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Regioregular poly[3-butyl-2,5-thienylene-*alt*-1,4-phenylene]: synthesis, preliminary characterization aspects and application in the fabrication of light-emitting diodes

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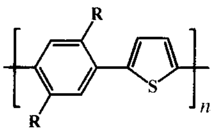
A novel regioregular polymer comprising alternating 1,4-phenylene and 3-butyl-2,5-thienylene repeat units has been synthesized and characterized using ^{1}H NMR, FTIR, UV–VIS absorption and fluorescence emission spectroscopy. The derived polymer showed strong fluorescence with a solution quantum yield of 48% relative to quinine sulfate and a film phase photoluminescence yield of 17%. Green light-emitting diodes were fabricated using the polymer as the emitter layer.

Introduction

Commercially available light-emitting diodes (LEDs) are dominated by inorganic materials, as exemplified by the family of GaAs and InGaAs LEDs. However, research impetus over the past decade or so has been focused largely on organic-based polymers on account of the facile tunability of their emissive wavelength *via* synthetic structural modifications as well as their ease of processability and consequent amenity to the fabrication of large area displays. Electroluminescent (EL) phenomena from organic compounds were first demonstrated in the early sixties by Pope *et al.*[1] and Helfrich *et al.*[2] In the following decade, electroluminescence in polyethylene terephthalate (PET) films was reported by Yoshino and coworkers.[3] However, these organic EL devices were severely limited by their high operating voltages and/or low quantum efficiencies. A research breakthrough in this area came about in the late 1980s when Tang *et al.*[4] and Adachi *et al.*[5] demonstrated that by application of a sophisticated multilayer structure comprising emissive dyes and carrier transport layers, the driving voltage may be dramatically lowered and also a higher device efficiency achieved. The next step forward appeared shortly after when the Cambridge group of Friend and Holmes[6] reported that conjugated polymers may be utilized as the active materials for electroluminescence under relatively low driving voltages. Subsequently, further interest in polymer-based LEDs was spurred by the reports of Ohmori et al.,[7] Byaun and Heeger,[8] as well as Gustaffason *et al.*[9] on facile device fabrication processes using soluble conjugated polymers. Thereafter, intensive research work was conducted in this field using a variety of structurally divergent conjugated polymers, amongst which are poly(*p*-phenylene) (PPP),[10] poly(*p*-phenylenevinylene) (PPV),[11] pyridine-based and pyridyl vinylene-based polymers[12] and functionalised polythiophenes with different pendant substituents,[13] with recent reports on the application of alternating copolymers of 2,5-thienylene and functionalised 1,4-phenylene moieties[14,15] [**1** (R = *n*-pentyl and *n*-heptyl)].



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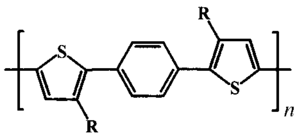

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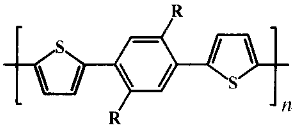

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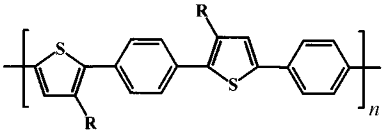

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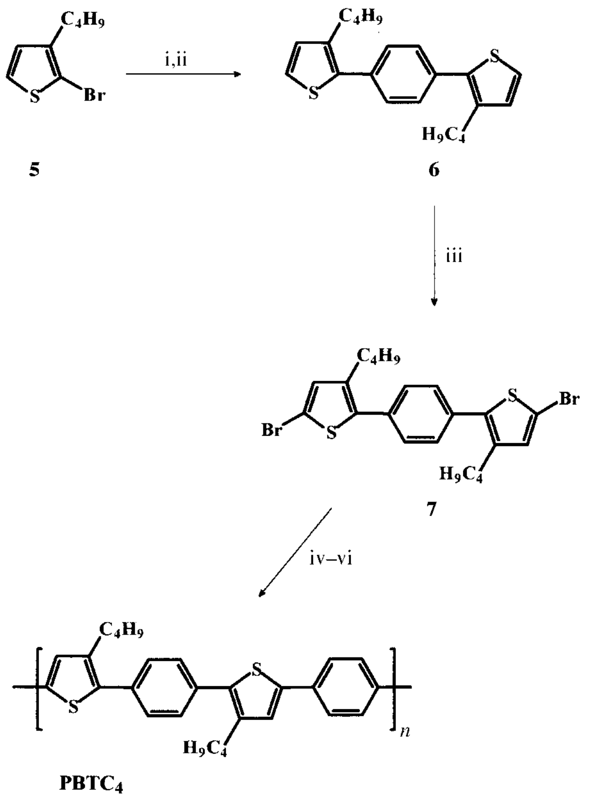
Meanwhile, one of our research group has been actively pursuing the structure–property correlation studies and applications of functional polythiophenes and alternating copolymers incorporating 3-functionalised 2,5-thienylene.[16–18] As part of this work, we recently reported on regioregular alternating copolymers of 4,4′-dialky-2,2′-bithienyl-5,5′-diyl and 1,4-phenylene units[17] [**2** (R = *n*-butyl, *n*-octyl and *n*-dodecyl)] which appeared highly fluorescent in comparison to functionalised polythiophenes. Similar fluorescent characteristics were also observed by other researchers on analogous polymers of structural type **3** (R = methyl, methoxy or *n*-butyl)].[19,20]

Invariably, in all such work on alternating copolymers of thienylene (bithienylene) and 1,4-phenylene units, only functionalisation on the latter moiety was reported, with no work, to the best of our knowledge, on related materials with functional derivatisation on the thienylene moieties. Accordingly, for comparative purposes, we report herein our findings on the synthesis and preliminary characterization aspects of regioregular poly(3-butyl-2,5-thienylene-*alt*-1,4-phenylene) [PBTC$_4$ **4** (R = *n*-butyl)] and its application as the active emissive layer in LED fabrication. Our experimental results revealed that LED devices fabricated using PBTC$_4$ afforded an obvious green emission similar to that of PPV.

Experimental

Polymer synthesis

Synthesis of the polymer PBTC$_4$ was effected in accordance with the synthetic route depicted in Scheme 1. The starting



Scheme 1 *Reagents and conditions*: i, Mg, Et_2O; ii, 1,4-dibromobenzene, $Ni(dppp)Cl_2$; iii, Br_2, AcOH–$CHCl_3$; iv, Bu^nLi, THF; v, $MgBr_2{\cdot}Et_2O$; vi, 1,4-dibromobenzene, $Ni(dppp)Cl_2$, THF.

material 2-bromo-3-butylthiophenes **5** was synthesized using the approach of McCullough *et al.*[21] Thereafter, **5** was reacted with magnesium to afford the corresponding Grignard reagent, whereupon cross-coupling with 1,4-dibromobenzene in the presence of catalytic amounts of $Ni(dppp)Cl_2$ [dppp = $Ph_2P(CH_2)_3PPh_2$] afforded the monomer **6** which was then brominated to afford compound **7**. Polymerization was effected by lithiating **7** by addition of 2 equiv. of *n*-butyllithium followed by addition of $MgBr_2{\cdot}Et_2O$ to afford the corresponding 5,5′-dimagnesio bromide Grignard reagent, which was then cross-coupled with 1,4-dibromobenzene in THF with $Ni(dppp)Cl_2$ as catalyst at room temperature over 24 h. The resulting polymer ($PBTC_4$) was precipitated upon pouring the reaction mixture into acidified methanol. Purification was effected by washing the crude polymer in turn with methanol, water and methanol again. Thereafter, oligomeric materials were removed *via* Soxhlet extraction with methanol, followed by acetone. The final polymer was obtained as brown–yellow powder.

Doping studies were effected by placing polymer pellets (*ca.* 0.1 g) inside a desiccator containing ground iodine crystals.

Instrumentation

Elemental analyses of all monomer and polymer samples were performed at the NUS Microanalytical Laboratory on a Perkin-Elmer 240C elemental analyser for C, H and S determinations. Halogen determinations were done either by ion chromatography or the oxygen flask method. FTIR spectra of the polymer dispersed in KBr disks were recorded on a Bio-Red TFS 156 spectrometer. Solution phase absorption and fluorescence spectrum measurements were conducted on a Hewlett Packard 8452A spectrophotometer and Shimadzu RF5000 fluorescence spectrophotometer, respectively. Dilute polymer solutions dissolved in spectro-grade chloroform (10^{-5} M) were used for analysis and coumarin (Aldrich) was used as the calibration standard. Optical absorption and photoluminescence (PL) measurements from thin polymer films deposited onto indium-tin-oxide coated glass plates were obtained on a Hitachi 330 spectrophotometer and Hitachi F-2000 fluorescence spectrophotometer, respectively. Film state fluorescence quantum efficiency measurements were conducted by excitation of the polymer film using a Spectra-Physics BeamLok 2060 continuous wave argon laser, whose beam intensity is modulated by passing it through a HMS light-beam chopper 220 operated at 200 rpm. Emitted light intensity was measured using an Oriel 70491 integrating sphere attached to a Stanford Research System Model SR830 DSP lock in amplifier. ^1H NMR spectra were recorded on a Bruker ACF 300 FT-NMR spectrometer operating at 300 MHz. Deuterated solvents were used as indicated and tetramethylsilane (TMS) was used as the internal reference. Thermogravimetric analysis (TGA) was conducted on a Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyser in air (75 ml min^{-1}). A heating rate of 10 °C min^{-1} was used. The temperature regime was room temperature to 1000 °C. Modulated differential scanning calorimetry (MDSC) experiments were conducted on a TA Instruments 2920 temperature modulated DSC machine in argon (70 ml min^{-1}). A heating rate of 1 °C min^{-1} was used in the temperature range from −60 to 170 °C. Conductivity measurements were carried out on polymer pellets of known thickness using a four-point probe connected to a Keithley constant current source. Conductivity was calculated from at least 10 pairs of consistent readings taken at different points of the pressed pellet. Cyclic voltammetry of polymer films was conducted using a single-compartment, three electrode cell comprising an indium-tin-oxide (ITO) working electrode with the polymer spin-coated on it, a platinum counter electrode and a silver quasi-reference electrode[22] using a HB-105 Hokuto Denko Ltd. arbitrary function generator and HA-501 Hokuto Denko Ltd. potentiostat. Tetrabutylammonium tetrafluoroborate in acetonitrile was used as the electrolyte solution. To ensure that our results were comparable with those of other literature reports, the widely used reference electrode, ferrocence couple (Fc/Fc^+), was examined previously by one of us in tetrabutylammonium tetrafluoroborate/acetonitrile system and the usual electrochemical behavior was observed.[23] Gel permeation chromatography (GPC) analyses were carried out using a Perkin-Elmer Model 200 HPLC system with Phenogel™ MXL and MXM columns (300 mm × 4.6 mm ID) calibrated using polystyrene standards and THF as eluant.

Device fabrication

Single layer devices were fabricated by spin-coating a chloroform solution of the polymer $PBTC_4$ (*ca.* 10 mg ml^{-1}) onto an ITO coated quartz substrate which has a sheet resistance of 10 Ω and then depositing the top magnesium-indium electrode on top of the polymer layer. The Mg-In alloy was evaporated in a bell jar under vacuum ($<10^{-6}$ Torr). The active area was *ca.* 4 mm^2. The emission spectrum and light intensity characteristics were measured by a Nikon P-250 spectrometer with a photomultiplier (R928 Hamamatsu Photonics Co.) and a silicon photodiode. All measurements were carried out in air under DC biased conditions.

Results and discussion

Polymer physical properties

$PBTC_4$ was obtained as a brown–yellow powder and exhibited good solubility in chloroform, tetrahydrofuran, dichloromethane, toluene and benzene and partial solubility in acetone. Its solubility in common organic solvents appeared greatly enhanced in comparison to poly[1,4-bis(3-alkyl-2-thienyl)-phenylenes] ($PBTBC_4$ **2**).[17] The number-averaged molecular weight (M_n) and polydispersity index (PDI) of $PBTC_4$ were

3900 and 2.2, respectively, as determined from GPC using polystyrene as standard. GPC results indicated there are *ca.* 18 thienylenephenylene repeating units in the polymer chain of $PBTC_4$, which is close to that of soluble $PBTBC_4$.

After doping with iodine, the conductivity of the $PBTC_4$ polymer was raised by an order of 10^5 with an accompanying color change from brown–yellow to black. The conductivity of the doped polymer increases with increasing iodine intake and the maximum conductivity obtained is 7.4×10^{-4} S cm^{-1} when I_2 uptake correspounds to 100 wt%. This conductivity value is lower than that of $PBTBC_4$, a result of the modification of polymer backbone with the ratio of thienylene to phenylene units decreased from 2 : 1 to 1 : 1.

TGA reveals that $PBTC_4$ is stable up to 410 °C in nitrogen with maximum degradation rate occurring at about 500 °C. MDSC results show distinct endothermic peaks at 45 and 100 °C which are attributed to melting of the side chains and the backbone of the polymer, respectively. A sharp glass transition temperature (T_g) was also observed at 52 °C. These results indicate that $PBTC_4$ is semicrystalline. Similar thermal transitions have been reported by Ruiz *et al.*[24] for similar centrosymmetric polymers with the long chain substituents located on the phenylene moieties.

Characterization studies

The elemental composition of the neutral polymers, as determined from microanalyses, showed good agreement between the expected ($C_{14}H_{14}S_1$), and observed ($C_{12.6}H_{14.4}S_{1.0}Br_{0.1}$) empirical formulae, with the low bromine content due to the end groups. Characterization studies were conducted by means of FTIR and ^{1}H NMR spectroscopy. The FTIR spectrum for the polymer is shown in Fig. 1. Thiophene ring stretching vibrations are observed at 1440–1500 cm^{-1} with phenylene ring vibrational bands seen at 1605 and 1545 cm^{-1}. In addition, the thienylene C_β–H out-of-plane bending vibration at about 830 cm^{-1} and the C_β–H stretching mode at 3057 cm^{-1} are indicative of 2,3,5-trisubstituted thiophenes.[25] The C–H aromatic out-of-plane bending mode at *ca.* 875 cm^{-1} is consistent with the *para*-substitution pattern of the phenylene moiety.

Fig. 2 depicts the ^{1}H NMR spectra for the monomer **6** and polymer $PBTC_4$. In the monomer spectrum, the two doublets centered at δ 7.23 and 6.99 with a coupling constant of 5.2 Hz are assigned respectively to the thiophene C_α–H and C_β–H resonances whilst the singlet at δ 7.47 is attributed to the protons on the phenylene moiety. The remaining four sets of resonances at the aliphatic region are consistent with the presence of the *n*-butyl pendant. After polymerization, the two sets of doublets (unshifted from δ 7.23 and 6.99) due now to the protons on the terminal thienylene depicted greatly attenuated intensities. Meanwhile, the internal thienylene C_β–H resonances on the internal thiophene rings and the phenylene protons are manifested at *ca.* δ 7.10 and 7.50 respectively. The splitting of these resonances is ascribable to the differing chemical environments of the protons on the thienylene and phenylene moieties within the polymer backbone. In addition, the existence of terminal bromophenylene moieties are evidenced by the resonance at δ 7.64.

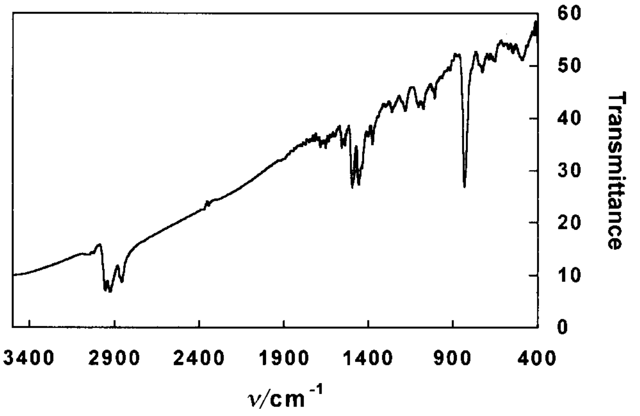


Fig. 1 FTIR spectrum of the polymer $PBTC_4$.

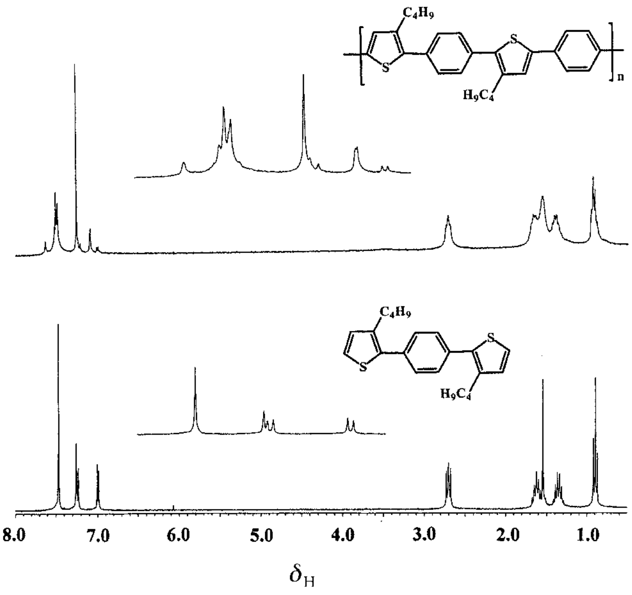


Fig. 2 ^{1}H NMR spectra of monomer **6** and $PBTC_4$.

Optical properties

Solution spectroscopy measurements were carried out carefully with freshly prepared solutions in accordance with the method described by Demas *et al.*[26] The spectra were determined in dilute chloroform solution (*ca.* 10^{-5} M), in order to avoid the possibility of concentration quenching or reabsorption and reemission, and all the solutions were purged with N_2 prior to measurement. The polymer exhibited an absorption maximum at 388 nm in $CHCl_3$ solution, which is 10 nm blue-shifted in comparison to $PBTBC_4$. As the molecular weight is almost the same as that of $PBTBC_4$ measured under identical conditions, this may be caused by the change in the torsion angle between aromatic rings because of structure modification,[14,20] thereby reducing coplanarity in the polymer backbone.

In solution, $PBTC_4$ exhibited a fluorescent emission maximum at 488 nm corresponding to a blue–green emission. It is quite close to that of $PBTBC_4$ (492 nm) and, therefore, an increase of Stokes shift is observed. The fluorescence quantum yield of the polymer relative to quinine sulfate as calculated by the approach of Davey *et al.*[27] is 48%, higher than that of $PBTBC_4$ (26%) reported earlier. This effect could be attributed to the higher content of 1,4-phenylene moieties, contributing to a more rigid polymer structure with the effect that relaxation from the excited state through non-radiative (*e.g.* thermal) processes will be reduced with consequently higher fluorescence quantum yield.[27,28] Another plausible answer as to why thiophene containing polymers seem to posses low fluorescence quantum yield is that the presence of heavy atoms, such as sulfur, favours intersystem crossing (ISC) due to spin-orbital coupling, and ISC can be an efficient route for quenching fluorescence.[29]

Light-emitting diodes

Despite the moderate molecular weight, our polymer may be spin-coated on glass or quartz substrates to afford pinhole-free films of good quality. Fig. 3 depicts the absorption and

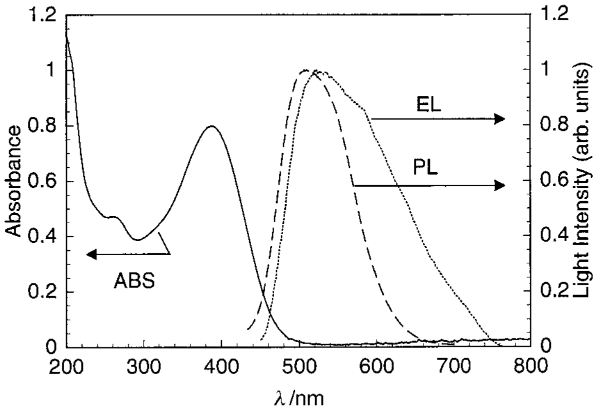


Fig. 3 UV–VIS absorption, photoluminescence and electroluminescence spectra of $PBTC_4$ film.

photoluminescence spectrum of a thin film of the polymer. The absorption maximum remained unshifted at 388 nm from that measured in the solution phase, which is suggestive of the current polymer being rigid with minimal conformational changes in going from its solution to condensed phase. However, both the absorption and emission maxima of the polymer film are bathochromically shifted with reference to that of an analogue polymer **1** (R = *n*-heptyl) reported by Fahlman *et al.*[14] From the extrapolation of the low energy edge of the optical absorption spectrum, the band-gap energy of $PBTC_4$ was estimated to be 2.7 eV. On the basis of the absorption spectrum measurements and a consideration of the polymer's onset oxidation (1.1 V *vs.* Ag/Ag^+) as evaluated from the cyclic voltammogram of spin-cast films on ITO substrates, which may be correlated to the polymer's ionisation potential,[30] the band scheme (Fig. 4) of $PBTC_4$ may be derived and contrasted with that of the polymer **1** (R = *n*-heptyl).[14] In comparison, our polymer has a much lower band-gap, an effect ascribable not just to the shorter pendant chain, but also to the diminished steric effects arising from a regioregular orientation of the alkyl pendants on the thienylene moieties, separated by 1,4-phenylene moieties with a consequently enhanced conjugation along the polymer backbone.

In the film state the emission maximum (upon excitation at 458 nm) occurs at 517 nm with an emitted green light clearly visible. The corresponding film-phase photoluminescence quantum yield (under excitation by an argon laser at 458 nm) as determined using an integrating sphere was 17%. The electroluminescence spectrum of an ITO/$PBTC_4$/Mg-In device, shown in Fig. 3, is almost identical to that for photoluminescence, indicating that the same excited state is involved in the two processes.

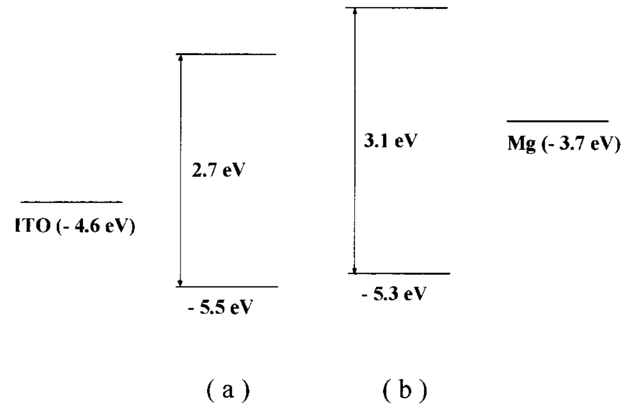


Fig. 4 Schematic energy band diagram of the conduction and valence bands of polymers: (*a*) $PBTC_4$; (*b*) structure **1** (R = *n*-heptyl).

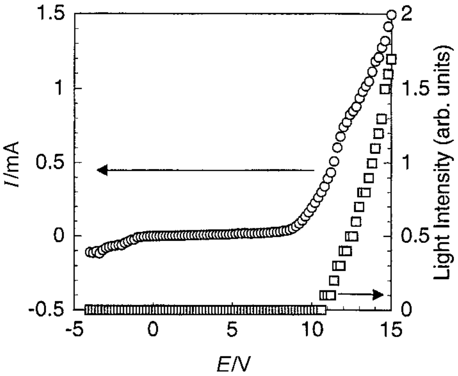


Fig. 5 (○) Current–voltage and (□) luminescence–voltage characteristics of an ITO/ $PBTC_4$/Mg-In device.

Fig. 5 represents typical current–voltage and luminescence–voltage characteristics in a device. Current and light emission arise almost at the same voltage, with the turn-on voltage at *ca.* 10 V. This is comparable to that reported earlier in devices fabricated from polymer **1** (R = *n*-pentyl)[14] and is promising despite the use of a non-optimized device configuration.

Conclusion

We have synthesized and characterized a new soluble blue–green light-emitting polymer composed of a regioregular arrangement of alternating 3-butyl-2,5-thienylene and 1,4-phenylene moieties by means of a Grignard cross-coupling approach. The derived polymer has good solubility in common organic solvents and was electrically conductive, attaining a maximum conductivity of 7.4×10^{-4} S cm^{-1} upon doping with iodine. DSC results indicate that the polymer is a semicrystalline. The polymer displayed highly fluorescent characteristics with a maximum solution fluorescence quantum yield of 48% relative to quinine sulfate. The photoluminescence quantum yield was determined to be about 17%. LED device fabricated with the polymer as emitter layer afforded a green light emission.

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References

1 M. Hope, H. P. Kallmann and P. Magnante, *J. Chem. Phys.*, 1963, **38**, 2042.
2 W. Helfrich and W. G. Schneider, *Phys. Rev. Lett.*, 1965, **14**, 229.
3 K. Kaneto, K. Yoshino, K.-C. Kao and Y. Inuishi, *Jpn. J. Appl. Phys.*, 1974, **13**, 1023.
4 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913.
5 C. Adachi, T. Tsutsui and S. Saito, *Appl. Phys. Lett.*, 1989, **56**, 799.
6 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539.
7 (*a*) Y. Ohmori, M. Uchida, Keiro Muro and K. Yoshino, *Jpn. J. Appl. Phys.*, 1991, **30**, L1938; (*b*) Y. Ohmori, M. Uchida, Keiro Muro and K. Yoshino, *Jpn. J. Appl. Phys.*, 1991, **30**, L1941.
8 D. Byaun and A. J. Heeger, *Appl. Phys. Lett.*, 1991, **58**, 1982.
9 G. Gustaffason, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri and A. J. Heeger, *Nature*, 1992, **357**, 477.
10 (*a*) G. Grem, G. Leditzky, B. Ullrich and G. Leising, *Adv. Mater.*,

1992, **4**, 36; (*b*) G. Leising, S. Tasch, F. Meghdadi, L. Athouel, G. Froyer and U. Sherf, *Synth. Met*., 1996, **81**, 185.
11 (*a*) N. C. Greenham, S. C. Moratti, D. D. C. Bardley, R. H. Friend and A. B. Holmes, *Nature*, 1993, **356**, 628; (*b*) N. Tessler, N. T. Harrison and R. H. Friend, *Adv. Mater*., 1998, **10**, 64.
12 A. J. Epstein, J. W. Blatchford, Y. Z. Wang, S. W. Jessen, D. D. Gebler, L. B. Lin, T. L. Gustafsson, H. L. Wang, Y. W. Park, T. M. Swager and A. G. MacDiarmid, *Synth. Met.*, 1996, **78**, 253.
13 M. Berggren, O. Inganas, G. Gustaffason, J. Rasmusson, M. R. Andersson, T. Hjertberg and O. Wennerstrom, *Nature*, 1994, **372**, 444.
14 M. Fahlman, J. Birgersson, K. Kaeriyama and W. R. Salaneck, *Synth. Met*., 1995, **75**, 223.
15 H. Saadeh, T. Goodson III and L. Yu, *Macromolecules*, 1997, **30**, 4608.
16 (*a*) S. C. Ng, P. Fu, W. L. Yu, H. S. O. Chan and K. L. Tan, *Synth. Met.*, 1996, **87**, 119; (*b*) S. C. Ng, H. S. O. Chan, P. Miao and K. L. Tan, *Synth. Met*., 1997, **90**, 25; (*c*) S. C. Ng, W. L. Yu and A. C. H. Huan, *Adv. Mater*., 1997, **9**, 887; (*d*) S. C. Ng, P. Miao and H. S. O. Chan, *Chem. Commun*., 1998, 153; (*e*) S. C. Ng, X. C. Zhou, P. Miao, H.S.O. Chan, S. F. Y. Li and P. Fu, *Langmuir*, 1998, **14**, 1748; (*f*) S. C. Ng, P. Miao, Z. K. Chen and H. S. O. Chan, *Adv. Mater*., 1998, **10**, 782.
17 S. C. Ng, J. M. Xu and H. S. O. Chan, *Synth. Met*., 1998, **92**, 33.
18 (*a*) S. C. Ng, L. G. Xu and H. S. O. Chan, *Synth. Met*., 1998, **94**, 185; (*b*) S. C. Ng, L. G. Xu and H. S. O. Chan, *J. Mater. Sci. Lett*., 1997, **16**, 1738; (*c*) S. C. Ng and L. G. Xu, *Adv. Mater*., 1998, **10**, in press.
19 A. Pelter, J. M. Maud, I. Jenkins, C. Sadeka and G. Coles, *Tetrahedron Lett*., 1989, **30**, 3461.
20 J. R. Reynolds, J. P. Ruiz, A. D. Child, K. Nayak and D. S. Marynick, *Macromolecules*, 1991, **24**, 678.
21 R. D. McCullough, R. D. Lowe, M. Jayaraman and D. L. Anderson, *J. Org. Chem*., 1993, **58**, 904.
22 T. Kawai, T. Kuwabara, S. Wang and K. Yoshino, *J. Electrochem. Soc.*, 1990, **137**, 3793.
23 T. Kawai, S. Nagame, M. Nakazono and K. Yoshino, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 1934.
24 J. P. Ruiz, J. R. Dharia, J. R. Reynolds and L. J. Buckley, *Macromolecules*, 1992, **25**, 849.
25 J.-E. Osterholm, J. Laakso, P. Nyholm, H. Isotalo, H. Stubb, O. Inganas and W. R. Salaneck, *Synth. Met*., 1989, **28**, C435.
26 J. N. Demas and G. A. Crosby, *J. Phys. Chem*., 1971, **75**, 991.
27 A. P. Davey, S. Elliott, O. O'Connor and W. Blau, *J. Chem. Soc., Chem. Commun*., 1995, 1433.
28 T. J. Kang, J. Y. Kim, K. J. Kim, C. Lee and S. B. Rhee, *Synth. Met*., 1995, **69**, 377.
29 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings Publ. Co., New York, 1978, p. 48.
30 H. Eckhardt, L. W. Shacklette, K. Y. Jen and R. L. Elsenbaumer, *J. Chem. Phys*., 1989, **91**, 1303.

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