

# Linear 1,4-coupled oligoanilines of defined length: preparation and spectroscopic properties

Izabela Różalska, Paulina Kułyk and Irena Kulszewicz-Bajer\*

Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland. E-mail: [ikulsz@chemix.ch.pw.edu.pl](mailto:ikulsz@chemix.ch.pw.edu.pl)

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A facile synthetic method involving  $S_NAr$  coupling of 4-fluoronitrobenzene to arylamines, followed by reduction of the nitro groups, has been developed. The method allows the preparation of symmetric ( $NH_2/NH_2$  end-capped) and asymmetric ( $Ph/NH_2$  end-capped) oligoanilines of even or odd chain lengths. The preparation of the  $NH_2/NH_2$  end-capped trimer to octamer and  $Ph/NH_2$  end-capped trimer to pentamer is described. The effect of the chain length on the spectroscopic properties of the oxidized oligomers has been investigated by UV-Vis-NIR spectroscopy.

## Introduction

Polyaniline is a technologically very important conducting polymer, commercially available today. Its electrical conductivity can exceed  $10^2 \text{ S cm}^{-1}$ . However, it should be noted that several factors, for example the molecular conformation, molecular configuration, or the length of conjugation have an enormous impact on its electrical properties. For this reason oligoanilines can be considered as good model compounds of polyaniline. The study of the properties of oligoanilines allows a better understanding of the complexity of the molecular interactions in a polymer. Moreover, oligomers of well-defined structure can show quantum confinement effects similar to those of classical semiconducting quantum dots; thus, they can have potential applications in molecular electronics and nanotechnology.

Two types of aniline oligomers have been prepared and studied to date, namely phenyl-capped oligomers (*i.e.*, capped with a phenyl ring at both ends, denoted  $Ph/Ph$ ) and oligomers capped with a phenyl ring at one end and with an amine group at the other (denoted as  $Ph/NH_2$ ). The first phenyl-capped oligomer of defined chain length was prepared by Honzl and Tlustakova.<sup>1</sup> They obtained the tetramer by the condensation of *N*-phenyl-1,4-phenylenediamine with diethyl succinylsuccinate, followed by hydrolysis, decarboxylation and aromatization. Similarly, the same authors synthesized the hexamer; however, they did not isolate the aniline octamer. Wudl and co-workers<sup>2</sup> modified Honzl's method and prepared phenyl-capped octaaniline. Other synthetic methods involving different types of condensation have also been reported. Rebourt *et al.*<sup>3</sup> used an Ullmann-type coupling reaction between acetanilides and 4-iodonitrobenzene to prepare the  $Ph/NH_2$  trimer and tetramer. The same type of tetramer was synthesized by Zhang *et al.*<sup>4</sup> who condensed *N*-phenyl-1,4-phenylenediamine in the presence of  $FeCl_3 \cdot 6H_2O$ . The oxidative coupling was also employed to prepare phenyl-capped oligomers. Wei *et al.*<sup>5</sup> obtained the  $Ph/Ph$  tetramer using *p*-phenylenediamine, diamine and  $(NH_4)_2S_2O_8$  as an oxidizing agent. Gao *et al.*<sup>6</sup> synthesized the phenyl-capped pentamer and hexamer using the corresponding amines and the  $Ph/NH_2$  tetramer in the pernigraniline oxidation state as a suitable oxidizer. Another synthetic method involves the condensation of aromatic amines and phenol or hydroquinone. Ochi *et al.*<sup>7</sup> have performed the reaction of *p*-phenylenediamine with *p*-anilinophe-

nol and prepared the phenyl-capped tetramer. Wang and MacDiarmid<sup>8</sup> used the condensation of *N*-phenyl-1,4-phenylenediamine with hydroquinone in the presence of titanium *n*-butoxide. However, it should be noted that the most general way to prepare different types of oligomers is the palladium catalyzed amination of aryl halides. Buchwald's group<sup>9</sup> synthesized the phenyl-capped heptaaniline through decaaniline, a series of end-functionalized octamers and the phenyl-capped 16-mer and 24-mer using tris(dibenzylideneacetone)dipalladium and S-BINAP. Hartwig's group studied the preparation of alternating *meta*- and *para*-anilines.<sup>10</sup> They used  $Pd(OAc)_2$  and tri(*tert*-butyl)phosphine or tris(*o*-methoxymethylphenyl)phosphine as catalysts. The condensation of activated fluoroarenes to arylamines can also serve as another convenient method for the preparation of nitroamino compounds, which can be reduced to oligoamines. Lantz and Obellianne<sup>11</sup> have performed the reaction of aromatic amines with 4-fluoronitrobenzene in the presence of  $MgO$  and water at  $200^\circ C$  and prepared linear nitroamino compounds. The same method was applied by Gebert *et al.*<sup>12</sup> to obtain the aniline trimer in poor yield, as mentioned by the authors. Very recently, Brown *et al.*<sup>13</sup> described the synthesis of aniline oligomers by the high-pressure-promoted  $S_NAr$  reaction of aromatic amines with fluoronitrobenzene.

In this paper, we present a simple method for the synthesis of symmetric ( $NH_2/NH_2$  end-capped) and asymmetric ( $Ph/NH_2$  end-capped) oligoanilines by the  $S_NAr$  reaction of 4-fluoronitrobenzene with the corresponding aromatic amines under atmospheric pressure. The same method was used by us earlier for the preparation of the shortest polyaniline model compounds, namely tetramers  $NH_2/NH_2$  and  $Ph/NH_2$ ,<sup>14</sup> which were studied in the leucoemeraldine and emeraldine oxidation states. Now we focus on the conditions of the  $S_NAr$  reaction. To overcome limitations in the preparation of linear oligomers we have studied the use of different types of bases added to the reaction mixtures. The coupling reaction is followed by the reduction of nitro groups to arylamines. The iterative coupling/reduction sequence allows us to prepare the linear  $NH_2/NH_2$  capped trimer to octamer and  $Ph/NH_2$  capped trimer to pentamer. The oligomers thus obtained are characterized by elemental analyses, mass spectroscopy, NMR and IR. Special attention is paid to the characterization of oxidized oligomers of different chain lengths as followed by UV-Vis-NIR spectroscopy.

## Experimental

### General methods and materials

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Mercury (400 and 100 MHz) spectrometer and referenced with respect to TMS and solvent, respectively. IR spectra were recorded on Bio-RAD FTS-165 spectrometer using KBr pellets. UV-Vis-NIR spectra were registered using a Lambda 2 (Perkin-Elmer) spectrometer in the spectral range 200–1100 nm. Mass spectra were measured by the EI method on a AMD 604 mass spectrometer. All compounds studied were subjected to elemental analyses. C, H and N were determined by combustion analysis.

*N*-Phenyl-1,4-phenylenediamine, 4,4'-diaminodiphenylamine sulfate, triethylamine, dimethyl sulfoxide (DMSO), 4-fluoronitrobenzene, ammonium persulfate and Sn powder were purchased from Aldrich Chemical Co. Acetone, dichloromethane, ethyl acetate, sodium pyrosulfite, HCl, KOH, NaOH were purchased from POCh (Poland). *N*-Phenyl-1,4-phenylenediamine was crystallized from water and dried over KOH in a vacuum desiccator. Triethylamine was dried over KOH. DMSO was stored over thermally activated 4 Å molecular sieves. 4-Fluoronitrobenzene, Sn powder, the oxidant and the solvents were used as supplied.

### Syntheses

**Synthesis of 4,4'-diaminodiphenylamine.** 4,4'-Diaminodiphenylamine sulfate (*ca.* 1.2 g) was dissolved in 50 ml of 1%<sub>w/v</sub> KOH solution; 0.6 g of sodium pyrosulfite,  $\text{Na}_2\text{S}_2\text{O}_5$ , were added to the solution and the mixture was boiled for 15 min, then filtered and crystallized. White crystals were dried over KOH in a vacuum desiccator. M.p. 158–160 °C.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  6.76 (s, 1H), 6.63 (s, 4H), 6.45 (m, 4H), 4.46 (s, 4H). IR ( $\text{cm}^{-1}$ ) 3409, 3390, 3034, 1612, 1515, 1312, 1275, 823. Anal. calcd for  $\text{C}_{12}\text{H}_{13}\text{N}_3$ : C, 72.36; H, 6.53; N, 21.11. Found: C, 69.68; H, 6.50; N, 20.39.

**General procedure for the substitution reactions.** Aromatic amine (5 mmol) and 4-fluoronitrobenzene (10 mmol for reactions in Scheme 1, 2, 3 and 5 mmol for reactions in Scheme 4) were dissolved in 15 ml of DMSO.  $\text{K}_2\text{CO}_3$  (20 mmol for reactions in Scheme 1 and 2) or triethylamine (10 mmol for reactions in Scheme 3 and 5 mmol for reactions in Scheme 4) was added to the solution and the mixture was stirred and heated at 90 °C for 3 days under an argon atmosphere to avoid oxidation of the amine. Then the solution was allowed to cool to room temperature and poured into 200 ml of distilled water. The brown-orange solid was precipitated, washed several times with distilled water and dried in air. The crude product was purified by a liquid chromatography.

**General procedure for the reduction of nitro compounds.** The nitro compound (2 mmol) was stirred with 4 ml of 37% HCl under an argon atmosphere for 15 min at room temperature. Tin powder (29.0 mmol for reductions in Scheme 3 and 15 mmol for reductions in Scheme 4) and 37% HCl (20 ml) were added in portions and the mixture was refluxed for *ca.* 3 h until a yellowish white precipitate was formed. After cooling to room temperature 10 ml of 20%<sub>w/v</sub> NaOH solution and then NaOH granules were slowly added with constant stirring. The pH of the mixture was adjusted to 12. The white precipitate was filtered under an argon atmosphere and the product was washed several times with 20%<sub>w/v</sub> NaOH solution, then with distilled water to pH = 7. The greyish-white powder was dried over KOH in a vacuum desiccator.

**General procedure for the oxidation of oligoanilines.** The UV-Vis-NIR spectra of *ca.*  $5 \times 10^{-5}$  M of the oligoaniline in

DMSO were recorded for each compound. Then an oxidizing solution containing *ca.*  $3 \times 10^{-4}$  M of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in 0.1 M HCl was added dropwise. The absorption spectra were registered after the addition of each drop of oxidizing agent.

### Characterization of synthesized compounds

***N*-(4-Nitrophenyl)-1,4-phenylenediamine (1).** 0.11 g, 10% yield, m.p. 206–208 °C.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.89 (s, 1H), 8.00–7.98 (m, 2H), 6.91–6.89 (m, 2H), 6.76–6.74 (m, 2H), 6.61–6.59 (m, 2H), 5.09 (s, 2H). IR ( $\text{cm}^{-1}$ ) 3457, 3372, 1624, 1592, 1523, 1515, 1496, 1464, 1299, 1254, 1176, 1112, 842, 833, 752. Anal. calcd for  $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_2$ : C, 62.89; H, 4.80; N, 18.34. Found: C, 62.39; H, 4.88; N, 17.85.

***N,N*-Di(4-nitrophenyl)-1,4-phenylenediamine (2).** 1.14 g, 65% yield, m.p. 232–234 °C.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.15–8.13 (m, 4H), 7.17–7.14 (m, 4H), 6.91–6.89 (m, 2H), 6.65–6.63 (m, 2H), 5.43 (s, 2H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  152.0, 148.5, 141.3, 132.0, 128.8, 125.5, 121.3, 115.2. IR ( $\text{cm}^{-1}$ ) 3552, 3474, 3383, 3072, 1618, 1579, 1494, 1341, 1326, 1308, 1278, 1180, 1110, 848, 751. Anal. calcd for  $\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}_4$ : C, 61.71; H, 4.00; N, 16.00. Found: C, 61.85; H, 4.31; N, 15.56.

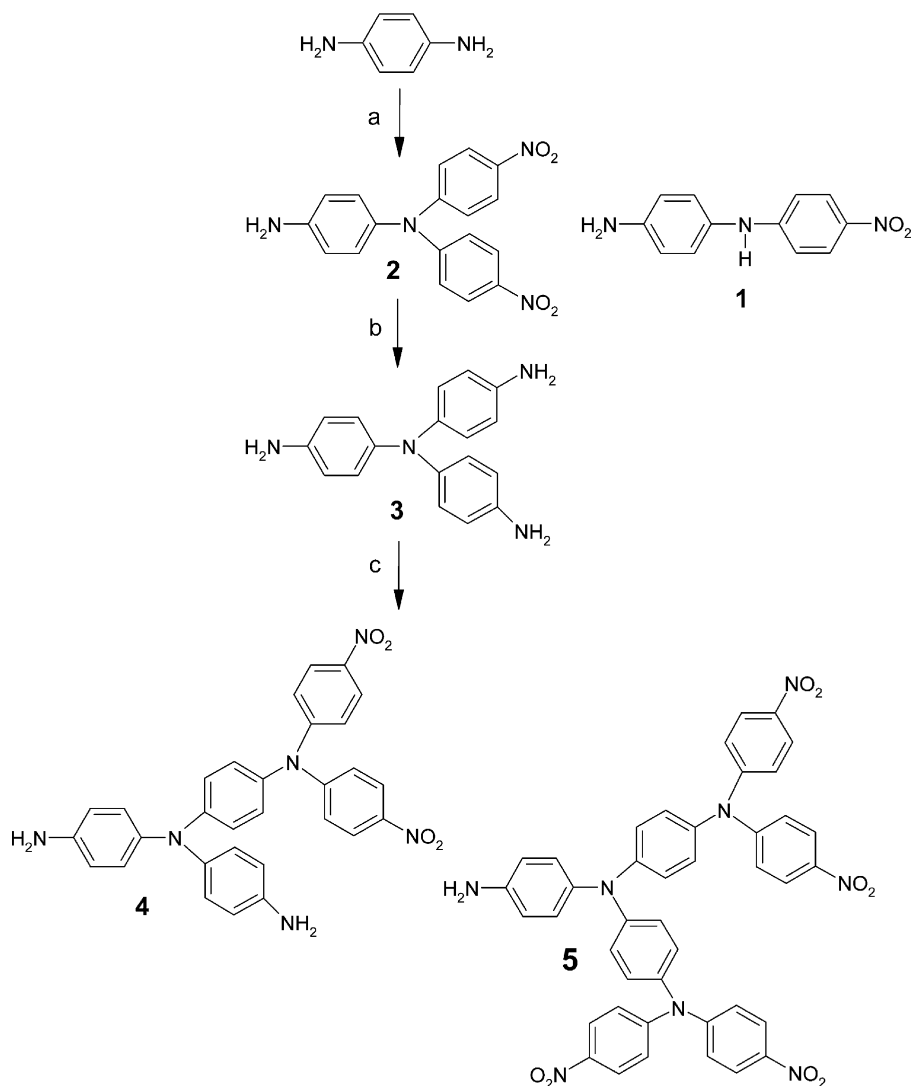
**Tris(4-Aminophenyl)amine (3).** 0.45 g, 78% yield,  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  6.43–6.41 (m, 12H), 5.0–4.1 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  127.2, 114.9, 105.6. IR ( $\text{cm}^{-1}$ ) 3553, 3474, 3383, 1618, 1602, 1579, 1494, 1308, 1278, 1110, 848, 751. Anal. calcd for  $\text{C}_{18}\text{H}_{18}\text{N}_4$ : C, 74.48; H, 6.21; N, 19.31. Found: C, 73.60; H, 6.15; N, 19.04. MS  $m/z$  = 290.4.

***N,N*-Di(4-nitrophenyl)-*N',N'*-di(4-aminophenyl)-1,4-phenylenediamine (4).** 0.53 g, 20% yield, m.p. 245–248 °C.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.16–8.14 (m, 4H), 7.18–7.16 (m, 4H), 6.96–6.94 (m, 2H), 6.90–6.88 (m, 4H), 6.61–6.59 (m, 2H), 6.56–6.54 (m, 4H), 5.05 (s, 4H). IR ( $\text{cm}^{-1}$ ) 3448, 3364, 1603, 1580, 1502, 1344, 1307, 1278, 1265, 1111, 842, 831, 750, 696. Anal. calcd for  $\text{C}_{30}\text{H}_{24}\text{N}_6\text{O}_4 \cdot (\text{H}_2\text{O})_{1.14}$ : C, 65.16; H, 4.76; N, 15.20. Found: C, 64.35; H, 4.38; N, 14.54.

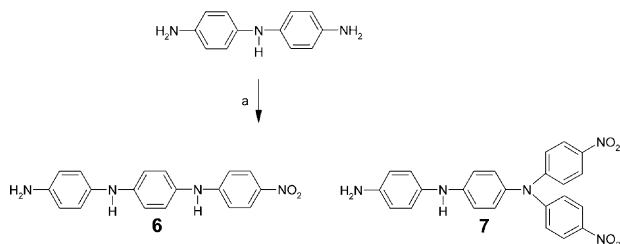
**Branched heptamer (5).** 2.08 g, 54% yield,  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.18–8.16 (m, 8H), 7.22–7.20 (m, 8H), 7.15–7.13 (m, 4H), 7.07–7.04 (m, 4H), 6.95–6.93 (m, 2H), 6.63–6.61 (m, 2H), 5.20 (s, 2H). IR ( $\text{cm}^{-1}$ ) 3465, 3381, 1603, 1581, 1503, 1494, 1344, 1307, 1280, 1266, 1178, 1111, 843, 831, 750, 695. Anal. calcd for  $\text{C}_{42}\text{H}_{30}\text{N}_8\text{O}_8 \cdot (\text{H}_2\text{O})_{2.34}$ : C, 61.76; H, 4.25; N, 13.75. Found: C, 61.09; H, 4.03; N, 13.07.

***N*-(4-Nitrophenyl)-*N'*-(4-aminophenyl)-1,4-phenylenediamine (6).** 0.18 g, 11% yield, m.p. 178–181 °C.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.00 (s, 1H), 8.02–7.99 (m, 2H), 7.55 (s, 1H), 7.00–6.98 (m, 2H), 6.84–6.79 (m, 6H), 6.55–6.52 (m, 2H), 4.78 (s, 2H). IR ( $\text{cm}^{-1}$ ) 3401, 3329, 2969, 1600, 1514, 1501, 1470, 1334, 1307, 1262, 1186, 1115, 835, 813, 750. Anal. calcd for  $\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_2$ : C, 67.50; H, 5.00; N, 17.50. Found: C, 66.85; H, 4.70; N, 17.25.

***N,N*-Di(4-nitrophenyl)-*N'*-(4-aminophenyl)-1,4-phenylenediamine (7).** 1.5 g, 68% yield, m.p. 227–230 °C.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.16–8.14 (m, 4H), 7.81 (s, 1H), 7.19–7.16 (m, 4H), 7.00–6.97 (m, 2H), 6.86–6.81 (m, 4H), 6.56–6.54 (m, 2H), 4.86 (s, 2H). IR ( $\text{cm}^{-1}$ ) 3367, 3067, 1596, 1577, 1512, 1491, 1334, 1320, 1308, 1272, 1177, 1109, 829, 751. Anal. calcd for  $\text{C}_{24}\text{H}_{19}\text{N}_5\text{O}_4$ : C, 65.31; H, 4.31; N, 15.87. Found: C, 64.00; H, 4.22; N, 15.57.



**Scheme 1** The condensation of 4-fluoronitrobenzene to *p*-phenylenediamine in the presence of K<sub>2</sub>CO<sub>3</sub>: (a) 4-fluoronitrobenzene (2 equiv), K<sub>2</sub>CO<sub>3</sub> (4 equiv), DMSO, 90 °C, (b) Sn, HCl<sub>conc</sub>, (c) 4-fluoronitrobenzene (6 equiv), K<sub>2</sub>CO<sub>3</sub> (12 equiv), DMSO, 90 °C.



**Scheme 2** The condensation of 4-fluoronitrobenzene to 4,4'-diaminodiphenylamine in the presence of K<sub>2</sub>CO<sub>3</sub>: (a) 4-fluoronitrobenzene (2 equiv), K<sub>2</sub>CO<sub>3</sub> (4 equiv), DMSO, 90 °C.

**Trimer NO<sub>2</sub>/NO<sub>2</sub>—*N,N'*-di(4-nitrophenyl)-1,4-phenylenediamine (8).** The crude product was chromatographed using acetone–CH<sub>2</sub>Cl<sub>2</sub> (1 : 3) and crystallized from methanol (0.735 g, 42% yield), m.p. 133–135 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 9.29 (s, 2H), 8.08–8.06 (m, 4H), 7.26 (s, 4H), 7.03–7.01 (m, 4H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 151.1, 137.7, 135.7, 126.3, 122.4, 113.1. IR (cm<sup>−1</sup>) 3384, 3333, 1597, 1538, 1511, 1475, 1324, 1300, 1113, 831, 749. Anal. calcd for C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>: C, 61.71; H, 4.00; N, 16.00. Found: C, 61.36; H, 3.89; N, 15.80.

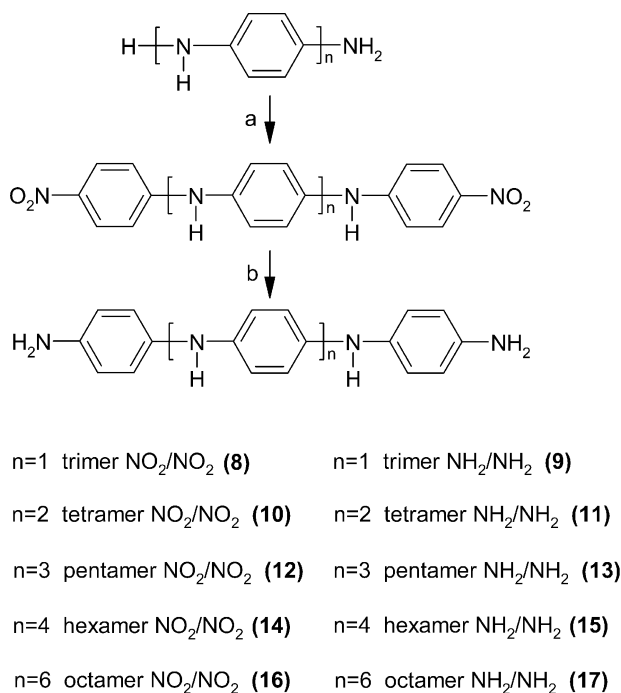
**Trimer NH<sub>2</sub>/NH<sub>2</sub>—*N,N'*-di(4-aminophenyl)-1,4-phenylenediamine (9).** A white powder was obtained (0.42 g, 72% yield).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.01 (s, 2H), 6.71–6.69 (m, 8H), 6.48–6.46 (m, 4H), 4.57 (s, 4H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 142.1, 138.0, 134.3, 119.6, 116.9, 114.9. IR (cm<sup>−1</sup>) 3396, 3365, 1525, 1517, 1440, 1303, 1263, 879, 821. Anal. calcd for C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>: C, 74.48; H, 6.21; N, 19.31. Found: C, 73.44; H, 6.02; N, 18.74. *M/z* = 290.6.

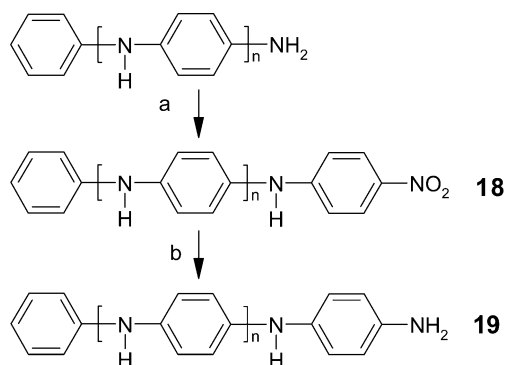
**Tetramer NO<sub>2</sub>/NO<sub>2</sub> (10).** The experimental data are given in ref. 14. <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 152.1, 140.3, 137.0, 131.7, 126.4, 123.7, 117.6, 112.3.

**Tetramer NH<sub>2</sub>/NH<sub>2</sub> (11).** The experimental data are given in ref. 14. <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 142.4, 138.8, 136.6, 133.9, 120.0, 118.1, 116.5, 114.9.

**Pentamer NO<sub>2</sub>/NO<sub>2</sub> (12).** The crude product was purified by liquid chromatography using acetone–CH<sub>2</sub>Cl<sub>2</sub> (1 : 4). The powder was recrystallized from methanol as orange-brown crystals (1.34 g, 50.5% yield after recrystallization), m.p. 187–189 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 9.08 (s, 2H), 8.04–8.01 (m, 4H), 7.96 (s, 2H), 7.09–7.00 (m, 12H), 6.87–6.85 (m, 4H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 152.4, 141.9, 136.8, 136.5, 130.5, 126.4, 124.0, 119.5, 116.1, 112.2. IR (cm<sup>−1</sup>) 3547, 3353, 1597, 1512, 1497, 1314, 1293, 1183, 1111, 819, 750. Anal.



**Scheme 3** The synthesis of linear symmetric nitroanilines and aminooligoanilines: (a) 4-fluoronitrobenzene (2 equiv),  $\text{Et}_3\text{N}$  (2 equiv), DMSO,  $90^\circ\text{C}$ , (b)  $\text{Sn}$ ,  $\text{HCl}_{\text{conc}}$ .



**Scheme 4** The synthesis of linear asymmetric nitroanilines and aminooligoanilines: (a) 4-fluoronitrobenzene (1 equiv),  $\text{Et}_3\text{N}$  (1 equiv), DMSO,  $90^\circ\text{C}$ , (b)  $\text{Sn}$ ,  $\text{HCl}_{\text{conc}}$ .

calcd for  $\text{C}_{30}\text{H}_{24}\text{N}_6\text{O}_4$ : C, 67.67; H, 4.51; N, 15.80. Found: C, 66.23; H, 4.55; N, 14.32.

**Pentamer  $\text{NH}_2/\text{NH}_2$  (**13**).** A greyish-white powder was obtained (0.64 g, 68% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.27 (s, 2H), 7.09 (s, 2H), 6.81–6.79 (m, 8H), 6.74–6.72 (m, 8H), 6.49–6.47 (m, 4H), 4.59 (s, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  142.4, 139.0, 137.5, 136.2, 133.8, 120.1, 118.5, 117.6, 116.4, 114.9. IR ( $\text{cm}^{-1}$ ) 3384, 3022, 1508, 1499, 1299, 1263, 815. Anal. calcd for  $\text{C}_{30}\text{H}_{28}\text{N}_6$ : C, 76.27; H, 5.93; N, 17.80. Found: C, 75.84; H, 5.82; N, 17.61. MS  $m/z$  = 472.5.

**Hexamer  $\text{NO}_2/\text{NO}_2$  (**14**).** The crude product was purified by liquid chromatography using acetone– $\text{CH}_2\text{Cl}_2$  (1 : 4). The pow-

der was recrystallized from methanol as orange-brown crystals (0.57 g, 68% yield after recrystallization), m.p.  $185\text{--}187^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  9.04 (s, 2H), 8.03–8.00 (m, 4H), 7.86 (s, 2H), 7.69 (s, 1H), 7.07–7.05 (m, 4H), 7.00–6.94 (m, 12H), 6.86–6.83 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  152.5, 142.4, 138.3, 136.7, 135.2, 130.1, 126.4, 124.1, 120.2, 117.8, 115.6, 112.1. IR ( $\text{cm}^{-1}$ ) 3394, 1595, 1503, 1348, 1320, 815. Anal. calcd for  $\text{C}_{36}\text{H}_{29}\text{N}_7\text{O}_4$ : C, 69.34; H, 4.65; N, 15.73. Found: C, 69.11; H, 4.76; N, 15.53.

**Hexamer  $\text{NH}_2/\text{NH}_2$  (**15**).** A greyish-white powder was obtained (0.40 g, 77% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.32 (s, 1H), 7.28 (s, 2H), 7.09 (s, 2H), 6.82–6.80 (m, 12H), 6.75–6.73 (m, 8H), 6.50–6.47 (m, 4H), 4.60 (s, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  142.4, 139.1, 137.7, 137.0, 136.1, 133.8, 120.1, 118.6, 118.0, 117.5, 116.4, 114.9. IR ( $\text{cm}^{-1}$ ) 3383, 1598, 1499, 1294, 815. Anal. calcd for  $\text{C}_{36}\text{H}_{33}\text{N}_7$ : C, 76.73; H, 5.86; N, 17.41. Found: C, 75.78; H, 5.77; N, 16.92. MS  $m/z$  = 563.0.

**Octamer  $\text{NO}_2/\text{NO}_2$  (**16**).** The crude product was purified by liquid chromatography using acetone– $\text{CH}_2\text{Cl}_2$  (1 : 4). The powder was recrystallized from methanol as orange-brown crystals (0.097 g, 17% yield after recrystallization), m.p.  $210\text{--}213^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  9.04 (s, 2H), 8.03–8.00 (m, 4H), 7.81 (s, 2H), 7.57 (s, 2H), 7.51 (s, 1H), 7.06–7.03 (m, 4H), 6.98–6.91 (m, 20H), 6.85–6.83 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  152.5, 145.3, 143.0, 140.3, 139.4, 137.6, 136.7, 130.4, 126.4, 124.1, 120.5, 118.8, 117.9, 117.0, 115.4, 112.1. IR ( $\text{cm}^{-1}$ ) 3379, 1595, 1499, 1321, 1293, 817. Anal. calcd for  $\text{C}_{48}\text{H}_{39}\text{N}_9\text{O}_4$ : C, 71.55; H, 4.84; N, 15.65. Found: C, 70.36; H, 4.58; N, 15.15.

**Octamer  $\text{NH}_2/\text{NH}_2$  (**17**).** A greyish-white powder was obtained (0.069 g, 77% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.72 (s, 1H), 7.51 (s, 2H), 7.36 (s, 2H), 7.28 (s, 2H), 7.12–7.10 (m, 8H), 6.94–6.65 (m, 20H), 6.49–6.47 (m, 4H), 4.61 (s, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  142.9, 141.5, 140.3, 139.1, 138.5, 137.7, 136.6, 133.5, 120.2, 119.5, 118.3, 117.9, 117.4, 116.6, 115.8, 114.4. IR ( $\text{cm}^{-1}$ ) 3590, 3380, 1597, 1498, 1298, 814. Anal. calcd for  $\text{C}_{48}\text{H}_{43}\text{N}_9$ : C, 77.32; H, 5.77; N, 16.91. Found: C, 76.70; H, 5.78; N, 16.66. MS  $m/z$  = 745.4.

**Trimer  $\text{Ph}/\text{NO}_2$ —*N*-(4-nitrophenyl)-*N'*-phenyl-1,4-phenylenediamine (**18**).** The experimental data are given in ref. 14.  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  152.0, 143.6, 140.0, 137.0, 131.8, 129.2, 126.3, 123.6, 119.4, 117.9, 116.3, 112.3.

**Trimer  $\text{Ph}/\text{NH}_2$ —*N*-(4-aminophenyl)-*N'*-phenyl-1,4-phenylenediamine (**19**).** The experimental data are given in ref. 14.  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  145.9, 142.8, 141.0, 133.4, 133.0, 129.0, 121.4, 121.0, 117.4, 115.5, 114.9, 114.1.

**Tetramer  $\text{Ph}/\text{NO}_2$  (**20**).** The experimental data are given in ref. 14.  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  152.4, 144.9, 141.8, 136.7, 136.6, 136.3, 130.5, 129.1, 126.3, 124.0, 119.8, 119.4, 118.3, 116.1, 115.0, 112.1.

**Tetramer  $\text{Ph}/\text{NH}_2$  (**21**).** The experimental data are given in ref. 14.  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  145.7, 142.7, 139.9, 135.1, 134.0, 133.4, 129.0, 121.0, 120.5, 119.6, 117.6, 116.3, 116.0, 114.9, 114.3.

**Pentamer  $\text{Ph}/\text{NO}_2$  (**22**).** The crude product was purified by chromatography (silica gel, ethyl acetate– $\text{CH}_2\text{Cl}_2$ : 1 : 4), then recrystallized from methanol (0.67 g, 74% yield), m.p.  $184\text{--}186^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  9.04 (s, 1H), 8.02–8.01 (m, 2H), 7.85 (s, 1H), 7.78 (s, 1H), 7.68 (s, 1H), 7.15–7.13 (m, 2H), 7.07–

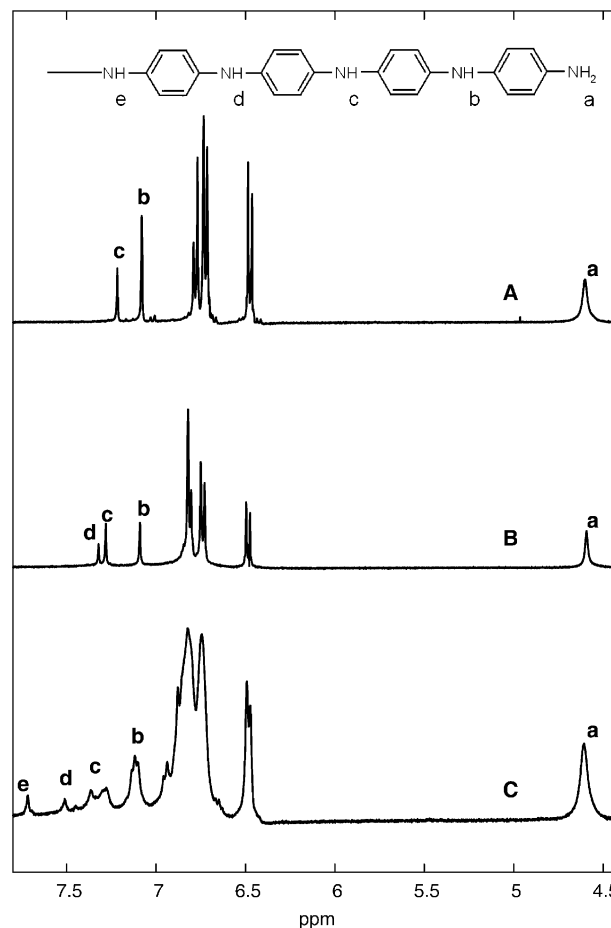


7.04 (m, 2H), 7.00–6.93 (m, 10H), 6.91–6.89 (m, 2H), 6.85–6.83 (m, 2H), 6.68–6.65 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  152.5, 145.3, 142.4, 138.3, 138.2, 136.7, 135.2, 135.1, 130.1, 129.1, 126.3, 124.1, 120.5, 120.2, 117.9, 117.8, 117.7, 115.6, 114.6, 112.1. IR ( $\text{cm}^{-1}$ ) 3388, 3024, 1597, 1525, 1510, 1497, 1322, 1296, 1113, 818, 750, 695. Anal. calcd for  $\text{C}_{30}\text{H}_{25}\text{N}_5\text{O}_2$ : C, 73.92; H, 5.13; N, 14.37. Found: C, 74.47; H, 4.83; N, 14.17.

**Pentamer Ph/ $\text{NH}_2$  (23).** The obtained white powder was dried over KOH in a vacuum desiccator (0.49 g, 78% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  7.71 (s, 1H), 7.51 (s, 1H), 7.36 (s, 1H), 7.13 (s, 1H), 7.12–7.11 (m, 2H), 6.96–6.94 (m, 2H), 6.90–6.83 (m, 10H), 6.76–6.74 (m, 4H), 6.66–6.64 (m, 1H), 6.50–6.48 (m, 2H), 4.58 (s, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  145.6, 142.5, 139.5, 139.4, 138.6, 135.9, 135.7, 134.3, 133.7, 129.0, 120.9, 120.3, 119.2, 119.0, 117.7, 117.0, 116.7, 116.2, 114.9, 114.4. IR ( $\text{cm}^{-1}$ ) 3390, 3022, 1598, 1527, 1509, 1498, 1303, 1218, 817, 747, 693. Anal. calcd for  $\text{C}_{30}\text{H}_{27}\text{N}_5$ : C, 78.77; H, 5.91; N, 15.32. Found: C, 77.78; H, 6.01; N, 15.07. MS  $m/z$  = 457.5.

## Results and discussion

Diarylamines are readily formed by the  $\text{S}_{\text{N}}\text{Ar}$  reaction of activated fluoroarenes with arylamines in dipolar aprotic solvents. The reaction is activated by a base such as  $\text{K}_2\text{CO}_3$  or KF, which are frequently recommended.<sup>15,16</sup> Condensation conditions are well-established for compounds containing one amine group; however, the use of aromatic diamine compounds can change the preference for the substitution reaction. We have studied this type of reaction with the goal to prepare linear symmetric ( $\text{NH}_2/\text{NH}_2$  end-capped) and asymmetric ( $\text{Ph}/\text{NH}_2$  end-capped) oligoanilines. We found that 4-fluoronitrobenzene reacts with *p*-phenylenediamine (Scheme 1) or 4,4'-diaminodiphenylamine (Scheme 2) in the presence of  $\text{K}_2\text{CO}_3$  to afford a mixture of branched triarylamine and monosubstituted arylamine. Branched amines are preferentially formed, even with an excess of starting amine. Yields of reactions at  $90^\circ\text{C}$  are *ca.* 70% with both starting amines. The decrease of the reaction temperature lowers the yield but two products are still formed. After the substitution of a first nitrobenzene ring, the secondary amine proton becomes more acidic than the protons of the terminal  $\text{NH}_2$  group; thus, carbonate deprotonates it easily, which leads to preferential formation of triarylamines. We have not studied the mechanism of the deprotonation and we cannot corroborate whether carbonate forms a hydrogen-bonded adduct with  $-\text{NH}-$  or deprotonates the amine group completely to nitranion. Similarly, the reaction of tris(4-aminophenyl)amine (3) with 4-fluoronitrobenzene under the same conditions gives a mixture of branched asymmetric arylnitroamines 4 and 5 (Scheme 1).



**Fig. 1** The  $^1\text{H}$  NMR spectra in  $\text{DMSO-d}_6$  solution of (a) tetramer  $\text{NH}_2/\text{NH}_2$  11, (b) hexamer  $\text{NH}_2/\text{NH}_2$  15 and (c) octamer  $\text{NH}_2/\text{NH}_2$  17.

The substitution reaction involves one or two terminal amine groups. The preparation of symmetric branched arylamines requires heating at  $140^\circ\text{C}$ . Nevertheless, this type of reaction establishes an easy way to prepare dendrimeric arylamines. It should be mentioned that we have also studied  $\text{S}_{\text{N}}\text{Ar}$  coupling in the presence of KF. In this case the mixture of the same products is obtained; however, the reaction yields do not exceed 50%.

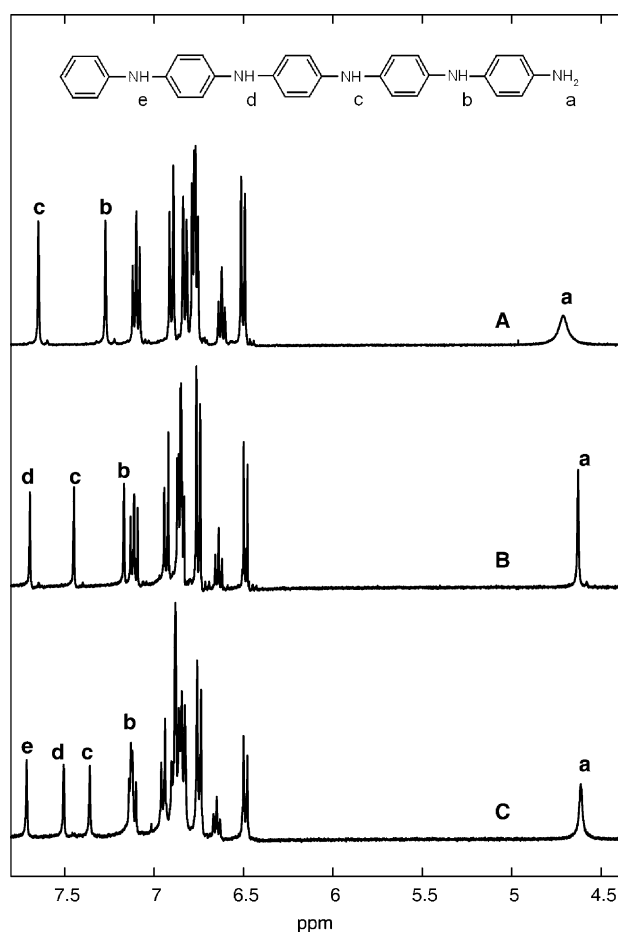
We conclude that the use of a less basic agent than  $\text{K}_2\text{CO}_3$ , for example triethylamine, can ensure the formation of linear arylnitroamines. In such a case the reaction fulfils the normal criterion for  $\text{S}_{\text{N}}\text{Ar}$  and the substitution involves two terminal amine groups. The reaction of *p*-phenylenediamine with 4-fluoronitrobenzene leads to the formation of a linear  $\text{NO}_2/\text{NO}_2$

**Table 1** Substitution of 4-fluoronitrobenzene to give symmetric and asymmetric aromatic amines and their subsequent reduction to oligoanilines.

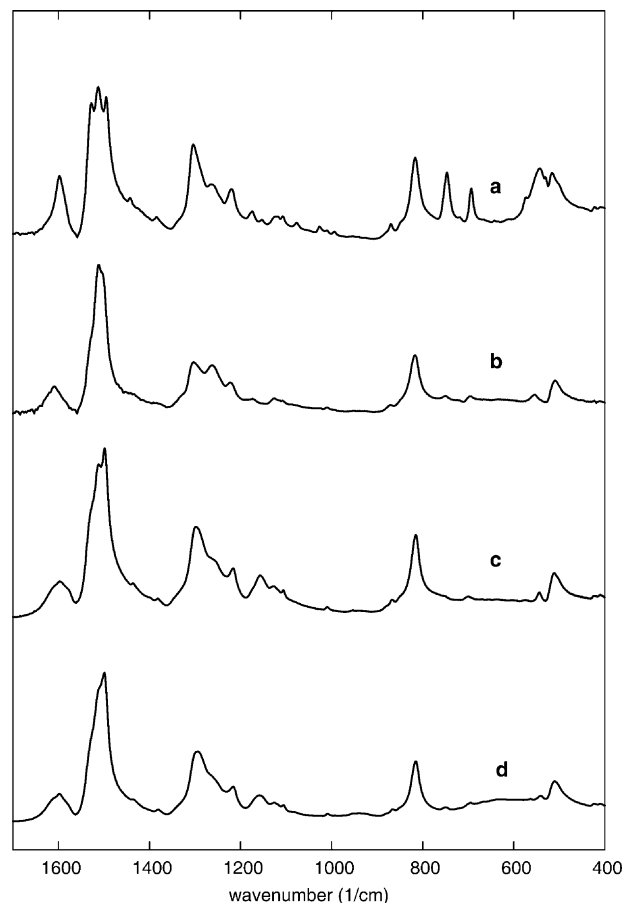
| Aromatic amine                | Nitrooligoaniline     | Yield (%) | Aminoaligoaniline     | Yield (%) |
|-------------------------------|-----------------------|-----------|-----------------------|-----------|
| <b>Symmetric</b>              |                       |           |                       |           |
| <i>p</i> -Phenylenediamine    | Trimer 8 ( $n=1$ )    | 42        | Trimer 9 ( $n=1$ )    | 72        |
| 4,4'-Diaminodiphenylamine     | Tetramer 10 ( $n=2$ ) | 61        | Tetramer 11 ( $n=2$ ) | 75        |
| Trimer 9 ( $n=1$ )            | Pentamer 12 ( $n=3$ ) | 51        | Pentamer 13 ( $n=3$ ) | 68        |
| Tetramer 11 ( $n=2$ )         | Hexamer 14 ( $n=4$ )  | 68        | Hexamer 15 ( $n=4$ )  | 77        |
| Hexamer 15 ( $n=4$ )          | Octamer 16 ( $n=6$ )  | 17        | Octamer 17 ( $n=6$ )  | 67        |
| <b>Asymmetric</b>             |                       |           |                       |           |
| N-Phenyl-1,4-phenylenediamine | Trimer 18 ( $n=1$ )   | 47        | Trimer 19 ( $n=1$ )   | 72        |
| Trimer 19 ( $n=1$ )           | Tetramer 20 ( $n=2$ ) | 46        | Tetramer 21 ( $n=2$ ) | 73        |
| Tetramer 21 ( $n=2$ )         | Pentamer 22 ( $n=3$ ) | 74        | Pentamer 23 ( $n=3$ ) | 78        |

trimer (**8**; Scheme 3). The reduction of nitroamine **8** affords an amine trimer **9**, which can be used as the starting amine to prepare an NO<sub>2</sub>/NO<sub>2</sub> pentamer (**12**; Scheme 3). The iterative coupling/reduction sequence allows oligomers of controlled length to be synthesized, all containing amine groups coupled in 1,4 positions to aromatic rings; thus, the use of an amine with an odd number of benzene rings leads to the formation of odd-length oligomers. Similarly, the use of a starting amine with an even number of benzene rings affords the formation of even-length oligomers (Table 1). In the case of asymmetric oligomers the length of the molecule increases by one ring in each coupling step (Table 1). It should be emphasized that the S<sub>N</sub>Ar reaction is carried out in mild conditions and therefore there is no need for protection of secondary amine groups. We have not detected the formation of branched products. Yields of coupling reactions are 42–74% for different molecules (Table 1). Only the yield of the preparation of octamer **17** is low, at ca. 17%. Presented yields are lower than the yields reported by Brown *et al.*<sup>13</sup> for a high-pressure synthesis; however, in the cases presented here we do not need any special apparatus to apply high pressure and all reactions can be carried out in standard laboratory equipment.

Obtained oligoanilines of both types were characterized using elemental analyses, mass spectroscopy, NMR, IR and UV-Vis-NIR spectroscopies. In Fig. 1 the <sup>1</sup>H NMR spectra in DMSO-d<sub>6</sub> solutions of the symmetric even oligomers, tetramer **11**, hexamer **15** and octamer **17** are presented. The signal of the terminal NH<sub>2</sub> groups' protons appears at 4.59 ppm, independent of the length of the molecule. The location of the other –NH– signals is influenced by their position in the chain; thus, different types of secondary amine groups' protons can be easily distinguished. The signal of the –NH<sub>b</sub>– protons appears at 7.08 ppm and that of –NH<sub>c</sub>– at 7.21 ppm in the tetramer **11**



**Fig. 2** The <sup>1</sup>H NMR spectra in DMSO-d<sub>6</sub> solution of (a) trimer Ph/NH<sub>2</sub> **19**, (b) tetramer Ph/NH<sub>2</sub> **21** and (c) pentamer Ph/NH<sub>2</sub> **23**.

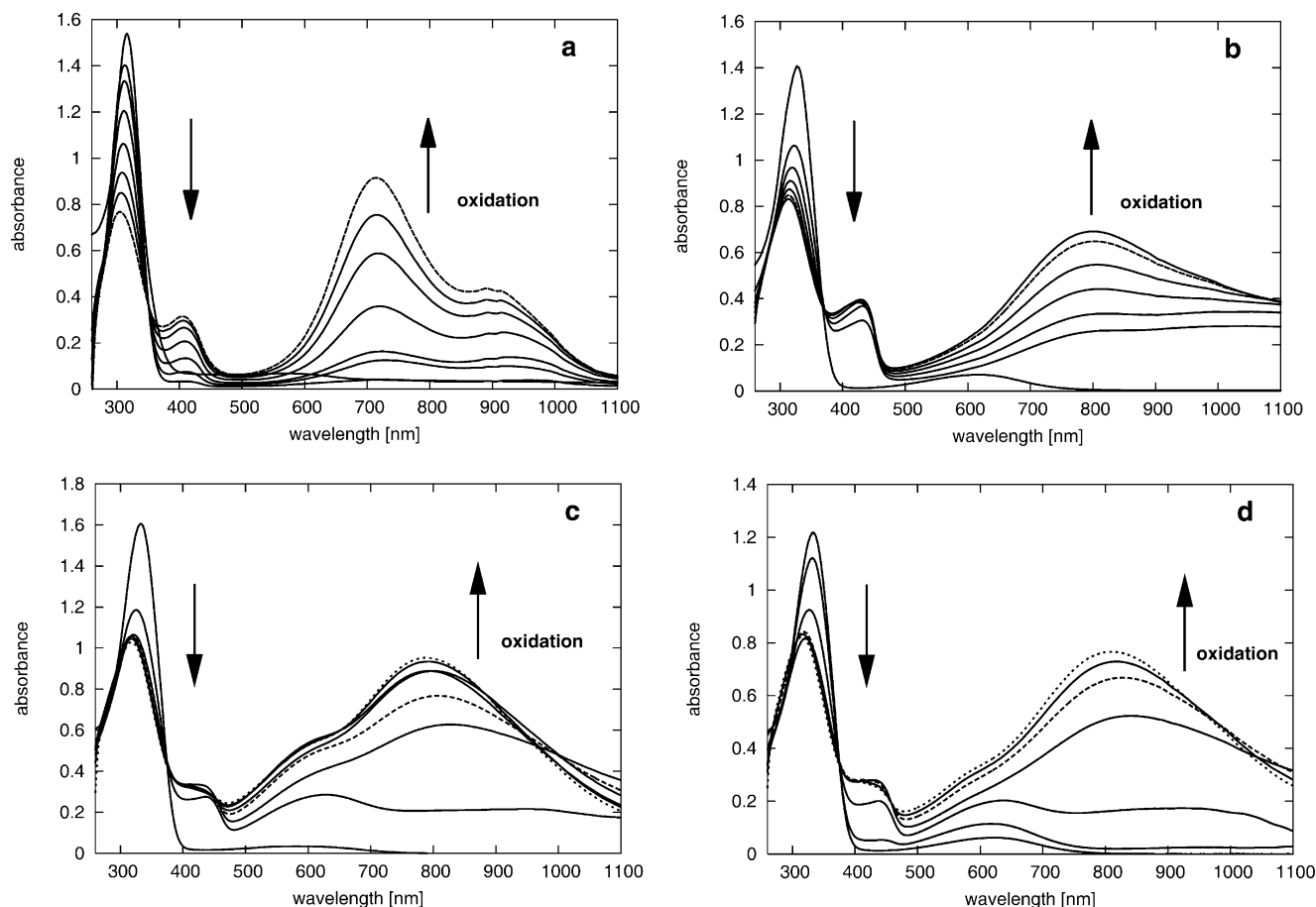


**Fig. 3** IR spectra of (a) tetramer Ph/NH<sub>2</sub> (**21**), (b) tetramer NH<sub>2</sub>/NH<sub>2</sub> (**11**), (c) hexamer NH<sub>2</sub>/NH<sub>2</sub> (**15**) and (d) octamer NH<sub>2</sub>/NH<sub>2</sub> (**17**).

spectrum, which is displaced to 7.28 ppm in the octamer **17** spectrum. The signal of the –NH<sub>d</sub>– proton appears at 7.32 ppm in the spectrum of hexamer **15** and at 7.51 ppm in the spectrum of octamer **17**.

In Fig. 2 the <sup>1</sup>H NMR spectra of the asymmetric oligoanilines are presented. These spectra are richer as compared to those of the symmetric oligomers. We can observe that the positions of the amine group protons are strongly influenced by the length of the molecule. The signal of the terminal NH<sub>2</sub> protons appears at 4.78 ppm in the spectrum of trimer **19** and shifts to 4.61 ppm in the spectrum of pentamer **23**. Positions of other secondary amine groups' protons are displaced with increase of the chain length. For example, the signal attributed to –NH<sub>b</sub>– is located at 7.27 ppm in the spectrum of trimer **19** and displaced to 7.13 ppm in the spectrum of pentamer **23**. Similarly, signals of –NH<sub>c</sub>– are shifted by 0.29 ppm from trimer **19** to pentamer **23** and that of –NH<sub>d</sub>– is shifted by 0.19 ppm from tetramer **21** to pentamer **23**. In these spectra we can also observe two multiplets (similar to triplets), the appearance of which confirms the presence of a terminal phenyl ring. The multiplets are located at 6.62 and 7.11 ppm, and their positions do not depend on the length of the molecule. <sup>1</sup>H NMR spectra presented here agree with the postulated structures of the synthesized oligomers.

In Fig. 3 the IR spectra of an asymmetric oligomer (tetramer **21**) and of symmetric ones (tetramer **11**, hexamer **15** and octamer **17**) are collected. They exhibit features typical of oligoanilines in the leucoemeraldine oxidation state. The character of the spectrum, especially in the low energy region, depends on the type of oligomer (symmetric or asymmetric) but is not influenced by the length of the molecule. Bands attributed to the –NH– or NH<sub>2</sub> stretching vibrations (not presented in Fig. 3) appear at 3388 cm<sup>–1</sup>. Modes due to a combination of C–H bending and C–C stretching vibrations



**Fig. 4** The UV-Vis-NIR spectra in DMSO of (a) trimer  $\text{NH}_2/\text{NH}_2$  **9**, (b) pentamer  $\text{NH}_2/\text{NH}_2$  **13**, (c) hexamer  $\text{NH}_2/\text{NH}_2$  **15** and (d) octamer  $\text{NH}_2/\text{NH}_2$  **17** oxidized with ammonium persulfate in 0.1 M HCl solution (the dashed line corresponds to the theoretical removal of 2 electrons, the dotted line to the removal of 4 electrons from each oligomer molecule).

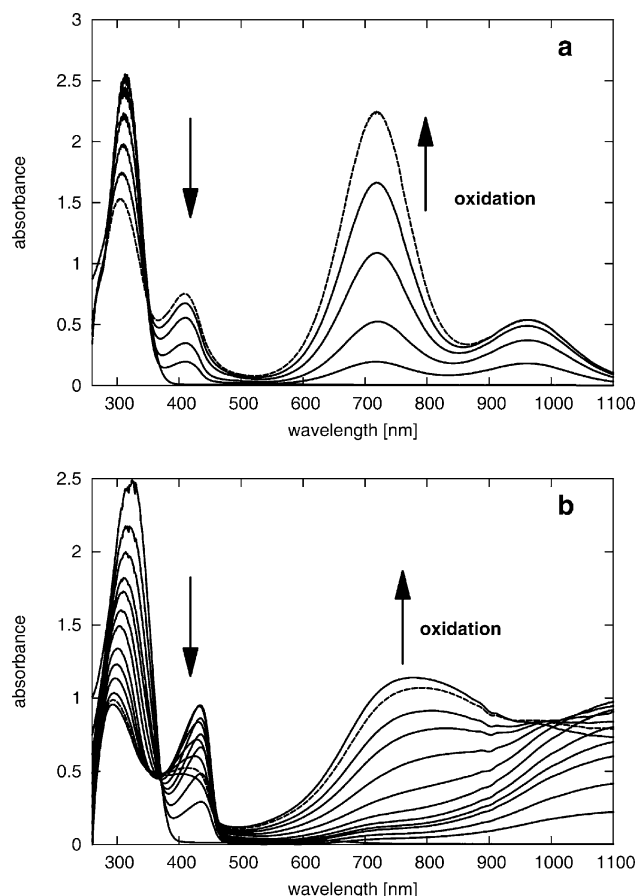
are located at 1598, 1512 and  $1498\text{ cm}^{-1}$ . The peak at  $1264\text{ cm}^{-1}$  can be ascribed to a C–N stretching vibration.<sup>17</sup> In all spectra of symmetric oligomers one band due to the C–H out-of-plane deformation of the 1,4-disubstituted ring at  $815\text{ cm}^{-1}$  is observed, whereas in the spectrum of asymmetric oligoanilines three peaks at 816, 746 and  $696\text{ cm}^{-1}$  appear. The presence of the two last peaks in this region confirms the presence of the terminal phenyl ring in the asymmetric molecule. The IR spectra of symmetric oligoanilines are perfectly compatible with the spectrum of polyleucoemeraldine.<sup>17,18</sup>

It was mentioned that oligoanilines can be considered as model compounds of polyaniline. The most interesting form of polyaniline is emeraldine, which contains *ca.* 50% of amine and *ca.* 50% of imine groups, that is one of the 4 rings is quinoid, the remaining three being benzoid. The best model compounds for emeraldine are therefore tetramer or octamer. We have shown before that  $\text{NH}_2/\text{NH}_2$  tetramer **11** can be oxidized to the emeraldine oxidation state with the formation of a positional isomer A and two geometrical isomers *syn* and *anti*.<sup>14</sup> The oxidation of the  $\text{Ph}/\text{NH}_2$  tetramer **21** gave a mixture of positional isomers A and B.<sup>14</sup> However, in the case of the polymer the distribution of imine groups and quinoid ring can be random. For this reason we have studied the oxidation of oligomers of both types and of different chain lengths using UV-Vis-NIR spectroscopy.

All absorption spectra of oligoanilines show only one peak related to the  $\pi$ - $\pi^*$  transition. However, it should be noticed that oligoanilines with a long chain (pentamer, hexamer, octamer) are easily oxidized and are very sensitive even to trace amounts of oxygen; thus, the spectra of long oligomers are contaminated by a small peak at *ca.* 600 nm due to the presence of residual quinoid units. Nevertheless, the position of the  $\pi$ - $\pi^*$  peak depends on the length of the molecule. In the

spectrum of a trimer (**9**) this peak appears at 316 nm and it shifts gradually to 333 nm in the spectrum of an octamer (**17**). Similarly, in the case of the spectrum of asymmetric oligomers the position of this peak changes from 314 nm for a trimer (**19**) to 325 nm for a pentamer (**23**). This suggests that for a well-defined structure of the molecule the conjugation length influences the  $\pi$ - $\pi^*$  energy gap, which is not unexpected.

Oligomers were oxidized using ammonium persulfate in 0.1 M HCl and the absorption spectra monitored for each step of oxidation. Absorption spectra are presented in Fig. 4 for symmetric oligomers and in Fig. 5 for asymmetric ones. The oxidation process gives rise to new peaks in the less energetic regions of the spectra. The character of the spectra does not depend on the end-capping groups (phenyl/ $\text{NH}_2$  or  $\text{NH}_2/\text{NH}_2$ ) but is significantly influenced by the length of the molecule. In particular, for a trimer (**9**) and a trimer (**19**) [Figs 4(a) and 5(a)] three new peaks appear at 410, 720 and 950 nm. Further oxidation causes an increase of the intensities of these peaks with a simultaneous decrease of the intensity of the  $\pi$ - $\pi^*$  peak. It is characteristic for both trimers that the low energy peak (950 nm) does not disappear during the oxidation. The location of these peaks is similar to that observed by Sun *et al.*<sup>19</sup> for a  $\text{Ph}/\text{Ph}$  trimer -CSA salt in THF solution. In the case of tetramers **11** and **21** the spectra were presented before.<sup>14</sup> In the first step of the oxidation three new peaks can also be observed at 426, 775 and *ca.* 1050 nm. However, after further oxidation the peak at 1050 nm disappears, while the other two shift to higher energy (412 and 730 nm, respectively) and dominate the spectra. The spectra of oxidized tetramers differ from that observed by Sun *et al.*,<sup>19</sup> who stated that only the peak at 425 nm and a broad band at *ca.* 1000 nm were observed for the  $\text{Ph}/\text{Ph}$  tetramer -CSA salt in THF solution. In our opinion the conjugation in the  $\text{Ph}/\text{Ph}$  tetramer is higher than in



**Fig. 5** The UV-Vis-NIR spectra in DMSO of (a) trimer Ph/NH<sub>2</sub> **19** and (b) pentamer Ph/NH<sub>2</sub> **23** oxidized with ammonium persulfate in 0.1 M HCl solution (the dashed line corresponds to the theoretical removal of 2 electrons from each oligomer molecule).

NH<sub>2</sub>/NH<sub>2</sub> or Ph/NH<sub>2</sub> tetramers and on the other hand salts with HCl acid have a more localized cation-radical than salts with camphorsulfonic acid, as was frequently observed for polyaniline; thus, the differences are not surprising.

The oxidation of pentamers **13** and **23** [Figs 4(b) and 5(b)] leads to the appearance of a new peak at 435 nm and an increase of the absorption in the NIR region. Further oxidation causes the localization of a new peak at 800 nm but increased absorption in the NIR region is still observed. Similar to the spectra of trimers, the dashed lines correspond to the theoretical removal of 2 electrons from each pentamer molecule. The character of these spectra suggests that radical-cations are formed with possible delocalization of charge carriers along the chain. The increase of the radical-cation concentration is manifested by the peak localization at 800 nm. In the case of hexamer **15** [Fig. 4(c)] in the first step of oxidation two new peaks can be observed at 436 and 630 nm. Further oxidation leads to the appearance of a broad band located at 810 nm with a shoulder at ca. 600 nm. This spectrum (dashed line) corresponds to the theoretical removal of 2 electrons from each hexamer molecule. The prolonged oxidation to the nigraniline state (dotted line) causes localization of the peak at 790 nm, still with a shoulder at 600 nm. The character of this spectrum indicates that the concentration of oxidized units is high; some imine groups are poorly protonated in 0.1 M HCl–DMSO solution and the delocalization of charge carriers is strongly limited.

The oxidation of octamer **17** [Fig. 4(d)] proceeds similarly to the oxidation of the hexamer in the first two steps; however, further oxidation leads to a spectra whose character is similar to that of tetramer **11**. The peaks of the octamer, theoretically oxidized to the emeraldine state, at 438 and 820 nm dominating

the spectra are broader and bathochromically shifted by 20 and 70 nm, respectively, as compared to the spectra of the tetramer.

Spectra collected for different oligomers unequivocally show that the stability of the radical-cations formed after oxidation depends strongly on the length of the molecule. Spectra presented before for oxidized tetramers and for an octamer are similar to the spectrum of protonated emeraldine,<sup>20</sup> which confirms that the imine groups and quinoid ring appear within every set of four aromatic rings in the polymer. Our spectra of oxidized octamer **17** differ from that presented by Sadighi *et al.*<sup>9</sup> However, these authors present absorption spectra of phenyl/phenyl end-capped octaanilines, thus the conjugation length of such a molecule is higher than for the NH<sub>2</sub>/NH<sub>2</sub> end-capped octamer. These authors did not observe an important correlation between the length of the oligomers and their absorption spectra. In our opinion the increase of the chain length lowers this type of dependence.

## Conclusions

Two types of oligoanilines, namely NH<sub>2</sub>/NH<sub>2</sub> and Ph/NH<sub>2</sub> end-capped oligomers, were synthesized by an S<sub>N</sub>Ar coupling under atmospheric pressure, followed by the reduction of the nitro groups. This synthetic method allows preparation of symmetric and asymmetric oligoanilines with even or odd chain lengths. The spectroscopic properties of the oxidized oligomers depend on the length of the molecule. The oxidation of oligoanilines leads to the formation of radical-cations that are not structurally equivalent. In the case of even oligomers, like tetramers or an octamer, the charge on the radical-cations are distributed similarly to protonated emeraldine, whereas in the case of the hexamer the charge distribution of radical-cations is comparable to the nigraniline oxidation state. The oxidation of odd oligomers creates radical-cations that are not equivalent—some of them behave like radical-cations of emeraldine, while others cannot dimerize and a strong absorption is observed in the NIR region.

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