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Triphenylpyridine-based star-shaped π-conjugated oligomers with triphenylamine core: synthesis and photophysical properties

Debabrata Jana, Binay K. Ghorai *

Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah 711 103, India

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ABSTRACT

Two novel star-shaped π-conjugated oligomers bearing a triphenylpyridine moiety as peripheral units and triphenylamine as a core have been synthesized via the threefold Heck/Sonogoshira coupling reaction protocol and their absorption and fluorescence properties have been examined. These oligomers showed excellent solubility in common organic solvents, emit light in blue and violet regions, and have high thermal stability.

Star-shaped triphenylamine based π-conjugated systems constitute one of the most extensively studied classes of organic compounds.[1] Research efforts in this field cover a broad spectrum of topics ranging from purely fundamental investigations to exploring the potential applications of individual compounds and their ensembles in nanoelectronics and solar energy conversion.[2] Triphenylamine cored compounds have found to be used as wide band gap energy transfer materials as well as promising applications in the area of hole-transporting.[3] Specifically, the molecular architecture and strong absorption and emission properties of this type complexes separated by different lengths of linkers have rendered these molecules useful as emitters in organic light-emitting diodes (OLEDs)[4], sensitizers in dye-sensitized solar cells (DSSCs),[5] and photovoltaic cells.[6] It has been found that the molecular and optical properties of these materials can be controlled by modifying the peripheral units.

Pyridine has been a key building block in constructing functional materials in view of its outstanding mechanical and dielectric properties.[7] As part of our continuing interest in this area, we were interested in the synthesis of 2,4,6-triphenylpyridine-based π-conjugated oligomers with triphenylamine core. In this Letter, we wish to report the synthesis, characterization, and photophysical properties of two representative new molecular structures having triphenylamine as the core molecule with three branches extending outward connected to 2,4,6-triphenylpyridine units. The triphenylamine moiety is carefully chosen and intensely employed in each structure as the core, since triphenylamine group is highly electron rich and possesses a propeller-shaped structure[8] and it can maintain uninterrupted conjugation between central nitrogen lone pair electrons and the arms[9] as well as function as a strong electron donor to the conjugation system.

The synthetic pathway leading to 2,6-diphenyl-4-(4-vinylphenyl)pyridine (**1**) and 4-(4-ethynylphenyl)-2,6-diphenylpyridine (**2**) is outlined from 4-(4-bromophenyl)-2,6-diphenylpyridine (**3**) in Scheme 1. Diphenylpyridine **3** was obtained in a good yield by the condensation of 3-(4-bromophenyl)-1-phenylpropenone and acetophenone in the presence of ammonium acetate, using the literature procedure.[7d] Treatment of **3** with *n*-BuLi in THF at −78 °C for 2 h, followed by addition of *N*-formylpiperidine, gave the expected aldehyde **4** in a 70% yield. Wittig condensation of aldehyde **4** and methylphosphoniumbromide salts in the presence of *n*-BuLi at −20 °C temperature afforded vinyl derivative **1** in a 65% yield. The Sonogashira coupling reaction of **3** with 2-methyl-3-butyn-2-ol in toluene at 90 °C for 12 h, afforded 4-[4-(2,6-diphenylpyridin-4-yl)-phenyl]-2-methylbut-3-yn-2-ol (**5**) in an 85% yield. The desired terminal alkyne **2** was obtained from **5** by removal of the acetone with powdered KOH in a 76% yield.

In order to synthesize oligomers **TPA-TPP1** and **TPA-TPP2**, two different strategies have been explored which involve threefold Heck/Sonogoshira coupling reaction (Scheme 2). The core molecule tris-(4-iodophenyl)amine (**6**) was readily prepared from triphenylamine in a good yield following the literature procedure.[10] The **TPA-TPP1** was prepared using a threefold Heck coupling of **6** with vinyl compound **1** [10% $Pd(OAc)_2$, $P(o\text{-tol})_3$, Et_3N, DMF, 90 °C] in a 75% yield. The **TPA-TPP2** was synthesized utilizing threefold Sonogoshira coupling of **6** with alkynyl derivative **2** in the presence of $CuI/Pd(PPh_3)_2Cl_2/NEt_3$ in an 86% yield.

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* Corresponding author. Tel.: +91 33 26684561; fax: +91 33 26682916.
E-mail address: bkghorai@yahoo.co.in (B.K. Ghorai).

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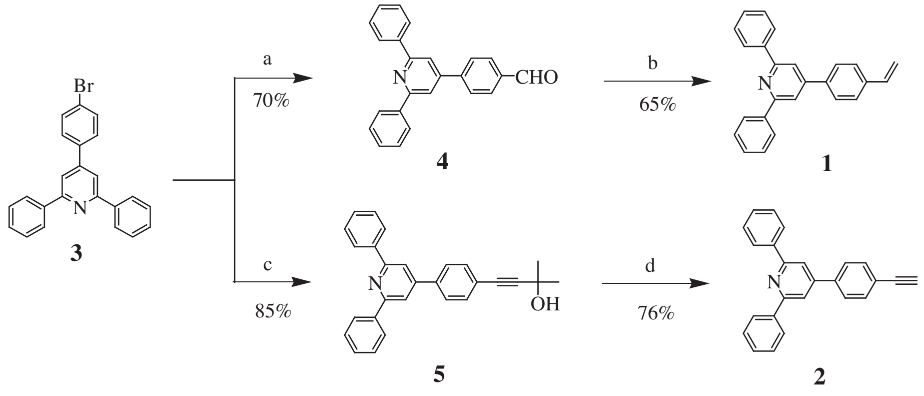
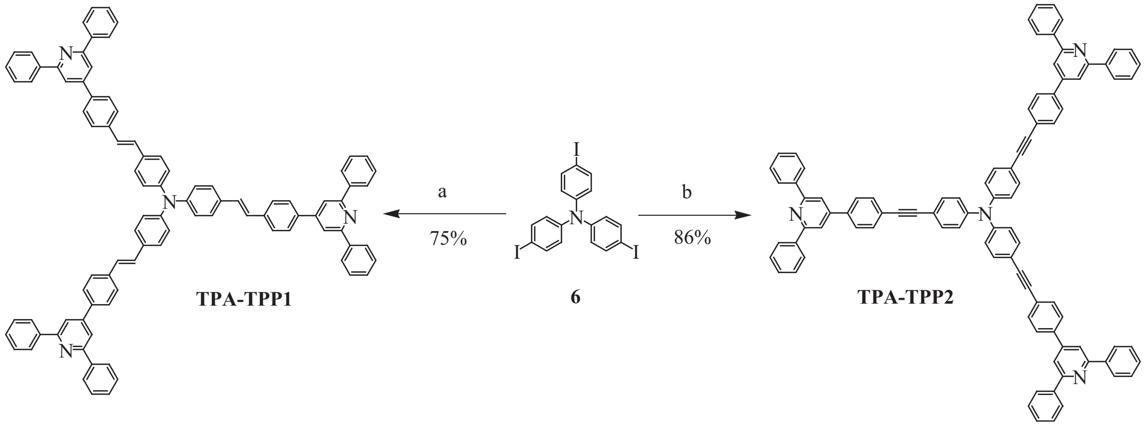


Scheme 1. Reagents and conditions: (a) *n*-BuLi (1.5 equiv), THF, −78 °C, 2 h, then *N*-formylpiperidine (2 equiv), rt, 12 h; (b) $Ph_3P^+CH_3Br^-$, *n*-BuLi, THF, −20 °C; (c) 2-Methyl-3-butyn-2-ol, $Pd(PPh_3)_2Cl_2$, Et_3N, PPh_3, CuI, toluene, 90 °C, 12 h; (d) Powdered KOH, toluene, reflux, 6 h.



Scheme 2. Reagents and conditions: (a) **1** (3.5 equiv), $Pd(OAc)_2$, P(*o*-tol)$_3$, Et_3N, DMF, 90 °C, 16 h; (b) **2** (3.5 equiv), $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, Et_3N, THF, rt, 24 h.

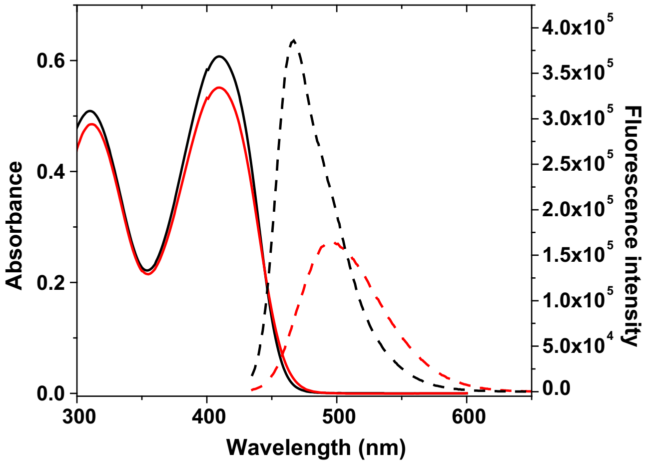


Figure 1. Absorption spectra (solid lines) and fluorescence emission spectra (dashed lines) performed at $\lambda_{ex} = \lambda_{max}$ (abs) of **TPA-TPP1** in toluene (black) and in tetrahydrofuran (red) in dilute solution (~10^{-6} M) at room temperature.

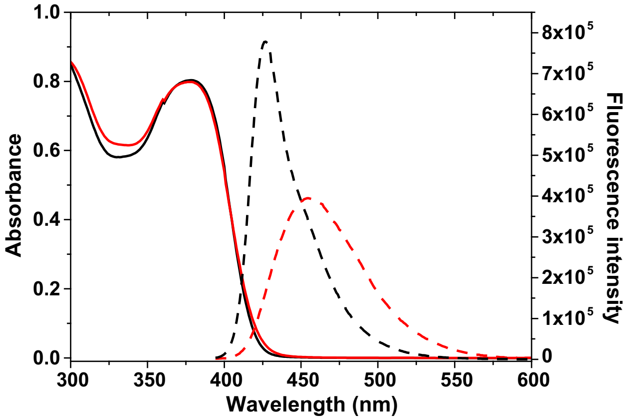


Figure 2. Absorption spectra (solid lines) and fluorescence emission spectra (dashed lines) performed at $\lambda_{ex} = \lambda_{max}$ (abs) of **TPA-TPP2** in toluene (black) and in tetrahydrofuran (red) in dilute solution (~10^{-6} M) at room temperature.

The UV–vis absorption and fluorescence properties of two synthesized compounds **TPA-TPP1** and **TPA-TPP2** in toluene and tetrahydrofuran are shown in Figures. 1 and 2. Their comprehensive photophysical characteristics are presented in Table 1. The absorption spectra of the compounds **TPA-TPP1**/**TPA-TPP2** are almost identical in toluene and tetrahydrofuran and exhibit maximum absorption wavelengths at 410 nm and 378 nm, respectively. The maximum absorption peak of the alkenyl bridged oligomer **TPA-TPP1** was red shifted by 32 nm with respect to the alkyne bridged oligomer **TPA-TPP2**. The π–π* energy gap (Δ*E*) of these oligomers was calculated from the UV–vis absorption maximum. It was obvious that the Δ*E* value of **TPA-TPP1** could be reduced by the introduction of alkenyl spacers at the backbone.

Table 1
Photophysical properties of derivatives **TPA-TPP1** and **TPA-TPP2**.

Compound	UV–vis (λ_{abs}, nm)		PL (λ_{max}, nm, Φ_{fl}[a])		Stokes shifts[b] (10^3 cm^{-1})		ΔE[c] (eV)	T_d (°C)
	Tol	THF	Tol	THF	Tol	THF		
TPA-TPP1	410	411	466 (0.14)	496 (0.08)	0.29	0.42	2.73	212
TPA-TPP2	378	379	426 (0.16)	455 (0.12)	0.30	0.44	2.98	270

[a] Fluorescence quantum yields, measured in solution using 9,10-diphenylanthracene (Φ_{fl} = 0.90, in CH_2Cl_2) as standard, excited at 365 nm.
[b] Stokes shift = $(1/\lambda_{abs} - 1/\lambda_{em})$.
[c] Determined from UV–vis absorption maximum.

The photoluminescence (PL) spectra of **TPA-TPP1** (exited at 410 nm, Fig. 1) and **TPA-TPP2** (exited at 378 nm, Fig. 2) in toluene showed maximum emission bands at 466 and 426 nm, respectively. In comparison to alkyne spacer **TPA-TPP2**, vinyl spacer **TPA-TPP1** showed a red shift of emission band. This is due to the much more delocalisation through vinyl π-spacers when compared to the alkyne π-spacers. A significant positive solvatochromic shift was also observed in the emission. The maximum emission peak of **TPA-TPP1** was red shifted ca. 30 nm in the tetrahydrofuran with respect to the toluene and in the case of **TPA-TPP2**, it was 29 nm. These results indicated that there was some charge-transfer character which is probably due to the electron-withdrawing effect of the pyridine moiety and it is spacer independent. We also noted an increase of the Stokes shifts with the solvent polarity. This distinct positive solvatochromic behavior suggests that significant charge redistribution takes place upon excitation leading to highly polar excited state. The fluorescence quantum yields of **TPA-TPP1** and **TPA-TPP2** in toluene solution are measured to be 0.14 and 0.16 (0.08 and 0.12 in tetrahydrofuran), respectively, by using diphenylanthracene as a standard. The thermal stability of these oligomers was checked by the TGA method, which showed that both final products exhibit good thermal stabilities. Their decomposition (5% weight loss) temperatures are found to be 212 °C for **TPA-TPP1** and 270 °C for **TPA-TPP2**.

To assess the HOMO values of the synthesized compounds cyclic voltammetry (CV) measurements were carried out. The E_{onset}^{ox} values (1.12 V and 1.36 V for **TPA-TPP1** and **TPA-TPP2**) were determined electrochemically at a platinum electrode as 0.2 mM solutions in anhydrous dichloromethane containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAHP) as the supporting electrolyte at a scan rate 100 mV/s and at 25 °C. On the basis of the roughly evaluated onset oxidation potentials (E_{onset}^{ox}), the HOMO energy levels of **TPA-TPP1** and **TPA-TPP2** are estimated as -5.78 and -6.02 eV, respectively $[\text{HOMO} = -e(E_{onset}^{ox} + 4.66)]$. The LUMO energy levels of **TPA-TPP1** and **TPA-TPP2** are -3.05 and -3.04 eV respectively, calculated from the HOMO energy level and ΔE (LUMO = HOMO + ΔE). These results indicate that the introduction of alkenyl π-spacers between the core and peripheral unit increases the electron donating ability of the compound and resulted in the enhancement of the HOMO energy level. **TPA-TPP2** can be viewed as a suitable candidate for hole-blocking material due to the lower HOMO energy level.

In summary, we have designed and efficiently prepared two new star-shaped π-conjugated oligomers bearing triphenylpyridine moiety as peripheral units and triphenylamine as a core through a convergent synthetic strategy by the way of the threefold Heck/Sonogoshira coupling reaction. These compounds have excellent solubility in common organic solvents such as chloroform, tetrahydrofuran, toluene, and methanol. Their fluorescence quantum yields 0.14 and 0.16, emit light in the blue and violet regions, the HOMO–LUMO energy gaps are 2.73 and 2.98 eV, and the decomposition (5% weight loss) temperatures are 212 and 270 °C, respectively.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2012.01.116.

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