Aggregation-Induced Emission of *cis,cis*-1,2,3,4-Tetraphenylbutadiene from Restricted Intramolecular Rotation

Junwu Chen,*,† Bin Xu,† Xiaoying Ouyang,† Ben Zhong Tang,‡ and Yong Cao*,†

Institute of Polymer Optoelectronic Materials & Devices, South China University of Technology, Guangzhou 510640, People's Republic of China, and Department of Chemistry, Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, People's Republic of China

Received: April 6, 2004; In Final Form: June 16, 2004

cis,cis-1,2,3,4-Tetraphenylbutadiene (TPBD) exhibits aggregation-induced emission (AIE) in the UV-blue band: the photoluminescence (PL) quantum yield of TPBD aggregates can differ from that of molecularly dissolved species by 2 orders of magnitude (>200). When the isolated molecules in solutions are cooled to extremely low temperature, they also emit intense light comparable to that in the solid state. TPBD thin layer shows on−off fluorescence switching behavior that can be utilized for the sensing of organic vapors. The phenyl substituents in TPBD are twisted in the solid state, and excimer formation is greatly prohibited. The cooling-enhanced emission of the TPBD solution and the fluorescence switching behavior suggest that the aggregation-induced emission is caused by restricted intramolecular rotation of the phenyl groups. The intramolecular phenyl rotations of TPBD can be regarded as rotational relaxations around their equilibrium positions, from which mean relaxation time is defined based on an Arrhenius equation. All the PL behaviors of TPBD can be well explained qualitatively by the magnitude of the relaxation time.

Introduction

Many conjugated organic emitters are highly emissive in their dilute solutions but become weakly luminescent when fabricated into thin films.[1] This is believed to be caused by aggregate formation: in the solid state, the molecules aggregate to form less emissive species such as excimers, leading to a reduction in the luminescence efficiency.[2] The conjugated materials are practically utilized in the solid state commonly as thin films, and mitigation of the aggregation quenching has been a thorny problem in the development of light-emitting diodes (LED). Many groups have attempted to obstruct aggregate formation through elaborate chemical, physical, and engineering approaches, which have, however, met with only limited success. Aggregation is in some sense inherent in film formation,[3] and it would be ideal if a molecule can emit intense light in its aggregation state. Swager and co-workers elegantly observed an unusual phenomenon that the photoluminescence (PL) quantum yield (Φ_F) of an aggregated film of a poly(*p*-phenylenethynylene) (PPE) was 3.5 times that of its solution.[4] The same phenomenon with Φ_F of neat film of about 8−10 times higher compared to its solution was also found for four diphenyl-substituted phenylenevinylene and diphenylenevinylene polymers (PPVs).[5] Interestingly, 2,3,4,5-tetraphenylsiloles[6] and 1-cyano-*trans*-1,2-bis(4′-methylbiphenyl)ethylene (CN-MBE)[7] were virtually nonemissive in solutions, but their aggregates or solid films are highly luminescent; a several hundreds of times change of Φ_F of the aggregated phase to the solution was found. Thus a concept of aggregation-induced emission (AIE) was proposed.[6a] Very recently, AIE effects were realized in silole-containing polyacetylenes[8] and also found for bis(4-(*N*-(1-naphthyl)phenylamino)phenyl)fumaronitrile (NPAFN).[9] AIE-active materials are promising emitters for the fabrications of highly efficient LEDs.[9,10] AIE-active molecules are normally highly emissive in their crystal forms; therefore, they are promising candidates for the realization of electrically pumped lasers[11] since crystals of conjugated molecules possess higher carrier mobilities to afford the high current injection, compared to their amorphous forms.[12]

Several models, such as exciton diffusion, rotational deactivation, and noncoplanarity, have been proposed for the lower PL quantum yield or PL quenching in solutions, compared with the enhanced emission in the solid state.[5−8] Belton et al. reported that the PPV chains had greater spatial freedom in solutions to explore more planar conformations that reduced the energy barriers for exciton diffusion along the polymer backbone, increasing the number of nonradiative routes and decreasing the PL yield.[5a] Holzer et al. reported that both the vibrational, librational, and rotational freedoms of motion of the side chain substituents of PPVs and the distortions of the main chain units in solutions seemed to be responsible for the fast nonradiative relaxation and reduced fluorescence quantum yield.[5b] They further pointed out that the lower PL quantum yield in solution was due to rotational deactivation.[13] Park et al.[7] proposed that twisted structure or noncoplanarity was responsible for the PL quenching of CN-MBE in solution while coplanarization in the solid state caused their aggregation-induced emission. The crystal structures of siloles, however, are not consistent with the former coplanarity hypothesis:[6a] the phenyl peripheries of siloles are twisted to a great extent (up to 87°) in the solid state.[6b,14] Based on further experimental results of enhanced emissions of silole solutions upon cooling and thickening, we pointed out that deactivations of excitons by phenyl rotations were responsible for the PL quenching of the siloles in solutions.[6b,8,14]

To enlarge the family of materials with enhanced emissions in the solid state, it is necessary to carry out more extensive studies in the field, particularly to discover the structural

---

* To whom correspondence should be addressed. Phone: 8620-8711-4609. Fax: 8620-8711-4535. E-mail: psjwchen@scut.edu.cn (J.C.); poycao@scut.edu.cn (Y.C.).

† South China University of Technology.

‡ Hong Kong University of Science & Technology.

10.1021/jp048475q CCC: $27.50

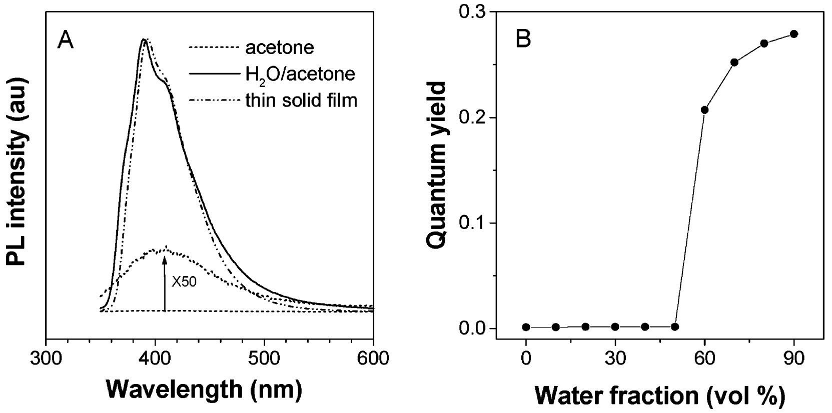
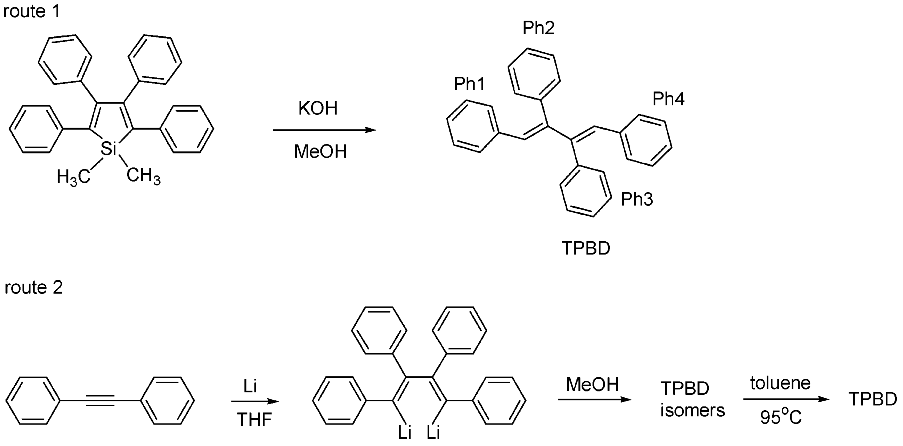


Figure 1. (A) PL spectra of TPBD in acetone, TPBD in water/acetone mixture (90:10 by volume), and its thin solid film (80 nm). Concentration of TPBD 10 μM; excitation wavelength 345 nm. (B) PL quantum yield of TPBD vs solvent composition of the water/acetone mixture.

SCHEME 1



characteristics of AIE-active molecules. In this paper, we report the aggregation-induced UV-blue emission of *cis*,*cis*-1,2,3,4-tetraphenylbutadiene (TPBD) and its origin from the restrictions of the rotations of the phenyl substituents on the butadiene core. We also demonstrate that the intense emission in aggregation state can be quenched upon fuming with solvent vapor, showing on−off fluorescence switching behavior. We point out that phenyl rotations are rotational relaxations around their equilibrium positions, and the mathematical description for the rotational relaxations is established and discussed.

Results and Discussion

Two synthetic methods can be used to prepare TPBD (Scheme 1). According to a similar procedure by Yamaguchi et al.,[15] TPBD was readily obtained in a yield of 76% by the desilylation of 1,1-dimethyl-2,3,4,5-tetraphenylsilole[16] (route 1 in Scheme 1). Alternatively, according to a classic report by Smith and Hoehn,[17] quenching of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene[6b] with methanol first gave complicated isomers; further heating of the isomers in toluene at 95 °C for 10 min and then recrystallization from toluene−heptane mixture also afforded the same TPBD in 70% yield (route 2 in Scheme 1). The spectroscopic data of TPBD are listed in the Experimental Section.

Compared to 1,1,4,4-tetraphenylbutadiene,[18] a typical blue emitter, TPBD derivatives are normally not regarded as fluorescent materials.[15] Indeed, upon excitation at 345 nm, the fluorescence of TPBD is very faint in common organic solvents such as acetone (Figure 1A), chloroform, tetrahydrofuran, etc. The 50 times magnified data of the emission of the acetone solution shows a noisy spectrum, peaking at about 408 nm. When water, the nonsolvent of TPBD, is added to the acetone solution, TPBD molecules form aggregates in the water−acetone mixture. The aggregates are highly fluorescent and emit an UV-blue light with a maximum at 390 nm and a vibronic shoulder at 410 nm (Figure 1A), indicating that TPBD is AIE-active. Compared to the TPBD aggregates, its thin solid film (80 nm) prepared by thermal evaporation under high vacuum also emits an intense light, with a 3 nm red shift of the emission peak and the same position of the vibronic shoulder. The emission maxima of the neat films of the reported PPE and PPVs with the enhanced solid-state emissions are around 520 nm.[4,5] Tetraphenylsiloles, silole-containing linear and hyperbranched polymers, and CN-MBE normally emit blue-green light while NPAFN emits light in the red region.[6−9] Therefore, the UV-blue emission of TPBD is unique. Highly efficient UV-blue emission is valuable for full color display based on color converters.[19]

To have a quantitative picture of the AIE process, we estimated the PL quantum yields (Φ_F) of TPBD in water−acetone mixtures, using 9,10-diphenylanthracene as the reference.[20] The Φ_F of the acetone solution is as low as 0.0011. The Φ_F is almost unchanged upon addition of water up to 50 vol %, but starts to swiftly increase afterward (Figure 1B). When the volume fraction of water in the water/acetone mixture is increased to 90%, Φ_F rises to 0.28, which is about 250 times higher than that of the acetone solution. The trajectory of the Φ_F change suggests that TPBD molecules start to aggregate at a water fraction of >50% and that the size and

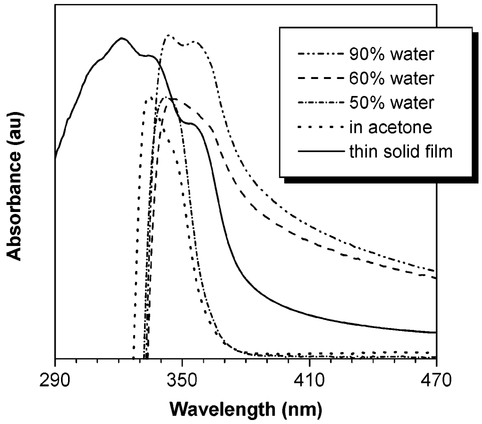


Figure 2. UV absorption spectra of TPBD thin solid film (80 nm) and TPBD in water/acetone mixtures with different volume fractions of water.

population of the aggregates continue to increase as the water fraction is increased.

The UV absorption spectra of TPBD thin solid film and TPBD in water/acetone mixtures with different volume fractions of water are shown in Figure 2. The absorption spectrum of the thin solid film peaks at 322 nm, with two vibronic shoulders at 336 and 354 nm. The difference between the absorption peak and the first vibronic shoulder is 14 nm, which is close to that in the emission spectrum of the thin solid film. The UV absorption spectrum of TPBD in acetone peaks at 334 nm, which is practically identical to the first vibronic shoulder of the thin solid film. The absorption maxima for the 50, 60, and 90% mixtures red shift to 342, 344, and 344 nm, respectively, and similar results were found for siloles in nonsolvent/solvent mixtures.[6] For the 90% mixture, a new peak at 356 nm can be observed. Notably, the UV absorptions for 60 and 90% mixtures in the long-wavelength region are greatly intensified. This is a signature of the aggregate formation, due to light scattering of aggregates,[21] which effectively decreases the light transmission through the TPBD mixtures. The abrupt increase in the absorbance from >50% water fraction agrees well with the sudden jump in the quantum yield shown in Figure 1B, doubly confirming that TPBD molecules start to aggregate when >50% of poor solvent (water) is added to the acetone solution. The large influence of the light scattering of the aggregates on the absorption results in the big absorption difference between the aggregates and the thin solid film.

Twisted intramolecular charge transfer (TICT) has been known to greatly affect the emission properties of some chromophoric molecules containing donor and acceptor groups.[22,23] In such systems, the polarity of the solvent has been found to alter both the ground and excited states of the molecules. Increasing the polarity of the solvents of 4-*N*,*N*′-dimethylaminoflavone solutions, for example, red-shifted their absorption and emission maxima by up to >100 nm and enhanced their Φ_F by up to ~143 times.[24] The TPBD is, however, not a push−pull molecule. The UV absorption maxima of TPBD in cyclohexane, ethyl acetate, and acetonitrile are at 330, 330, and 328 nm, respectively; the solvent polarity exerts little effect on the absorption transitions. TPBD is also virtually nonemissive in the solutions of the three solvents. The TICT mechanism does not contribute to the AIE process of TPBD.

The crystal structure of TPBD, as reported by Karle and Dragonette,[25] shows that TPBD is a centrosymmetric molecule, and the butadiene core of TPBD is almost coplanar while the four phenyls are twisted. The angle between Ph2 and the butadiene core is 75° while that between Ph1 and the chain is 34° in the TPBD crystal (Ph1 and Ph2 are labeled in Scheme 1). Similar to 2,3,4,5-tetraphenylsiloles,[6b] coplanarity is not responsible for the AIE mechanism of TPBD. The twisted structures of phenyl substituents in TPBD and 2,3,4,5-tetraphenylsiloles should be very important for their intense emissions in the solid state and probably prohibit excimer formations in the solid state. The absorption and emission of the thin solid film of TPBD are both blue shifted compared with those of TPBD solution. This is evidence that excimer hardly forms in the aggregates of TPBD.

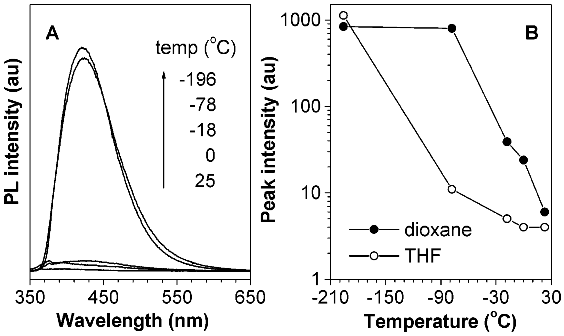


Figure 3. (A) Photoluminescence spectra of TPBD in 1,4-dioxane at different temperatures. (B) Effect of temperature on the peak intensity of the photoluminescence of TPBD in dioxane and THF. Concentration of TPBD 10 μM; excitation wavelength 345 nm.

Cooling-enhanced emission was found for isolated species of siloles, demonstrating that phenyl rotations of siloles are thermally activated.[6b] We check the temperature effect on the photoluminescence of TPBD in dilute solutions. Two solvents, dioxane (mp = 11.8 °C) and THF (mp = −108 °C), were selected as solvents for low-temperature PL measurements. When a dilute dioxane solution of TPBD (10 μM) was cooled, the intensity of its PL spectrum was increased (Figure 3A). When cooled from room temperature to below the melting point of dioxane, the liquid solution changed to a solid “glass”. The PL intensity progressively increased when the temperature was successively decreased from 25 to −78 °C, indicating that the cooling is gradually limiting the thermally activated intramolecular rotations of phenyls of TPBD. Further decreasing the temperature from −78 to −196 °C caused little change in the peak intensity, implying that the intramolecular rotations may have already been frozen at −78 °C. When THF was used as the solvent, no significant enhancement of PL intensity was found from 25 to −18 °C (Figure 3B) since THF possesses a higher solvating power and much lower melting point compared to dioxane. Restriction of the thermally activated intramolecular rotations began to be effective at −78 °C, although the PL intensity was much lower than that of the frozen dioxane at −78 °C. Further cooling the THF solution to a frozen temperature (−196 °C) brought the PL intensity to a level comparable to that of dioxane. The PL intensity at −196 °C is ~280-fold higher than that at room temperature, which is comparable to a Φ_F increase of aggregates at 90% water fraction in the acetone solution, indicating that the restrictions of the rotations of the phenyl groups of isolated TPBD molecules in the solid “glasses” at much lower temperature (−196 °C) are similar to those of TPBD aggregates.

Although the intramolecular phenyl rotations of TPBD are restricted in the solid state, they can still be activated by solvent vapors, causing fluorescence quenching like that in solutions. As shown in Figure 4, a TPBD thin layer developed on a TLC silica plate emits bright and deep blue light under illumination with a 365 nm UV lamp at room temperature; the fluorescence

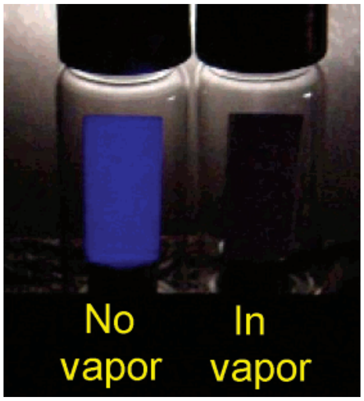


Figure 4. On−off fluorescence switching of TPBD thin layer developed on the TLC plate without vapor (left) and in vapor (dichloromethane) (right) under UV light (365 nm) illumination at room temperature.

turns off reversibly in the atmosphere of dichloromethane vapor. The on−off fluorescence switching behavior of TPBD thin layer can thus be utilized for the sensing of organic vapors. The same behavior was found for CN-MBE, an AIE-active molecule.[7] Thus the on−off fluorescence switching behavior could be a common property for AIE-active chromophores.[26]

It is evident that the extent of intramolecular phenyl rotation plays a dominant role in the PL behaviors of TPBD and tetraphenylsiloles. Here we point out that the intramolecular rotations can be regarded as rotational relaxations around their equilibrium positions and the mean relaxation time (τ) can be expressed with the following well-known Arrhenius equation:

$$\tau = \tau_0\, e^{(\Delta E/RT)} \tag{1}$$

where τ_0 is a constant, ΔE is the activation energy for the rotational relaxation, R is the gas constant, and T is the absolute temperature (K).

All the PL behaviors of TPBD can be well explained qualitatively with eq 1. For TPBD molecularly dissolved in a solvent at room temperature, the activation energy ΔE for the rotational relaxation is very small due to the strong solvation power of the solvent, giving a very small τ which opens the nonradiative channel. For the case of TPBD aggregates, ΔE can be very high due to the big intramolecularly steric restrictions to the intramolecular phenyl rotations in the solid state, giving a large τ which effectively closes the nonradiative channel and populates the radiative decay. The activation energy ΔE in the solid state decreases again when a TPBD thin layer on a TLC plate is fumed by a solvent vapor, which causes the on−off fluorescence switching behavior. The τ increases with decreasing of temperature, and this causes the cooling-enhanced emission.

In summary, TPBD is an AIE-active molecule: virtually invisible in common organic solvents while highly emissive in the UV-blue band in the aggregation state. Upon cooling, the isolated TPBD molecules in frozen glasses (−196 °C) also emit intense light comparable to that in the solid state. The on−off fluorescence switching behavior of TPBD thin layer can be utilized for the sensing of organic vapors. Restricted intramolecular rotation contributes to the AIE behavior. The intramolecular phenyl rotations of TPBD can be regarded as rotational relaxations around their equilibrium positions, from which mean relaxation time is defined based on an Arrhenius equation. All the PL behaviors of TPBD can be well explained qualitatively by the magnitude of the relaxation time.

Experimental Section

Materials. THF and 1,4-dioxane (Aldrich) were predried over 4 Å molecular sieves and distilled from sodium benzophenone ketyl immediately prior to use. Diphenylacetylene and lithium wire were purchased from Aldrich and used as received without further purification. 1,1-Dimethyl-2,3,4,5-tetraphenylsilole was prepared according to a previous report.[16]

Instrumentation. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX 400 spectrometer. The UV−visible absorption spectra were recorded on an HP 8453. Gas chromatography−mass spectrometry (GC−MS) was performed on a Finnigan Trace 2000. Melting points were measured on a Model X-4 of Beijing Taike Instruments. The fluorescence display of a TPBD thin layer on a TLC plate was photographed on a Sony DSC-5P digital camera.

The PL spectra of the silole solutions and the nanoaggregate mixtures were recorded on a Jobin Yvon Fluorolog-3 spectrofluorometer. The sample chamber of the spectrofluorometer was dehumidified with P_2O_5. The nanoaggregate mixtures were freshly prepared by adding poor solvents into the TPBD solutions with vigorous shaking. For example, a nanoparticle mixture of TPBD was prepared by adding 8 mL of water into 2 mL of an acetone solution in a 10 mL volumetric flask. The concentrations of all the aggregate mixtures were adjusted to 10 μM.

PL characterization of TPBD on a TLC plate was measured according to a previous report,[6b] performed on the Jobin Yvon Fluorolog-3 spectrofluorometer. Merck TLC plates (Silica 60 F_{254}) were used for TLC-fluorescence measurement. The TPBD thin layer was developed from its chloroform solution (2 mg/mL).

Synthesis of TPBD by Desilylation (Route 1). According to a similar preparation method by Yamaguchi et al.,[15] a mixture of 1,1-dimethyl-2,3,4,5-tetraphenylsilole (1.24 g, 3 mmol) and potassium hydroxide (1.68 g, 30 mmol) in toluene/water 2:1 mixed solvent (15 mL) was heated to reflux for 20 h. After dilution with an aqueous solution of HCl (0.1 N), the mixture was extracted with ether several times. The combined extract was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. Recrystallization from a toluene/heptane mixture afforded 0.81 g of TPBD in 76% yield. White solids; mp = 183−184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.43−7.33 (m, 10H), 7.04 (m, 6H), 6.76 (m, 4H), 6.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ [ppm]: 145.6, 139.8, 137.3, 131.7, 130.4, 129.5, 128.8, 127.8, 127.4, 126.6; GC−MS: m/z 358 (M^+); UV ($CHCl_3$) λ_{max} (nm)/ϵ_{max} (dm^3 mol^{-1} cm^{-1}): 334/3.05 × 10^4.

Synthesis of TPBD by Route 2. Under dry nitrogen, 177 mg (25.4 mmol) of freshly cut lithium shavings were added to a solution of diphenylacetylene (5 g, 28.0 mmol) in 25 mL of THF. The mixture was stirred for 12 h at room temperature. Methanol (2 mL) was dropwise added to the resultant THF solution of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene. The mixture was further stirred for 1 h. The crude product was purified on a silica gel column using hexane/chloroform mixture (15:1 by volume) as eluent. Heating of the product (TPBD isomers) in toluene at 95 °C for 10 min and then recrystallization from toluene−heptane mixture afforded 3.18 g of pure TPBD in 70% yield (based on lithium).

Acknowledgment. Financial support from the Natural Science Foundation of China (No. 50303006) and the Ministry of Science and Technology of China (No. 2002CB613404) is gratefully acknowledged.

References and Notes

(1) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.

(2) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765.

(3) *Film Formation in Coatings: Mechanisms, Properties, and Morphology*; Provder, T., Urban, M. W., Eds.; American Chemical Society: Washington, DC, 2001.

(4) Deans, R.; Kim, J.; Machacek, M. R.; Swager, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 8565.

(5) (a) Belton, C.; O'Brien, D. F.; Blau, W. J.; Cadby, A. J.; Lane, P. A.; Bradley, D. D. C.; Bryne, H. J.; Stockmann, R.; Horhold, H. H. *Appl. Phys. Lett.* **2001**, *78*, 1059. (b) Holzer, W.; Penzkofer, A.; Stockmann, R.; Meysel, H.; Liebegott, H.; Horhold, H. H. *Polymer* **2001**, *42*, 3183.

(6) (a) Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. *Chem. Commun.* **2001**, 1740. (b) Chen, J.; Law, C. C. W.; Lam, J. W. Y.; Dong, Y.; Lo, S. M. F.; Williams, I. D.; Zhu, D.; Tang, B. Z. *Chem. Mater.* **200**3, *1*5, 1535.

(7) An, B. K.; Kwon, S. K.; Jung, S. D.; Park, S. Y. *J. Am. Chem. Soc.* **2002**, *124*, 14410.

(8) Chen, J.; Xie, Z.; Lam, J. W. Y.; Law, C. C. W.; Tang, B. Z. *Macromolecules* **200**3, *3*6, 1108.

(9) Yeh, H. C.; Yeh, S. J.; Chen, C. T. *Chem. Commun.* **2003**, 2632.

(10) Chen, H. Y.; Lam, J. W. Y.; Luo, J. D.; Ho, Y. L.; Tang, B. Z.; Zhu, D. B.; Wong, M.; Kwok, H. S. *Appl. Phys. Lett.* **2002**, *81*, 574.

(11) Though Schön et al. claimed that electrically pumped lasers were realized (Schön, J. H.; et al. *Science* **2000**, *289*, 599; *Science* **2000**, *290*, 963), the papers have since been retracted by the journal (*Science* **2002**, *298*, 961).

(12) (a) Funahashi, M.; Hanna, J. *Phys. Rev. Lett.* **1997**, *78*, 2184. (b) Schein, L. B.; McGhie, A. R. *Phys. Rev. B* **1979**, *20*, 1631.

(13) Holzer, W.; Penzkofer, A.; Stockmann, R.; Meysel, H.; Liebegott, H.; Horhold, H. H. *Synth. Met.* **2002**, *125*, 343.

(14) Chen, J.; Peng, H.; Law, C. C. W.; Dong, Y.; Lam, J. W. Y.; Williams, I. D.; Tang, B. Z. *Macromolecules* **2003**, *36*, 4319.

(15) Yamaguchi, S.; Endo, T.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Tamao, K. *Chem. Eur. J.* **2000**, *6*, 1683.

(16) Tang, B. Z.; Zhan, X.; Yu, G.; Lee, P. P. S.; Liu, Y.; Zhu, D. *J. Mater. Chem.* **2001**, *11*, 2874.

(17) Smith, L. I.; Hoehn, H. H. *J. Am. Chem. Soc.* **1941**, *63*, 1184.

(18) See, for example: (a) Kim, J. H.; Noh, S.; Kim, K.; Lim, S. T.; Shin, D. M. *Synth. Met.* **2001**, *117*, 227. (b) Huang, J. S.; Yang, K. X.; Xie, Z. Y.; Liu, S. Y.; Jiang, H. J. *Opt. Quantum Electron.* **2001**, *33*, 165. (c) Gardecki, J. A.; Maroncelli, M. *Appl. Spectrosc.* **1998**, *52*, 1179. (d) Wen, W. K.; Jou, J. H.; Chiou, J. F.; Chang, W. P.; Whang, W. T. *Appl. Phys. Lett.* **1997**, *71*, 1302.

(19) Qiu, C. F.; Wang, D.; Chen, H. Y.; Wong, M.; Kwok, H. S. *Appl. Phys. Lett.* **2001**, *79*, 2276.

(20) Morris, J. V.; Mahaney, M. A.; Huber, J. R. *J. Phys. Chem.* **1976**, *80*, 969.

(21) (a) Tang, B. Z.; Xu, H.; Lam, J. W. Y.; Lee, P. P. S.; Xu, K.; Sun, Q.; Cheuk, K. K. L. *Chem. Mater.* **2000**, *12*, 1446. (b) Tang, B. Z.; Geng, Y.; Lam, J. W. Y.; Li, B.; Jing, X.; Wang, X.; Wang, F.; Pakhomov, A. B.; Zhang, X. X. *Chem. Mater.* **1999**, *11*, 1581.

(22) (a) Rettig, W.; Baumann, W. In *Progress in Photochemistry and Photophysics*; Rabek, J. F., Ed.; CRC Press: Boca Taton, FL, 1990; Vol. 6, Chapter 3, p 79. (b) Suppan, P. *Chemistry and Light*; Royal Society of Chemistry: London, 1994.

(23) (a) Morozumi, T.; Anada, T.; Nakamura, H. *J. Phys. Chem. B* **2001**, *105*, 2923. (b) Bajorek, A.; Paczkowski, J. *Macromolecules* **1998**, *31*, 86. (c) Soujanya, T.; Fessenden, R. W.; Samanta, A. *J. Phys. Chem.* **1996**, *100*, 3507. (d) Grabowski, Z. R. *Pure Appl. Chem.* **1993**, *65*, 1751.

(24) Wang, P.; Wu, S. *J. Lumin.* **1994**, *62*, 33.

(25) Karle, I. L.; Dragonette, K. S. *Acta Crystallogr.* **1965**, *19*, 500.

(26) We have found that siloles also possess the same property.