Pergamon

Tetrahedron Letters 43 (2002) 3517–3520

TETRAHEDRON
LETTERS

Tetraphenylmethane based tectons in dendrimer synthesis: preparation and energy transfer properties of a dendritic stilbene–anthracene dyad

Saumitra Sengupta* and Nilasish Pal

Department of Chemistry, Jadavpur University, Kolkata 700 032, India

Received 30 January 2002; revised 13 March 2002; accepted 21 March 2002

Abstract—A topologically new stilbene–anthracene dendrimer has been prepared using a highly branched tristilbenyl dendron derived from tetraphenylmethane. Steady-state photophysical studies on this dendrimer showed energy transfer from the peripheral stilbene units to the anthracene core. © 2002 Elsevier Science Ltd. All rights reserved.

The photosynthetic unit of purple bacteria is a supramolecular assembly composed of a central reaction center surrounded by chlorophyll and carotenoid chromophores.[1] The latter act as the light harvesting antennae which absorb incident photons and transfer the energy to the central reaction center with high efficiency. Dendrimers are highly branched macromolecules that have attracted considerable current attention due to their potential application in a number of functional devices.[2] They usually consist of a multiarmed core from which numerous branches radiate outwards in a three dimensional array. The degree of branching in a dendrimer increases with successive generations as a result of which higher generation dendrimers are globular in shape and possess high functional densities at their periphery. These features bear close resemblance to the composition of a natural photosynthetic unit and in recent years, have triggered widespread activity in the synthesis of photoresponsive dendrimers as artificial light harvesting modules.[3] Photoresponsive dendrimers are also gaining interest as the active material for other photonic applications viz. organic LEDs, optical power limiting devices and in non-linear optics.[4] In view of these, we have initiated a program on the synthesis and photophysical studies of dendritic bichromophoric (donor–acceptor) systems and report here the synthesis and energy transfer properties of a dendritic stilbene–anthracene dyad.

Stilbene–anthracene dyads are a promising class of energy transfer modules in which stilbene units act as the donor and anthracene acts as the acceptor chromophore. Spectral overlap between stilbene fluorescence and anthracene absorbance concurs with the Förster's type ($S_1^D \rightarrow S_1^A$) energy transfer process.[5] A few reports on cross-conjugated dendrimers comprised of *meta*-distyrylbenzene dendrons and an anthracene core have recently appeared in the literature.[6] However, effective energy transfer was only possible in a second generation dendrimer having 12 stilbene units at the periphery.[6a] We now describe a topologically new stilbene–anthracene dendrimer **5** in which a tetraphenylmethane based tristilbenyl dendron has been used as the peripheral chromophore and show that, by virtue of the highly branched nature of these dendrons resulting in a greater number of energy collection sites, energy transfer to the core is possible even in a first generation dendrimer.

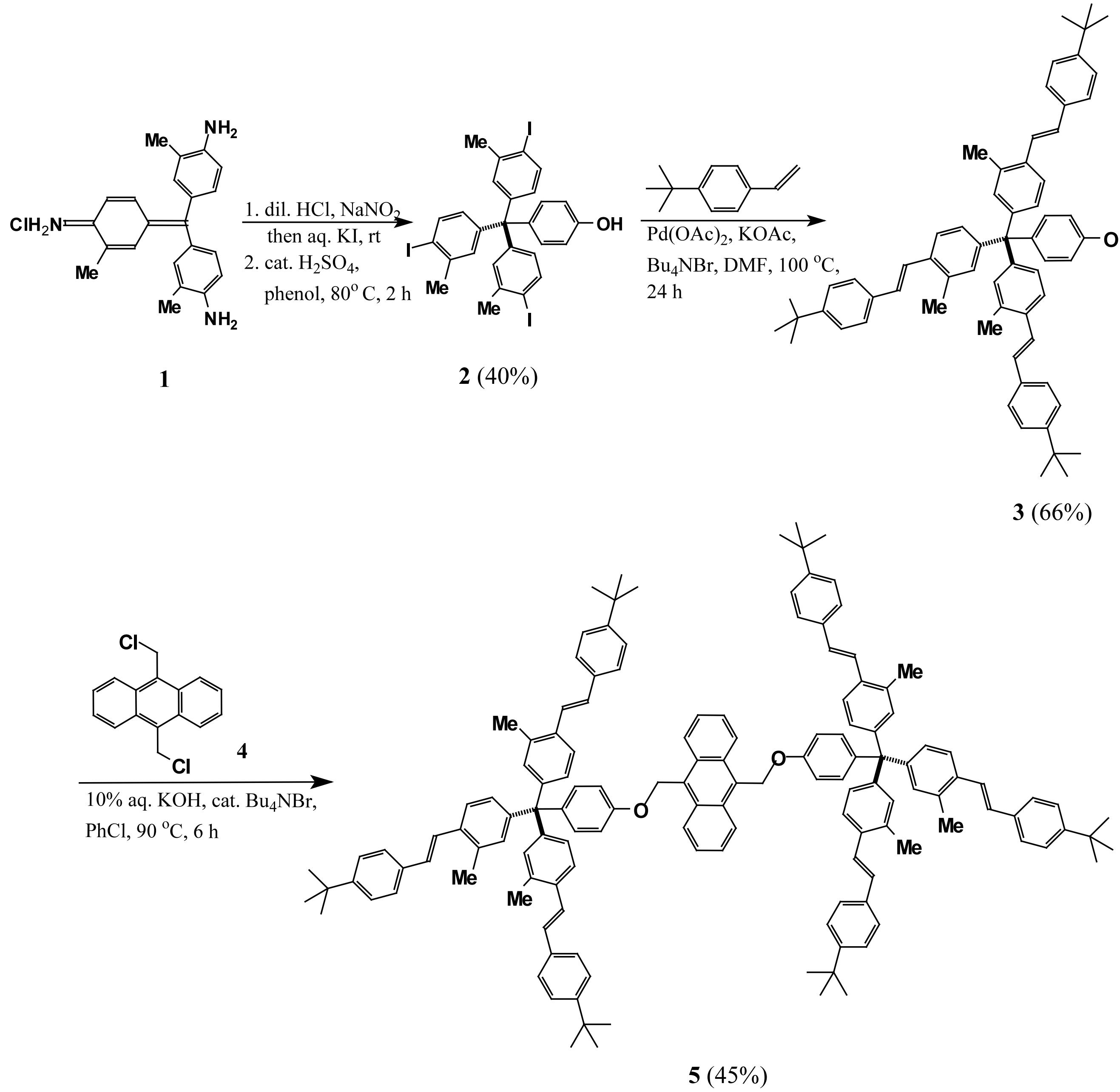
Our synthesis started with the cheap dyestuff, New Fuchsin **1** which was easily converted to the (triiodophenyl)methyl phenol **2** by a two-step procedure previously described by us (Scheme 1).[7] Threefold Heck reaction of **2** with *p*-*tert*-butylstyrene under Jeffery's conditions (cat. $Pd(OAc)_2$, Bu_4NBr, KOAc, DMF, 100°C, 24 h)[8] then produced the desired tristilbenyl dendron **3** in 66% yield.[9] The ^1H NMR spectrum of **3** showed large coupling constants ($J \sim 16$ Hz) for the olefinic protons indicating a *trans*-geometry for the stilbene moieties. The dendron **3** was then coupled to the 9,10-bis-(chloromethyl)anthracene **4** core, under phase transfer catalysis (10% aq. NaOH, cat. Bu_4NBr, PhCl, 90°C, 6 h),[10] to produce the first generation

---

Keywords: dendrimer; stilbene; anthracene; energy transfer.

* Corresponding author. Fax: 91 033 4734266; e-mail: jusaumitra@yahoo.co.uk

0040-4039/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(02)00588-9



Scheme 1.

dendrimer **5** in 45% yield after purification by preparative thin layer chromatography on silica gel.[9] The coupling reaction between **3** and **4** was best carried out under the PTC conditions described above since other methods (NaH, DMF, rt to 100°C or K_2CO_3, DMF, rt to 100°C) either led to incomplete reaction or produced a complex mixture of products. The ^{1}H NMR spectrum of **5** clearly showed the presence of the 9,10-bis-(oxymethylene)anthracene core in the dendrimer structure. Thus, a four proton singlet was found at δ 5.97 due to the core methylene groups together with a four proton multiplet at δ 8.38 due to the anthracene ring α-hydrogens. The anthracene ring β-hydrogens remained embedded along with the other aromatic protons in a broad multiplet ranging from 6.97 to 7.72 ppm.

The absorption and photoluminescence (PL) spectra of the dendron **3** is shown in Fig. 1. The absorption maximum at 318 nm is due to the stilbene units and is red-shifted from that of *trans*-stilbene[11] by ca. 20 nm indicating some electronic interaction between the three stilbene units through the central sp^3-carbon. Recently, Bazan et al. have reported similar homoconjugative effects in some tetrastilbenylmethane derivatives.[12] The 318 nm peak is also associated with a large molar extinction coefficient (ε_{max} 11.0×10^4 M^{-1} cm^{-1}) which is significantly more than three times the value of *trans*-stilbene (ε_{max} 2.7×10^4 M^{-1} cm^{-1}),[11] indicating constructive excitonic coupling between the three stilbenoid arms in **3**. Such a constructive interaction is perhaps due to the rigid tetrahedral arrangement of the chromophores in **3**.[13] The dendron **3** produced a strong

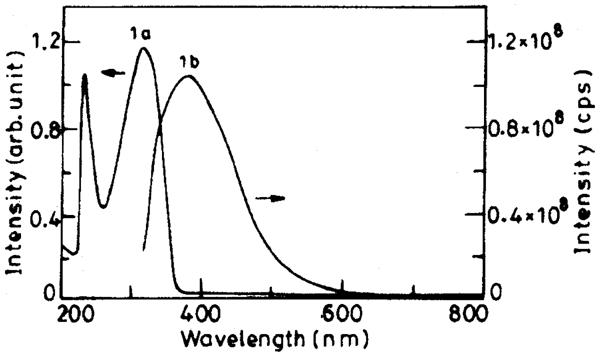
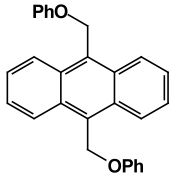


Figure 1. Absorption (1a) and PL spectra (1b) of **3** in CH_2Cl_2.

fluorescence with a maximum at 387 nm (λ_{exc} 318 nm) which is also red-shifted from the stilbene fluorescence by ca. 20 nm.

The absorption spectrum of the dendrimer **5** is shown in Fig. 2. The peaks at 234 (ε_{max} 16.6×10^4 M^{-1} cm^{-1}) and 321 nm (ε_{max} 22.8×10^4 M^{-1} cm^{-1}) are due to the stilbene dendrons (cf. Fig. 1). The molar absorbtivity of the latter peak is twice that of the 318 nm peak of **3** since two dendron moieties are present in the dendrimer. Weak absorptions were also found at 373 and 394 nm (log ε 3.6) which were assigned to the anthracene core [λ_{max} (nm) for the model 9,10-bis-(phenoxymethyl)anthracene (**6**):[14] 230 (log ε 3.86), 246 (log ε 3.87), 354 (log ε 3.44), 374 (log ε 3.62) and 394 (log ε 3.62)]. The spectrum is thus a superimposition of peaks arising out of the peripheral stilbenoid dendrons and the anthracene core. This was as expected since the two types of chromophores in **5** are connected by a nonconjugated linker.



6

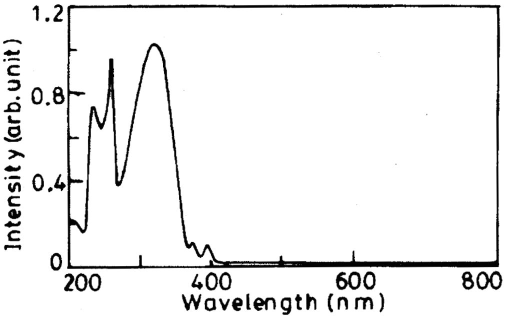


Figure 2. Absorption spectrum of **5** in CH_2Cl_2.

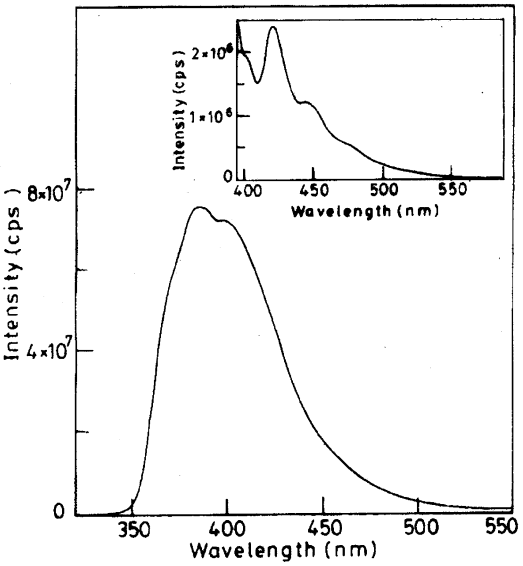


Figure 3. PL spectrum of **5** (λ_{exc} 318 nm; inset λ_{exc} 394 nm).

The PL spectrum of the dendrimer is shown in Fig. 3. Excitation at 394 nm, where absorption is only due to the anthracene core, led to a structured emission with peaks at 402, 422 and 446 nm (see inset, Fig. 3). On the other hand, excitation at 318 nm, where the stilbene moieties have strong absorption, produced peaks at 387 and 400 nm (Fig. 3). The former peak corresponds to emission from the stilbenoid moieties (cf. Fig. 1) whereas the latter is due to emission from the anthracene unit indicating energy transfer from the surface stilbene units to the dendrimer core. In a control experiment, an equimolar mixture of **3** and the model core **6** in CH_2Cl_2 was irradiated at 318 nm which produced an emission spectrum (λ_{max} 387 nm) which was fully superimposable on the PL spectrum of **3** showing that the energy transfer in **5** is purely an intramolecular process. The fluorescence intensity of **5** at 400 nm is nearly 500 times that of the emission peak produced by direct core excitation (cf. inset, Fig. 3), again pointing to light harvesting by the stilbenoid periphery and subsequent energy transfer to the anthracene core. Further proof of energy transfer in **5** comes from its photoluminescence excitation (PLE) spectrum monitored at 420 nm (Fig. 4) which showed a strong peak at 320 nm indicating effective coupling between the stilbene units and the anthracene core. Notably, the emission spectrum of **5**

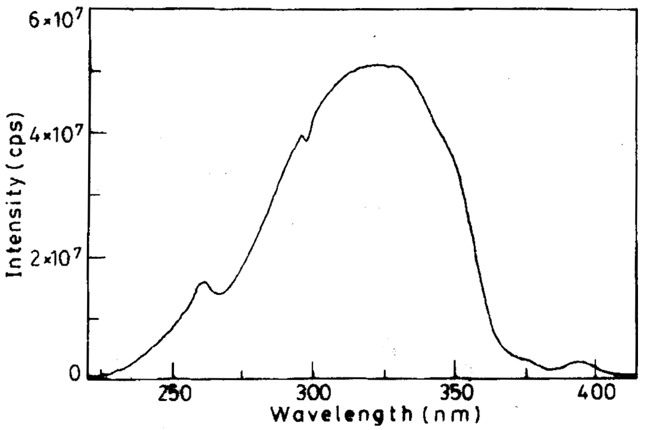


Figure 4. PLE spectrum of **5** monitored at 420 nm.

was devoid of much red-tailing, a phenomenon previously observed by us for a first generation *m*-distyrylbenzene–anthracene dendrimer,[6b] suggesting that the highly branched nature of the tetraphenylmethane based dendrons in **5** probably discourages aggregate formation. However, the energy transfer in **5** is less than quantitative, perhaps due to the presence of only six energy collection sites in the dendrimer periphery. A higher generation dendrimer with more energy collecting sites might provide improved efficiency. Moreover, in an anthracene-cored dendrimer, the acceptor wavelength (370–390 nm) where the energy is being transferred, has a low absorptivity which may also account for the inefficient energy transduction in our system. An acceptor chromophore having a strong absorbance in the long wavelength region capped by numerous stilbenoid energy collecting sites could provide a superior energy transfer module. We are currently investigating these possibilities.

Acknowledgements

Professor Nitin Chattopadhya is thanked for access to the fluorescence spectrometer and Pradipta Purkayastha for some fluorescence experiments. One of us (N.P.) thanks CSIR, New Delhi for a research fellowship.

References

1. (a) McDermott, G.; Prince, S. M.; Freer, A. A.; Hawthornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaacs, N. W. *Nature* **1995**, *374*, 517; (b) Hu, X.; Damjanovic, A.; Ritz, T.; Schulten, K. *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 5935.
2. Reviews: (a) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Macromolecules: Concepts, Syntheses, Perspectives*; VCH: Weinheim, 1996; (b) Chow, H. F.; Mong, T. K. K.; Nongrum, M. F.; Wan, C. W. *Tetrahedron* **1998**, *54*, 8543; (c) Smith, D. K.; Diederich, F. *Chem. Eur. J.* **1998**, *4*, 1353; (d) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 884; (e) Grayson, S. M.; Fréchet J. M. J. *Chem. Rev.* **2001**, *101*, 3819.
3. Reviews: (a) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701; (b) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 74.
4. See, for example: (a) Put, E. J. H.; Clays, K.; Persoons, A.; Biemans, H. A. M.; Luijkx, C. P. M.; Meijer, E. W. *Chem. Phys. Lett.* **1996**, *260*, 136; (b) Wang, P.-W.; Liu, Y.-J.; Devadoss, C.; Bharathi, P.; Moore, J. S. *Adv. Mater.* **1996**, *8*, 237; (c) Mongin, O.; Gossauer, A. *Tetrahedron* **1997**, *53*, 6835; (d) Halim, M.; Pillow, J. N. G.; Samuel, I. D. W.; Burn, P. L. *Adv. Mater.* **1999**, *11*, 371; (e) Freeman, A. W.; Fréchet, J. M. J.; Koene, S. C.; Thompson, M. E. *Polym. Prepr.* **1999**, *40*, 1246; (f) Spangler, C. W.; Elandaloussi, E. H.; Reeves, B. *Polym. Prepr.* **2000**, *41*, 789; (g) Robinson, M. R.; Wang, S.; Bazan, G. C. *Adv. Mater.* **2000**, *12*, 1701; (h) Yokoyama, S.; Nakahama, T.; Ohtono, A.; Mashiko, S. *J. Am. Chem. Soc.* **2000**, *122*, 3174; (i) Maus, M.; De, R.; Lor, M.; Weil, T.; Mitra, S.; Wiesler, U. M.; Herrmann, A.; Hofkens, J.; Vosch, T.; Müllen, K.; De Schryver, F. C. *J. Am. Chem. Soc.* **2001**, *123*, 7668; (j) Weil, T.; Wiesler, U. M.; Herrmann, A.; Bauer, R.; Hofkens, J.; De Schryver, F. C.; Müllen, K. *J. Am. Chem. Soc.* **2001**, *123*, 8101; (k) Meskers, S. C. J.; Bender, M.; Hübner, J.; Romanovskii, Y. V.; Oestereich, M.; Schenning, A. P. H. J.; Meijer, E. W.; Bässler, H. *J. Phys. Chem. A* **2001**, *105*, 10220.
5. Spieser, S. *Chem. Rev.* **1996**, *96*, 1953.
6. (a) Pillow, J. N. G.; Halim, M.; Lupton, J. M.; Burn, P. L.; Samuel, I. D. W. *Macromolecules* **1999**, *32*, 5985; (b) Sengupta, S.; Sadhukhan, S. K.; Singh, R. S.; Pal, N. *Tetrahedron Lett.* **2002**, *43*, 1117.
7. (a) Sengupta, S.; Sadhukhan, S. K. *Tetrahedron Lett.* **1999**, *40*, 9157; (b) Sengupta, S.; Sadhukhan, S. K. *Organometallics* **2001**, *20*, 1889.
8. Jeffery, T. *Tetrahedron* **1996**, *52*, 10113.
9. **3**: mp 220–224°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.33 (s, 27H), 2.34 (s, 9H), 4.67 (br s, 1H), 6.72 (d, 2H, $J=8.5$ Hz), 6.98 (d, 3H, $J=16$ Hz), 7.04–7.11 (m, 6H), 7.14 (d, 2H, $J=8.3$ Hz), 7.26 (d, 3H, $J=16$ Hz), 7.37 (d, 6H, $J=8.2$ Hz), 7.45 (d, 6H, $J=8.8$ Hz), 7.48 (d, 3H, $J=9.2$ Hz). **5**: mp>250°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.33 (s, 54H), 2.37 (s, 18H), 5.97 (s, 4H), 6.97–7.72 (m, 66H), 8.38 (m, 4H).
10. Cao, D.; Meier, H. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 186.
11. Meier, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1399.
12. (a) Oldham, W. J., Jr.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 2987; (b) Wang, S.; Oldham, W. J., Jr.; Hudack, R. A., Jr.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695.
13. The molar absorbtivity of tetraphenylmethane is 2020 compared to 212 for benzene. For constructive excitonic couplings, see: (a) Kasha, M.; Rawls, H. R.; Ashraf El-Bayoumi, M. *Pure Appl. Chem.* **1965**, *11*, 371; (b) Langhals, H.; Wagner, C.; Ismael, R. *New. J. Chem.* **2001**, *25*, 1047.
14. Prepared by phase transfer catalyzed alkylation reaction of **4** with excess phenol.