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Thienyl Triarylamines. Reactivity and Spectra of Cation Radicals and Dications

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Dedicated to Professor Lennart Eberson on the occasion of his 65th birthday

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The α-thienyl substituted triarylamines, bis(4-bromophenyl)-4-(2-thienyl)-phenylamine (**1**), (4-bromophenyl)bis-[4-(2-thienyl)phenyl]amine (**2**) and tris[4-(2-thienyl)phenyl]amine (**3**) were prepared as novel molecular systems for photoelectrical conversion. Electrochemical oxidations using solvents like hexafluoroisopropanol were performed to evaluate the stability of the corresponding cation radicals. The dimer 5,5′-{bis[4-di(4-bromophenyl)amino]phenyl}-2,2′-bithiophene (**1D**) was prepared by an electrochemical oxidation–reduction sequence. Chemical and electrochemical oxidations of **1D** were studied and UV–VIS–NIR spectra of the neutral, cation radical and dication are reported.

Organic molecules and polymers are receiving much attention as active components in optoelectronic devices such as electrophotographic receptors, light emitting diodes (LEDs) and photovoltaic cells.[1–4] These materials have to possess useful dye properties, charge transport properties, thermal stability, photo-stability, and good film-forming properties. Because many of these applications involve transient formation of ion radicals, stability of these ions is also important. A variety of compounds have been studied,[5–10] but most attention has been given to conjugated polymers like poly(phenylenevinylene) and triarylamines.

Triarylamine derivatives have good spectral properties and are well known hole transport materials with high charge transport mobility. Recently, Shirota and co-workers designed and synthesized new low-molecular weight materials with triarylamine and thienyl moieties related to those reported here. These are of special interest for the formation of LEDs because they form amorphous films with relatively high glass-transition temperatures.[11–17]

In this paper, we describe the synthesis of [4-(2-thienyl)phenyl]bis(4-bromophenyl)amine (**1**) which is transformed to dimer **1D** by an oxidation–reduction sequence. **1D**, containing dithiophene and triarylamine moieties forms stable cation radicals with intense near IR absorbance. (4-Bromophenyl)bis[4-(2-thienyl)phenyl]-amine (**2**) and tris[4-(2-thienyl)phenyl]amine (**3**) which might lead to new linear and starburst polymers, are also reported. The present investigation explores the reactivity of cation radicals of monomers **1–3** as well as the redox behavior of the dimer **1D** and the spectra of its cation radical and dication in solution.

Results and discussion

Monomer synthesis. The monomers (**1–3**) were prepared from tris(4-bromophenyl)amine (**0**) by a slightly modified Grignard coupling reaction. Use of the Grignard reagent prepared *in situ* gave the monomers in good yields as shown in Scheme 1. Using a molar ratio of three thienyl Grignard to one amine (**0**) compound, **3** was isolated in 85% yield. By using two equivalents of the Grignard reagent a mixture of unchanged **0** (8%), **1** (24%), **2** (43%) and **3** (20%) was prepared and separated by column chromatography. The structure and purity of **1–3** were confirmed by UV–VIS, FTIR, ^{1}H NMR and high resolution FABMS as described in the Experimental section.

Cyclic voltammetry and electronic absorption spectra. Electroanalytical data were obtained by cyclic voltammetry in acetonitrile using a platinum or glassy carbon working electrode. At fast sweep rate the compounds listed in Table 1 show chemically (peak current ratio $i_{pc}/i_{pa}=1$) and electrochemically ($E_{pa}-E_{pc}\approx 60$ mV) reversible first oxidation waves forming the cation radical. In the case of **2** the electron transfer is sluggish and the peak separation is larger ($E_{pa}-E_{pc}=95$ mV). The

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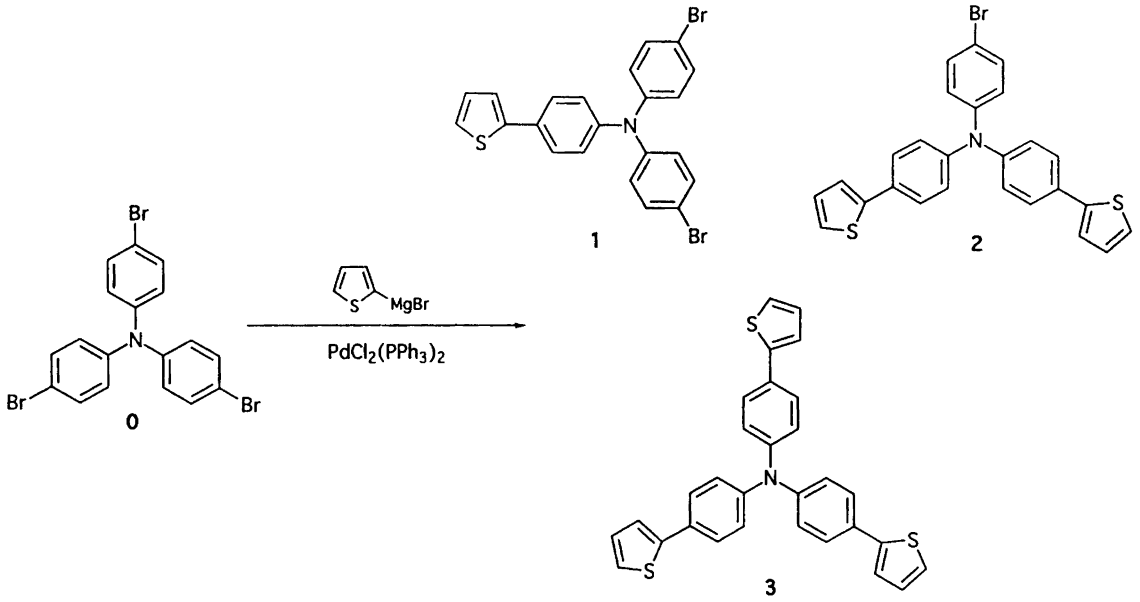


Scheme 1.

second wave corresponding to the dication was irreversible for all of the compounds listed in Table 1, which is in accordance with other substituted triarylamines.[18] The data for tris(4-bromophenyl)amine (**0**) are also given for the purpose of comparison.

The E° values for **1**–**3** are lower than that for the compound **0** indicating the greater resonance and electron-donating ability of α-thienyl compared with bromo substituents for stabilization of the cation radical. The chemical reversibility was observed at different scan rates ($v > 10$ V s^{-1} for **1**, $v > 3$ V s^{-1} for **2** and $v > 0.2$ V s^{-1} for **3**). These results suggest that the rate of the coupling of the cation radicals to dimers is decreased by increasing the number of thiophene rings from **1** to **3**, which is in agreement with previous results on thiophene oligomers.[19] The electronic absorption spectra have two bands in the UV–VIS region for compounds **1**–**3** and show shifts to longer wavelength as the number of thiophene units increases. The observed λ_{max} values correlate qualitatively with the measured E° values. These shifts in E° and λ_{max} suggest that despite cross conjugation all three thiophenes of **3** are conjugated through the amine.

Table 1. Oxidation potentials[a] and absorption maxima.

Compound	E°/V[b]	Sweep rate/V s^{-1}	E_p^2/V[c]	λ_{max}/nm (log ε)
0	0.98	0.005	1.72	312 (4.53)[d]
1	0.87	10	1.38	262 (5.37), 326 (4.69)
2	0.78	3	1.30	263 (4.62), 344 (4.75)
3	0.67	0.2	1.25	275 (4.55), 368 (4.71)

[a]Potentials versus SCE in MeCN–0.1M $LiClO_4$. [b]$E^\circ = (E_{pc} - E_{pa})/2$. [c]Sweep rate: 50 mV s^{-1}. [d]From Ref. 30.

Electrochemistry of ***1****. Synthesis of dimer* ***1D*** *by an oxidation–reduction sequence.* The cyclic voltammogram for **1** shows two irreversible waves at 0.86 V and 1.38 V (Fig. 1b). A reverse sweep after the first oxidation wave showed the appearance of a new redox couple with the anodic peak potential at 0.71 V (Fig. 1a) corresponding to the oxidation of the dimer **1D** formed through fast dimerization of the cation radical **1a** (Scheme 3) and

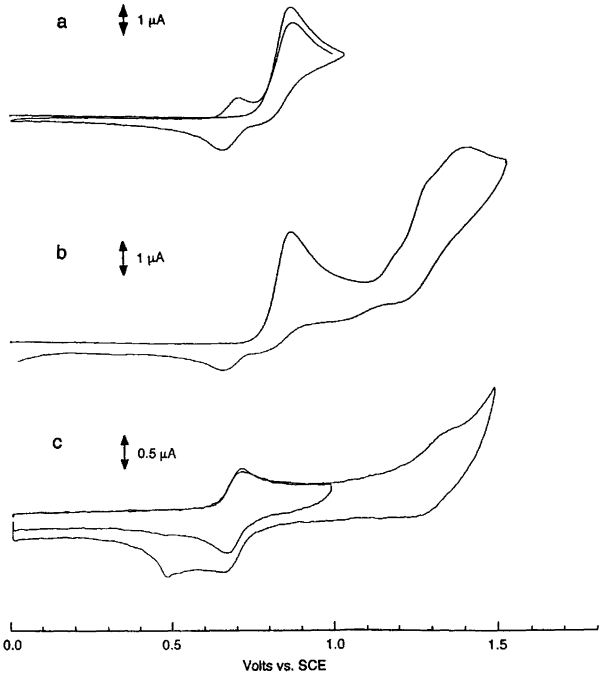


Fig. 1. Cyclic voltammograms run in 0.1 M $LiClO_4$–CH_3CN; $v = 50$ mV s^{-1}; Pt-anode ($2r = 1$ mm); (a) and (b) **1** (0.8 mM); (c) **1D** (0.1 mM).

deprotonation. Such electrochemical behavior of **1** is similar to that reported earlier for other triarylamines.[20] The cyclic voltammogram of the dimer **1D** (Fig. 1c) shows the first reversible wave at 0.71 V corresponding to the two electron oxidation of **1D** to dication $\mathbf{1D}^{2+}$ which is then reduced in the cathodic sweep at 0.65 V (see below). The second irreversible wave of **1D** appeared at 1.3 V. Importantly, the first redox couple of **1D** matches with the redox couple shown in Fig. 1a.

The shift of the half peak potential, $E_{p/2}$, measured for **1** in acetonitrile solution using the method given by Aalstad and Parker,[21] showed the variation of $E_{p/2}$ with $\log v$ of 21 ± 1.2 mV per decade of sweep rate and 19.6 ± 0.6 mV with concentration of **1**. These values are close to the theoretical values of 19.7 mV for an EC(dim) mechanism.[22] The half-peak widths for different sweep rates (0.01–0.5 V s^{-1}) correspond closely to expectations for Nernstian electron transfer ($E_p - E_{p/2} = 47.7$ mV).[23] The rate of the homogeneous coupling rate constant can be obtained by use of the following eqn. (1)[24] adopted for an anodic process,

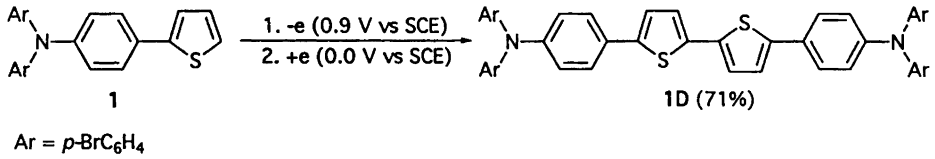
$$E_p = E^\circ + RT/nF\,0.902 - RT/3nF \ln(2/3\lambda) \qquad (1)$$

where $\lambda = kC_0(RT/Fv)$, k is a second-order rate constant of a homogeneous dimerization reaction, v is the sweep rate, C_0 is the concentration of **1**, $E^\circ = 0.87$ V determined by fast cyclic voltammetry, E_p is the peak potential and R, T and F have their usual meanings. The average value of the rate constant, k, obtained was 2.4×10^4 M^{-1} s^{-1}.

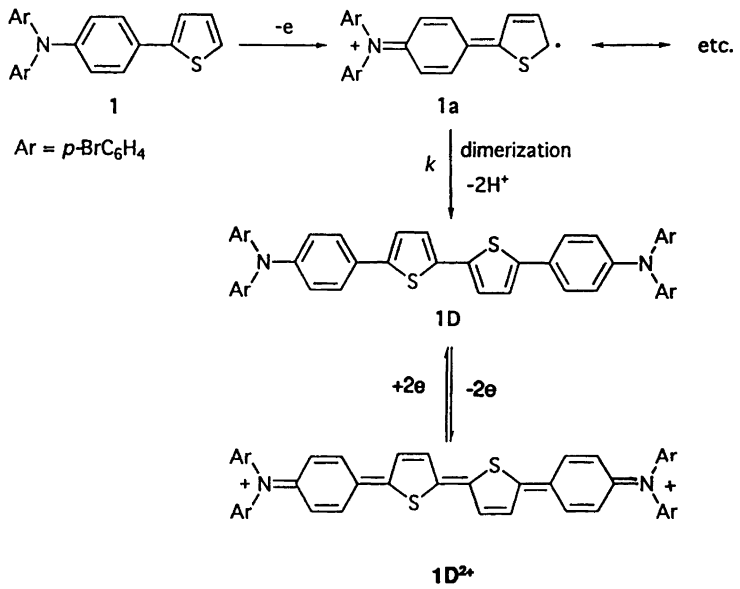
The one-pot electrochemical synthesis of the dimer **1D** by an oxidation–reduction sequence was performed in a divided cell in 0.1 M $LiClO_4$–CH_3CN solution by using a Pt gauze anode (3×5 cm) and graphite cathode. The controlled potential oxidation at 0.9 V (1.5 F mol^{-1}) followed by the controlled potential cathodic reduction at 0.0 V (0.5 F mol^{-1}) resulted in the formation of 5,5′-{bis[4-di(4-bromophenyl)amino]phenyl}-2,2′-bithiophene, **1D**, which was isolated in 71% yield (Scheme 2).

The oxidation–reduction process can be explained according to Scheme 3. Compound **1** is oxidized to cation radical **1a**, which dimerizes and is deprotonated to **1D**. Since the oxidation potential of **1D** is lower than the applied potential ($E_{app} = 0.9$ V) the dimer is further oxidized to the stable $\mathbf{1D}^{2+}$. This dication is reduced by adjusting the potential to 0.0 V vs. SCE.

The electronic absorption spectra of **1D** showed two strong absorption bands at 316 ($\log \varepsilon = 4.46$) and 412 ($\log \varepsilon = 4.59$) nm, respectively. The emission spectra of **1D** in CH_2Cl_2 showed maxima at 492 and 519 nm with a quantum efficiency of 42%. FTIR spectra of **1D** showed no absorption band around 695 cm^{-1}, which is present in monomer **1**, resulting from an α C–H in-plane deformation of the thiophene ring.[25] This indicates the position of coupling of two cation radicals. The high



Scheme 2.



Scheme 3.

resolution FAB mass spectra of **1D** showed (M^+) molecular peaks at m/z 963.8412, which is in accordance with molecular formula $C_{44}H_{28}Br_4N_2S_2$. The structure of **1D** was supported by ^1H NMR spectra with appropriate chemical shifts, integration and splittings.

*Oxidation of **1D** and optical spectra.* The spectra of the cation radical were of some interest since they were expected to be at very long wavelength in the NIR and there was the possibility that the species would be mixed valence, i.e. that the odd electron and charge would be localized on one side of the molecule or the other, not delocalized over both. Electrochemical and chemical oxidation of **1D** was studied in methylene chloride solution. A solution of **1D** was oxidized at room temperature by adding 1 equiv. of $NOPF_6$. The VIS–near-IR spectra in CH_2Cl_2 showed peaks at 731 nm ($\log \varepsilon = 4.30$) and 1710 nm ($\log \varepsilon = 4.34$) (Fig. 2). This is as expected for a delocalized cation radical of **1D** since the spectra of similar cation radicals show two $\pi \rightarrow \pi^*$ excitations (HOMO to SOMO and SOMO to LUMO) each with vibronic structure.[26] A PPP molecular orbital calculation led to orbital energies that could be translated into the absorption maximum for the long wavelength (HOMO–SOMO) band.[27] The calculation gave 1550 nm, in reasonable agreement with the observed 1700 nm experimental result. This result and the band shape confirm that the cation radical has delocalized, not mixed valence, ground and excited states. In the solvent hexafluoroisopropanol, which is known to stabilize cation radicals,[28] the cation radical was not very soluble. Formation of the dication was, however, confirmed by its NIR absorbance.

When the dimer **1D** was oxidized with 2 equiv. of $NOPF_6$ one broad absorption peak appeared at 1110 nm ($\log \varepsilon = 4.66$) due to the dication of **1D**. By adding 1 equiv. of neutral dimer **1D** into the solution of the dication, the spectra showed the presence of cation radical from reproportionation. One peak for the dication at wavelengths between the two peaks for the cation radical is consistent with model oligothiophene spectra.[26]

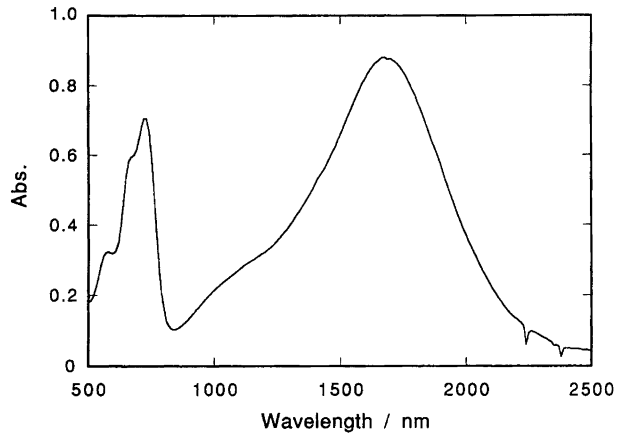


Fig. 2. VIS–near-IR spectra of 0.4 mM **1D**$^+$ in CH_2Cl_2.

Controlled potential oxidation of **1D** was performed in 0.1 M Bu_4NPF_6–CH_2Cl_2 solution. We were able to demonstrate that the oxidation products depend on the applied potential of oxidation. When the potential was maintained at the rising part of the first wave ($E_{app} = 0.75$ V) of the cyclic voltammogram (Fig. 4), and the electrolysis was terminated after passage of 1 F mol^{-1} the VIS–near IR spectra showed the presence of the absorption bands at 731 and 1710 nm, corresponding to the cation radical and small absorption at 1110 nm due to the dication. When the oxidation was performed at 1.0 V, only dication was formed and the quantity of electricity corresponded to 2 F mol^{-1}.

The electrochemical oxidation was monitored by UV–VIS spectroscopy (Fig. 5) which revealed that the peaks of neutral **1D** at 316 and 412 nm nearly disappeared after passage of 1 F mol^{-1} at 0.75 V (Fig. 5a) and completely disappeared after passage of 2 F mol^{-1} (Fig. 5b) at 1.0 V. In both cases, it was possible to recover quantitatively starting substrate **1D** by reduction of the solution at the controlled cathodic potential

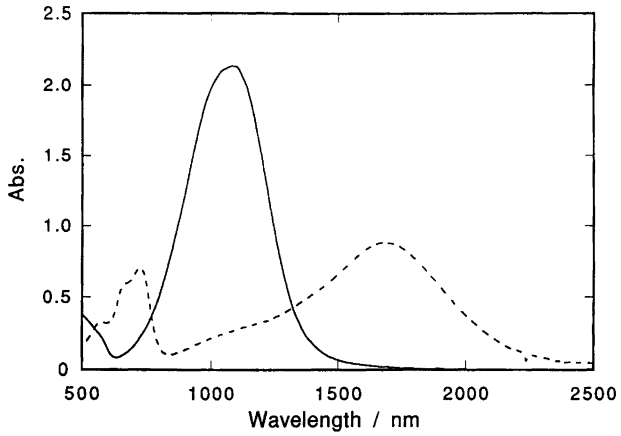


Fig. 3. VIS–near-IR spectra of (solid line) 0.4 mM **1D**$^{2+}$ in CH_2Cl_2 and (dashed line) of 0.4 mM **1D**$^{2+}$ plus 0.4 mM **1D** in CH_2Cl_2.

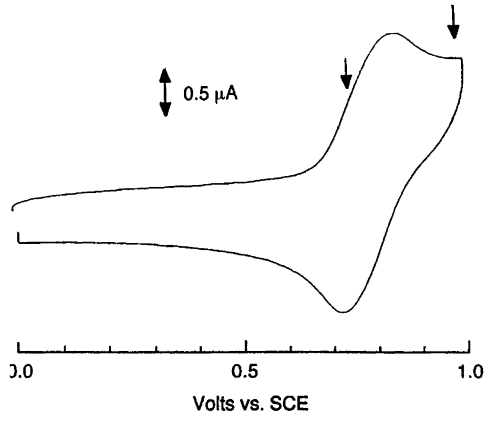


Fig. 4. Cyclic voltammogram of **1D** (0.32 mM) run in 0.1 M Bu_4NPF_6–CH_2Cl_2; $v = 50$ mV s^{-1}; Pt anode ($2r = 1$ mm). Arrows indicate the potentials of controlled potential oxidations.

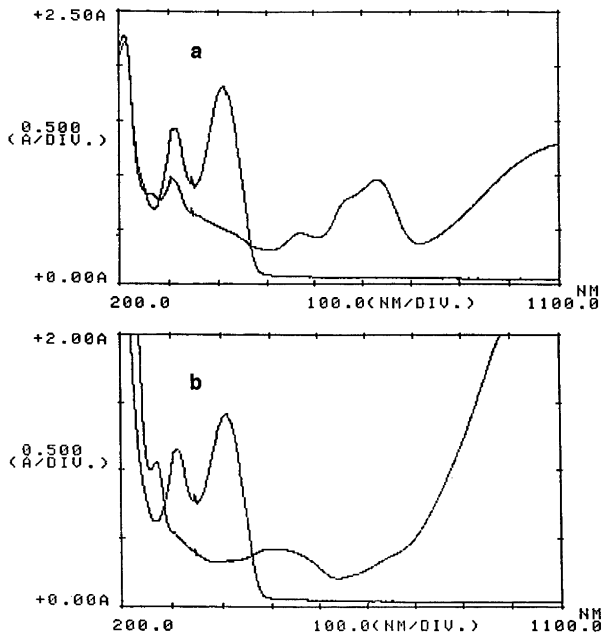


Fig. 5. UV–VIS spectra: (a) **1D** (0.47 mM) after oxidation at 0.75 V; (b) **1D** (0.32 mM) after oxidation at 1.0 V.

(E_{app} = 0.0 V). One-electron oxidation at 0.75 V showed a peak at 731 nm due to the presence of $\mathbf{1D}^+$ and two-electron oxidation at 1.0 V showed the peak of $\mathbf{D}^{2+}$ at 1110 nm. The results clearly demonstrate that the first peak in the cyclic voltammogram of **1D** includes two one-electron oxidation processes eventually leading to $\mathbf{D}^{2+}$. This peak has a breadth of more than 100 mV, which allows the formation of cation radical with little disproportionation to neutral and dication, as observed.

Experimental

Melting points were recorded with an electrothermal apparatus and are uncorrected. The molecular orbital, electrochemical, and spectroscopic methods and the equipment have been previously reported.[29] The reference electrode was SCE.

Tris[4-(2-thienyl)phenyl]amine **3**. A mixture of Mg (560 mg, 23.1 mmol), one I_2 crystal and some drops of 2-bromothiophene in Et_2O (10 ml) was refluxed under argon until the reaction was initiated, then a solution of 2-bromothiophene (3.0 g, 18.4 mmnol) in Et_2O was added dropwise. After being stirred under reflux for 1 h, the solution of the Grignard reagent was added dropwise to a mixture of tris(4-bromophenyl)amine (2.51 g, 5.21 mmol) and $PdCl_2(PPh_3)_2$ (400 mg) in THF (30 ml). The reaction was refluxed for 4 h and cooled at room temperature. The reaction mixture was poured into saturated aq. NH_4Cl solution and extracted with EtOAc. The combined organic layers were dried (Na_2SO_4) and evaporated to dryness. Purification of the residue by flash chromatography (silica gel; hexane–CH_2Cl_2 9:1) furnished compound **3** (1.89 g; 85%) as a pale yellow solid: m.p. 138–140 °C. FABMS Calcd. for $C_{30}H_{21}NS_3$ 491.0836. Found (M^+) 491.0856. FTIR (KBr): 1597, 1531, 1498, 1322, 1289, 1274, 1182, 848, 815, 698 cm^{-1}; 1H NMR ($CDCl_3$, 500 MHz): δ 7.09 (m, 3 H), 7.16 (d, 6 H, J_{AB} = 8.5 Hz), 7.24–7.28 (m, 6 H) 7.54 (d, 6 H, J_{AB} = 8.5 Hz).

Following the above procedure, but using only 2 equiv. of 2-bromothiophene, a mixture of unchanged **0** (8%), **1** (24%), **2** (23%) and **3** (20%) was isolated by flash chromatography.

Bis(4-bromophenyl)-4-(2-thienyl)phenylamine **1**. Pale yellow solid: m.p. 59–60 °C. FABMS Calcd. for $C_{22}H_{15}Br_2NS$ 482.9292. Found (M^+) 482.9292. FTIR (KBr): 3067, 2927, 1586, 1284, 1176, 1102, 1071, 958, 816, 695 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 6.92 (d, 4 H, J_{AB} = 8.5 Hz), 7.05 (d, 2 H, J_{AB} = 8.5 Hz), 7.06–7.09 (m, 1 H), 7.24–7.27 (m, 2 H), 7.37 (d, 4 H, J_{AB} = 8.5 Hz), 7.54 (d, 2 H, J_{AB} = 8.5 Hz).

4-Bromophenylbis[4-(2-thienyl)phenyl]amine **2**. M.p. 110–113 °C. FABMS Calcd. for $C_{26}H_{18}BrNS_2$ 487.0064. Found (M^+) 487.0089. FTIR (KBr): 1580, 1532, 1483, 1430, 1315, 1294, 1073, 1007, 850, 839, 823, 690 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.03 (d, 2 H, J_{AB} = 8.5 Hz), 7.07–7.09 (m, 2 H), 7.10 (d, 4 H, J_{AB} = 8.5 Hz), 7.24–7.28 (m, 4 H), 7.38 (d, 2 H, J_{AB} = 8.5 Hz), 7.52 (d, 4 H, J_{AB} = 8.5 Hz).

Electrochemical synthesis of 5,5'-{bis[4-di(4-bromophenyl)amino]phenyl}-2,2'-bithiophene **1D**. Into the anodic compartment of a divided cell equipped with a Pt gauze anode (3 × 5 cm) and a graphite cathode, filled with 0.1 M solution of $LiClO_4$ in acetonitrile (40 ml) were added 241 mg of **1**. The anode potential was maintained at 1.0 V and electrolysis was continued until 1.5 F mol^{-1} had been passed. The potential was adjusted at 0.0 V vs. SCE and the reduction was carried out until 0.5 F mol^{-1} had been passed. After the electrolysis, the dark solution was evaporated under reduced pressure and 70 ml of 40% aqueous solution of hydrazine was added. The reaction mixture was sonicated for 15 min and extracted with CH_2Cl_2 (3 × 30 ml). The combined organic layers were dried (Na_2SO_4) and evaporated to dryness. Purification of the residue by flash chromatography (silica gel; hexane–CH_2Cl_2 9:1) gave **1D** (170 mg, 71%) as a yellow solid m.p. 224–227 °C. FABMS Calcd. for $C_{44}H_{18}Br_4N_2S_2$ 963.8427. Found (M^+) 963.8412. FTIR (KBr): 1586, 1530, 1485, 1384, 1313, 1273, 1072, 1007, 820, 794 cm^{-1}. ^{1}NMR ($CDCl_3$ 500 MHz): δ 6.98 (d, 8 H, J_{AB} = 8.5 Hz), 7.05 (d, 4 H, J_{AB} = 8.5 Hz), 7.13–7.18 (m, 4 H), 7.70 (d, 8 H, J_{AB} = 8.5 Hz) 7.49 (d, 4 H, J_{AB}–78.5 Hz).

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