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Effect of Transannular $\pi-\pi$ Interaction on Emission Spectral Shift and Fluorescence Quenching in Dithia[3.3]paracyclophane−Fluorene Copolymers

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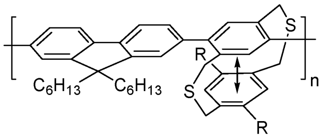
ABSTRACT: A series of dithia[3.3]paracyclophane−fluorene copolymers **1a**−**c** and **3**−**5** were synthesized by a palladium-catalyzed reaction between 9,9-di-*n*-hexylfluorene-2,7-bis(trimethylene boronate) and the corresponding dithiacyclophane precursors. The transannular $\pi-\pi$ interaction in the dithiaparacyclophane 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.

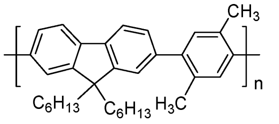
Introduction

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 $\pi-\pi$ interaction has been particularly emphasized in supramolecular assembly[6] 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 $\pi-\pi$ 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 backbone[11] or chromophores introduced as a pendant group[12] 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 $\pi-\pi$ 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 $\pi-\pi$ interaction and electron-transfer process remain significant in the series.



1a: R = H
1b: R = OMe
1c: R = CN



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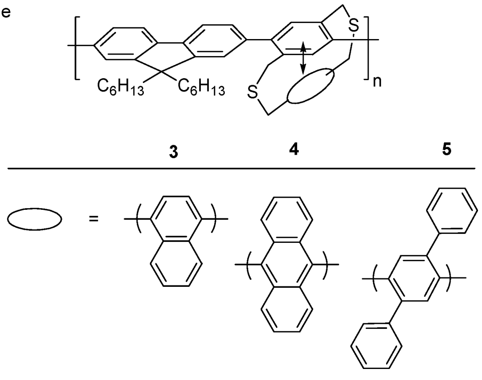

Results and Discussion

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 $Pd(PPh_3)_4$ to afford **8a**. Treatment of **8a** with $HBr-CHCl_3$ 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 conditions[13] 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−

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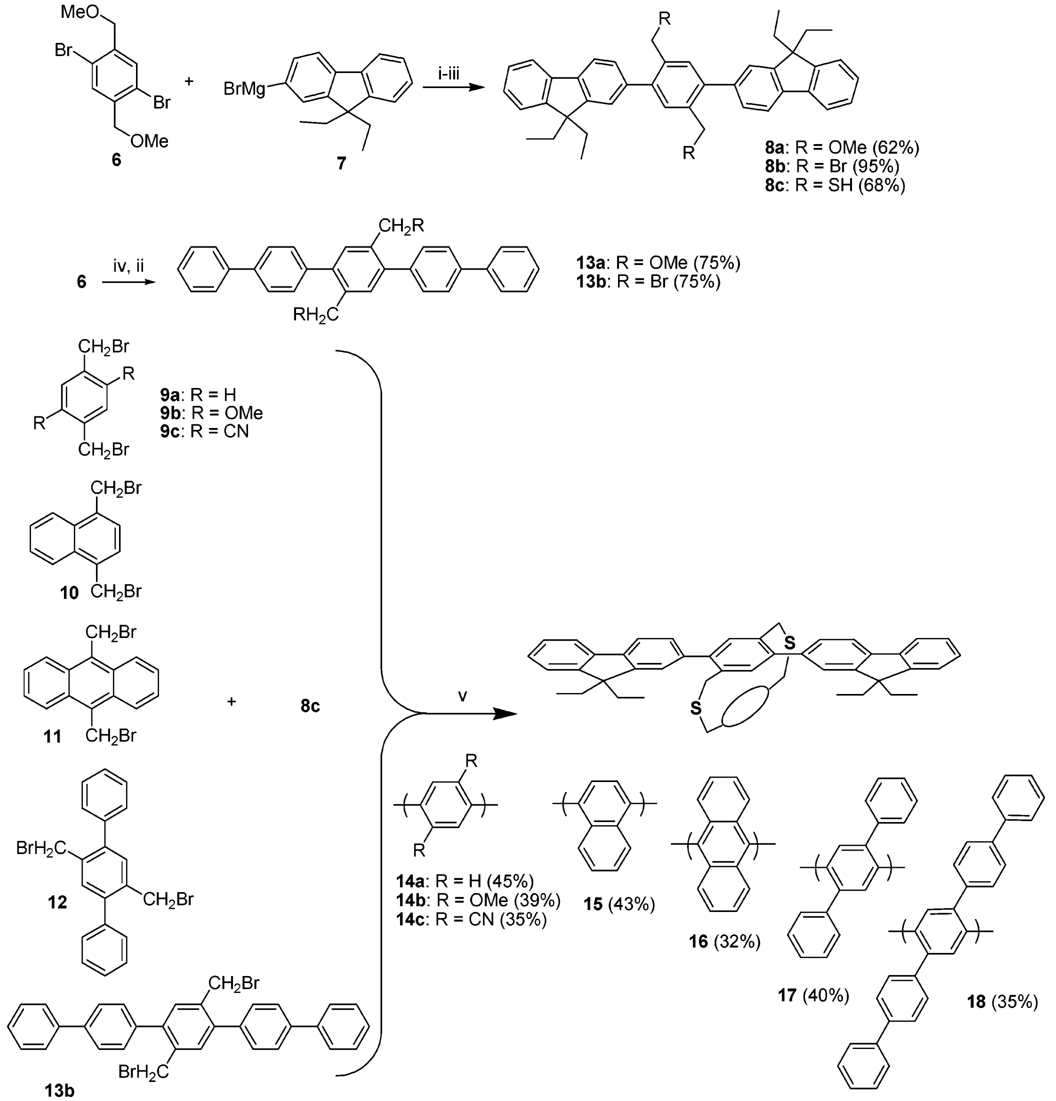
Scheme 1. Synthetic Routes to Model Compounds 14−18[a]



[a] Reagents and conditions: (i) $Pd(PPh_3)_4$, THF, reflux; (ii) $HBr-CHCl_3$, room temperature; (iii) $NH_2C(S)NH_2$, ethanol, $NaHCO_3$, reflux; (iv) biphenylboronic acid, 2 M K_2CO_3, n-Bu_4NBr, $Pd(PPh_3)_4$, 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 ^{1}H 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 $Pd(PPh_3)_4$ 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 ^{1}H 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 CH_2 groups. Like **14a**−**c**, two methyl groups of ethyl substituents at 9-position of fluorene showed two sets of triplets, indicating that two flurenyl 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.

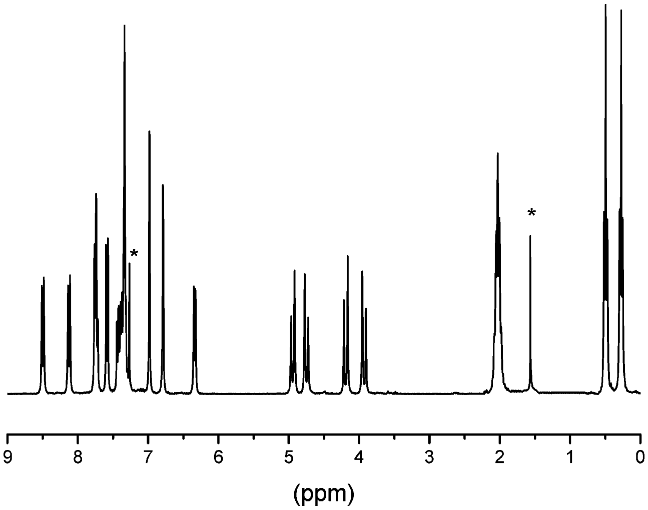
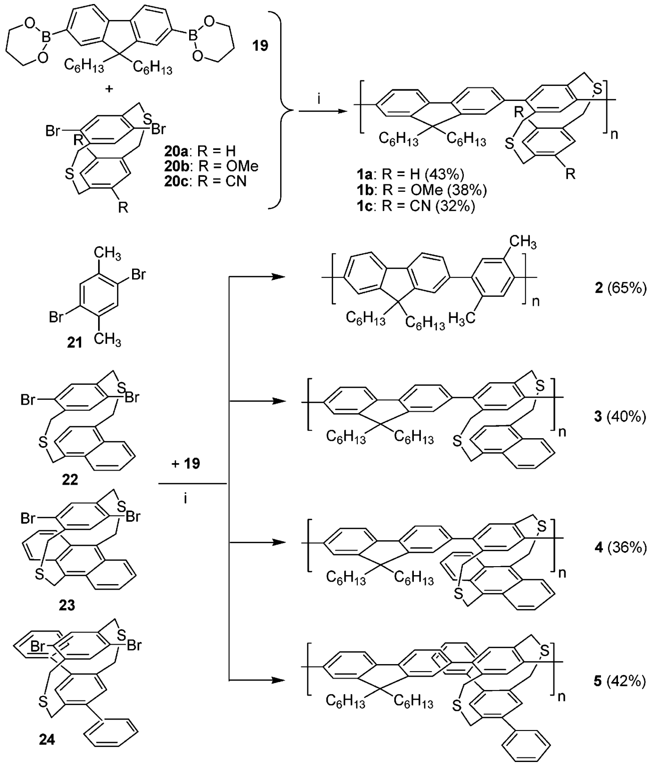


Figure 1. ^{1}H NMR spectrum of compound **16** in $CDCl_3$ at room temperature. *Residual solvent.

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

Scheme 2. Synthetic Routes to Copolymers 1−5[a]



[a] Reagents and conditions: (i) Pd(PPh$_3$)$_4$ (5 mol %), toluene/2 M K$_2$CO$_3$ (1:1), (n-Bu)$_4$NBr, 105 °C, 3 d. The yields are included in parentheses.

Table 1. Molecular Weights and Thermal Properties of Polymers

polymer	M_w	M_n	M_w/M_n	T_d
3	8400	4300	1.95	279
4	4900	3650	1.34	298
5	6460	4650	1.39	298

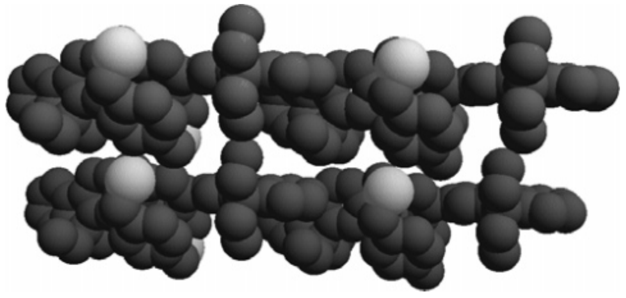
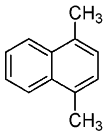


Figure 2. Crystal packing of **14a**.

Table 2. Optical Properties of Compounds 8a, 14a, 15−18, 25, and 26[a]



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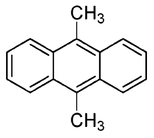

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compd	λ_{max} (THF) (nm) abs	λ_{max} (THF) (nm) em	λ_{max} (films) (nm) abs	λ_{max} (films) (nm) em	Φ_{PL} solution
8a	273, 293, 313	372	318	377	0.20
14a	322	378	327	372	0.17
15	323	382	327	379	0.12
16	318, 403, 427	450, 465	322, 407, 433	471	0.07
17	322	404	325	396	0.30
18	316	402	319	399	0.25
25	278, 289, 300	326, 338, 355			0.07
26	342, 359, 378, 400	408, 427, 453, 483			0.96

[a] The PL efficiency (ϕ_{PL}) of the model compounds in THF solutions was measured by using quinine sulfate (ca. 1 × 10^{-5} M solution in 0.1 M H$_2$SO$_4$, assuming ϕ_{PL} of 0.55) as a standard. Absorption maxima were taken as λ_{ex} for **14a**, **15**, **17**, and **18**. The λ_{ex} values for **8a**, **16**, **25**, and **26** are 293, 403, 300, and 378 nm, respectively.

procedures, the reactions between **19** and **21**−**24** gave the copolymers **2**−**5**, respectively, in isolated yields of 65%, 40%, 36%, and 42%. In general, the ^{1}H NMR spectra of the copolymers **3**−**5** clearly showed signals in the range of δ 3−5 corresponding to characteristic benzylic protons of dithiacyclophanes, indicating that the paracyclophane units remained intact during the polymerization in the formation of these polymers.

Polymers **3**−**5** were found to be readily soluble in common organic solvents, such as THF, chloroform, toluene, and xylenes. They were structurally characterized by various spectroscopic and elemental analyses. Their molecular weights against the polystyrene standards were determined by gel permeation chromatography (GPC) and are summarized in Table 1. The molecular weights of polymers were constantly relatively low even if various palladium catalysts ((Pd(PPh$_3$)$_4$, Pd$_2$(dba)$_3$/P(t-Bu)$_3$), etc.) and bases (K$_2$CO$_3$, Cs$_2$CO$_3$, diisopropylamine, CsF, KF) for Suzuki cross-coupling reaction[15] at different reaction temperatures were attempted in the polymerization process. In their structures determined by X-ray crystallography, the interplanar distances of the two central aromatic rings in the model compounds **14a** and **22** were found to be 3.33 and 3.32 Å, respectively. These are slightly shorter than that of the normal packing distance of benzenoid rings in organic molecules (3.4 Å),[16] indicating that transannular $\pi-\pi$ interaction is likely. The crystal packing of **14a** is illustrated in Figure 2 (crystallographic data in CIF format reported earlier),[9a] and it shows no significant intermolecular $\pi-\pi$ stacking among molecules of **14a**. This may suggest that the optical properties in the solid state described in a later discussion are unlikely to be derived from intermolecular transannular $\pi-\pi$ interactions in **14**−**18** or such interactions between polymer chains in **1** and **3**−**5**.

The UV−vis absorption and photoluminescence (PL) characteristics of **15**−**18** in THF and in film (ca. 1 × 10^{-5} M) are summarized in Table 2. A comparison of the electronic spectrum of **15** with those of 1,4-dimethylnaphthalene **25** and **8a** as references shows considerable absorption red shifts (Figure 3a) similar to the optical behavior of **14a**.[9a] Qualitatively, the absorption spectrum of **15** is clearly not a summation of the individual spectra of **8a** and **25**, suggesting that the observed red shift in **15** is a result of a significant transannular $\pi-\pi$ interaction. Progressive red shifts are also clearly visible going from **25** to **8a** to **15** in their emission spectra (Figure 3b). The dithiaanthracenophane **16** displayed an even larger red shift of 78 (93) nm in its PL spectrum relative to that of **8a** (Figure 4). Going from the dithiacyclophane **14a** to those with polyphenyl units in **17** and **18** also resulted in significant emission shifts of about 25 nm in their PL spectra, in both solution and thin film (Table 2). This indicates that the introduction of a dithiacyclophane unit with either a higher benzenoid or a polyphenyl moiety will have a significant transannular effect on the emission spectral properties of these oligomeric model compounds. It is noteworthy that similar results were observed going from the terphenyl in **17** to the quinquephenyl in **18**. Thus, only the polymer **5** was prepared for a comparative study of the polymers **1**−**5** (refer to later discussion). All oligomeric model compounds

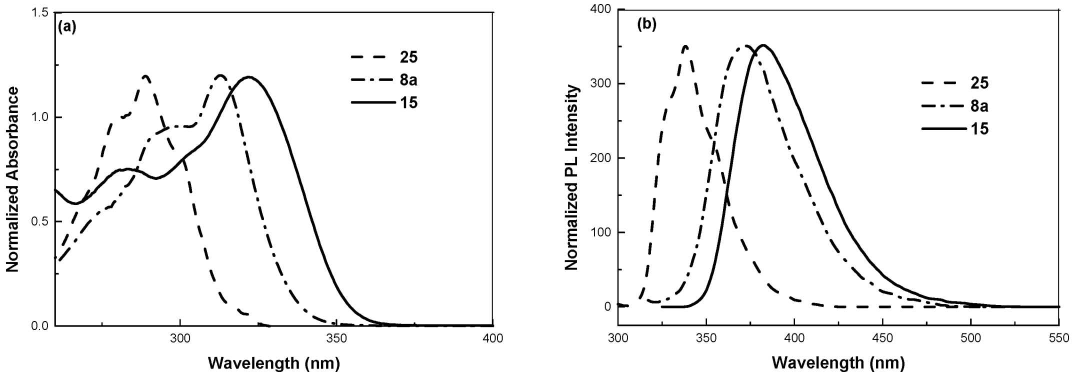

Figure 3. (a) UV−vis absorption and (b) PL spectra of **8a**, **15**, and **25** measured in solution (THF; ca. 1 × 10^{-5} M) at room temperature.

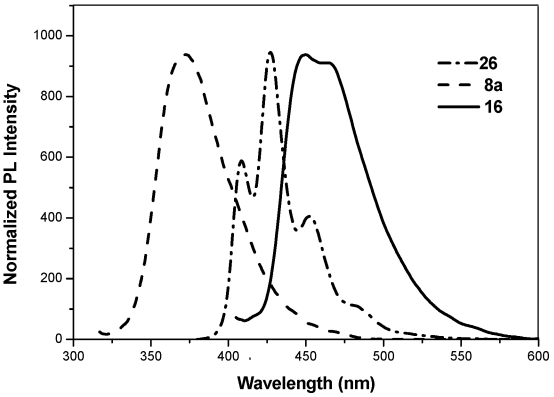

Figure 4. PL spectra of **8a**, **16**, and **26** measured in solution (THF; ca. 1 × 10^{-5} M) at room temperature.

except **16** exhibited small absorption red shifts of 3−5 nm and emission blue shifts of 3−8 nm going from solution to solid state. Such small shifts are in fact in accordance with little intermolecular $\pi-\pi$ interaction in the crystalline state as mentioned earlier for **14a** (Figure 2).

A comparison of the relative PL intensity of the emission λ_{max} of **14**−**18** in solution is illustrated in Figure 5. In the benzenoid series going from **14a** to **15** and **16**, the quantum yield of the emission signal decreased by 30% and 59%, respectively (Table 2). On the contrary, in the polyphenyl series going from **14a** to **17** and **18**, an increase of 76% and 47% in quantum efficiency, respectively, was observed. It is evident that the transannular $\pi-\pi$ interaction in the cyclophane unit not only affects emission spectral properties of these compounds but also acts as a fluorescence quencher in some examples such as **15** and **16**. On the other hand, such through-space interaction may also enhance the quantum efficiency as in **17** and **18** relative to the reference compound **14a**. It would thus be interesting to investigate whether the above observation remains consistent in the corresponding copolymers **1**−**5**.

Table 3 summarizes the optical properties of polymers **1a** and **2**−**5**. The PL spectra of polymers **1a** and **2**−**5** in solution and solid state are shown in Figure 6. Transparent and uniform films of polymers were prepared on quartz plates by spin-casting their solutions in chloroform at room temperature. Resembling the corresponding model compounds, polymers **1**−**5** showed only a small red shift of the 0−0 absorption bands in film as compared to that in solution ($\Delta\lambda_{max}$ = 3−6 nm; Table 3), suggesting that there is little change in molecular conformation going from solution to solid state. This is also supported by the fact that all of these polymers displayed only small emission shifts going from solution to solid state ($\Delta\lambda_{max}$ = 4−9 nm; Table 3). Using copolymer **2** as a reference, all of the dithiacyclophane−fluorene copolymers **1a** and **3**−**5** showed significant red shifts in their emission λ_{max} (Figure 5; Table 3) in both solution and thin film. Going from **1a** ($\Phi_{PL} = 0.75$) to **3** ($\Phi_{PL} = 0.50$) and **4** ($\Phi_{PL} = 0.05$), the introduction of the higher benzenoids in the latter again led to significant to nearly complete quenching of the emission signal in solution. Similarly, the quantum yields of polymers **1a** ($\Phi_{PL} = 0.42$), **3** ($\Phi_{PL} = 0.28$), and **4** ($\Phi_{PL} = 0.02$) in film state showed the same trend as that in solution. Replacing the higher benzenoids with a terphenyl unit in **5** ($\Phi_{PL} = 0.78$ in solution and 0.57 in film state) returned to an enhanced quantum efficiency in its PL spectrum.

The electrochemical behaviors were examined on **8a**, **14a**−**c**, and **15**−**18** in CH_2Cl_2 and on the polymers **1a**−**c** and **2**−**5**, in THF vs Ag/AgCl, using $[CH_3(CH_2)_3]_4NPF_6$ as the supporting electrolyte. The anodic peak potentials of the model compounds and polymers were summarized in Table 4. As can be seen clearly from Table 4, the transannular $\pi-\pi$ interaction in **14a**−**c** significantly lowers the anodic peak potentials (E_{pa}). The CV of the planar **8a** exhibited a one-electron oxidation wave with E_{pa} of +1.71 V, corresponding to oxidations from neutral form to the radical cation. However, the E_{pa}'s of **14a** and **14b** downshifted by 0.32 and 0.40 V, respectively, in comparison with its counterpart **8a**. This is comparable to the decrease in the oxidation potential of [2.2]paracyclophane (+1.57 V/SCE[17]) when compared to xylene (+2.30 V/SCE[18]). Therefore, the decrease in the E_{pa}'s in **14a**−**c** could be attributed to the transannular $\pi-\pi$ interaction between two co-facial aromatic rings, which enhances the delocalization of the cationic charge. Compound **14c** exhibits the highest E_{pa} among the model compounds **14a**−**c** because of the presence of electron-withdrawing cyano substituents that make it difficult to be oxidized. For **15**−**18**, they show a similar trend in the decrease of the E_{pa} (+1.25−1.49 V) with respect to **8a**. The relatively lower E_{pa} for **16** (+1.25 V) as compared to other model compounds should be attributed to the presence of an electron-rich anthracene unit in the opposite deck of cyclophane, which easily undergoes an oxidation process.

Similar to the oligomeric model compounds, it was found that E_{pa}'s of the corresponding polymers **1a**−**c** (+1.14−1.34 V) and **3**−**5** (+1.13−1.45 V) are lower than that of their planar reference counterpart **2** (E_{pa} = +1.60 V) ranging from 0.47 to 0.15 V. This is in fact in good agreement with the results obtained from the oligomeric model compounds that stacked paracyclophanes alter the electronic structure of the polymer backbone, thus leading to the drop of oxidation potentials.

In general, the overall change in free energy ($\Delta G^{\ddagger}$) for intermolecular electron transfer is estimated in terms of the equation:[10] $\Delta G^{\ddagger} = E(P/P^{+\bullet}) - \Delta E_{0-0} - E(Q/Q^{-\bullet})$, where $E(P/P^{+\bullet})$,

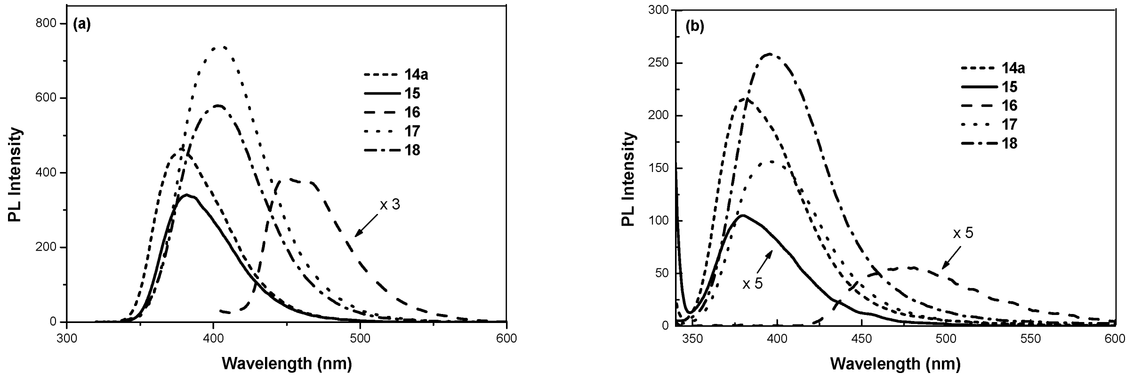

Figure 5. PL spectra of compounds **14a** and **15**−**18** in (a) solution (THF) and (b) film on quartz plate at room temperature.

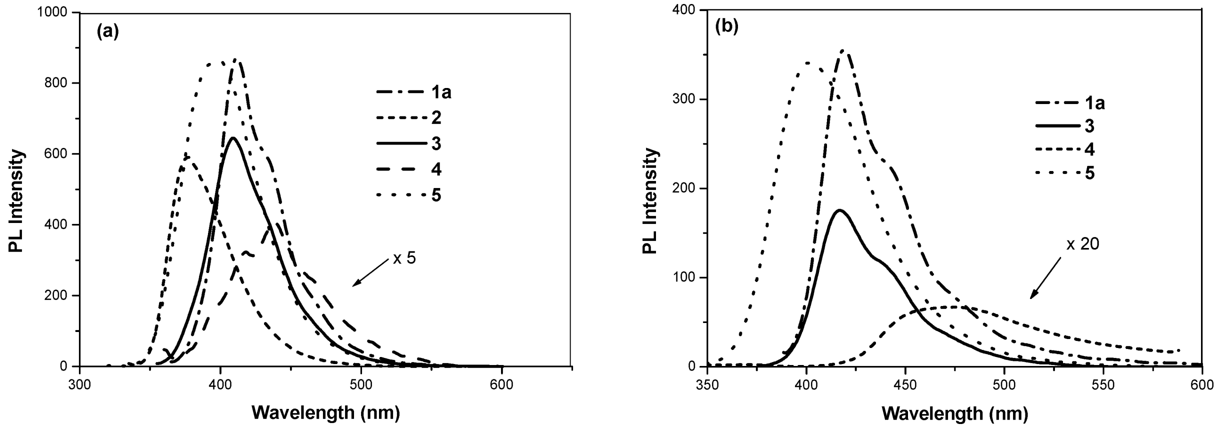

Figure 6. PL spectra of (a) polymers **1a** and **2**−**5** in solution (THF) and (b) polymers **1a** and **3**−**5** in film on quartz plate at room temperature.

Table 3. Optical Properties of Copolymers 1−5[a]

	λ_{max} (THF) (nm)		λ_{max} (films) (nm)		Φ_{PL}	
polymer	abs	em	abs	em	solution	film
1a	361	411, 428	367	417, 440	0.75	0.42
2	330	376	333	385	0.50	0.33
3	352	410, 426	355	416, 442	0.50	0.28
4	314, 362, 385, 408	417, 439, 469	312, 387, 413	473	0.05	0.02
5	321	396	327	402	0.78	0.57

[a] The PL efficiency (ϕ_{PL}) of the polymers in THF solutions was measured by using quinine sulfate (ca. 1×10^{-5} M solution in 0.1 M H_2SO_4, assuming ϕ_{PL} of 0.55) as a standard. The PL efficiency (ϕ_{PL}) in film state was estimated by using 9,10-diphenylanthracene (1×10^{-3} M dispersed in PMMA films, which has a quantum efficiency of 83%) as a standard. Absorption maxima were taken as λ_{ex} for **1a**, **2**, **3**, and **5**. The λ_{ex} value for **4** is 362 nm.

Table 4. Anodic Peak Potential (E_{pa}) of Model Compounds and Polymers

compd	E_{pa} (V)	polymer	E_{pa} (V)
8a	+1.71	**2**	+1.60
14a	+1.39	**1a**	+1.17
14b	+1.31	**1b**	+1.34
14c	+1.60	**1c**	+1.34
15	+1.39	**3**	+1.45
16	+1.25	**4**	+1.42
17	+1.49	**5**	+1.13
18	+1.45		

ΔE_{0-0}, and $E(Q/Q^{-\bullet})$ 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. This equation could in fact be employed in our work to give a qualitative evaluation of the extent of a probable intramolecular electron-transfer process, thus an estimate of the degree of fluorescence quenching in the series of copolymers studied. The main polymer backbone could be considered as an electron donor, whereas the parallel-stacked "external" aromatic moiety of the cyclophane unit could serve as an electron acceptor. Thus, the electron-transfer $\Delta G^{\ddagger}$ values for **3**−**5** could be estimated. The values of $E(P/P^{+\bullet})$ and ΔE_{0-0} for a general benzene−fluorene polymer backbone are 1.19 (vs SCE) and 3.34 eV,[2a] respectively. The $E(Q/Q^{-\bullet})$ values for naphthalene, anthracene, and *p*-terphenyl were reported to be −2.29,[19] −1.93,[20] and −2.82[20] eV, respectively. The $\Delta G^{\ddagger}$ values for **3**−**5** are thus estimated to be +0.14, −0.22, and +0.67, respectively, indicating that the driving force for electron transfer is the most favorable for **4** but lowest for **5**. This is in satisfactory agreement with the earlier observation that **4** showed nearly complete quenching in Φ_{PL} but the PL efficiency of **5** was the highest (Table 3). The above results and those reported earlier in our preliminary work[9a] on quenching effect in copolymers **1** due to electronic effects of the substituents collectively support an electron-transfer quenching mechanism accounting for the significant attenuation of Φ_{PL} values in copolymers **1**−**5**. The quenching phenomenon should involve a transannular $\pi-\pi$ interaction in the cyclophane units in these polymers.

The fluorescence lifetime of selected fluorene-based copolymers **1a**,**b** and model compounds **14a**,**b** and **8a** was determined by using time-correlated single photon counting on a picosecond time scale. Figure 7a and b illustrates the dynamics decay of model compound **14a** and planar reference compound **8a**, and polymer **1a**,**b**, respectively. The fluorescence decay profiles for compounds **14a**,**b** and **8a** and polymers **1a**,**b** are fitted using a monoexponential, and the resulting parameters are summarized

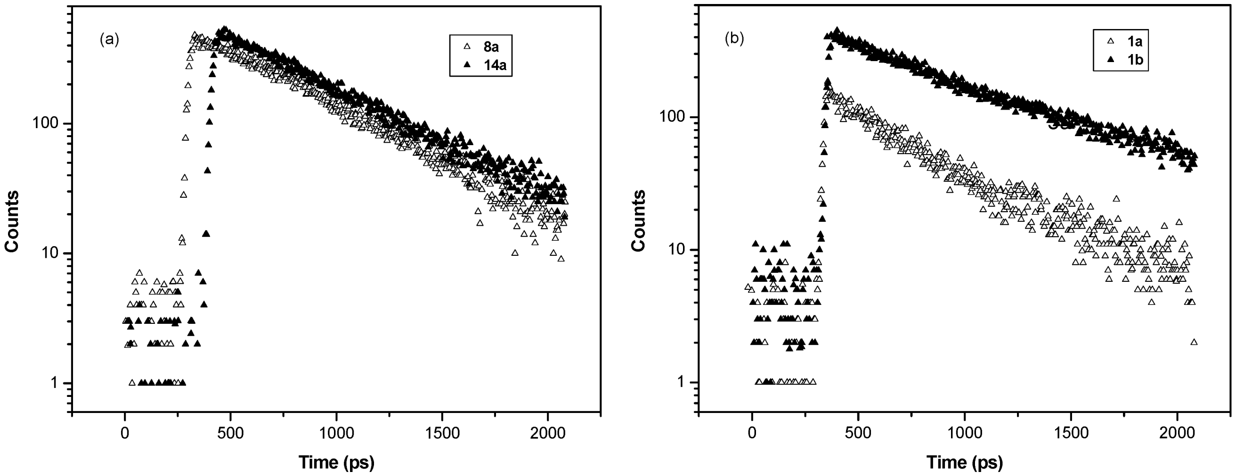

Figure 7. Fluorescence lifetime measurements of (a) compounds **8a** and **14a**, and (b) polymers **1a** and **1b**.

Table 5. Fluorescence Decay Analyses of Polymers and Model Compounds at 298 K[a]

compd	τ (ps)	γ^r (ps^{-1}) $\times 10^{-3}$	Φ_{PL}
1a	440	1.7	0.75
1b	750	0.48	0.36
14a	570	0.30	0.17
14b	660	0.015	0.010
8a	740	0.30	0.20

[a] Excited at 378 nm.

in Table 5. To study fluorescence dynamics, fluorescence decay rates were estimated by using $\gamma^r = \Phi_{PL}/\tau$, where the values for Φ_{PL} and fluorescence lifetime (τ) are also given in Table 5. It is found that the fluorescence decay rate of **14a** is approximately 20-fold greater than that of **14b**. The ratio of the fluorescence decay rates of **1a** and **1b** is approximately 4:1. The polymer **1b** has a lower radiative rate as compared to **1a** due to the fast relaxation to singlet state, which leads to the slightly longer fluorescence lifetime. The characteristics of fluorescence decays profiles for polymers and model compounds are similar to those of the reported pseudo-*p*-distyryl[2.2]paracyclophane, which shows a monoexponential decay on a long time scale.[21] It is noteworthy that the τ values for fluorine-containing model compounds **8a**, **14a**,**b**, and polymers **1a**,**b** are close to the reported value of poly(dioctylfluorene).[22] The compounds **14a**,**b** showed a shorter lifetime than the planar counterpart **8a**. It is likely due to the presence of $\pi-\pi$ interaction and stacked nonplanar structural features in **14a**,**b** and subsequently resulted in a relative short fluorescence lifetime as compared to that of compound **8a**.

Conclusions

Transannular $\pi-\pi$ interaction via dithiaparacyclophanes incorporated in selected conjugated polymers has been shown to induce significant emission shifts in both solution and the solid state. This is in some cases accompanied by an enhanced PL quantum yield, making it a positive parameter for tuning the color and intensity of the emitting light. The introduction of substituents or higher benzenoids in the cyclophane units may, on the other hand, lead to significant fluorescence quenching. A qualitative correlation between the quantum yield and the reduction potential [$E(Q/Q^{-\bullet})$] of the quencher segment of the cyclophane could, however, be established. This will allow the prediction of any undesirable quenching effect in future design of cyclophane-based conjugated polymers.

Experimental Section

Instrumentation. ^{1}H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were obtained as solutions in $CDCl_3$. TMS was used as the internal reference. Elemental analyses were obtained in the Chemical and Molecular Analysis Center, Department of Chemistry, National University of Singapore. Cyclic voltammetry was performed with a three-electrode cell in a solution of $[CH_3(CH_2)_3]_4NPF_6$ (0.10 M) in acetonitrile at a scan rate of 100 mV/s under N_2. A platinum electrode was coated with a thin polymer film and was used as the working electrode. A Pt wire was used as the counter electrode, and a Ag/AgCl electrode was used as the reference electrode. Cyclic voltammetry were performed on an EG & G Parc model 273A potentiostat/galvanostat system with a three-electrode cell in a solution of $[CH_3(CH_2)_3]_4NPF_6$ (0.10 M) in acetonitrile at a scan rate of 100 mV/s under N_2. A platinum electrode was coated with a thin polymer film and was used as the working electrode. A Pt wire was used as the counter electrode, and a Ag/AgCl electrode was used as the reference electrode. The PL efficiency (ϕ_{PL}) of the model compounds and polymers in THF solutions was measured by using quinine sulfate (ca. 1×10^{-5} M solution in 0.1 M H_2SO_4, assuming ϕ_{PL} of 0.55) as a standard. Quantum yields in film state were estimated by using 9,10-diphenylanthracene (1×10^{-3} M dispersed in PMMA films, which has a quantum efficiency of 83%) as a standard. The fluorescence lifetime was determined on a frequency-tripled output femtosecond laser from a Ti:sapphire. The samples were excited by the excitation pulses centered at 378 nm with a pulse duration of 200 fs and a repetition rate of 82 MHz. The PL was dispersed by a 0.25 m monochromator and recorded through a streak camera with a time resolution of 15 ps.

1,4-Bis(9,9-diethylfluorenyl)-2,5-bis(methoxymethyl)benzene (8a). A solution of 2-bromo-9,9-diethylfluorene[23] (9.04 g, 30 mmol) in THF (100 mL) was added slowly to a suspension of magnesium turnings (1.80 g, 75 mmol) in THF under nitrogen, and the mixture was heated at reflux for 6 h. The Grignard reagent was added dropwise into a stirred solution of **6**[24] (3.24 g, 10 mmol) and a catalytic amount of $[Pd(PPh_3)_4]$ in THF (50 mL) at room temperature. The reaction mixture was heated at reflux for 20 h, cooled to room temperature, and poured into crushed ice containing hydrochloric acid. The mixture was extracted with ether, and the combined organic extracts were evaporated to give a yellow solid. The residue was chromatographed on silica gel using hexane/dichloromethane (2:1) to afford **8a** as a white solid (3.75 g, 62%); mp 192−195 °C. ^{1}H NMR: δ 7.80−7.74 (m, 4H), 7.58 (s, 2H), 7.46−7.30 (m, 10H), 4.40 (s, 4H), 3.38 (s, 6H), 2.10−2.03 (m, 8H), 0.38 (t, $J = 7.3$ Hz, 12H). ^{13}C NMR: δ 150.06, 149.68, 141.60, 141.26, 140.58, 139.21, 134.84, 131.18, 127.98, 127.03, 126.84, 124.04, 122.89, 119.65, 119.24, 58.24, 56.12, 32.75, 8.53. Anal. Calcd for $C_{44}H_{46}O_2$: C, 87.09; H, 7.64. Found: C, 86.86; H, 7.89. MS (EI, *m*/*z*): 606 (M$^+$).

1,4-Bis(9,9-diethylfluorenyl)-2,5-bis(bromomethyl)benzene (8b). HBr gas was bubbled vigorously through a solution of **8a** (6.06 g, 10 mmol) in $CHCl_3$ (100 mL) for 1 h. The reaction mixture was stirred for an additional 10 h and neutralized with aqueous 2 M Na_2CO_3 solution. The product was extracted into ether, washed with brine, and dried over magnesium sulfate. The crude product obtained after solvent removal was chromatographed on silica gel with hexane as eluent to give **8b** as a white solid (6.69 g, 95%); mp 186−190 °C. ^{1}H NMR: δ 7.87−7.75 (m, 4H), 7.56 (s, 2H), 7.55−7.35 (m, 10H), 4.51 (s, 2H), 2.11−2.09 (m, 8H), 0.40 (t, $J = 7.1$ Hz, 12H). ^{13}C NMR: δ 150.15, 142.27, 141.17, 141.02, 137.93, 135.70, 132.95, 127.71, 127.28, 126.92, 123.57, 122.97, 119.81, 119.59, 56.27, 32.76, 31.73, 8.58. Anal. Calcd for $C_{42}H_{40}Br_2$: C, 71.60; H, 5.72; Br, 22.68. Found: C, 71.34; H, 5.92; Br, 22.39. MS (EI, *m*/*z*): 702 (M$^+$).

1,4-Bis(9,9-diethylfluorenyl)-2,5-bis(mercaptomethyl)benzene (8c). A solution of **8b** (7.04 g, 10 mmol) and thiourea (1.67 g, 22 mmol) in ethanol (100 mL) was heated at reflux for 4 h. The solvent was removed in vacuo. The dithiouronium salt was suspended in aqueous 4% sodium bicarbonate and heated at reflux for 3 h. The mixture was extracted with ether and washed sequentially with water and brine. The combined organic extracts were dried over anhydrous Na_2SO_4. The product mixture was chromatographed on silica gel using hexane/methanol (10:1) as eluent to give **8c** as a white solid (4.15 g, 68%); mp 152−154 °C. ^{1}H NMR: δ 7.87−7.75 (m, 4H), 7.48 (s, 2H), 7.46−7.32 (m, 10H), 3.78 (d, $J = 7.3$ Hz, 4H), 2.10−2.08 (m, 8H), 1.77 (t, $J = 8.0$ Hz, 2H), 0.41 (t, $J = 7.3$ Hz, 12H). ^{13}C NMR: δ 150.10, 141.39, 141.11, 140.85, 138.96, 137.66, 131.38, 127.81, 127.21, 126.93, 123.79, 122.95, 119.76, 119.57, 56.21, 32.79, 26.50, 8.60. Anal. Calcd for $C_{42}H_{42}S_2$: C, 82.57; H, 6.93; S, 10.50. Found: C, 82.42; H, 6.68; S, 10.33. MS (EI, *m*/*z*): 610 (M$^+$).

2′,5′-Bis(bromomethyl)-[1,1′;4′,1″]terphenyl (12). A mixture of 2′,5′-dimethyl-*p*-terphenyl[25] (2.58 g, 10 mmol), NBS (3.92 g, 22 mmol), and a catalytic amount of benzoyl peroxide in CCl_4 (50 mL) was heated at reflux under IR radiation for 6 h. The reaction mixture was cooled to room temperature and extracted with CH_2Cl_2. The organic phase was washed with water and brine and then dried over anhydrous Na_2SO_4. The residue obtained after solvent removal was chromatographed on silica gel using hexane/CH_2Cl_2 as eluant to give **12** as a white solid (1.66 g, 40%); mp 180−184 °C. ^{1}H NMR: δ 7.52−7.47 (m, 10H), 4.48 (s, 4H). ^{13}C NMR: δ 141.68, 139.30, 135.54, 132.99, 129.00, 128.47, 127.79, 31.41. Anal. Calcd for $C_{20}H_{16}Br_2$: C, 57.72; H, 3.88; Br, 38.40. Found: C, 57.88; H, 3.85; Br, 38.55. MS (EI, *m*/*z*): 414 (M$^+$).

2″,5″-Bis(methoxymethyl)-[1,4′;1′,1″;4″,1‴;4‴,1⁗]quinquephenyl (13a). A mixture of **6** (3.24 g, 10 mmol), biphenylboronic acid[26] (3.92 g, 30 mmol), $Pd(PPh_3)_4$ (0.577 g, 5% mmol), toluene (30 mL), and aqueous 2 M K_2CO_3 (40 mL) was heated at reflux for 24 h under nitrogen. It was cooled, diluted with water, and extracted with ether. The organic phase was dried over Na_2SO_4, and the residue was chromatographed on silica gel using hexane/CH_2Cl_2 (1:1) as eluant to afford **13a** as a white solid (3.53 g, 75%); mp 238−240 °C. ^{1}H NMR: δ 7.70−7.37 (m, 20H), 4.45 (s, 4H), 3.39 (s, 6H). ^{13}C NMR: δ 140.74, 140.58, 140.01, 139.39, 134.86, 130.97, 129.72, 128.79, 127.32, 127.06, 126.80, 72.32, 58.19. Anal. Calcd for $C_{34}H_{30}O_2$: C, 86.77; H, 6.43. Found: C, 86.98; H, 6.61. MS (EI, *m*/*z*): 470 (M$^+$).

2″,5″-Bis(bromomethyl)-[1,4′;1′,1″;4″,1‴;4‴,1⁗]quinquephenyl (13b). This was prepared by a procedure similar to that described for **8b**. Compound **13b** was isolated as a white solid (75%); mp 231−234 °C. ^{1}H NMR: δ 7.74−7.39 (m, 20H), 4.53 (s, 4H). ^{13}C NMR: δ 141.37, 140.71, 140.58, 138.25, 135.68, 133.11, 129.45, 128.88, 127.53, 127.19, 127.14, 31.45, 29.70. Anal. Calcd for $C_{32}H_{24}Br_2$: C, 67.63; H, 4.26; Br, 28.12. Found: C, 67.49; H, 4.15; Br, 28.03. MS (EI, *m*/*z*): 566 (M$^+$).

General Procedure for the Preparation of Dithiacyclophanes 14−18. A solution of **8c** (3.0 mmol) and **9a**, **9b**,[27] **9c**,[28] **10**,[29] **11**, **12**, or **13b** (3.0 mmol), respectively, in degassed toluene was added dropwise with stirring to a solution of KOH (0.336 g, 6.0 mmol) in ethanol (1 L). After the addition was completed, the reaction was stirred for 2 d at room temperature. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel using hexane/CH_2Cl_2 (5:1) as eluant to afford a white solid. The product was further purified by recrystallization from benzene/methanol to afford compounds **14−18**, respectively, as colorless crystals.

5,8-Bis[2-(9,9-diethylfluorenyl)]-2,11-dithia[3.3]paracyclophane (14a). Yield: 45%; mp 281−283 °C. ^{1}H NMR: δ 7.87 (d, $J = 8.0$ Hz, 2H), 7.77−7.82 (m, 2H), 7.48 (d, $J = 7.7$ Hz, 2H), 7.43−7.32 (m, 10H), 7.21 (d, $J = 7.7$ Hz, 2H), 6.91 (d, $J = 8.0$ Hz, 2H), 4.11 (d, $J = 15.3$ Hz, 2H), 3.88 (d, $J = 15.3$ Hz, 2H), 3.76 (d, $J = 14.5$ Hz, 2H), 3.53 (d, $J = 14.5$ Hz, 2H), 2.14−2.08 (m, 8H), 0.52 (t, $J = 7.3$ Hz, 6H), 0.38 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR: δ 150.10, 149.99, 141.18, 140.53, 139.77, 139.36, 135.94, 133.20, 132.41, 129.21, 128.29, 128.03, 127.12, 126.93, 124.17, 122.93, 119.75, 119.66, 56.09, 38.55, 35.84, 32.99, 32.66, 8.75, 8.50. Anal. Calcd for $C_{50}H_{48}S_2$: C, 84.22; H, 6.78; S, 8.99. Found: C, 84.51; H, 6.98; S, 8.84. MS (EI, *m*/*z*): 712 (M$^+$).

5,8-Bis[2-(9,9-diethylfluorenyl)]-14,17-dimethoxy-2,11-dithia-[3.3]paracyclophane (14b). Yield: 39%; mp 287−290 °C. ^{1}H NMR: δ 7.87−7.76 (m, 4H), 7.58−7.33 (m, 12H), 6.57 (s, 2H), 4.13 (d, $J = 15.4$ Hz, 2H), 4.08 (d, $J = 15.4$ Hz, 2H), 3.91 (d, $J = 14.8$ Hz, 2H), 3.84 (s, 6H), 3.34 (d, $J = 14.8$ Hz, 2H), 2.11−2.02 (m, 8H), 0.48 (t, $J = 7.3$ Hz, 6H), 0.33 (t, $J = 7.3$ Hz, 6H). ^{13}C NMR: δ 151.59, 150.08, 149.85, 141.33, 140.39, 139.82, 133.17, 132.04, 127.82, 126.98, 126.91, 126.85, 123.75, 122.85, 119.65, 116.46, 58.43, 56.12, 36.60, 33.07, 32.68, 32.16, 8.68, 8.47. Anal. Calcd for $C_{52}H_{52}O_2S_2$: C, 80.79; H, 6.78; S, 8.30. Found: C, 80.54; H, 6.67; S, 8.38. MS (EI, *m*/*z*): 772 (M$^+$).

5,8-Dicyano-14,17-bis[2-(9,9-diethylfluorenyl)]-2,11-dithia[3.3]-paracyclophane (14c). Yield: 35%; mp 279−281 °C. ^{1}H NMR: δ 7.90−7.75 (m, 4H), 7.56 (s, 2H), 7.51−7.35 (m, 12H), 4.28 (d, $J = 15.4$ Hz, 2H), 4.14 (d, $J = 15.4$ Hz, 2H), 3.98 (d, $J = 15.4$ Hz, 2H), 3.61 (d, $J = 15.4$ Hz, 2H), 2.27−1.57 (m, 8H), 0.47 (t, $J = 7.1$ Hz, 6H), 0.40 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR: δ 150.87, 150.14, 141.25, 141.10, 141.06, 140.61, 138.64, 133.53, 133.08, 132.31, 127.47, 127.31, 126.95, 123.07, 122.94, 120.07, 119.82, 116.86, 116.36, 56.47, 36.91, 35.97, 32.88, 32.77, 8.72, 8.55. Anal. Calcd for $C_{52}H_{46}S_2N_2$: C, 81.85; H, 6.08; S, 8.40; N, 3.67. Found: C, 81.70; H, 6.38; S, 8.24; N, 3.69. MS (EI, *m*/*z*): 762 (M$^+$).

5,8-Bis[2-(9,9-diethylfluorenyl)]-2,11-dithia[3]paracyclo[3]-(1,4)naphthalenophane (15). Yield: 43%; mp 299−302 °C. ^{1}H NMR: δ 7.88 (d, $J = 8.4$ Hz, 1H), 7.84−7.30 (m, 16H), 7.06 (d, $J = 7.0$ Hz, 1H), 7.01 (s, 1H), 6.82 (d, $J = 7.0$ Hz, 1H), 6.71 (s, 1H), 5.41 (d, $J = 7.6$ Hz, 1H), 4.42−3.75 (m, 8H), 2.36−1.91 (m, 8H), 0.56 (t, $J = 7.1$ Hz, 3H), 0.44−0.37 (m, 6H), 0.20 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR: δ 150.23, 150.16, 150.01, 148.98, 141.43, 141.02, 140.82, 140.07, 139.28, 139.23, 139.07, 133.65, 132.74, 132.51, 132.44, 132.36, 132.11, 131.48, 131.06, 127.99, 127.67, 127.28, 127.00, 126.84, 126.77, 125.74, 125.51, 125.44, 125.31, 124.50, 123.01, 122.72, 122.56, 119.91, 119.81, 119.52, 119.34, 56.14, 55.88, 38.04, 37.50, 36.57, 35.99, 32.97, 32.87, 32.66, 32.55, 8.85, 8.62, 8.54, 8.36. Anal. Calcd for $C_{54}H_{50}S_2$: C, 84.99; H, 6.60. Found: C, 84.76; H, 6.43. MS (EI, *m*/*z*): 762 (M$^+$).

5,8-Bis[2-(9,9-diethylfluorenyl)]-2,11-dithia[3]paracyclo[3]-(9,10)anthracenophane (16). Yield: 32%; mp 271−275 °C. ^{1}H NMR: δ 8.49 (d, $J = 9.1$ Hz, 2H), 8.12 (d, $J = 9.1$ Hz, 2H), 7.76−7.31 (m, 14H), 6.97 (s, 2H), 6.78 (s, 2H), 6.33 (d, $J = 7.7$ Hz, 2H), 4.93 (d, $J = 15.4$ Hz, 2H), 4.74 (d, $J = 15.4$ Hz, 2H), 4.18 (d, $J = 15.4$ Hz, 2H), 3.92 (d, $J = 15.4$ Hz, 2H), 2.04−1.97 (m, 8H), 0.48 (t, $J = 7.3$ Hz, 6H), 0.27 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR: δ 150.04, 149.02, 141.34, 140.26, 138.82, 138.20, 132.09, 131.15, 129.98, 129.60, 129.41, 128.27, 126.88, 126.81, 125.84, 125.14, 124.85, 123.38, 122.82, 119.56, 118.89, 55.98, 36.35, 33.05, 32.38, 29.75, 8.73, 8.49. Anal. Calcd for $C_{58}H_{52}S_2$: C, 85.67; H, 6.45. Found: C, 85.42; H, 6.39. MS (ESI, *m*/*z*): 812 (M$^+$).

5,8-Bis[2-(9,9-diethylfluorenyl)]-14,17-diphenyl-2,11-dithia-[3.3]paracyclophane (17). Yield: 40%; mp 276−278 °C. ^{1}H NMR: δ 7.74−7.22 (m, 28H), 4.26 (d, $J = 14.9$ Hz, 2H), 4.24 (d, $J = 14.9$ Hz, 2H), 3.99 (d, $J = 14.9$ Hz, 2H), 3.72 (d, $J = 14.9$ Hz, 2H), 2.02−1.73 (m, 8H), 0.40 (t, $J = 7.2$ Hz, 12H). ^{13}C NMR:

δ 150.22, 150.09, 141.31, 140.76, 140.34, 140.25, 139.64, 139.56, 133.60, 133.40, 132.17, 132.12, 129.92, 128.38, 128.15, 127.11, 126.95, 126.79, 123.84, 122.86, 119.68, 119.30, 56.13, 35.88, 35.00, 32.74, 32.51, 8.64, 8.49. Anal. Calcd for $C_{62}H_{56}S_2$: C, 86.06; H, 6.52. Found: C, 86.21; H, 6.64. MS (EI, *m*/*z*): 864 (M^+).

5,8-Bis(4-biphenyl)-14,17-bis[2-(9,9-diethylfluorenyl)]-2,11-dithia[3.3]paracyclophane (18). Yield: 35%; mp 304−305 °C. ^{1}H NMR: δ 7.72−7.23 (m, 36H), 4.30 (d, $J = 15.0$ Hz, 2H), 4.29 (d, $J = 15.0$ Hz, 2H), 4.04 (d, $J = 15.0$ Hz, 2H), 3.74 (d, $J = 15.0$ Hz, 2H), 1.96−1.73 (m, 8H), 0.34 (t, $J = 7.1$ Hz, 12H). ^{13}C NMR: δ 150.23, 149.99, 141.30, 140.60, 140.34, 139.90, 139.68, 139.22, 133.83, 133.37, 132.22, 132.08, 130.41, 128.85, 128.11, 127.40, 127.02, 126.93, 126.77, 123.69, 122.84, 119.66, 119.29, 56.14, 35.96, 34.99, 32.66, 32.54, 8.62, 8.49. Anal. Calcd for $C_{74}H_{64}S_2$: C, 87.36; H, 6.34. Found: C, 87.21; H, 6.29. MS (EI, *m*/*z*): 1016 (M^+).

General Procedure for the Preparation of Dithiacyclophanes 20a−c. A solution of 1,4-dibromo-2,5-bis(bromomethyl)benzene[30] (3.0 mmol) and 1,4-bis(mercaptomethyl)benzene, 1,4-bis(mercaptomethyl)-2,5-dimethoxybenzene,[31] or 1,4-dicyano-2,5-bis(mercaptomethyl)benzene (prepared from **9c**)[29] (3.0 mmol), respectively, in degassed toluene was added dropwise with stirring to a solution of KOH (0.336 g, 6.0 mmol) in ethanol (1 L). After the addition was completed, the reaction mixture was stirred for 20 h at room temperature. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel using CH_2Cl_2 as eluent. The product was further purified by recrystallization from toluene.

5,8-Dibromo-2,11-dithia[3.3]paracyclophane (20a). Yield 60%; mp 239−241 °C. ^{1}H NMR: δ 7.18 (s, 2H), 7.17 (d, $J = 9.4$ Hz, 2H), 7.02 (d, $J = 9.4$ Hz, 2H), 4.15 (d, $J = 15.1$ Hz, 2H), 3.89 (d, $J = 15.1$ Hz, 2H), 3.80 (d, $J = 15.1$ Hz, 2H), 3.62 (d, $J = 15.1$ Hz, 2H). ^{13}C NMR: δ 136.85, 135.24, 135.15, 129.37, 128.08, 123.31, 37.76, 36.57. Anal. Calcd for $C_{16}H_{14}Br_2S_2$: C, 44.67; H, 3.28; Br, 37.15; S, 14.91. Found: C, 44.69; H, 3.17; Br, 36.94; S, 15.13. MS (EI, *m*/*z*): 428 (M^+).

5,8-Dibromo-14,17-dimethoxy-2,11-dithia[3.3]paracyclophane (20b). Yield: 50%; mp 240−242 °C. ^{1}H NMR: δ 7.32 (s, 2H), 6.74 (s, 2H), 4.05 (d, $J = 15.0$ Hz, 2H), 3.91 (d, $J = 15.0$ Hz, 2H), 3.90 (s, 6H), 3.65 (d, $J = 15.0$ Hz, 2H), 3.48 (d, $J = 15.0$ Hz, 2H). ^{13}C NMR: δ 150.39, 136.84, 134.13, 124.19, 123.25, 112.66, 55.78, 37.01, 31.82. Anal. Calcd for $C_{18}H_{18}O_2Br_2S_2$: C, 44.10; H, 3.70; S, 13.08; Br, 32.59. Found: C, 43.94; H, 3.60; S, 12.79; Br, 32.60. MS (EI, *m*/*z*): 488 (M^+).

5,8-Dibromo-14,17-dicyano-2,11-dithia[3.3]paracyclophane (20c). Yield: 65%; mp 313−318 °C. ^{1}H NMR: δ 7.75 (s, 2H), 7.42 (s, 2H), 4.09 (d, $J = 15.2$ Hz, 2H), 3.99 (d, $J = 15.2$ Hz, 2H), 3.86 (d, $J = 15.2$ Hz, 2H), 3.76 (d, $J = 15.2$ Hz, 2H). ^{13}C NMR: δ 140.29, 136.55, 135.12, 133.55, 123.72, 116.85, 115.63, 37.08, 35.00. Anal. Calcd for $C_{18}H_{12}N_2Br_2S_2$: C, 45.02; H, 2.52; N, 5.83; Br, 33.28; S, 13.35. Found: C, 45.30; H, 2.51; N, 5.68; Br, 33.15; S, 13.38. MS (EI, *m*/*z*): 478 (M^+).

General Procedure for the Preparation of Dithiayclophanes 22−24. These were prepared by a procedure similar to that described for **20a−c** between a reaction of 1,4-bis(mercaptomethyl)-2,5-dibromobenzene (prepared from 1,4-dibromo-2,5-bis(bromomethyl)benzene)[26] (3.0 mmol) and **10**, **11**, or **12** (3.0 mmol), respectively.

5,8-Dibromo-2,11-dithia[3]paracyclo[3](1,4)naphthalenophane (22). Yield: 44%; mp 257−259 °C. ^{1}H NMR: δ 8.16 (d, $J = 8.2$ Hz, 1H), 8.01 (d, $J = 8.2$ Hz, 1H), 7.59−7.48 (m, 2H), 7.29 (s, 1H), 7.14 (d, $J = 7.1$ Hz, 2H), 7.02 (d, $J = 7.1$ Hz, 2H), 6.74 (s, 1H), 4.64 (d, $J = 15.7$ Hz, 2H), 4.42 (d, $J = 14.3$ Hz, 2H), 4.25 (d, $J = 16.4$ Hz, 2H), 4.10−3.99 (m, 3H), 3.71 (d, $J = 14.3$ Hz, 2H), 3.57 (d, $J = 16.0$ Hz, 2H). ^{13}C NMR: δ 136.97, 136.21, 134.60, 134.52, 134.35, 131.91, 131.69, 131.12, 127.05, 125.71, 125.44, 125.23, 125.14, 124.06, 123.58, 122.81, 37.39, 37.08, 36.52, 34.71. Anal. Calcd for $C_{20}H_{16}Br_2S_2$: C, 50.02; H, 3.36; Br, 33.27. Found: C, 49.91; H, 3.13; Br, 32.78. MS (EI, *m*/*z*): 478 (M^+).

5,8-Dibromo-2,11-dithia[3]paracyclo[3](9,10)anthracenophane (23). Yield: 40%; mp 300−305 °C. ^{1}H NMR: δ 8.47−8.35 (dd, $J = 27.2$, 8.7 Hz, 4H), 7.62−7.47 (m, 4H), 7.14 (d, $J = 7.1$ Hz, 2H), 7.02 (d, $J = 7.1$ Hz, 2H), 6.84 (s, 2H), 5.25 (d, $J = 15.4$ Hz, 2H), 4.65 (d, $J = 15.4$ Hz, 2H), 4.12 (d, $J = 15.4$ Hz, 2H), 3.50 (d, $J = 15.4$ Hz, 2H). ^{13}C NMR: δ 135.54, 133.60, 130.19, 129.64, 127.85, 126.05, 125.13, 124.93, 124.90, 122.45, 35.72, 29.38. Anal. Calcd for $C_{24}H_{18}Br_2S_2$: C, 54.35; H, 3.42; Br, 30.13. Found: C, 54.07; H, 3.19; Br, 30.13. MS (EI, *m*/*z*): 528 (M^+).

5,8-Dibromo-14,17-diphenyl-2,11-dithia[3.3]paracyclophane (24). Yield: 42%; mp 225−228 °C. ^{1}H NMR: δ 7.65−7.39 (m, 12H), 7.16 (s, 2H), 4.12 (d, $J = 15.3$ Hz, 2H), 4.03 (d, $J = 15.3$ Hz, 2H), 3.84 (d, $J = 15.3$ Hz, 2H), 3.49 (d, $J = 15.3$ Hz, 2H). ^{13}C NMR: δ 140.64, 139.95, 137.18, 133.88, 133.02, 131.57, 129.05, 128.50, 127.09, 122.96, 37.74, 36.24. Anal. Calcd for $C_{28}H_{22}Br_2S_2$: C, 57.74; H, 3.81; Br, 27.44. Found: C, 57.57; H, 3.74; Br, 27.66. MS (EI, *m*/*z*): 580 (M^+).

General Procedure for the Preparation of Copolymers 1−5. A mixture of **19**[2a] (251 mg, 0.5 mmol), $Pd(PPh_3)_4$ (28 mg), (n-$C_4H_9)_4NBr$ (16 mg), and **20a**, **20b**, **20c**, **21**, **22**, **23**, or **24** (0.5 mmol), respectively, in degassed toluene (3 mL) was added to a 2 M aqueous K_2CO_3 solution (3 mL). The mixture was vigorously stirred at 105 °C for 3 d under nitrogen. The mixture was then cooled to room temperature and poured into a stirred mixture of hydrazine and deionized water (1:1). The mixture was extracted with $CHCl_3$, and the combined organic extracts were slowly poured into cold methanol. The precipitated white solid was filtered and washed sequentially and thoroughly with methanol, acetone, and THF in a Soxhlet apparatus. The THF solution was slowly poured into cold methanol to reprecipitate the copolymer. The polymer was then filtered and dried under vacuum at room temperature.

Copolymers 1a−c. The spectroscopic and elemental data of these copolymers were reported in an earlier communication.[9a]

Poly[2,7-(9,9-di-*n*-hexylfluorene)-*co-alt*-2,5-(dimethylbenzene)] (2). Yield: 65%. ^{1}H NMR (main signals): δ 7.82−7.79 (br, d), 7.40 (br, s), 7.31 (br, s), 2.83 (br, s), 2.10−1.10 (br, m), 0.89−0.77 (br, m). Anal. Calcd for $(C_{33}H_{40})_n$: C, 90.77; H, 9.23. Found: C, 90.01; H, 9.08.

Poly{2,7-(9,9-di-*n*-hexylfluorene)-*co-alt*-5,8-(2,11-dithia[3]-paracyclo[3](1,4)naphthalenophane)} (3). Yield: 40%. ^{1}H NMR: δ 7.76−6.79 (br, m), 4.82−3.69 (br, d), 2.17−2.08 (br, m), 1.25−0.71 (br, m). FT-IR (KBr): 3064, 3034, 2926, 2857, 2360, 1890, 1595, 1514, 1458, 1411, 1373, 1250, 1220, 1047, 886, 817, 756 cm^{-1}. Anal. Calcd for $(C_{45}H_{48}S_2)_n$: C, 82.77; H, 7.41. Found: C, 82.01; H, 7.05.

Poly{2,7-(9,9-dihexylfluorene)-*co-alt*-5,8-(2,11-dithia[3]-paracyclo[3](9,10)anthracenophane)} (4). Yield: 36%. ^{1}H NMR: δ 8.45−6.83 (br, m), 5.25−3.45 (br, d), 1.92−0.71 (br, m). FT-IR (KBr): 3052, 2926, 2852, 2400, 1850, 1673, 1610, 1458, 1371, 1218, 1051, 895, 819, 759, 615 cm^{-1}. Anal. Calcd for $(C_{45}H_{48}S_2)_n$: C, 82.77; H, 7.41. Found: C, 82.06; H, 7.01.

Poly{2,7-(9,9-dihexylfluorene)-*co-alt*-5,8-(14,17-diphenyl-2,11-dithia[3.3]paracyclophane)} (5). Yield: 42%. ^{1}H NMR: δ 7.28−7.14 (br, m), 4.33−3.47 (br, d), 1.87−0.65 (br, m). FT-IR (KBr): 3055, 3024, 2924, 2852, 2337, 1949, 1896, 1599, 1460, 1415, 1373, 1219, 1049, 1022, 893, 827, 741, 702, 530 cm^{-1}. Anal. Calcd for $(C_{53}H_{54}S_2)_n$: C, 84.30; H, 7.21. Found: C, 83.65; H, 7.03.

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References and Notes

(1) (a) Pei, Q.; Yu, G.; Zhang, C.; Heeger, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 3922. (b) Hide, H.; Díaz-García, M. A.; Schwartz, B. J.; Andersson, M. R.; Pei, Q.; Heeger, A. J. *Science* **1996**, *273*, 1833. (c) Halls, J. J. M.; Walsh, C. A.; Marseglia, E. A.; Frienf, R. H.; Moratti, S. C.; Holmes, A. B. *Nature* **1995**, *376*, 498.

(2) (a) Liu, B.; Yu, W.-L.; Lai, Y.-H.; Huang, W. *Chem. Mater.* **2001**, *13*, 1984. (b) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608. (c) Döettinger, S. E.; Hohloch, M.; Segura, J. L.; Steinhuber, E.; Hanack, M.; Tompert, A.; Oelkrug, D. *Adv. Mater.*

1997, *9*, 233. (d) Staring, E. G. J.; Demandt, R. C. J. E.; Braun, D.; Rikken, G. L. J.; Kessener, Y. A. R. R.; Venhuizen, A. H. J.; van Knippenberg, M. M. F.; Bouwmans, M. *Synth. Met.* **1995**, *71*, 2179. (e) Moratti, S. C.; Cervini, R.; Holmes, A. B.; Baigent, D. R.; Friend, R. H.; Greenham, N. C.; Grüner, J.; Hamer, P. J. *Synth. Met.* **1995**, *71*, 2117. (f) Meng, H.; Huang, W. *J. Org. Chem.* **2000**, *65*, 3894.

(3) (a) Yu, W.-L.; Meng, H.; Pei, J.; Chua, S.-J.; Huang, W.; Lai, Y.-H. *Chem. Commun.* **1998**, 1957. (b) Yu, W.-L.; Meng, H.; Pei, J.; Huang, W. *J. Am. Chem. Soc.* **1998**, *120*, 11808. (c) Fou, A. C.; Rubner, M. F. *Macromolecules* **1995**, *28*, 7115. (d) Baskar, C.; Lai, Y.-H.; Valiyaveettil, S. *Macromolecules* **2001**, *34*, 6255.

(4) (a) Monkman, A. P.; Pålsson, L.-O.; Higgins, R. W. T.; Wang, C.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K. *J. Am. Chem. Soc.* **2002**, *124*, 6049. (b) Eichen, Y.; Nakhmanovich, G.; Gorelik, V.; Epshtein, O.; Poplawski, J. M.; Ehrenfreund, E. *J. Am. Chem. Soc*. **1998**, *120*, 10463.

(5) (a) Jin S.-H.; Kang, S.-Y.; Yeom, I.-S.; Kim, J. Y.; Park, S. H.; Lee, K.; Gal, Y.-S.; Cho, H.-N. *Chem. Mater.* **2002**, *14*, 5090. (b) Ego, C.; Marsitzky, D.; Becker, S.; Zhang, J.; Grimsdale, A. C.; Müllen, K.; MacKenzie, J. D.; Silva, C.; Friend, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 437.

(6) (a) Hunter, C. A.; Meah, M. N.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5773. (b) Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154. (c) Ranganathan, D.; Haridas, V.; Gilardi, R.; Karle, I. L. *J. Am. Chem. Soc.* **1998**, *120*, 10793. (d) Asakawa, M.; Ashton, P. R.; Hayes, W.; Janssen, H. M.; Meijer, E. W.; Menzer, S.; Pasini, D.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 920. (e) Raymo, F. M.; Houk, K. N.; Stoddart, J. F. *J. Org. Chem.* **1998**, *63*, 6523.

(7) (a) Griffiths-Jones, S. R.; Searle, M. S. *J. Am. Chem. Soc*. **2000**, *122*, 8350. (b) Guckian, K. M.; Krugh, T. R.; Kool, E. T. *J. Am. Chem. Soc.* **2000**, *122*, 6841. (c) Burley, S. K.; Petsko, G. A. *Science* **1985**, *229*, 23. (d) Gorin, A. A.; Zhurkin, V. B.; Olson, W. K. *J. Mol. Biol*. **1995**, *247*, 34. (e) Hunter, C. A.; Singh, J.; Thornton, J. M. *J. Mol. Biol.* **1991**, *218*, 837. (f) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

(8) (a) Morisaki, Y.; Chujo, Y. *Macromolecules* **2002**, *35*, 587. (b) Morisaki, Y.; Ishida, T.; Chujo, Y. *Macromolecules* **2002**, *35*, 7872. (c) Salhi, F.; Collard, D. M. *Adv. Mater*. **2003**, *15*, 81. (d) Salhi, F.; Lee, B.; Meta, C.; Bottomley, L. A.; Collard, D. M. *Org. Lett.* **2002**, *4*, 3195.

(9) (a) Wang, W.; Xu, J.; Lai, Y.-H. *Org. Lett.* **2003**, *5*, 2765. (b) Wang, W.; Xu, J.; Lai, Y.-H.; Wang, F. *Macromolecules* **2004**, *37*, 3546.

(10) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(11) (a) Morita, S.; Zarkhidov, A. A.; Yoshino, K. *Solid State Commun.* **1992**, *82*, 249. (b) Yu, G.; Gao, J.; Hummelen, J.; Wudl, F.; Heeger, A. J. *Science* **1993**, *270*, 1789. (c) Gao, J.; Hide, F.; Wang, H. *Synth. Met.* **1994**, *84*, 979. (d) Lin, H.; Yang, J.; Zheng, M.; He, Q.; Huang, H.; Bai, F. *Polym. Adv. Technol.* **2003**, *14*, 303.

(12) (a) Tang, H.; Luo, J.; Qin, H.; Kang, H.; Ye, C. *Macromol. Rapid Commun.* **2000**, *21*, 1125. (b) Nešpůrek, S.; Schauer, F.; Kadashchuk, A. *Monatsh. Chem.* **2001**, *132*, 159. (c) Tachibana, H.; Kishida, H.; Tokura, Y. *Appl. Phys. Lett*. **2000**, *77*, 2443. (d) Zhao, C.; Horiuchi, H.; Okutsu, T.; Tobita, S.; Takigami, S.; Hiratsuka, H. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 961.

(13) (a) Rossa, L.; Vögtle, F. *Top. Curr. Chem.* **1983**, *113*, 1. (b) Knops, P.; Sendhoff, N.; Mekelburger, H.-B.; Vögtle, F. *Top. Curr. Chem.* **1991**, *161*, 1. (c) Ostrowicki, A.; Koepp, E.; Vögtle, F. *Top. Curr. Chem.* **1991**, *161*, 37.

(14) Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers: New York, 1985.

(15) (a) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020. (b) Bellina, F.; Carpita, A.; Rossi, R. *Synthesis* **2004**, 2419.

(16) Robertson, J. M. *Organic Crystals and Molecules*; Cornell University Press: Ithaca, NY, 1953.

(17) (a) Sato, T.; Torizuka, K. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1199. (b) Sato, T.; Torizuka, K.; Komaki, R.; Atobe, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 561.

(18) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Phys. Chem.* **1986**, *90*, 3747.

(19) Berlman, J. B. *Handbook of Fluorescence Spectra of Aromatic Compounds*; Academic Press: New York, 1965.

(20) Meites, L.; Zuman, P. *CRC Handbook Series in Organic Electrochemistry*; CRC Press: Cleveland, OH, 1976.

(21) Ruseckas, A.; Namdas, E. B.; Lee, J. Y.; Mukamel, S.; Wang, S.; Bazan, G. C.; Sundstrom, V. *J. Phys. Chem. A* **2003**, *107*, 8029.

(22) Herz, L. M.; Phillips, R. T. *Phys. Rev. B* **2000**, *61*, 13691.

(23) Kannan, R.; He, G. S.; Yuan, L.; Xu, F.; Prasad, P. N. *Chem. Mater.* **2001**, *13*, 1896.

(24) McCoy, R. K.; Karasz, F. E.; Sarker, A.; Lahti, P. M. *Chem. Mater*. **1991**, *3*, 941.

(25) Merlet, S.; Birau, M.; Wang, Z. Y. *Org. Lett.* **2002**, *4*, 2157.

(26) (a) Superchi, S.; Donnoli, M. I.; Rosini, C. *Org. Lett.* **1999**, *1*, 2093. (b) Sun, W. M.; Ji, X. Y.; Kricka, L. J.; Dunford, H. B. *Can. J. Chem.* **1994**, *72*, 2159.

(27) Shinmyozu, T.; Sakai, T.; Uno, E.; Inazu, T. *J. Org. Chem*. **1985**, *50*, 1959.

(28) Cassidy, P. E.; Wallace, R. J.; Aminabhavi, T. M. *Polymer* **1986**, *27*, 1131.

(29) Hart, H.; Reilly, J. L.; Jiang, J. B. C. *J. Org. Chem.* **1977**, *42*, 2684.

(30) Kim, J. E.; Song, S.-Y.; Shim, H.-K. *Synth. Met.* **2001**, *121*, 1665.

(31) Staab, H. A.; Appel, W. K. *Liebigs Ann. Chem*. **1981**, 1065.

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