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Synthesis of dendritic stilbenoid compounds: Heck reactions for the periphery and the core

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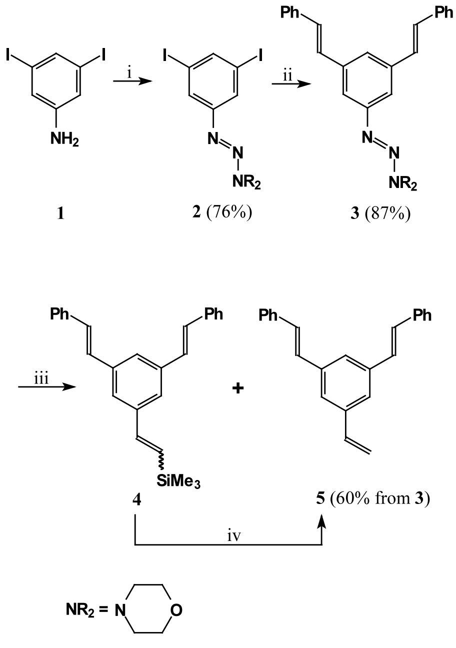
Abstract—A convergent synthetic strategy for stilbenoid dendrimers is described in which multifold Heck reactions have been used to construct both the peripheral and the core stilbene units. Solution optical properties of one of the dendrimers indicated some energy transfer having taken place from the periphery to the core. © 2002 Elsevier Science Ltd. All rights reserved.

Since 1990, when Holmes et al. first reported that poly(p-phenylenevinylenes) (PPVs) can be effectively used as the emitting layer in light emitting diodes (LEDs),[1] interest in the synthesis and optical properties of stilbenoid compounds has increased substantially.[2,3] While most studies have dealt with linear oligophenylenevinylenes,[3] it has been recognized recently that dendritic stilbenoid compounds are promising candidates for applications in organic LEDs.[4] Stilbenoid dendrimers offer a number of advantages over the linear PPVs. Due to their highly branched structures, such dendrimers are expected to be less aggregated and hence, should not suffer from fluorescence-quenching due to intermolecular interactions.[5] Moreover, their optical properties, especially the emitted color and quantum yields, can be fine tuned via appropriate choice of the fluorescent core. However, despite such promise and given the fact that the synthesis of functional dendrimers has rapidly burgeoned in recent years,[6] there are only a handful of reports on the synthesis of dendritic stilbenoid compounds.[4,7] In continuation of our interest in the synthesis of novel conjugated aromatic architectures for optoelectronic applications, we now present a convergent synthesis of stilbenoid dendrimers via the strategic use of multifold Heck reactions.

Until now, Wittig or Horner–Emmons reactions have been mostly used for the synthesis of stilbenoid dendrimers.[7] For such strategies, special bifunctional synthons are usually required, both for dendron preparation as well as for the core-coupling reactions. Syntheses of stilbenoid dendrimers via a sequential Heck reaction (for dendron propagation) and Horner–Emmons condensation (for core-coupling) have also been reported.[4,7a] However, stilbene synthesis via Wittig or Horner–Emmons reactions usually give rise to a



Scheme 1. (i) $NaNO_2$, conc. H_2SO_4, 0°C to rt then morpholine, aq. Na_2CO_3; (ii) styrene, $Pd(OAc)_2$, Bu_4NBr, KOAc, DMF, 90°C; (iii) $CH_2{=}CHSiMe_3$ (10 equiv.), $Pd(dba)_2$, CH_3CN, 0°C to rt; (iv) TFA, CH_2Cl_2, rt.

Keywords: stilbenoid dendrimers; Heck reaction; fluorescence; energy transfer.

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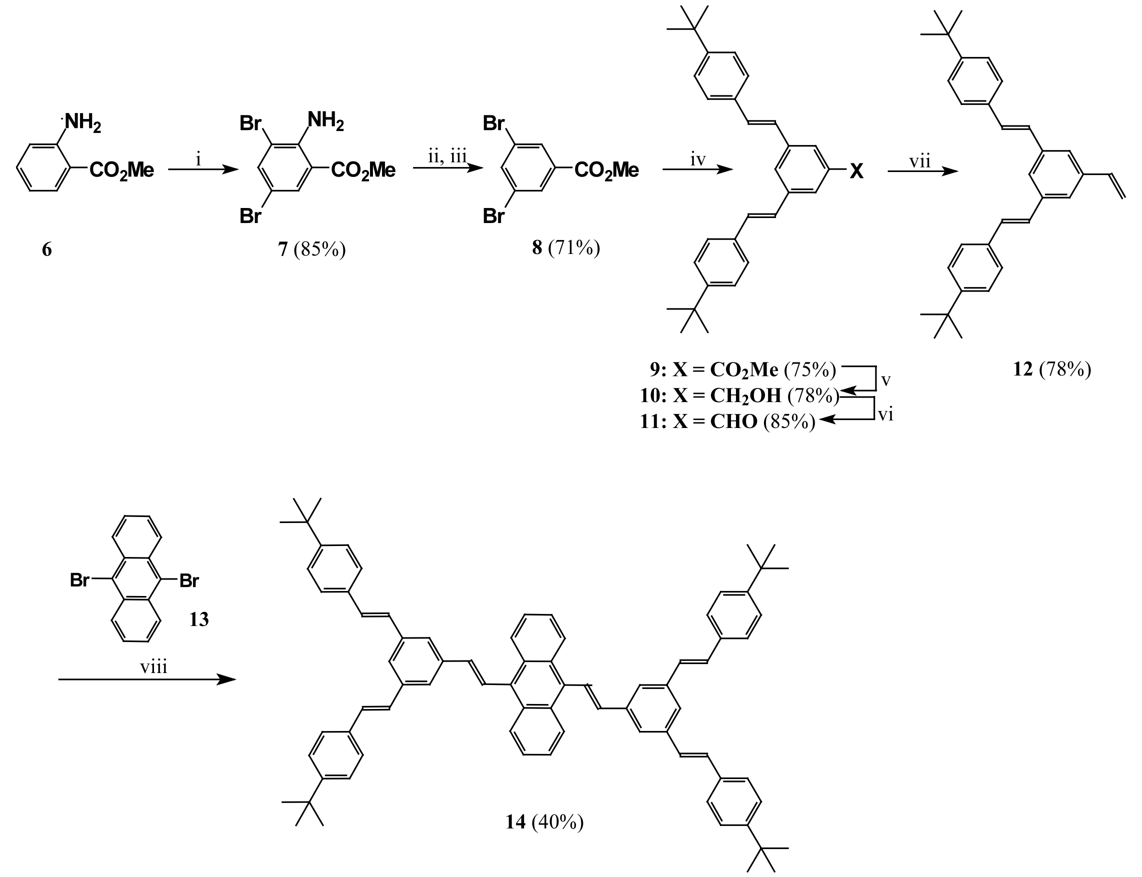
cis/*trans* mixture of products which is indeed the case for all the reported synthesis of stilbenoid dendrimers,[4,7] necessitating an extra isomerization step to produce the desired *trans*-stilbene linkages. It must be mentioned that lack of stereochemical homogeneity in the dendrimer structure can severely affect its optoelectronic properties. In view of these and given the fact that Heck arylation of styrenes provides a highly *trans*-selective synthetic route to stilbenoid compounds,[8] we decided to use the Heck arylation reaction to construct all the stilbenoid linkages (both at the core and in the periphery) of our dendrimers.

For a convergent approach, our immediate goal was to find an efficient synthetic route to a 3,5-distyryl styrene dendron. Towards this goal, 3,5-diiodoaniline **1** was converted to the corresponding triazene **2** (76%) and the latter subjected to twofold Heck reaction with styrene under Jeffery's conditions ($Pd(OAc)_2$, Bu_4NBr, KOAc, DMF, 90°C)[8c] to produce *trans*,*trans*-3,5-distyryl triazene **3** in 87% yield (Scheme 1).[9] Protection of the amino group in **1** as a triazene[9] was necessary to drive the Heck reaction to completion. The triazene moiety in **3** was then converted to the diazonium tetrafluoroborate (HBF_4, ether) and then subjected to a Heck reaction with excess vinyl trimethylsilane ($Pd(dba)_2$, CH_3CN, 0°C to rt),[10] which led to a mixture of the styrylsilane **4** and the desired distyryl styrene **5** in good yield. Protodesilylation of **4** (to **5**) could be easily carried out by treatment of the mixture with TFA, resulting in a 60% overall yield of **5** from **3**.[11] However, despite its brevity and synthetic novelty, the above sequence became prohibitively expensive on a large scale due to the high cost of vinyl trimethylsilane which was required in large excess.

In an alternative approach, we started with methyl anthranilate **6** which via dibromination (to give **7**, 85%) followed by diazotization ($NaNO_2$, conc. HCl then aq. $NaBF_4$) and protodediazoniation reactions ($FeSO_4$, DMF) gave methyl 3,5-dibromobenzoate **8** (71%) in a good overall yield on a multigram scale (Scheme 2). Twofold Heck reaction on **8** with 4-*t*-butylstyrene under Jeffery's conditions then produced **9** in 75% yield. The ester group in **9** was reduced ($LiAlH_4$, THF, rt) to give the benzyl alcohol **10** (78%) and the latter oxidized (MnO_2, CH_2Cl_2, rt) to produce the 3,5-bis-styryl benzaldehyde **11** in 85% yield.[12] A more convergent route to **11** via twofold Heck reaction on 3,5-dibromobenzaldehyde was also examined but gave inferior yields (ca. 15%) under the above conditions, presumably due to the sensitive nature of the aldehyde function in the starting material and/or the product.[4] Wittig reaction of **11** ($Ph_3P^+MeI^-$, *n*-BuLi, THF) then



Scheme 2. (i) Br_2, HOAc; (ii) $NaNO_2$, conc. HCl, 0°C then satd aq. $NaBF_4$; (iii) $FeSO_4$, DMF, rt; (iv) 4-*t*-butyl styrene, $Pd(OAc)_2$, Bu_4NBr, KOAc, DMF, 90°C; (v) $LiAlH_4$, THF, rt; (vi) MnO_2, CH_2Cl_2, rt; (vii) $Ph_3P^+MeI^-$, *n*-BuLi, THF; (viii) $Pd(OAc)_2$, Bu_4NBr, KOAc, DMF, 90°C.

produced the desired 3,5-distyryl styrene dendron **12** in 78% yield after chromatographic purification on silica gel.

The dendron **12** was used to prepare a stilbenoid dendrimer having a low band-gap anthracene core. The anthracene core was chosen for its high fluorescence yields as well as to create an energy sink in our dendrimer.[13] Thus, twofold Heck reaction of **12** with 9,10-dibromoanthracene **13**, again under Jeffery's phase transfer conditions, gave rise to the first generation dendrimer **14** in 40% yield (Scheme 2). The dendrimer was characterized by its ^{1}H and ^{13}C NMR spectra.[14] The ^{1}H NMR spectrum of **14** showed uniformly large coupling constants for the vinylic protons (J 15–16 Hz) indicating an all-*trans* configuration, thereby attesting to the superior stereoselectivity of the Heck reaction vis-à-vis Wittig methodologies in *trans*-stilbene synthesis.

The absorption spectrum of **14** (1.08×10^{-5} M in CH_2Cl_2) is shown in Fig. 1. The peaks at 228 (log ε 4.7) and 318 nm (log ε 5.0) were assigned to the peripheral stilbene units [λ_{max} for **11**: 230 and 316 nm] whereas those at 268 (log ε 4.9) and 412 nm (log ε 4.2) were due to the anthracene core [λ_{max} for the model 9,10-bis-(*p*-*t*-butylstyryl)anthracene:[15] 228, 266, 310 (shoulder) and 414 nm]. The spectrum is thus a superimposition of peaks arising from the peripheral and central chromophores. This was as expected in view of the *meta*-orientation of the peripheral and central chromophores in **9**. At higher concentrations of **9**, the shape and chromicity of the spectral bands changed, perhaps due to aggregation effects. Similar concentration dependent spectral changes have also been reported for a number of stilbenoid and anthracene derivatives and ascribed to aggregate formation.[5,7,13]

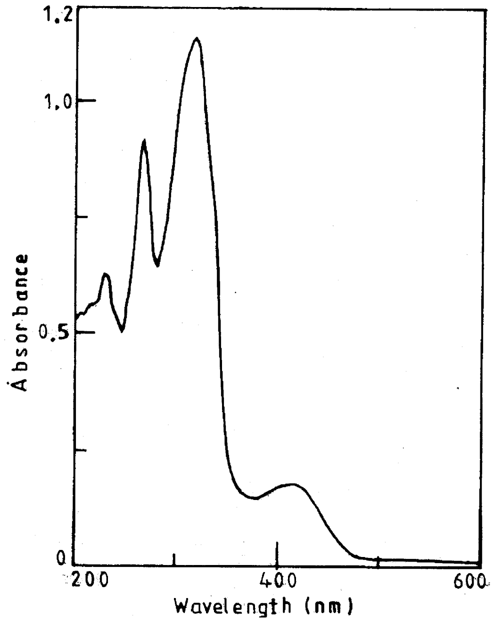


Figure 1. Absorption spectrum of **14**.

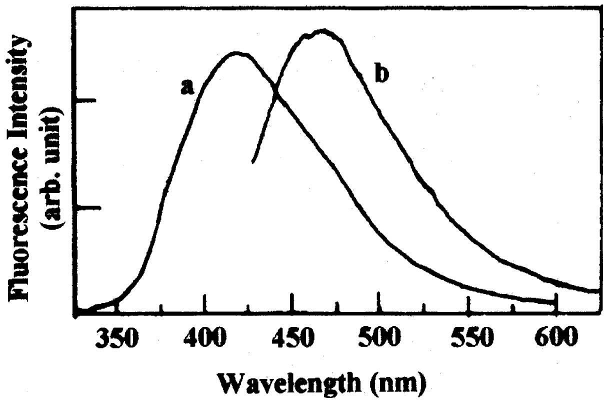


Figure 2. PL spectrum of **14**: (a) $\lambda_{exc}=318$ nm; (b) $\lambda_{exc}=414$ nm.

The photoluminescence (PL) spectrum of **14** in CH_2Cl_2 (excitation at 412 nm) showed an emission band at 470 nm due to the anthracene core (Fig. 2b). Excitation at 318 nm i.e. at the absorption maximum of the stilbene units, resulted in an emission band at 418 nm, typical of stilbenoid compounds, together with a shoulder at 470 nm (Fig. 2a). The appearance of this shoulder at 470 nm indicated that some energy transfer had taken place from the peripheral stilbene units to the anthracene core.[4,16] Both these emission spectra, however, showed considerable tail emission extending to ca. 650 nm, probably arising from the eximer states of the anthracene core. The photoluminescence excitation (PLE) spectrum of **14** obtained by monitoring the emission at 470 nm produced a large excitation band at 316 nm with a shoulder at 416 nm (Fig. 3). This also suggests that there is some optical coupling between the surface and the core chromophores of the dendrimer. Since the peripheral stilbene units in **14** are mutually *meta*-oriented and hence cross-conjugated, it is unlikely that energy transfer would take place via a through-bond mechanism (Dexter's mechanism), although in view of the short distance between the stilbene units and the

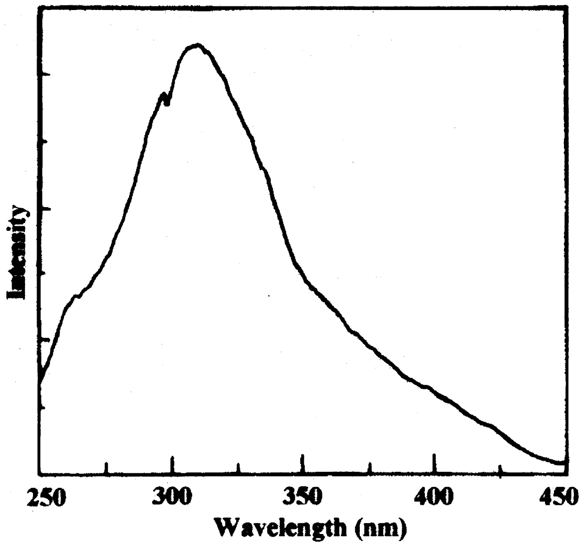
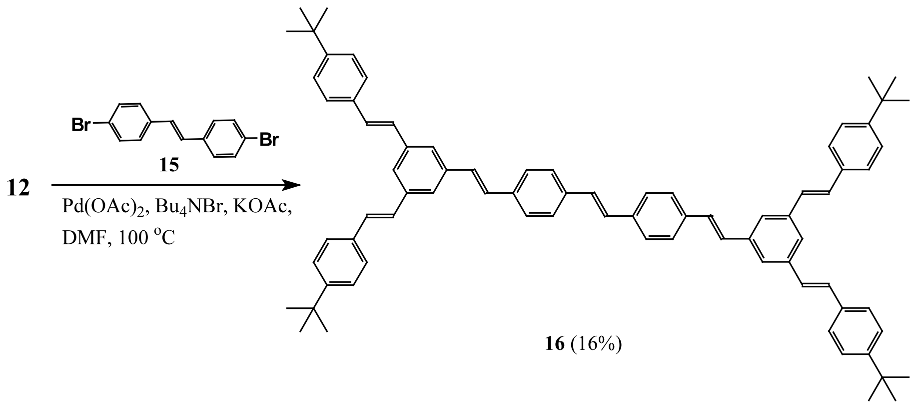


Figure 3. PLE spectrum of **14** monitored at 470 nm.



Scheme 3.

anthracene core, some contribution from orbital overlap cannot be ruled out. A Förster's type through-space (singlet→singlet) mechanism is more likely to operate in this system, especially in view of spectral overlap between the stilbene fluorescence and the core absorption bands. Although, at this moment, we do not have a satisfactory explanation for the inefficient energy transfer in **14**, the presence of only four peripheral energy collection sites and also that these are in the form of *para*-substituted stilbene units which usually have very short fluorescence lifetimes,[17] may be the reason for the low transduction of energy.[18]

As an additional example of our Heck reaction strategy, a twofold Heck reaction of **12** was also carried out with *trans*-4,4′-dibromostilbene (**15**)[19] which led to the highly fluorescent dumb-bell shaped dendrimer **16**[20] having an all-*trans* distyrylstilbene core (Scheme 3). However, the isolated yield of **16** was poor (16%), mainly due to limited solubility of the *mono*- and bis-coupled products which led to incomplete conversions together with a considerable loss of material during the isolation and purification steps. Nevertheless, **16** should serve as a good oligomeric model for end-capped PPVs in photophysical studies.[3a,21]

In conclusion, a new synthetic strategy for dendritic stilbenoid compounds has been described which uses multifold Heck reactions to construct both the peripheral and core stilbene units. Since multifold Heck reactions on poly-haloarenes is currently an established synthetic repertoire,[8] synthesis of stilbenoid dendrimers having high core-branching can be readily achieved via the present strategy. We are presently exploring these possibilities.

Acknowledgements

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12. **9**: δ_H ($CDCl_3$, 300 MHz) 1.34 (s, 18H), 3.96 (s, 3H), 7.12 (ABq, *J* 16.5 Hz, 4H), 7.44 (AA′BB′, 8H), 7.77 (br s, 1H), 8.06 (d, *J* 1.5 Hz, 2H). **11**: δ_H ($CDCl_3$, 300 MHz) 1.34 (s, 18H), 7.18 (ABq, *J* 16.2 Hz, 4H), 7.45 (AA′BB′, 8H), 7.82 (br s, 1H), 7.88 (d, *J* 1.2 Hz, 2H), 10.06 (s, 1H).
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