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Synthesis and optical properties of novel blue fluorescent conjugated polymers

Martin Baumgarten* and Timucin Yüksel

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz.
E-mail: baumgart@mpip-mainz.mpg.de

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In the present paper we describe new approaches towards the synthesis of conjugated polymers with defined conjugation length, resulting in a blue or green fluorescence. The new approach reported here is to use 1,3-phenylene (type 1) and 10,10′-bianthrylene (type 2) bridges of conjugated segments such as stilbenes and thiophenes which can easily be varied to further change the optical properties.

Introduction

Conjugated or conducting polymers have been shown to possess high potential for application in advanced materials, *e.g.* in photonic, electronic or even magnetic devices.[1,2] While for conducting properties the search towards very small band gap continues, new applications of conjugated polymers in the field of materials science have increased the interest in, *e.g.*, a large band gap combined with high yield blue fluorescence or large dipole moments.[1–4] Recently, we have therefore concentrated our efforts on the control of conjugation in extended π-systems, using changes in topology and geometry.[5] Consequently, we developed a more general approach towards fully conjugated polymers with defined conjugation length, as given in Scheme 1. Thereby we combine the bifunctional alkyl-substituted *m*-phenylene (type 1) or bianthrylene (type 2) units with conjugated π-molecules/segments, *e.g.* stilbenes, phenyl substituted stilbenes, and bi- or terthiophenes which also carry solubilizing groups.

Here we describe synthetic approaches and some optical characterizations of *m*-phenylene and 9,10-bianthrylene bridged π-conjugated polymers to demonstrate the wide variety of these conjugated polymers for producing readily predictable optical properties.

Experimental

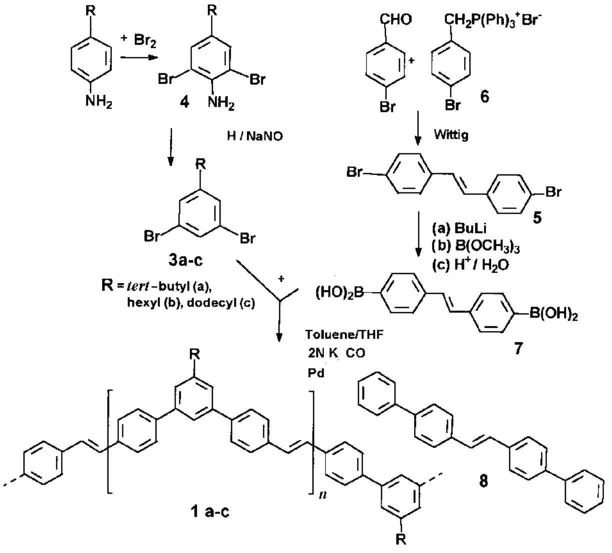
Synthesis

3,5-Dibromo-1-alkyl-benzenes (3a–c). The general procedure is exemplified for 3,5-dibromo-1-*tert*-butylbenzene **3a** (see Scheme 2 opposite).

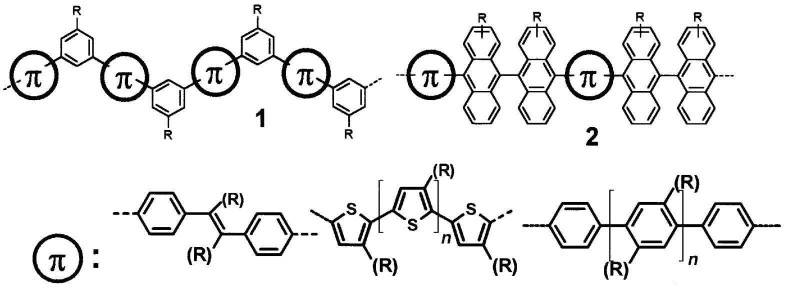
2,6-Dibromo-4-*tert*-butylaniline (4). According to the procedure of Ishida and Iwamura,[6] bromine (12 ml) was added within 1 h to a solution of *p*-*tert*-butylaniline (10.76 g; 72 mmol), in concentrated HCl (6.6 ml) and water (320 ml). The mixture was stirred for 3 h and the resulting slurry was then treated with a diluted aqueous solution of $NaHCO_3$, $Na_2S_2O_3$ and diethyl ether (300 ml). The organic layer was separated, washed with water and dried over $MgSO_4$. The concentrated, red-colored oily product was passed through a short column (silica-gel/CH_2Cl_2) to give 19.13 g (86%) of **4**.

^{1}H NMR [250 MHz, CD_2Cl_2, room temperature (RT)], δ (ppm) = 1.27 (s, 9H); 4.38 (br, 2H); 7.39 (s, 2H). ^{13}C NMR (62.5 MHz, CD_2Cl_2, RT), δ (ppm) = 30.5; 33.89; 122.02; 126.43; 130.17; 135.80. FD MS (70 eV): m/z (%) = 307.2 (100%).

3,5-Dibromo-1-*tert*-butylbenzene (3a). A solution of **4** (19 g; 61 mmol) in ethanol (100 ml), benzene (34 ml) and concen-



Scheme 2 Preparation of poly(*m*-terphenylenevinylene)s.



Scheme 1 Approaches to conjugated polymers with a defined conjugation length.

trated H_2SO_4 (9 ml) was treated with $NaNO_2$ (9 g) and then boiled under reflux for 3 h. After addition of diethyl ether, the organic layer was separated, washed with water, dried ($MgSO_4$) and chromatographed on silica-gel and light petroleum (bp 40–60 °C) (R_f 0.93), to give 7.13 g (51%) of nearly pure **3** as a slightly yellow product, mp 28 °C.

^1H NMR (250 MHz, CD_2Cl_2), δ (ppm) = 1.29 (s, 9H); 7.48 (s, 2H); 7.65 (s, 1H). ^{13}C NMR (62.5 MHz, CD_2Cl_2, RT), δ (ppm) = 31.51; 35.79; 124.06; 128.46; 131.77; 156.33. FD MS (70 eV): m/z (%) = 291.8 (100%).

3,5-Dibromo-1-hexylbenzene (3b). ^1H NMR (250 MHz, CD_2Cl_2, RT), δ (ppm) = 0.89 (t, 3H); 1.30 (m, 6H); 1.58 (q, 2H); 2.56 (t, ^3J = 7.5 Hz, 2H); 7.29 (s, 2H); 7.49 (s, 1H). ^{13}C NMR (62.5 MHz, CD_2Cl_2), δ (ppm) = 14.69; 23.37; 29.60; 31.78; 32.40; 36.12; 123.34; 131.10; 131.92; 147.91. FD MS (70 eV): m/z (%) = 320.2 (100%).

3,5-Dibromo-1-dodecylbenzene (3c). mp 53 °C. ^1H NMR (250 MHz, CD_2Cl_2, RT), δ (ppm) = 0.87 (t, 3H); 1.26 (m, 18H); 1.51 (m, 2H); 2.54 (t, 2H); 7.27 (s, 2H); 7.48 (s, 1H). ^{13}C NMR (62.5 MHz, CD_2Cl_2, RT), δ (ppm) = 14.71; 23.51; 29.89; 30.17; 30.32; 30.44; 30.47; 31.82; 32.73; 36.10; 123.31; 131.12; 131.90; 148.02. FD MS (70 eV): m/z (%) = 404.0 (100%).

***trans*-4,4′-Dibromostilbene (5).** In a 1000 ml three-necked flask 80 ml dimethyl sulfoxide (DMSO) is added dropwise to NaH (0.94 g; 39 mmol) under inert conditions. After the evolution of hydrogen has stopped the mixture is cooled to 10 °C and 4-bromobenzyltriphenylphosphonium bromide **6** (20 g; 39 mmol), which is dissolved in 100 ml DMSO, is added. The color of the mixture turns red. After 30 min stirring at room temperature a solution of 4-bromobenzaldehyde (7.22 g; 39 mmol) in 40 ml DMSO is added dropwise. The mixture is then heated slowly and boiled under reflux for 3 h and stirred for an additional 24 h at 80 °C. At room temperature the product precipitates and can be separated by filtration. Purification by dissolving in chloroform and washing the solution several times with water and recrystallization from chloroform gave 8.7 g (66%) of *trans*-4,4′-dibromostilbene; mp 182 °C.

^1H NMR (250 MHz, $CDCl_3/CCl_4$/25:75, RT), δ (ppm) = 6.97 (s, 2H); 7.31 (d, 4H); 7.43 (m, 4H). ^{13}C NMR (62.5 MHz, $CDCl_3/CCl_4$/25:75, RT), δ (ppm) = 122.15; 128.30; 128.50; 132.24; 136.17. FD MS (70 eV): m/z (%) = 338.0 (100%).

4,4′-bis(dihydroxyborylstilbene (7). At −70 °C *n*-butyllithium (80 ml; 1.6 M in hexane) was added dropwise to a solution of *trans*-4,4′-dibromostilbene (10 g; 29.5 mmol) in dry THF (400 ml). The resultant yellowish suspension was then stirred for additional 1 h at −70 °C. At −30 °C, trimethylborate (20.1 ml; 0.18 mol) was added within 15 min. The resulting pale yellowish solution was stirred for 15 h at room temperature.

After removing 50% of the solvent, 2 M HCl 100 ml, and *tert*-butylmethyl ether (100 ml) were added and the separated organic layer was washed with water carefully. After further removal of the solvent, the residue is recrystallized from *tert*-butylmethyl ether/propan-2-ol to give 6.98 g (89%) of **7**, as a white powder; mp 270 °C.

^1H NMR (250 MHz, $[^2H_6]$DMSO), δ (ppm) = 7.29 (s, 2H); 7.54 (d, 4H); 7.76 (d, 4H); 8.05 (s,br 4H). ^{13}C NMR (62.5 MHz, $[^2H_6]$DMSO), δ (ppm) = 124.8; 125.9; 129.26; 134.89; 138.84.

Polymers 1a–c. The general procedure for polymers **1a**–**f** is exemplified for **1a**.

Under light and oxygen protected conditions 3,5-dibromo-1-*tert*-butylbenzene (1 g; 2.48 mmol) and 4,4′-dihydroxyborylstilbene (0.7 g; 2.48 mmol) were dissolved in a mixture of toluene (15 ml), tetrahydrofuran (10 ml) and *n*-butanol (3 ml). To the stirred mixture a solution of K_2CO_3 in water (2 M; 10 ml) and tetrakis(triphenylphosphine)palladium(0) (0.18 g; 0.15 mmol) was added. The reaction mixture was warmed slowly to reflux temperature and boiled under reflux for 96 h. After that it was allowed to cool to room temperature and methylene chloride (100 ml) was added. After filtration, the filtrate was washed with water several times and dried over $MgSO_4$. Precipitation by adding methanol gives 0.92 g (99%) of the polymer (**1a**) as a bluish – grey solid.

^1H NMR (250 MHz, $CDCl_3$, RT), δ (ppm) = 1.39 (br, 18H); 1.46 (br, 9H); 7.10 (br, 42H). ^{13}C NMR (62.5 MHz, $CDCl_3$, RT), δ (ppm) = 30.40; 30.48; 33.81; 34.00; 122.31; 123.06; 123.18; 125.96; 126.51; 126.63; 127.14; 127.30; 127.51; 135.22; 135.43; 139.91; 140.08; 150.63; 151.23. UV–VIS (chloroform): λ_{max} = 348 nm. Gel permeation chromatography (GPC) or size exclusion chromatography (SEC, synonyms) (THF/polystyrene): number average molar mass (M_n) = 2124; weight average molar mass (M_w) = 4561; degree of polymerization (P_n) = 7; polydispersity (PDI) = 2.15.

Polymer **1b**, yield 74%. ^1H NMR (250 MHz, $CDCl_3$, RT), δ (ppm) = 0.9 (br); 1.33 (br); 1.62 (br); 2.60 (br); 7.00 (br). ^{13}C NMR (62.5 MHz, $CDCl_3$, RT), δ (ppm) = 13.09; 21.56; 21.62; 27.93; 28.13; 30.27; 30.64; 30.75; 34.76; 35.21; 121.73; 124.73; 125.17; 125.95; 126.16; 126.32; 126.48; 126.97; 127.20; 127.51; 127.67; 129.18; 130.99; 135.26; 135.38; 135.81; 137.94; 139.53; 140.16; 144.55. UV–VIS (chloroform): λ_{max} = 347 nm. GPC or SEC (THF/polystyrene): M_n = 3650; M_w = 7005; P_n = 11; PDI = 1.90.

Polymer **1c**, yield 74%. ^1H NMR (250 MHz, $CDCl_3$, RT), δ (ppm) = 0.8 (br); 1.18 (br); 1.59 (br); 2.63 (br); 7.10 (br). ^{13}C NMR (62.5 MHz, $CDCl_3$, RT), δ (ppm) = 13.11; 14.12; 21.68; 22.69; 28.35; 28.45; 28.55; 28.67; 29.36; 29.69; 30.64; 30.91; 31.92; 36.21; 123.24; 124.25; 125.93; 126.21; 126.51; 126.94;127.41;127.52; 127.68; 142.49. UV–VIS (chloroform): λ_{max} = 348 nm. GPC or SEC (THF/polystyrene): M_n = 5722; M_w = 8990; P_n = 14; PDI = 1.60.

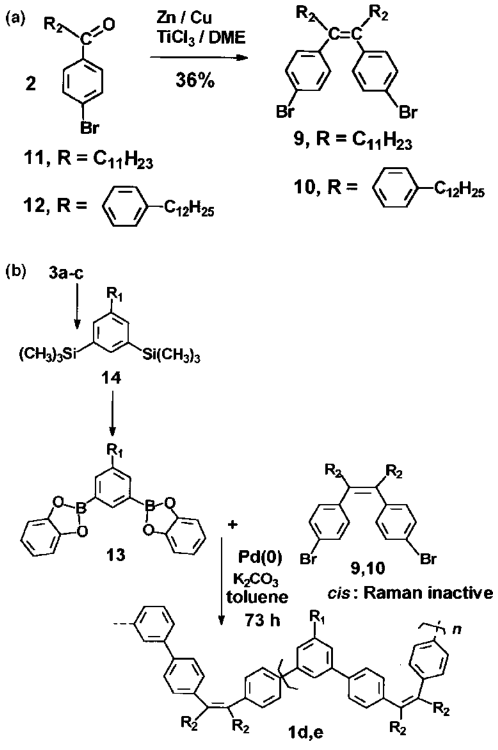
Substituted stilbenes **9** and **10** were prepared *via* the McMurry reaction (see Scheme 3 on next page).

4-bromododecanoylbenzene (11). To an ice cooled mixture of bromobenzene (38.64 g; 0.25 mol) and aluminum chloride (18.8 g; 0.14 mol) lauric acid chloride (26.92 g; 0.12 mol) was added dropwise within 1 h. The resultant red solution was stirred vigorously and slowly allowed to come to room temperature. The mixture was then warmed to 90 °C and stirred for 5 h at this temperature. After an additional 24 h stirring at room temperature the mixture was added to a mixture of ice/water (500 ml) and 50 ml conc. HCl. The mixture was first extracted with chloroform (200 ml three times). The separated organic layer was then washed with a solution of sodium hydroxide (2% in water) and then with water. After removing the solvent the residue was recrystallized from a mixture of methanol and acetone (2 : 5) to give a white powder (61%); mp 54 °C.

^1H NMR (250 MHz, CD_2Cl_2, RT), δ (ppm) = 0.88 (t, ^3J = 6.28 Hz, 3H); 1.27 (m, 16H); 1.63 (m, 2H); 2.92 (t, 2H); 7.59 (d, ^3J = 8.5 Hz, 2H); 7.80 (d, ^3J = 8.8 Hz, 2H). ^{13}C NMR (62.5 MHz, CD_2Cl_2, RT), δ (ppm) = 14.67; 23.48; 24.97; 30.06; 30.13; 30.27; 30.31; 30.41; 32.71; 39.30; 128.44; 130.32; 132.55; 136.76; 199.91. FD MS (70 eV): m/z (%) = 339.9 (100%).

α,α′-bis-undecyl-4,4′-dibromostilbene (9). Zinc–copper couple: zinc dust (19.6 g; 0.3 mol) and copper(II) sulfate were added to deoxygenated water (80 ml) and stirred at room temperature for 1 h. The black suspension was carefully filtered under argon, washed with deoxygenated water, diethyl ether and acetone. After that it was stored under inert conditions.

In a three-necked 250 ml flask, fitted with a condenser, dimethoxyethane–$(TiCl_3)_{1/2}$ (7.2 g; 25 mmol) and the zinc–



Scheme 3

copper couple (6.7 g) were suspended in deoxygenated dimethoxyethane (140 ml) and heated to reflux with vigorous stirring. After 2 h, 4-bromododecanoylbenzene (**11**) (2.1 g; 6.3 mmol) dissolved in 15 ml deoxygenated dimethoxyethane was added carefully through a cannula. The resulting mixture was boiled under reflux for 9 h and then left to cool to room temperature. After addition of pentane (200 ml) and filtration the solvent was removed. The resultant oily product was purified by column chromatography (SiO_2/CCl_4). Yield 49%, colourless oil.

^1H NMR (250 MHz, $CDCl_3$, RT), δ (ppm) = 0.86 (t, 6H); 1.23 (m, 36 H); 2.45(t, 4H); 6.74 (d, ^3J = 8.5 Hz, 4H); 7.16 (d, ^3J = 8.5 Hz, 4H). ^{13}C NMR (62.5 MHz, CD_2Cl_2, RT), δ (ppm) = 14.68; 23.49; 29.02; 30.14; 30.24; 30.37; 30.43; 32.72; 34.96; 120.17; 131.39; 131.88 138.76; 143.10. FD MS (70 eV): *m*/*z* (%) = 644.3 (100%). UV (ethanol): λ_{max} = 255 nm.

4-Bromo-4′-dodecylbenzophenone (12). In a three-necked 1000 ml flask fitted with a condenser and a dropping funnel 4-bromobenzoyl chloride (24.25 g; 0.098 mol) and dodecyl benzene (7.3 g; 0.033 mol) were mixed under dry and inert conditions. To this mixture trifluoromethanesulfonic acid (0.05 g; 0.3 mmol) was added carefully through a cannula and the whole warmed to reflux temperature slowly. After 20 h stirring, the mixture was allowed to cool down and methylene chloride (300 ml) added and the resultant solution washed carefully with water and then dried over magnesium sulfate. After removing the solvent, the residue was purified by column chromatography (SiO_2), using light petroleum (bp 40–60 °C and methylene chloride (5 : 4), followed by recrystallization of the product from methanol/tetrahydrofuran. Yield 59%, mp 111 °C.

^1H NMR (250 MHz, $CDCl_3$, RT), δ (ppm) = 0.86 (t, ^3J = 6.6 Hz, 3H); 1.24 (m, 18 H); 1.57 (m, 2H); 2.66 (t, ^3J = 7.85 Hz, 2H); 7.25 (d, ^3J = 8.17 Hz, 2H); 7.58 (m, 6H). ^{13}C NMR (62.5 MHz, CD_2Cl_2, RT), δ (ppm) = 16.51; 25.09; 31.70; 31.76; 31.87; 31.97; 32.05; 33.54; 34.33; 38.46; 129.56; 130.87; 132.61; 133.87; 133.94; 137.10; 139;16; 150.56; 197.74. FD MS (70 eV): *m*/*z* (%) = 428.4 (100%). Elemental analysis calculated: (%) C: 69.92, H: 7.75, Br: 18.61, O: 3.73; found: (%) C: 69.90, H: 7.69, Br: n.m., O: n.m.

4,4′-dibromo,-4″,4‴-bis-dodecyltetraphenylethylene (10). Zinc–copper couple (4.9 g; 69 mmol) and $TiCl_3$ (18 ml; 1 M in methylene chloride) were added to deoxygenated dimethoxyethane (100 ml) under inert conditions. The mixture was stirred and heated to reflux for 2.5 h. A solution of 4-bromo-4′-dodecylbenzophenone (**12**) (1.93 g; 4.5 mmol) in deoxygenated dimethoxyethane (10 ml) was added through a cannula and the resulting mixture was boiled under reflux for an additional 20 h. The solvent was removed and the residue was dissolved in hexane (150 ml) and filtrated over a thin pad of florisil to remove inorganic salts. The filtrate was concentrated and, after addition of chloroform, washed with water and dried over sodium sulfate. Purification by column chromatography (SiO_2/light petroleum (bp 40–60 °C) gave 26% of a white powder; mp 92 °C.

^1H NMR (500 MHz, $CDCl_3$, RT), δ (ppm) = 0.86 (t, ^3J = 6.7Hz, 6H); 1.25 (m, 36 H); 1.57 (m, 4H); 2.47 (m, 4H); 6.83 (m, 12H); 7.17 (d, ^3J = 8.5 Hz, 2H); 7.21 (d, ^3J = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, RT), δ (ppm) = 14.56; 23.12; 29.65; 29.69; 29.79; 29.92; 30.09; 31.58; 32.35; 36.00; 120.92; 120.77; 128.15; 128.37; 131.15; 131.38; 131.43; 131.49; 133.35; 133.39. FD MS (70 eV): *m*/*z* (%) = 827.0 (100%). UV–VIS (ethanol): λ_{max} = 326 nm. Elemental analysis: calculated: (%) C: 72.63, H: 8.05, Br: 19.33; found: (%) C: 72.57, H: 8.07, Br: n.m.

3,5-bis(trimethylsilyl)-*tert*-butylbenzene (14). Within 1 h a solution of 1,3-dibromo-5-*tert*-butylbenzene (3 g; 0.01 mol) in dry THF (10 ml), was added to a mixture of magnesium (0.56 g; 0.23 mol), trimethylsilyl chloride and THF (4 ml). To initiate and to complete the reaction, the mixture was heated to reflux for 18 h. After cooling the mixture to room temperature, hexane (60 ml) was added and the whole was washed with a saturated solution of ammonium chloride. The organic layer was collected and poured into a short column which was filled with silica-gel. Drying over magnesium sulfate and removing the solvent the filtrate gave 3,5-bis(trimethylsilyl)-*tert*-butylbenzene (**14**) as a colorless oily product (85%).

^1H NMR (250 MHz, $CDCl_3$, RT), δ (ppm) = 0.33 (s, 18H); 1.39 (s, 9H); 7.54 (s, 1H); 7.60 (d, 2H). ^{13}C NMR (62.5 MHz, CD_2Cl_2, RT), δ (ppm) = 0.41; 32.51; 35.93; 131.76; 136.72; 140.05; 150.31. EI-MS (70 eV): *m*/*z* (%) = 263 (100% M − CH_3), 279 (20% M^+), 247 (10% M − $2CH_3$). Elemental analysis: calculated: (%) C: 68.98, H: 10.85, Si: 20.16; found: (%) C: 69.09, H: 10.76, Si: n.m.

5-*tert*-Butyl-1,3-phenylenebis(1,3,2-benzodioxaborol) (13). 1,3-bis(trimethylsilyl)-*tert*-butylbenzene (**14**) (1.53 g; 5.5 mmol) was dissolved in dry methylene chloride (29 ml). At −78 °C a solution of boron tribromide (2.75 g; 11 mmol) in methylene chloride (10 ml) was added slowly within 1 h. After the reaction mixture reached room temperature it was gently heated up to reflux, which was maintained for 25 h. At 0 °C 1,2-dihydroxybenzene (1.22 g; 11 mmol) was added in one portion and the mixture was stirred at room temperature for a further 24 h. The precipitated product was filtered off and crystallized twice from chloroform. Yield (79%), mp 168 °C.

^1H NMR (250 MHz, CD_2Cl_2, RT), δ (ppm) = 1.45 (s, 9H); 7.14 (m, 4H); 7.34 (m, 4H); 8.32 (d, 2H); 8.61 (s, 1H). ^{13}C NMR (62.5 MHz, CD_2Cl_2, RT), *δ* (ppm) = 31.80; 35.87; 110.47; 113.27; 123.64; 132.63; 136.43; 139.64; 149.34. FD MS (70 eV): *m*/*z* (%) = 370.02 (100%). Elemental analysis: calculated: (%) C: 71.41, H: 5.45, B: 5.84, O: 17.30; found: (%) C: 71.49, H: 5.42, B: n.m., O: n.m.

5-Hexyl-1,3-phenylenbis(1,3,2-benzodioxaborol) (13b). Yield (49%); mp 136 °C.

^1H NMR (250 MHz, $CDCl_3$, RT), δ (ppm) = 0.88 (t, 3H); 1.32 (m, 6H); 1.64 (m, 2H); 2.73 (t, 2H); 7.12 (m, 4H); 7.33 (m, 4H); 8.07 (d, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$, RT), δ (ppm) = 14.49; 22.99; 29.43; 31.95; 32.12; 36.29; 112.98; 123.23; 139.23; 139.67; 143.01; 148.92. FD MS (70 eV): *m*/*z* (%) = 398.10 (100%). Elemental analysis: calculated: (%) C: 72.42, H: 6.08, B: 5.43, O: 16.08; found: (%) C: 72.26, H: 5.98, B: n.m., O: n.m.

Polymer 1d: Poly[(5-*tert*-butyl-*m*-phenylene)-*Z*-(α,α′-diundecylethenylene)(undecylstilbene)]. According to the general procedure as given for polymers **1a**–**f**, 5-*tert*-butyl-1,3-phenylenebis(1,3,2-benzodioxaborol) (**13**) (1 g; 2.7 mmol) and 4,4′-dibromo-α,α′-diundecylstilbene (**9**) (1.75 g; 2.7 mmol) were used in a mixture of toluene (15 ml), THF (10 ml) and *n*-butanol (5 ml). After adding a solution of potassium carbonate (10 ml; 2 M) and tetrakis(triphenylphosphino)palladium catalyst (0.18 g; 1.6 mmol) the mixture was boiled under reflux for 83 h and worked up as already described. Yield 90%.

^{1}H NMR (250 MHz, $CDCl_3$, RT), δ (ppm) = 0.85 (m, br); 1.24 (m, br); 2.55 (m, br); 6.60 (m, br). ^{13}C NMR (62.5 MHz, $CDCl_3$, RT), δ (ppm) = 13.11; 21.67; 27.57; 28.35; 28.52; 28.66; 30.42; 30.90; 121.66; 125.22; 126.39; 127.62; 129.09; 136.92; 137.42; 139.88; 141.40. UV (methylene chloride): λ_{max} = 265 nm. GPC or SEC (THF/polystyrene): M_n = 3181; M_w = 6405; P_n = 5; PDI = 2.00.

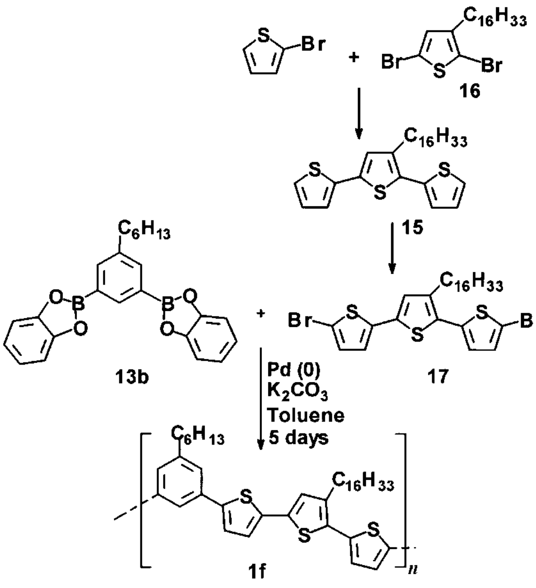
Polymer 1e: Poly(5-hexyl-*m*-phenylene)-*Z*-(α,α′-bis(4,4′-dodecylphenyl)-α,α′-diphenylethenylene. 4,4′-Dibromo,-4″,4‴-bis(dodecyl)tetraphenylethylene (10) (0.2 g; 0.24 mmol) and 5-hexyl-1,3-phenylene-(1,3,2-benzodioxaborol) (0.09 g; 0.24 mmol) were dissolved in toluene (3 ml), THF (2 ml) and *n*-butanol (1 ml). After addition of a solution of sodium carbonate (1 ml; 2 M) and tetrakis(triphenylphosphino)palladium catalyst (4 mg), the reaction mixture stirred for 80 h at reflux temperature. Work up gave 89% of the polymer.

^{1}H NMR (250 MHz, [$^2H_8$]THF, RT), δ (ppm) = 0.88 (m, br); 1.30 (m, br); 156 (m, br); 253 (m, br); 6.70 (m, br). ^{13}C NMR (62.5 MHz, [$^2H_8$]THF, RT), δ (ppm) = 13.11; 22.13; 22.20; 23.31; 23.63; 23.95; 24.27; 24.59; 28.95; 29.04; 29.26; 31.26; 31.37; 31.51; 35.08; 125.31; 125.58; 126.52; 127.05; 128.03; 130.85; 131.35; 138.58; 139.90; 140.61; 140.89; 143.17. UV-VIS (chloroform): λ_{max} = 338 nm. GPC or SEC (THF/polystyrene): M_n = 3183; M_w = 6305; P_n = 4; PDI = 1.9.

3-Hexadecyl-2,2′;5′,2″-terthiophene (15). The alkylated terthiophene **15** was prepared by the coupling reaction of 3-alkyl-2,5-dibromoterthiophene **16** with two equivalents of 2-bromothiophene (see Scheme 4 above) according to a procedure described by Delabouglise *et al.*[15] In turn, 3-hexadecylthiophene was used as precursor for **16** and was characterized as follows.

^{1}H NMR (250 MHz, $CDCl_3$, RT), δ (PPM) = 0.87 (t, ^3J = 6.9Hz, 3H); 1.24 (m, 22H); 1.54 (m, 2H); 2.57 (t, ^3J = 7.8 Hz, 2H); 6.93 (m, 1H); 7.20 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$, RT), δ (PPM) = 14.54; 23.14; 29.76; 29.89; 30.01; 30.07; 30.97; 32.34; 120.14; 125.42; 128.70; 143.68. FD MS (70 eV): *m*/*z* (%) = 306.6 (100%). Elemental analysis: calculated: (%) C: 77.85, H: 11.76, S: 10.39; found: (%) C: 77.89, H: 11.65, S: 10.32.

2,5-Dibromo-3-hexadecylthiophene (**16**) was characterized as follows. ^{1}H NMR (250 MHz, $CDCl_3$, RT), δ (ppm) = 0.86 (t, ^3J = 6.6 Hz, 3H); 1.24 (m, 22H); 1.48 (m, 2H); 2.45 (t, ^3J = 7.7 Hz, 2H); 6.75 (s, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$, RT), δ (ppm) = 14.54; 23.11; 29.50; 29.78; 29.87; 29.94; 29.98; 30.11; 32.34; 108.30; 131.35; 143.39. FD MS (70 eV): *m*/*z* (%) = 466.2 (100%). Elemental analysis: calculated: (%) C: 51.51, H: 7.35, S: 6.87, Br: 34.27; found: (%) C: 50.05, H: 7.85, S: 5.98, Br: n.m.



Scheme 4 Synthesis of polymer **1f**.

Finally, **15** was produced: diethyl ether (30 ml) and magnesium (2.4 g; 96 mmol) were put into a 500 ml three-necked flask fitted with a condenser and a dropping funnel. The apparatus was purged with nitrogen several times and 2-bromothiophene (15.9 g; 96 mmol), which was dissolved in diethyl ether (30 ml), was added dropwise under stirring within 1 h. After all the magnesium was dissolved, the reaction mixture was stirred for further 2 h at room temperature. The resultant Grignard compound was then transferred into a dropping funnel and added into an ice cooled mixture of 2,5-dibromo-3-hexadecylthiophene (**16**) (15 g; 32 mmol), diethyl ether (50 ml) and Ni(dppp)Cl_2 (0.71 g; 1.3 mmol) within 20 min under vigorous stirring. The reaction mixture was kept at room temperature. After 24 h the mixture was added to water and the organic layer was separated and washed with water carefully and dried over magnesium sulfate. After removing the solvent the residue was chromatographed [SiO_2/light petroleum (bp 40–60 °C)]. Yield 55%, mp 39 °C.

^{1}H NMR (250 MHz, CD_2Cl_2, RT), δ (ppm) = 0.88 (t, ^3J = 6.7Hz, 3H); 1.26 (m, 26H); 1.59 (m, 2H); 2.73 (t, 2H); 7.00 (m, 7H). ^{13}C NMR (62.5 MHz, CD_2Cl_2, RT), δ (ppm) = 14.66; 23.47; 30.05; 30.14; 30.26; 30.36; 30.47; 31.30; 32.71; 124.33; 125.19; 126.15; 126.64; 128.67; 135.75; 136.58; 137.90; 141.27. FD MS (70 eV): *m*/*z* (%) = 472.5 (100%). UV-VIS (chloroform): λ_{max} = 346 nm. Elemental analysis: calculated: (%) C: 71.13, H: 8.53, S: 20.34; found: (%) C: 73.51, H: 8.50, S: 18.70.

Dibromohexadecylterthiophene (17). A three-necked flask (250 ml) was fitted with a condenser and a dropping funnel and purged with nitogene. After addition of *N*-bromosuccinimide (5 g; 0.011 mol) in chloroform (35 ml), 3-hexadecyl-2,2′;5′,2″-terthiophene (**5**) (3.8 g; 0.021 mol) and concentrated acetic acid (35 ml) were added and the whole mixture was stirred for 8 h at room temperature. Chloroform (50 ml) was then added to the reaction mixture. The solution was washed with a solution of sodium hydrogencarbonate and water. The organic layer was separated and the solvent was evaporated. The residue was puified by column chromatography (SiO_2/heptane). Recrystallization from ethanol gave 98% of a yellow powder (mp 62 °C).

^{1}H NMR (250 MHz, CD_2Cl_2, RT), δ (ppm) = 0.88 (t, ^3J = 6.6 Hz, 3H); 1.27 (m, 26H); 1.56 (m, 2H); 2.68 (t, 2H); 6.89 (d, ^3J = 4.08 Hz, 1H); 6.92–6.94 (d, ^3J = 3.77 Hz, 1H); 6.97 (s, 1H); 6.99–7.01 (d, ^3J = 3.77 Hz, 1H); 7.04–7.06 (d, *J* = 3.77 Hz, 1H). ^{13}C NMR (62.5 MHz, CD_2Cl_2, RT), δ (ppm) = 14.70; 23.50; 30.01; 30.18; 30.22; 30.36; 30.51; 32.74; 124.86; 127.05; 129.70; 131.52; 135.21; 137.98; 139.29; 141. FD MS (70 eV): *m*/*z* (%) = 630.6 (100%). UV-VIS (chloroform): λ_{max} = 357 nm. Elemental analysis: calculated:

(%) C: 52.77 H: 6.39, S: 15.25, Br: 25.34; found: (%) C: 52.56, H: 6.03, S: 15.25, Br: 26.08.

Polymer 1f: Poly[(5-hexyl-*m*-phenylene)-1-(3-hexadecyl)terthiophenylene]. According to the general procedure for polymers **1a–f** 5-hexyl-1,3-phenylene-(1,3,2-benzodioxaborol) (0.4 g; 1 mmol), 5,5″-dibromo-3-hexadecylterthiophene (0.63 g; 1 mmol), palladium catalyst (90 mg) and potassium carbonate (1 ml; 2 M) were boiled under reflux for 83 h in a mixture of toluene (14 ml), THF (10 ml) and *n*-butanol (1 ml). Work up gave 90% of polymer **1f**.

^{1}H NMR (250 MHz, $CDCl_3$, RT), δ (ppm) = 0.84 (m, br); 1.23–150 (m, br); 169 (m, br); 2.66–2.79 (m, br); 7.05–7.62 (m, br). ^{13}C-NMR (62.5 MHz, $CDCl_3$, RT), δ (ppm) = 13.13; 21.64; 21.68; 28.09; 28.37; 28.52; 28.67; 28.72; 29.46; 30.40; 30.74; 30.92; 34.97; 122.71; 123.02; 123.34; 123.92; 125.48; 128.75; 133.60; 133.99; 134.54; 135.58; 139.35; 141.69; 143.37. UV–VIS (chloroform): λ_{max} = 403 nm. GPC or SEC (THF/polystyrene): M_n = 4487; M_w = 6828; P_n = 7; PDI = 1.5.

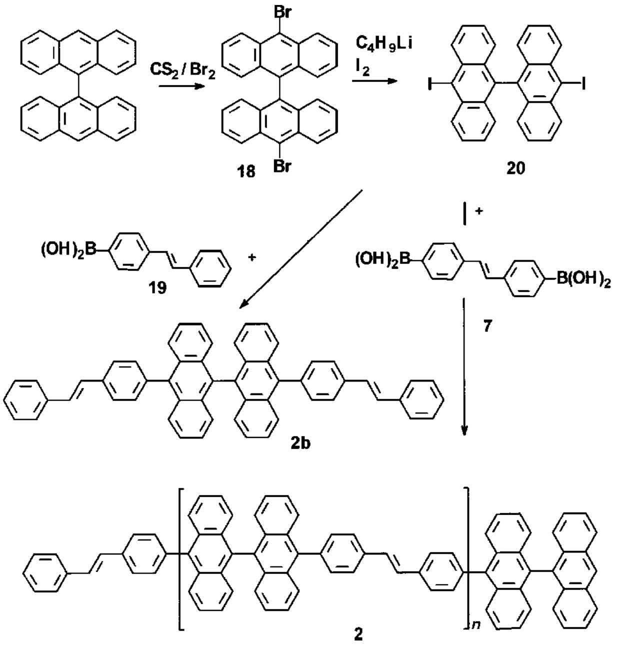
9,9′-Bianthryl. Anthrone (7 g; 0.036 mol) and zinc (7 g; 0.11 mol) were suspended in hot acetic acid (45 ml). To this mixture concentrated HCl (15 ml) was added. After stirring for 15 min at room temperature the reaction was kept refluxing for 1 h.

The precipitate was then filtered off, washed with water/HCl, dried and recrystallized from acetic anhydride, to give 0.97 g of 9,9′-bianthryl (15%).

^{1}H NMR (250 MHz, $C_2D_2Cl_4$, RT), δ (ppm) = 7.07–7.20 (m, 8H); 7.42–7.50 (m, 4 H); 8.14–8.20 (m, 4H); 8.70 (s, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$, RT), δ (ppm) = 125.80; 126.30; 127.27; 127.70; 129.05; 132.15; 132.18; 133.35. FD MS (70 eV): *m*/*z* (%) = 354.30 (100%).

10,10′-Dibromo-9,9′-bianthryl (18). 9,9′-Bianthryl (1.2 g; 3.4 mmol) was dissolved in CS_2 (70 ml) and then treated with bromine (1.2 g; 7.5 mmol) in CS_2 (30 ml). After 30 h stirring at room temperature the solvent was removed. Recrystallization of the residue from ethanol gave 1.6 g (92%) of **18** (see Scheme 5 below).

^{1}H NMR (250 MHz, $CDCl_3$, RT), δ (ppm) = 7.40 (m, 8H); 7.59 (m, 4 H); 8.73. ^{13}C NMR (62.5 MHz, $CDCl_3$, RT), δ (ppm) = 124.36; 126.76; 127.53; 127.66; 128.53; 130.83; 132.60; 133.62. FD MS (70 eV): *m*/*z* (%) = 512.2 (100%).



Scheme 5 Synthesis of poly[(bianthrylene)stilbenylene].

10,10′-Distilbenylbianthryl (2b). 10,10′-Dibromo-9,9′-bianthryl (**18**) (0.65 g; 1.27 mmol) and 4-dihydroxyborylstilbene (**19**) (0.6 g; 2.68 mmol) were mixed with toluene (15 ml), THF (10 ml), butanol (3 ml) and potassium carbonate (10 ml; 2 M). After addition of palladium catalyst (0.3 g; 0.26 mmol) the mixture was heated to reflux temperature and stirred for 80 h. The crude material was dissolved in tetrachloroethane (100 ml) and filtered through a short layer of florisil. The filtrate was then washed with water and dried over magnesium sulfate. Purification of the crude product by column chromatography (SiO_2/light petroleum: chloroforme (4 : 1)) gave a yellow powder. Crystallization from tetrachloroethane gave a product yield of 82%, mp 285 °C.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 393 K), δ (ppm) = 7.11–7.14 (m, 2H); 7.19–7.23 (m, 4 H); 7.28 (m, 8H); 7.38 (m, 8H); 7.59 (m, 8H); 7.82 (m, 8H). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 393 K), δ (ppm) = 126.46; 126.76; 127.84; 128.24; 129.26; 129.60; 130.04; 131.17; 131.41; 132.31; 132.47; 133.07; 134.52; 137.61; 138.40; 138.73; 139.49. FD MS (70 eV): *m*/*z* (%) = 710.3 (100%). UV–VIS (chloroform): λ_{max} = 403 nm. Elemental analysis: calculated: (%) C: 94.41, H: 5.39; found: (%) C: 93.97, H: 6.02.

10,10′-Diiodo-9,9′-bianthryl (20). 10,10′-Dibromo-9,9′-bianthryl (1 g; 2 mmol) was dissolved in dried diethyl ether (20 ml) under inert conditions. At room temperature butyllithium (3.3 ml; 1.6 M in hexane) was added within 30 min. The mixture was stirred for further 15 min at room temperature and then a solution of iodine (1.7 g; 6.7 mmol) dissolved in diethyl ether (10 ml) was added. After 2 h the resultant brownish solution was diluted with diethyl ether (100 ml) and then washed with sodium thiosulfate (25% in water). The organic phase was dried with sodium sulfate. After evaporation of the solvent, the residue was purified by crystallization from a mixture of tetrachloroethane and chloroform. Yield 41%.

1H NMR (250 MHz, $CDCl_3$, RT), δ (ppm) = 7.25 (m, 8H); 7.45 (m, 4 H); 8.59 (m, 4H). FD MS (70 eV): *m*/*z* (%) = 606.24 (100%).

Poly(bianthrylenestilbenylene) (2). According to general procedure for polymers **1a–f**, 10,10′-dibromo-9,9′-bianthryl (0.3 g; 0.6 mmol) and 4,4-bis(dihydroxyboryl)stilbene (0.16 g; 0.6 mmol), in a mixture of THF (6 ml), toluene (2 ml) and potassium carbonate (2 ml; 2 M) and after addition of palladium catalyst (3 mg), were refluxed for 98 h. Work up gave a 60% yield of polymer **2**.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 393 K), δ (ppm) = 7.08–7.12 (m, br); 7.32 (m, br); 7.49 (m, br); 7.72 (m, br); 7.76 (m, br). UV–VIS (methanol): λ_{max} = 405 nm.

Results and discussion

To obtain access to polymers of type **1** and type **2** the palladium-induced boronic acid coupling according to Suzuki[8] was considered. As shown in Scheme 2 for polymers of type **1** this route implies access to the 1,3-dibromo-5-alkylbenzenes **3a–c** or 1,3-diboronic acid derivatives and mono- or dibromo (or their mono- and diboronic acid) π-moieties.[9] Even more additional solubilizing groups had to be considered to obtain soluble polymers and good film-forming properties. In the first approach the synthesis of dibromostilbenes **5** was achieved by Wittig coupling[10] of the 4-bromaldehyde with the phosphonium salt **6**. The 3,5-dibromo-1-alkylbenzenes **3a–c**, were synthesized from the appropriate alkylphenylamine according to Ishida and Iwamura.[6,11] Since it turned out to be difficult to obtain the diboronic acid of the phenyl unit, the dibromostilbene moiety was transferred to the diboronic acid **7** and coupled (Pd induced) to the poly(*m*-terphenylenevinylene).

Table 1 Comparison of M_w, M_n(GPC) and P_n(NMR) for different *m*-phenylene coupling units

	$10^{-3}\ M_w$/g mol^{-1}	$10^{-3}\ M_n$/g mol^{-1}	M_w/M_n	P_n	Yield (%)
1a	4.561	2.124	2.1	7	99
1b	7.005	3.650	1.9	11	74
1c	8.990	5.722	1.6	14	87

The preparation of polymers **1a–c** by palladium-induced boronic acid coupling strongly depends on the solvent mixtures.[12] We found that the yields were best when a combination of toluene/THF/*n*-butanol (5 : 3 : 1) with aqueous potassium carbonate was used. The degree of polymerization was controlled by GPC and NMR and demonstrates further the dependence on the length of the solubilizing alkyl groups R (*t*-butyl, *n*-hexyl, *n*-dodecyl, see Table 1) and the purity of the boronic acid derivative. Upon using R = *n*-dodecyl, up to now, the highest degree of polymerization, $M_w = 9000$, $M_n = 5700$, was found (see Table 1). Obviously the amount of catalyst has only a minor influence on the polymerization, since we used 1 to 4 mol% of the catalyst and did not find any remarkable difference in the degree of polymerization.

Although the degree of polymerization differed, and thus the length of intact conjugation, as supposed, the 1,3-phenylene bridging interrupts the conjugation and the optical absorption maxima of the polymers **1a–c** were identical, with $\lambda_{max} = 348$ nm (Table 2). This holds also for the fluorescence and excitation emission spectra presented for **1c** both as solution and film cast on quartz in Fig. 1. For **1a–c** the transition from solution to film is combined with an increased Stokes shift and further bathochromically moved excitation maxima, presumably due to some intermolecular π-interaction. Thus the experiments confirm the suggested model, limiting the effective conjugation to a 4,4′-diphenyl substituted stilbene (**8**), independent of the number of repeat units. This is in complete agreement with model calculations by the AM1-CI/PPP approach (Table 2).

Table 2 Fluorescence and excitation emission data for polymers **1a-c** and absorption and fluorescence data from AM1-CI and PPP calculations for a 4,4′-diphenylstilbene (**8**)

	Absorption/exc. emission		Fluorescence/solution	
Compounds	λ_{max} (nm)	$E_{a,max}$ eV	λ_{max} nm	$E_{f,max}$ eV
1a	348[a]	3.57	416[b] 437	2.99 2.85
1b	348[a]	3.57	416[b] 437	2.99 2.85
1c	348[a]	3.57	416[b] 436	2.99 2.85
8 (AM1)	340	3.65	421	2.94
8 (PPP)	335	3.70	379	3.27

Solvents: [a] $CHCl_3$. [b] CH_2Cl_2. Underlined values denote absolute maxima.

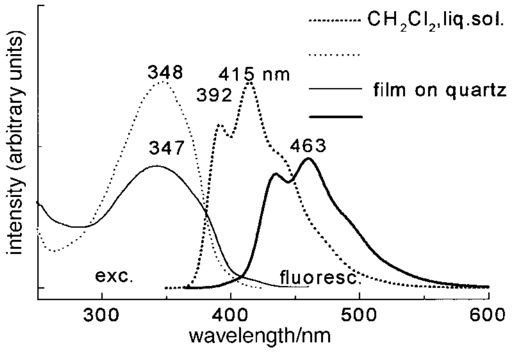


Fig. 1 Fluorescence and excitation (exc.) emission spectra for **1c** in methylene chloride solution and for a spin-coated film on quartz.

To further verify this approach, and to increase the solubility of 5,6-alkyl and 5,6-alkylphenyl substituted stilbenes, compounds **9** and **10** were considered. They can be synthesized by the McMurry[13] reaction of the ketone precursors **11** and **12**. Interestingly, unlike the Wittig coupling where *trans* products are formed, we found sole formation of the *cis* products for **9** (and very minor *trans* configuration for **10**) as evidenced by Raman spectroscopy, where they did not show any signal where only the symmetric (*trans*) compounds contribute (as checked for **5**). The transformation into the diboronic acids, on the other hand, seemed more difficult to achieve than for a naked stilbene.[9] Therefore we prepared the 1,3-diboronic acid ester **13** of the phenyl coupling unit **3b**,[14] *via* a Grignard reaction (Scheme 3a,b) to a di(trimethylsilane) intermediate **14**. Then Suzuki coupling of **9** and **10** with **13** to polymers **1d** and **1e** proceeded smoothly in high yield.

For **1d** and **1e** the optical absorptions and excitation spectra (Figs. 2(a) and 2(b), respectively) are clearly dominated by the *cis* arrangement, leading to hypsochromic shifts compared with the *trans* stilbene moieties in **1a–c**. However, the fluorescences still appear in the range attributable to the *trans* stilbene, with nearly the same λ_{max} ($\lambda_{exc.} = 447$ nm) for **1d** (alkylated stilbene moiety) while the fluorescence maximum of the dialkylphenyl substituted, polymer **1e** is further shifted to

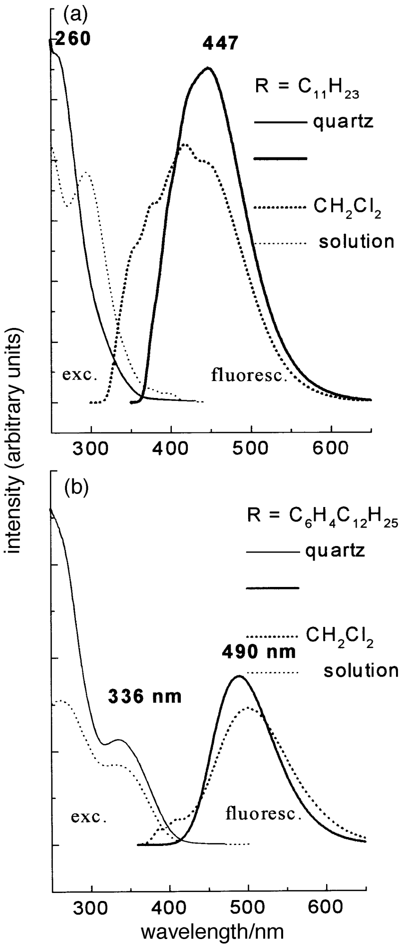


Fig. 2 Fluorescence and exc. emission spectra in methylene chloride solution and for spin-coated films on quartz for (a) **1d** and (b) **1e**.

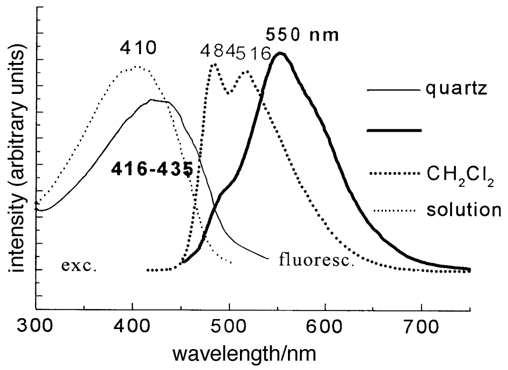


Fig. 3 Fluorescence and exc. emission spectra in methylene chloride solution and for a spin-coated film on quartz for **1f**.

the region of green light ($\lambda_{exc.} = 500$ (sol.) and 490 nm (quartz)). This effect can easily be explained by a very small amount of *trans*-configurations (1–5%) which act as an energetic sink within the polymer. Although we tried the photochemical *cis* to *trans* transformation we have not yet achieved this approach in considerable yield. Remarkably, it should be noted that the transition from solution to a thin film on quartz now no longer exhibits large changes in the excitation maxima. The substitution of the ethenylene units seems to hinder further intermolecular aggregation.

In a further extension of type **1** polymers we synthesized an alkylated terthiophene (**15**) by coupling 3-alkyl-2,5-dibromothiophene **16** with two equivalents of 2-bromothiophene.[15] The bromination of the obtained terthiophene succeeded by addition of *N*-bromosuccinimide to a solution of terthiophene in chloroform and acetic acid. The desired dibromoterthiophene **17** was purified by column chromatography and coupled with the boronic acid ester **13** (Scheme 4) to the corresponding polymer **1f**. The alkyl groups lead to high solubility and good film forming properties (*e.g.* spin coating) of the polymer. Here the longest absorption wavelength so far was measured ($\lambda_{max} \sim 420$–430 nm) and the fluorescence now occurs in the green spectral region (500–550 nm) (Fig. 3). Here again the ease in shifting the absorption and fluorescence properties can be recognized, since the conjugated segment can be diminished or extended by one thiophene unit.

According to the general approach outlined in Scheme 1 we also synthesized compounds of type 2. Since the steric demands for anthryl substitution are much larger than for phenyl substituion we first optimized the synthesis of the reference compound distilbenylbianthryl **2b**. Upon coupling 10,10′-dibromo-9,9′-bianthryl (**18**) with 4-dihydroxyborylstilbene (**19**) we obtained **2b** in 69% yield, but separation of the mono substituted product proved difficult. In the hope that the corresponding diiodobianthryl would have a higher reactivity, in a further experiment, the dibromobianthryl was converted into the diiodo compound **20**.[16] We obtained 10,10′-diiodo-9,9′-bianthryl by quenching of the dilithiated bianthryl with iodine (Scheme 5).

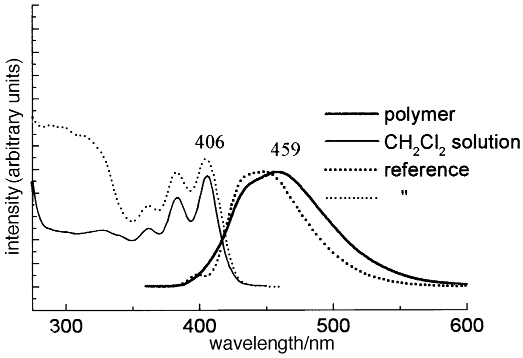
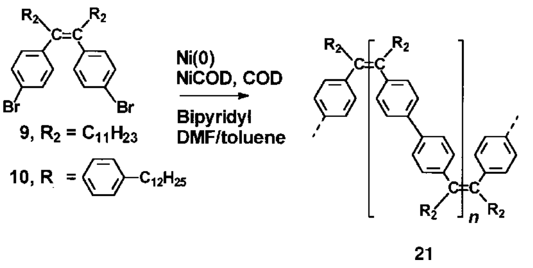


Fig. 4 Fluorescence and exc. emission spectra in methylene chloride solutions for the reference **2b** and the polymer **2**.

The coupling reaction of the diiodobianthryl **15** with the boronic acid of the stilbene to the reference **2b** succeeded in 52% yield. Unfortunately an alkyl-substituted 9,9′-bianthryl was not yet accessible, therefore the Suzuki coupling yielded only low molecular weight oligomers ($P_n \sim 5$) due to low solubility. However, again as expected from our predictions, the optical absorption and fluorescence spectra of solutions of the reference compound distilbenylbianthryl **2b** (abs.: 405 nm, fluores.: 448 nm) and the higher oligomers **2** (406 nm; fluoresc.: 459 nm) were nearly identical (see Fig. 4).

Conclusions

As outlined in the results section, the use of 1,3-phenylene and 9,10-bianthryl bridging of conjugated moieties such as stilbenes and thiophenes can be used to synthesize a broad range of new fully conjugated polymers with well-defined conjugation lengths that are independent of the number of repeat units. In addition, the optical absorption and fluorescence properties can easily be shifted by extension or reduction of the size of the intermediate π-moieties. Furthermore, this approach also enables one to use differently sized π-moieties in the polymerization (*e.g.* use different dibromooligothiophenes or mix alkylphenyl-substituted and unsubstituted stilbenes) to cover a very broad range of absorption and fluorescence with a high yield of light absorption and emission. As discussed at the Bunsen meeting in Heidelberg, 1998,[17] the stilbene moieties themselves are of great interest, and upon shortening and simplifying the synthetic aspects the 9,10-dibromostilbenes could easily be used for Ni(0)-induced Yamamoto coupling towards new soluble poly(biphenylenevinylene)s (**21**) (Scheme 6; such work is now in progress.



Scheme 6

Acknowledgement

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References

1 *Handbook of Conducting Polymers*, ed. T. A. Skotheim, Marcel Dekker, New York, 1st edn., 1986; 2nd edn., 1997.
2 *Conjugated Polymers*, ed. J. L. Brédas and R. Silbey, Kluwer Academic, Dordrecht, 1991.
3 J. L. Segura, *Acta Polym.*, 1998, **49**, 319.
4 J. J. Wolff and R. Wortmann, *J. Prakt. Chem.*, 1998, **340**, 99.
5 M. Baumgarten, *Acta Chem. Scand.*, 1997, **51**, 193.
6 T. Ishida and H. Iwamura, *J. Am. Chem. Soc.*, 1991, **113**, 4238.
7 F. Bell and D. H. Waring, *J. Chem. Soc.*, 1949, 267.
8 M. Suzuki, S. Saweda and T. Saegusa, *Macromolecules*, 1989, **22**, 1505.
9 I. G. C. Coutts, H. R. Goldschmid and O. C. Musgrave, *J. Chem. Soc.*, 1970, 488.
10 W. W. S. Wittig, *Org. React.*, 1977, **25**, 73.
11 G. H. Coleman and W. F. Talbot, *Org. Synth.*, 1943, Coll. vol. II, 592.
12 N. Miyaura, K. Yamada, H. Suginome and A. Suzuki, *J. Am. Chem. Soc.*, 1985, **107**, 972.

13 J. E. McMurry, T. Lectka and J. G. Rico, *J. Org. Chem.*, 1989, **54**, 3748.

14 M. M. Murray, P. Kaszynski, D. A. Kaisaki, W. Chang and D. A. Dougherty, *J. Am. Chem. Soc.*, 1994, **116**, 8152.

15 D. Delabouglise, M. Hmyne, G. Horrowitz, A. Yassar and F. Garnier, *Adv. Mater.*, 1992, **4**, 107.

16 B. F. Duerr, Y. S. Chung and A. W. Czarnik, *J. Org. Chem.*, 1988, **53**, 2120.

17 H-H. Hörhold, private communication at the Bunsen discussion meeting, Heidelberg, 1998.

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