

Synthesis and spectral properties of functionalized oligoarylenes containing a nitro group

Haiying Ji, Zhan Zhang, Ying An, Xianlei Fu, Yu Yang, Guohua Gao*

Shanghai Key Laboratory of Green Chemistry and Chemical Process, Department of Chemistry,
East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, China

E-mail: ghgao@chem.ecnu.edu.cn

Abstract

The synthesis of symmetrical oligoarylenes using a reliable double Suzuki cross-coupling strategy is presented here. These novel compounds were identified by ^1H NMR, ^{13}C NMR, IR, and HRMS. It was found that UV-vis absorptions were in the range of 295~348 nm and fluorescence emissions were detected between 387 and 395 nm in CHCl_3 . Substituent effects on absorption and fluorescence spectra are also discussed.

Keywords: Oligoarylenes, double Suzuki cross coupling, UV-vis, fluorescence spectra

Introduction

Conjugated organic oligomers and polymers have been the focus of intense research over the past few decades because of their interesting optical, electrical and optoelectrical properties. Oligo-*p*-phenylenes are excellent model compounds for developing a profound understanding of the spectroscopic and redox properties of polyaromatic systems.¹ These compounds have been recognized as prospective materials for opto-electronic applications (for example, organic light-emitting diodes² (OLEDs)).³ They exhibit non-linear optical properties, high quantum efficiency, and efficient light emission in the blue region of spectra.^{3c} Recently, systematic theoretical optoelectronic properties research of the oligo-*p*-phenylenes were widely reported.⁴ Heteroaryls (thiophenes) are incorporated into the oligoarylenes structures, which attract much attention as potentially useful materials⁵ for electronic devices such as thin-film transistors⁶ and OLEDs.⁷ Thiophene-phenylene co-oligomers crystals exhibit good performance in field-effect transistors.⁸

In order to influence the optical properties, introduction of functional groups such as nitro substituent into the oligoarylenes has been a valid approach.⁹ The nitro substituent is easily introduced and is a valuable starting point for the synthesis of more complex target molecules. For example, polyindolocarbazole and polydiindolocarbazole can be synthesized from polyaromatic systems containing nitro groups, which show good optical, electrochemical, magnetic and conductive properties.¹⁰

Encouraged by these reports, we developed the idea of introducing nitro groups and heteroaryls into oligoarylenes with the aim of tuning their optical properties. To the best of our knowledge, oligoarylenes compounds (Figure 1) containing nitro groups have not been reported so far. According to previous reports,¹¹ the Suzuki cross coupling reaction is a reliable protocol for the synthesis of oligoarylenes. Here, we used a double Suzuki cross coupling reaction to synthesize novel symmetrical oligoarylenes compounds (Figure 1) of general structure **3a-d** and **5a-d**, which might allow for the construction of electroluminescent devices in the future. The relationship between structure and spectral properties was also discussed.

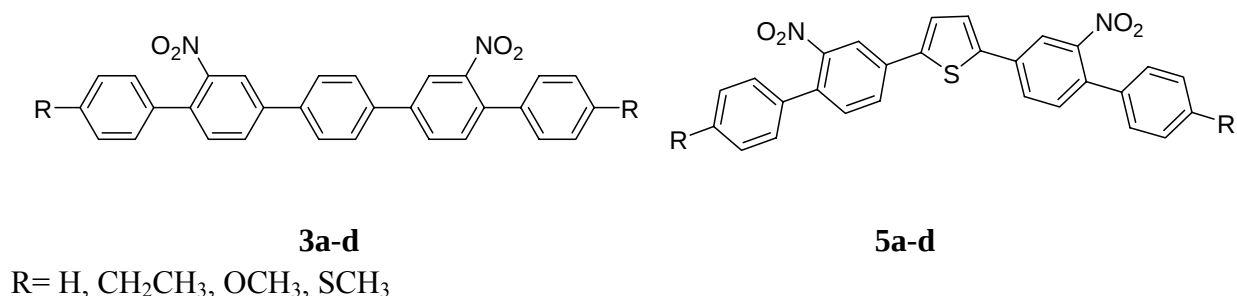


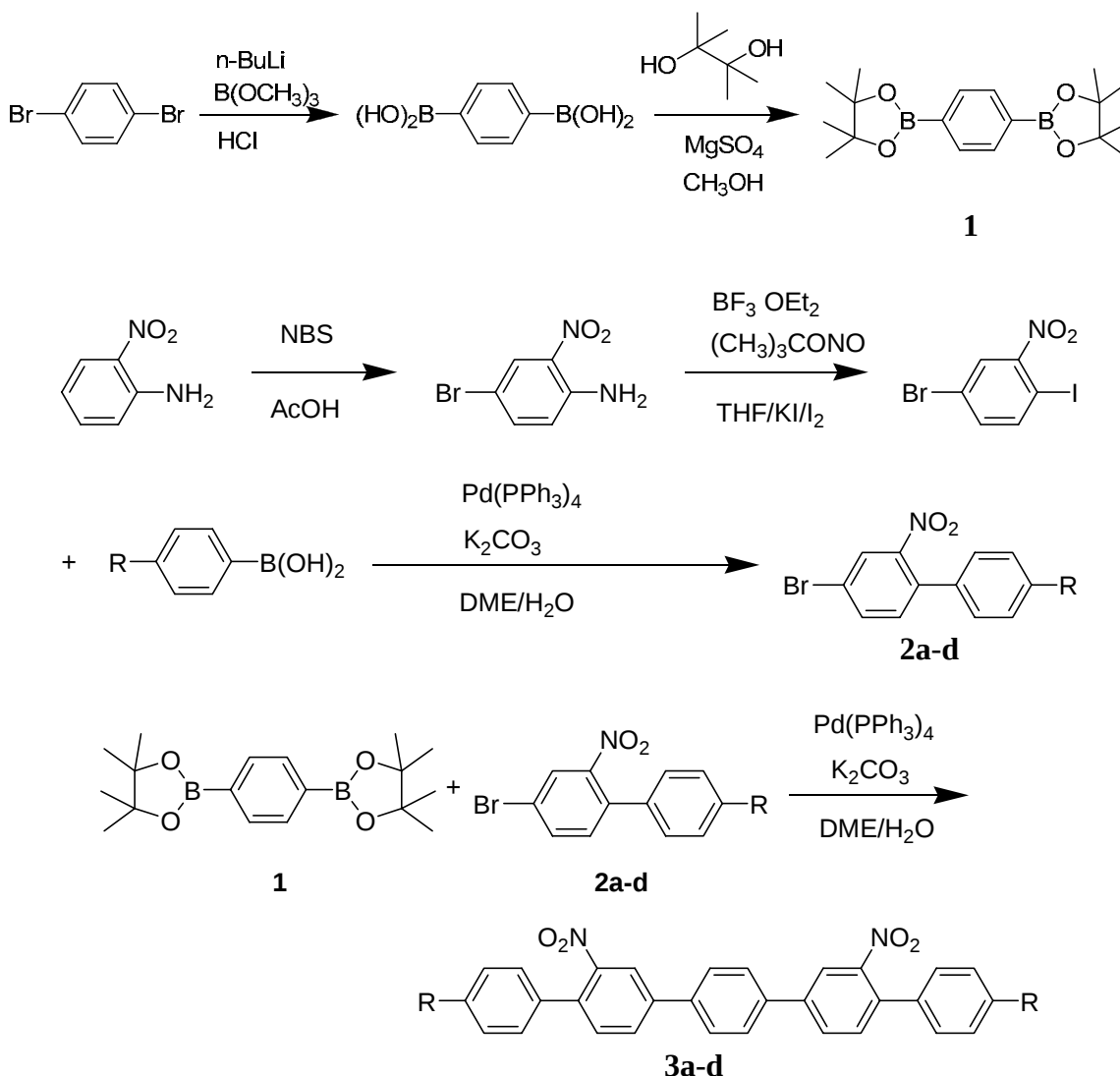
Figure 1. Oligoarylenes.

Results and Discussion

Synthesis

The sequence of the reactions leading to the syntheses of compounds **3** in this study is outlined in Scheme 1. As is shown in Scheme 1, syntheses of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene¹² was started from 1,4-dibromobenzene. Firstly, 1,4-dibromobenzene reacted with n-butyllithium at -78 °C for 30 min, and then the reaction was allowed to warm to room temperature and stirred for 1 hour. When the mixture was recooled to -78 °C, trimethyl borate was added to form the desired diboronic acid. Next, the conversion of the diacid to the pinacol diester proceeded smoothly at room temperature and gave **1** in an overall yield of 15%. The synthetic route of compounds **2a-d** starts with *o*-nitroaniline.¹³ Firstly, *o*-nitroaniline was brominated with N-bromosuccinimide (NBS) to afford 4-bromo-2-nitroaniline. Then, diazotization of 4-bromo-2-nitroaniline followed by iodination afforded the desired 4-bromo-1-iodo-2-nitrobenzene which was highly selectively coupled with various phenyl boronic acids to give substituted 4-bromo-2-nitrobiphenyls (**2a-d**). Sequentially, compounds **3a-d** were synthesized by a double Suzuki cross coupling reaction of compounds **1** and **2a-d** in 44-75% yields. Reactions were carried out using 5 mol % tetrakis (triphenylphosphine) palladium(0) as catalyst and potassium carbonate (K₂CO₃) as base in 1,2-dimethoxyethane (DME) and H₂O at reflux temperature. Various substituents (R) had influence on the yield of **3a-d**. The yield of **3a** (R = H) was 44%. The yield was increased to 75% when R was ethyl group. It was found that the

yields of **3c** and **3d** (changing R from H to methoxy and methylthio group) were 67% and 70%, respectively.

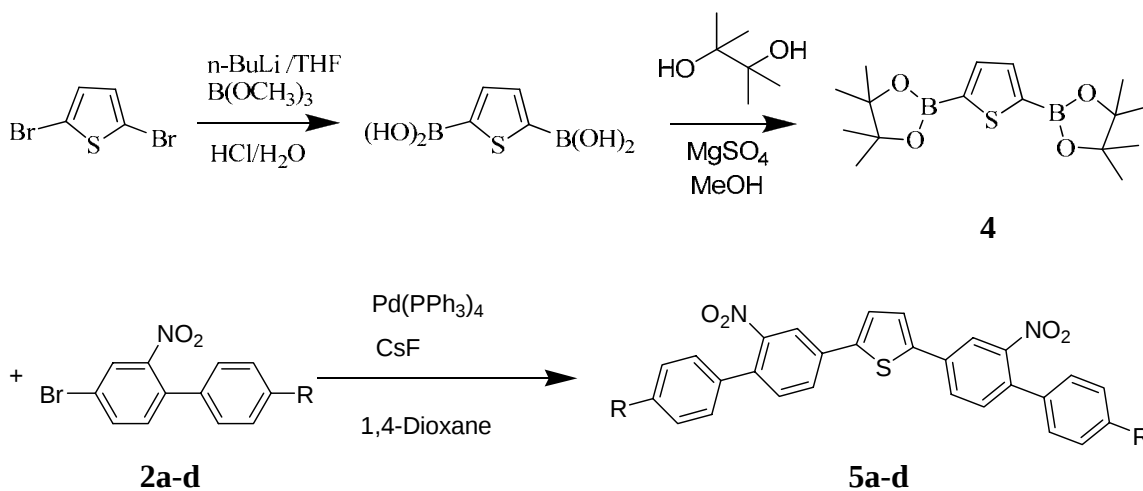


R= H (**3a**), CH₂CH₃ (**3b**), OCH₃ (**3c**), SCH₃ (**3d**)

Scheme 1. Synthesis of 4,4'-disubstituted-2',3'-dinitro-*p*-pentaphenyls (**3a-d**).

Next, our attention focused on the introduction of a thiophene in the centre of the oligoarylenes. The synthesis of compounds **5** was outlined in Scheme 2. First, 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (**4**)¹⁴ was prepared from 2,5-dibromothiophene and the overall yield of the two steps was 17%. Then, compounds **5a-d** were synthesized by a double Suzuki cross coupling reaction between compounds **4** and **2a-d** in moderate (30-80%) yields.¹⁵ Reactions were carried out using 5 mol % tetrakis (triphenylphosphine) palladium(0) as catalyst and cesium fluoride (CsF) as base in 1,4-dioxane at reflux temperature.

IR spectra of the synthesized compounds displayed a strong N=O group absorption (symmetric stretching vibration and antisymmetric stretching vibration) at 1365-1335 and 1550-1510 cm^{-1} .



R= H (**5a**), CH_2CH_3 (**5b**), OCH_3 (**5c**), SCH_3 (**5d**)

Scheme 2. Synthesis of 4'-substituted-2,5-bis(2-nitrophenyl-4-yl)thiophene (**5a-d**).

Spectral properties

To study the influence of the substituent, the spectral properties of compounds **3a-d** and **5a-d** were investigated. The UV-vis spectra of compounds **3a-d** and **5a-d** were recorded in chloroform (CHCl_3) solution using 10×10 mm quartz cells and a spectral range of 200-800 nm. The fluorescence spectra were recorded in CHCl_3 . The absorption maxima ($\lambda_{\text{abs}}^{\text{max}}$), molar absorption coefficient (ϵ), and the emission maxima ($\lambda_{\text{em}}^{\text{max}}$) of the studied compounds **3a-d** and **5a-d** are listed in Table 1.

Table 1. The UV-vis absorption and fluorescence spectra of compounds **3** and **5**

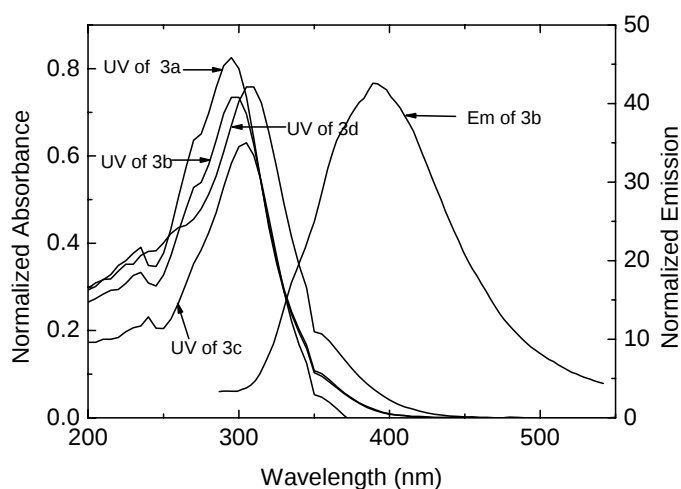
Compounds	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	ϵ (L/mol/cm)	$\lambda_{\text{em}}^{\text{max}}$ (nm)
3a	295	4.00×10^4	394
3b	297	3.85×10^4	390
3c	303	3.46×10^4	387
3d	307	5.95×10^4	395
5a	343	3.44×10^4	393
5b	346	3.85×10^4	390
5c	348	3.11×10^4	390
5d	348	3.44×10^4	395

The maximum absorption spectra of **3a-d** and **5a-d** was observed in the range of 295~348 nm. When R was H and ethyl groups, the absorption maxima of compounds (**3a**, **3b**) were 295 and 297 nm, respectively. When R was methoxy or methylthio group, the absorption maxima of compounds (**3c**, **3d**) gave a red shift from 8 to 12 nm compared with **3a**. This is due to compounds **3c** and **3d** having an auxochromic methoxy group and methylthio group which can shift the absorption maxima ($\lambda_{\text{abs}}^{\text{max}}$). Because thiophene was introduced into oligoarylenes in the centre, the absorption maxima of compounds **5** gave a large red shift compared with compounds **3**. The compounds (**5b**, **5c**, **5d**) gave a red shift from 3 to 5 nm compared with **5a**. In general, electron donating groups have a bathochromic effect on the absorption and the largest bathochromic shift in $\lambda_{\text{abs}}^{\text{max}}$ occurred when there was a methylthio group at the R position of oligoarylenes containing heteroaryls (thiophene).

Literature¹⁶ reported that $\lambda_{\text{abs}}^{\text{max}}$ of *p*-quinquephenyl (PPPPP) and 2,5-bisbiphenyl-4-yl-thiophene (PPTPP) are 309 and 356 nm in CHCl₃, respectively. The $\lambda_{\text{abs}}^{\text{max}}$ of **3a** gave blue shift of 14 nm compared with PPPPP (nitro free analogue) and **5a** also generated blue shift of 13 nm compared with PPTPP (nitro free analogue). From this it can be seen that introducing nitro substituent into PPPPP and PPTPP produced blue shift of $\lambda_{\text{abs}}^{\text{max}}$.

The band position of fluorescence spectra of **3a-d** and **5a-d** was observed between 387 and 395 nm. The charge density of the substituent has a small influence on the fluorescence emission peak. According to literature¹⁶, $\lambda_{\text{em}}^{\text{max}}$ of PPPPP and PPTPP are 370 and 434 nm in CHCl₃, respectively. The $\lambda_{\text{em}}^{\text{max}}$ of **3a** gave red shift of 24 nm compared with nitro free analogue PPPPP and **5a** generated blue shift of 41 nm compared with nitro free analogue PPTPP. This shows that introducing nitro substituent into PPPPP and PPTPP have influence on fluorescence spectra.

The absorption spectra (**3a-d**, **5a-d**) and emission spectra (**3b**, **5b**) in CHCl₃ were shown in Figure 2.



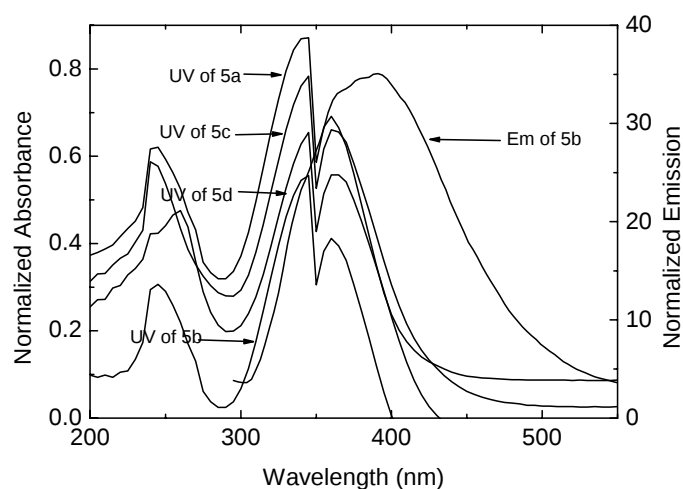


Figure 2. The absorption spectra (**3a-d**, **5a-d**) and emission spectra (**3b**, **5b**) in CHCl_3 .

Conclusions

In conclusion, we have developed a reliable protocol for the synthesis of symmetrical oligoarylenes containing nitro groups using a double Suzuki cross coupling. The maximum UV-vis absorption of title compounds were between 295 and 348 nm and their maximum fluorescence emissions were at 387~395 nm in CHCl_3 . Electron donating groups have a bathochromic effect on the absorption.

Experimental Section

General Procedures. Unless stated otherwise, reactions were performed in dry, nitrogen-flushed glassware, using freshly distilled solvents. Reagent grade tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Reagent grade chloroform (CHCl_3) and ethyl acetate (EtOAc) was used without further distillation. Melting points were measured by using a XT5 melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 500MHz spectrometer using TMS as an internal reference. Chemical shift values (δ) were given in ppm. Infrared spectra were obtained on a NEXUS670 spectrophotometer using potassium bromide pellets and are reported as wave numbers (cm^{-1}).

1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (1). A solution of *n*-butyllithium (16 mL, 1.6 M in hexane) was added dropwise to a stirred, cooled (-78°C) solution of 1,4-dibromobenzene (2.36 g, 10 mmol) in dry THF (50 mL) under an atmosphere of dry nitrogen,

and the mixture was stirred at -78 °C for 2 hour. Then the mixture was allow to warm to room temperature and stirred for 1 hour. Trimethyl borate (6.8 mL) was added dropwise at -78 °C and the mixture was allowed to attain room temperature overnight, and 10% aqueous hydrochloric acid (50 mL) was added. The product was extracted into EtOAc (twice) and the combined organic layers were washed with water and dried (MgSO₄). The solvent was removed in vacuo and the crude product was rinsed with n-hexane to yield a white powder. The crude product, 2,3-dimethylbutane-2,3-diol (4.72 g, 40 mmol), MgSO₄ (12 g), and methanol (80 mL) was stirred at room temperature for 48 hour. The reaction mixture was removed in vacuo, and the residue was poured into water. The product was extracted into EtOAc (twice) and the combined organic extracts were dried (MgSO₄). The solvent was removed in vacuo and the residue was rinsed with n-hexane to yield a white powder which was crystallized from ethanol to yield a white crystalline solid (0.495 g). Yield, 15%. m.p. 230-232 °C (lit.¹⁷ 235-236 °C). ¹H NMR (400 MHz, CDCl₃) δ 1.27 (s, 24H, CH₃), 7.73 (s, 4H, Ar-H). ¹³C NMR (100 MHz, CDCl₃) δ 24.8, 83.8, 133.9. GC-MS: m/z (EI): 330.

General procedure for the preparation of 4'-substituted-4-bromo-2-nitrobiphenyl (2)

To a mixture of 4-bromo-1-iodo-2-nitrobenzene (1 mmol) and tetrakis (triphenylphosphine) palladium(0) (5 mol %) in DME (10 mL) was added a solution of K₂CO₃ (4 equiv.) in water (2 mL), and the mixture was purged with nitrogen for 10 min. Arylboronic acid (1 equiv.) was added, and the mixture was heated to reflux and stirred. After consumption of 4-bromo-1-iodo-2-nitrobenzene (monitored by TLC) the reaction mixture was concentrated under reduced pressure. The residue was poured into water (30 mL), extracted with ethyl acetate (3×20 mL). The combined organic solutions were washed with saturated brine (40 mL) and dried over MgSO₄. After removal of the solvent, the residue was chromatographed on silica gel with petroleum ether/chloroform to afford the title compounds.

4-Bromo-2-nitrobiphenyl (2a). Yield, 91%, colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.25-7.33 (m, 3H, Ar-H), 7.41-7.43 (m, 3H, Ar-H), 7.73 (q, 1H, *J* = 1.9 Hz, Ar-H), 7.99 (d, 1H, *J* = 1.85 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 121.3 (s), 127.0 (d), 127.7 (d), 128.6 (d), 128.8 (d), 133.2 (d), 135.2 (s), 135.3 (d), 136.3 (s), 149.6 (s). GC-MS: m/z (EI): 277. Anal. Calcd for C₁₂H₈BrNO₂: C, 51.83; H, 2.90; N, 5.04; Found: C, 51.94; H, 2.89; N, 5.12.

4-Bromo-4'-ethyl-2-nitrobiphenyl (2b). Yield, 46%, yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 1.26 (t, 3H, *J* = 7.6 Hz, CH₃), 2.70 (q, 2H, *J* = 7.6 Hz, CH₂), 7.20 (d, 2H, *J* = 8.1 Hz, Ar-H), 7.25 (d, 2H, *J* = 8.1 Hz, Ar-H), 7.31 (d, 1H, *J* = 8.3 Hz, Ar-H), 7.71 (q, 1H, *J* = 2 Hz, Ar-H), 7.95 (d, 1H, *J* = 1.9 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 15.6 (q), 28.5 (t), 120.9 (s), 126.9 (d), 127.7 (d), 128.4 (d), 133.2 (d), 133.4 (s), 133.8 (s), 135.2 (d), 144.8 (s), 149.6 (s). GC-MS: m/z (EI): 305. Calcd for C₁₄H₁₂BrNO₂: C, 54.92; H, 3.95; N, 4.58; Found: C, 54.84; H, 4.03; N, 4.49.

4-Bromo-4'-methoxy-2-nitrobiphenyl (2c). Yield, 81%, yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 3.76 (s, 3H, CH₃), 6.86-6.88 (m, 2H, Ar-H), 7.13-7.15 (m, 2H, Ar-H), 7.23 (d, 1H, *J* = 8 Hz, Ar-H), 7.63 (dd, 1H, *J* = 4 Hz, Ar-H), 7.86 (d, 1H, *J* = 4 Hz, Ar-H). ¹³C NMR (100 MHz,

CDCl_3) δ 55.3 (q), 114.4 (d), 120.8 (s), 126.9 (d), 128.3 (s), 129.0 (d), 133.2 (d), 134.8 (s), 135.1 (d), 149.7 (s), 159.9 (s). GC-MS: m/z (EI): 307. Calcd for $\text{C}_{13}\text{H}_{10}\text{BrNO}_3$: C, 50.67; H, 3.27; N, 4.55; Found: C, 50.77; H, 3.53; N, 4.61.

(4'-Bromo-2'-nitrobiphenyl-4-yl)(methyl)sulfane (2d). Yield, 87%, yellow solid. m.p. 92.3-93.8 °C. ^1H NMR (400 MHz, CDCl_3) δ 2.43 (s, 3H, CH_3), 7.11-7.24 (m, 5H, Ar-H), 7.64 (d, J = 8 Hz, 1H, Ar-H), 7.90 (d, J = 4 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 15.3 (q), 121.2 (s), 126.3 (d), 127.1 (d), 128.1 (d), 132.6 (s), 133.1 (d), 134.6 (s), 135.3 (d), 139.8 (s), 149.4 (s). FT-IR (KBr) 807 (m), 963 (w), 999 (w), 1090 (m), 1261 (w), 1358 (m), 1383 (w), 1429 (w), 1464 (w), 1522 (s), 1600 (w), 1629 (w), 2918 (w), 3096 (w), 3445 (br) cm^{-1} . GC-MS: m/z (EI): 325 (M^{2+}). Calcd for $\text{C}_{13}\text{H}_{10}\text{BrNO}_2\text{S}$: C, 48.16; H, 3.11; N, 4.32; Found: C, 48.34; H, 3.03; N, 4.45.

General procedure for the preparation of compounds 3

The mixture of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (1 mmol), 4'-substituted-4-bromo-2-nitrobiphenyl (2 mmol) and tetrakis (triphenylphosphine) palladium(0) (5 mol%, according to 2) in DME (10 mL) and EtOH (0.5 mL) was purged with nitrogen for 30 min, then aqueous of K_2CO_3 (6 mmol) was added and the mixture was heated to reflux. After consumption of 4'-substituted-4-bromo-2-nitrobiphenyl (monitored by TLC) the reaction mixture was concentrated under reduced pressure. The residue was poured into water (30 mL), extracted with CHCl_3 (3×30 mL). The combined organic solutions were washed with saturated NaCl solution (40 mL) and dried over MgSO_4 . After removal of the solvent, the residue was chromatographed on silica gel with chloroform to afford the title compounds.

2', 3'-Dinitro-*p*-pentaphenyls (3a). Yield, 44%, yellow solid. m.p. 280.2-281.3 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.37 (d, 4H, J = 13.4 Hz, Ar-H), 7.45 (s, 6H, Ar-H), 7.56 (d, 2H, J = 7.95 Hz, Ar-H), 7.79 (s, 4H, Ar-H), 7.90 (d, 2H, J = 6.1 Hz, Ar-H), 8.13 (s, 2H, Ar-H). FT-IR (KBr) 704 (m), 754 (m), 775 (m), 826 (m), 878 (w), 1006 (w), 1094 (w), 1346 (s), 1474 (w), 1513 (vs), 3037 (w) cm^{-1} . HRMS m/z : calcd for $\text{C}_{30}\text{H}_{20}\text{N}_2\text{O}_4$ 472.1423, found 472.1426. Calcd for $\text{C}_{30}\text{H}_{20}\text{N}_2\text{O}_4$: C, 76.26; H, 4.27; N, 5.93; Found: C, 76.34; H, 4.45; N, 5.87.

2', 3'-Dinitro-4, 4'-diethyl-*p*-pentaphenyls (3b). Yield, 75%, light yellow solid. m.p. 245.2-246.6 °C. ^1H NMR (500 MHz, CDCl_3) δ 1.28 (t, 6H, J = 7.6 Hz, CH_3), 2.71 (q, 4H, J = 7.6 Hz, CH_2), 7.29 (s, 8H, Ar-H), 7.54 (d, 2H, J = 7.9 Hz, Ar-H), 7.76 (s, 4H, Ar-H), 7.86 (q, 2H, J = 1.7 Hz, Ar-H), 8.08 (d, 2H, J = 1.7 Hz, Ar-H). ^{13}C NMR (125 MHz, CDCl_3) δ 15.3 (q), 28.6 (t), 122.3 (d), 127.7 (d), 127.8 (d), 128.3 (d), 130.3 (d), 132.5 (s), 134.1 (s), 135.2 (d), 138.4 (s), 140.2 (s), 144.6 (s), 149.8 (s). FT-IR (KBr) 757 (w), 826 (s), 884 (w), 1007 (w), 1057 (w), 1117 (w), 1184 (w), 1254 (w), 1280 (w), 1363 (s), 1479 (s), 1524 (vs), 1611 (w), 2874 (w), 2931 (w), 2969 (w), 3028 (w) cm^{-1} . HRMS m/z : calcd for $\text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_4$ 528.2049, found 528.2070. Calcd for $\text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_4$: C, 77.25; H, 5.34; N, 5.30; Found: C, 77.39; H, 5.47; N, 5.42.

2', 3'-Dinitro-4, 4'-dimethoxy-*p*-pentaphenyls (3c). Yield, 67%, light yellow solid. m.p. >300 °C. ^1H NMR (500 MHz, CDCl_3) δ 3.86 (s, 6H, CH_3), 6.96 (t, 8H, J = 7.5 Hz, Ar-H), 7.26-7.30 (m, 2H, Ar-H), 7.53 (d, 4H, J = 8 Hz, Ar-H), 7.74-7.78 (m, 2H, Ar-H), 7.96 (s, 2H, Ar-H).

FT-IR (KBr) 802 (m), 1026 (m), 1095 (m), 1179 (w), 1258 (m), 1352 (w), 1476 (w), 1512 (m), 1611 (w), 2963 (w) cm^{-1} . HRMS m/z : calcd for $\text{C}_{32}\text{H}_{24}\text{N}_2\text{O}_6$ 532.1634, found 532.1642. Calcd for $\text{C}_{32}\text{H}_{24}\text{N}_2\text{O}_6$: C, 72.17; H, 4.54; N, 5.26; Found: C, 72.09; H, 4.45; N, 5.39.

2', 3'-Dinitro-4, 4'-dithiomethyl-*p*-pentaphenyls (3d). Yield, 70%, yellow solid. m.p. >300 °C. ^1H NMR (400 MHz, CDCl_3) δ 2.47 (s, 6H, CH_3), 7.21-7.27 (m, 10H, Ar-H), 7.46 (d, J = 8 Hz, 4H, Ar-H), 7.71 (s, 2H, Ar-H), 8.04 (d, J = 4 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 15.5 (q), 122.5 (d), 126.5 (d), 127.8 (d), 128.3 (d), 130.5 (d), 132.5 (s), 133.4 (s), 134.7 (d), 138.4 (s), 139.5 (s), 140.5 (s), 149.7 (s). FT-IR (KBr) 819 (s), 1091 (m), 1352 (s), 1474 (m), 1514 (vs), 1597 (w), 2924 (w), 3224 (m), 3405 (br) cm^{-1} . HRMS m/z : calcd for $\text{C}_{32}\text{H}_{24}\text{N}_2\text{O}_4\text{S}_2$ 564.1177, found 564.1183. Calcd for $\text{C}_{32}\text{H}_{24}\text{N}_2\text{O}_4\text{S}_2$: C, 68.06; H, 4.28; N, 4.96; Found: C, 68.34; H, 4.42; N, 5.12.

2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (4). The experimental procedure was as described for the preparation of compound 1. Yield, 17%, white solid. m.p. 215-217 °C (lit.¹⁸ 224 °C). ^1H NMR (400 MHz, CDCl_3) δ 1.33 (s, 24H, CH_3), 7.67 (s, 2H, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 24.7, 84.1, 137.6. GC-MS: m/z (EI): 336.

General procedure for the preparation of compounds 5

The mixture of 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (1 mmol), 4'-substituted-4-bromo-2-nitrobiphenyl (2 mmol) and tetrakis(triphenylphosphine) palladium(0) (5 mol%, according to 2) in 1,4-dioxane (10 mL) was purged with nitrogen for 30 min, then CsF (12 mmol) was added and the mixture was heated to refluxed. After consumption of 4'-substituted-4-bromo-2-nitrobiphenyl (monitored by TLC) the reaction mixture was concentrated under reduced pressure. The residue was poured into water (30 mL), extracted with CHCl_3 (3×30 mL). The combined organic solutions were washed with saturated NaCl solution (40 mL) and dried over MgSO_4 . After removal of the solvent, the residue was chromatographed on silica gel with chloroform to afford the title compounds.

2,5-Bis(2-nitrobiphenyl-4-yl)thiophene (5a). Yield, 80%, yellow solid. m.p. 214.8-216.1 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.34-7.35 (m, 4H, Ar-H), 7.41-7.50 (m, 10H, Ar-H), 7.84 (q, 2H, J = 1.8 Hz, Ar-H), 8.09 (d, 2H, J = 1.7 Hz, Ar-H). ^{13}C NMR (125 MHz, CDCl_3) δ 120.9 (d), 125.9 (d), 127.8 (d), 128.4 (d), 128.8 (d), 128.9 (d), 132.7 (d), 134.1 (s), 135.3 (s), 136.8 (s), 141.9 (s), 149.7 (s). FT-IR (KBr) 700 (m), 768 (m), 801 (m), 867 (w), 1014 (w), 1095 (w), 1264 (w), 1353 (s), 1445 (w), 1478 (w), 1523 (vs), 1547 (m), 1611 (w), 2924 (w), 2962 (w), 3060 (w) cm^{-1} . HRMS m/z : calcd for $\text{C}_{28}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$ 478.0987, found 478.1008. Calcd for $\text{C}_{28}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$: C, 70.28; H, 3.79; N, 5.85; Found: C, 70.35; H, 3.91; N, 5.94.

2,5-Bis(4'-ethyl-2-nitrobiphenyl-4-yl)thiophene (5b). Yield, 30%, yellow solid. m.p. 148.5-150.2 °C. ^1H NMR (500 MHz, CDCl_3) δ 1.28 (t, 6H, J = 7.6 Hz, CH_3), 2.70 (q, 4H, J = 7.6 Hz, CH_2), 7.23-7.28 (m, 8H, Ar-H), 7.42 (s, 2H, Ar-H), 7.46 (q, 2H, J = 8.1 Hz, Ar-H), 7.80 (q, 2H, J = 1.9 Hz, Ar-H), 8.04 (d, 2H, J = 1.8 Hz, Ar-H). ^{13}C NMR (125 MHz, CDCl_3) δ 15.3 (q), 28.6 (t), 120.8 (d), 125.8 (d), 127.7 (d), 128.3 (d), 128.8 (d), 132.6 (d), 133.8 (s), 133.9 (s), 135.2 (s), 141.9 (s), 144.7 (s), 149.8 (s). FT-IR (KBr) 795 (m), 827 (m), 1268 (w), 1357 (m), 1481 (w),

1529 (vs), 1612 (w), 2870 (w), 2928 (w), 2965 (w) cm^{-1} . HRMS m/z : calcd for $\text{C}_{32}\text{H}_{26}\text{N}_2\text{O}_4\text{S}$ 534.1613, found 534.1638. Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{N}_2\text{O}_4\text{S}$: C, 71.89; H, 4.90; N, 5.24; Found: C, 71.83; H, 5.04; N, 5.12.

2,5-Bis(4'-methoxy-2-nitrophenyl-4-yl)thiophene (5c). Yield, 74%, orange yellow solid. m.p. 226-227.2 $^{\circ}\text{C}$. ^1H NMR (500 MHz, CDCl_3) δ 3.85 (s, 6H, CH_3), 6.97 (d, 4H, $J = 8.5$ Hz, Ar-H), 7.27 (d, 4H, $J = 8.5$ Hz, Ar-H), 7.43 (s, 2H, Ar-H), 7.47 (d, 2H, $J = 8$ Hz, Ar-H), 7.83 (q, 2H, $J = 2$ Hz, Ar-H), 8.03 (d, 2H, $J = 1.5$ Hz, Ar-H). ^{13}C NMR (125 MHz, CDCl_3) δ 55.3 (q), 114.3 (d), 120.8 (d), 125.7 (d), 128.8 (d), 128.9 (d), 129.1 (s), 132.6 (d), 133.7 (s), 134.8 (s), 141.9 (s), 149.8 (s), 159.9 (s). FT-IR (KBr) 754 (w), 803 (m), 827 (m), 1034 (m), 1110 (w), 1178 (m), 1253 (s), 1351 (s), 1384 (m), 1480 (w), 1519 (s), 1610 (m), 2962 (w) cm^{-1} . HRMS m/z : calcd for $\text{C}_{30}\text{H}_{22}\text{N}_2\text{O}_6\text{S}$ 538.1199, found 538.1222. Calcd for $\text{C}_{30}\text{H}_{22}\text{N}_2\text{O}_6\text{S}$: C, 66.90; H, 4.12; N, 5.20; Found: C, 67.05; H, 4.22; N, 5.11.

2,5-Bis(4'-(methylthio)-2-nitrophenyl-4-yl)thiophene (5d). Yield, 57%, yellow solid. m.p. 214.2-215.3 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 2.46 (s, 6H, CH_3), 7.21-7.25 (m, 8H, Ar-H), 7.35-7.42 (m, 4H, Ar-H), 7.75 (d, $J = 8$ Hz, 2H, Ar-H), 8.00 (s, 2H, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 15.5 (q), 121.0 (d), 125.9 (d), 126.5 (d), 128.2 (d), 128.9 (d), 132.6 (d), 133.2 (s), 134.1 (s), 134.7 (s), 139.6 (s), 141.9 (s), 149.7 (s). FT-IR (KBr) 803 (s), 1021 (s), 1099 (s), 1261 (s), 1351 (m), 1476 (m), 1523 (m), 1545 (m), 2921 (w), 2963 (m), 3445 (br) cm^{-1} . HRMS m/z : calcd for $\text{C}_{30}\text{H}_{22}\text{N}_2\text{O}_4\text{S}_3$ 570.0742, found 570.0747. Calcd for $\text{C}_{30}\text{H}_{22}\text{N}_2\text{O}_4\text{S}_3$: C, 63.14; H, 3.89; N, 4.91; Found: C, 63.25; H, 4.02; N, 5.01.

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