

Effect of Transannular π – π Interaction on Emission Spectral Shift and Fluorescence Quenching in Dithia[3.3]paracyclophane–Fluorene Copolymers

Wei-Ling Wang,^{*,†} Jianwei Xu,[‡] Zhe Sun,[†] Xinhai Zhang,[‡] Yong Lu,[†] and Yee-Hing Lai[†]

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, and Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602

Received March 7, 2006; Revised Manuscript Received August 1, 2006

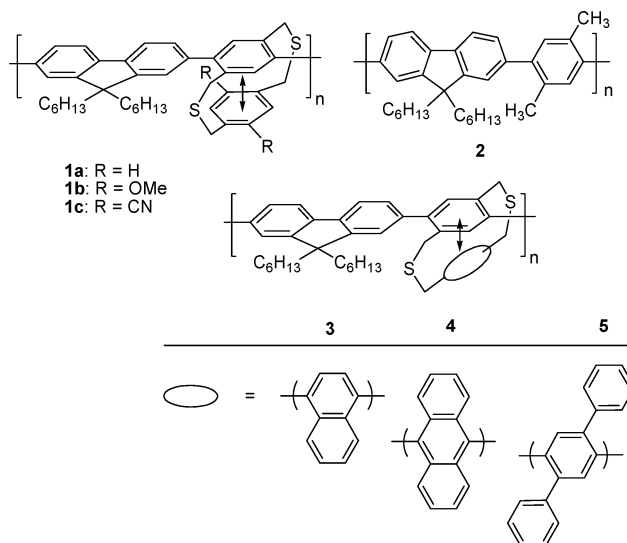
ABSTRACT: A series of dithia[3.3]paracyclophane–fluorene copolymers **1a–c** and **3–5** were synthesized by a palladium-catalyzed reaction between 9,9-di-*n*-hexylfluorene-2,7-bis(trimethylene boronate) and the corresponding dithiacyclophane precursors. The transannular π – π interaction in the dithiacyclophane modified the electronic and optical properties of the copolymers significantly, resulting in emission red shifts relative to a reference polymer **2**. The observed shift in **1a** and **5** was accompanied by enhanced photoluminescence (PL) efficiency, whereas that in **1b**, **1c**, **3**, and **4** experienced a significant to nearly complete fluorescence quenching. The quenching effect is likely to involve an electron-transfer process and could be correlated qualitatively to the reduction potential of the “external” aromatic moiety in the cyclophane unit.

Introduction

Organic conjugated polymers have been investigated for their promising electronic and optical applications.¹ One of the current research interests on conjugated polymers focuses on tuning their spectral and electrical properties. Many approaches to tuning the property of conjugated polymers have been achieved by means of a variety of modifications of the polymer backbone, such as attachment of side chains or substituents with varied electronic properties,² incorporation of p or n block of different nature,³ and a change in pH,⁴ to name a few. These attempts aimed at increasing luminescence efficiency and selection of color,⁵ thus resulting in the desirable properties. As a kind of noncovalent interaction, aromatic π – π interaction has been particularly emphasized in supramolecular assembly⁶ due to the implication of biological significance,⁷ but it is rarely used as a tuning element to control the properties of conjugated polymers. It was, however, employed as a “linker” to extend conjugation in a number of organic conjugated polymers.⁸

Recently, we reported our preliminary results on the optical properties of fluorene–[3.3]paracyclophane conjugated polymers.⁹ It was demonstrated that the transannular π – π interaction in the paracyclophane could serve as a sensitive internal regulator of the polymers’ emission properties. For example, **1a** emitted blue light but exhibited a significant red shift accompanied by an enhanced fluorescence quantum yield as compared to the reference polymer **2**. On the contrary, the substituted benzene ring in the paracyclophane in **1b** and **1c** acts as an internal fluorescence quencher via a probable intramolecular electron-transfer mechanism.¹⁰ Examples of the effect of electron-transfer processes on the optical properties of polymers via chromophores in the polymer backbone¹¹ or chromophores introduced as a pendant group¹² covalently bonded to the polymer backbone have been reported, but chromophores exhibiting quenching effect via through-space interaction have not been established. To substantiate the relationship between transannular π – π interaction and electron-transfer process in **1** and their effect on the optical properties

of such copolymers, we report a study of a series of oligomeric model compounds **15–18** and copolymers **3–5**. The condensed benzenoid or the terphenyl unit would exhibit varied electronic properties and thus alter the optical properties of the copolymers should the transannular π – π interaction and electron-transfer process remain significant in the series.



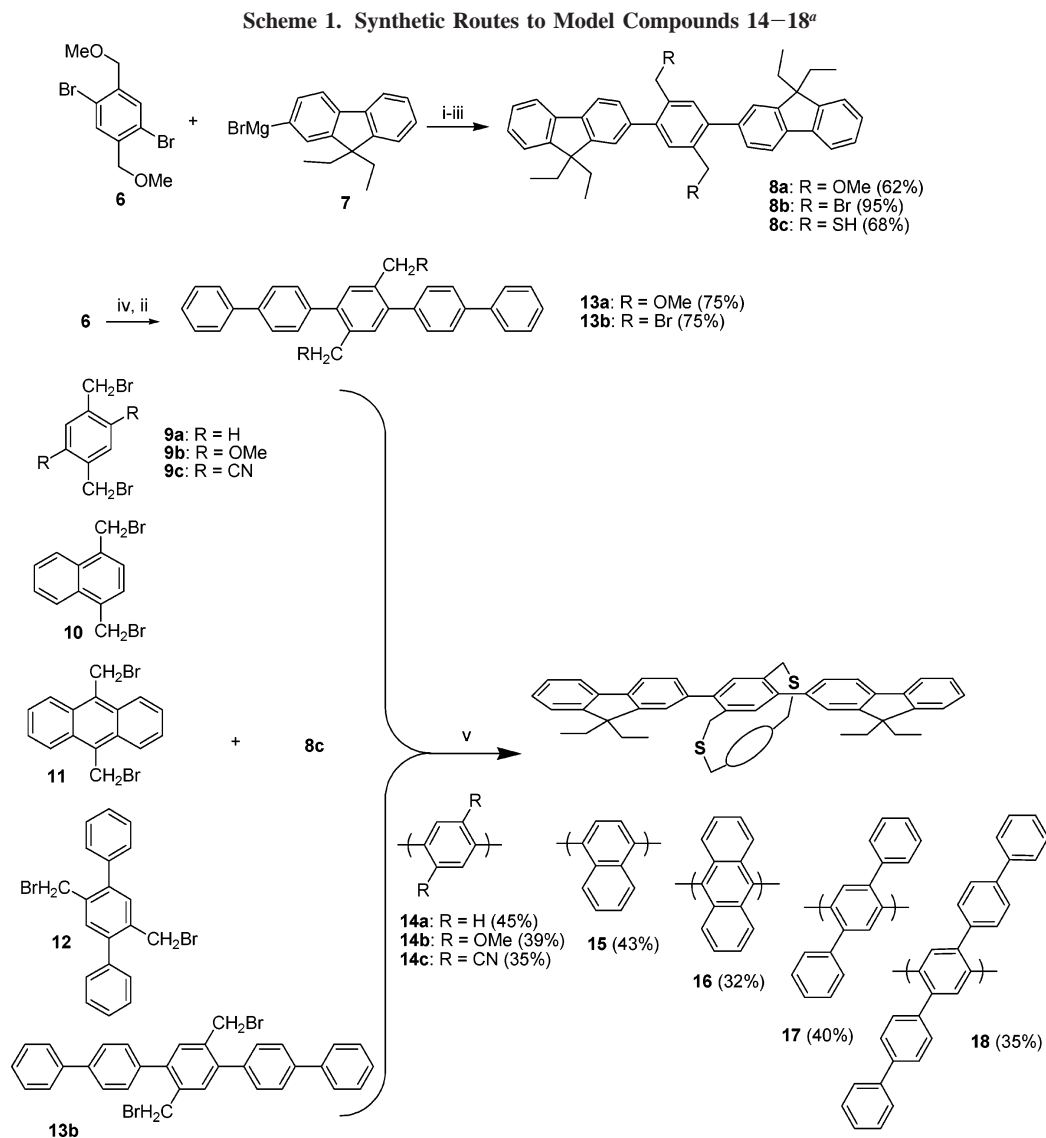
Results and Discussion

A series of model compounds **14–18** was synthesized by the synthetic approach to [3.3]paracyclophanes as illustrated in Scheme 1. The Grignard reagent **7** in THF was coupled with **6** catalyzed by Pd(PPh₃)₄ to afford **8a**. Treatment of **8a** with HBr–CHCl₃ gave the desired dibromide **8b**, which reacted with thiourea, followed by base hydrolysis to give **8c** as a common precursor to the desired series of dithiacyclophanes. Cyclization reactions between **8c** and **9a–c** under high dilution conditions¹³ produced **14a–c**, respectively. Interestingly, two sets of triplets at δ 0.36 and δ 0.50 corresponding to methyl protons were observed in the respective ¹H NMR spectra of **14a–c**. This indicates that the central cyclophane unit exerts a relatively large steric effect that restricts free rotation about the fluorene–

* Corresponding author. E-mail: wlwang@imcb.a-star.edu.sg.

[†] National University of Singapore.

[‡] Institute of Materials Research and Engineering.



^a Reagents and conditions: (i) Pd(PPh₃)₄, THF, reflux; (ii) HBr–CHCl₃, room temperature; (iii) NH₂C(S)NH₂, ethanol, NaHCO₃, reflux; (iv) biphenylboronic acid, 2 M K₂CO₃, *n*-Bu₄NBr, Pd(PPh₃)₄, toluene, reflux; (v) KOH, ethanol/toluene, high dilution conditions. The yields are included in parentheses.

benzene bonds in these molecules at room temperature. In fact, there was no coalescence of the methyl signals up to 383 K in several dynamic ¹H NMR studies of these polyaryls, corresponding to a conformational barrier of >80 kJ mol⁻¹ estimated on the basis of the coalescence temperature method.¹⁴

A Suzuki coupling reaction between biphenylboronic acid and **6** in the presence of Pd(PPh₃)₄ yielded compound **13a**, which upon treatment with HBr gas afforded the dibromide **13b**. The dithiacyclophanes **15–18** were then similarly prepared by coupling reactions between **8c** and the corresponding dibromides **10**, **11**, **12**, and **13b**, respectively. All new compounds prepared in this work were characterized by spectroscopic methods and element analyses. As an example, Figure 1 gives the ¹H NMR spectrum of **16**. Compound **16** appeared as two doublets at δ 4.93, 4.72, 4.18, and 3.92, assigned to two groups of magnetically inequivalent bridge CH₂ groups. Like **14a–c**, two methyl groups of ethyl substituents at 9-position of fluorene showed two sets of triplets, indicating that two fluorenyl groups are hindered sterically and hence will not freely rotate along the central cyclophane part.

The general synthetic route toward the desired polymers employing the common precursor **19** is outlined in Scheme 2.

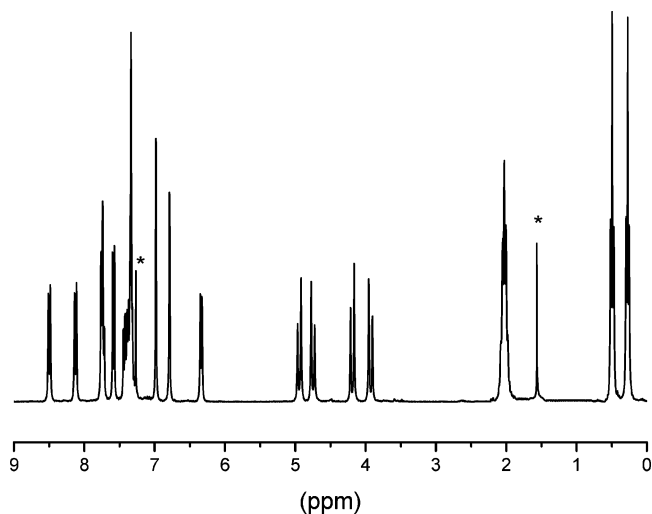


Figure 1. ¹H NMR spectrum of compound **16** in CDCl₃ at room temperature. *Residual solvent.

The palladium-catalyzed coupling reaction between **19** and **20a–c** afforded polymers **1a–c**. Using similar experimental

Download English Version:

<https://daneshyari.com/en/article/4993883>

Download Persian Version:

<https://daneshyari.com/article/4993883>

[Daneshyari.com](https://daneshyari.com)