

High Charge Mobility of a Perylene Bisimide Dye with Hydrogen-bond Formation Group

Jing Zhi SUN*

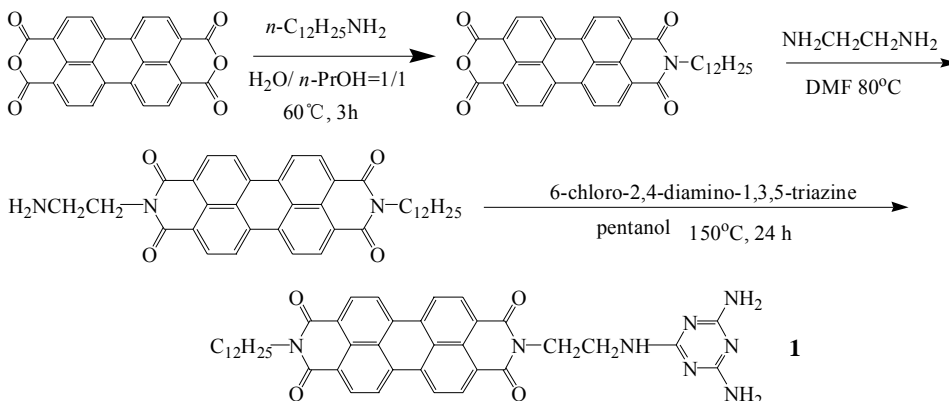
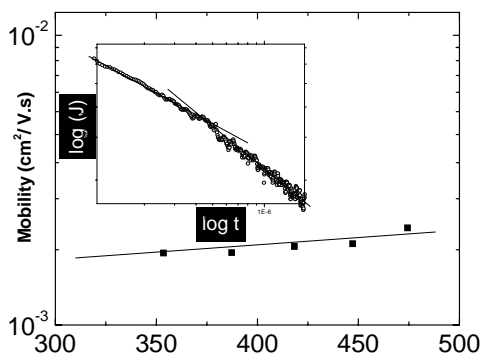
Department of Polymer Science & Engineering and State Key Laboratory for Silicon Materials,
Zhejiang University, Hangzhou 310027

Abstract: A perylene bisimide dye covalently bonded with a hydrogen-bond formation group of 1, 3, 5-triazine-2, 4-diamine has been synthesized. Its casting films show a charge carrier mobility over 10^{-3} cm^2/Vs , which is in the range of the highest values found for other promising charge transport materials suitable for solution processable technique.

Keywords: Mobility, perylene bisimide, casting film.

Charge carrier mobility is one of the most important parameters concerning the performance of organic electronic devices¹. High mobility usually leads to high calculation speed in computer and high short-circuit current in organic solar cells. Unfortunately, the intrinsic charge mobilities for organic semiconductors are of orders of magnitude lower than amorphous silicon. As a promising *n*-type organic semiconductor, *N,N'*-*n*-alkyl-perylene bisimides have shown their electron mobility to be up to 10^{-1} cm^2/Vs^2 , but these results are recorded only in smectic discotic liquid crystal phases, which are usually impractical in the fabrication of large-area films with convenient solution processable techniques. Polymeric perylene bisimides allow of good processability, but their characteristic amorphous state leads to low charge mobilities in the same level as those found in conjugated polymers (10^{-5} - 10^{-7} cm^2/Vs)^{3,4}. Recently, self-assembling methodology based on hydrogen-bond (H-bond) has been used in the construction of well-ordered structures containing perylene bisimide chromophores and their photoinduced charge transfer process and photoluminescent properties have been investigated^{5,6}, no reports so far describe the charge mobility of thin films of perylene bisimide derivatives fabricated by using H-bond constituents. In consideration that the well-ordered structure is crucial for charge carrier transportation, we prepared a perylene bisimide derivative with a 1, 3, 5-triazine-2, 4-diamine function group, which provides H-bonds interactions between molecules, the electron mobility of solution cast films was investigated with time of flight (TOF) technique.

* E-mail: sunjz@zju.edu.cn

Scheme 1 Synthetic route towards compound **1****Figure 1** Electric field dependent charge mobility of perylene bisimide **1** for casting films, inset shows a typical transient conductivity signal.

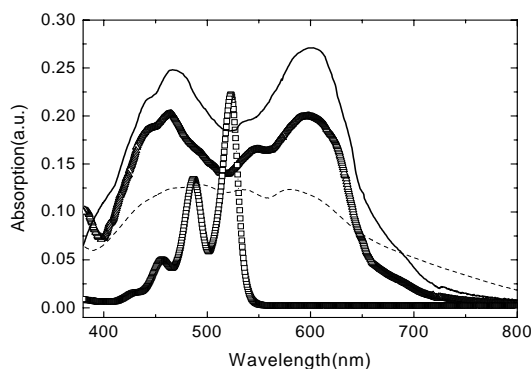
The final perylene bisimide **1** (**Scheme 1**) was derived from a two-step condensation of perylene-3, 4, 9, 10-tetracarboxylic dianhydride with dodecylamine and ethylenediamine in sequence and a nucleophilic replacement of N-dodecyl-N'-β-aminoethyl-3, 4, 9, 10-tetracarboxylic-bisimide with 6-chloro-2, 4-diamino-1, 3, 5-triazine. The characterization data are included in the note⁷. Thin films were fabricated by solution casting onto ITO (indium tin oxide) coated glass substrates, the solution was prepared by dissolving 200 mg of compound **1** in tetrahydrofuran/chloroform mixture (1/1 by volume). As a comparison, thin films were also fabricated by vapor deposition of **1** on ITO coated glass in a rate of about -2 \AA/s in high vacuum. After deposition an aluminum electrode (in thickness of 150 nm) on the organic layer, the charge mobilities were measured by using a standard TOF technique. The wavelength of the excitation light is 532nm and the duration of the laser pulse is 5 ns.

The data of the charge mobility obtained from solution casting films in thickness of 2 μm are displayed in **Figure 1**. At room temperature, a mobility of $1\text{-}2 \times 10^{-3} \text{ cm}^2/\text{Vs}$ was recorded under the electric field of 1×10^5 to $2.5 \times 10^5 \text{ V/cm}$. A comparative experiment on vacuum-deposition films gave a similar mobility of about $2 \times 10^{-3} \text{ cm}^2/\text{Vs}$.

These data are approaching to the best results found for α -sexithienyl in single crystal films ($2 \times 10^{-3} \text{ cm}^2/\text{Vs}$)⁸ and 4, 5, 7-trinitrofluorenone in self-organized columnar phase ($2.3 \times 10^{-3} \text{ cm}^2/\text{Vs}$)⁶. The inset of **Figure 1** is a typical transient conductivity signals, such transient features indicate a highly dispersive transport. This phenomenon is similar to that observed in liquid crystal perylene derivatives², but different from those observed in well-ordered columnar phase of discotic liquid crystals⁹. The good linear dependence of mobility on the field and the transient feature suggested that the hopping mechanism dominates the transport process of photogenerated carriers.

The hopping rate of a charge carrier was determined by the distance between two nearest hopping sites¹⁰. With respect to the solids of **1**, the gap can be considered to be equivalent to the π - π stacking space between adjacent perylene chromophores. Based on well-established experiment data, UV-visible spectroscopy is a helpful technique to examine the π - π stacking arrangements in perylene bisimide derivatives. The in-phase overlap between the π -orbitals of adjacent molecules resulted in an intermolecular charge-transfer absorption band around 600-630 nm, and the solids were referred as "black phase"¹¹. In comparison with the solution spectrum, the casting films of **1** (200nm) displayed an additional absorption band red-shifted to 604 nm (**Figure 2**), which suggested the formation of an in-phase close packing between perylene cores.

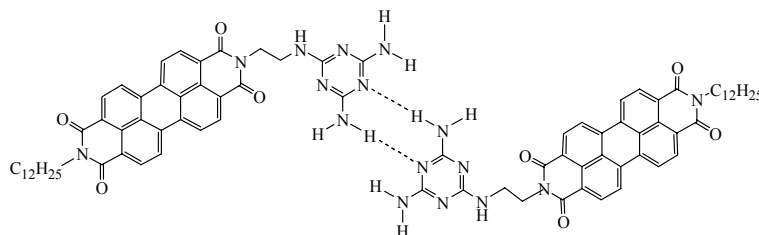
Figure 2 Absorption spectrum of molecule **1** in casting film (solid line), vacuum-deposition films (up triangle), solution of tetrahydrofuran (open square), respectively, the curve in dashed line was recorded from casting-film of N,N'-dodecylperylene bisimide.



In contrast, without the 2, 4-diamino-1, 3, 5-triazine group, the red-shifted absorption band at about 570 nm can be observed for the casting films (200 nm) of reference compound N,N'-*n*-dodecylperylene bisimide. This is normal to perylene bisimides and often referred as 'red phase'¹². For some derivatives, a 'red phase' can be transformed into a black phase with solvent vapor annealing. But in our case, both of the crystals from precipitation and sublimation are in dark red-brown, similar to the results reported by S. G. Liu *et al.* in brown phase of a liquid crystal perylene bisimide derivative¹¹. Their optical absorption features showed little changes after annealing with THF or CHCl₃ vapor. This phase stability may be associated with the H-bond

interactions between two 2, 4-diamino-1, 3, 5-triazine groups, holding two perylene cores together to form a “coupled” or enlarged building block (see **Scheme 2**).

Scheme 2 Illustration of H-bond interactions between two perylene bisimide molecules



In summary, we have covalently linked perylene bisimide with a H-bonds formation group of 2, 4-diamino-1, 3, 5-triazine. A charge mobility over $1.0 \times 10^{-3} \text{ cm}^2/\text{Vs}$ has been observed for its solution casting films, which is in the same order of magnitude of self-organized transport materials reported recently. Furthermore, the molecular aggregation states of this material are different from its counterpart of N,N'-*n*-alkyl-peryene bisimides. These unique properties may be endowed by the supramolecular structure held together by H-bonds, which are of new research interests in the field of perylene bisimides.

Acknowledgment

This research was supported by the National Natural Scientific Foundation of China (No. 90101008) and 973 project (No.2002CB613401) of the MST of P. R. China.

References and Notes

1. P. Strohriegel, J. V. Grazulevicius, *Adv. Mater.*, **2002**, *14*, 1439.
2. C. W. Struijk, A.B. Sieval, J. E. J. Dakhorst, *et al.*, *J. Am. Chem. Soc.*, **2000**, *122*, 11057.
3. *Handbook of Organic Conductive Molecules and Polymers*, Vol.4, Ed. H.S.Nalwa, John Wiley & Sons, N.Y., Chapter 1, 1997.
4. V. Percec, M. Glodde, T. K. Bera, *et al.*, *Nature*, **2002**, *419*, 384.
5. P. Jonkheijm, F. J. M. Hoeben, R. Kleppinger, *et al.*, *J. Am. Chem. Soc.*, **2003**, *125*, 15941.
6. E. E. Neuteboom, S. C. J. Meskers, P. A. van Hal, *et al.*, *J. Am. Chem. Soc.*, **2003**, *125*, 8625.
7. Selected data of **1**: $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ ppm 0.94 (t, 3H, $J=6.8\text{Hz}$, CH_3), 1.33-1.62 (m, 18H, CH_2), 2.08 (quin, 2H, $J=7.0\text{Hz}$, CH_2), 4.44-4.52 (m, 6H, $-\text{N-CH}_2$), 6.80-6.82 (br, 5H,) 8.70-8.78 (m, 8H, Ar); Elem. Anal. calcd. for $\text{C}_{41}\text{H}_{42}\text{N}_8\text{O}_4$: C, 69.30, H, 5.92, N 15.77; found: C, 70.17, H, 6.27, N, 15.43.
8. A. Dodabalapur, L. Torsi, H. E. Katz, *Science*, **1995**, *268*, 270.
9. D. Adam, P. Schuhmacher, J. Simmerer, *et al.*, *Nature*, **1994**, *371*, 141.
10. J. Cornil, D. Beljonne, J. -P. Calbert, *et al.*, *Adv. Mater.*, **2001**, *13*, 1053.
11. S. G. Liu, G. Sui, R. A. Cormier, *et al.*, *J. Phys. Chem. B*, **2002**, *106*, 1307.
12. R. A. Cormier, B. A. Gregg, *J. Phys. Chem. B*, **1997**, *101*, 11004.

Received 16 November, 2004