ORGANIC LETTERS

2003
Vol. 5, No. 16
2765−2768

Alternating Conjugated and Transannular Chromophores: Tunable Property of Fluorene-Paracyclophane Copolymers via Transannular π–π Interaction

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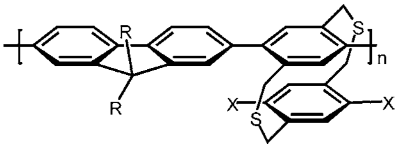
Received March 8, 2003 *(Revised Manuscript Received July 3, 2003)*

ABSTRACT



A series of fluorene-dithia[3.3]paracyclophane copolymers was synthesized by Suzuki coupling reactions of suitable precursors. Transannular π–π interactions altered the electronic and optical properties of the polymer backbone significantly. A large red shift in the emission spectrum of the unsubstituted polymer was accompanied by enhanced photoluminescence (PL) efficiency. Substitution in the cyclophane unit resulted in PL quenching.

Transannular $\pi-\pi$ interaction is one type of significant nonbonding interaction commonly observed between π-aromatic systems in chemical and biological systems.[1] The unique through-space[2] interaction associated with a high degree of structural rigidity in *para*-cyclophanes was recently used ingeniously to explore the optical properties of π-conjugated oligomers **1** and **2**[3] and polymers **3**.[4] In these systems, a *para*-[2.2]cyclophane was employed as a core and two chromophores are attached to the different aromatic rings. Thus, "conjugation" along the polymer backbone, for example, in **3**, could only be propagated via effective transannular interactions in the whole series of cyclophane units. Much work was focused on the investigation of the effect of stacking on delocalized excitons of chromophore-substituted cyclophanes in **1** and **2**.[3,5] Effective transannular interactions were also observed in the polymer **3**,[4] which exhibited novel optical properties. We propose a new type of alternating conjugated and transannular chromophores represented by oligomer **4** and polymer **5**. In these systems, there is linear conjugation in the polymer skeleton, and transannular $\pi-\pi$ interactions via the "external" aryl rings in the cyclophane units will be used to tune the properties

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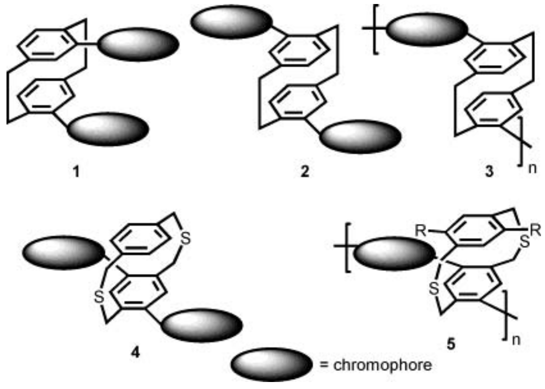
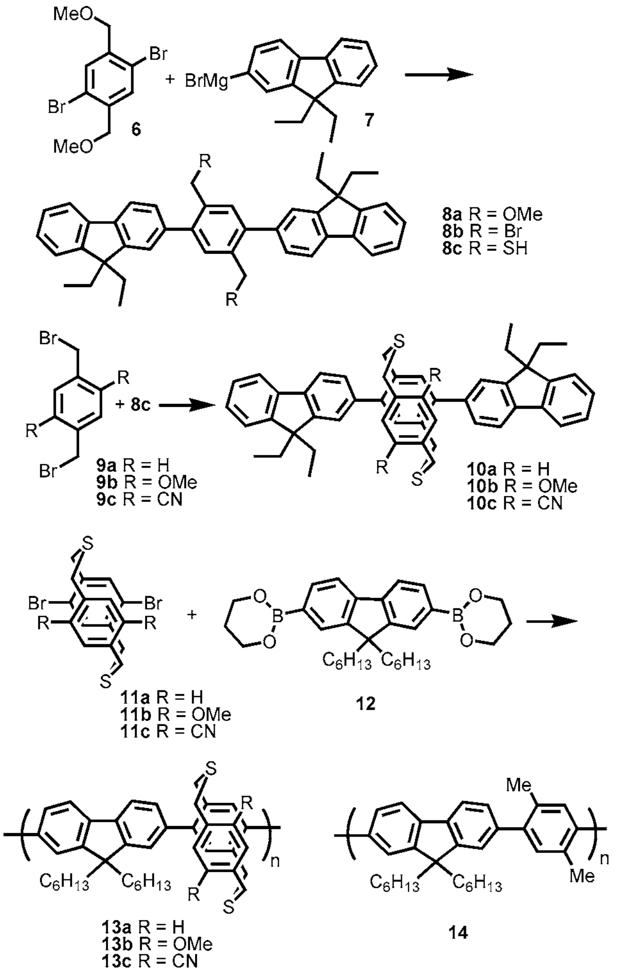
10.1021/ol034413r CCC: $25.00

of the polymer. Altering the properties of conjugated polymers via structural modifications and/or introduction of substituents with varied electronic properties,[6,7] the incorporation of *p* or *n* block,[8] and the change in pH[9] have been well documented, and this transannular effect may add a new and useful dimension in tuning the properties of conjugated polymers. In conjunction with our efforts in the study of fluorene-based conjugated polymers,[6,10] we wish to report the synthesis of a series of novel fluorene-dithia[3.3]-paracyclophane copolymers **13** and a preliminary study on the $\pi-\pi$ transannular effect on their optical properties.



Scheme 1. Synthetic Routes to Oligomers **10** and Polymers **13**[a]



[a] Reaction conditions. **6** + **7** → **8a**: Pd(PPh$_3$)$_4$, THF, reflux, 20 h. **8a** → **8b**: HBr−CHCl$_3$, room temperature, 10 h. **8b** → **8c**: NH$_2$C(S)NH$_2$, ethanol, NaHCO$_3$, reflux, 4 h. **8c** + **9** → **10**: KOH, ethanol/toluene, high dilution conditions. **11** + **12** → **13**: Pd(PPh$_3$)$_4$ (5 mol %), toluene/2 M K$_2$CO$_3$ (1:1), (n-Bu)$_4$NBr, 105 °C, 3 days.

The fluorene-paracyclophane polymers **13a**−**c** were synthesized using Suzuki coupling[11] reaction (these polymers were characterized by ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy, elemental analyses, and gel permeation chromatography). The difluorenylbenzene **8a** was prepared by a coupling of 1,4-dibromo-2,5-bis(methoxymethyl)benzene **6**[12] with the Grignard reagent of 2-bromo-9,9-diethylfluorene catalyzed by Pd(PPh$_3$)$_4$. Treatment of **8a** with HBr gave the dibromo compound **8b**, which was converted to the dimercaptan **8c** by a reaction with thiourea followed by base hydrolysis. Separate coupling reactions between **8c** and **9a**−**c** under high dilution conditions[13] produced the oligomers **10a**−**c**, respectively. Employing the Suzuki coupling strategy afforded the synthesis of polymers **13a**−**c** by the reactions of **11a**−**c** (details on the synthesis of these dithiacyclophanes will be published separately) with **12**.[14] Polymer **14** prepared from 1,4-dibromo-2,5-dimethylbenzene and **12** was used as a reference for later discussion. All polymers are readily dissolved in common organic solvents such as THF, chloroform, toluene, and xylene. The structure of **10a** was determined by X-ray crystallography, and an ORTEP drawing of **10a** is shown in Figure 1. The two fluorene units deviate from the central aromatic plane of the dithia[3.3]-cyclophane by 49.7 and 46.5°, respectively, in inverse

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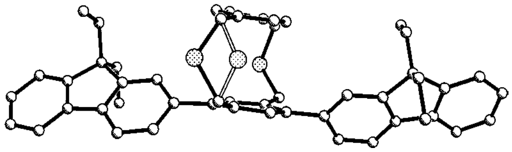

Figure 1. ORTEP drawing of compound **10a** (one of the sulfur atoms is disordered; hydrogen atoms are omitted for clarity).

directions. There is no significant deviation from planarity (mean deviation < 0.03 Å) for the two benzene rings in the cyclophane unit, but they tilt at a very small inter-ring angle of 2.4°. The interplane distance of the two benzene rings of 3.332 Å is less than the normal packing distance of aromatic rings in organic aromatic molecules (3.4 Å),[15] thus supporting potential transannular $\pi-\pi$ interaction between the two rings in the cyclophane unit.

The UV−vis absorption and photoluminescence (PL) spectra of **8a** (a reference) and **10a−c** are shown in Figure 2. In Figure 2a, **10a** (PL efficiency, $\phi_{PL} = 17\%$) exhibits a red shift of about 10 nm relative to **8a**, while that observed for **10b** and **10c** is about 14 nm, suggesting that **4b** and **4c** have more effective $\pi-\pi$ interaction than **4a**. An unexpected observation was that while the PL intensity of **10a** is significantly higher than that of **8a**, the PL of **10b** ($\phi_{PL} =$ 1%) and that of **10c** ($\phi_{PL} = \sim 0\%$) were essentially quenched thoroughly (Figure 2b). The dicyanobenzene in **10c** should behave as an electron acceptor inducing a transannular, intramolecular electron transfer between the polymer backbone and the dicyanobenzene units, thus resulting in a complete quenching of the PL of **10c**. Electronically the dimethoxybenzene in **10b** is normally considered to be an electron-donating unit.[16] It could, however, also be viewed as a "quencher" in some cases in a more general discussion on energy/electron transfer [17,18] (refer to a the discussion on polymers **13a−c** below).

The UV−vis absorption and PL spectra of polymers **13a−c** and **14** (as a reference) in THF and in film are shown in Figures 3 and 4, respectively. Only a smaller red shift of about 7 nm in the 0−0 absorption bands was observed comparing Figures 3a and 4a, implying that there is no considerable molecular conformational change in polymers **13a−c** going from solution to solid state. In both solution and thin film, **13a** exhibits a large red shift (>30 nm), while **13c** shows a significant blue shift (about 15 nm) in absorption bands in comparison to those of the reference **14**. The above is a good indication that the incorporation of [3.3]paracyclophane units causes significant changes to the electronic and optical properties of the polymer backbone via transannular $\pi-\pi$ interactions, although similar shifts are not apparent in the case of **13b**. Interestingly, **13b** shows a much larger red shift (46 nm) emission going from solution to solid film, while the shift observed for **13a** was significantly smaller (6 nm). The dependence of PL spectra of polymers **13a−c** on their concentration in a range from 10^{-4} to 2.5×10^{-6} M in THF was examined, but no emission of excimer was observed. This suggests that there is no significant interaction between the polymer chains due to perhaps the steric demand of the [3.3]paracyclophane units that discourage the formation of aggregates.

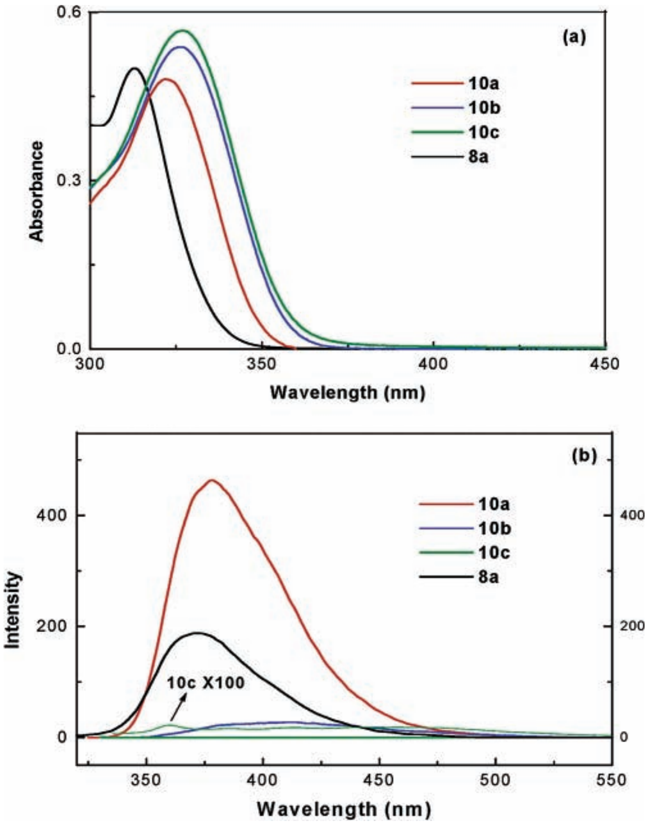

Figure 2. (a) UV−vis and (b) PL spectra of oligomers **10a−c** and **8a** measured from solutions (ca. 1×10^{-5} M) in THF at room temperature.

The ϕ_{PL} of **13a** (75%) is considerably larger (about 20%) than those of **14** both in solution and thin film. This could be a result of restricted rotation about the fluorene−cyclophane bonds in **13a**, giving it a more rigid molecular structure accountable for the higher observed ϕ_{PL}. Going from **13a** to **13b** ($\phi_{PL} = 36\%$) is accompanied by a significant drop (about 50%) in PL efficiency, while the PL for **13c** ($\phi_{PL} = 0\%$) is again completely quenched. The quench in **13c** could be readily attributed to an intramolecular electron-transfer from the polymer backbone to the dicyanobenzene units via transannular interactions, but the dimethoxybenzene units in **13b** seem to behave like quenchers as well. In general, the overall change in free energy ($\Delta G^{\ddagger}$) for

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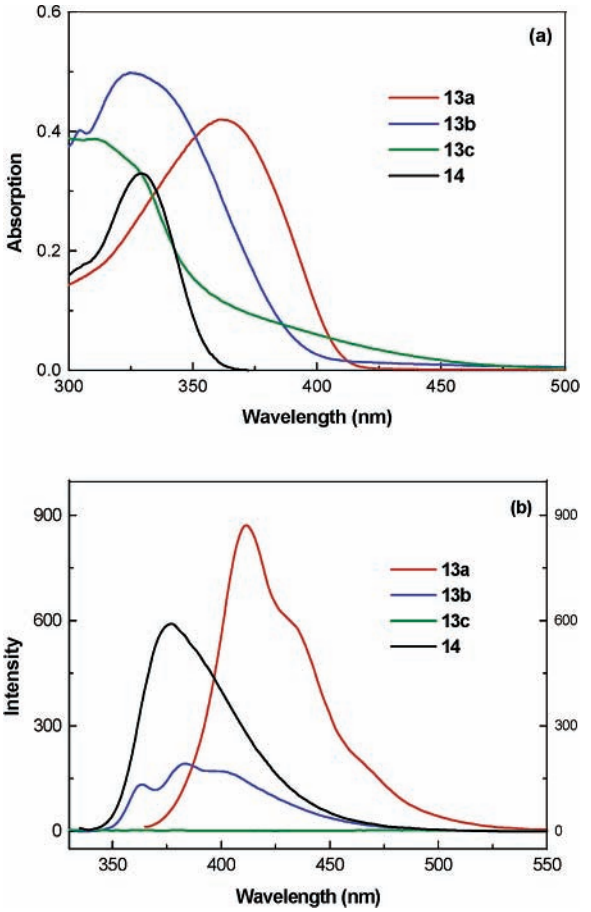

Figure 3. (a) UV−vis and (b) PL spectra of polymers **13a**−**c** and **14** measured from solutions (ca. 1 × 10^{-5} M) in THF at room temperature.

intermolecular electron-transfer could be estimated by the following equation:[18a] $\Delta G^{\ddagger} = E(\mathrm{P/P}^{\bullet+}) - \Delta E_{0-0} - E(\mathrm{Q/Q}^{\bullet-})$, where $E(\mathrm{P/P}^{\bullet+})$, ΔE_{0-0}, and $E(\mathrm{Q/Q}^{\bullet-})$ are defined as the oxidation potential of the polymer, the lowest singlet 0−0 excitation energy of the polymer, and the reduction potential of the quencher, respectively. In polymers **13a**−**c**, the polymer backbone is considered the electron donor and the substituted benzene rings in the cyclophane units are the quencher (electron acceptor). The values of $E(\mathrm{P/P}^{\bullet+})$ and ΔE_{0-0} for a general fluorene-benzene polymer backbone are 1.19 (vs SCE) and 3.34 eV, respectively.[6] The $E(\mathrm{Q/Q}^{\bullet-})$ values for benzene, 1,4-dimethoxybenzene, and 1,4-dicyanobenzene were reported to be −3.42,[19] <−2[18b], and −1.64 V,[18a] respectively. The estimated $\Delta G^{\ddagger}$ values are thus +1.27, >−0.15, and −0.51 eV, respectively, for **13a**−**c**, indicating that the driving force in energy for both **13b** and **13c** is favorable to electron transfer. This is in agreement with the "unexpectedly" low ϕ_{PL} observed for **13b** and with **13c** being a nonfluorescent polymer.

In conclusion, a series of proof-of-concept experiments show that there are significant transannular $\pi-\pi$ interactions in polymers **13a**−**c**, which alter the electronic and optical properties of the polymer backbone. A large red shift in the emission spectrum of **13a** was accompanied by an enhanced PL efficiency, although substitution in **13b** and **13c** seems to result in significant or complete quenching of the PL. The precursor **8c** could in principle be coupled with different types of benzenoid or heteroaromatic rings to construct the dithiacyclophane unit. Desulfurization of dithia[3.3]cyclophanes would also lead to a separate series of [2.2]cyclophanes with perhaps stronger transannular $\pi-\pi$ interactions. Work in both the above aspects is in progress in our laboratory.

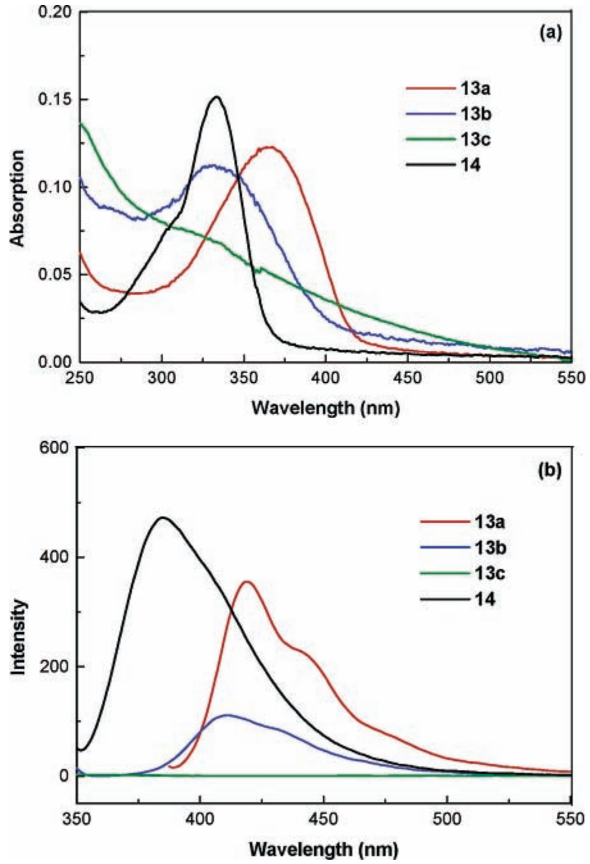

Figure 4. (a) UV−vis and (b) PL spectra of polymers **13a**−**c** and **14** measured from spin-coated films on quartz plates at room temperature.

Acknowledgment. This work was supported by the National University of Singapore (NUS). The authors thank the staff at the Chemical and Molecular Analysis Center, Department of Chemistry, NUS, for their technical assistance.

Supporting Information Available: Crystallographic data of **10a** (in CIF format) and molecular weights, quantum yields, and spectroscopic/elemental data of polymers **13a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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