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COMMUNICATION

Fullerene Derivatives with Increased Dielectric Constant

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The invention of new organic materials with high dielectric constant is of extreme importance for development of organic-based devices such as organic solar cells. We report on a synthetic way to increase the dielectric constant of fullerene derivatives. It is demonstrated that introducing triethylene glycol monoethyl ether (TEG) side chains to fulleropyrrolidines increases the dielectric constant by ~ 46 percent without devaluation of optical properties, electron mobility and energy level of the compound.

The dielectric properties of molecular materials are crucial to a host of important phenomena, including enzyme function,[1] electron transfer,[2,3] chemical sensors[4,5] and a variety of electronic applications[6,7] such as in self-assembled nanoscale dielectric materials for gating thin-film transistors[8–10] as well as in thin interfacial extraction/blocking layers for organic light-emitting diodes and photovoltaic cells.[11–15] Yet, there are no common synthetic tools for affecting dielectric properties as there are, for example, for tuning band gaps, hydrophobicity, etc.

The dielectric constant, ε_r, expresses the quantity of electrical energy that can be stored in a material under an applied electric field and can be translated to the ability of a material to polarize in response to an applied field. Ceramics are traditionally known as materials with high dielectric constants, however, their limitations such as fragility, heaviness and low break down strength have drawn attention towards their organic counterparts, which are more flexible with better large-scale processability. Thus, efforts have been made to increase the ε_r of organic materials by blending inorganic, conductive fillers or electron-rich organic dopants[16,17] to polymers. However, this approach results in a high dielectric loss, reduces breakdown field strength and glass transition temperature. Attempts have been made to raise ε_r by introducing cyano[18] groups to polyimides, which increased ε_r from 3.16 to 3.73. Recently, a

polyacrylate was reported in which polar terthiophene groups, via the formation of nano-crystalline domains, dramatically increased ε_r across a wide range of frequencies.[19] If generalizable, this strategy could prove effective for non-conjugated polymers. Although there is nothing inherently wrong with the general strategy of installing polar pendant groups, a generalizable route to prepare high dielectric constant π-*conjugated* organic materials has proven elusive; e.g., what constitutes a polarizable pendant group and how strongly does it influence the properties of a conjugated material? Little focus has been devoted to improving dielectric constants in conjugated organic materials; there are only few examples of ε_r greater than 3–4 in these materials. A poly (*p*-phenylenevinylene) derivative bearing polar oligoethylene oxide side-chains (PEO-PPV) gave ε_r = 4 - 5.5[20] and fluorine atoms have been used to increase ε_r from 4.2 to 5.5.[21] We are particularly interested in conjugated organic materials with high values of ε_r for applications in organic photovoltaics (OPV). In a recent theoretical study, we showed that increasing ε_r reduces the exciton binding energy and recombination losses, making solar cells with power conversion efficiencies above 20% feasible.[22]

Although much research focuses on modifying the electronic, optical and solubility properties of fullerenes, increasing ε_r without sacrificing these properties is an important challenge in organic solar cells that has not yet been solved. This paper describes the improvement of the dielectric constant of fullerene derivatives by introducing polarizable side groups. We show that fulleropyrrolidines PTEG-1 and PTEG-2 (Figure 1) with triethylene glycol monoethyl ether (TEG) side chains exhibit a considerable increase in ε_r and excellent solubility in organic solvents without any significant changes to electron mobility, UV-vis absorption, and electrochemical properties.

Phenyl-C_{61}-butyric acid methyl ester (PCBM) is the most widely used fullerene acceptor in OPV devices, but fullerenes

in general are widely utilized as acceptors. Fulleropyrrolidines are easily prepared via the Prato method,[23] a 1,3-dipolar cycloaddition of an azomethineylide, generated in situ from the corresponding aldehyde and *N*-methylglycine. This methodology has proven to be a powerful procedure for the functionalization of C_{60} due to its versatility and the ready availability of the starting materials, while making methano[60]fullerenes has some limitations in terms of molecule design and method. For instance the preparation of ylides and, in particular, diazo compounds can be difficult.
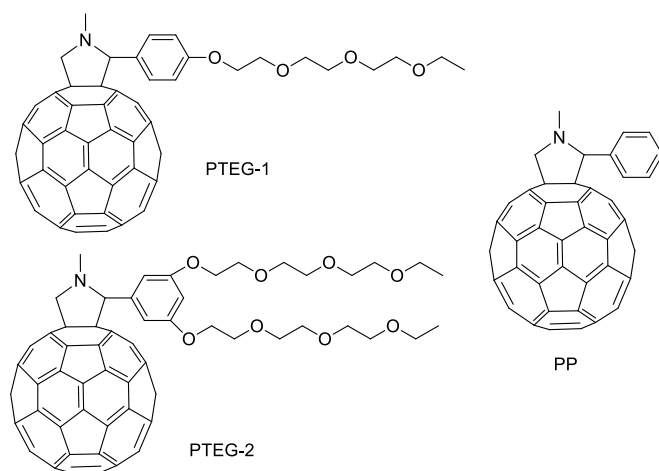

Figure 1. Chemical structure of PTEG-1, PTEG-2 and PP.

The synthetic route to prepare PTEG-1, PTEG-2 and PP is shown in Scheme S1 and detail of materials synthesis is shown in the supporting information (SI). For comparison, PP without TEG chains is also prepared (Figure 1).

The structures of the synthesized compounds were confirmed by analytical and spectroscopic data. The ^1H NMR spectra of PTEG-1 and PTEG-2, recorded in $CDCl_3$, exhibit the expected signals of a TEG moiety and the characteristic peaks of the pyrrolidine ring as two doublets (AB quartet) and one singlet as well as a singlet for the *N*-CH_3 group. In fulleropyrrolidines the signals of the *ortho*-hydrogen atoms of the phenyl group directly attached to the pyrrolidine ring appear as broad singlet at room temperature due to restricted rotation of phenyl group.

A notable feature of the fulleropyrrolidine PTEG-1 is its improved solubility compared to PCBM in wide range of organic solvents such as *o*-dichlorobenzene (ODCB), PhCl, $CHCl_3$, $PhCH_3$, and THF. For example, PCBM is reasonably soluble in $CHCl_3$ (~25 mg/ml), ODCB (~30 mg/ml) and $PhCH_3$ (10 mg/ml), but much less soluble in THF, while PTEG-1 is easily dissolved in ODCB (~65 mg/ml), $CHCl_3$ (~45 mg/ml), $PhCH_3$ (~36 mg/ml) and THF (~15 mg/ml). This enhancement of solubility is not only an important property for the fabrication of electronic devices, but also opens the possibility of using sustainable and/or less harmful solvents. PTEG-2, with two TEG chains, shows even better solubility in organic solvents.

The UV-vis absorption spectra of compounds PTEG-1 and PTEG-2, together with that of reference compound PP, in 10^{-5} M $CHCl_3$ is shown in Figure S1 in the SI. C_{60} derivatives generally display strong absorption in the UV region and broad, weak absorption in visible region. The absorption of PTEG-1 and PTEG-2 is almost the same as PP, especially the characteristic peak of fullerene moiety at 430 and 704 nm. This similarity indicates that TEG chains do not have any significant effect on the fulleropyrrolidine chromophore, in solution.

The electrochemistry of fullerenes is one of their most important properties as conjugated materials. Therefore, we investigated the electrochemical properties of PTEG-1 and PTEG-2 by cyclic voltammetry. We also studied PP and PCBM for comparison (SI Figure S2). The measured half-wave potentials of the reduction processes of all compounds are listed in Table 1. The first reduction potential, which approximates the LUMO energy level of these compounds, is almost the same for PTEG-1, PTEG-2, and the controls, PP and PCBM. This similarity implies that TEG chains do not affect the LUMO energy of fullerene derivatives (because they do not shift the reduction potentials). In addition, there is no significant change in the potential of the second reduction.

Table 1. Electrochemical properties, ε_r and electron mobility (μ_e) of PTEG-1, PTEG-2 and PP

Compound	$E_{1/2}$ 1, red[a]	$E_{1/2}$ 2, red[a]	ε_r	μ_e[cm²/Vs]
PCBM	-1.092	-1.482	3.9 ± 0.1	2×10⁻⁷
PTEG-1	-1.113	-1.511	5.7 ± 0.2	2×10⁻⁷
PTEG-2	-1.106	-1.504	5.3 ± 0.2	3.5×10⁻⁷
PP	-1.114	-1.508	3.6 ± 0.4	-[b]

[a]V vs Fc/Fc+ [b] Insufficient film quality.

It is well known that, as polarizability increases, the dielectric constant increases, and the more available polarization mechanisms a material possesses, the larger the dielectric constant. We expected the addition of TEG chain(s) to fullerenes to increase the relative permittivity of fullerene compound by increasing the mechanisms of polarization via the reorientation of the dipole moments of the ethers in TEG.

We investigated the dielectric properties of the fullerene derivatives presented in this paper by spectral impedance measurements. The average values obtained for the dielectric constant of PTEG-1, PTEG-2, PP and PCBM, upon equivalent circuit (SI Figure S4) fitting over the frequency range of 100Hz-1MHz, are shown in Table 1. Interestingly, the dielectric constant for both PTEG-1 and PTEG-2 increased significantly to 5.7 and 5.3 respectively, in comparison to PCBM (ε_r~3.9) and PP (ε_r~3.6). The determined dielectric constant for all three compounds is constant from 100 to 10^6 Hz (Figure 2). This enhancement of the dielectric properties clearly shows the influence of the increased polarizability afforded by TEG side chains. The measured dielectric constants of PTEG-1 and PTEG-2 differ only by the sum of their standard deviations. This observation is counterintuitive, because one might expect

that two TEG moieties per molecule would have a greater influence than one. We therefore tentatively conclude that the measured permittivity results from a complex interplay between the fullerene cages and their substituents and is not simply a result of increasing the volume fraction of glycol units in the film. This situation is quite different from that of the addition of macroscopic high-k fillers.

Having already determined that the optical HOMO/LUMO gap and the absolute position of these orbitals (from reduction potentials) are unaffected by the inclusion of TEG chains, we investigated the electron mobility of films of the fullerene derivatives by measuring the current-voltage characteristics of electron-only devices with the following architecture at room temperature: Au/fullerene derivative/LiF/Al. The experimental J-V curves show that current density quadratically depends on the voltage, which is a characteristic behavior for space-charge limited current (SCLC).[24] The J-V curves of PTEG-1 and PTEG-2 are shown in Figure S5 corrected for built-in voltage of V_{bi}=0.5 V and 0.05 V, respectively.

We found similar values for the electron mobility of the fullerenes with single and double TEG side chains (PTEG-1 and PTEG-2), PCBM of $\sim 2 \times 10^{-7}$ m^2/Vs (Table 1). Thus, in addition to the electro-optical properties of the molecules being unaffected by inclusion of TEG chains, their bulk electron mobility did not change with respect to that of the benchmark fullerene derivative, PCBM.
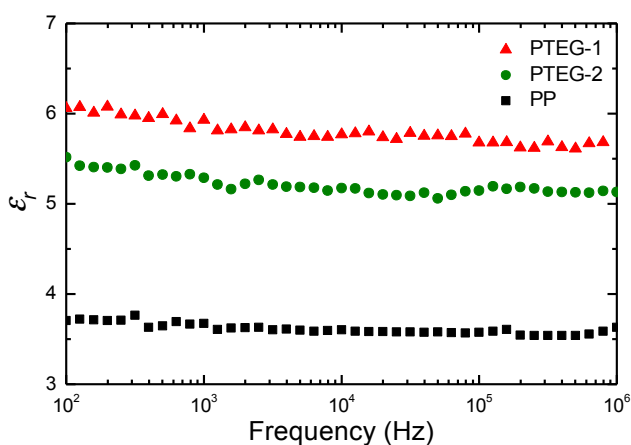

Figure 2. Dielectric constant versus frequency at room temperature for PTEG-1, PTEG-2 and PP.

In conclusion, we synthesized fullerene derivatives with dielectric constants significantly higher than C_{60} and PCBM, without negatively impacting molecular properties (optical absorption and reduction potentials) as well as bulk properties (electron mobility). Our strategy of increasing polarizability by including TEG chains also improved the solubility compared to PCBM in a wide range of organic solvents. This work is one of the first efforts unambiguously demonstrating a synthetic route for the orthogonal tuning the dielectric constant (a bulk property) of a conjugated organic material. This orthogonality is critical to the tailoring of high-dielectric-constant materials

because it precludes the need to balance the negative impacts of simpler strategies such as the inclusion of additives and the re-optimization of each combination of material/additive. While there are scattered reports of small increases in the dielectric constant of conjugated polymers through the inclusion of polar pendant groups, the strategy presented in this paper opens up new opportunities to improve the power conversion efficiencies of heterojunction OPV devices without perturbing HOMO/LUMO energies or electron mobility of fullerene acceptors. Ultimately this strategy of synthetically manipulating the dielectric properties of materials may lead to single-component, non-excitonic OPV devices.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental methods, synthetic routes, UV spectra, dielectric constant and mobility measurements, electrochemical properties and NMR spectra. See DOI: 10.1039/c000000x/

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