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Synthesis and properties of novel bis(triarylamines) based on a 3,3′-diphenyl-2,2′-bithiophene core

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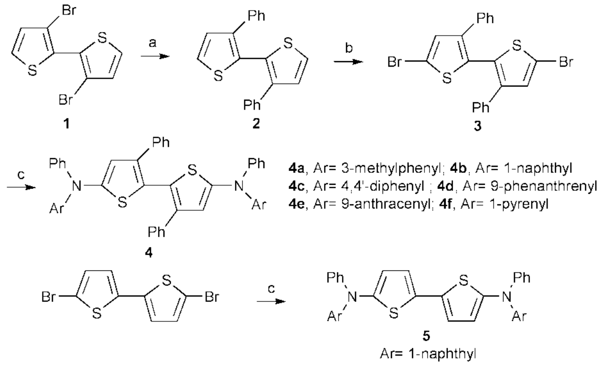
An efficient synthesis of 3,3′-diphenyl-2,2′-bithiophene based bis(triarylamines) and their physical properties are reported.

Amorphous triarylamines with high glass transition temperatures (T_g) are widely used as hole-transporting materials in organic light-emitting devices (OLED).[1] Thiophene and oligothiophene-linked triarylamines and bis(triarylamines), with phenyl rings separating the thiophene system from the terminal diarylamino groups were first introduced by Shirota *et al.*[2] These amorphous materials form thin films with high morphological stability and also show interesting hole-transporting properties, resulting in their successful use as colour-tunable emitting materials for OLED devices. Triarylamines with diarylamino group(s) directly attached to thiophene are one of the least exploited class of hole-transporting materials.[3,4] Recently, Watanabe and co-workers[5] have accomplished a systematical study on Pd-catalysed amination for the synthesis of 2-diarylaminothiophenes and 2,5-bis(diarylamino)thiophenes. In addition to this, a new synthetic strategy involving transition-metal free cyclization followed by thermal decarboxylation has also been introduced for the synthesis of triarylamines bearing a thiophene moiety.[6] However, the physical properties of thiophene based triarylamines are still limited.[5,6] In this communication, we report the synthesis and physical properties of a new class of bis(triarylamines) based on 3,3′-diphenyl-2,2′-bithiophene as a central linkage. It is well documented that the physical properties of oligothiophenes and polythiophenes strongly depend on the nature of the substituents. However, the similar oxidation potential and absorption λ_{max} of bithiophene and 3,3′-diphenyl-2,2′-bithiophene have been attributed to counterbalancing the resonance effect of phenyl substituents by the steric effect.[7] Interestingly, polythiophenes with phenyl substituent(s) at its 3- and 4-position exhibit higher thermal stability and lower oxidation potentials.[8] Accordingly, the resulting new class of bis(triarylamines) based on 3,3′-diphenyl-2,2′-bithiophene could enhance the thermal and morphological stability, which are crucial for their application in optoelectronic devices.

Cu-promoted Ullman reaction for the synthesis of 3,3′-diphenyl-2,2′-bithiophene was first reported by Johnson in 1976.[9] Further synthetic efforts based on the Ni-catalysed Kumada coupling reaction of 2-halo-3-phenylthiophene with 2-magnesium-3-phenylthiophene gave 3,3′-diphenyl-2,2′-bithiophene in poor yields.[7,8] We report herein a more efficient synthetic pathway (Scheme 1). In the presence of a catalytic amount of $Pd(PPh_3)_4$, 3,3′-dibromo-2,2′-bithiophene **1**[10] was treated with phenylboronic acid in DME to afford 3,3′-diphenyl-2,2′-bithiophene (**2**) in 86% yield. Regioselective bromination[11] of **2** was accomplished by treating **2** with bromine in AcOH–$CHCl_3$ (1:2) solution, which afforded 5,5′-dibromo-3,3′-diphenyl-2,2′-bithiophene **3** in 95% yield. Six different diarylamines were screened to react with **3** respectively in the presence of a catalytic amount of $Pd(OAc)_2$ and PBu^t_3 in toluene[12] at reflux temperature, resulting in compounds **4a**–**4f** as bright yellow solids in moderate yields (Table 1). For a comparative study of the influences of phenyl



Scheme 1 Reagents and conditions: a, $PhB(OH)_2$, $Pd(PPh_3)_4$, Na_2CO_3, DME, reflux 2 d, 86%; b, Br_2, AcOH–$CHCl_3$ (1:2), 0 °C to rt 98%; c, diarylamine, $Pd(OAc)_2$, PBu^t_3, $NaOBu^t$, toluene, reflux overnight.

Table 1 Chemical yields and physical properties of 5,5′-bis(diarylamino)-3,3′-diphenyl-2,2′-bithiophenes **4** and model compound **5**

Compound	Yield (%)[a]	λ_{max}/nm, log ε[b]	λ_{em}/nm[c]	E_{pa}, E_{pc} /mV[d]	T_g/°C[e]
4a	62	263 (4.59), 367 (4.12)	535	550, 430	55
4b	56	262 (4.69), 365 (4.26)	535	595, 440	85
4c	60	260 (4.96), 317 (4.87)	538	570, 465	83
4d	52	254 (4.90), 363 (4.09)	539	605, 470	114
4e	51	256 (4.99), 376 (4.54)	494	(545, 455), (650, 570)	119
4f	53	265 (4.94), 381 (4.48)	458, 503	600, 500	124
5	62	273 (4.38), 392 (4.42)	480	(460, 385), (695, 610)	67

[a] Isolated yield by column chromatography on SiO_2 (hexane–CH_2Cl_2 = 4:1) with satisfactory spectral analyses (^1H, ^{13}C, mass, HRMS, and IR). [b] Recorded in EtOAc; units of ε mol^{-1} dm^3 cm^{-1}. [c] Recorded in EtOAc and excited at λ_{max}. [d] Performed in 0.1 M solution of n-Bu_4NPF_6 in CH_2Cl_2, carbon electrode was used as the working electrode, scan rate 100 mV s^{-1}, Ag/AgCl as reference electrode. [e] Analyzed by differential scanning calorimetry (DSC), T_g was recorded from heating (10 °C min^{-1}) a liquid nitrogen quenched melt-sample.

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† Electronic supplementary information (ESI) available: experimental details and NMR spectra. See http://www.rsc.org/suppdata/cc/b1/b103194p/

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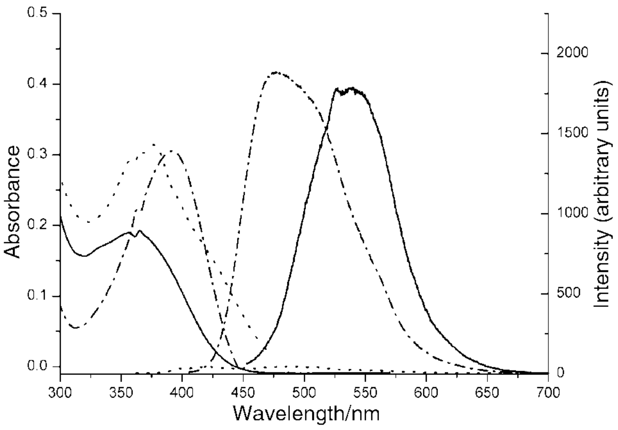

Fig. 1 Absorption and photoluminescence spectra of **4b** (solid), **4e** (dot), and **5** (dash-dot) in EtOAc (1.0×10^{-5} M)

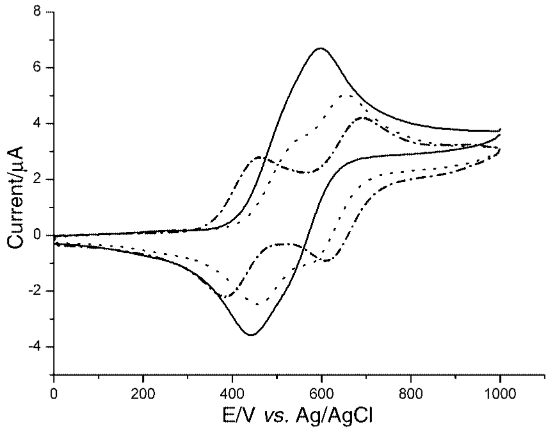

Fig. 2 Cyclic voltammogram of **4b** (solid), **4e** (dot), and **5** (dash-dot) in CH_2Cl_2.

substituents on the physical properties, model compound **5** was also synthesized by the Pd-catalysed amination of 5,5′-dibromo-2,2′-bithiophene.

The absorption spectra of **4a**–**4f** in ethyl acetate showed similar behaviour, displaying two absorption maxima (Table 1). The second bands of **4e** and **4f** were slightly red-shifted compared to that of **4a**–**4d**. Compound **4a**–**4d** were highly fluorescent. These results indicate that the absorption $\lambda_{\max}$ is relatively insensitive to the nature of the diarylamino substitutents. However, the photoluminescence efficiency and emission maxima are strongly dependent on the structural feature of the terminal diarylamino groups. Thus, bis(triarylamines) (**4a**–**4d**) with less conjugated diarylamino substituents showed more efficient photoluminescence than when compared with those bearing more conjugated terminal diarylamino groups (**4e**–**4f**). The significant Stokes shift (*ca.* 170 nm for **4a**–**4d**) reveals that the 3,3′-diphenyl-2,2′-bithiophene linkage may be highly twisted in the ground state. The emission maxima with relatively long wavelength could be attributed to the relaxation from an excited state with a more coplanar conformation. The influence of phenyl substituents of the bithiophene linkage on the photophysical properties are demonstrated by a comparison of the UV-Vis and photoluminescent spectra of **4b**, **4e**, and **5** (Fig. 1). Bis(triarylamine) **5** exhibited a sharper, red-shifted absorption and a blue-shifted emission compared to that of **4b**. The longer emission wavelength of **4b** further confirms a more conjugated excited state.

Compounds **4a**–**4f** exhibited only quasi-reversible anodic oxidation (Table 1). The onset of oxidation and E_{pa} (V *vs.* Ag/AgCl) varied with the nature of the terminal diarylamino groups. Differing from the conventional bis(triarylamines),[13] only one redox couple (E_{pa} 550 mV, E_{pc} 430 mV *vs.* Ag/AgCl) was detected for **4a** and **4c**. Coulometry in a thin layer cell showed the redox process of **4a** to be a two-electron oxidation. The lack of co-planarity of the central 3,3′-diphenyl-2,2′-bithiophene linkage prevents the extension of π-conjugation along the molecular axis. The rate of second oxidation in **4a** may be faster than the conformational change reaching a more coplanar conformation. Therefore, the first radical cation can not efficiently delocalise in the whole molecule, the two triarylamine systems behave independently but are oxidized simultaneously without any communication. Fig. 2 shows a comparison of the cyclic voltammogram of **4b, 4e**, and **5**. Two partially resolved redox processes (E_{pa} 545 mV, E_{pc} 455 mV and E_{pa} 650 mV, E_{pc} 570 mV *vs.* Ag/AgCl) of **4e** were detected, which were assigned to be a two-step one-electron redox couple corresponding to removal of an electron from each triarylamine system. The redox potential difference (110 mV) of **4e** indicates that the second oxidation could occur *via* a radical cation with more coplanar conformation. **4b**, **4d**, and **4f** showed similar redox behaviour but were less resolved when compared with that of **4e**. The model compound **5** exhibited two well-resolved redox couples (E_{pa} 460 mV, E_{pc} 385 mV and E_{pa} 695 mV, E_{pc} 610 mV *vs.* Ag/AgCl). The lower oxidation onset and larger potential difference (230 mV) reveal that the the central bithiophene linkage is in a coplanar conformation.

All the compounds in this study exhibited an amorphous nature evidenced by the presence of the glass transition temperature (Table 1). The asymmetric diarylamino substituent and the diphenyl substituted central bithiophene linkage significantly contribute to the high T_{g}s. Compounds (**4d**, **4e**, **4f**) with higher molecular weight aryl groups showed higher T_{g}s compared to that of **4a**, **4b** and **4c** bearing a lower molecular weight aryl group in the terminal diarylamino substituents.

In summary, we have successfully established an efficient method for the synthesis of a new class of bis(triarylamines) bearing 3,3′-diphenyl-2,2′-bithiophene as a central linkage. The introduction of phenyl substituents on the central linkage apart from improving the morphological stability, twists the conformation of the central bithiophene linkage in the ground state, which results in interesting photophysical and electrochemical properties. Further studies on the modification of the central bithiophene linkage by introducing bulkier aryl groups and their applications in OLED are under way and will be reported in due course.

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