Synthesis of Monofunctionalized *p*-Quaterphenyls

Ivonne Wallmann,[a] Manuela Schiek,[b] Rainer Koch,[c] Arne Lützen*[a]

[a] Kekulé-Institute of Organic Chemistry and Biochemistry, University of Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany
Fax +49(228)739608; E-mail: arne.luetzen@uni-bonn.de

[b] Mads Clausen Institute, University of Southern Denmark, Alsion 2, 6400 Sønderborg, Denmark

[c] Institute of Pure and Applied Chemistry, Centre of Interphase Science, University of Oldenburg, P.O. Box 2503, 26111 Oldenburg, Germany

Received 28 February 2008

Abstract: *p*-Oligophenyls have proven to be versatile building blocks for the generation of self-assembled nanoaggregates via vapor deposition on solid supports whose optical properties and morphologies can be influenced by the introduction of functional groups. Nonsymmetrically functionalized *p,p′*-disubstituted derivatives could even be demonstrated to form nanoaggregates that can act as frequency doublers due to their nonlinear optical properties.

Similar properties can be expected from monofunctionalized derivatives. Thus, we developed a general approach for the synthesis of monofunctionalized 1,1′:4′,1″:4″,1‴-quaterphenyls (*p*-quaterphenylenes) through the application of a reliable Suzuki cross-coupling strategy.

Key words: cross-coupling reaction, *p*-oligophenyls, rodlike molecules, Suzuki cross-coupling

π-Conjugated rodlike molecules[1] such as oligothiophenes,[2] perylenes,[3] pentacenes,[4] and *p*-oligophenyls (*p*-oligophenylenes)[5] have been used extensively over the last years to build up organic materials, because of their optical, electrical, and optoelectrical properties.[6]

Among these molecules, the *p*-oligophenyls, especially the *p*-hexaphenyl and 4,4‴-disubstituted *p*-quaterphenyls (1,1′:4′,1″:4″,1‴-quaterphenyls), show a high tendency to self assemble to mutually aligned fiberlike aggregates on muscovite mica upon vapor deposition by a sophisticated high-vacuum surface growth process.[5c,d,6h,7] These structures can reach lengths of up to one millimeter and show high quantum yields of anisotropic blue luminescence, which make them very interesting for optoelectronic devices such as organic light emitting diodes (OLEDs). Interestingly, not only the nanoaggregates' optical properties like their luminescence properties (efficiency and emission wavelength), but also their morphologies can be tailored by the choice of suitable functional groups.[8] Nonsymmetrically 4,4‴-functionalized *p*-quaterphenyls,[9] however, were not only shown to have interesting linear optical properties,[8,10] but they could also be demonstrated to exhibit exciting nonlinear optical activity such as frequency doubling.[8b,11] Obviously, (at least most of) the molecular building blocks arrange themselves in a head-to-tail-orientation in the aggregates that transfers the noncentrosymmetric properties of the molecules to the nanofiber, which is a prerequisite for nonlinear optical activity.

Monofunctionalized derivatives like 4-substituted species also fulfill this requirement, of course, and quantum chemical studies suggest that they should have very interesting nonlinear optical properties on a molecular level.[12] However, since there are hardly any known examples they have not yet been tested with regard to their ability to form nanofibers. Thus, we started an investigation to develop a general approach for the synthesis of these compounds.

Although *p*-quaterphenyl has been known for almost 130 years,[13] and it is even commercially available, a direct (regio-)selective functionalization[14] of this compound is very difficult to achieve mainly because of the notoriously low solubility of these compounds. In order to gain access to these molecules it is, therefore, mandatory to introduce the desired functional group(s) into smaller units and then employ these to assemble the quaterphenyl scaffold. Although some other approaches were also used in the past,[15] modern homo- and cross-coupling procedures, especially Karash- and Suzuki-type couplings, have been shown to be very efficient in this content.[16] However, most of the compounds prepared in this way bear long alkyl or alkoxy chains to improve the solubility in organic solvents and there are only a few reports[9,17,18] that also give rise to the desired *p*-quaterphenyls that are only functionalized in 4,4‴-positions.

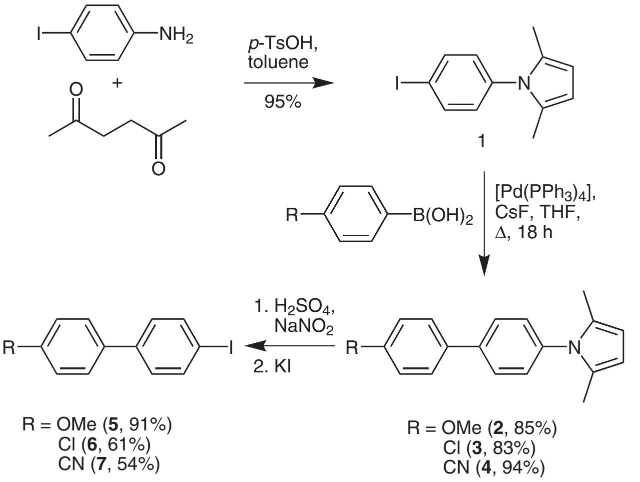
According to our previous protocol, we again used Suzuki cross-coupling reactions as the key steps in the synthesis of the monosubstituted target compounds.

Since the solubility of *p*-oligophenyls decreases already drastically from biphenyls to *p*-terphenyls it seemed reasonable to build up *p*-quaterphenyls from two biphenyl building blocks. Thus, one either needs a biphenyl-4-yl halide and a 4′-functionalized biphenyl-4-ylboronic acid derivative or the nonsubstituted boronic acid derivative and the respective biphenyl-4-yl halide furnished with the desired functional group.

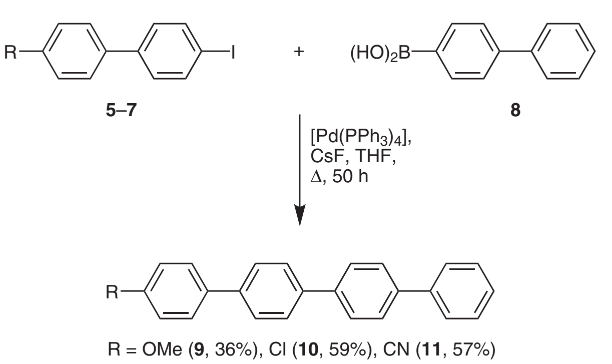
The latter strategy requires the formation of 4′-functionalized 4-iodobiphenyls **5**–**7**, which were prepared starting from 4-iodoaniline following a three-step protocol that we reported earlier (Scheme 1).[9] 4′-Functionalized 4-iodobiphenyls **5**–**7** were then coupled with commercially available biphenyl-4-ylboronic acid (**8**) to give the first set of *p*-quaterphenyls **9**–**11** (Scheme 2). The use of 3 mol% of

SYNTHESIS 2008, No. 15, pp 2446–2450
Advanced online publication: 08.07.2008
DOI: 10.1055/s-2008-1067163; Art ID: Z05508SS

tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] and cesium fluoride proved to be efficient in the catalysis of both the Suzuki cross-couplings to obtain the biphenyls and the *p*-quaterphenyl in moderate to acceptable yields of 39% (**9**), 59% (**10**), and 57% (**11**).

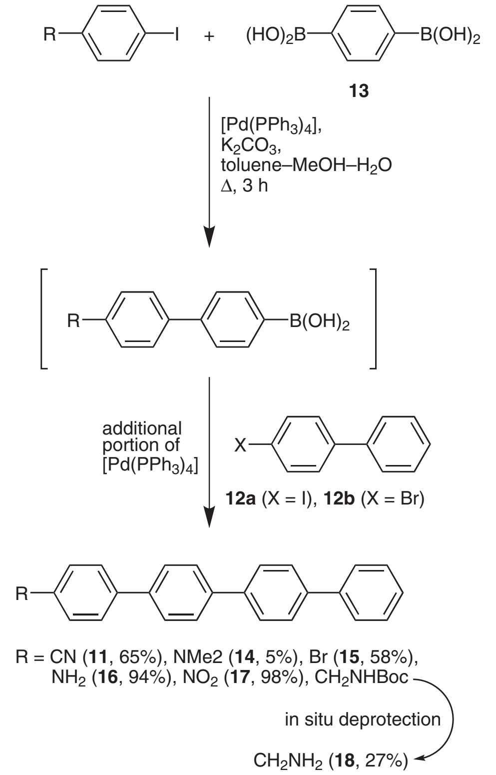


Scheme 1 Synthesis of 4′-functionalized 4-iodobiphenyls **5**–**7** from 4-iodoaniline



Scheme 2 Synthesis of monofunctionalized *p*-quaterphenyls **9**–**11**

The other strategy involves 4′-functionalized biphenyl-4-ylboronic acid derivatives, which are then reacted with commercially available 4-iodo- (**12a**) or 4-bromobiphenyl (**12b**). Of course, one can prepare, isolate, and purify the functionalized boronic acids in a stepwise manner like the iodides **5**–**7** shown previously, however, during the course of our study we found that there is a much more elegant way to gain access to our target compounds: In fact, we were able to show that one can perform two Suzuki cross-coupling reactions with commercially available benzene-1,4-yldiboronic acid (**13**) in a stepwise manner in a one-pot reaction. Therefore, **13** was first reacted with the readily available 4-functionalized iodobenzene to give the functionalized biphenylylboronic acid, which was then transformed without further purification into the desired *p*-quaterphenyl in a second Suzuki reaction upon addition of commercially available 4-iodobiphenyl (**12a**) and some further palladium catalyst directly to the reaction mixture of the first coupling (Scheme 3). It should be noted at this point, that we had to change the base to potassium carbonate and, thus, also the solvent to a mixture of toluene, methanol, and water in order to obtain satisfying results. However, this is actually an improvement because the base is inexpensive and the solvents no longer need to be anhydrous. Thus, this procedure is less time consuming and much less expensive (despite the higher amount of palladium catalyst) due to the fact that most starting materials are commercially available and several isolation and purification steps can be saved. As can be seen by the yield of 65% for **11**, which was obtained when we followed this approach, this procedure is equally well suited for the synthesis of these compounds, although the purification of the product proved to be more tedious than in the other case. It should be noted, however, that this approach also has its limitations, since we were able to obtain the dimethylamino-substituted target compound **14** and also benzylamine **18**, but only in low yields of 5% and 27% (after in situ deprotection of the Boc group), respectively, but it allowed an elegant access to the desired bromo **15**, amino **16**, and nitro **17** derivative in good to excellent yield of 58–98%.



Scheme 3 Synthesis of monofunctionalized *p*-quaterphenyls **11**, **14**–**18**

All products **9**–**11**, and **14**–**18** are even less soluble than their 4,4‴-difunctionalized analogues. Thus, they precipitated from the reaction mixture and were purified by repeated washing with water and organic solvents in some cases also with diluted trifluoroacetic acid. Unfortunately, this purification method usually leads to retention of residual solvents in the products, which cannot always be removed upon drying under normal laboratory high vacuum but only by out-gassing under ultrahigh vacuum.

Actually, the solubility proved to be so low, that we were not even able to record ^1H NMR spectra of these compounds that show all the expected resonances. Nevertheless, we were able to characterize these compounds by (high resolution) mass spectrometry, UV/Vis, and fluorescence spectroscopy, and elemental analysis (in some cases).

In conclusion we have developed two reliable protocols for the synthesis of monofunctionalized *p*-quaterphenyls by using Suzuki cross-coupling reactions, which allow the isolation of the target compounds in sufficient purity to perform vapor deposition studies. These compounds are promising candidates for the formation of well-defined nanoaggregates with interesting linear and nonlinear optical properties.

Solvents were dried, distilled, and stored under argon according to standard procedures. Reactions with air- and moisture-sensitive transition metal compounds were performed under an argon atmosphere in oven-dried glassware using standard Schlenk techniques.

TLC was performed on aluminum TLC plates (silica gel 60 F254) from Merck and the products were visualized under UV light (254 or 366 nm). Products were purified either by column chromatography on silica gel 60 (70–230 mesh or 230–400 mesh) from Merck or by extraction and washing procedures. Because of the low solubility of the quaterphenyls it was not possible to record ^1H and ^{13}C NMR spectra that show all the expected resonances, thus, they are not listed here. Mass spectra were recorded on a Finnigan MAT-95XL. UV/Vis spectra were measured on a Jena Analytic Specord 200 spectrometer in a 1-cm quartz cuvette. Fluorescence spectra were taken on a Aminco Bowman AB2 spectrometer in a 1-cm quartz cuvette. Since the *p*-quaterphenyls were obtained as amorphous solids they usually contain residual amounts of solvents from the extraction and washing procedure that could not be removed completely in all cases even after heating for longer periods of time under standard laboratory high vacuum (10^{-3} mbar). Thus, not all of the quaterphenyls gave satisfactory elemental analysis. Thus, we also give HRMS data in all cases.

4-Bromophenylboronic acid, 4-chlorophenylboronic acid, 4-methoxyphenylboronic acid, 4-nitrophenylboronic acid, 4-cyanophenylboronic acid, biphenyl-4-ylboronic acid (**8**), 4-iodobiphenyl (**12a**), 4-bromobiphenyl (**12b**), benzene-1,4-diyldiboronic acid (**13**), 1-iodo-4-nitrobenzene, 4-iodobenzonitrile, CsF, and $Pd(PPh_3)_4$ were purchased from Sigma-Aldrich, Alfa Aesar, Merck, Lancaster, or Strem and used as received.

1-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-4-iodobenzene (**1**),[19] 4-iodo-*N*,*N*-dimethylaniline,[20] 4-(2,5-dimethyl-1*H*-pyrrol-1-yl)-4′-methoxybiphenyl (**2**),[9] 4-chloro-4′-(2,5-dimethyl-1*H*-pyrrol-1-yl)biphenyl (**3**),[9] 4-cyano-4′-(2,5-dimethyl-1*H*-pyrrol-1-yl)biphenyl (**4**),[9] 4-iodo-4′-methoxybiphenyl (**5**),[9] 4-chloro-4′-iodobiphenyl (**6**),[9] 4-cyano-4′-iodobiphenyl (**7**),[9] and *N*-Boc-protected 4-bromobenzylamine[21] were prepared according to published procedures.

1,1′:4′,1″:4″,1‴-Quaterphenyls; General Procedure 1

A 2-necked flask equipped with a condenser was charged with biphenyl-4-boronic acid (**8**, 1.05 equiv). A 4′-substituted 4-iodobiphenyl, CsF (3 equiv), and $Pd(PPh_3)_4$ (3 mol%) were added and dissolved in anhyd THF under an argon atmosphere. The mixture was refluxed for 15 h. The mixture was cooled to r.t. and the precipitate was collected and washed with THF, CH_2Cl_2, and H_2O to obtain the desired quaterphenyl.

1,1′:4′,1″:4″,1‴-Quaterphenyls; General Procedure 2

A 2-necked flask equipped with a condenser was charged with benzene-1,4-diyldiboronic acid (**13**, 1 equiv). A 4-substituted iodobenzene, K_2CO_3 (3 equiv), and $Pd(PPh_3)_4$ (5 mol%) were added and dissolved in a mixture of toluene, MeOH, and H_2O. The mixture was refluxed until TLC monitoring indicated the complete consumption of the starting material (~3 h). The mixture was allowed to cool to r.t. and 4-iodobiphenyl (**12a**, 1.2 equiv) and an additional portion of $Pd(PPh_3)_4$ (5 mol%) were added. The soln was refluxed for a further 36 h. The mixture was cooled to r.t. and the precipitate collected and washed with different organic solvents and H_2O to give the desired quaterphenyl.

1-Methoxy-1,1′:4′,1″:4″,1‴-quaterphenyl (9)[22]

Following general procedure 1 using 4-iodo-4′-methoxybiphenyl (**5**, 2.0 g, 6.44 mol) with **8** (1.33 g, 6.77 mmol), CsF (2.93 g, 19.3 mmol), and $Pd(PPh_3)_4$ (223 mg, 0.19 mmol) in THF (120 mL) gave **9** as a slightly yellow amorphous solid; yield: 780 mg (36%).

MS (EI): *m*/*z* = 336.2 ([M^+], 100).

HRMS (EI): *m*/*z* calcd for $C_{25}H_{20}O$: 336.1514; found: 336.1516.

UV/Vis (CH_2Cl_2): λ_{max} = 265 nm.

Fluorescence (CH_2Cl_2): λ_{max} = 384 nm.

4-Chloro-1,1′:4′,1″:4″,1‴-quaterphenyl (10)

Following general procedure 1 using 4-chloro-4′-iodobiphenyl (**6**, 1.16 g, 3.69 mmol) with **8** (0.76 g, 3.87 mmol), CsF (1.68 g, 11.07 mmol), and $Pd(PPh_3)_4$ (127 mg, 0.11 mmol) in THF (70 mL) gave **10** as an off-white amorphous solid; yield: 740 mg (59%).

MS (EI): *m*/*z* = 340.2 ([M^+], 100).

HRMS (EI): *m*/*z* calcd for $C_{24}H_{17}Cl$: 340.1019; found: 340.1022.

Anal. Calcd for $C_{24}H_{17}Cl \cdot 0.5\ H_2O$: C, 82.39; H, 5.29. Found: C, 82.68; H, 5.20.

UV/Vis (CH_2Cl_2): λ_{max} = 301.5 nm.

Fluorescence (CH_2Cl_2): λ_{max} = 356 nm.

4-Cyano-1,1′:4′,1″:4″,1‴-quaterphenyl (11)

Following general procedure 1 using 4-cyano-4′-iodobiphenyl (**7**, 1.68 g, 5.51 mmol) with **8** (1.14 g, 5.78 mmol), CsF (2.51 g, 16.53 mmol), and $Pd(PPh_3)_4$ (191 mg, 0.17 mmol) in THF (70 mL) gave **11** as a slightly brownish amorphous solid; yield: 1.04 g (57%);.

Following general procedure 2 using 4-iodobenzonitrile (1.5 g, 6.6 mmol) with **13** (1.09 g, 6.6 mmol), K_2CO_3 (2.73 g, 19.7 mmol), and $Pd(PPh_3)_4$ (380 mg, 0.33 mmol) in toluene–MeOH–H_2O (70 mL:50 mL:0.5 mL) gave the respective biphenylboronic acid, which was reacted in situ with **12a** (2.21 g, 7.9 mmol) and an additional portion of $Pd(PPh_3)_4$ (380 mg, 0.33 mmol) to give **11**; yield: 1.42 g (65%).

MS (EI): *m*/*z* = 331.1 ([M^+], 100)

HRMS (EI): *m*/*z* = calcd for $C_{25}H_{17}N$: 331.1361; found: 331.1361.

Anal. Calcd for $C_{25}H_{17}N \cdot 0.5\ CH_2Cl_2$: C, 81.92; H, 4.85; N, 3.75. Found: C, 82.13; H, 5.02; N, 3.55.

UV/Vis (CH_2Cl_2): λ_{max} = 312 nm.

Fluorescence (CH_2Cl_2): λ_{max} = 390 nm.

4-(Dimethylamino)-1,1′:4′,1″:4″,1‴-quaterphenyl (14)

Following general procedure 2 using 4-iodo-*N*,*N*′-dimethylaniline (0.75 g, 3.04 mmol) with **13** (0.5 g, 3.04 mmol), K_2CO_3 (1.26 g, 9.12 mmol), and $Pd(PPh_3)_4$ (176 mg, 0.15 mmol) in toluene–MeOH–H_2O (45 mL:30 mL:0.5 mL) gave the respective biphenylboronic acid, which was reacted in situ with **12a** (1.02 g, 3.65

mmol) and an additional portion of Pd(PPh$_3$)$_4$ (176 mg, 0.15 mmol) to give **14** as an off-white amorphous solid; yield: 53 mg (5%). (A further increase in the amount of the palladium catalyst unfortunately did not increase the yield.)

MS (EI): *m*/*z* = 349.2 ([M$^+$], 100)

HRMS (EI): *m*/*z* calcd for $C_{26}H_{23}N$: 349.1830; found: 349.1833.

UV/Vis (CH_2Cl_2): λ_{max} = 331.5 nm.

Fluorescence (CH_2Cl_2): λ_{max} = 448 nm.

4-Bromo-1,1′:4′,1″:4″,1‴-quaterphenyl (15)[23]

Following general procedure 2 using 1-bromo-4-iodobenzene (0.75 g, 2.66 mmol) with **13** (0.45 g, 2.66 mmol), K_2CO_3 (1.10 g, 7.98 mmol), and Pd(PPh$_3$)$_4$ (153 mg, 0.13 mmol) in toluene–MeOH–H_2O (45 mL:30 mL:0.5 mL) gave the respective biphenylboronic acid, which was reacted in situ with **12a** (0.89 g, 3.19 mmol) and an additional portion of Pd(PPh$_3$)$_4$ (153 mg, 0.13 mmol) to give **15** as a brownish amorphous solid; yield: 585 mg (58%).

MS (EI): *m*/*z* = 384.1 ([M$^+$], 100)

HRMS (EI): *m*/*z* calcd for $C_{24}H_{17}Br$: 384.0514; found: 384.0515

Anal. Calcd for $C_{24}H_{17}Br\cdot H_2O$: C, 71.47; H, 4.75. Found: C, 71.84; H, 4.59.

UV/Vis (CH_2Cl_2): λ_{max} = 303.5 nm.

Fluorescence (CH_2Cl_2): λ_{max} = 378 nm.

4-Amino-1,1′:4′,1″:4″,1‴-quaterphenyl (16)[24]

Following general procedure 2 using 4-iodoaniline (1.5 g, 6.88 mmol) with **13** (1.14 g, 6.88 mmol), K_2CO_3 (2.85 g, 20.64 mmol), and Pd(PPh$_3$)$_4$ (398 mg, 0.34 mmol) in toluene–MeOH–H_2O (90 mL:60 mL:0.5 mL) gave the respective biphenylboronic acid, which was reacted in situ with **12a** (2.31 g, 8.26 mmol) and an additional portion of Pd(PPh$_3$)$_4$ (398 mg, 0.34 mmol) to give **16** as a slightly yellow-green solid; yield: 2.08 mg (94%).

MS (EI): *m*/*z* = 349.2 (M$^+$, 100)

HRMS (EI): *m*/*z* calcd for $C_{26}H_{23}N$: 349.1830; found: 349.1833.

UV/Vis (CH_2Cl_2): λ_{max} = 311 nm.

Fluorescence (CH_2Cl_2): λ_{max} = 386 nm.

4-Nitro-1,1′:4′,1″:4″,1‴-quaterphenyl (17)[24]

Following general procedure 2 using 1-iodo-4-nitrobenzene (2 g, 8.06 mmol) with **13** (1.34 g, 8.06 mmol), K_2CO_3 (3.34 g, 24.18 mmol), and Pd(PPh$_3$)$_4$ (466 mg, 0.40 mmol) in toluene–MeOH–H_2O (90 mL:60 mL:0.5 mL) gave the respective biphenylboronic acid which was reacted in situ with **12a** (2.8 g, 9.67 mmol) and an additional portion of Pd(PPh$_3$)$_4$ (466 mg, 0.40 mmol) to give **17** as an off-white amorphous solid; yield: 2.78 g (98%).

MS (EI): *m*/*z* = 351.2 (M$^+$, 100)

HRMS (EI): *m*/*z* calcd for $C_{24}H_{17}NO_2$: 351.1259; found: 351.1258.

UV/Vis (CH_2Cl_2): λ_{max} = 323.5 nm.

Fluorescence (CH_2Cl_2): λ_{max} = 390 nm.

4-(Aminomethyl)-1,1′:4′,1″:4″,1‴-quaterphenyl (18)

Following general procedure 2 using *N*-Boc-protected 4-iodobenzylamine (952 mg, 3.5 mmol) with **13** (580 mg, 3.5 mmol), K_2CO_3 (1.45 g, 10.5 mmol), and Pd(PPh$_3$)$_4$ (202 mg, 0.175 mmol) in toluene–MeOH–H_2O (45 mL:30 mL:0.5 mL) gave the respective biphenylboronic acid, which was reacted in situ with **12b** (979 mg, 4.2 mmol) and an additional portion of Pd(PPh$_3$)$_4$ (202 mg, 0.175 mmol) to give *N*-Boc-protected quaterphenyl, which was suspended in CH_2Cl_2 (100 mL). The mixture was cooled to 0 °C and TFA (10 mL) was added dropwise to give an intense yellow soln. The mixture was allowed to warm up to r.t. and stirred for a further 1 h. The soln was made alkaline by dropwise addition of concd aq NaOH resulting in a bulky light yellow precipitate. The crude product was collected by filtration and washed repeatedly with H_2O and CH_2Cl_2. Following recrystallization (hot DMSO) gave **18** as a yellow-green amorphous solid; yield: 319 mg (27%).

MS (EI): *m*/*z* = 335.2 (M$^+$, 100)

HRMS (EI): *m*/*z* calcd for $C_{25}H_{21}N$: 335.1674; found: 335.1670

UV/Vis (CH_2Cl_2): λ_{max} = 319 nm.

Acknowledgment

Financial support from the DFG is gratefully acknowledged.

References

(1) (a) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863. (b) Schwab, P. F. H.; Smith, J. R.; Michl, J. *Chem. Rev.* **2005**, *105*, 1197.

(2) Ziegler, G. In *Handbook of Organic Conductive Molecules and Polymers*, Vol. 3; Nalwa, H. S., Ed.; Wiley: New York, **1997**, Chap. 13.

(3) (a) Krause, B.; Dürr, A. C.; Ritley, K.; Schreiber, F.; Dosch, H.; Smilgies, D. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2002**, *66*, 235404. (b) Würthner, F. *Chem. Commun.* **2004**, 1564.

(4) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891.

(5) (a) James, D. K.; Tour, J. M. *Top. Curr. Chem.* **2005**, *257*, 33. (b) Resel, R. *Thin Solid Films* **2003**, 433 1. (c) Balzer, F.; Rubahn, H.-G. *Adv. Funct. Mater.* **2005**, *14*, 17.
(d) Balzer, F.; Rubahn, H.-G. *Phys. Unserer Zeit* **2005**, *36*, 36.

(6) (a) Müllen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, **1998**.
(b) Fichou, D. *Handbook of Oligo- and Polythiophenes*; Wiley-VCH: Weinheim, **1999**. (c) Nalva, H. S. *Handbook of Advanced Electronic and Photonic Materials and Devices*; Academic Press: San Diego, **2000**. (d) Witte, G.; Woell, C. *J. Mater. Res.* **2004**, *19*, 1889. (e) Hertel, D.; Müller, C. D.; Meerholz, K. *Chem. Unserer Zeit* **2005**, *39*, 336. (f) Müllen, K.; Scherf, U. *Organic Light Emitting Devices – Synthesis,Properties and Applications*; Wiley-VCH: Weinheim, **2006**. (g) Klauk, H. *Organic Electronics – An Industrial Perspective*; Wiley-VCH: Weinheim, **2006**.
(h) Al-Shamery, K.; Rubahn, H.-G.; Sitter, H. *Organic Nanostructures for Next Generation Devices*; Springer Series in Material Science 101: Berlin, **2008**.

(7) (a) Balzer, F.; Rubahn, H.-G. *Appl. Phys. Lett.* **2001**, *79*, 2860. (b) Balzer, F.; Rubahn, H.-G. *Surf. Sci.* **2002**, *507*, 588.

(8) (a) Schiek, M.; Balzer, F.; Al-Shamery, K.; Lützen, A.; Rubahn, H.-G. *Soft Matter* **2008**, *4*, 277. (b) Schiek, M.; Balzer, F.; Al-Shamery, K.; Brewer, J.; Rubahn, H.-G. *Small* **2008**, *4*, 176.

(9) Schiek, M.; Al-Shamery, K.; Lützen, A. *Synthesis* **2007**, 613.

(10) (a) Schiek, M.; Lützen, A.; Koch, R.; Al-Shamery, K.; Balzer, F.; Frese, R.; Rubahn, H.-G. *Appl. Phys. Lett.* **2005**, *86*, 153107. (b) Schiek, M.; Lützen, A.; Al-Shamery, K.; Balzer, F.; Rubahn, H.-G. *Surf. Sci.* **2006**, *600*, 4030.
(c) Schiek, M.; Lützen, A.; Al-Shamery, K.; Balzer, F.; Rubahn, H.-G. *Crystal Growth Des.* **2007**, *7*, 229.

(11) Brewer, J.; Schiek, M.; Lützen, A.; Al-Shamery, K.; Rubahn, H.-G. *Nano Lett.* **2006**, *6*, 2656.

(12) Koch, R.; Finnerty, J. J.; Bruhn, T. *J. Phys. Org. Chem.* submitted for publication.

(13) Schmidt, H.; Schultz, G. *Justus Liebigs Ann. Chem.* **1880**, *203*, 129.

(14) (a) Scheinbaum, M. L. *J. Chem. Soc., Chem. Commun.* **1969**, 1235. (b) Pavlopoulos, T. G.; Hammond, P. R. *J. Am. Chem. Soc.* **1974**, *96*, 6568. (c) Péres, L. O.; Guileet, F.; Froyer, G. *Org. Biomol. Chem.* **2004**, *2*, 452.

(15) In the past *p*-quaterphenyl syntheses were achieved by cyclotrimerizations of acetylenes, Diels–Alder reactions of cyclopentadienones and subsequent aromatization, Wittig reactions of cinnamaldehydes followed by Diels–Alder reactions with acetylenedicarboxylates and subsequent aromatization, addition of Grignard reagents to arenes, Grignard reactions with *p*-quinones and subsequent dehydration, or Ullmann-type coupling reactions. For a detailed list of references see citations 20–25 listed in ref 9.

(16) For a detailed list of references see citations 26–30 listed in ref 9.

(17) (a) Fran, J.; Karakaya, B.; Schäfer, A.; Schlüter, A. D. *Tetrahedron* **1997**, *53*, 15459. (b) Hensel, V.; Schlüter, A.-D. *Chem. Eur. J.* **1999**, *5*, 421.

(18) (a) Percec, V.; Okita, S. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 877. (b) Morikawa, A. *Macromolecules* **1998**, *31*, 5999. (c) Li, Z. H.; Wong, M. S.; Tao, Y.; D'Iorio, M. *J. Org. Chem.* **2004**, *69*, 921. (d) Lee, M.; Jang, C.-J.; Ryu, J.-H. *J. Am. Chem. Soc.* **2004**, *126*, 8082. (e) Ryu, J.-H.; Jang, C.-J.; Yoo, Y.-S.; Lim, S.-G.; Lee, M. *J. Org. Chem.* **2005**, *70*, 8956. (f) Welter, S.; Salluce, N.; Benetti, A.; Rot, N.; Belser, P.; Sonar, P.; Grimsdale, A. C.; Müllen, K.; Lutz, M.; Spek, A. L.; de Cola, L. *Inorg. Chem.* **2005**, *44*, 4706.

(19) Thiemann, F.; Piehler, T.; Haase, D.; Saak, W.; Lützen, A. *Eur. J. Org. Chem.* **2005**, 1991.

(20) Umzawa, H.; Okada, S.; Oikawa, H.; Matsuda, H.; Nakanishi, H. *J. Phys. Org. Chem.* **2005**, *18*, 468.

(21) Howell, S. J.; Spencer, N.; Philp, D. *Tetrahedron* **2001**, *57*, 4945.

(22) This compound has been described in some Japanese patents, however, without any data concerning its synthesis no characterization.

(23) This compound has been described before, however, using a different synthetic approach giving **15** in considerably lower yield, see ref 14c. It has also been described in a recent Japanese patent (written in Japanese): Yabunouchi, N.; Moriwaki, F. WO 2007,080,704, **2007**; *Chem. Abstr.* **2007**, *147*, 166040.

(24) The nitro compound **17** and the amino compound **16** have been described before, however, they were obtained in very low yields by nitration of *p*-quaterphenyl to give **17** and subsequent reduction to give **16**, see ref 14a. Furthermore, these compounds are also listed in some Japanese patents, however, without any data concerning their synthesis or characterization. Finally, **17** has also been described in a theoretical study concerning organic electrodes: Solak, A. O.; Eichhorst, L. R.; Clark, W. J.; McCreery, R. L. *Anal. Chem.* **2003**, *75*, 296.