

Synthesis of Fluorescent Thiophene-derivatized Pentytiptycenes and Their Aggregate Behaviors

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Abstract

Thiophene-derivatized pentytiptycenes were synthesized and characterized by NMR and UV-Vis spectroscopy. Aggregation behavior of thiophene-derivatized pentytiptycenes was monitored by the measurement of fluorescence. Fluorescence intensities for the thiophene-derivatized pentytiptycenes and thiophene-derivatized pentytiptycenes aggregates were compared. There is no shift in the maximum of the emission wavelength. In the range of water fraction between 20% and 40%, the emission intensity of thiophene-derivatized pentytiptycene aggregates remains almost identical. Fluorescence efficiency increased by about 5 times higher when the thiophene-derivatized pentytiptycenes forms the aggregates in solution.

Key words : Thiophene, Iptycene, Fluorescence, Quenching

1. Introduction

Recently, the electronic structure and molecular bonding properties of the valence shell orbitals of thiophene and the mono halogenated thiophenes have been investigated both experimentally and theoretically.^[1] New approaches to the detection of analytes are a central challenge in the field of chemical sensors.^[2-4] Detection sensitivity has been principally determined by the transduction method and the new materials has been focused upon endowing selectivity. This has led to their use as new materials with tailored photoluminescence and electroluminescence properties, for example as the emitting layer or as an electron-transport, hole-blocking (ETHB) layer in organic light emitting devices (OLEDs).^[5,6] More often, thiophene was incorporated into calamitic mesogens and lower transition temperatures were usually achieved.^[7-10] The aggregation of highly emissive organics and polymers into a solid state causes an emission-quenching effect, since the aggregation of molecules forms less emissive species such as excimers. Reduction of emission efficiency in the solid state has been a major problem in device applications

of light-emitting organic molecules. Many attempts to prevent aggregate formation have been made through chemical, physical, and engineering approaches. In contrast, few results on aggregation-induced emission (AIE) properties have been recently reported. An aggregation-induced emission enhancement of polysiloles was reported. In this paper, the synthesis of thiophene-derivatized pentytiptycenes was reported and their aggregation behaviors were investigated. The key feature of thiophene-derivatized pentytiptycenes was the incorporation of rigid three-dimensional pentytiptycene moieties in the thiophene-derivatized pentytiptycenes that prevent p-stacking or excimer formation. The fluorescence of thiophene-derivatized pentytiptycenes in comparison to an other fluorescence compounds verifies the important role of their porosity. The porosity is a result of the rigid pentytiptycene groups, which provide cavities for analyte binding.

2. Experimental

2.1. Materials

Pentytiptyene diacetylene has been synthesized by the procedures described in the literature.^[4] All synthesis manipulations were carried out under an atmosphere of dry argon gas using standard vacuum-line Schlenk techniques. All solvents were purified and degassed before use according to standard literature methods: diethyl-

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ether, tetrahydrofuran (THF), methanol were purchased from Aldrich Chemical Co. Inc. and distilled from sodium/benzophenone ketyl. All other reagents (Aldrich) such as anthracene, benzoquinone, 2-iodothiophene, CuI, triethylamine, and $\text{Pb}(\text{PPh}_3)_2\text{Cl}_2$ were purchased and used without any purification. Spectroscopic grade THF from Fisher Scientific was used for the fluorescence measurements. Spectroscopy grade THF and water from Fisher Scientific were used for the fluorescence measurements. NMR grade deuteriochloroform was stored over 4 Å molecular sieves. NMR data were collected with 300 MHz spectrometer for ^1H NMR. Chemical shifts are reported in parts per million (δ ppm); downfield shifts are reported as positive values from tetramethylsilane (TMS) standard at 0.00 ppm. UV-vis absorption spectrum and fluorescence emission spectrum were recorded with the use of a Shimadzu UV-2401 spectrophotometer and a Perkin-Elmer luminescence spectrometer LS 50B, respectively. The solvents were determined to be free of emitting impurities prior to use. To avoid changing the concentrations of the emitting compound, the experiments were carried out with solution by preparing the quencher in the same solution of the emitting compound.

The concentration of thiophene penttiptycene polymers and their aggregates for the fluorescence measurement was $1 \text{ mg}/1 \text{ L} = 1 \text{ ppm}$.

2.2. Synthesis of lptycene Quinones

To a mixture of anthracene (17.8 g, 0.1 mol) and benzoquinone (5.4 g, 0.05 mol) in a 200 mL round bottomed flask fitted with a condenser was added 75 mL of mesitylene. The mixture was refluxed for 24 h and then the solid was filtered after cooling to room temperature. The hydroquinone solid was digested in 100 mL of hot xylene twice and filtered (16.5 g). The crude hydroquinones (8 g) were dissolved in hot glacial acetic acid (ca 300 mL) and then a solution of 1.5 g of potassium bromate (9 mmol) in 100 mL of hot water was added. A deep orange color and precipitate developed immediately. The solution was boiled for a few minutes and then an additional 100 mL of hot water was added and the heat was removed. The orange quinone solid was collected after the solution was cooled. The quinones were washed with acetic acid and then with water. The crude quinones were dissolved in chloroform (ca. 120 mL) and washed with sodium bicarbonate and

brine. The organic layer was separated and dried (MgSO_4). The dark-colored impurities were removed by filtering the chloroform solution through a thin layer of silica gel. The resulting orange solution was adsorbed onto ca. 50 g of silica gel. The resulting yellow silica gel solid mixture was chromatographed with hexane/ethyl acetate (5:1) as the eluent to obtain triptycene quinone in 80-95% purity, which can be further purified by column chromatography with pure chloroform as the eluent. Penttiptycene quinone stays bound to the silica gel and was obtained as a pure material by extraction of the silica gel with chloroform. The overall yields for triptycene quinone and penttiptycene quinone were 13% and 39%, respectively. Triptycene quinone (mp 294.0°C , lit. mp $292\text{-}296^\circ\text{C}$): ^1H NMR (300 MHz, CDCl_3) 5.80 (s, 2H), 6.60 (s, 2H), 7.04 (dd, $J = 3.3$ and 5.3 Hz, 4H), 7.43 (dd, $J = 3.3$ and 5.3 Hz, 4H) ppm; ^{13}C NMR (75 MHz, CDCl_3) 47.36, 124.40, 125.56, 135.36, 143.57, 151.90, 183.48 ppm. penttiptycene quinone (mp $>350^\circ\text{C}$, lit. mp $>370^\circ\text{C}$): ^1H NMR (300 MHz, CDCl_3) 5.75 (s, 4H), 6.97 (dd, $J = 3.2$ and 5.3 Hz, 8H), 7.36 (dd, $J = 3.2$ and 5.3 Hz, 8H) ppm; ^{13}C NMR (75 MHz, CDCl_3) 47.39, 124.24, 125.46, 143.65, 150.95, 179.96 ppm.

2.3. Synthesis of Bis(trimethylsilyl)ethynyl Penttiptycene

Under an atmosphere of argon, 1 equivalent of *n*-butyllithium (2.5 mmol) in hexane was added dropwise to a solution of (trimethylsilyl)acetylene (0.35 mL, 2.5 mmol) in THF at 0°C . The mixture was then kept at 0°C for another 40 min before it was transferred to a solution of penttiptycene quinone (0.46 g, 1 mmol) in THF at 0°C . The mixture was warmed to room temperature and stirred overnight. The reaction was quenched with 1 mL of 10% HCl and then subjected to a $\text{CHCl}_3/\text{H}_2\text{O}$ workup. The solvent was removed and hexane was then added to the residue. The resulting white solid (0.59 g, 90%, 0.90 mmol), which is a mixture of the trans and cis isomers, was collected by filtration. This crude solid was dissolved in 10 mL of acetone and then a solution of tin(II) chloride dihydrate (0.51 g, 2.25 mmol) in 50% of acetic acid (10 mL) was added dropwise. This mixture was stirred at room temperature for another 24 h and the resulting solid product was filtered. The solid was then dissolved in CHCl_3 and washed with water and sodium bicarbonate and then dried (MgSO_4). The CHCl_3 was removed in vacuo and the residue was washed with hexane to remove the yellow impurities.

The resulting white solid was collected (yield 85%). Bis(trimethylsilylethynyl) pentiptycene (mp 419°C): ^1H NMR (300 MHz, CDCl_3) 0.51 (s, 18H), 5.80 (s, 4H), 6.96 (dd, $J = 3.2$ and 5.3 Hz, 8H), 7.36 (dd, $J = 3.2$ and 5.3 Hz, 8H) ppm; ^{13}C NMR (62.5 MHz, CDCl_3) 0.31, 52.2, 100.7, 102.5, 114.8, 123.8, 125.2, 144.1, 144.9 ppm.

2.4. Synthesis of Pentiptyene Diacetylene

The deprotection of the trimethylsilyl group was carried out by dissolving bis(trimethylsilylethynyl) pentiptycene in a mixture of KOH (two tablets in 1 mL of H_2O), THF, and MeOH and stirring at room temperature for 5 h. The resulting solid product was filtered and washed with water and then dried in vacuo. Pentiptyene diacetylene (mp 439.5°C): ^1H NMR (300 MHz, CDCl_3) 3.69 (s, 2H), 5.82 (s, 4H), 6.95 (dd, $J = 3.2$ and 5.4 Hz, 8H), 7.36 (dd, $J = 3.2$ and 5.4 Hz, 8H)

2.5. Synthesis of Thiophene-derivatized Pentiptyene

Pentiptyene diacetylene (1 g, 2.0913 mmol) in dry THF (650 mL) 24 h were added to solution of 2-iodothiophene (0.878 g, 4.1826 mmol), CuI (0.0398 g, 0.20912 mmol), $\text{Pb}(\text{PPh}_3)_2\text{Cl}_2$ (0.1454 g, 0.20716 mmol), triethylamine (1.632 ml). The reaction mixture was 1.5 h stirred at room temperature and then 2.5 h 65°C reflux. The solution was cooling to room temperature and filtered, The solvent was removed in vacuo, and the crude iptycene thiophene were dissolved in chloroform (100 mL) and then solution washed with sodium bicarbonate. The solution was dried with MgSO_4 . The white impurities were removed by filtering the chloroform solution, removed in vacuo and then dissolved in ethyl acetate. The resulting mixture were chromatographed with hexane/chloroform (9:1)mixture eluent to obtain product. Solvent is removed and the residue was washed with hexane. The resulting white solid was obtained in 70% yield: ^1H NMR : (300 MHz, CDCl_3) 5.82 (s, 4H), 6.9(s, 2H), 6.95 (dd, $J = 3.2$ and 5.3 Hz, 8H), 7.36 (dd, $J = 3.2$ and 5.3 Hz, 8H) ppm.

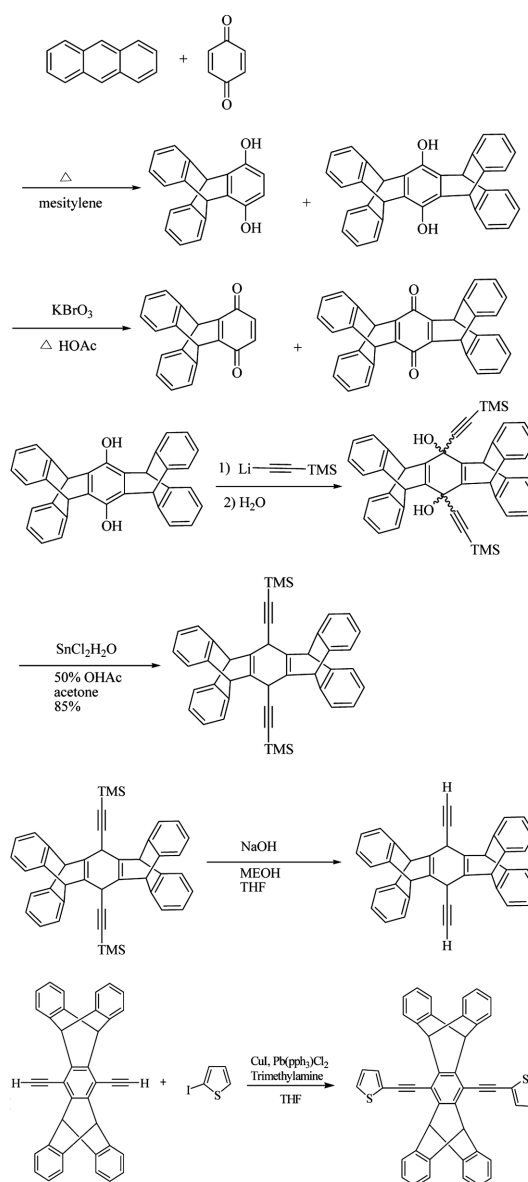
2.6. Instrumentation and Experimental Condition

Fluorescence emission and excitation spectra were recorded on Perkin-Elmer Luminescence spectrometer LS 50B. The solvents were determined to be free of emitting impurities prior to use. To avoid changing the concentrations of the emitting compound, the experiments were carried out with solution by preparing the

quencher in the same solution of compound. The UV-vis spectra were obtained from Shimadzu UV-2401 diode array spectrometer.

3. Result and Discussion

Scheme 1 illustrated the preparation of thiophene-derivatized pentiptycene starting from the petiptycene diacetylene, in the presence of CuI/ $\text{Pb}(\text{PPh}_3)_2\text{Cl}_2$, as an effective activating agent.



Scheme 1. synthesis of thiophene-derivatized pentiptycene.

Fluorescence spectra for both thiophene-derivatized pentiptycene and thiophene-derivatized pentiptycene aggregates exhibit one emission band (λ_{max} , 344 nm) when excited at 214 nm. There is no shift in the maximum of the emission wavelength. Fig. 1 shows the fluorescence spectra of thiophene-derivatized pentiptycene and thiophene-derivatized pentiptycene aggregates. For thiophene-derivatized pentiptycene solution in pure THF, the photoluminescence (PL) intensity is very weak.

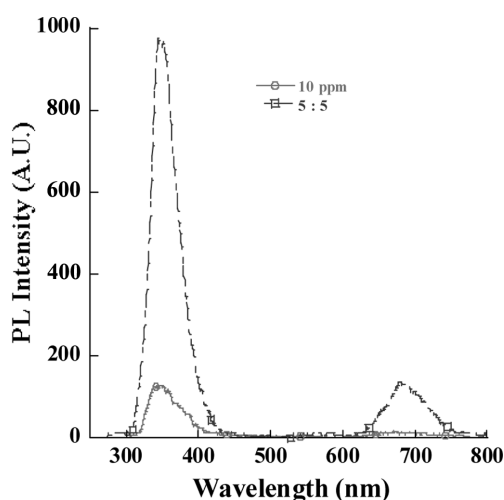


Fig. 1. Fluorescence spectra of thiophene-derivatized pentiptycene (solid line) and thiophene-derivatized pentiptycene aggregates (dashed line).

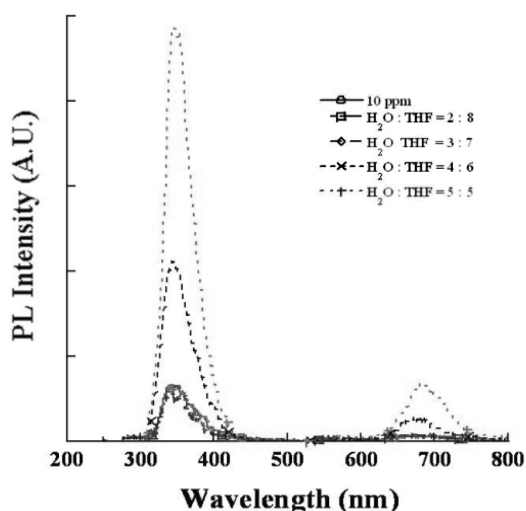


Fig. 2. Photoluminescence spectra of thiophene-derivatized pentiptycene aggregates in water-THF mixtures.

In solutions between 0% and 40% water by volume, the emission intensity of thiophene-derivatized pentiptycene aggregates does not increase. However, the intensity of the emission band increases by about 5 times when the solution is 50% water by volume, indicating that the thiophene-derivatized pentiptycenes form the aggregates in solution. Fig. 2 shows the fluorescence spectra in water-THF mixture for the thiophene-derivatized pentiptycene aggregates exhibiting on emission band (λ_{max} , 344 nm) when excited at 214 nm. In the range of water fraction between 20% and 40%, the emission intensity of thiophene-derivatized pentiptycene aggregates remains almost identical. A minimum volume-fraction of 40% water is required to increase the luminescence, which indicates the onset of aggregation.

As increasing water fraction, the emission intensity of thiophene-derivatized pentiptycene aggregates increases dramatically above the volume-fraction of 40% water. There is no shift in the maximum of the emission wavelength. The intensity of emission band increases by 11 times at the volume-fraction of 40% water. Fig. 3 shows the plot for relative fluorescence intensity of thiophene-derivatized pentiptycene vs thiophene-derivatized pentiptycene aggregates.

The large increase in photoluminescence from thiophene-derivatized pentiptycene aggregates could be attributed to the incorporation of rigid three-dimensional pentiptycene moieties in the thiophene-derivatized pen-

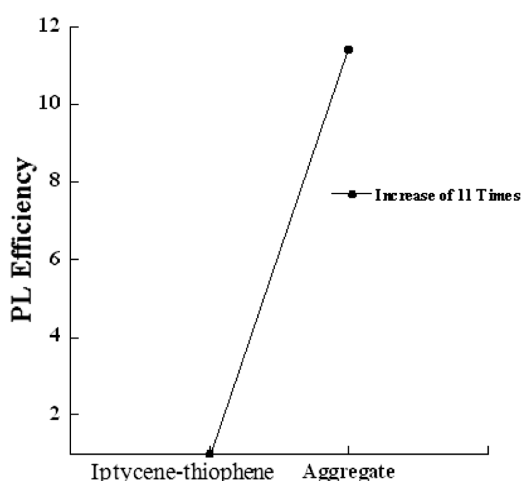


Fig. 3. Plot of the relative intensity of thiophene-derivatized pentiptycene vs thiophene-derivatized pentiptycene aggregates.

tiptycenes aggregates that prevent p-stacking or excimer formation, which limits the nonradiative decay pathways or inhibits the solvent assisted quenching resulting from aggregation. The stability of thiophene-derivatized pentiptycenes aggregates in 50% water solutions has been investigated, and the fluorescence intensity remains unchanged over a month. This indicates that thiophene-derivatized pentiptycenes aggregates show neither further aggregation nor degradation.

4. Conclusion

New thiophene-derivatized pentiptycene and thiophene-derivatized pentiptycene aggregates have been synthesized and characterized by photoluminescence spectroscopy. The thiophene-derivatized pentiptycene aggregates exhibit 11 times better PL efficiency at 50% water fraction than iptycene-thiophene dissolved in THF. The large increase in photoluminescence from thiophene-derivatized pentiptycene aggregates could be attributed to the incorporation of rigid three-dimensional pentiptycene moieties in the thiophene-derivatized pentiptycenes aggregates.

References

- [1] A. B. Trofimov, J. Schirmer, D. M. P. Holland, A. W. Potts, L. Karlsson, R. Maripuu and K. Siegbahn, "The influence of electron correlation and relativistic effects on the valence shell photoelectron spectrum of iodothiophene", *J PHYS B-AT MOL OPT.* vol. 35, pp. 5051-5058, 2002.
- [2] J. P. Czarnik and A. W. Eds. "Chemosensors of Ion and Molecule Recognition Desvergne", Kluwer Academic Publishers: Boston, 1997.
- [3] A. P. De Silva, H. Q. N. Gunaratne, T.G unnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.* "Signaling recognition events with fluorescent sensors and switches", Vol. 97, pp. 1515, 1997.
- [4] J. S. Yang and T. M. Swanger. *J. AM. Chem. Soc.* vol. 120, pp. 1184, 1998.
- [5] A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew "Electroluminescent conjugated polymers - Seeing polymers in a new light"*, *Chem., Int. Ed.*, vol. 37, p. 402, 1998.
- [6] Y. Shirota, J. Mater, Y. Shirota and J. Mater, *Chem.*, "Organic materials for electronic and optoelectronic devices", vol. 10, pp. 1, 2000.
- [7] A. P. H. J. Kilbinger, A. F. M. Biscarini, F. Cavallini, M. Cooper, H. J. Derrick, P. J. Feast, W. J. Lazaroni, R. Leclere, P. H. McDonell, L. A. Meijer and E. W. Meesters, *J. Am. Chem. Soc.* "Supramolecular Organization of [alpha],[alpha]-Disubstituted Sexithiophenes find it", vol. 124, pp. 1269, 2002.
- [8] R. Azumi, H. Tachibana, H. Sakai, M. Abe, P. Bauerle and M. Matsumoto, *Chem. Lett.* "Liquid crystalline behavior of α -substituted oligothiophenes", p. 1022, 2001.
- [9] P. Liu, H. Nakano and Y. Shirota *Liq. Cryst.* "Synthesis and mesogenic properties of a novel family of oligothiophene derivatives", vol. 28, pp. 581, 2001.
- [10] H. Zhang, S. Shiino, A. hishido, A. Kanazawa, O. Tsutsumi and T. Shiono, *Adv. Mater.* "A Thiophene Liquid Crystal as a Novel -Conjugated Dye for Photo-Manipulation of Molecular Alignment", vol. 12, pp. 1336, 2000.