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A Novel Approach Toward Low Optical Band Gap Polysquaraines

A. Ajayaghosh* and J. Eldo

Photochemistry Research Unit, Regional Research Laboratory, CSIR,
Trivandrum 695 019, India

aajayaghosh@rediffmail.com

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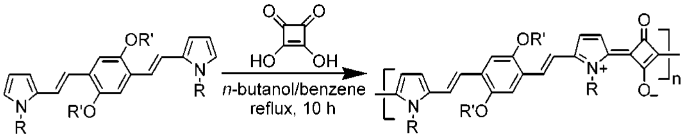
ABSTRACT



Polycondensation of 2,5-dialkoxydivinylbenzene-bridged bispyrroles and squaric acid resulted in extensively conjugated polymers with strong near-infrared (NIR) absorption around 800–1000 nm, which is a signature of their low band gap (E_g). Conjugated polymers with such a strong NIR absorption are rare. One of the synthesized polysquaraines showed a significantly low E_g of 0.79 eV with an intrinsic conductivity of 5.3×10^{-4} S/cm.

Since optical absorption in π-conjugated systems plays a key role in determining the HOMO−LUMO energy gap and the intrinsic electronic properties, control of these parameters by molecular engineering is of great significance to the design of low band gap (E_g) polymers.[1] To a large extent, this has been achieved with the help of strategies such as rigidification of the polymer backbone and enhancement of a polymer's nonclassical quinoid character.[2,3] Among several recent approaches, the twist inhibition between consecutive repeating units of conjugated polymers using ladder-type bonds,[4] reversible noncovalent linkages,[5] and strong donor−acceptor interactions[6] are shown to be effective in achieving reduced E_g. Even though several oxidative polymerization methods are available for the synthesis of conjugated polymers with E_g below 1 eV, a reasonably viable nonoxidative polymerization pathway towards intrinsically semiconducting polymers with adequate solubility in organic solvents remains elusive.[7]

A novel class of polymers that has generated considerable interest in recent years is polysquaraines in anticipation of their low HOMO−LUMO separation due to a strong donor−acceptor interaction.[8,9] Unfortunately, none of these reports

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* Fax: +91 471 490 186.

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(6) Donor−acceptor strategies reported earlier are not very successful in producing extremely low E_g polymers; see: (a) Yamamoto, T.; Zhou, Z.-h.; Kanbara, M.; Kizu, K.; Maruyama, T.; Nakamura, Y.; Fukuda, T.; Lee, B.-L.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K.; Sasaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 10389. (b) Van Mullekom, Vekemans, J. A. J. M.; Meijer, E. W. *Chem. Eur. J.* **1998**, *4*, 1235. (c) Zhang, T. Q.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 5065. (d) Zhang, T. Q.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *120*, 5355.

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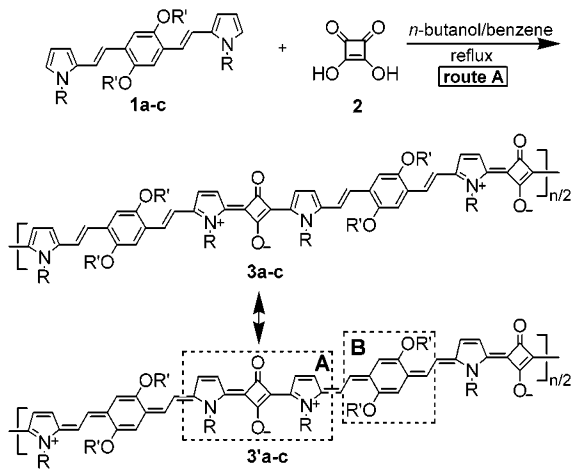
were successful in realizing a soluble low E_g polymer despite the recent theoretical prediction that squaraine dyes can be used to construct intrinsically semiconducting polymers with extremely small band gaps.[10] Here, we describe a rational approach toward the synthesis of low E_g polysquaraines that are reasonably soluble and intrinsically semiconducting with intense NIR sensitivity.[11] The idea involves a non-oxidative polycondensation of logically selected molecular components via the in situ generation of an organic dye **A** at well-defined positions of a conjugated backbone, which is capable of electronically communicating with each repeating segment with the aid of a strongly electron-donating moiety **B**. This has been illustrated by the polycondensation of electron-rich bispyrroles with squaric acid, leading to the formation of low E_g polymers **3a**−**c** (Scheme 1).

Scheme 1



3a, R = $C_{12}H_{25}$, R' = C_8H_{17}; **3b**, R = $C_{12}H_{25}$, R' = CH_3; **3c**, R = CH_3, R' = C_4H_9

We speculated that the positive charge on the zwitterionic dye moieties could be delocalized along the conjugated backbone, thus generating quinoid resonance structures **3′a**−**c**. For this reason, bispyrroles **1a**−**c** were prepared by the Wittig−Horner−Emmons reaction of the corresponding *N*-alkylpyrrole-2-carboxaldehyde with appropriate bisphosphonate esters.[12] Compounds **1a**−**c** showed absorption maxima due to $\pi-\pi^*$ transition around 400−420 nm with strong fluorescence emission around 470−480 nm. Polycondensation of **1a**−**c** with squaric acid in stoichiometric quantities resulted in the formation of intensely colored products (**3a**−**c**), which were isolated in 69−75% yields after repeated precipitation and washing with hexane and diethyl ether, respectively, in the form of powders or ribbons with metallic luster. The reaction conditions could be optimized by changing the dilution of the reactants and composition of the solvents. The progress of the reaction was monitored by following the changes in the absorption spectra of the reaction mixtures at different time intervals (Figure 1).

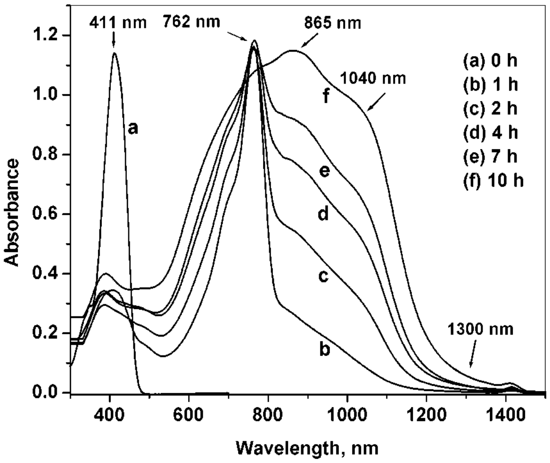


Figure 1. The evolution of the absorption spectra of polysquaraines **3c** with time.

Polysquaraines with long alkyl chains on the benzene and the pyrrole moieties were soluble in organic solvents such as dichloromethane, chloroform, tetrahydrofuran, and toluene.

All new compounds were characterized by spectral data, which were in agreement with their structures (see Supporting Information). ^{1}H NMR spectrum of the soluble polymer **3a** showed considerable broadening of the resonance bands corresponding to the aromatic protons, indicating strong $\pi-\pi$ interaction of the rigid backbone. For a better insight into the structure of the polymers, the model compound **4** was prepared under controlled conditions (Scheme 2). Spectral characteristics of this compound were identical with that of the intermediate compound corresponding to the 762 nm band in Figure 1. Structures of these compounds were established by NMR and HRMS analyses. These compounds were subsequently used for the synthesis of **3c** (route B), which showed identical spectral properties and thereby established their structural identity. The average molecular weight (M_n) of the most soluble polymer **3a** was around 17000−18000 g/mol ($M_w/M_n \approx 10.2$) as determined by the size exclusion chromatography (SEC) using polystyrene

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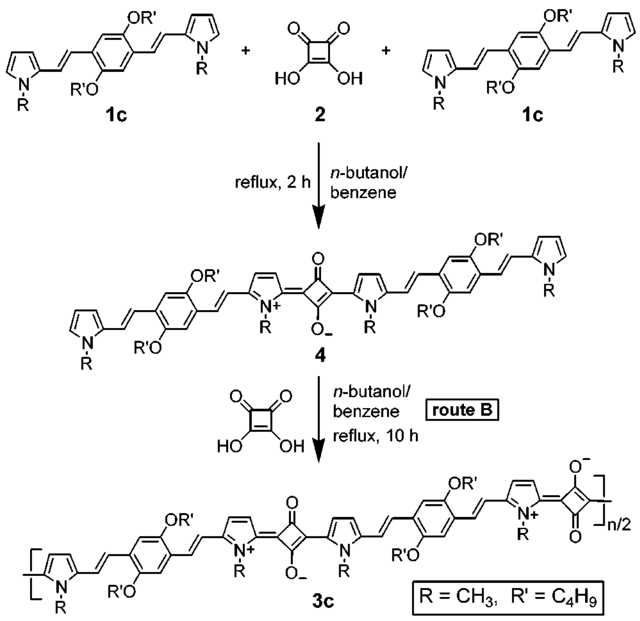
Scheme 2



standards.[13] Further purification of the polymer did not show any change in the broad dispersity, indicating that this could be due to the possible aggregation of the polysquaraines. Thermogravimetric analysis (TGA) under nitrogen atmosphere revealed a decomposition temperature around 300 °C for **3a**−**c**.

The UV−vis−NIR absorption spectra of **3a**−**c** revealed several interesting properties, which are unique to the new polymers. For example, the intense and broad NIR absorption of **3a**−**c** in toluene with vibronic features around 750−1050 nm in comparison with the sharp absorption of **4** is an indication of a high degree of conjugation and planarity of the former (Figure 2). Since the ground-state S_0 and the first excited singlet state S_1 of squaraines represent intramolecular charge transfer states of the donor−acceptor−donor type interaction, we anticipated that the introduction of a strong conjugated electron donor bridge and elongation of the conjugation length will substantially improve the absorption properties of the resulting polysquaraines. The observed spectral properties strongly support this argument. The optical and electronic properties of **3a**−**c** are summarized in Table 1 and reveal that the alkoxy substituents have considerable influence on their absorption properties, E_g, and electrical conductivities. The solution band gap of **3c** is one of the lowest values reported for any conjugated polymer.[14]

Table 1. Solution and Solid-State Electronic Properties of **3a**−**c**

	solution[a]			solid-state[b]			intrinsic
polymer	λ_{max} (nm)	λ_{onset} (nm)	E_g[c] (eV)	λ_{max} (nm)	λ_{onset} (nm)	E_g[c] (eV)	conductivity (S/cm)[d]
3a	998	1160	1.07	905	1208	1.02	6.2×10^{-6}
3b	870	1170	1.06	870	1390	0.89	2.2×10^{-5}
3c	871	1300	0.95	880	1570	0.79	5.3×10^{-4}

[a] In toluene. [b] Film cast from chloroform solution. [c] Calculated from the onset of absorption. [d] Measured on rectangular pellets by two-point probe method using a Kiethley Electrometer.

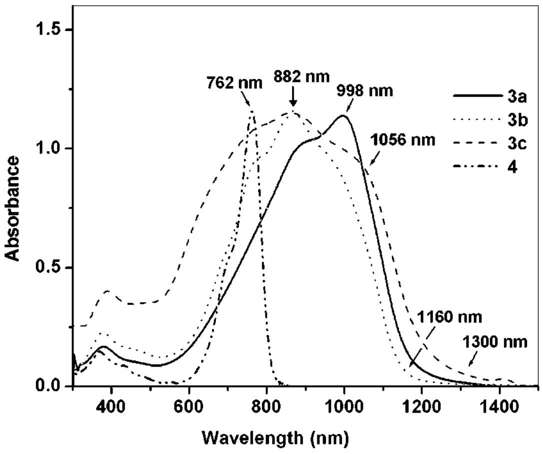


Figure 2. Absorption spectra of polysquaraines **3a**−**c** and **4** in toluene.

The intrinsic conductivity of **3a** is 6.2×10^{-6} S/cm, whereas **3c** showed an enhanced conductivity of 5.3×10^{-4} S/cm, which reveals that the length of the alkyl chains plays a key role in the conducting properties of these materials. X-ray data reveal that steady increase in the alkyl chain length could produce disruption of the stacking by increasing the *d*-spacing within the layered assemblies as observed in the case of regioregular polythiophenes.[15] For example, **3c** showed an interplanar distance of 11 Å with an interlayer π-stacking distance of 3.4 Å, indicating compact molecular packing with ordered microstructural domains. The ordered domains present in such self-organized microstructures of π-conjugated polymers have a crucial role in their charge carrier mobilities and photopysical properties.[16] On increasing the length of the hydrocarbon side chains from **3b** to **3a**, both interplanar and interlayer spacing increased from 17 to 20.5 and 3.8 to 4.3 Å, respectively, indicating considerable disruption of the π-stacking. Consequently, the conductivities showed a drastic decrease while going from **3c** to **3a**.

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In conclusion, we have shown that the optical and electronic properties of polysquaraines can be significantly altered to the low band gap region when coupled with a strongly electron-donating conjugated moiety. The broad and structured NIR absorption spectra of the new polysquaraines suggest a high degree of conjugation and planarization of the polymer backbone. This is one of the simplest examples to demonstrate how optical and electronic properties of donor−acceptor-type conjugated polymers can be tuned by the logical selection of their molecular components. We foresee a wider use of the present approach for the designing of new π-conjugated materials with novel optoelectronic properties.

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Supporting Information Available: Experimental procedures and characterization data of **1a**−**c**, **3a**−**c**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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