the polymer is shown in Figure 1. When excited at 450 nm, the films of pristine MDMO-PPV show a broad emission band with maxima at 580 and 625 nm. The PL

Table 2 Relative intensities (I/I_0) of a band at 585 nm band in the emission spectra of the MDMO-PPV films blended with different amounts of fullerene compounds.

Fullerene concentration (%)	Compound							
	1a	**1b**	**1c**	**1d**	**1e**	**1f**	PCBM	C_{60}
0	1	1	1	1	1	1	1	1
0.26	0.589	0.470	0.720	0.652	0.685	0.795	0.815	0.754
0.5	0.503	0.303	0.522	0.371	0.407	0.547	0.515	0.470
1	0.326	0.176	0.302	0.213	0.170	0.289	0.405	0.326
2	0.129	0.090	0.209	0.110	0.067	0.185	0.190	0.165
4	0.105	0.051	0.073	0.052	0.056	0.106	0.083	0.067
7.7	0.030	0.013	0.022	0.024	0.009	0.044	0.042	0.032

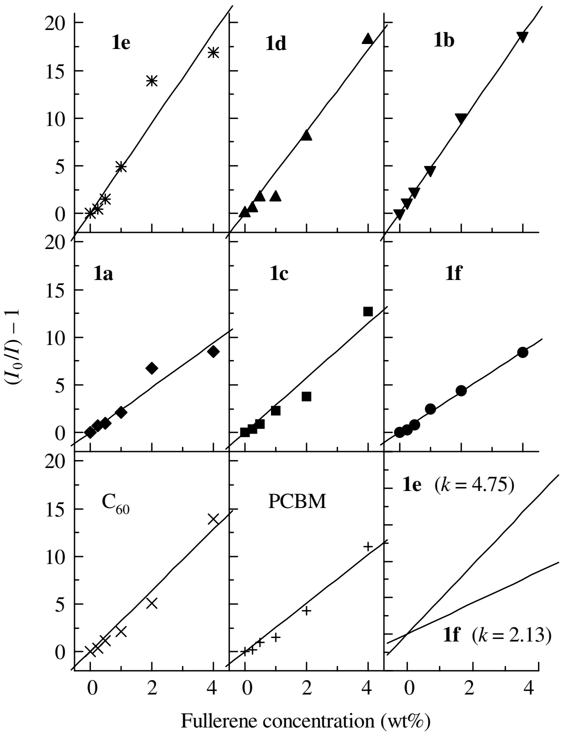


Figure 2 Stern–Volmer plots for polymer PL quenching by fullerene derivatives.

intensity decreases very strongly when just 0.2% of a fullerene or its derivative is mixed with the polymer (Figure 2). A further increase in the concentration of the fullerene acceptor in the blends results in more complete PL quenching; the MDMO-PPV luminescence becomes virtually undetectable by our instrument in the films with the fullerene content above 7%.

The relative intensities of the band at 580 nm (I/I_0, where I_0 is the intensity of this band in the spectrum of pristine polymer) in the emission spectra of the films with different fullerene contents are listed in Table 2 (the I/I_0–fullerene concentration plot is shown in supplementary materials). These data indicate that [60]fullerene and its derivatives exhibit considerably different PL quenching efficiencies.

For a quantitative evaluation of the quenching ability of various fullerene acceptors, we used the Stern–Volmer plot (Figure 2). The quenching factor Q defined by the equation $Q = (I_0/I) - 1$ was plotted against the fullerene concentration in the blends (C, wt%). The experimental points can be linearly fitted by the function $Q = kC$. The resulting linear fits are shown in Figure 2. The slopes k of such linear fits can be used for the quantitative characterization of the PL quenching ability of the fullerene compounds; higher values of k correspond to more efficient PL quenching. The calculated values of k are given in Table 3. Compounds **1e**, **1d** and **1b** (R = Bu, Pr and Et, respectively) are the most efficient quenchers of MDMO-PPV photoluminescence, while other compounds show significantly lower k values.

The electronic properties (electron affinities *etc.*) of **1a**–**f** and PCBM are very similar, as can be concluded from cyclic voltammetry data (Table 1). Therefore, other factors should be responsible for the different PL quenching abilities of these compounds. We assume that long and non-branched alkyl chains like in **1e**, **1d** and **1b** interact quite efficiently with MDMO-PPV side chains through the van der Waals bonding; hence, the activation energy of the photoinduced electron transfer can be significantly lowered for these compounds that is reflected in their superior PL quenching abilities. We believe that such a supramolecular approach to control the efficiency of photoinduced charge separation in the polymer–fullerene blends will allow one to improve further power conversion efficiencies in the plastic solar cells.

Table 3 Quenching abilities (k values) of **1a**–**f** and reference fullerene compounds derived from the Stern–Volmer plots shown in Figure 2.

Fullerene	k	Fullerene	k
1e	4.75	**1c**	2.87
1b	4.72	PCBM	2.56
1d	4.30	**1a**	2.36
C$_{60}$	3.21	**1f**	2.13

According to the preliminary results, the substituent modifications of fullerene acceptors **1a**–**f** scales the power conversion efficiencies of solar cells from very low (0.1%) to appreciably high values (> 3.5%). Some of the materials showed a better performance than PCBM in the tests under identical conditions.

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Online Supplementary Materials

Supplementary data associated with this article [list of ^{1}H and ^{13}C NMR shifts for all compounds, plots of ^{13}C NMR spectra for **1a**–**f**, 2D COSY and HSQC NMR spectra for **1e**, the plot I_0/I against C (fullerene) illustrating PL quenching abilities of different compounds] can be found in the online version at doi:10.1016/j.mencom.2007.05.015.

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