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Synthesis of novel 1,3-bis(5-diarylaminothiophen-2-yl)isothianaphthenes

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We report the synthesis, electrochemical and optical properties of novel 1,3-bis(5-diarylaminothiophen-2-yl)isothianaphthenes obtained by palladium-catalysed amination of 1,3-bis(5-bromothiophen-2-yl)isothianaphthene with diarylamines.

Low molecular weight hole injecting and transporting compounds belonging to the classes of triarylamines and thiophenes are widely studied for potential applications in solar cells, organic light emitting diodes, field effect transistors *etc.*[1–4] In the case of triarylamines the HOMO energy value can be appreciably manipulated in the range of −5 eV to −5.5 eV by chemical modification to suit the hole injection from electrodes.[5] In the case of thiophenes the band gap energy and wavelength of maximum absorption can be varied over a wide range in the visible region up to 600 nm, mainly by variation of the LUMO energy value.[6] Moreover, the modification of thiophene ring into benzo[*c*]thiophene results in a new class of compounds generally called isothianaphthenes which are well known for their low band gap energy values of about 1 eV.[7] Isothianaphthene monomers are relatively unstable and poly(isothianaphthene) has a very low solubility. Polymers containing an isothianaphthene moiety with solubilizing substituents have been reported for application in solar cells.[8,9]

Oligomeric compounds can meet the criteria for materials used in the preparation of advanced electronic devices. Low molecular weight compounds not only allow the preparation of materials with high purity, but also allow easy control of the electronic properties. In this respect, a combination of an isothianaphthene moiety and a triarylamine unit in a low molecular weight compound is a challenging task in the development of hole transporting light harvesting dyes. Some oligomeric thiophenes containing diarylamine substituents have recently been reported as potential hole transport materials.[2,10,11] But these compounds show absorption only in the range of about 400 nm making them unsuitable as dyes for application in solar cells. An alternative approach is to synthesize well-defined oligothiophenes carrying isothianaphthene units.[12]

In this work, we report for the first time the successful incorporation of an isothianaphthene moiety into oligothiophenes containing triarylamine units by Pd-catalysed amination of 1,3-bis(5-bromothiophen-2-yl)isothianaphthene. This allows us to combine the efficient hole-transport property of the triarylamines and the low band gap nature of the isothianaphthene unit into one molecule. The optical and electrochemical properties of these novel compounds are studied and compared with 5,5′-bis(phenylnaphthylamino)-2,2′-bithiophene, a compound which does not contain an isothianaphthene moiety.[11] The synthetic strategy is selected in such a way as to obtain well defined low molecular weight compounds with high solubility and stability.

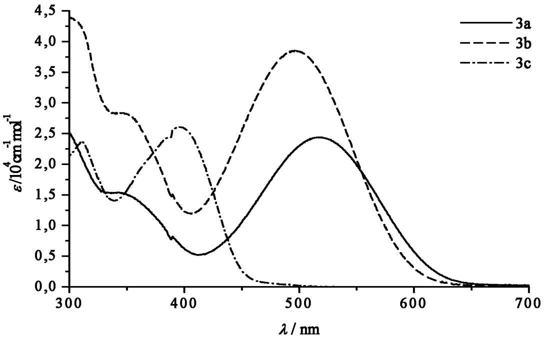
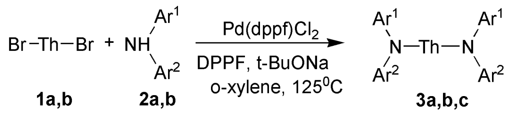


Fig. 1

The scheme of synthesis and the structures of diarylamines and 1,3-bis(5-bromothiophen-2-yl)benzo[c]thiophene are given in Table 1. The 1,3-bis(5-diarylaminothiophen-2-yl)isothianaphthenes (**3a**† and **3b**) were obtained by the reaction of 1,3-bis(5-bromothiophen-2-yl)benzo[*c*]thiophene (**1a**) with the corresponding diarylamines (**2a** and **2b**) in the presence of $Pd(dppf)Cl_2$ in combination with DPPF and *t*-BuONa as base (Table 1). The 5,5′-bis(phenylnaphthylamino)-2,2′-bithiophene (**3c**)[11] was obtained by a similar method using 5,5′-dibromobithiophene. Palladium-catalysed amination of aryl halides developed and studied in detail by Hartwig *et al.* and Buchwald *et al.* for the preparation of the secondary amines as well as triarylamines was used here to obtain the target molecules in good yields.[13] The starting dibromo compound, 1,3-bis(5-bromothiophen-2-yl)benzo[*c*]thiophene (**1a**) was prepared by a standard bromination with NBS in $CHCl_3$ and CH_3COOH (1:1) solution at −40 °C of 1,3-bis(thiophen-2-yl)benzo[*c*]thiophene, which was prepared by a similar method as reported by Kiebooms *et al.* by a three-step synthesis.[14] The first step is the preparation of 1,2-di[*S*-(2-pyridinyl)]benzenedithioate from phthaloyl dichloride and

Table 1 Synthesis of 1,3-bis(5-diarylaminothiophen-2-yl)isothianaphthenes



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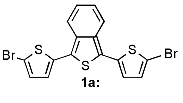
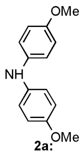
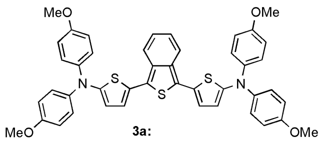
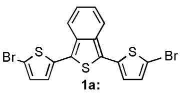
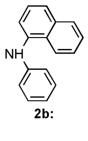
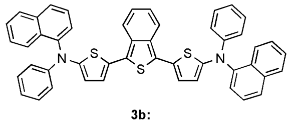
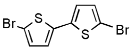
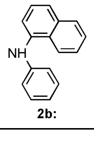
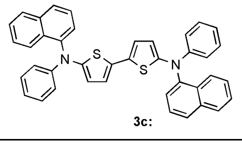
 1a:	 2a:	 3a:
 1a:	 2b:	 3b:
 1b:	 2b:	 3c:

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2-mercaptopyridine in a solution of TEA in THF at 0 °C, the second step being the conversion of 1,2-di[*S*-(2-pyridinyl)]benzenedithioate into 1,2-dithienoylbenzene by reaction with 2-magnesiumbromothiophene in THF at 0 °C and the final step is a ring closure reaction with Lawesson reagent of 1,2-dithienoylbenzene in CH_2Cl_2 at 60 °C.

The absorption, fluorescence (measured in cyclohexane) and electrochemical properties of all the compounds are given in Table 2. The optical measurements of **3a** were carried out in dioxane due to its poor solubility in cyclohexane. The molecules **3a** and **3b** with an isothianaphthene group in the middle show extended absorption in the visible range with a red shift of 100 nm compared to **3c** without an isothianaphthene group (Fig. 1). In order to use these model compounds as strongly absorbing dyes, for example, in solar cells, the molar extinction coefficient should be high enough. Compound **3b** shows a highest value of ε equal to 39 000 cm^{-1} mol^{-1} dm^3, which is in the same range as many of the light harvesting dyes like perylene bisimides and Ru-bipyridyl dyes presently used in solar cells.

Table 2 Electrochemical and optical properties of novel bis(diarylamino-)thiophenes

Compound	λ^{abs}_{max}/nm	ε/10^4 cm^{-1} mol^{-1}	λ^{em}_{max}/nm	E_{ox1}/V	HOMO/eV
3a	518	2.4	640	−0.21	−4.59
3b	497	3.9	610	−0.08	−4.72
3c	397	2.6	464	0.04	−4.84

HOMO energy values were obtained from first oxidation potential values (E_{ox1}) measured in THF against ferrocene and calculated by taking the HOMO energy value of ferrocene to be −4.8 eV with respect to zero energy level.

As expected, compounds **3a** and **3b** exhibit intense fluorescence emission in the red wavelength region (640 and 610 nm) compared to **3c**, which show emission at 464 nm. The electrochemical stability and reversibility of redox processes were studied using cyclic voltammetry in THF containing 0.1 M tetrabutylammonium hexafluorophosphate by a three-electrode assembly system. Each measurement was calibrated with ferrocene as the internal standard. All the three compounds exhibit reversible two-stage oxidation processes. The first oxidation potential of **3c** is in agreement with the published value of 0.43 V *vs.* Ag/AgCl[11] taking into consideration the oxidation potential of ferrocene as 0.4 V *vs.* Ag/AgCl. Due to the presence of the isothianaphthene group, the compounds **3a** and **3b** have lower oxidation potentials making them suitable candidates for use in organic solar cells. The first oxidation potential E_{ox1} of **3a** equal to −0.21 V *vs.* ferrocene which corresponds to a HOMO value of −4.6 eV (with respect to zero vacuum energy level) is one of the lowest ever reported for air-stable hole conductors.

In summary, we were able to incorporate an isothianaphthene group into bis(arylamino)oligothiophenes using palladium-catalysed coupling reactions resulting in novel hole transport dyes with high molar extinction coefficient. In comparison to the bis(arylamino)oligothiophenes, the compounds reported here have a characteristic absorption in the long wavelength region of the visible spectra as well as low oxidation potentials. The fluorescence quenching studies of these compounds in combination with an electron acceptor like TiO_2 as well as the suitability of these compounds for application in solar cells are the current topic of research and will be reported later.

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Notes and references

† *Synthesis:* 1,3-bis(5-bromothiophen-2-yl)benzo[*c*]thiophene (**1a**) was synthesized according to a similar procedure as reported by U. Mitschke and P. Baeuerle[15], but by using a mixture of chloroform and acetic acid as solvent. 5,5′-Dibrom-2,2′-bithienyl (**1b**) and the diarylamines (**2a**, **2b**) were purchased from Aldrich and were purified by sublimation. The solvents and other reagents were dried *in vacuo*.

The syntheses of **3a–c** were performed in *o*-xylene with 3 mol% $Pd(dppf)Cl_2$, 9 mol% DPPF and 2.2 equiv. of Bu^tONa and 2.3 equiv. of diarylamine for 1 equiv. of the dibromo compound at 125 °C for 18 h under Ar. After completion of the reaction, the mixture was filtered through a Si-gel column to remove the salts. *o*-Xylene was removed *in vacuo* and final purification by column chromatography (Si-gel, Et_2O–n-Hex 1 : 1) yielded pure products. **3a** (1.53g, 58%) deep red–violet solid. mp 229.0 °C; ^1H NMR (C_6D_6) 3.28 (s, 12H), 6.48 (d, 2H), 6.73 (m, 8H), 6.78 (m, 2H), 6.98 (d, 2H), 7.19 (m, 8H), 7.94 (m, 2H); IR (KBr, *ν*, cm^{-1}) 2929, 1503, 1463, 1242, 1180, 1037, 828; *m*/*z* 755 (M^+).

3b Purification by column chromatography (Si-gel, Tol–n-Hex 1 : 1), (0.12 g, 28%) deep red solid. mp 186.4 °C; ^1H NMR (DMSO) 6.81 (d, 2H), 7.14–7.24 (m, 8H), 7.32–7.43 (m, 12H), 7.60 (d, 2H), 7.77–7.91 (m, 8H); IR (KBr, *ν*, cm^{-1}) 3058, 1627, 1592, 1538, 1492, 1465, 1288, 743, 695, 475; *m*/*z* 735 (M^+).

3c[11] was purified by column chromatography (Si-gel, Et_2O–n-Hex 1:9); yield: **3c** (2.8 g, 50%) as a yellow solid. mp 208.4 °C; ^1H NMR (DMSO) 6.67 (d, 2H), 7.01 (d, 2H), 7.06–7.15 (m, 6H), 7.24–7.40 (m, 10H), 7.49 (s, 2H), 7.72 (d, 2H), 7.83 (m, 4H); IR (KBr, *ν*, cm^{-1}) 3055, 1627, 1592, 1523, 1491, 1465, 1281, 747, 693, 476; *m*/*z* 600 (M^+).

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