Synthesis and coplanarity-dependent HOMO–LUMO separation of π-conjugated dimers

Takashi Murashima,*[a] Daiki Shiga,[a] Keiji Nishi,[a] Hidemitsu Uno[b] and Noboru Ono*[a]

[a] *Department of Chemistry, Faculty of Science, Ehime University, Bunkyo-cho 2–5, Matsuyama 790-8577, Japan*
[b] *Advanced Instrumentation Center for Chemical Analysis, Ehime University, Bunkyo-cho 2–5, Matsuyama 790-8577, Japan*

Received (in Cambridge, UK) 20th April 2000, Accepted 29th June 2000
Published on the Web 24th July 2000

Three series of dimers containing pyrrolo[3,4-*e*][2,1,3]benzothiadiazole units have been prepared by application of the Pd-catalyzed Suzuki coupling. The dependence of the HOMO–LUMO separation on coplanarity has been evaluated by means of electronic absorption spectra and cyclic voltammetry. The pyrrole dimer **5c** shows a narrow HOMO–LUMO separation owing to its intrinsically planar structure, as confirmed by ^{1}H NMR.

Introduction

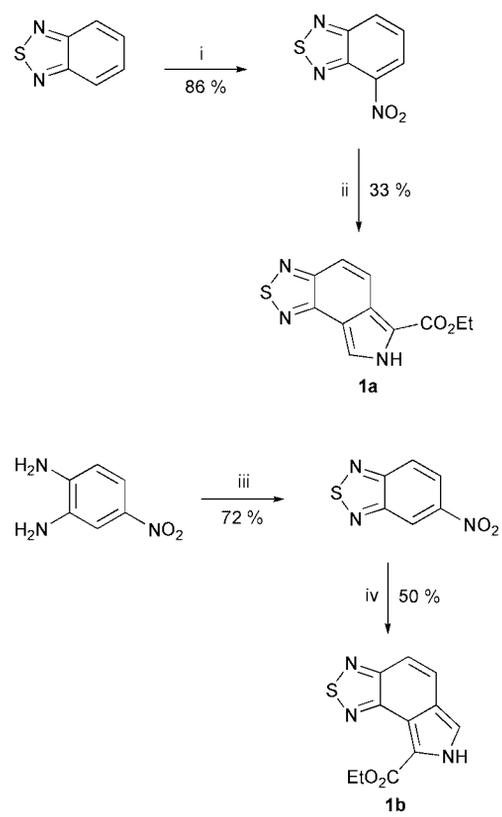
Organic conducting materials have attracted much attention, and extensive research is being focused on the preparation of materials with higher conductivity. The copolymerization of donor and acceptor units is an effective strategy for improving the electronic conductivity.[1] Another promising strategy for band gap reduction of polymers is the polymerization of monomers having expanded π-electron conjugation systems.[2]

According to the latter concept, varieties of low band gap polymers such as polypyrrole, polythiophene, poly(pyrrolenevinylene) and poly(thienylenevinylene)s were prepared with a view to forming materials with high conductivity and high optical nonlinearity. However, most of the polymers with an expanded π-electron system exhibit lower conductivity than predicted by theoretical investigations because the presence of a bulky expanded ring can cause successive monomer units to be tilted out of plane relative to one another with a resultant reduction in the degree of conjugation of the polymer.

We prepared some highly conjugated pyrroles and their polypyrroles using extended Barton–Zard pyrrole synthesis.[2f,2h,3] Among these polypyrroles prepared, poly(pyrrolo[3,4-*e*][2,1,3]-benzothiadiazolene) showed relatively high electronic conductivity.[2f] The high conductivity of this compound arises mainly from the high coplanarity of the π-conjugation units. While the improvement in planarity could be explained on the basis of the hydrogen bond between the thiadiazole ring nitrogen and neighboring pyrrole NH, we could not estimate the contribution to the overall reduction of band gap by ignoring the complexity of the polymer structure. Although several researchers have recently reported the preparation and properties of oligomers and polymers with a thiadiazole ring moiety with intramolecular and intermolecular hydrogen bond networks,[4] more detailed studies seem to be required to reveal their basic properties. Thus, in this paper, we report the preparation of some aryl dimers containing a pyrrolo[3,4-*e*][2,1,3]benzothiadiazole unit as a key structure in the hope of determining the contribution of coplanarity to the reduction of the band gap.

Results and discussion

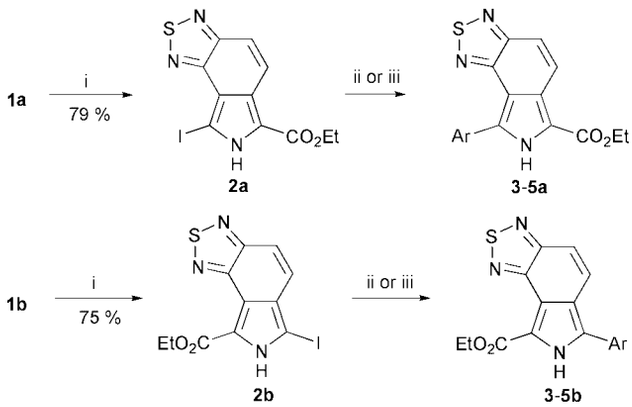
The key structure of the target compound, pyrrolobenzothiadiazole,[2f,3a,b,5] was constructed by the reaction of 4-nitro-2,1,3-benzothiadiazole or 5-nitro-2,1,3-benzothiadiazole with ethyl isocyanoacetate in the presence of an appropriate non-ionic base (Scheme 1). One intrinsic advantage of this synthetic strategy is the availability of two regioisomeric pyrrolobenzothiadiazoles **1a** and **1b**. By using whichever we choose of these two compounds **1a**,**b**, the pyrrole α-hydrogen could be replaced by aromatic rings to give regioisomeric dimers.



Scheme 1 *Reagents*: (i) HNO_3, H_2SO_4; (ii) $CNCH_2CO_2Et$, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU); (iii) $SOCl_2$, Et_3N; (iv) $CNCH_2CO_2Et$, *tert*-butyliminotri(pyrrolidino)phosphorane (BTPP).

Compounds **1a**,**b** were converted to α-iodo derivatives **2a**,**b** by the reaction with iodine, iodic acid and acetic acid.[6] The aryl dimers **3a**,**b**, **4a**,**b** and **5a**,**b** were prepared from **2a**,**b** by

DOI: 10.1039/b003211p



		a	b
3	Ar = Ph	36%	90%
4	Ar = 2-Thienyl	68%	94%
5	Ar = Pyrrol-2-yl	15%	40%

Scheme 2 *Reagents*: (i) I_2, HIO_3, AcOH; (ii) arylboronic acid, Pd cat., base; (iii) (1-*tert*-butoxycarbonylpyrrol-2-yl)boronic acid, Pd cat., base, then NaOEt.

Suzuki coupling[7] using the corresponding arylboronic acids (Scheme 2). The ester function of these dimers was removed by hydrolysis and subsequent decarboxylation using potassium hydroxide. When these reactions were conducted in an ethylene glycol solution, only decomposition occurred and no expected product was obtained. The desired products could be obtained in moderate yields by the addition of 20% v/v of toluene. These α-free compounds are labile and they should be handled under nitrogen in the dark.

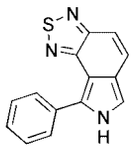
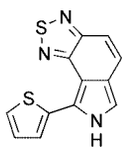
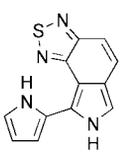
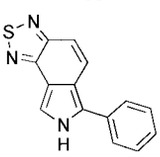
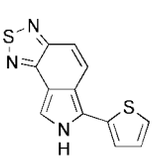
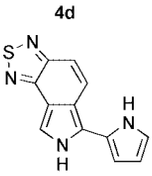
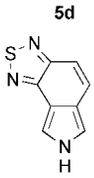
The structural characterizations of three series of aryl dimers, phenylpyrroles, thienylpyrroles and pyrrolylpyrroles, were discussed on the basis of their UV-visible spectroscopic data (Table 1). The UV data for 8-(pyrrol-2-yl)pyrrolo[3,4-*e*][2,1,3]-benzothiadiazole **5c** were consistent with a high degree of coplanarity. Therefore, a bathochromic shift was observed upon the incorporation of an unsubstituted pyrrole into the mother unit, pyrrolo[3,4-*e*][2,1,3]benzothiadiazole **6** (λ_{max} shifting from 370 nm for **6** to 442 nm for **5c**). By contrast, the isomeric dimer, 6-(pyrrol-2-yl)pyrrolo[3,4-*e*][2,1,3]benzothiadiazole **5d** showed only a small bathochromic shift (412 nm for **5d**), reflecting the lack of coplanarity. The large bathochromic shift observed in **5c** was due to the intramolecular hydrogen bond between the thiadiazole ring nitrogen and neighboring pyrrole NH.[8]

The UV data of the thienylpyrrolobenzothiadiazoles **4c** and **4d** also indicated the existence of intramolecular interaction between thiophene and the thiadiazole ring, but this interaction is weaker than that observed in the pyrrolylpyrrolobenzothiadiazoles. Both **4c** and **4d** showed similar bathochromic shifts, reflecting the expansion of the π-electron conjugated system. The absorption bands of the 8-substituted dimer **4c** and 6-substituted dimer **4d** were observed at 408 and 403 nm, respectively. This slightly larger shift of **4c** meant the weak interaction overruled the steric hindrance between thiophene and thiadiazole.

In both the pyrrole and thiophene containing dimers, the intramolecular charge transfer from the electron-donating part to the electron-withdrawing part also contributed to the red-shifts.[1]

The physical properties of the phenyl substituted dimers **3c** and **3d** showed a sharp contrast to those of the pyrrolylpyrrolobenzothiadiazoles. In the case of 8-pyrrolyl substituted dimer **5c**, the intramolecular interaction causes an improvement in coplanarity as described above. On the other hand, in the case of an 8-phenyl substituted dimer, there is no effective interaction between the two aromatic rings and they are both tilted out by the steric bulkiness. Thus, the phenyl dimer **3c** showed smaller bathochromic shift than the 6-substituted one **3d** (396 nm for **3c** and 416 nm for **3d**). Such steric hindrance often causes a reduction in the electrical conductivity of the polymers.

Table 1 UV-Visible spectral data and electrochemical properties of dimers

Compounds	λ_{max}/nm [a]	Absorption edge/nm [a,b]	Peak potential/V [c]
 **3c**	396 (3.13 eV)	431 (2.88 eV)	0.52
 **4c**	408 (3.04 eV)	459 (2.70 eV)	0.50
 **5c**	442 (2.81 eV)	503 (2.47 eV)	0.22
 **3d**	416 (2.98 eV)	477 (2.60 eV)	0.60
 **4d**	403 (3.08 eV)	462 (2.68 eV)	0.54
 **5d**	412 (3.01 eV)	479 (2.59 eV)	0.36
 **6**	370 (3.35 eV)	420 (2.95 eV)	0.71

[a] Calculated values of HOMO–LUMO separation are listed in parentheses. [b] The absorption edge was determined from the differential curve of the corresponding spectra. [c] Oxidation potentials were measured by cyclic voltammetry. Potential values were *versus* Ag/AgCl. Bu_4NClO_4 (0.1 M CH_3CN solution) was used as supporting electrolyte. Scan rate was 100 mV s^{-1}.

In order to estimate the contribution of planarity to electronic conductivity, we measured the HOMO–LUMO energy separations of the dimers prepared. The HOMO–LUMO separations calculated from the absorption edges of **3c**,**d**, **4c**,**d** and **5c**,**d** are listed in Table 1 together with their absorption maxima. The absorption of **5c** was observed at a longer wavelength compared to those of the other dimers, suggesting that **5c** had a smaller HOMO–LUMO separation. The energy gap

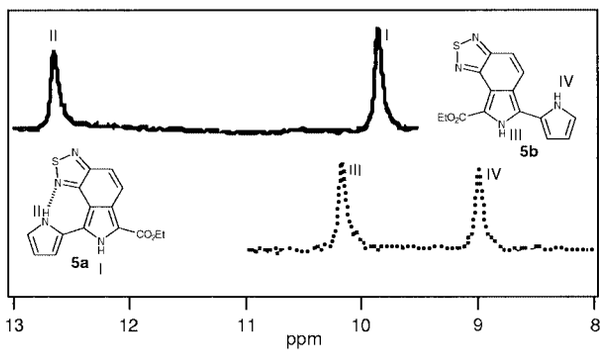


Fig. 1 ^{1}H-NMR spectra of dimers **5a** (solid line) and **5b** (dotted line) in $CDCl_3$.

of **5c** (2.47 eV for absorption edge and 2.81 eV for absorption maximum) was the narrowest among these dimers, and was comparable to that of a pyrrole–benzothiadiazole dimer which was completely coplanar by virtue of hydrogen bonding.[8b]

The interdependence of coplanarity and HOMO–LUMO separation for these aromatic dimers was evaluated with cyclic voltammetry. The low oxidation potential of compound **5c** (0.22 V *vs.* Ag/AgCl) and relatively high oxidation potential (0.36 V *vs.* Ag/AgCl) of **5d** again suggested the high coplanarity of **5c** (Table 1).

The ^{1}H NMR data of the pyrrolylpyrrolobenzothiadiazoles **5c**,**d** could not be used to indicate the existence of an intramolecular hydrogen bond due to their low solubility. Therefore, the precursor dimers **5a**,**b** were used instead. The N–H absorption of the β-unsubstituted pyrrole (**5a**, II in Fig. 1) was shifted downfield to 12.6 ppm, suggesting that the intramolecular hydrogen bond was sufficiently strong to diminish the electron density of the pyrrolic proton. This low-field N–H signal showed no concentration dependence and no detectable temperature dependence. The corresponding N–H absorption of **5b** appeared at 9.0 ppm, indicating the absence of a hydrogen bond.

In conclusion, various aromatic dimers, consisting of pyrrolo[3,4-*e*][2,1,3]benzothiadiazole as an essential moiety, can be synthesized in moderate to good yields by means of Suzuki coupling. In the case of the pyrrole containing dimer **5c**, the absorption maximum is shifted to 442 nm, whereas the absorption maximum of isomeric dimer **5d** is observed at 412 nm, reflecting the absence of a hydrogen bond. The difference between these shifts (30 nm) is comparable to the bathochromic shift observed with one unit elongation from bipyrrole to terpyrrole.[9] While the use of donor–acceptor (D–A) dimers is a well-established methodology for preparing narrow band gap polymers, the main reason for the narrow HOMO–LUMO separation of compound **5c** is obviously an intramolecular hydrogen bond. The ^{1}H-NMR spectra and cyclic voltammetry data also suggest a high degree of coplanarity and a narrow HOMO–LUMO separation in **5c**.

Experimental

General procedures

Melting points were measured on a Yanaco micro melting point apparatus and are uncorrected. NMR spectra were recorded on a JEOL-JNM-GSX 270 or JNM-EX 400 spectrometer by using $CDCl_3$, acetone-d_6 or DMSO-d_6 as solvent and tetramethylsilane as an internal standard for ^{1}H and ^{13}C; *J* values are given in Hz. IR spectra were obtained with a Hitachi 260–10 or Horiba FT-720 spectrophotometer. UV-Vis spectra were recorded on a Shimadzu UV-2200 or JASCO V-570 spectrophotometer. Mass spectra were measured with a Hitachi M80B-LCAPI spectrometer under the following ionizing conditions: electron impact, 20 eV; high boiling PFK (Aldrich, bp 210–240 °C) as a standard. FAB mass spectra were measured with a JEOL JMS-LX 2000 spectrometer; samples were dissolved in *m*-nitrobenzyl alcohol as a matrix. Electrochemical measurements were performed with a dual potentiostat (BSA BS-1), a Ag/AgCl reference electrode, and a platinum wire counter electrode in CH_3CN/Bu_4NClO_4 (0.1 mol dm^{-3}) at 298 K, scan rate 100 mV s^{-1}, potential *vs.* Ag/AgCl calibrated with Fc/Fc$^+$ (0.101 V). Elemental analysis was performed with a Yanaco MT-5 Me instrument. THF was freshly distilled from sodium benzophenone ketyl. Catalysts for Suzuki coupling were prepared according to literature procedures.[10]

Ethyl pyrrolo[3,4-*e*][2,1,3]benzothiadiazole-6-carboxylate (1a)

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was added dropwise to a solution of 4-nitro-2,1,3-benzothiadiazole (1.81 g, 10 mmol) and ethyl isocyanoacetate (1.0 cm^3, 10 mmol) in THF (100 cm^3) at 0 °C under Ar. The resulting mixture was stirred at ambient temperature for 5 h. After dil. hydrochloric acid (50 cm^3) was added, the crude mixture was extracted with chloroform (3 × 20 cm^3). The organic phase was washed with aq. sodium hydrogen carbonate, water and brine, and dried over Na_2SO_4. The solvent was removed and the residue was purified by silica gel column chromatography (ethyl acetate–hexane) to give the title compound **1a** (0.81 g, 33% yield), mp 183–184 °C; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 1.49 (t, J = 7.1, 3H, CH_3CH_2), 4.49 (q, J = 7.1, 2H, CH_3CH_2), 7.62 (d, J = 9.6, 1H, Ar-*H*), 7.97 (d, J = 3.3, 1H, pyrrole-α), 8.19 (d, J = 9.6, 1H, Ar-*H*) and 10.23 (br, 1H, N*H*); ^{13}C-NMR ($CDCl_3$, 270 MHz) δ 14.38, 60.20, 115.24, 115.57, 118.30, 119.14, 125.00, 125.49, 150.39, 153.91 and 160.42; ν_{max} (KBr)/cm^{-1} 1689, 1392, 1340, 1277, 1146, 839, 804, 768, 741 and 609; *m*/*z* (EI) 247 (M$^+$, 100%), 201 (M$^+$ − EtOH, 98) and 173 (32); λ_{max} (CH_2Cl_2)/nm 359 (log ε 4.15), 308 (3.93), 296 (4.08), 267 (4.23) and 242 (4.15); Anal. calcd. for $C_{11}H_9N_3O_2S$: C, 53.43; H, 3.67; N, 16.99; found: C, 53.66; H, 3.67; N, 16.99%.

Ethyl pyrrolo[3,4-*e*][2,1,3]benzothiadiazole-8-carboxylate (1b)

Compound **1b** was prepared by a similar procedure to that described above using 5-nitro-2,1,3-benzothiadiazole as a starting material. Yield 50%; mp 172–173 °C; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 1.52 (t, J = 7.1, 3H, CH_3CH_2), 4.55 (q, J = 7.1, 2H, CH_3CH_2), 7.47 (d, J = 3.4, 1H, pyrrole-α), 7.51 (d, J = 9.5, 1H, Ar-*H*), 7.68 (d, J = 9.5, 1H, Ar-*H*) and 10.12 (br, 1H, N*H*); ^{13}C-NMR ($CDCl_3$, 270 MHz) δ 14.49, 61.24, 116.94, 117.18, 117.44, 117.62, 124.49, 124.92, 149.60, 156.15 and 160.31; ν_{max}(KBr)/cm^{-1} 3265, 1672, 1427, 1379, 1331, 1259, 1188, 1024, 768 and 619; *m*/*z* (EI) 247 (M$^+$, 64%), 201 (M$^+$ − EtOH, 100) and 175 (18); λ_{max} (CH_2Cl_2)/nm 364 (log ε 3.95), 288 (4.26), 279 (4.23), 264 (4.36) and 256 (4.28); Anal. calcd. for $C_{11}H_9N_3O_2S$: C, 53.43; H, 3.67; N, 16.99; found: C, 53.08; H, 3.64; N, 16.94%.

Iodination of 1a,b with iodine and iodic acid

To a stirred solution of **1a** or **1b** (6 mmol), iodic acid (0.81 g, 4.5 mmol) and iodine (2.28 g, 9 mmol) in chloroform (20 cm^3), acetic acid (29 cm^3) and water (2.0 cm^3) were added at ambient temperature and the resulting mixture was stirred for 3 h at reflux temperature. After cooling, the mixture was quenched with aqueous sodium carbonate, then neutralized with sodium carbonate. The crude precipitate was recrystallized from THF–chloroform to give a pure compound.

Ethyl 8-iodopyrrolo[3,4-*e*][2,1,3]benzothiadiazole-6-carboxylate (2a). Yield 79%; mp >300 °C; ^{1}H-NMR (DMSO-d_6, 270 MHz) δ 1.47 (t, J = 7.1, 3H, CH_3CH_2), 4.46 (q, J = 7.1, 2H, CH_3CH_2), 7.73 (d, J = 9.3, 1H, Ar-*H*), 8.24 (d, J = 9.3, 1H, Ar-*H*) and 13.91 (br, 1H, N*H*); ^{13}C-NMR (DMSO-d_6, 270 MHz) δ 14.35, 60.37, 72.64, 118.92, 119.62, 119.85, 124.97, 126.08, 149.97, 154.31 and 159.57; ν_{max} (KBr)/cm^{-1} 3196, 1588,

1436, 1390, 1336, 1240, 1218, 1172, 1086, 1032, 840, 826, 816 and 763; *m*/*z* (EI) 373 (M^+, 100%), 327 (M^+ − EtOH, 56), 299 (10) and 172 (36); λ_{max} (CH_2Cl_2)/nm 366, 322, 308 and 270; Anal. calcd. for $C_{11}H_8IN_3O_2S$: C, 35.41; H, 2.16; N, 11.26; found: C, 35.68; H, 2.23; N, 11.13%.

Ethyl 6-iodopyrrolo[3,4-*e*][2,1,3]benzothiadiazole-8-carboxylate (2b). Yield 75%; mp 235 °C; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 1.52 (t, J = 7.1, 3H, CH_3CH_2), 4.55 (q, J = 7.1, 2H, CH_3CH_2), 7.45 (d, J = 9.5, 1H, Ar-*H*), 7.56 (d, J = 9.5, 1H, Ar-*H*) and 10.06 (br, 1H, N*H*); ^{13}C-NMR (DMSO-d_6, 270 MHz) δ 14.34, 60.36, 74.92, 116.38, 117.26, 121.41, 126.13, 128.12, 148.90, 155.88 and 159.18; ν_{max} (KBr)/cm^{-1} 3200, 1658, 1480, 1430, 1414, 1378, 1334 and 1250; *m*/*z* (EI) 373 (M^+, 92%), 327 (M^+ − EtOH, 100) and 172 (40); λ_{max} (CH_2Cl_2)/nm 376, 322 and 290; Anal. calcd. for $C_{11}H_8IN_3O_2S$: C, 35.41; H, 2.16; N, 11.26; found: C, 35.30; H, 2.20; N, 11.03%.

General procedure of Suzuki coupling

Method A.[7b] A solution of iodopyrrole (1.0 mmol), areneboronic acid (1.5 mmol), Pd catalyst (0.10 mmol) and the appropriate base (neat or saturated aqueous solution) (3.0 mmol) in DMF was stirred for 3 to 6 h at 80 °C under Ar. The resulting mixture was cooled to ambient temperature and worked up. The solvent was removed under vacuo and the residue was purified by silica gel column chromatography (chloroform–hexane or toluene) to give the expected dimers.

Method B.[7d,f] In the case of the reaction of pyrrol-2-ylboronic acid with iodopyrrole **2a**, part of the protecting group, *tert*-butoxycarbonyl, still remained after completion of the reaction described above. Thus, the crude mixture was dissolved in THF (10 cm^3) and the solution was treated with sodium methoxide (20% ethanol solution, 2.35 cm^3, 4.8 mmol) at ambient temperature for 30 min. After removal of solvent, the residue was purified by silica gel column chromatography (chloroform) to give pure compound **5a**.

Ethyl 8-phenylpyrrolo[3,4-*e*][2,1,3]benzothiadiazole-6-carboxylate (3a). *Method A*: Catalyst, $Pd(PPh_3)_4$; base, sat. Na_2CO_3 aq. Yield 36%; mp 202–203 °C; ^{1}H-NMR (DMSO-d_6, 270 MHz) δ 1.30 (t, J = 7.2, 3H, CH_3CH_2), 4.31 (q, J = 7.2, 2H, CH_3CH_2), 7.34–7.44 (m, 3H, Ar-*H*), 7.58 (d, J = 9.3, 1H, Ar-*H*), 8.00 (d, J = 7.3, 2H, Ar-*H*), 8.17 (d, J = 9.3, 1H, Ar-*H*) and 13.40 (br, 1H, N*H*); ^{13}C-NMR ($CDCl_3$, 270 MHz) δ 14.58, 61.03, 113.42, 115.42, 119.75, 125.35, 127.08, 128.10, 128.85, 129.33, 130.54, 132.78, 150.88, 155.13 and 161.29; ν_{max} (KBr)/cm^{-1} 3280, 2921, 2852, 1678, 1460, 1308, 1290, 1275, 1227, 1207, 1119, 1107 and 1070; *m*/*z* (EI) 323 (M^+, 100%), 277 (M^+ − EtOH, 55), 249 (76) and 223 (13); λ_{max} (CH_2Cl_2)/nm 380 (log ε 4.11), 334 (4.26) and 253 (4.32); Anal. calcd. for $C_{17}H_{13}N_3O_2S$: C, 63.14; H, 4.05; N, 12.99; found: C, 62.96; H, 4.13; N, 12.96%.

Ethyl 8-(2-thienyl)pyrrolo[3,4-*e*][2,1,3]benzothiadiazole-6-carboxylate (4a). *Method A*: Catalyst, $Pd(PPh_3)_4$; base, sat. Na_2CO_3 aq. Yield 68%. Catalyst, $Pd(OAc)_2$, PPh_3; base, Et_3N. Yield 58%. Catalyst, $Pd(PPh_3)_2Cl_2$; base, sat. Na_2CO_3 aq. Yield 68%. Mp 205–206 °C; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 1.51 (t, J = 7.1, 3H, CH_3CH_2), 4.51 (q, J = 7.1, 2H, CH_3CH_2), 7.28 (dd, J = 5.2, 3.8, 1H, thiophene-β), 7.48 (dd, J = 5.2, 0.9, 1H, thiophene-β), 7.66 (d, J = 9.8, 1H, Ar-*H*), 8.23 (d, J = 9.8, 1H, Ar-*H*), 8.59 (dd, J = 3.8, 0.9, 1H, thiophene-α) and 9.82 (br, 1H, N*H*); ^{13}C-NMR (DMSO-d_6, 270 MHz) δ 14.38, 60.40, 112.01, 115.40, 118.81, 125.58, 126.19, 127.11, 127.40, 127.85, 129.08, 131.34, 150.07, 154.53 and 160.27; ν_{max} (KBr)/cm^{-1} 3300, 1666, 1462, 1276, 1254, 1196, 1120, 860, 850, 816 and 720; *m*/*z* (EI) 329 (M^+, 96%), 283 (M^+ − EtOH, 79) and 255 (100); λ_{max} (CH_2Cl_2)/nm 354 (log ε 4.30) and 273 (4.36); Anal. calcd. for $C_{15}H_{11}N_3O_2S_2$: C, 54.70; H, 3.37; N, 12.76; found: C, 54.30; H, 3.43; N, 12.65%.

Ethyl 8-(pyrrol-2-yl)pyrrolo[3,4-*e*][2,1,3]benzothiadiazole-6-carboxylate (5a). *Method B*: Catalyst, $Pd(PPh_3)_4$; base, sat. Na_2CO_3 aq. Yield 15%; mp 275–280 °C (decomp.); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.43 (t, J = 7.2, 3H, CH_3CH_2), 4.42 (q, J = 7.2, 2H, CH_3CH_2), 6.36 (s, 1H, pyrrole-α), 6.72 (s, 1H, pyrrole-β), 7.04 (s, 1H, pyrrole-β), 7.51 (d, J = 9.8, 1H, Ar-*H*), 8.12 (d, J = 9.8, Ar-*H*), 9.84 (br, 1H, N*H*) and 12.6 (br, 1H, N*H*); ^{13}C-NMR ($CDCl_3$, 400 MHz) δ 14.18, 61.00, 106.52, 110.35, 113.91, 115.68, 119.36, 120.19, 122.99, 123.32, 123.57, 126.13, 149.11, 150.75 and 154.68; ν_{max} (KBr)/cm^{-1} 3325, 2922, 2850, 1743, 1680, 1468 and 1020; *m*/*z* (EI) 312 (M^+, 74%), 266 (M^+ − EtOH, 63) and 238 (100); λ_{max} (CH_2Cl_2)/nm 372; Anal. calcd. for $C_{15}H_{12}N_4O_2S$: C, 57.68; H, 3.87; N, 17.94; found: C, 57.32; H, 3.91; N, 17.81%.

Ethyl 6-phenylpyrrolo[3,4-*e*][2,1,3]benzothiadiazole-8-carboxylate (3b). *Method A*: Catalyst, $Pd(PPh_3)_4$; base, sat. Na_2CO_3 aq. Yield 90%; mp 240–242 °C; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 1.53 (t, J = 7.1, 3H, CH_3CH_2), 4.56 (q, J = 7.1, 2H, CH_3CH_2), 7.42–7.61 (m, 3H, Ar-*H*), 7.55 (d, J = 9.5, 1H, Ar-*H*), 7.72 (d, J = 7.0, 2H, Ar-*H*), 7.90 (d, J = 9.5, 1H, Ar-*H*) and 10.13 (br, 1H, N*H*); ^{13}C-NMR (DMSO-d_6, 270 MHz) δ 14.38, 60.28, 116.07, 117.16, 117.37, 120.42, 125.32, 128.48, 128.81, 128.91, 130.02, 131.52, 149.43, 155.74 and 160.07; ν_{max} (KBr)/cm^{-1} 3278, 1670, 1448, 1302, 1271, 1203, 1024, 762 and 687; *m*/*z* (EI) 323 (M^+, 100%), 277 (M^+ − EtOH, 86) and 249 (55); λ_{max} (CH_2Cl_2)/nm 386 (log ε 3.96), 331 (4.28) and 302 (4.28); Anal. calcd. for $C_{17}H_{13}N_3O_2S$: C, 63.14; H, 4.05; N, 12.99; found: C, 63.10; H, 4.14; N, 13.07%.

Ethyl 6-(2-thienyl)pyrrolo[3,4-*e*][2,1,3]benzothiadiazole-8-carboxylate (4b). *Method A*: Catalyst, $Pd(PPh_3)_4$; base, sat. Na_2CO_3 aq. Yield 94%; mp 225–226 °C; ^{1}H-NMR (DMSO-d_6, 270 MHz) δ 1.45 (t, J = 7.1, 3H, CH_3CH_2), 4.46 (q, J = 7.1, 2H, CH_3CH_2), 7.28 (dd, J = 3.6, 5.2, 1H, thiophene-β), 7.58 (d, J = 9.5, 1H, Ar-*H*), 7.78 (dd, J = 5.2, 1.0, 1H, thiophene-β), 7.82 (dd, J = 3.6, 1.0, 1H, thiophene-α), 8.06 (d, J = 9.5, 1H, Ar-*H*) and 13.49 (br, 1H, N*H*); ^{13}C-NMR (DMSO-d_6, 270 MHz) δ 14.51, 60.63, 116.56, 117.36, 117.42, 120.47, 125.02, 125.19, 127.48, 127.76, 128.20, 131.21, 149.35, 155.76 and 160.16; ν_{max} (KBr)/cm^{-1} 1649, 1458, 1269, 1194, 1026, 825, 800 and 694; *m*/*z* (EI) 329 (M^+, 74%), 283 (M^+ − EtOH, 100) and 255 (60); λ_{max} (CH_2Cl_2)/nm 349 (log ε 4.26) and 251 (4.52); Anal. calcd. for $C_{15}H_{11}N_3O_2S_2$: C, 54.70; H, 3.37; N, 12.76; found: C, 54.37; H, 3.43; N, 12.59%.

Ethyl 6-(pyrrol-2-yl)pyrrolo[3,4-*e*][2,1,3]benzothiadiazole-6-carboxylate (5b). *Method B*: Catalyst, $Pd(PPh_3)_4$; base, sat. Na_2CO_3 aq. Yield 40%; mp 243–246 °C; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 1.54 (t, J = 7.2, 3H, CH_3CH_2), 4.56 (q, J = 7.2, 2H, CH_3CH_2), 6.44 (d, J = 3.5, 1H, pyrrole-α), 6.71 (s, 1H, pyrrole-β), 7.20 (s, 1H, pyrrole-β), 7.53 (d, J = 9.2, 1H, Ar-*H*), 7.87 (d, J = 9.2, 1H, Ar-*H*), 8.98 (br, 1H, N*H*) and 10.20 (br, 1H, N*H*); ^{13}C-NMR (DMSO-d_6, 270 MHz) δ 14.46, 60.25, 109.34, 109.57, 115.20, 115.46, 117.50, 118.76, 120.41, 121.66, 125.30, 125.91, 149.36, 155.89 and 160.17; ν_{max} (KBr)/cm^{-1} 3313, 2925, 2852, 1645, 1466, 1269 and 1211; *m*/*z* (EI) 312 (M^+, 64%), 266 (M^+ − EtOH, 100), 283 (80) and 194 (36); λ_{max} (CH_2Cl_2)/nm 348 and 250; Anal. calcd. for $C_{15}H_{12}N_4O_2S\cdot\frac{1}{2}H_2O$: C, 56.06; H, 4.08; N, 17.44; found: C, 56.09; H, 3.87; N, 17.14%.

General procedure of decarboxylation

A mixture of ester compounds (1.0 mmol) and potassium hydroxide (0.28 g, 5.0 mmol) was dissolved in ethylene glycol (10 cm^3) and toluene (2.5 cm^3). The solution was stirred at 170 °C for 2 h under Ar, then quenched. The resulting mixture was extracted with chloroform (3 × 30 cm^3) and the organic phase was dried and evaporated. The crude mixture was purified by silica gel column chromatography with the exclusion of light using hexane–chloroform as eluent. Most of the

decarboxylated compounds were fairly labile and insoluble, thus mps and absorption coefficients were not determined.

Pyrrolo[3,4-*e*][2,1,3]benzothiadiazole (6). Yield 82%; mp 158–159 °C; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 7.27 (d, J = 1.8, 1H, pyrrole-α), 7.33 (d, J = 9.5, 1H, Ar-*H*), 7.63 (dd, J = 9.5, 0.6, 1H, Ar-*H*), 7.79–7.81 (m, 1H, pyrrole-α) and 9.20 (br, 1H, N*H*); λ_{max} (CH_2Cl_2)/nm 370.

8-Phenylpyrrolo[3,4-*e*][2,1,3]benzothiadiazole (3c). Yield 40%; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 7.34 (d, J = 2.7, 1H, Ar-*H*), 7.37 (d, J = 9.3, 1H, Ar-*H*), 7.42–7.58 (m, 3H, Ar-*H*), 7.63 (d, J = 9.3, 1H, Ar-*H*), 8.14 (dd, J = 8.2, 1.2, 2H, Ar-*H*) and 9.19 (br, 1H, N*H*); *m*/*z* (EI) 251 (M^+, 100%); λ_{max} (CH_2Cl_2)/nm 396 and 300.

8-(2-Thienyl)pyrrolo[3,4-*e*][2,1,3]benzothiadiazole (4c). Yield 60%; ^{1}H-NMR (acetone-d_6, 270 MHz) δ 7.28 (dd, J = 5.1, 3.9, 1H, thiophene-β), 7.35 (d, J = 9.5, 1H, Ar-*H*), 7.56 (dd, J = 5.1, 1.0, 1H, thiophene-β), 7.57 (d, J = 2.9, 1H, pyrrole-α), 7.79 (d, J = 9.5, 1H, Ar-*H*), 8.50 (dd, J = 3.9, 1.0, 1H, thiophene-α) and 11.71 (br, 1H, N*H*); *m*/*z* (EI) 257 (M^+, 100%); λ_{max} (CH_2Cl_2)/nm 408, 333 and 263.

8-(Pyrrol-2-yl)pyrrolo[3,4-*e*][2,1,3]benzothiadiazole (5c). Yield 52%; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 6.39 (m, 1H, pyrrole-β), 6.56 (m, 1H, pyrrole-β), 7.06 (m, 1H, pyrrole-α), 7.19 (d, J = 2.8, 1H, pyrrole-α), 7.30 (d, J = 9.3, 1H, Ar-*H*), 7.60 (d, J = 9.3, 1H, Ar-*H*), 9.1 (br, 1H, N*H*) and 12.50 (br, 1H, N*H*); *m*/*z* (EI) 240 (M^+, 100%); λ_{max} (CH_2Cl_2)/nm 442 and 344.

6-Phenylpyrrolo[3,4-*e*][2,1,3]benzothiadiazole (3d). Yield 63%; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 7.37–7.42 (m, 2H, Ar-*H*), 7.53 (t, J = 7.6, 2H, Ar-*H*), 7.63–7.66 (m, 2H, Ar-*H*), 7.86–7.90 (m, 2H, Ar-*H*) and 9.21 (br, 1H, N*H*); *m*/*z* (FAB) 251 (M^+, 100%); λ_{max} (CH_2Cl_2)/nm 394, 305 and 254.

6-(2-Thienyl)pyrrolo[3,4-*e*][2,1,3]benzothiadiazole (4d). Yield 55%; ^{1}H-NMR (acetone-d_6, 270 MHz) δ 7.22 (dd, J = 3.6, 5.2, 1H, thiophene-β), 7.39 (d, J = 9.5, 1H, Ar-*H*), 7.52 (d, J = 3.6, 1H, thiophene-β), 7.56 (d, J = 5.2, 1H, thiophene-α), 7.92 (s, 1H, pyrrole-α), 8.15 (d, J = 9.5, 1H, Ar-*H*) and 11.82 (br, 1H, N*H*); *m*/*z* (EI) 257 (M^+, 100%); λ_{max} (CH_2Cl_2)/nm 403 and 319.

6-(Pyrrol-2-yl)pyrrolo[3,4-*e*][2,1,3]benzothiadiazole (5d). Yield 58%; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 6.35 (dd, J = 6.0, 2.6, 1H, pyrrole-β), 6.52–6.55 (m, 1H, pyrrole-β), 6.89–6.92 (m, 1H, pyrrole-α), 7.28 (d, J = 9.8, 1H, Ar-*H*), 7.69 (d, J = 2.6, 1H, pyrrole-α), 7.83 (d, J = 9.8, 1H, Ar-*H*), 9.56 (br, 1H, N*H*) and 10.53 (br, 1H, N*H*); *m*/*z* (EI) 240 (M^+, 100%); λ_{max} (CH_2Cl_2)/nm 412.

References

1 (*a*) J. Kürti, P. R. Surjàn and M. Kertesz, *J. Am. Chem. Soc.*, 1991, **113**, 9865; (*b*) M. Pomerantz, B. Chaloner-Gill, L. O. Harding, J. J. Tseng and W. J. Pomerantz, *J. Chem. Soc., Chem. Commun.*, 1992, 1672; (*c*) C. Kitamura, S. Tanaka and Y. Yamashita, *Chem. Lett.*, 1996, 63; (*d*) T. Yamamoto, Z. Zhou, T. Kanbara, M. Shimura, K. Kizu, T. Maruyama, Y. Nakamura, T. Fukuda, B. Lee, N. Ooba, S. Tomaru, T. Kurihara, T. Kaino, K. Kubota and S. Sasaki, *J. Am. Chem. Soc.*, 1996, **118**, 10389; (*e*) Q. T. Zhang and J. M. Tour, *J. Am. Chem. Soc.*, 1997, **119**, 5065.

2 (*a*) F. Wudl, M. Kobayashi and A. J. Heeger, *J. Org. Chem.*, 1984, **49**, 3382; (*b*) M. Kobayashi, N. Colaneri, M. Boysel, F. Wudl and A. J. Heeger, *J. Chem. Phys.*, 1985, **82**, 5717; (*c*) J. L. Brédas, *Synth. Met.*, 1987, **17**, 115; (*d*) T. L. Lambert and J. P. Ferraris, *J. Chem. Soc., Chem. Commun.*, 1991, 752; (*e*) S. Musmanni and J. P. Ferraris, *J. Chem. Soc., Chem. Commun.*, 1993, 172; (*f*) N. Ono, H. Hironaga, K. Simizu, K. Ono, K. Kuwano and T. Ogawa, *J. Chem. Soc., Chem. Commun.*, 1994, 1019; (*g*) T. Yamamoto, K. Sugiyama, T. Kushida, T. Inoue and T. Kanbara, *J. Am. Chem. Soc.*, 1996, **118**, 3930; (*h*) N. Ono, C. Tsukamura, Y. Nomura, H. Hironaga, T. Murashima and T. Ogawa, *Adv. Mater.*, 1997, **9**, 149.

3 (*a*) T. Murashima, K. Fujita, K. Ono, T. Ogawa, H. Uno and N. Ono, *J. Chem. Soc., Perkin Trans. 1*, 1996, 1403; (*b*) T. Murashima, R. Tamai, K. Fujita, H. Uno and N. Ono, *Tetrahedron Lett.*, 1996, **37**, 8391; (*c*) T. Murashima, R. Tamai, K. Nishi, K. Nomura, K. Fujita, H. Uno and N. Ono, *J. Chem. Soc., Perkin Trans. 1*, 2000, 995.

4 Y. Yamashita, M. Tomura and K. Imaeda, *Chem. Commun.*, 1996, 2021; Y. Yamashita, K. Ono, M. Tomura and K. Imaeda, *Chem. Commun.*, 1997, 1851; T. M. Barclay, A. W. Cordes, N. A. George, R. C. Haddon, M. E. Itkis, M. S. Mashuta, R. T. Oakley, G. W. Patenaude, R. W. Reed, J. F. Richardson and H. Zhang, *J. Am. Chem. Soc.*, 1998, **120**, 352; T. Suzuki, H. Fujii, Y. Yamashita, C. Kabuto, S. Tanaka, M. Harasawa, T. Mukai and T. Miyashi, *J. Am. Chem. Soc.*, 1992, **114**, 3034; T. M. Barclay, L. Beer, A. W. Cordes, R. T. Oakley, K. E. Preuss, N. J. Taylor and R. W. Reed, *Chem. Commun.*, 1999, 531; S. Tanaka and Y. Yamashita, *Synth. Met.*, 1995, **69**, 599; Y. Yamashita, K. Ono, S. Tanaka, K. Imaeda, H. Inokuchi and M. Sano, *J. Chem. Soc., Chem. Commun.*, 1993, 1803; T. Naito, H. Kobayashi, A. Kobayashi and A. E. Underhill, *Chem. Commun.*, 1996, 521; T. M. Barclay, A. W. Cordes, R. C. Haddon, M. E. Itkis, R. T. Oaklay, R. W. Reed and H. Zhang, *J. Am. Chem. Soc.*, 1999, **121**, 969; T. M. Barclay, A. W. Cordes, N. A. George, R. C. Haddon, R. T. Oakley, T. T. M. Palstra, G. W. Patenaude, R. W. Reed, J. F. Richardson and H. Zhang, *Chem. Commun.*, 1997, 873.

5 T. D. Lash, P. Chandrasekar, A. T. Osuma, S. T. Chaney and J. D. Spence, *J. Org. Chem.*, 1998, **63**, 8455.

6 M. Farnier and P. Fournari, *Bull. Soc. Chim. Fr.*, 1973, 351; R. Guilard, M. A. Aukauloo, C. Tardieux and E. Vogel, *Synthesis*, 1995, 1480.

7 (*a*) W. J. Thompson and J. Gaudino, *J. Org. Chem.*, 1984, **49**, 5237; (*b*) T. Ishiyama, M. Murata and N. Miyaura, *J. Org. Chem.*, 1995, **60**, 7508; (*c*) A. Giroux, Y. Han and P. Presit, *Tetrahedron Lett.*, 1997, **38**, 3841; (*d*) C. N. Johnson, G. Stemp, N. Anand, S. C. Stephen and T. Gallagher, *Synlett*, 1998, 1025; (*e*) C. Franc, F. Denonne, C. Cuisinier and L. Ghosez, *Tetrahedron Lett.*, 1999, **40**, 4555; (*f*) G. W. Gribble, M. G. Saulnier, J. A. Obaza-Nutaitis and D. M. Ketcha, *J. Org. Chem.*, 1992, **57**, 5891.

8 (*a*) H. A. M. van Mullekom, J. A. J. M. Vekemans and E. W. Meijer, *Chem. Commun.*, 1996, 2163; (*b*) H. A. M. van Mullekom, J. A. J. M. Vekemans and E. W. Meijer, *Chem. Eur. J.*, 1998, **4**, 1235.

9 K. Müllen and G. Wegner, *Electronic Materials: the oligomer approach*, Wiley–VCH Verlag, Weinheim, 1998, pp. 242–249.

10 J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1939, 1622; D. R. Coulson, *Inorg. Synth.*, 1972, **13**, 121; D. H. R. Barton, J. Khami, N. Ozbalik, M. Ramesh and J. C. Sarma, *Tetrahedron Lett.*, 1989, **30**, 4661.