Supporting Information:

EXPERIMENTAL

Preparation of 2-(N,N-Diphenylamino)thiophene **2a**:

Method A:
Methyl 2-(*N,N*-diphenylamino)thiophene-5-carboxylate **5a**[14] (10 mmol, 3.1 g) was heated in a mixture of KOH (2.0 g) in 50% aqueous methanol (50 mL) for 2 h. After cooling, the reaction mixture was acidified by addition of aqueous hydrochloric acid and the precipitate formed in nearly quantitative yield was isolated by filtration. By heating the 2-(*N,N*-diphenylamio)thiophene-5-carboxylic acid **6a** so obtained at their melting point the evaluation of carbon dioxide occurs. After the end of the decarboxylation the smelt crystallizes by cooling. For purification the product obtained was recrystallized from toluene.

Method B:
The 2-(*N,N*-diphenylamio)thiophene-5-carboxylic acid **6a** obtained by the previous procedure was heated in acetic acid (25 mL) at reflux temperature for 5 min. After cooling the reaction mixture and addition of water (5 mL) the precipitate was isolated by filtration and recrystallized, after drying, from toluene.
All other 2-(*N,N*-diarylamino)thiophenes **2b** – **2g** listed in Table 1 were obtained by means of the method A and by starting from their corresponding 2-(*N,N*-diphenylamino)thiophene-5-carboxylic acids **6** prepared by saponification of their alkyl carboxylates **5**.

Preparation of 5,5'-Bis-(N,N-diphenylamino)-2,2'-bithiophene **7a**:
To a solution of 2-(*N,N*-diphenylamino)thiophene (**5a**, 10 mmol, 2.5 g) in dichloromethane (50 mL) titanium tetrachloride (15 mmol, 2.8 g) in dichloromethane (20 mL) was added dropwise under strirring at 0 °C. After stirring for 4h at room temperature a saturated aqueous potassium carbonate solution (100 mL) was added to the reaction mixture. The organic layer separated after some standing was dried with anhydrous sodium sulphate and evaporated at reduced pressure. The remaining solid was absorbed at silica and eluated with toluene. Yield 2.0 g; mp. 189.7 °C; ^{1}H NMR (δ-values, measured in C_6D_6): 6.35 (d, *J* 3.9 Hz, 2H), 6.64 (d, J 3.9 Hz, 2H), 6.84 (m, 4H), 7.04 (m, 8H), 7.13 (m, 16 H).

Table 1: Yields and ^{1}H NMR spectroscopic data of the *N*-diarylated 2-aminothiophenes **2**

Entry	Yield [%] (method)	^{1}H NMR (in $CDCl_3$), δ-values
6a	92 (A) 90 (B)	6.68 - 6.72 (m, 1H), 6.83 - 6.89 (m, 1H), 6.94 - 7.02 (m, 3H), 7.06 - 7.13 (m, 4H), 7.18 - 7.27 (m, 4H)
6b	58 (A)	2.29 (s, 6H, CH_3), 6.62 (d, 1H, CH), 6.83 (t, 1H, CH), 6.89 (d, 1H, CH), 7.00 (d, 2H, CH), 7.04 (d, 2H, CH)
6c	74 (A)	6.74 - 6.78 (m, 1H), 6.88 - 6.94 (m, 1H), 7.00 - 7.09 (m, 2H), 7.15 - 7.20 (m, 2H), 7.22 - 7.44 (m, 5H), 7.45 - 7.50 (m, 1H), 7.59 - 7.65 (m, 1H), 7.70 - 7.77 (m, 2H)
6d	86 (A)	6.73 (d, *J* 3.2 Hz, 1H), 6.80 - 6.85 (m, 1H), 6.88 - 6.96 (m, 3H), 7.17 (t, *J* 7.7 Hz, 2H), 7.40 - 7.52 (m, 4H), 7.78 - 7.84 (m, 1H), 7.89 (d, *J* 8.1 Hz, 2H), 8.05 (d, *J* 8.1 Hz, 1H)
6e	46 (A)	6.69 - 6.74 (m, 2H), 6.84 - 6.90 (m, 2H), 6.94 - 7.00 (m, 4H), 7.03 (s, 4H), 7.08 - 7,12 (m, 4H), 7.20 - 7.28 (m, 4H)
6f	44 (A)	6.61 - 6.67 (m, 2H), 6.84 - 6.90 (m, 2H), 6.91 - 6.99 (m, 2H), 7.01 - 7.06 (m, 2H), 7.07 - 7.10 (m, 1H), 7.11 - 7.16 (m, 1H), 7.35 - 7.39 (m, 1H)
6g[c]	52[e]	3.11 (t, ^3J 4.7 Hz, 4H, CH_2), 3.82 (t, ^3J 4.7 Hz, 4H, CH_2), 6.15 (d, ^4J 3.2 Hz, 1H) 6.62 (d, ^3J 5.2 Hz, 1H), 6.78 (dd, ^3J 5.2 Hz, ^4J 3.2 Hz, 1H),

[a] measured towards the SCE, irreversible potentials

[b] reversible potential

[c] 2-morpholinothiophene-5-carboxylic acid[12]

[d] 2-morpholinthiophene

[e] H. Hartmann, S. Scheithauer, *J. Prakt. Chem.*, **1969**, *311*, 827