Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 76 (2008) 569–573

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Optical and nonlinear optical properties of an octasubstituted liquid crystalline copper phthalocyanine

Nan He [a], Yu Chen [a,*], James Doyle [b], Ying Liu [a], Werner J. Blau [b]

[a] *Lab for Advanced Materials, Department of Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China*

[b] *Materials Ireland Polymer Research Centre, Department of Physics, Trinity College Dublin, Dublin 2, Ireland*

Received 20 September 2006; received in revised form 9 November 2006; accepted 16 November 2006
Available online 9 January 2007

Abstract

The optical and nonlinear optical properties of an octasubstituted, liquid crystalline copper phthalocyanine, which was synthesized by the reaction of 1,2-dibromo-4,5-bis[dodecanoxymethyl]-benzene with a small excess of CuCN in dilute anhydrous *N*,*N*′-dimethylacetamide solution, are described. The ratio of the excited to ground state absorption cross-section ($\kappa = \sigma_{ex}/\sigma_0$) and the linear optical absorption coefficient of the compound were measured in dry toluene solution; their values were about 2.4 ± 0.5, and $1.4\ cm^{-1}$, respectively. In the solid state the compound shows signs of irreversible thermal damage when illuminated by laser at the lowest energy per pulse setting used. In solution, the values of both the nonlinear absorption coefficient and the third-order nonlinear susceptibility decreased with increasing incident intensity, this being indicative of saturation effects arising from higher triplet excitations.

Keywords: Organic compounds; Optical materials; Chemical synthesis; Optical properties

1. Introduction

Copper(II) phthalocyanine (CuPc) is planar and displays the gradually falling long-wavelength absorption of a simple, nearly vertical ‘‘deck-of-cards’’ structure [1]; it has attracted much attention in the last 10 years because of its potential applications in chemical sensors, optical data storage, organic solar cells, and organic field-effect transistors [2]. The presence of the paramagnetic Cu^{II} atom in the cavity of the phthalocyanine molecule creates a very fast path for the internal conversion $S_1 \rightarrow T_1$. The fluorescence yield of monomeric CuPc in solution is <0.01%, implying an intersystem crossing rate constant of $>10^{12}\ s^{-1}$ [3]. Organic field-effect transistors that employ CuPc as the semiconducting layer can function as p-channel accumulation-mode devices [4]. When the substrate temperature for deposition of CuPc is 125 °C, a mobility of $0.02\ cm^2/V\ s$ and an on/off ratio of 4×10^5 can be achieved [4a]. A 2.4-inch organic light emitting diode panel (device structure: ITO/CuPc/NPD/DPVBi/Alq3/LiF/Al:Li (0.1 wt%)) with blue monochrome emission and resolution of 160 × 160 has been fabricated using vacuum evaporation [2d]. An external power conversion efficiency of a p/n-junction photovoltaic device with a configuration ITO/CuPc/PTCBI/BCP/Ag (ITO: indium–tin-oxide as conducting anode; PTCBI: 3,4,9,10-perylene-tetracarboxylic-bisbenzimidazole as acceptor; BCP: bathocuproine as an organic exciton-blocking layer) reached $2.4 \pm 0.3\%$ [5]. This device structure demonstrates that control of exciton diffusion in solid-state organic devices leads to a significant increase in the photo-to-carrier conversion efficiency.

Many experimental results have demonstrated that the liquid crystalline phthalocyanine can adopt a high interfacial surface area morphology and a vertically ordered composition and exhibit exciton diffusion lengths of a few hundred nanometers as well as high charge-carrier mobility ($0.1–1\ cm^2/V\ s$) [6]. This

---

* Corresponding author. Tel.: +86 21 64253135; fax: +86 21 64252485.
E-mail address: oematerials@yahoo.com (Y. Chen).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.11.005

is undoubtedly beneficial for the further improvement of the performance of the CuPc based optoelectronic devices. Piechocki et al. [7] reported briefly the first peripherally octakis (dodecyloxymethyl) substituted CuPc displaying a disordered, hexagonal columnar mesophase over a wide temperature range. Subsequently, the influence of the number of side chains, type of linking group and the central metal ion, length of the side chains and branching of the chains on both the mesophase stability and optoelectronic properties of phthalocyanines have been investigated [8]. In this contribution, we report the optical and nonlinear optical (NLO) properties of an octasubstituted liquid crystalline copper phthalocyanine, which was simply synthesized by the reaction of 1,2-dibromo-4,5-bis[dodecanoxymethyl]-benzene with a small excess of CuCN in dilute anhydrous *N*,*N*′-dimethylacetamide solution, as shown in Scheme 1. The compounds **2** and **3** were synthesized according to the procedures reported in the literatures [7,9].

2. Experimental

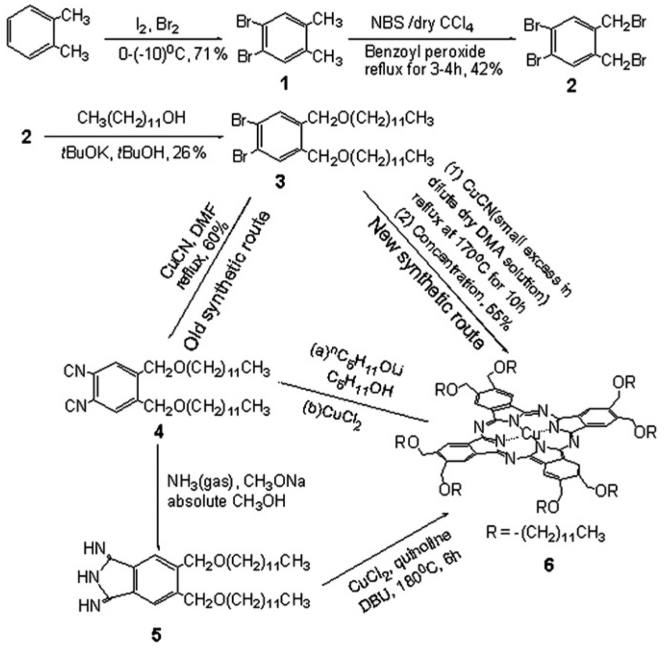
The operations for synthesis prior to the termination reaction were carried out under purified argon. All chemicals were purchased from Aldrich and were used without further purification. Solvents were purified, dried and distilled under dry nitrogen. UV/vis absorption spectra were recorded on a Jasco V-530 UV/vis spectrophotometer; photoluminescence spectra were measured by Shimadzu spectrofluorophotometer; ^{1}H NMR spectra were performed on a JEOL Lambda 400 NMR spectrometer (^{1}H: 250.131 MHz; $CDCl_3$ as solvent). Analytical thin layer chromatography (TLC) was performed using aluminium coated Merck Kiesegel 60 F254 plates. MALDI-TOF-MS measurements were performed on a Bruker REFLEX III-S mass spectrometer [10] and elemental analyses were performed using a Carlo–Erba elemental analyzer 1104, 1106. The texture of compound **6** was observed with an Axiolab Zeiss polarizing microscope.

Cyclic voltammetric data were obtained on a BAS CV-50W voltammetric analyzer using a scan rate of 100 mV/s. A glassy carbon, platinum wire and Ag/Ag^+ were used as the working, counter and reference electrodes, respectively; tetrabutylammonium hexafluorophosphate (TBAH, 0.1 M) in dry acetonitrile was used as electrolyte. Before scanning, solutions were saturated with nitrogen. The HOMO/LUMO values of the phthalocyanines were estimated by the onset of the redox potentials taking the known reference level for ferrocene, 4.8 eV below the vacuum level.

Nanosecond transient absorption measurements were carried out using third harmonic generation (THG, 355 nm) employing a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, 6 ns FWHM) as exciting source. For transient absorption spectra in the near-IR region (600–1400 nm), monitoring light from a pulsed Xe-lamp was detected with a Ge-avalanche photodiode (Hamamatsu Photonics, B2834). For transient absorption spectra in the visible and near-IR regions (400–1000 nm), monitoring light from a pulsed Xe-lamp was detected using an Si-PIN photodiode (Hamamatsu Phonics, S1722-02).

Open aperture Z-scanning was used to probe total transmittance through the samples. The second harmonic, 532 nm, of a Q-switched Nd:YAG laser with a pulse repetition rate of 10 Hz was used, the beam having been spatially filtered to remove the higher order modes and tightly focused with a 9 cm focal length lens. The solution based NLO experiments were undertaken in quartz cuvettes with a path length of 1 mm.

*Synthesis of compound **1***. To *o*-xylene (95 ml) containing iodine (0.4 g) was added, dropwise, Br_2 (80 ml) over 2 h at 0 °C; the reaction mixture was then allowed to attain room temperature. The resultant solid was left at room temperature



Scheme 1.

overnight before being dissolved in Et_2O (600 ml), washed with 2 N NaOH (600 ml), H_2O (600 ml), dried over Na_2SO_4, filtered, and concentrated under vacuum to give a white oil which crystallized upon standing. Recrystallization from MeOH gives a white crystalline solid in the yield of 71%. ^1H NMR (in $CDCl_3$): δ/ppm = 2.2 (6H, s, 1,2-Me), 7.3 (2H, s, 3,6-H).

*Synthesis of compound **6***. To the stirred solution of compound **3** (1.20 g) in anhydrous *N*,*N*′-dimethylacetamide (DMA, 50 ml) was added CuCN (0.54 g). The reaction mixture was heated for 10 h at 170 °C under reflux, and then concentrated to 10 ml under slightly decreased pressure. The residual solution soon turned bluish green. After continuing reaction for an additional 4 h at the same temperature, the solvent was evaporated and the greenish residue was subjected to column chromatography (Al_2O_3, eluent: toluene) in order to remove the excess of metallic salt. The green fraction was collected, the solvent evaporated and the resultant copper phthalocyanine was recrystallized from heptane. Yield: 55%. ^1H NMR: δ/ppm = 1.2 (br m, 184H, paraffin), other peaks were not observed due to paramagnetic copper ion. MALDI-TOF-MS: calcd for $C_{136}H_{224}O_8N_8Cu$: m/z = 2162.8); found: 2162.8 (M^+), 1977.6 [$M^+ - CH_3(CH_2)_{11}O$], 1793.5 [$M^+ - 2CH_3(CH_2)_{11}O$]. Its UV/vis absorption is strongly concentration dependent, implying some aggregation process.

3. Results and discussion

o-Xylene is treated with bromine to give compound **1**; the methyl groups are then brominated with *N*-bromosuccinimide (NBS) via a radical mechanism. It should be noted that light must be strictly excluded during this step in order to avoid the multi-substitution of methyl groups. The reaction of compound **3** with a small excess of CuCN in dilute DMF or *N*,*N*′-dimethylacetamide (DMA) solution produces dicyano-compound **4**. However, the formation of **4** depends greatly on the experimental conditions used. In our work, the resultant dark-green copper phthalocyanine **6** ($[CH_3(CH_2)_{11}OCH_2]_8CuPc$) was obtained in 55% yield. The molecular ion peak at m/z = 2162.8 was detected from the MALDI-TOF mass spectrum of **6**. Like most of the discotic mesophases, the mesophase of **6** is of a typical hexagonal columnar phase.

The polarized optical images and electron diffraction pattern of compound **6** are shown in Fig. 1. The sharp spots of reflections in the electron diffraction pattern displayed at room temperature imply the existence of larger particles in the solid state. Upon heating at 120 °C for several minutes, the solid crystalline phase of **6** is transformed into a viscous, birefringent liquid. When the sample was slightly cooled, a typical fan-like pattern of discotic liquid crystals was obtained with a two-dimensional hexagonal lattice.

The UV/vis absorption spectrum of **6** exhibits strong concentration dependence, suggesting aggregation; the maximum peak of the Q-band is located at 683 nm ($\varepsilon = 2.2 \times 10^5$). Fig. 2 compares the influence of the laser irradiation on the Q-band in the UV/vis absorption spectrum of **6**. The results indicate that this compound is unstable under long-term laser irradiation. In the solid states the sample shows signs of irreversible thermal damage at lowest energy per pulse under laser illumination. This means compound **6** is unsuitable for the fabrication of solid photonic devices, especially optical limiters. The HOMO/LUMO values of the phthalocyanines were experimentally estimated by the onset of the redox potentials [11]

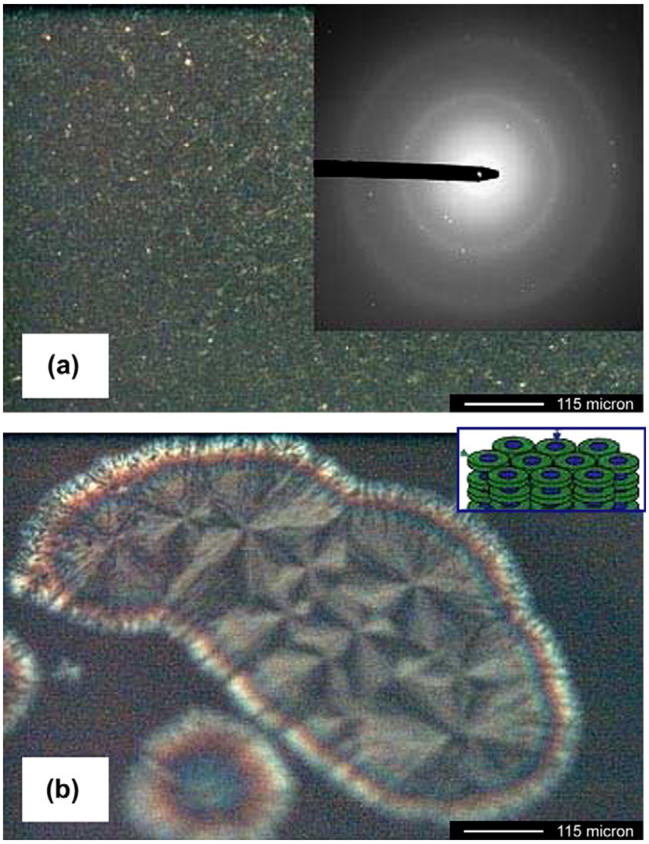


Fig. 1. Polarized optical images of $[CH_3(CH_2)_{11}OCH_2]_8CuPc$: (a) at room temperature; (b) after heating at about 120 °C for several minutes. *Inset*: (a) electron diffraction pattern; and (b) characteristic structure of the discotic mesophases.

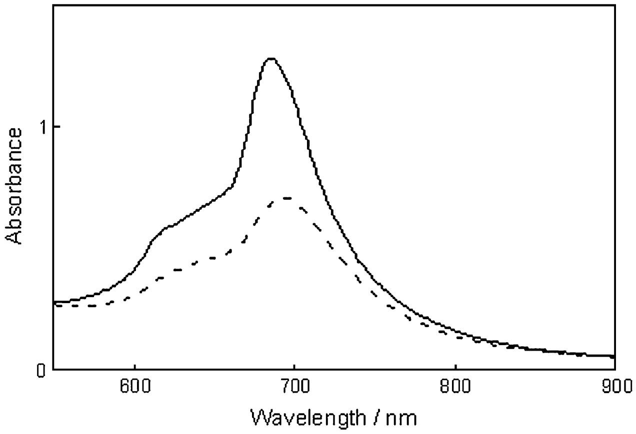


Fig. 2. The Q-bands in the UV/vis absorption spectra of $[CH_3(CH_2)_{11}OCH_2]_8$-CuPc in chloroform (1×10^{-4} M) before (solid line) and after (dashed line) laser irradiation.

taking the known reference level for ferrocene, 4.8 eV below the vacuum level, according to the following equation: HOMO/LUMO $= -[E_{\text{onset}} - E_{\text{ox.(ferrocene)}}] - 4.8$ eV. For **6**, the HOMO and LUMO positions are located at −5.2 eV and −3.4 eV, respectively; from which the HOMO/LUMO gap is calculated to be 1.8 eV. The absolute HOMO position may be measured by UV photoelectron spectroscopy (UPS). In order to give an efficient n/p characteristic for the photovoltaic cells, the materials should not only have the appropriate conduction type but also have their frontier orbitals in a position that leads to a junction which separates the light-induced charge carriers in a way so that the electrons end up in the n-type material and defect-electrons (holes) end up in the p-type material [12]. For the phthalocyanines as p-type materials, the ideal n-type materials are usually 3,4,9,10-perylenetetracarboxylic acid diimide derivatives (PTCDI) [1,12]. The energy levels of **6** are well-matched with those of PTCDI (as an example, for *N*,*N*′-bismethyl-3,4,9,10-perylenebiscarboximide (PTCDIa), its HOMO and LUMO values are −6.8 and −4.6 eV, respectively). This suggests that compound **6** might be used as a p-type material for organic solar cells with such a configuration "ITO/**6**/PTCDI/Au". Further studies on this issue are currently in progress.

Upon excitation with nanosecond laser pulse at 355 nm (i.e., roughly at the centre of the B band) the transient absorption spectra of **6** were observed in argon-saturated anhydrous chloroform. The transient absorption band at 520 nm after the laser pulse irradiation is attributable to the triplet–triplet absorption of the phthalocyanine compounds [13]. Stronger triplet excited state absorption in the high-transmittance optical window comprised between Q- and B-bands in the UV/vis absorption spectrum of **6** ensures that the absorption cross-section of the excited state is always larger than that of the ground state. From photophysical experiments, one can easily measure the ratio of the excited to ground state absorption cross-section ($\kappa = \sigma_{\text{ex}}/\sigma_0$), and the linear optical absorption coefficient (α_0). For **6**, these two values obtained in dry toluene solution are about 2.4 ± 0.5, and 1.4 cm^{-1}, respectively.

Open aperture Z-scanning has been used to study the imaginary third-order nonlinear optical processes in molecular materials; by moving the sample along the *z* axis through the focus, the intensity-dependent absorption can be measured as a change of the transmission through the sample using a detector in the far field [14]. On approaching the focus the intensity increases by several orders of magnitude relative to the intensity away from focus, thus inducing nonlinear absorption in the sample. For **6**, a clear decrease of transmittance about the focus was observed, typical of an induced positive nonlinear absorption (Fig. 3). The absorption mechanism, in which the transmission decreases as a function of intensity, is due to population of excited states through a multi-step nonlinear absorption. For focal intensities of 0.14 and 0.29 GW cm^{-2}, the nonlinear absorption coefficients (β_{I}) measured in solution were 4.53×10^{-8} and 2.13×10^{-8} cm W^{-1}, respectively, while the corresponding effective third-order nonlinear susceptibilities ($\text{Im}\{\chi^{(3)}\}$) are 1.71×10^{-12} and 8.04×10^{-13} esu. The results show that both the β_{I} and $\text{Im}\{\chi^{(3)}\}$ values decreased with increasing incident intensity, being indicative of saturation effects arising from higher level triplet excitations. The optical limiting data plotted with the normalized transmission (T_{norm}) against the incident energy density per pulse (J cm^{-2}) are depicted in Fig. 4. The solid line represents theoretical fits to the experimental data. The saturation energy density (F_{sat}) value of **6** was determined to be (17 ± 7.27) J cm^{-2}, smaller than that of *t*Bu$_4$PcInCl (24.2 ± 0.8 J cm^{-2}) and *t*Bu$_4$PcGaCl (27.0 ± 1.0 J cm^{-2}) [15].

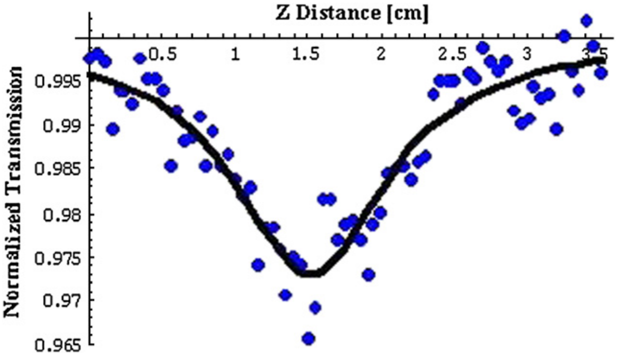


Fig. 3. Open aperture Z-scan spectra of compound **6** in toluene at 532 nm with normalized transmission plotted as a function of sample position in the *z* direction.

4. Conclusions

A new one-pot synthesis of an octasubstituted liquid crystalline copper phthalocyanine from 1,2-dibromo-4,5-bis[dodecanoxymethyl]-benzene is described. The ratio of the excited:ground state absorption cross-section ($\kappa = \sigma_{\text{ex}}/\sigma_0$), and the linear optical absorption coefficient of this compound were measured in dry toluene solution, producing values of 2.4 ± 0.5, and 1.4 cm^{-1}, respectively. The NLO experimental results obtained at 532 nm show that both the β_{I} and $\text{Im}\{\chi^{(3)}\}$

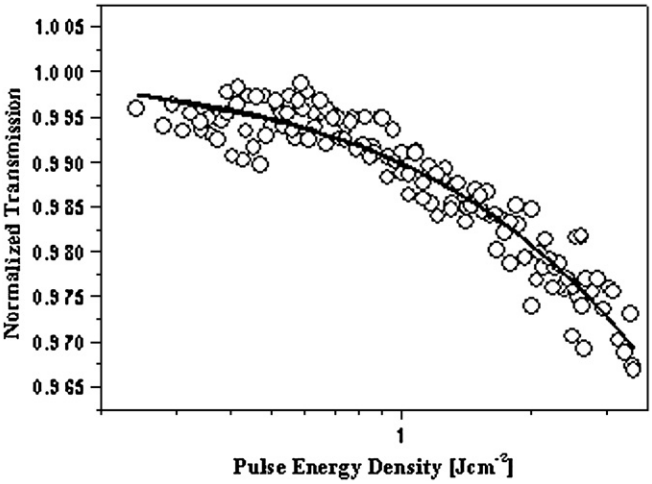


Fig. 4. Plot of normalized transmission against pulse energy density for **6** in toluene.

values decreased with increasing incident intensity, being indicative of saturation effects arising from higher level triplet excitations.

Acknowledgements

We are grateful for the financial support of National Natural Science Foundation of China (20546002, 20676034), ECUST (YJ0142124), China/Ireland Science and Technology Collaboration Research Foundation (CI-2004-06), SRF for ROCS, NCET (050413), Shanghai Shuguang project (05SG35) and STCSM (05XD14004).

References

[1] Whitlock JB, Panayotatos P, Sharma GD, Cox MD, Sauers RR, Bird GR. Opt Eng 1993;32:1921–34.

[2] (a) Law KY. Chem Rev 1993;93:449–86;
(b) Kadhum M, Makhseed S, McKeown NB. J Mater Chem 2001;11:2784–9;
(c) Pustelny T, Ignac-Nowicka J, Opilski Z. Opt Appl 2004;34:249–64;
(d) Kim SW, Hwang BH, Lee JH, Kang JI, Min KW, Kim WY. Curr Appl Phys 2002;2:335–8;
(e) Il'chuk GA, Nikitin SE, Nikolacv YA, Rud VY, Rud YV, Terukov EI. Semiconductors 2004;38:1308–11;
(f) Beck K, Kunzelmann T, von Schickfus M, Hunklinger S. Sens Actuators Part A Phys 1999;76:103–6;
(g) Healy TWB, Ewing CT. J Phorphyrins Phthalocyanines 1999;3:522–9;
(h) Haensel H, Zettl H, Krausch G, Schmitz C, Kisselev R, Thelakkat M, et al. Appl Phys Lett 2002;81:2106–8.

[3] Vincett PS, Voight EM, Riechoff KE. J Chem Phys 1971;55:4131–40.

[4] (a) Bao Z, Lovinger AJ, Dodabalapur A. Appl Phys Lett 1996;69:3066–8;
(b) Sakai M, Iizuka M, Nakamura M, Kudo K. Jpn J Appl Phys Part 1 2004;43:2362–5.

[5] Peumans P, Bulovic V, Forrest SR. Appl Phys Lett 2000;76:2650–2.

[6] (a) Tant J, Brussels B, Geerts Y, Brussels B. In: Proceedings of the fifth international symposium on functional π-electron systems, Ulm, Germany; May 30–June 4, 2002. p. 231;
(b) Blasse G, Dirksen GJ, Meijerink A, van der Pol JF, Neeleman E, Drenth W. Chem Phys Lett 1989;154:420–4;
(c) Adam D, Schuhmacher P, Simmerer J, Haussling L, Siemensmeyer K, Etzbach KH, et al. Nature 1994;371:141–3;
(d) Hanna J. In: Proceedings of SPIE: organ photovoltaics III, vol. 4801; 2003. p. 99–113.

[7] Piechocki C, Simon J, Skoulios A, Guillon D, Weber P. J Am Chem Soc 1982;104:5245–8.

[8] Sleven J, Cardinaels T, Görller-Walrand C, Binnemans K. Arkivoc 2003;IV:68–82.

[9] (a) Pawlowski O, Hanack M. Synthesis 1980;287–9;
(b) Kingsberg E. Synthesis 1972;29–31;
(c) Piechocki C, Simon J. Nouv J Chim 1985;9:159–66.

[10] Preparation method of samples for the MALDI-TOF-MS measurements: the samples were dissolved in dry THF, and then mixed 1:1 (0.8 μl each) with a methanol solution of α-cyano-4-hydroxycinnamic acid as matrix.

[11] Chen Y, El-Khouly ME, Sasaki M, Araki Y, Ito O. Org Lett 2005;7:1613–6.

[12] Woehrle D, Kreienhoop L, Schnurpfeil G, Elbe J, Tennigkeit B, Hiller S, et al. J Mater Chem 1995;5:1819–29.

[13] Chen Y, Araki Y, Fujitsuka M, Hanack M, Ito O, O'Flaherty SM, et al. Solid State Commun 2004;131:773–8.

[14] Chen Y, Hanack M, Araki Y, Ito O. Chem Soc Rev 2005;34:517–29.

[15] O'Flaherty SM, Hold SV, Cook MJ, Torres T, Chen Y, Hanack M, et al. Adv Mater 2003;15:19–32.