Alternative acceptor materials for organic photovoltaic cells

Troisi L.,[1] Bona F.,[1] Citti C.,[1] Giancane G.,[2] Granito C.,[1] Liu T.,[3] Troisi A.[3]

[1] Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Organic Chemistry Laboratory, University of Salento, via Monteroni, 73100 Lecce, Italy. Corresponding author: luigino.troisi@unisalento.it
[2] Dipartimento di Beni Culturali, Università del Salento, via Dalmazio Birago, 73100 Lecce, Italy.
[3] Department of Chemistry and Centre for Scientific Computing University of Warwick, Coventry CV4 7AL, UK.

Abstract

Synthesis and spectroscopic characterization of perylene derivatives (perylene monoimides and diimides) are reported. The aim of the present work is to investigate the synthesis of these compounds in detail in order to highlight the crucial factors for obtaining a specific class of molecules. The final compounds of the synthetic pathway would be able to mimic the peculiar properties of fullerene derivatives, up to now the best candidates as accepting materials.

Introduction

Organic photovoltaics (OPV) is a young technology that was developed in recent decades[1] and has encouraged scientists to continue their efforts towards new classes of solar cells. Up to now fullerenes have been the best candidate as accepting materials because of their very low lying excited states of their anion[2].

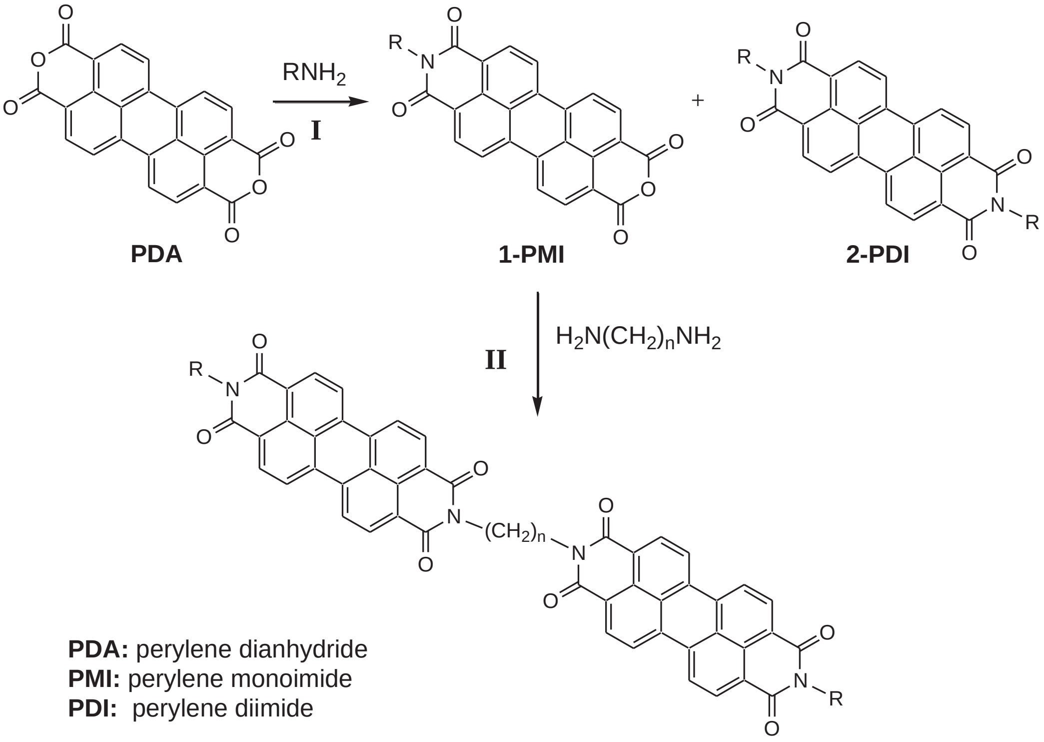
In this work we have designed and synthesized new accepting molecules that mimic the properties of fullerenes and can therefore substitute them in the development of alternative acceptors to be applied in new OPV cells.

The aim of the present study was to build a class of molecules with a “designed” degeneracy of the LUMO levels. A strategy to generate electron acceptors with quasi degenerate LUMOs may also be to connect identical conjugated electron acceptors through non-conjugated alkyl links. Changing the acceptor and the link it is possible to modulate the energy levels and their separation.

The new family of proposed acceptors is both easily accessible synthetically and virtually unrelated to any of the current attempts of matching the fullerene properties with different chemistries.

To realize our idea we have limited the synthetic work to a single class of compounds which includes one or more sp^3 carbon or nitrogen-based molecules coordinated to two identical acceptors (P) with the general formula $(CH_2)_nP_2$.

A possible approach to the realization of this synthesis involves perylene as the central core of the acceptor. Scheme 1 illustrates the general synthetic pathway we followed.



PDA: perylene dianhydride
PMI: perylene monoimide
PDI: perylene diimide

Scheme 1

The perylene derivatives are good fullerene mimic candidates showing the following strategic properties:

- large molar adsorption coefficients;
- good electron accepting properties[3];
- possible generation of highly conducting direction along the π-π stacking axis[4];
- robust, thermal stable, inexpensive[5]

Materials and methods

All used reagents were of commercial grade and used without any further purification.

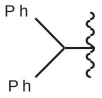
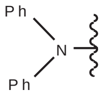
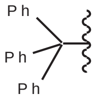
^{1}H and the ^{13}C NMR spectra were recorded with a Bruker Avance 400 apparatus (400.13 and 100.62 MHz, for ^{1}H and ^{13}C, respectively) with $CDCl_3$ as solvent and TMS as internal standard (δ = 7.26 ppm for ^{1}H spectra; δ = 77.0 ppm for ^{c}C spectra). FT-IR spectra were acquired with a Perkin Elmer Spectrum On spectrophotometer and the analysis were performed on solid samples. UV-Vis spectra were recorded with an Agilent Cary 5000 spectrophotometer using CH_2Cl_2 as solvent. Fluorescence emission spectra were acquired with a Perkin Elmer LS55 fluorimeter using CH_2Cl_2 as solvent and a polychromatic incident beam.

N-alkyl-perylene-3,4,9,10-tetracarboxylic monoimide (**1-PMI**) and *N,N'*-dialkyl-perylene-3,4,9,10-tetracarboxylic diimide (**2-PDI**) were synthesized following Dincalp's et al. methodology[6], but slightly modified. In a 50 ml fask primary amine (10.0 mmol), $Zn(AcO)_2$ (1.0 mmol), perylene-3,4:9,10-tetracarboxylic dianhidride (1.0 mmol) and quinoline (8 ml) were poured and stirred at reflux temperature of 210°C over night under a nitrogen atmosphere. The reaction mixture was poured into 160 ml of methanol/10% hydrochloric acid solution (V/V = 2/1) under stirring. The solid precipitate was filtered off and stirred in 40 ml of cold Na_2CO_3 solution (10%) for 2 hours. The precipitate was filtered off again and washed several times with water until the solid was colorless. The crude product was purified by silica gel column chromatography using methylene chloride as eluent.

Results and Discussion

The stage **I** (Scheme 1) was carried out according to a modified version of the methodology reported by Dincalp et al[6]. *N*-Alkyl-perylene-3,4,9,10-tetracarboxylic monoimide (**1-PMI**) and *N,N'*-dialkyl-perylene-3,4,9,10-tetracarboxylic diimide (**2-PDI**) were synthesized from perylene 3,4,9,10-tetracarboxylic dianhydride (**PDA**) by reaction with a primary amine in a $Zn(OAc)_2$ and quinoline (8 mL) solution. The obtained results are reported in Table 1.

Table 1: synthesis of *N*-alkyl-perylene-3,4:9,10-tetracarboxylic monoimide (**1-PMI**) and N,N'-bis-alkyl-perylene-3,4:9,10-tetracarboxylic diimide (**2-PDI**).

Entry	R	Products distribution (%)[a]		Total Yield (%)[a]
		PMI	PDI	
1		**1a** (27)	**2a** (73)	22
2		**1b** (33)	**2b** (67)	9
3		**1c** (36)	**2c** (64)	14

[a] Products distribution and total yield calculated on isolated products.

The low PMI yield recovered with this synthetic protocol did not allow us to perform the stage **II** for preparing the goal compounds $(CH_2)_nP_2$ (Scheme 1). Zafer et al.[7] reported the preparation of PMI through the PDI hydrolysis with KOH in *tert*-butanol. The hydrolysis of **2a**, using Zafer's conditions, gave a mixture of products whose separation was difficult. Therefore, we thought to modify Dincalp's methodology slightly changing the reagents stoichiometric ratios. In detail, the reagents used were: primary amine (0.2 mmol), $Zn(AcO)_2$ (1.0 mmol), perylene-3,4,9,10-tetracarboxylic dianhydride (1.0 mmol), quinoline (20 ml). The reaction mixture was stirred at reflux temperature of 210°C for 15h under a nitrogen atmosphere. The 90% of quinoline was removed by distillation under vacuum and the remained solution was treated with 20 ml of methanol/10% hydrochloric acid solution (V/V = 2/1) under stirring. The solid precipitate was washed with 5 ml of cold Na_2CO_3 solution (10%) and several time with water until the solid was colorless. The crude product was purified by silica gel column chromatography using methylene chloride as eluent. The pure PMI and the pure PDI were isolated with a total yield of 68% in a ratio of PMI/PDI = 62/38.

The pure products were characterized by ^1H, ^{13}C NMR and FT-IR spectroscopy. Moreover, UV-Vis absorption and Fluorescence emission measurements were performed (*Figures 1* and *2*).

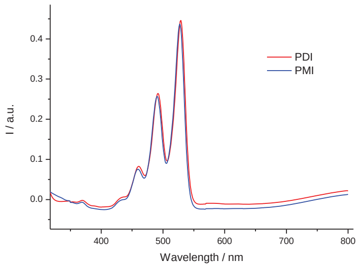


Figure 1. PDI (red) and PMI (blue) UV-Vis absorption spectra at the concentration of 12.5 µM.

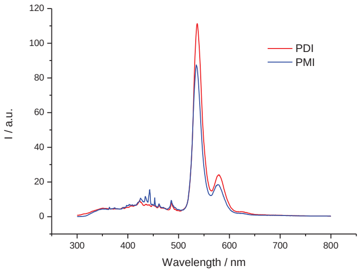


Figure 2. PDI (red) and PMI (blue) fluorescence emission spectra at the concentration of 0.1 µM.

The Fluorescence spectra showed that PDI has a fluorescence quantum yield much higher than PMI.
The bigger fluorescence of PDI due to the presence of two aromatic units compared to the PMI compound give a further contribution to their characterization.

The following step will be the reaction between **1a-PMI** and $H_2N(CH_2)_2NH_2$ (1,2-ethanediamine) in NMP (N-methylpyrrolidinone) in order to obtain the final compound of the general formula $(CH_2)_2P_2$.

Conclusions

An efficient synthesis for PMI has been developed giving an alternative pathway to the known methodology and allowing good yields of the desired product.
The final compound should be tested in combination with a donor in organic solar cells.
Once its activity is evaluated the class of compounds can be extended to many other molecules of similar typology to be applied in organic photovoltaic field.

References

[1] Tang, C. W. (Eastman Kodak Co., USA). Application: US1980-119328.
[2] Closs, G.; Miller, J.; *Science* (1988), 240, 440-447.
[3] Neuteboom, E. E.; Meskers, S. C. J.; Van Hal, P. A.; Van Duren, J. K. J.; Meijer, E. W.; Janssen, R. A. J.; Dupin, H.; Pourtois, G.; Cornil, J.; Lazzaroni, R.; Bredas, J. L.; Beljonne, D.; *J. Am. Chem. Soc.* (2003), 125, 8625.
[4] Boom, T.; Hayes, R. T.; Zhao, Y.; Bushard, P. J.; Weiss, E. A.; Wasielewski, M. R.; J. Am. Chem. Soc. (2002), 124, 9582.
[5] Liu, S. G.; Sui, G.; Cormier, R. A.; Leblanc, R. M.; Gregg, B. A.; *J. Phys. Chem. B*; (2002), 106, 1307.
[6] Dincalp, H.; Avcibasi, N.; Icli, S.; *J. Photoch. Photobio. A* (2007), 185, 1-12.
[7] Zafer, C.; kus, M.; Turkmen, G.; Dincalp; Demic, S.; Kuban, B.; Teoman, Y.; Icli, S.; *Sol. Energ. Mat. Sol. C.* (2007), 91, 427-431.