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Oxidation of Dithia[3.3]metacyclophane-Containing Through-Space π-Conjugated Polymer

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Summary

The oxidation reaction of dithia[3.3]metacyclophane-containing π-conjugated polymer (**3**) was performed by the treatment with *m*-chloroperbenzoic acid (*m*-CPBA). The reaction proceeded smoothly to obtain the corresponding oxidized polymer (**4**), and all sulfur atoms of the dithia[3.3]metacyclophane unit were converted to the sulfone group according to the ^{1}H, ^{13}C NMR, and IR spectra. The rapid *syn-[anti]-syn* interconversion of the oxidized dithia[3.3]metacyclophane moieties in polymer (**4**) and dithia[3.3]metacyclophane moieties in polymer (**3**) occured in solution at room temperature. Polymer (**4**) exhibited a blue emission in the same region as polymer (**3**).

Introduction

Over the last three decades, a considerable amount of interest in the design and preparation of novel conjugated polymers [1] due to their intriguing properties, such as electrical conductivity [1,2], electroluminescence [3], liquid crystallinity [4], and third-order nonlinear optical property [5]. One research area with regard to conjugated polymers focuses on customizing their spectral and electrical properties. For this purpose, a number of aromatic compounds have been incorporated into the conjugated polymer backbone, and their physical properties have been studied in detail.

[2.2]Paracyclophane and related compounds, which exhibit an intramolecular π-π interaction between two face-to-face benzene rings, have been widely investigated because of their unique structure [6]. Recently, we have reported the through-space conjugated polymers [7] prepared by using [2.2]paracyclophane as the key building block (Chart 1a) [7a]. These polymers exhibited an extension of the conjugation length via the through-space interaction and an intense photoluminescence in the visible purplish blue to orange region.

On the other hand, the incorporation of metacyclophanes into the conjugated chains has received very little attention, although a transannular π-π interaction exists between the two benzene rings of [2.2]metacyclophane and [3.3]metacyclophane. Mizogami and Yoshimura reported the synthesis and electrical conductivity of polymetacyclophane. The face-to-face structure of polymetacyclophane resulted in a high conductivity of 0.25 S cm^{-1} by doping with H_2SO_4 vapor (Chart 1b) [8]. Recently, we reported the preparation, stereochemistry, and optical properties of poly(*p*-phenylene-ethynylene)s that possessed a dithia[3.3]metacyclophane skeleton in the main chain (Chart 1c) [9]. 2,11-Dithia[3.3]metacyclophanes have been intensively used as synthetic precursors for the synthesis of [2.2]metacyclophanes and [2.2]metacyclophane-dienes [10]. Specifically, [2.2]metacyclophane can be prepared via 2,11-dithia[3.3]metacyclophane-2,2',11,11'-tetraoxide intermediates, which can be easily prepared by the oxidation reaction of 2,11-dithia[3.3]metacyclophane (Scheme 1). In this study, we subjected a 2,11-dithia[3.3]metacyclophane-containing polymer to this oxidation reaction to obtain a new conjugated polymer that contained the 2,11-dithia[3.3]metacyclophane-2,2',11,11'-tetraoxide unit in the main chain.

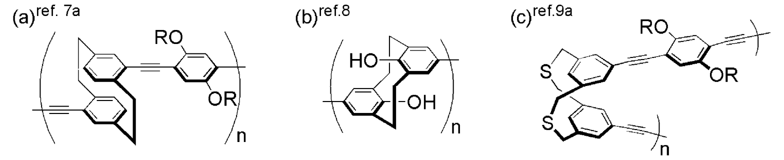
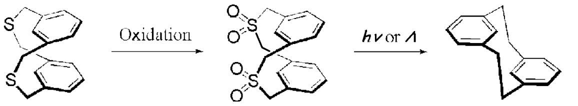


Chart 1. Cyclophane-containing polymers.



Scheme 1. Synthesis of [2.2]metacyclophane via 2,11-dithia[3.3]metacyclophane-2,2',11,11'-tetraoxide.

Experimental

General

^1H and ^{13}C NMR spectra were recorded on a JEOL EX400 instrument at 400 and 100 MHz, respectively. Samples were analyzed in $CDCl_3$, and the chemical shift values were expressed relative to Me_4Si as an internal standard. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer, and samples were analyzed in $CHCl_3$ solution at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in $CHCl_3$ solution at room temperature. Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8020 and RI-8020 (TSK gel α-3000 column) using $CHCl_3$ as an eluent after calibration with standard polystyrene.

Materials

NEt_3 was distilled from KOH. Dehydrated grade of toluene and $CHCl_3$, $PdCl_2(PPh_3)_2$, PPh_3, CuI, and *m*-chloroperbenzoic acid (*m*-CPBA) (ca. 75%) were obtained commercially, and used without further purification. 6,15-Dibromo-2,11-dithia[3.3]metacyclophane (**1**) [9a], 1,4-didodecyloxy-2,5-diethynylbenzene (**2**) [11], and dithia[3.3]metacyclophane-containing π-conjugated polymer (**3**) [9a] were prepared according to literature.

*Polymerization of **1** with **2***

A 50 mL Pyrex flask was charged with 6,15-dibromo-2,11-dithia[3.3]metacyclophane (**1**) (60 mg, 0.14 mmol), 1,4-didodecyloxy-2,5-diethynylbenzene (**2**) (69 mg, 0.14 mmol), $PdCl_2(PPh_3)_2$ (6.1 mg, 8.7 μmol), PPh_3 (8.2 mg, 0.031 mmol), CuI (2.4 mg, 0.013 mmol), toluene (3.0 mL), NEt_3 (3.0 mL), and a magnetic stirring bar under a flow of argon. The reaction was carried out at 90 ^oC for 60 h. After the reaction, the crude mixture was extracted with $CHCl_3$, and washed with aqueous NH_3 and H_2O. The organic layer was dried over Na_2SO_4 and evaporated. The residue was dissolved in a small amount of $CHCl_3$ and reprecipitated from a large amount of MeOH. The resulting polymer was separated by filtration, washed with MeOH, and dried in vacuo to give polymer (**3**) in 71% yield (76 mg, 0.10 mmol) as an yellowish orange solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.87 (br, 6H), 1.25 (br, 38H), 1.53 (br, 4H), 1.83 (br, 4H), 3.72 (br, 8H), 3.99 (br, 4H), 6.84-7.12 (br, 6H). ^{13}C NMR and IR data of **3** also matched the literature values reported previously [9a].

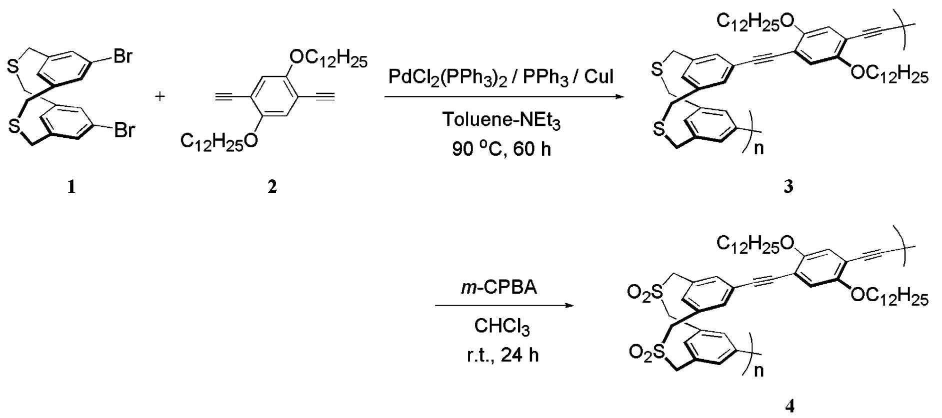
*Oxidation reaction of polymer (**3**)*

To a solution of polymer (**3**) (32mg, 0.042 mmol) in $CHCl_3$ (3.0 mL) was added *m*-CPBA (58 mg, 0.25 mmol) under a flow of argon. The reaction mixture was stirred at room temperature for 24 h. The reaction was quenched by adding aqueous NaOH. The mixture was extracted with $CHCl_3$, and the organic layer was washed with H_2O and then brine. The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by reprecipitation from MeOH. The resulting polymer was separated by filtration, and dried in vacuo to give polymer (**4**) in 93% yield (32 mg, 0.039 mmol) as a brown solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.87 (br, 6H), 1.24 (br, 38H), 1.66 (br, 4H), 1.84 (br, 4H), 3.99 (br, 4H), 4.30 (br, 8H), 6.99 (br, 2H), 7.53 (br, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 22.7, 26.0, 29.4, 29.7 (overlapping signals), 31.9, 61.1, 69.5, 87.9, 93.0, 117.6, 123.2, 128.6, 130.1, 132.0, 133.8, 153.5. IR (KBr): 1115, 1326 cm^{-1} (ν_{SO2}), 2204 cm^{-1} ($\nu_{C\equiv C}$).

Results and Discussion

The key monomer, 6,15-dibromo-2,11-dithia[3.3]metacyclophane (**1**), was prepared according to the procedure decribed in our previous study [9a]. The polymerization of **1** with 1,4-didodecyloxy-2,5- diethynylbenzene (**2**) was performed by the Sonogashira coupling reaction [12] in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ (3.0 mol%), PPh_3, and CuI in toluene-NEt_3 (v/v = 1:1) at 90 ^oC for 60 h under an argon atmosphere (Scheme 2). Metacyclophane-containing polymer (**3**) was obtained by reprecipitation from MeOH in 71% yield as an yellowish brown powder.

The oxidation reaction of polymer (**3**) was carried out by adding an excess amount of *m*-CPBA to $CHCl_3$ solution at room temperature for 24 h under an argon atmosphere according to literature [10,13] (Scheme 2). After the reaction, the reaction mixture was washed with aqueous NaOH to quench the excess amount of *m*-CPBA. The crude product was purified by reprecipitation from MeOH to obtain oxidized polymer (**4**) in 93% yield as a brown solid. Both polymers (**3**) and (**4**) were readily soluble in common organic solvents such as THF, CH_2Cl_2, $CHCl_3$, and toluene.



Scheme 2. Synthesis of polymer (**3**) and oxidized polymer (**4**).

Table 1. Polymerization results and the optical properties of polymers (**3**) and (**4**).

polymer	yield/%[a]	M_w[b]	M_n[b]	M_w/M_n[b]	UV λ_{max}/nm (log ε)[c]	PL λ_{max}/nm[c,d]	Φ_F[d,e]
3	71	3900	2400	1.6	310, 374 (4.39)	440	0.41
4	93	2200	1200	1.8	302, 366 (3.87)	444	0.12

[a] Isolated yield. [b] GPC ($CHCl_3$), polystyrene as a standard. [c] UV-vis absorption (2 x 10^{-5} M) and fluorescence emission spectra were recorded in dilute $CHCl_3$ solutions at room temperature. [d] Excited at the absorption maxima. [e] PL efficiencies in $CHCl_3$ determined relative to 9-anthracenecarboxylic acid in CH_2Cl_2 (Φ_F = 0.442).

The molecular weight measurements were performed by GPC using $CHCl_3$ as an eluent and using a calibration curve of polystyrene as a standard. The results are summarized in Table 1. The number-average molecular weights (M_n) of **3** and **4** were 2400 with M_w/M_n of 1.6 and 1200 with M_w/M_n of 1.8, respectively. The molecular weight decreased after the oxidation. This might be due to bond cleavage in a part of the polymer backbone during the oxidation. However, ^{1}H, ^{13}C NMR, and IR spectra revealed that all sulfur atoms underwent oxidation (vide infra).

Polymers (**3**) and (**4**) were characterized by ^{1}H, ^{13}C NMR, and IR spectra. In the ^{1}H NMR spectrum of **3**, the aryl protons of the dithia[3.3]metacyclophane unit appeared at 6.84-7.12 ppm (Figure 1a). The signals corresponding to the bridge methylene protons appeared at 3.72 ppm. These observations suggest that the *syn* form of the dithia[3.3]metacyclophane skeleton is the predominant conformation due to the rapid *syn-[anti]-syn* isomerization in solution [9a]. In the ^{1}H NMR spectrum of **4**, the signals for the bridge methylene protons of the -CH_2SCH_2- moieties disappeared, and new signals appeared at 4.30 ppm as a broad singlet peak (Figure 1b). It is known that the signals of the methylene protons of 2,11-dithia[3.3]metacyclophane-2,2',11,11'-tetraoxide and 2,11-dithia[3.3]metacyclophane appear at 4.67 and 3.62 ppm, respectively [14]. Therefore, the signals at 4.30 ppm in Figure 1b were attributed to the -$CH_2SO_2CH_2$- moieties. These results suggest that all sulfur atoms of dithia[3.3]metacyclophane were oxidized to the sulfone group. The aryl protons of **4** were downfield shifted to 7.5 ppm relative to those of **3**. The internal aromatic protons were also observed at around 7.5 ppm in the normal aromatic region. This implies that the dithia[3.3]metacyclophane tetraoxide unit of **4** exists predominantly as the *syn* conformation due to the rapid *syn-[anti]-syn* isomerization in solution at room temperature similar to the case in polymer (**3**). In addition, the bridge methylene carbon peak of **4** appeared at 61.1 ppm, which was downfield shifted in comparison with that of **3** (37.6 ppm) [9a] in the ^{13}C NMR spectra. The acetylenic moieties of **4** were characterized by ^{13}C NMR spectrum (δ 87.9 and 93.0 ppm) and IR spectrum (ν = 2204 cm^{-1}). The sulfone group of **4** was characterized by IR spectrum (ν = 1115 and 1326 cm^{-1}) (Figure 2).

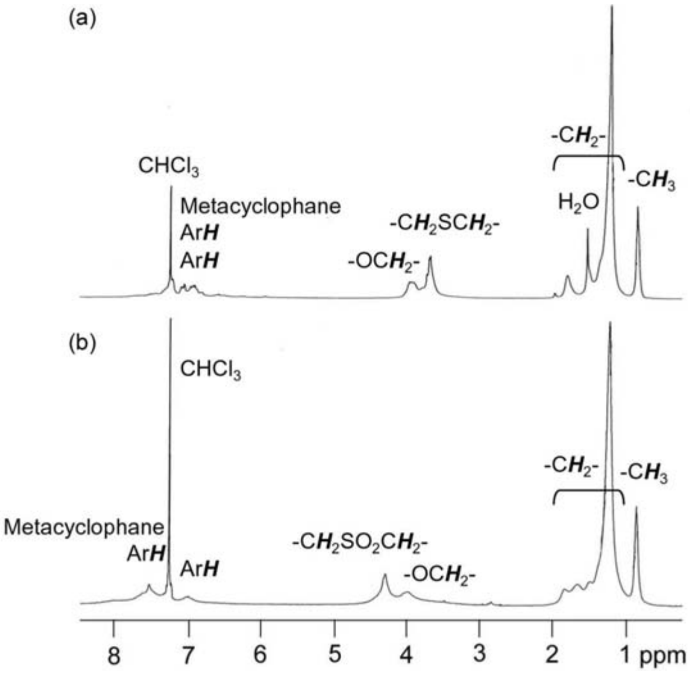


Figure 1. ^{1}H NMR spectra of polymers **3** (a) and **4** (b) in $CDCl_3$.

The optical properties of polymers (**3**) and (**4**) were examined, and the results are also summarized in Table 1. The UV-vis absorption spectrum of **3** in dilute $CHCl_3$ solution at room temperature exhibited absorption maxima at 310 and 374 nm (Table 1 and Figure 3a), which agreed with the absorption of the PPE backbone. The absorption spectrum of **4** exhibited the absorption maxima at 302 and 366 nm (Table 1 and Figure 3b). The absorption maxima were slightly blue shifted in comparison with those of **3**; however, the absorption edge did not change after the oxidation. The oxidation of sulfur atoms did not significantly affect the π-conjugation length of the polymer main chain, because the lone pairs of the two sulfur atoms in dithia[3.3]metacyclophane were not included in the π-conjugated system.

The fluorescence emission spectrum of **3** in dilute $CHCl_3$ solution at room temperature on excitation at 374 nm exhibited emission maxima at 408 and 440 nm in the visible blue region (Table 1 and Figure 3c). The emission maxima of **4** were observed at 419 and 444 nm in the visible blue region (Table 1 and Figure 3d). Polymer (**4**) exhibited a quantum efficiency of 0.12, which was determined by using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard ($\Phi_F = 0.442$) [15]. The emission of oxidized polymer (**4**) occurred in the same region as that of **3**. Additionally, it is reported that the emission maxima of compound (**5**) were observed at 402 and 426 nm [11a]. These spectra of **3**-**5** were similar and had vibrational structures. These results indicate that the emitting species are the phenylene-ethynylene units; in other words, the emissions of polymers (**3**) and (**4**) would occur in the monomer state rather than the phane state [16].

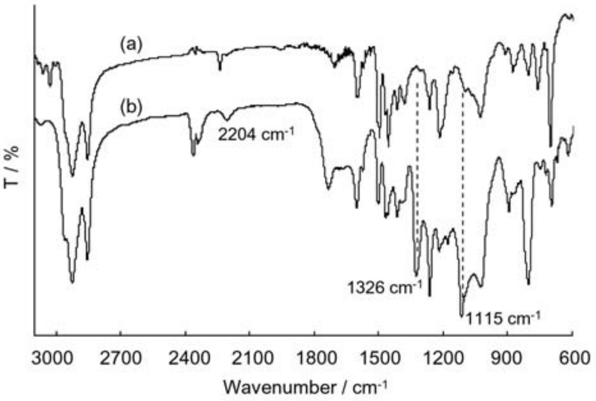


Figure 2. IR spectra (KBr) of polymers **3** (a) and **4** (b).

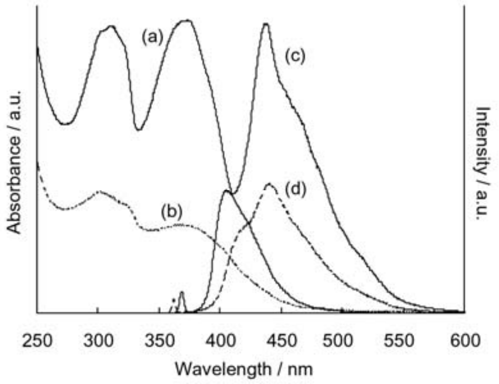
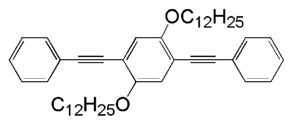


Figure 3. UV-vis absorption spectra of polymers **3** (a) and **4** (b) in $CHCl_3$, and fluorescence emission spectra of **3** (c) and **4** (d) in $CHCl_3$ at room temperature.



Compound 5[ref. 11a]

PL λ_{max} = 402 and 426 nm

Conclusion

The oxidation of the π-conjugated polymer having a dithia[3.3]metacyclophane in the main chain was performed and the product was characterized. The ^{1}H NMR spectrum revealed that the reaction efficiency was 100%. Polymer (**3**) and oxidized polymer (**4**) adopted the *syn* conformation in solution at room temperature due to the rapid *syn-[anti]-syn* isomerization. Further, the UV-vis absorption spectra revealed that in polymer (**4**), the oxidation of sulfur atoms did not affect the π-conjugation length of the polymer main chain. The synthesis of the [2.2]metacyclophane-containing conjugated polymer by the additional polymer reaction is currently underway.

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References

1. SkotheimTA, Elsenbaumer RL, Reynolds JR, Eds. (1998) Handbook of Conducting Polymers, 2nd ed. Marcel Dekker, New York
2. (a) Shirakawa H (2001) Angew Chem Int Ed 40:2574 (b) MacDiarmid AG (2001) Angew Chem Int Ed 40:2581. (c) Heeger AJ (2001) Angew Chem Int Ed 40:2591
3. (a) Kraft A, Grimsdale AC, Holmes AB (1998) Angew Chem Int Ed 37:402 (b) Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, Bradley DDC, Dos Santos DA, Bredas JL, Lögdlund M, Salaneck WR (1999) Nature 397:121 (c) Mitschke U, Bauerle P (2000) J Mater Chem 10:1471. (d) Bernius MT, Inbasekaran M, O'Brien J, Wu W (2000) Adv Mater 121:1737 (e) Akcelrud L (2003) Prog Polym Sci 28:875
4. (a) Nehring J, Amstutz H, Holmes PA, Nevin A (1987) Appl Phys Lett 51:1283 (b) Moll A, Siegfried N, Heitz W (1990) Makromol Chem Rapid Commun 11:485 (c) Witteler H, Lieser G, Wegner G, Schulze M (1993) Makromol Chem Rapid Commun 14:471
5. (a) Messir J, Kajzar F, Prasad PN, Ulrich DR, Eds. (1989) Nonlinear Optical Effects in Organic Polymers (NATO ASI Series E: Applied Sciences vol. 162). Kluwer Academic Publishers, Dordrecht (b) Pasad PN, Williams DJ (1991) Introduction to Nonlinear Optical Effects in Molecules and Polymers. Wiley-Interscience, New York (c) Bredas JL, Adant C, Tackx P, Persoons A, Pierce BM (1994) Chem Rev 94:243
6. (a) Vögtle F (1993) Cyclophane Chemistry. Wiley&Sons, New York (b) Shultz J, Vögtle F (1994) Top Curr Chem 172:42 (c) Cleiter R, Hopf H, Eds. (2004) Modern Cyclophane Chemistry. Wiley-VCH, Weinheim
7. (a) Morisaki Y, Chujo Y (2002) Macromolecules 35:587 (b) Morisaki Y, Chujo Y (2002) Chem Lett 194 (c) Morisaki Y, Ishida T, Chujo Y (2002) Macromolecules 35:7872 (d) Morisaki Y, Chujo Y (2002) Polym Bull 49:209 (e) Morisaki Y, Fujimura F, Chujo Y (2003) Organometallics 22:3553 (f) Morisaki Y, Chujo Y (2003) Macromolecules 36:9319 (g) Morisaki Y, Chujo Y (2004) Macromolecules 37:4099 (h) Morisaki Y, Ishida T, Tanaka H, Chujo Y (2004) J Polym Sci Part A Polym Chem 42:5891 (i) Morisaki Y, Wada N, Chujo Y (2005) Polym Bull 53:73 (j) Morisaki Y, Wada N, Chujo Y (2005) Polymer 46:5884 (k) Morisaki Y, Chujo Y (2005) Bull Chem Soc Jpn 78:288
8. Mizogami S, Yoshimura S (1985) J Chem Soc Chem Commun 1736
9. (a) Morisaki Y, Ishida T, Chujo Y (2003) Polym J 35:501 (b) Morisaki Y, Ishida T, Chujo Y (2006) Org Lett 8:1029
10. Givens RS, Olsen RJ (1979) J Org Chem 44:1608
11. (a) Li H, Powell DR, Hayashi RK, West R (1998) Macromolecules 31:52 (b) Moroni M, Le Moigne J (1994) Macromolecules 27:562

12. Sonogashira K, Tohda Y, Hagihara N (1975) Tetrahedron Lett 16:4467
13. Otsubo T, Kitasawa M, Misumi S (1979) Bull Chem Soc Jpn 52:1515
14. Sato T, Wakabayashi M, Hata K, Kainosho M (1971) Tetrahedron 27:2737
15. The absorbance (a.u.) of each sample was below 0.05 at the excitation wavelength in the measurement of the fluorescence quantum yield. The quantum yield (Φ_{unk}) of unknown sample was calculated by the following equation: $\Phi_{unk} = \Phi_{std}[A_{std}F_{unk}/A_{unk}F_{std}][n_{D,unk}/n_{D,std}]^2$ where A_{std} and A_{unk} are the absorbance of the standard and unknown sample, respectively, F_{std} and F_{unk} are the corresponding relative integrated fluorescence intensities, and n_D is the refractive index [CH_2Cl_2 ($n_D = 1.424$) and $CHCl_3$ ($n_D = 1.446$) were used.]
16. (a) Oldham Jr WJ, Miao YJ, Lachicotte RJ, Bazan GC (1998) J Am Chem Soc 120:419 (b) Bazan GC, Oldham Jr WJ, Lachicotte RJ, Tretiak S, Chernyak V, Mukamel S (1998) J Am Chem Soc 120:9188 (c) Wang S, Bazan GC, Tretiak S, Mukamel S (2000) J Am Chem Soc 122:1289