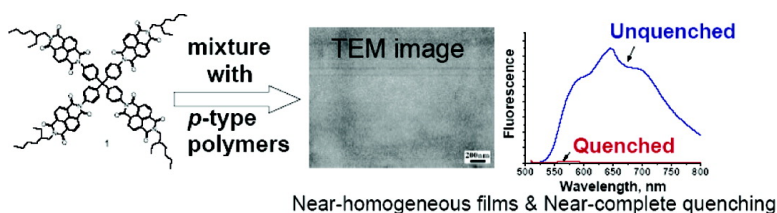


Tetrahedral *n*-Type Materials: Efficient Quenching of the Excitation of *p*-Type Polymers in Amorphous Films

Palaniswamy Ganesan, Xiaoniu Yang, Joachim Loos, Tom J. Savenije, Ruben D. Abellon, Han Zuilhof, and Ernst J. R. Sudhler

J. Am. Chem. Soc., **2005**, 127 (42), 14530-14531 • DOI: 10.1021/ja053689m • Publication Date (Web): 30 September 2005

Downloaded from <http://pubs.acs.org> on March 25, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 10 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Tetrahedral *n*-Type Materials: Efficient Quenching of the Excitation of *p*-Type Polymers in Amorphous Films

Palaniswamy Ganesan,^{†,§} Xiaoniu Yang,^{¶,§} Joachim Loos,[¶] Tom J. Savenije,[‡] Ruben D. Abellon,[‡] Han Zuilhof,^{*,†} and Ernst J. R. Sudhölter[†]

Laboratory of Organic Chemistry, Wageningen University, Dreijenplein 8, 6703 HB Wageningen, The Netherlands, Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, The Netherlands, Materials and Interface Chemistry, Eindhoven University of Technology, PO Box 513, Helix STO 0.41, 5600 MB Eindhoven, The Netherlands, and Opto-Electronic Materials Section, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands

Received June 6, 2005; E-mail: Han.Zuilhof@wur.nl

Recently, there has been a surge in the efforts directed to the development of all-organic solar cells.¹ Basically, two types of such solar cells have been envisaged: (1) *p*-*n* double layer cells, in which two layers of *p*- and *n*-type materials are deposited on top of each other;² and (2) bulk heterojunction cells, in which the *p*-type and *n*-type materials are blended, so as to form a bicontinuous phase to allow charge transport to both electrodes.³ The most well-known of these latter types of cells are based on a polymeric *p*-type material, such as MDMO-PPV and bucky-ball derivatives. The success of these devices⁴ hinges on many aspects, including proper energetics between *p*-type and *n*-type material, excellent light-absorbing properties of the *p*-type material, and an appropriately small degree of phase separation to obtain a bicontinuous phase. Limitations include (a) phase separation of the *n*-type material, which requires high amounts of the bucky-ball derivatives (~80 wt %) to obtain the optimal bicontinuous phase, (b) limited visible light absorption by C₆₀ derivatives,⁵ and (c) the fact that the ball-shape of the bucky ball that allows charge transport in nearly all directions with equal probability is intrinsically linked to its optical absorption properties and is therefore hard to improve systematically.

The present paper presents preliminary data of a new approach, in which the shape of the *n*-type material that yields the amorphous properties⁶ is decoupled from its optoelectronic properties, thus allowing a systematic improvement of the latter. This approach uses the nondirectionality available via tetrahedral cores, such as those of tetraphenyl methane. We present the first steady-state and transient optical and ground-state electrochemical properties of a novel *n*-type material, **1**,^{7,8} together with morphology and transient charge carrier studies of films of polymeric *p*-type materials and **1**.

Figure 1 presents relevant optical properties of this material in CHCl₃ solution. Basically, both the absorption (0.7 μM) and fluorescence (0.7 μM) are nearly identical to those of a model compound, *N*-phenyl-*N'*-(2-ethylhexyl)naphthalenediimide (**2**). Interestingly, at higher concentration (7 μM), the excitation spectrum of **1** shows the formation of ground state complexes that give rise to complex fluorescence with λ_{max} ~ 470 nm, which is absent at lower concentrations. Such ground state complex formation is also evident from absorption spectra at higher concentrations. This complex formation is likely advantageous for charge transport, as it indicates π-π interactions between adjacent molecules of **1**.

The Franck-Condon excited state of **1** rapidly (<1 ps)⁹ decays to a long-lived triplet state (τ = 859 ns), the absorption of which

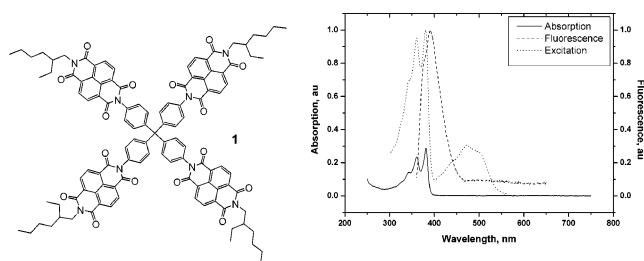


Figure 1. Structure and optical properties of **1**.

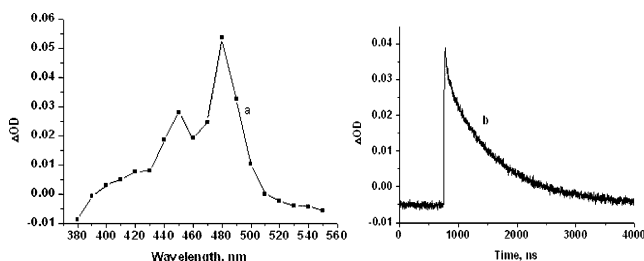


Figure 2. Transient absorption spectrum and decay of the T₁ state of **1**. (a) Transient absorption spectra 40 ns after the excitation pulse (λ_{exc} = 355 nm). (b) Decay profile of the transient at 480 nm.

is presented in Figure 2. This spectrum closely resembles triplet absorption spectra of *N,N'*-dialkyl-naphthalenediimides.¹⁰

The fully reversible electron-accepting properties of aromatic diimides¹¹ (for **1**, $E_{red}^1 = -1.23$ V and $E_{red}^2 = -1.72$ V vs Fc/Fc⁺ in CHCl₃) and a long-lived triplet state open the way to effective quenching of their excited states by electron donors, such as MDMO-PPV, and for the quenching of the excited states of such donors. The latter process occurs effectively in solution, which prompted us to study it in thin films of 50% MDMO-PPV and 50% of **1** (percentages by weight) spin-coated from chlorobenzene. The results of this quenching study are depicted in Figure 3 and show that **1** quenches the fluorescence of MDMO-PPV by 99% in film. This is linked to the near-homogeneity of the resulting films spin-coated from chlorobenzene, as observed in bright-field transmission electron microscopy (BF-TEM). A 50/50 wt % mixture of MDMO-PPV and **1** spin-coated from CHCl₃ does only yield ~70% fluorescence quenching and clearly displays inhomogeneous pocket formation at ~50 nm scale (Figure 4, left). Only upon spin-coating from chlorobenzene films are formed that show homogeneity on this scale (Figure 4, right), as also required for successful blends of MDMO-PPV and C₆₀ derivatives.^{3a} Even better observations were made for quenching of poly-(3-hexylthiophene) [P3HT] (50/50 wt %), another *p*-type polymer frequently used for all-organic

[†] Wageningen University.

[§] Dutch Polymer Institute.

[¶] Eindhoven University of Technology.

[‡] Delft University of Technology.

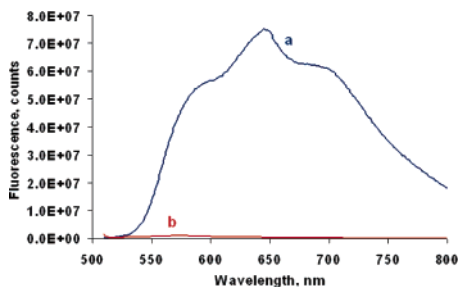


Figure 3. Fluorescence quenching of MDMO-PPV by **1** in a thin film. (a) Fluorescence of pure MDMO-PPV film, and (b) 50/50 wt % mixture of MDMO-PPV and **1**, spin-coated from chlorobenzene.

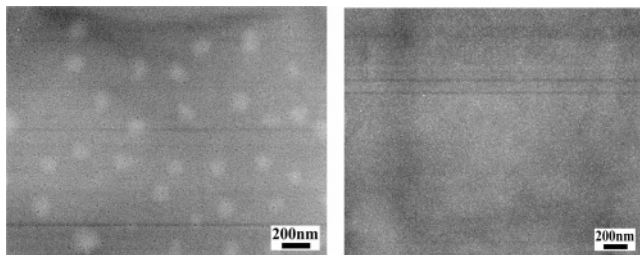


Figure 4. BF-TEM images show the detailed morphology of thin films containing mixtures of MDMO-PPV and **1**, spin-coated from chloroform (left) and chlorobenzene (right), respectively.

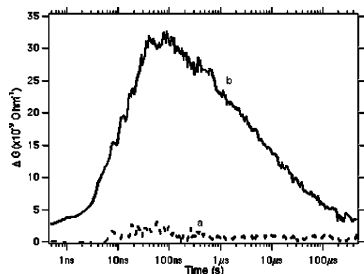


Figure 5. Change in conductivity, ΔG , obtained from FP-TRMC measurements ($\lambda_{\text{exc}} = 500$ nm, intensity = $28 \mu\text{J}/\text{cm}^2$ per pulse) for films of (a) pure P3HT and (b) 1:1 mixture of P3HT and **1**.

optoelectronic studies;¹² upon spin-coating from CHCl_3 and chlorobenzene, near-complete quenching of P3HT fluorescence by **1** was observed.

This prompted us to directly study the formation of transient charge carriers and their lifetimes in films of polymeric *p*-type materials and **1**. This can be accomplished via flash photolysis time-resolved microwave conductivity measurements (FP-TRMC).¹³ FP-TRMC probes the amount and mobility of charge carriers formed upon excitation with a short laser pulse (pulse fwhm = 4 ns; $\lambda_{\text{exc}} = 500$ nm) via the time-resolved absorption of microwaves that are passed through the irradiated sample. As an example of the versatility of our approach, we present in Figure 5 the change in conductance observed for a mixture of **1** with P3HT.

As obvious from Figure 5, pulsed excitation leads to near-instantaneous, highly efficient formation of long-lived charge carriers, with lifetimes in the order of tens of microseconds. Using 3 MeV electron pulses, a maximum one-dimensional mobility of $0.03 \text{ cm}^2/\text{V}\cdot\text{s}$ was measured,¹⁴ which is very high for an amorphous material and displays effective charge transfer between adjacent molecules of **1**. In other words, by use of a tetrahedral framework,

the nondirectionality required for optimal charge separation in a film and for charge transport through a film can be obtained. This approach can be optimized by variation of the aromatic diimides or other *n*-type materials with more extended π -systems. This can be done without compromising the nondirectionality that is essential for amorphous blends, while yielding layers with an absorption spectrum that overlaps better with the solar emission spectrum. As such, this approach adds significant flexibility to the construction of amorphous blends of *n*-type and *p*-type materials for optoelectronic devices, such as all-organic solar cells. Further studies with a variety of tetrahedral *n*-type materials in combination with a variety of *p*-type polymers are currently ongoing in our laboratories.

Acknowledgment. The authors thank the Dutch Polymer Institute (Functional Polymer Systems, Project 324) for financial support, Dr. Marc Koetse (TNO Industries, Eindhoven) for supplying the MDMO-PPV, Dr. Martijn Wienk (TU Eindhoven) for many stimulating discussions, and Barend van Lagen for spectroscopic assistance.

Supporting Information Available: Synthesis and characterization of **1** and **2** (6 pages, print/PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Nelson, J. *Curr. Opin. Solid State Mater.* **2002**, *6*, 87–95. (b) Gregg, B. J. *Phys. Chem. B* **2003**, *107*, 4688–4698. (c) Brabec, C. J. *Sol. Energ. Mater. Sol. C* **2004**, *83*, 273–292. (d) Hoppe, H.; Sariciftci, N. S. *J. Mater. Res.* **2004**, *19*, 1924–1945. (e) Sun, S.; Fan, Z.; Wang, Y.; Haliburton, J. *J. Mater. Sci.* **2005**, *40*, 1429–1443.
- (2) Hayashi, Y.; Yamada, I.; Takagi, S.; Takasu, A.; Soga, T.; Jimbo, T. *Jpn. J. Appl. Phys.* **2005**, *44*, 1296–1300.
- (3) (a) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15–26. (b) Svensson, M.; Zhang, F.; Veenstra, S. C.; Verhees, W. J. H.; Hummelen, J. C.; Kroon, J. M.; Inganäs, O.; Andersson, M. R. *Adv. Mater.* **2003**, *15*, 988–991.
- (4) Shaheen, S. E.; Brabec, C. J.; Sariciftci, N. S.; Padinger, F.; Frommertz, T.; Hummelen, J. C. *Appl. Phys. Lett.* **2001**, *78*, 841–843.
- (5) (a) Efforts to overcome this latter limitation have recently been published by Hummelen and co-workers using C_{70} derivatives, which are very expensive. (b) Wienk, M. M.; Kroon, J. M.; Verhees, W. J. H.; Knol, J.; Hummelen, J. C.; van Hal, P. A.; Janssen, R. A. *J. Angew. Chem., Int. Ed.* **2003**, *42*, 3371–3375.
- (6) Shirota, Y. *J. Mater. Chem.* **2005**, *15*, 75–93.
- (7) (a) Preliminary studies on tetrahedrally shaped *p*-type materials for OLEDs have been published (ref 7b), but to the best of our knowledge, no studies of any *p*-*n* mixture using tetrahedrally shaped materials have, as of yet, been reported. (b) Wang, S.; Oldham, W. J., Jr.; Hudack, R. A., Jr.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695–5709.
- (8) (a) Synthetic details are in Supporting Information, along routes developed by Neugebauer and Langhals. (b) Neugebauer, F. A.; Fischer, H.; Bernhardt, R. *Chem. Ber.* **1976**, *109*, 2389–2394. (c) Langhals, H.; Wagner, C.; Ismael, R. *New J. Chem.* **2001**, *25*, 1047–1049.
- (9) Ganesan, P.; Zhang, H.; Zuilhof, H.; Sudhölter, E. J. R. Unpublished results.
- (10) Green, S.; Fox, M. A. *J. Phys. Chem.* **1995**, *99*, 14752–14757.
- (11) (a) Abraham, B.; McMasters, S.; Mullan, M. A.; Kelly, L. A. *J. Am. Chem. Soc.* **2004**, *126*, 4293–4300. (b) Struijk, C. W.; Sieval, A. B.; Dakhorst, J. E. J.; van Dijk, M.; Kimkes, P.; Koehorst, R. B. M.; Donker, H.; Schaafsma, T. J.; Picken, S. J.; van de Craats, A. M.; Warman, J. M.; Zuilhof, H.; Sudhölter, E. J. R. *J. Am. Chem. Soc.* **2000**, *122*, 11057–11066.
- (12) (a) Schilinsky, P.; Waldauf, C.; Brabec, C. J. *Appl. Phys. Lett.* **2002**, *81*, 3885–3887. (b) Padinger, F.; Rittberger, R. S.; Sariciftci, N. S. *Adv. Funct. Mater.* **2003**, *13*, 85–88. (c) Yang, X. N.; Loos, J.; Veenstra, S. C.; Verhees, W. J. H.; Wienk, M. M.; Kroon, J. M.; Michels, M. A. J.; Janssen, R. A. *J. Nano Lett.* **2005**, *5*, 579–583. (d) Kim, Y.; Choulis, S. A.; Nelson, J.; Bradley, D. D. C.; Cook, S.; Durrant, J. R. *J. Mater. Sci.* **2005**, *40*, 1371–1376.
- (13) Kroeze, J. E.; Savenije, T. J.; Vermeulen, M. J. W.; Warman, J. M. *J. Phys. Chem. B* **2003**, *107*, 7696–7705.
- (14) (a) Measuring frequency of 30 GHz. (b) Schouten, P. G.; Warman, J. M.; de Haas, M. P. *J. Phys. Chem.* **1993**, *97*, 9863–9870.

JA053689M