Synthesis and Photophysical Properties of Stilbenoid Dendrimers via Heck Reaction on a Tetraphenylethylene Core

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Two new tetraphenylethylene-cored stilbenoid dendrimers have been efficiently prepared by fourfold Heck reaction with appropriate dendron molecules. The methodology permits highly *trans*-selective coupling. The optical absorption and emission properties of these systems were studied. The materials display strong emission in the blue region.

Organic light-emitting devices (OLEDs) have been attracting considerable attention because of their potential application within flat-panel displays.[1,2] Efficient blue-light OLEDs are of particular interest because they are desired for use as blue light sources in full-color display applications;[3–8] they can also serve as hosts for exothermic energy transfer to lower-energy fluorophores to realize white-light OLEDs.[9–13] High-performance blue-light-emitting materials exhibiting ideal color purity, good stability, and high fluorescence efficiency remain relatively rare. In particular, dendritic poly(phenylenevinylenes), also called stilbenoid dendrimers, represent an important group within this class of material. Several different studies have been published to date concerning the synthesis and properties of these materials.[14] For example, such compounds have been used successfully as molecular wires in molecular scale electronics,[15] and nanotechnological devices, light emitting diodes,[16] organic-based lasers for fabrication,[17] and optoelectronics.[17c]

For synthesis of fully conjugated stilbenoid dendrimer, we choose tetraphenylethylene two-dimensional scaffolds as a core. These systems usually have a fully conjugated backbone in three modes: diagonal conjugation, lateral conjugation, and cross conjugation. Since the three π-systems could potentially interact with each other, the overall photophysical properties of compound based on Figure 1 were expected to be different from those of the individual one-dimensional π-system. All four corners of this module are attached with identical stilbenoid peripheral units. Here, phenylenevinylene dendritic arms can function as light-harvesting antennae.[16b] This manuscript focuses on the synthesis and characterization of a tetraphenylethylene-cored first-generation stilbenoid dendrimers bearing phenylenevinylene arms as peripheral units. The optical absorption and emission properties were examined. By incorporation of *tert*-butyl groups to the terminal aryl rings as in the oligomeric series the solubility properties can be slightly enhanced.

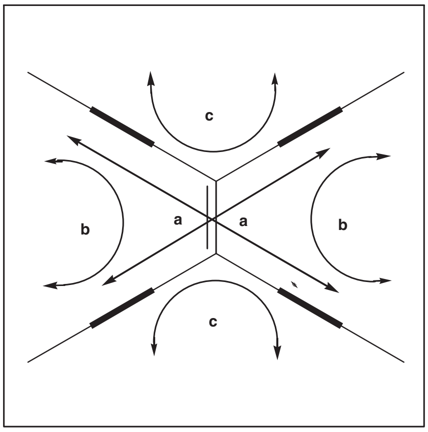
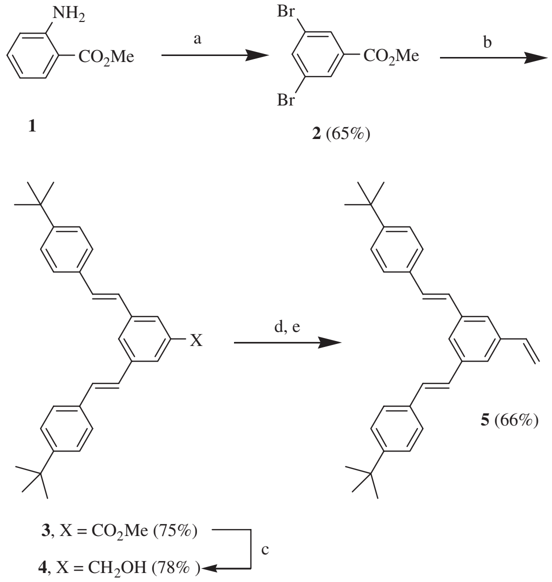


Figure 1. a: Diagonal conjugation (transoid), b: lateral conjugation (cisoid), c: cross conjugation, ▬: conjugated spacer.



Scheme 1. Reagents and conditions: (a) (i) Br_2, HOAc; (ii) *t*-BuONO, DMF, 60 °C; (b) 4-*t*-butylstyrene, $Pd(OAc)_2$, *n*-Bu_4NBr, KOAc, DMF, 90 °C, 24 h; (c) $LiAlH_4$, THF, rt; (d) PDC, CH_2Cl_2, rt; (e) $Ph_3P^+MeI^-$, *n*-BuLi, THF, −20 °C.

Results and Discussion

Our studies began with dendron **5**, which was prepared from methyl anthranilate (**1**) following a slightly modified procedure as reported by Sengupta and co-workers (Scheme 1).[18] Thus, dibromination of **1** followed by deamination (*t*-BuONO, DMF) gave methyl 3,5-dibromobenzoate (**2**) in 65% yield. Twofold Heck reaction on **2** with 4-*t*-butylstyrene under Jeffery's conditions[19] gave **3**, which on treatment with lithium aluminum hydride in THF afforded the benzyl alcohol **4**. Conversion of **4** to the corresponding terminal olefin **5** was then accomplished by pyridinium dichromate (PDC) oxidation followed by Wittig reaction.

We have chosen tetraphenylethylene as a core molecule to prepare stilbenoid dendrimer because this two-dimensional

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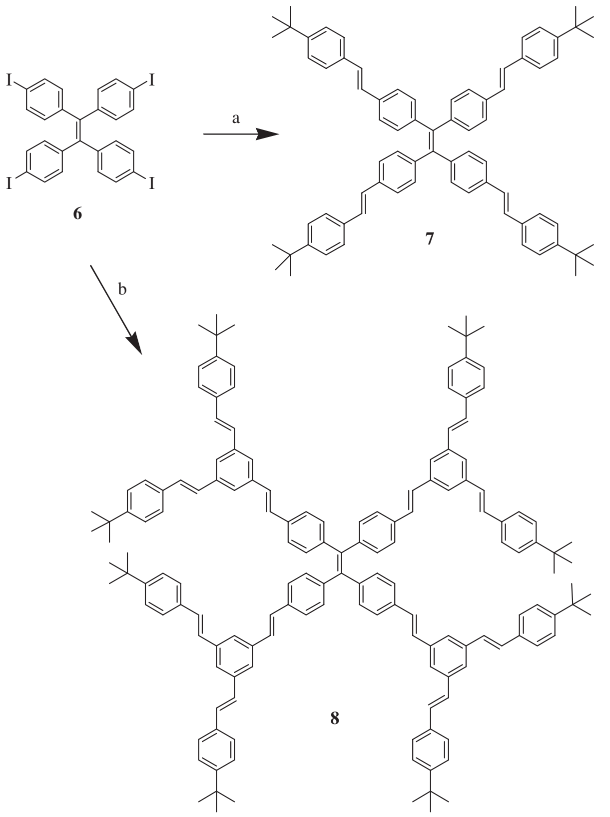

Scheme 2. Reagents and conditions: (a) 4-*t*-butylstyrene, $Pd(OAc)_2$, *n*-Bu_4NBr, PPh_3, KOAc, DMF, 100 °C, 24 h, 45%; (b) **5**, $Pd(OAc)_2$, *n*-Bu_4NBr, PPh_3, KOAc, DMF, 100 °C, 48 h, 21%.

scaffold facilitates additional conjugation due to the presence of four phenyl rings. Moreover, tetraphenylethylene has a strong emission property that provides opportunities for the synthesis of tetraphenylethylene-cored stilbenoid dendrimers. Particularly, in presence of *meta*-linkages in the phenylene-vinylene peripheral unit lowers the molecular conjugation. Both of these effects allow the system to emit blue light, the primary color that is the hardest to obtain with polymer light-emitting diodes (PLEDs).

Tetraiodide **6** was prepared from tetraphenylethylene[20] by the fourfold iodination with I_2–$PhI(OAc)_2$ in CH_2Cl_2 after stirring at room temperature for 60 h in the dark in 76% yield.[21] Generally, multifold Heck coupling reaction for stilbenoid dendrimer preparation afforded low yields due to the insolubility of partially coupled intermediates, which were observed to precipitate from solution during early reaction times.[22] Thus, fourfold Heck reaction of **6** with 4-*tert*-butylstyrene derivative under Jeffery's phase transfer conditions [10% $Pd(OAc)_2$, *n*-Bu_4NBr, KOAc, DMF, 100 °C] give rise to the first-generation dendrimer **7** in 45% yield (Scheme 2). Under the same conditions, fourfold Heck reaction of **6** with excess of styrene derivative **5** led to the fluorescent *meta*-branched X-shaped tetraphenylethylene-cored dendrimer **8** formed in 21% yield.

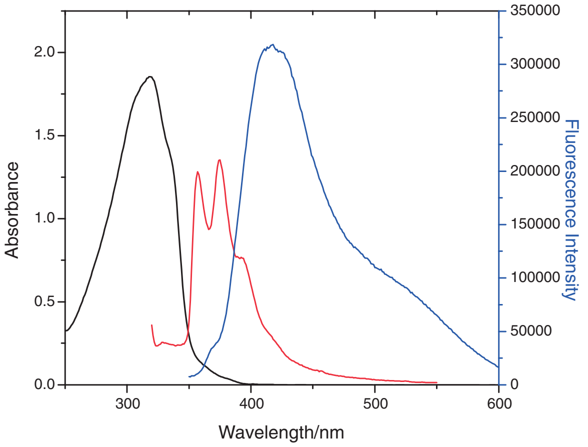

Figure 2. Absorption (black) and emission spectrum of **7** (blue), emission spectrum of tetraphenylethylene (red) in CH_2Cl_2 solutions at $C = 1.02 \times 10^{-6}$ M.

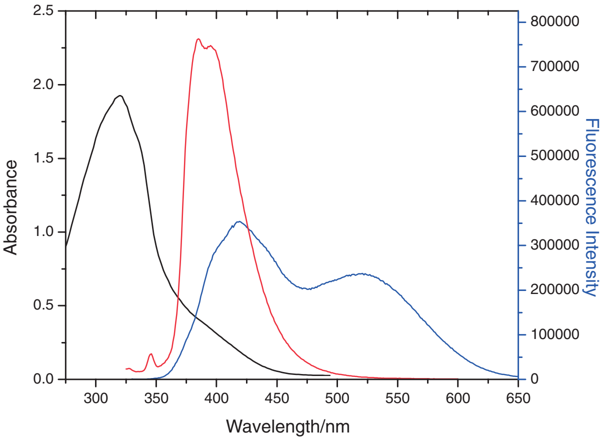

Figure 3. Absorption (black) and emission spectrum of **8** (blue), emission spectrum of **5** (red) in CH_2Cl_2 solutions at $C = 1.1 \times 10^{-6}$ M.

UV–Vis and PL Spectroscopy. The optical properties of the synthesized stilbenoid dendrimers **7** and **8** were investigated by UV–vis and photoluminescence (PL) spectroscopy on CH_2Cl_2 solutions at room temperature. The data obtained are shown in Figures 2 and 3. These compounds show maximum absorption wavelengths in the UV or visible region (320 nm). The peaks at 320 nm were assigned to the particularities of the stilbene units. The *meta*-arrangement through which the different units are linked prevents efficient delocalization throughout the conjugated backbone, and as a result, more or less the same phenomenon observed in absorption spectroscopy. The materials are strongly fluorescent and emit light in the blue region. Fluorescence quantum yields of **7** and **8** are 0.42 and 0.65.[23]

In both cases, excitation at 320 nm, that is, at the absorption maxima of the stilbene units, resulted in fluorescence in the region 418–420 nm, typical of stilbenoid compounds. Particularly for compound **8**, an additional shoulder peak at 521 nm was observed (Figure 3). The fluorescence excitation spectrum of **8** obtained by monitoring the emission at 420 nm and also 520 nm, for both cases produced an excitation band at 320 nm. It is shown that the compounds **7** and **8** exhibit two emission bands. The shorter wavelength emission bands of the compounds **7** and **8** coincide with that of the peripheral stilbene units. The emission bands at the longer wavelengths in both **7** and **8** are different from the emission of a simple tetraphenylethylene unit. The intriguing phenomenon can be explained by energy transfer mechanism. The conjugative effect of the peripheral stilbene unit with the central tetraphenylethylene unit in both **7** and **8** initiates an efficient energy transfer form the periphery to the central core for which centrally disposed tetraphenylethylene unit in each case gives a new emission band at the longer wavelength (for **7** at 512 nm and for **8** at 521 nm).

Conclusion

In conclusion, we have successfully synthesized and characterized a monodisperse stilbenoid first generation dendrimer in a straightforward manner using fourfold Heck coupling reaction between tetraphenylethylene derivatives and an appropriate stilbenoid unit. The protocol permits a highly *trans*-selective synthetic route to stilbenoid compounds. The *meta*-substitution pattern causes all chromophores to be independent, and all of the compounds present absorption wavelengths in the UV or visible region, and the materials exhibit strong emission in the blue region.

Experimental

General. Solvents and reagents were dried and purified by distillation before use as follows: tetrahydrofuran from sodium benzophenone ketyl, dichloromethane and chloroform from P_2O_5, DMF from CaH_2, and pyridine from solid KOH. Unless otherwise noted, all reactions were carried out under an inert atmosphere in flame dried flasks. After drying, organic extracts were evaporated under reduced pressure and the residue was column chromatographed on silica gel (Spectrochem, particle size 100–200 mesh), using an ethyl acetate–petroleum ether (60–80 °C) mixture as eluent unless specified otherwise.

Typical Experimental Procedure for Preparation of Stilbenoid Dendrimers 7 and 8. A mixture of dried KOAc (70 mg, 0.714 mmol), n-Bu_4NBr (153 mg, 0.476 mmol) in DMF (6 mL) was stirred for 15 min in a double necked round-bottomed flask in argon atmosphere at room temperature. To the reaction mixture were added **6** (100 mg, 0.119 mmol), PPh_3 (12 mg, 0.047 mmol), and 4-*tert*-butylstyrene (114 mg, 0.717 mmol) simultaneously. The mixture was stirred for another 15 min. A catalytic amount of $Pd(OAc)_2$ was added and heated for 24 h at 100 °C. The mixture was cooled to room temperature and extracted with hexane and ether mixture (1:1) (15 mL). The organic layer was washed with water (3×5 mL) and brine (5 mL), and dried over anhydrous Na_2SO_4. Solvent was removed in a rotary evaporator and the crude product was purified using column chromatography (silica gel/ethyl acetate: petroleum ether 1:99) to yield the compound **7** (51 mg, 45%) as white solids.

Compound 7: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, 8H, $J = 8.0$ Hz), 7.34 (d, 8H, $J = 8.0$ Hz), 7.03 (d, 4H, $J = 16.0$ Hz), 7.01 (d, 4H, $J = 16.0$ Hz), 1.31 (s, 36H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.7, 135.8, 134.7, 131.8, 129.7, 128.3, 127.7, 126.2, 126.0, 125.6, 34.6, 31.3; MALDI-TOF MS: m/e: 964.2755 (M^+).

Compound 8: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (br s, 8H), 7.51 (d, 8H, $J = 8.0$ Hz), 7.49 (br s, 4H), 7.48 (d, 16H, $J = 8.0$ Hz), 7.42 (d, 8H, $J = 8.0$ Hz), 7.40 (d, 16H, $J = 8.0$ Hz), 7.17 (d, 12H, $J = 16$ Hz), 7.10 (d, 12H, $J = 16$ Hz), 1.33 (s, 72H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.8, 138.1, 134.4, 131.9, 130.9, 130.4, 128.9, 127.5, 126.4, 126.3, 125.7, 125.6, 34.6, 31.2; MALDI-TOF MS: m/e: 2006.6907 (MH^+).

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