Tetrahedron Letters 53 (2012) 196-199

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

vents and emit light in the blue and violet regions.

Synthesis and photophysical properties of tetraphenylethylene-based conjugated dendrimers with triphenylamine core

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ARTICLE INFO

ABSTRACT

Article history: Received 29 September 2011 Revised 31 October 2011 Accepted 3 November 2011 Available online 9 November 2011

Keywords: Threefold Heck reaction Threefold Sonogashira reaction Tetraphenylethylene Dendrimers Fluorescence

In the past few decades, π -conjugated dendrimers have been extensively studied because of their unusual molecular structures and the potential of acting as the active chemical components, such as organic light emitting diodes (OLEDs),¹ photovoltaic cells,² optical power limiting,³ and field-effect transistors.^{4a} One of the important challenging goals of dendritic materials chemistry is to develop new families of π -conjugated dendritic molecules with novel branches and cores, to investigate their physical and chemical properties,^{4b,c} as well as to understand the structure-property relationship within such structures.⁵ Among these dendrimers, triphenylamine (TPA) derivatives have been widely investigated for almost two decades because these compounds have shown excellent thermal and electrochemical stabilities, electron donating ability, and optoelectronic properties.^{6,7} Considerable effort in synthetic chemistry, in particular by Shirota et al. has led to the development of many classes of TPA-based compounds as hole transporting⁸ or electroluminescent materials.^{6a-c}

The tetraphenylethylene (TPE) motif has attracted considerable attention by virtue of its rich electrochemical⁹ and excited state properties¹⁰ as well as its extensive usage as an electron transfer catalyst in a variety of polymerization,¹¹ aggregation induced emission properties.¹² Derivatives of TPE have been incorporated into organic polymers and oligomers with the resulting materials displaying fluorescence profiles that can be perturbed according to the overall density of TPE units within the polymer/oligomer and the environment surrounding the bulk material.¹³ Alternatively,

discrete fluorescent sensors, particularly for biomolecules and metal ions, have been prepared by the attachment of specific ligands to TPE scaffolds using flexible spacers.¹⁴ The extended π -systems based on tetraarylethylenes are also potentially important candidates for incorporation into various organic optoelectronic and optomechanical switching and storage devices,¹⁵ as well as for the preparation of two-dimensional molecular scaffolds for bichromophoric donor-acceptor dyads for energy/charge transport.¹⁶

Two new conjugated dendrimers bearing a tetraphenylethylene moiety as dendrons and triphenylamine

as a core have been synthesized through a convergent synthetic strategy using threefold Heck/threefold

Sonogashira coupling reaction. These dendrimers showed excellent solubility in common organic sol-

In this Letter, we report the design, synthesis, characterization, and photophysical properties of the two representative conjugated dendrimers having triphenylamine as the core with three tetraphenylethylene branches through a simple convergent procedure using threefold Heck/threefold Sonogashira coupling reaction.

The synthetic routes for the preparation of tetraphenylethylene peripheral units are shown in Scheme 1. Treatment of 4-bromobenzophenone with diphenylmethyllithium at a lower temperature (0 °C) followed by acid catalysed dehydration of the resulting alcohol afforded 1-(4-bromophenyl)-1,2,2-triphenylethylene $(\mathbf{1})^{9b}$ in a good yield. Although the reaction of $\mathbf{1}$ with *n*-BuLi in Et₂O or THF at temperatures (between -60 °C and room temperature), followed by addition of dimethylformamide, gave the expected aldehyde 2, but the isolated yield was not more than 50%. The yield of **2** was improved to 70% with the same halogen-metal exchange reaction conducted in benzene at 60 °C for 2 h, followed by quenching of the precipitated lithio intermediate with dimethylformamide. The Wittig reaction of aldehyde 2 with methylphosphoniumbromide salts in the presence of *n*-BuLi at $-20 \degree C$ afforded vinyl tetraphenylethylene 3 in a 70% yield. To attach alkynyl conjugation to the TPE peripheral unit, initially we have used





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^{0040-4039/\$ -} see front matter \odot 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.tetlet.2011.11.012



Scheme 1. Reagents and conditions: (a) *n*-BuLi (2 equiv), benzene, 60 °C, 2 h, then DMF, rt, 6 h; (b) Ph₃P⁺CH₃Br⁻, *n*-BuLi, THF, -20 °C to rt, 6 h; (c) CBr₄, PPh₃, CH₂Cl₂, -10 °C to rt, 4 h; (d) *n*-BuLi, THF, -78 °C, 1 h; (e) [Ph₃PCH₂Br]⁺ Br⁻, *t*-BuOK, THF, -78 °C, 1 h, then rt, 24 h.

Hagihara–Sonogashira coupling reaction. Thus, the reaction of **1** with (trimethylsilyl)acetylene/2-methyl-3-butyn-2-ol under the standard reaction-protocol afforded alkyne **5** in very low yield. In an alternative approach, the aldehyde **2** undergoes a Corey–Fuchs transformation¹⁷ with CBr₄/PPh₃ and a subsequent dehalogenation of the intermediated β , β -dibromotetraphenylethylene **4** with *n*-BuLi to give **5** in an overall 15% yield. Similarly, the desired terminal alkyne **5** was obtained in a 60% yield from a Wittig-type reaction¹⁸ of aldehyde **2** with (bromomethyl)triphenylphosphonium bromide in the presence of excess potassium *tert*-butoxide.

To achieve the synthesis of three branched dendrimers, two different strategies have been explored, involving threefold Heck or threefold Sonogashira cross-coupling reaction. The core molecule, tris-(4-iodophenyl)amine (**6**) was readily prepared in a good yield from triphenylamine employing iodine and mercury oxide following the literature procedure.¹⁹

The **TPA-TPE1** dendrimer was prepared using a threefold Heck coupling reaction of **6** with alkene **3** under Jeffery's phase transfer conditions²⁰ [10% Pd(OAc)₂, *n*-Bu₄NBr, K₂CO₃, DMF, 90 °C] in a 90% yield (Scheme 2). The **TPA-TPE2** dendrimer was synthesized utilizing threefold Sonogashira reaction of **6** with alkyne **5** in a 75% yield.

The absorption behaviour of dendrimers in dilute chloroform solution is presented in Figure 1. The UV–vis absorption spectra of **TPA-TPE1** display two absorption peaks at 275 and 412 nm, respectively and **TPA-TPE2** also displays two absorption peaks at 274 and 365 nm, respectively (Table 1). The first absorption peak in the short wavelength region at 275 nm was attributed to the



Figure 1. Absorption spectra of TPA-TPE1 (red) and TPA-TPE2 (black) in dilute chloroform solution (${\sim}10^{-6}\,M).$

tetraphenylethylene moiety. For **TPA-TPE1**, the second absorption peak at 412 nm is due to the TPA-vinylene bridged tetraphenylethylene unit. The absorption peak at 365 nm for **TPA-TPE2** was assigned to be TPA-alkynyl bridged TPE unit.

The fluorescence spectrum of **TPA-TPE1** (exited at 412 nm) showed a sharp emission band at 492 nm (Fig. 2). Particularly, the fluorescence spectrum of **TPA-TPE2** (excited at 365 nm)



Scheme 2. Reagents and conditions: (a) 5 (4 equiv), Pd(PPh_3)₂Cl₂, Cul, Et₃N, THF, rt, 24 h; (b) 3 (4 equiv), Pd(OAC)₂, PPh₃, n-Bu₄NBr, K₂CO₃, DMF, 90 °C, 16 h.

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Photophysical properties of derivatives TPA-TPE1 and TPA-TPE2

| Compd | $\lambda_{abs}(nm)$ | $\lambda_{\rm em}({\rm nm})$ | ${\Phi_{\mathrm{fl}}}^{\mathrm{a}}$ | $E_{\text{onset}}^{\text{ox}}$ (V) | HOMO ^c (eV) | LUMO ^d (eV) | $E_{\rm g}^{\rm e}$ (eV) |
|----------|---------------------|------------------------------|-------------------------------------|------------------------------------|------------------------|------------------------|--------------------------|
| TPA-TPE1 | 275, 412 | 492 | 0.98 | 0.83 | -5.49 | -2.87 | 2.62 |
| TPA-TPE2 | 274, 365 | 425 | 0.14 | 1.02 | -5.68 | -2.66 | 3.02 |

^a Fluorescence quantum yields, measured in CHCl₃ solution using 9,10-diphenylanthracene ($\Phi_{\rm fl}$ = 0.90, in CH₂Cl₂) as standard, excited at 365 nm.

^b E_{onser}^{2,} onset oxidation potential; potentials versus Ag/Ag+, working electrode glassy carbon, 0.1 M Bu₄NPF₆/CH₂Cl₂, scan rate 100 mVs⁻¹.

^c HOMO (eV) = $-e(E_{onset}^{ox} + 4.66)$.

^d LUMO (eV) = HOMO- E_g .

^e Determined from UV-vis absorption spectra.

resulted in an emission at 425 nm with a long tail emission extending to 650 nm. The emission peak of TPA-TPE1 was red shifted 67 nm than that of TPA-TPE2, which showed that there was an obvious much more π - π ^{*} delocalization with the introduction of the vinyl bridge into the dendrimer. The fluorescence quantum yields $(\Phi_{\rm fl})$ of **TPA-TPE1** and **TPA-TPE2** are measured in different solvents, by using 9,10-diphenylanthracene as a standard, presented in Table 2. Recently. Yuan et al.²¹ have synthesized similar type of derivative (**3TPETPA**), in which the tetraphenylethylene moieties are linked directly to the triphenylamine core. The $\Phi_{\rm fl}$ values of 3TPETPA, TPA-TPE1 and TPA-TPE2 in tetrahydrofuran are 0.42%, 57% and 4% respectively. TPA-TPE1 in particular shows a high fluorescence quantum yield in polar solvent such as chloroform ($\Phi_{\rm fl}$ = 98%), but a 3.7-fold lower efficiency in the non polar solvent e.g. in toluene ($\Phi_{\rm fl}$ = 26%). In case of **TPA-TPE2**, the $\Phi_{\rm fl}$ values are lower in both chloroform (14%) and toluene (3%). This may be due to multiple phenyl rings in the TPE units which undergo active intramolecular rotations in the solution,²² effectively quenching the light emission. But interestingly, for alkenyl spacer dendrimer (**TPA-TPE1**), Φ_{fl} values are high and solvent dependent, probably due to the charge separated state. The results of the quantum yield measurements have shown that alkene π -bridged dendrimers have somewhat superior photophysical properties over their alkyne π -bridged counterparts. As the quantum yield of TPA-TPE1 is considerably higher (0.98 vs 0.14), this compound could be viewed as a suitable candidate for practical applications. The band gaps (E_g) of **TPA-TPE1** and **TPA-TPE2** were 2.62 and 3.02 eV, respectively.

Cyclic voltammetry (CV) analyses were carried out to measure the HOMO values of the synthesized compounds. On the basis of the roughly evaluated onset oxidation potentials (E_{onset}^{α}), the HOMO energy levels of **TPA-TPE1** and **TPA-TPE2** are estimated as -5.49and -5.68 eV, respectively (HOMO = $-e(E_{onset}^{\alpha} + 4.66)$). The LUMO



Figure 2. Fluorescence spectra of TPA-TPE1 (red) and TPA-TPE2 (black) in dilute chloroform solution ($\sim 10^{-6}$ M).

| Table 2 | |
|---------|------|
| | |

| Fluorescence quantum yields | $(\Phi_{\rm fl},\%)$ in different solvents |
|-----------------------------|--|
|-----------------------------|--|

| Compd | Toluene | THF | CHCl ₃ |
|-----------------------|---------|------|-------------------|
| 3TPETPA ²¹ | _ | 0.42 | _ |
| TPA-TPE1 | 26 | 57 | 98 |
| TPA-TPE2 | 3 | 4 | 14 |

energy levels of **TPA-TPE1** and **TPA-TPE2** are -2.87 and -2.66 eV, respectively, calculated from the HOMO energy level and energy band gap (E_g), determined from the UV–vis absorption threshold (LUMO = HOMO– E_g). The electrochemical properties as well as the energy level parameters of the dendrimers are listed in Table 1. These results indicate that the introduction of alkenyl π -spacers between the core and peripheral unit, increases the conjugation as well as electron donating ability of the dendrimers. This results in the enhancement of the HOMO energy level^{6c} and lowers the barrier to hole injection from the most widely used anode material, indium tin oxide (ITO), which has a work function of 5.0 eV.

In conclusion, two new conjugated dendrimers bearing a tetraphenylethylene moiety as dendrons and triphenylamine as a core have been synthesized through a convergent synthetic strategy using three fold Heck/Sonogashira coupling reaction. These dendrimers showed excellent solubility in common organic solvents such as chloroform, tetrahydrofuran, and 1,1,2,2-tetrachloroethane. These conjugated dendrimers have high fluorescence quantum yields 0.98 and 0.14, their maximum emissive wavelengths in chloroform are at 492 and 425 nm, the band gaps are 2.62 and 3.02 eV, the HOMO energy level -5.49 eV for **TPA-TPE1** and -5.68 eV for **TPA-TPE2**. We are currently investigating the electroluminescent properties of these dendrimers.

Acknowledgments

Financial support from UGC [No.37-93/2009(SR)], Government of India is gratefully acknowledged. We thank IICB, Kolkata for providing us MALDI-MS facility. The CSIR, New Delhi, is also thanked for the award of Senior Research Fellowship to D.J.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.11.012.

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