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# Second-harmonic generation from floating monolayers and LB multilayers of poly(isocyanide)s

M.N. Teerenstra, J.G. Hagting, and A.J. Schouten\* et al.

## SUPPLEMENTARY DETAILS

Detailed description of the synthesis of the precursors and polymers used in this study.

### 4-[4-(*N,N*-Dibutylamino)phenylazo]benzoic acid (**8a**)

4-Aminobenzoic acid (6.5 g, 47.4 mmol) was dissolved in 20 ml of 4N aqueous HCl at 80°C and filtered through a glass pore filter (p4) to remove impurities. After cooling down to room temperature, 25 g of ice and 7.5 ml of conc. HCl were added. Subsequently a solution of 3.6 g (52.2 mmol) of NaNO<sub>2</sub> in 10 ml of water was added slowly at 3°C. The temperature was maintained at 3°C and 13.0 g (63.3 mmol) of *N,N*-dibutylaniline, was added at once. After stirring for 15 min. a solution of 3.4 g of sodium acetate in 5 ml water was added. After 1 h, again 3.4 g sodium acetate dissolved in 5 ml water was added and the temperature was raised to room temperature subsequently 5 ml of a 20 wt.% NaOH solution was added slowly. The red precipitate was collected by filtration and washed several times with water, subsequently with 10% acetic acid and water, and dried overnight in vacuo at 85°C. The crude product was purified by recrystallization from 80 ml of toluene. Yield: 8.65 g (24.5 mmol, 52%) of **8a**.

Elem. anal. calcd. for C<sub>21</sub>H<sub>27</sub>N<sub>3</sub>O<sub>2</sub>: %C 71.36; %H 7.70; %N 11.89. Found: %C 71.50; %H 7.86; %N 11.83.

IR:  $\nu$  (cm<sup>-1</sup>) 2957 ( $\nu_a$  CH<sub>3</sub>), 2931 ( $\nu_a$  CH<sub>2</sub>), 2871 ( $\nu_s$  CH<sub>2</sub>), 1692 ( $\nu$  C=O), 1596 ( $\delta$  C=C, aromatic ring), 1516 ( $\delta$  C=C, aromatic ring), 1362 ( $\nu$  C<sub>arom.</sub>-N), 820 ( $\delta$  C<sub>arom.</sub>-H, 1,4-disubst. benzenes).

<sup>1</sup>H NMR (60 MHz):  $\delta$  1.0 (t,6H), 1.4 (m,4H), 1.6 (m,4H), 3.3 (t,4H), 6.6 (d,2H), 7.8 (d,4H), 8.2 (d,2H), 9.5 (s,1H).

**(*R,S*)-2-*N*-Formylaminopropyl 4-[4-(*N,N*-dibutylamino)phenylazo]benzoate (8b)**

To a solution of 8.00 g (22.6 mmol) of **8a**, 2.57 g (24.9 mmol) of (*R,S*)-2-*N*-formylamino-1-propanol, and 215 mg (1.13 mmol) of *p*-toluenesulfonic acid monohydrate in 67 ml of dry pyridine was added 5.60 g (27.2 mmol) of dicyclohexylcarbodiimide and the mixture was stirred for 24 h at room temperature under nitrogen atmosphere. Acetic acid (7.5 ml) was added to allow the dicyclohexylurea to crystallize. The crystals were removed by filtration and washed with cold pyridine. The filtrate was diluted with 80 ml of chloroform and 80 g of ice, acidified with 13 ml of 5N aqueous HCl, washed with water, saturated aqueous NaHCO<sub>3</sub> solution, water, and dried (Na<sub>2</sub>SO<sub>4</sub>). After evaporation of the solvents the crude product was purified by chromatography (Al<sub>2</sub>O<sub>3</sub>, eluent acetone) and subsequently recrystallized from hexane/ethanol. Yield: 3.48 g (7.93 mmol, 35%) of **8b**.

Elem. anal. calcd. for C<sub>25</sub>H<sub>34</sub>N<sub>4</sub>O<sub>3</sub>: %C 68.47; %H 7.81; %N 12.77. Found: %C 68.50; %H 7.90; %N 12.64.

IR:  $\nu$  (cm<sup>-1</sup>) 3290 ( $\nu$  NH), 3055 (comb.  $\nu$  C=O and  $\delta$  NH), 2960 ( $\nu_a$  CH<sub>3</sub>), 2938 ( $\nu_a$  CH<sub>2</sub>), 2875 ( $\nu_s$  CH<sub>3</sub>), 1722 ( $\nu$  C=O, aromatic), 1680 (amide I), 1600 ( $\delta$  C=C, aromatic ring), 1516 ( $\delta$  C=C, aromatic ring), 1364 ( $\nu$  C<sub>arom.</sub>-N), 823 ( $\delta$  C<sub>arom.</sub>-H, 1,4-disubst. benzenes).

<sup>1</sup>H NMR (200 MHz):  $\delta$  0.95 (t,6H), 1.28 (d,3H), 1.36 (m,4H), 1.62 (m,4H), 3.36 (t,4H), 4.32 (d,2H), 4.48 (m,1H), 6.16 (d,1H), 6.68 (d,2H), 7.86 (m,4H), 8.12 (d,2H), 8.15 (s,1H).

<sup>13</sup>C NMR:  $\delta$  13.9 (q,2C), 17.3 (q,1C), 20.3 (t,2C), 29.5 (t,2C), 43.4 (d,1C), 50.9 (t,2C), 67.2 (t,1C), 111.1 (d,2C), 122.0 (d,2C), 125.9 (d,2C), 129.2 (s,1C), 130.6 (d,2C), 143.1 (s,1C), 151.2 (s,1C), 156.3 (s,1C), 160.8 (d,1C), 166.3 (s,1C).

**(*R,S*)-2-Isocyanopropyl 4-[4-(*N,N*-dibutylamino)phenylazo]benzoate (8c)**

To a solution of 1.00 g (2.28 mmol) of **8b** in 12 ml of triethylamine (distilled from CaH<sub>2</sub>) and 8 ml of tetrahydrofuran was slowly added at 0°C and under a nitrogen atmosphere 3.50 g (22.8 mmol) of phosphoryl chloride (POCl<sub>3</sub>) with a syringe. The mixture was stirred for 4 h at 0°C, 24 h at room temperature, and finally 4 h at 30°C. Dichloromethane (25 ml) was added and the mixture was poured into 250 ml of saturated aqueous NaHCO<sub>3</sub> solution. The organic phase was separated and washed several times with water, with saturated aqueous NaHCO<sub>3</sub> solution, and was subsequently dried (Na<sub>2</sub>SO<sub>4</sub>). After removal of the solvents, the crude product was purified by chromatography (SiO<sub>2</sub>, eluent chloroform). Yield: 0.70 g (1.66 mmol, 73%) of **8c**.

Elem. anal. calcd. for  $C_{25}H_{32}N_4O_2$ : %C 71.40; %H 7.67; %N 13.32. Found: %C 71.08; %H 7.76; %N 12.97.

IR:  $\nu$  ( $cm^{-1}$ ) 2957 ( $\nu_a$   $CH_3$ ), 2933 ( $\nu_a$   $CH_2$ ), 2872 ( $\nu_a$   $CH_3$ ), 2142 ( $\nu$   $C\equiv N$ ), 1723 ( $\nu$   $C=O$ ), 1598 ( $\delta$   $C=C$ , aromatic ring), 1518 ( $\delta$   $C=C$ , aromatic ring), 1366 ( $\nu$   $C_{arom.}-N$ ), 822 ( $\delta$   $C_{arom.}-H$ , 1,4-subst. benzenes), 773 ( $\delta$   $C_{arom.}-H$ ).

$^1H$  NMR (300 MHz):  $\delta$  1.0 (t,6H), 1.4 (m,4H), 1.5 (d,3H), 1.6 (m,4H), 3.4 (t,4H), 4.1 (m,1H), 4.4 (m,2H), 6.7 (d,2H), 7.9 (m,4H), 8.2 (d,2H).

### **Poly[(*R,S*)-1-(4-(4-(*N,N*-dibutylamino)phenylazo)benzoyloxymethyl)ethylisocyanide] (8d)**

Compound **8c** (0.50 g, 1.19 mmol) was dissolved in 5 ml of chloroform at 0 °C under a nitrogen atmosphere and polymerized by adding a solution of 1.4 mg of  $NiCl_2 \cdot 6 H_2O$  in 5 ml of methanol ( $[Ni^{2+}]/[8c] = 4.9 \cdot 10^{-3}$ ). The solution was stirred for 24 h at 0 °C and another 3 days at 30 °C. Polymer **8** was collected by repeated precipitations of the reaction mixture in a mixture methanol-water (3:1, v/v). After washing with water and methanol the polymer was dried in vacuo at 80 °C. Yield: 0.36 g (72%) of **8d**.

Elem. anal. calcd. for  $(C_{25}H_{32}N_4O_2)_n$ : %C 71.40; %H 7.67; %N 13.32. Found: %C 71.10; %H 7.67; %N 13.14.

IR:  $\nu$  ( $cm^{-1}$ ) 2958 ( $\nu_a$   $CH_3$ ), 1719 ( $\nu$   $C=O$ ), 1630 ( $\nu$   $C=N$ ), 1598 ( $\delta$   $C=C$ , aromatic ring), 1515 ( $\delta$   $C=C$ , aromatic ring), 1364 ( $\nu$   $C_{arom.}-N$ ), 819 ( $\delta$   $C_{arom.}-H$ , 1,4-subst. benzenes).

$^1H$  NMR (200 MHz):  $\delta$  0.8 (br), 1.2 (br), 1.6 (br), 3 (br), 6.4 (br), 7.5 (br).

Molecular weight:  $\bar{M}_n = 82 \cdot 10^3$  D.

### **(*S*)-2-*N*-Formylaminopropyl 4-[4-(*N,N*-dibutylamino)phenylazo]benzoate (9b)**

To a solution of 8.00 g (22.6 mmol) of **8a**, 2.80 g (27.2 mmol) (*S*)-2-*N*-formylamino-1-propanol, and 0.3 g (1.6 mmol) of *p*-toluenesulfonic acid monohydrate in 100 ml of pyridine was added 6.1 g (29.6 mmol) of dicyclohexylcarbodiimide subsequently the same procedure was followed as for **8b**. Yield: 3.00 g (6.84 mmol, 30%) of red crystals.

Elem. anal. calcd. for  $C_{25}H_{34}N_4O_3$ : %C 68.47; %H 7.81; %N 12.77. Found: %C 68.44; %H 7.84; %N 12.74.

IR:  $\nu$  ( $cm^{-1}$ ) 3291 ( $\nu$   $NH$ ), 3054 (comb.  $\nu$   $C=O$  and  $\delta$   $NH$ ), 2959 ( $\nu_a$   $CH_3$ ), 2934 ( $\nu_a$   $CH_2$ ), 2873 ( $\nu_s$   $CH_3$ ), 1718 ( $\nu$   $C=O$ , aromatic), 1690 (amide I), 1600 ( $\delta$   $C=C$ , aromatic ring), 1516 ( $\delta$   $C=C$ ,

aromatic ring), 1366 ( $\nu$  C<sub>arom.</sub>-N), 821 ( $\delta$  C<sub>arom.</sub>-H, 1,4-disubst. benzenes).

<sup>1</sup>H NMR (300 MHz):  $\delta$  1.0 (t,6H), 1.3 (d, 3H), 1.4 (m,4H), 1.6 (m,4H), 3.4 (t,4H), 4.35 (dd,2H), 4.5 (m,1H), 5.95 (d,1H), 6.7 (d,2H), 7.85 (m,4H), 8.1 (d,2H), 8.15 (s,1H). <sup>13</sup>C NMR: 13.9 (q,2C), 17.4 (q,1C), 20.3 (t,2C), 29.5 (t,2C), 43.5 (d,1C), 51.0 (t,2C), 67.2 (t,1C), 111.1 (d,2C), 122.0 (d,2C), 125.9 (d,2C), 129.2 (s,1C), 130.6 (d,2C), 143.1 (s,1C), 151.2 (s,1C), 156.2 (s,1C), 160.7 (d,1C), 166.3 (s,1C).

#### **(S)-2-Isocyanopropyl 4-[4-(N,N-dibutylamino)phenylazo]benzoate (9c)**

This compound was prepared starting from 1.5 g (3.42 mmol) of **9b** as described for **8c**. Crystallization afforded 1.02 g (2.43 mmol, 71%) of **9c** as red crystals.

Elem. anal. calcd. for C<sub>25</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub>: %C 71.40; %H 7.67; %N 13.32. Found: %C 69.81; %H 7.87; %N 12.90.

IR:  $\nu$  (cm<sup>-1</sup>) 2959 ( $\nu_a$  CH<sub>3</sub>), 2145 ( $\nu$  C $\equiv$ N), 1724 ( $\nu$  C=O), 1598 ( $\delta$  C=C, aromatic ring), 1519 ( $\delta$  C=C, aromatic ring), 1364 ( $\nu$  C<sub>arom.</sub>-N), 822 ( $\delta$  C<sub>arom.</sub>-H, 1,4-disubst. benzenes).

<sup>1</sup>H NMR (300 MHz):  $\delta$  1.0 (t,6H), 1.4 (m,4H), 1.5 (d,3H), 1.6 (m,4H), 3.4 (t,4H), 4.1 (m,1H), 4.4 (m,2H), 6.7 (d,2H), 7.85 (m,4H), 8.15 (d,2H).

#### **Poly[(S)-1-(4-(4-(N,N-dibutylamino)phenylazo)benzoyloxymethyl)ethylisocyanide] (9d)**

Polymer **9** was prepared starting from 0.32 g (0.76 mmol) of **9c** and [Ni<sup>2+</sup>]/[**9c**]=1.0·10<sup>-2</sup> according to the procedure described for polymer **8**. Yield: 0.22 g (70%) of a red solid.

Elem. anal. calcd. for (C<sub>25</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub>)<sub>n</sub>: %C 71.40; %H 7.67; %N 13.32. Found: %C 70.29; %H 7.73; %N 12.98.

IR:  $\nu$  (cm<sup>-1</sup>) 2957 ( $\nu_a$  CH<sub>3</sub>), 1720 ( $\nu$  C=O), 1630 ( $\nu$  C=N), 1600 ( $\delta$  C=C, aromatic ring), 1515 ( $\delta$  C=C, aromatic ring), 1364 ( $\nu$  C<sub>arom.</sub>-N), 822 ( $\delta$  C<sub>arom.</sub>-H, 1,4-disubst. benzenes).

<sup>1</sup>H NMR (300 MHz):  $\delta$  0.8 (br), 1.2 (br), 1.6 (br), 3.0 (br), 6.4 (br), 7.5 (br).

Molecular weight:  $\bar{M}_n = 40 \cdot 10^3$  D.

#### **4-[4-(N,N-Dibutylamino)phenylazo]-3-nitrobenzoic acid (10a)**

To a stirred mixture, of 10 g (54.9 mmol) of 4-amino-3-nitrobenzoic acid and 65 ml of 4N aqueous HCl at 0°C, was added dropwise a solution of 4.2 g (60.6 mmol) of NaNO<sub>2</sub> in 12 ml of water. To the homogeneous solution 9.02 g (43.9 mmol) of *N,N*-dibutylaniline was added. After

stirring for 2 h a solution of 8 g of sodium acetate dissolved in 30 ml of water and 15 ml of acetic acid was added. The product was collected by extracting the reaction mixture several times with chloroform. After washing with water, 10% aqueous acetic acid, water, and drying ( $\text{MgSO}_4$ ), of the solvent was removed under reduced pressure. Crystallization from conc. acetic acid afforded **10a** as a red solid. Yield 9.40 g (23.6 mmol, 43%).

Another more convenient route to **10a** is the following:

To 15 ml of conc. sulfuric acid was slowly added 1.725 g (25.0 mmol) of  $\text{NaNO}_2$ . After the mixture had become homogeneous 4.55 g (25.0 mmol) of 4-amino-3-nitrobenzoic acid was added. As soon as the mixture had turned dark, 125 ml of DMSO was added. The resulting solution was added to a solution of 5.13 g (25.0 mmol) of *N,N*-dibutylaniline, 15 g of sodium acetate, and 120 g of acetic acid in 200 ml of DMSO. After stirring overnight the crude product was obtained by pouring the mixture in a ten fold volume of icewater. Compound **10a** was purified by extraction with acetone and subsequent evaporation of this solvent. Yield 5.48 g (13.8 mmol, 55%) of **10a**.

Elem. anal. calcd. for  $\text{C}_{21}\text{H}_{26}\text{N}_4\text{O}_4$ : %C 63.30; %H 6.58; %N 14.06. Found: %C 63.09; %H 6.61%; %N 13.39.

IR:  $\nu$  ( $\text{cm}^{-1}$ ) 2956 ( $\nu_a \text{CH}_3$ ), 2929 ( $\nu_a \text{CH}_2$ ), 2871 ( $\nu_s \text{CH}_3$ ), 2858 ( $\nu_s \text{CH}_2$ ), 1694 ( $\nu \text{C=O}$ ), 1599 ( $\delta \text{C=C}$ , aromatic ring), 1533 ( $\nu_a \text{NO}_2$ ), 1517 ( $\delta \text{C=C}$ , aromatic ring), 1380 ( $\nu_s \text{NO}_2$ ), 1361 ( $\nu \text{C}_{\text{arom.}}-\text{N}$ ), 823 ( $\delta \text{C}_{\text{arom.}}-\text{H}$ , 1,4-disubst. benzenes), 766 ( $\delta \text{C}_{\text{arom.}}-\text{H}$ , 1,2,4-trisubst. benzenes).  $^1\text{H}$  NMR (300 MHz):  $\delta$  1.0 (t,6H), 1.4 (m,4H), 1.6 (m,4H), 3.4 (t,4H), 6.7 (d,2H), 7.85 (m,3H), 8.25 (d,1H), 8.55 (s,1H).  $^{13}\text{C}$  NMR:  $\delta$  14.8 (q,2C), 20.2 (t,2C), 29.5(t,2C), 51.1 (t,2C), 111.3 (d,2C), 118.7 (d,2C), 125.9 (d,1C), 127.2 (d,1C), 128.6 (s,1C), 133.8 (d,1C), 143.7 (s,1C), 146.9 (s,1C), 149.1 (s,1C), 152.3 (s,1C), 169.6 (s,1C).

### **2-(S)-N-Formylaminopropyl 4-[4-(N,N-dibutylamino)phenylazo]-3-nitrobenzoate (10b)**

To a solution of 3.93 g (9.86 mmol) of **10a**, 1.12 g (10.85 mmol) of (*S*)-2-*N*-formylamino-1-propanol, and 94 mg (0.49 mmol) of *p*-toluenesulfonic acid monohydrate in pyridine (50 ml) was added 2.45 g (11.8 mmol) of dicyclohexylcarbodiimide and the mixture was stirred for 24 h at room temperature and additionally 24 h at 45°C. Acetic acid (6 ml) was added and the remaining part of the procedure was identical as that described for **8b**. Yield: 3.81 g (7.89 mmol, 80%) of **10b**.

Elemental analysis calculated for  $C_{25}H_{33}N_5O_5$ : 62.10% C; 6.88% H; 14.48% N. Found: 62.05% C; 6.86% H; 14.50% N.

IR:  $\nu$  ( $cm^{-1}$ ) 2932 ( $\nu_a$   $CH_2$ ), 1724 ( $\nu$  C=O, aromatic), 1651 (amide I), 1598 ( $\delta$  C=C, aromatic ring), 1533 ( $\nu_a$   $NO_2$ ), 1517 ( $\delta$  C=C, aromatic ring), 1386 ( $\nu_s$   $NO_2$ ), 1362 ( $\nu$   $C_{arom.}-N$ ), 820 ( $\delta$   $C_{arom.}-H$ , 1,4-disubst. benzenes), 766 ( $\delta$   $C_{arom.}-H$ , 1,2,4-trisubst. benzenes).

$^1H$  NMR (300 MHz):  $\delta$  1.0 (t,6H), 1.3 (d,3H), 1.4 (m,4H), 1.6 (m,4H), 3.4 (t,4H), 4.4 (m,2H), 4.55 (m,1H), 5.75 (d,1H), 6.7 (d,2H), 7.8 (m,3H), 8.2 (s,1H), 8.23 (d,1H), 8.4 (s,1H).

### **(S)-2-Isocyanopropyl 4-[4-(N,N-dibutylamino)phenylazo]-3-nitrobenzoate (10c)**

Compound **10b** (0.78 g, 1.61 mmol) was dissolved in a mixture of 10 ml of triethylamine and 5 ml of THF. At 0°C, 2.47 g (16.1 mmol) of  $POCl_3$  was added dropwise through a syringe. The mixture was stirred for 6 h at 0°C and another 18 h at 30°C. The remaining part of the procedure was the same as that described for **8c**. Yield: 0.53 g (1.14 mmol, 71%) of **10c**.

Elem. anal. calcd. for  $C_{25}H_{31}N_5O_4$ : %C 64.50; %H 6.71; %N 15.04. Found: %C 64.32; %H 6.70; %N 14.92.

IR:  $\nu$  ( $cm^{-1}$ ) 2959 ( $\nu_a$   $CH_3$ ), 2930 ( $\nu_a$   $CH_2$ ), 2873 ( $\nu_s$   $CH_3$ ), 2860 ( $\nu_s$   $CH_2$ ), 2145 ( $\nu$   $C\equiv N$ ), 1729 ( $\nu$  C=O), 1601 ( $\delta$  C=C, aromatic ring), 1535 ( $\nu_a$   $NO_2$ ), 1519 ( $\delta$  C=C, aromatic ring), 1385 ( $\nu_s$   $NO_2$ ), 1363 ( $C_{arom.}-N$ ), 826 ( $\delta$   $C_{arom.}-H$ , 1,4-disubst. benzenes), 763 ( $\delta$   $C_{arom.}-H$ , 1,2,4-trisubst. benzenes).

$^1H$  NMR (200 MHz):  $\delta$  1.0 (t,6H), 1.3 (d,3H), 1.4 (m,4H), 1.6 (m,4H), 3.4 (t,4H), 4.4 (m,2H), 4.6 (m,1H), 6.7 (d,2H), 7.8 (m,3H), 8.25 (d,1H), 8.5 (s,1H).

### **Poly[(S)-1-(4-(4-(N,N-dibutylamino)phenylazo)-3-nitrobenzoyloxymethyl)ethylisocyanide] (10d)**

Isocyanide **10c** (0.53 g, 1.14 mmol) was dissolved in 5 ml of  $CHCl_3$ . The polymerization was initiated by adding at 0°C 2.7 mg (11.4  $\mu$ mol) of  $NiCl_2 \cdot 6 H_2O$  dissolved in 2.70 ml of methanol.  $[Ni^{2+}]/[10c]=1.0 \cdot 10^{-2}$ . The mixture was stirred for 10 h at 0°C. Temperature was raised to 30°C and stirring was continued until the IR vibration of the isocyanide group ( $\approx 2145$   $cm^{-1}$ ) had disappeared (3 days). The solvent was removed under reduced pressure and the red polymer was purified by repeated precipitation from chloroform solution (3 ml) into a vigorously stirred mixture of water-methanol (1:4, v/v). Yield: 0.35 g (66%) of **10d**.

Elem. anal. calcd. for  $(C_{25}H_{31}N_5O_4)_n$ : %C 64.50; %H 6.71; %N 15.04. Found: %C 64.58; %H 6.84; %N 14.25.

IR:  $\nu$  ( $\text{cm}^{-1}$ ) 2954 ( $\nu_a$   $\text{CH}_3$ ), 2913 ( $\nu_a$   $\text{CH}_2$ ), 2873 ( $\nu_s$   $\text{CH}_3$ ), 1726 ( $\nu$   $\text{C}=\text{O}$ ), 1630 ( $\nu$   $\text{C}=\text{N}$ ), 1600 ( $\delta$   $\text{C}=\text{C}$ , aromatic ring), 1534 ( $\nu_a$   $\text{NO}_2$ ), 1517 ( $\delta$   $\text{C}=\text{C}$ , aromatic ring), 1386 ( $\nu_s$   $\text{NO}_2$ ), 1363 ( $\nu$   $\text{C}_{\text{arom.}}-\text{N}$ ), 823 ( $\delta$   $\text{C}_{\text{arom.}}-\text{H}$ , 1,4-disubst. benzenes), 764 ( $\delta$   $\text{C}_{\text{arom.}}-\text{H}$ , 1,2,4-trisubst. benzenes).

$^1\text{H}$  NMR (200 MHz):  $\delta$  0-1.6 (br), 3.4 (br), 5.8-6.8 (br), 6.9-8 (br).

Molecular weight:  $\bar{M}_n = 46 \cdot 10^3$  D.

### ***N,N*-di(acetoxyethyl)aniline**

A mixture of 9.00 g (0.050 mol) of *N,N*-diethanolaniline, 12.5 g (0.12 mol) of tri-ethylamine, 0.30 g (2.5 mmol) of 4-*N,N*-dimethylaminopyridine (DMAP) and 11.25 g (0.11 mol) of acetic acid anhydride in THF (85 ml) were refluxed for 24 h. The volatile parts were removed under reduced pressure and the crude product was extracted with  $\text{CH}_2\text{Cl}_2$ , washed with water, aqueous  $\text{NaHCO}_3$  and water, and dried ( $\text{MgSO}_4$ ). The solvent was removed under reduced pressure. Yield 12.0 g (45.2 mmol, 91%) of a colourless liquid.

IR:  $\nu$  ( $\text{cm}^{-1}$ ) 2957 ( $\nu_a$   $\text{CH}_3$ ), 1740 ( $\nu$   $\text{C}=\text{O}$ ), 1600 ( $\delta$   $\text{C}=\text{C}$ , aromatic ring), 1506 ( $\delta$   $\text{C}=\text{C}$ , aromatic ring), 1381 ( $\delta_s$   $\text{CH}_3$ ), 1371 ( $\nu$   $\text{C}_{\text{arom.}}-\text{N}$ ), 1233 (O-C(O), coupled motions).

$^1\text{H}$  NMR (200 MHz):  $\delta$  2.05 (s,6H), 3.6 (t,4H), 4.2 (t,4H), 6.75 (m,3H), 7.20 (m,2H).

### **4-[4-(*N,N*-Di(acetoxyethyl)amino)phenylazo]-3-nitrobenzoic acid (11a)**

4-amino-3-nitrobenzoic acid (6.83 g, 37.5 mmol) was added to a solution of 2.59 g (37.5 mmol) of  $\text{NaNO}_2$  and 15 ml of conc.  $\text{H}_2\text{SO}_4$  at  $0^\circ\text{C}$ . The colour of the mixture turned dark and 80 ml of DMSO was added. This solution was then added to a mixture of 6.63 g (25 mmol) of *N,N*-di(acetoxyethyl)aniline, 15 g of sodium acetate, 100 g of acetic acid, and 150 ml of DMSO, and stirred for 20 h. The red solution was added slowly to a twenty fold excess of icewater and the precipitated product was collected by filtration. After extraction of the precipitate with hot acetone and subsequent purification by means of chromatography ( $\text{SiO}_2$ , eluent chloroform-methanol 10:1, v/v) the product was obtained as a red solid. Yield: 6.5 g (1.42 mmol, 57%) of

### **11a.**

Elem. anal. calcd. for  $\text{C}_{21}\text{H}_{22}\text{N}_4\text{O}_8$ : %C 55.02; %H 4.84; %N 12.22. Found: %C 52.64; %H 4.88; %N 11.09.



IR:  $\nu(\text{cm}^{-1})$  2962 ( $\nu_{\text{a}} \text{CH}_3$ ), 2923 ( $\nu_{\text{a}} \text{CH}_2$ ), 2854 ( $\nu_{\text{s}} \text{CH}_2$ ), 1739 ( $\nu \text{C}_{\text{aliph.}}=\text{O}$ ), 1696 ( $\nu \text{C}=\text{O}$ , acid), 1600 ( $\delta \text{C}=\text{C}$ , aromatic ring), 1533 ( $\nu_{\text{a}} \text{NO}_2$ ), 1380 ( $\delta_{\text{s}} \text{CH}_3$ ).

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  2.00 (s,6H), 3.75 (t,4H), 4.20 (t,4H), 6.98 (d,2H), 7.70 (m,3H), 8.22 (d,1H), 8.4 (d,1H).

**(S)-2-N-Formylaminopropyl 4-[4-(N,N-di(acetoxyethyl)amino)phenylazo]-3-nitrobenzoate (11b)**

A mixture of 5.00 g (10.93 mmol) of **11a**, 1.33 g (13.12 mmol) of (S)-2-N-formylamino-1-propanol, and 3.2 g (10.9 mmol) of 4-N,N-diaminopyridinetoluenesulfonate (DPTS)<sup>12</sup> were refluxed in 125 ml of  $\text{CH}_2\text{Cl}_2$  for 30 min. Subsequently 4.5 g (21.9 mmol) of dicyclohexylcarbodiimide was added at 0°C and the mixture was stirred overnight. The solvent was removed under reduced pressure. The crude product was dissolved in  $\text{CHCl}_3$ , washed with water (3x), dried ( $\text{MgSO}_4$ ), and purified by column chromatography ( $\text{SiO}_2$ , eluent acetone-pet. ether, 40:60 v/v). Yield: 4.40 g (8.09 mmol, 74%) of **11b**.

Elem. anal. calcd. for  $\text{C}_{25}\text{H}_{29}\text{N}_5\text{O}_9$ : %C 55.25; %H 5.38; %N 12.88. Found: %C 56.04; %H 5.74; %N 12.55.

IR:  $\nu(\text{cm}^{-1})$  3330 ( $\nu \text{N-H}$ ), 2933 ( $\nu_{\text{a}} \text{CH}_2$ ), 2856 ( $\nu_{\text{s}} \text{CH}_2$ ), 1740 ( $\nu \text{C}_{\text{aliph.}}=\text{O}$ ), 1702 ( $\nu \text{C}_{\text{arom.}}=\text{O}$ ), 1651 (amide I), 1600 ( $\delta \text{C}=\text{C}$ , aromatic ring), 1534 ( $\nu_{\text{a}} \text{NO}_2$ ), 1516 ( $\delta \text{C}=\text{C}$ , aromatic ring), 1382 ( $\delta_{\text{s}} \text{CH}_3$ ), 1231 (O-C(O), coupled motions).

$^1\text{H}$  NMR (200 MHz):  $\delta$  1.25 (d,3H), 2.00 (s,6H), 3.65 (t,4H), 4.25 (t,4H), 4.30 (d,2H), 4.40 (m,1H), 6.80 (d,2H), 7.65 (d,1H), 7.80 (d,2H), 8.10 (s,1H), 8.15 (dd,1H), 8.40 (d,1H).  $^{13}\text{C}$  NMR:  $\delta$  17.2 (q,1C), 20.8 (q,2C), 43.3 (d,1C), 49.8 (t,2C), 60.8 (t,2C), 67.8 (t,1C), 11.8 (d,2C), 118.8 (d,2C), 125.3 (d,1C), 126.6 (d,1C), 129.3 (s,1C), 133.6 (d,1C), 144.4 (s,1C), 146.6 (s,1C), 148.2 (s,1C), 151.6 (s,1C), 160.7 (d,1C), 162.2 (s,1C), 170.6 (s,2C).

**(S)-2-Isocyanopropyl 4-[4-(N,N-di(acetoxyethyl)amino)phenylazo]-3-nitrobenzoate (11c)**

This compound was prepared from 3.62 g (6.66 mmol) of **11b** as described for **8c**. Yield 1.93 g (3.7 mmol, 55%) of **11c**.

Elem. anal. calcd. for  $\text{C}_{25}\text{H}_{27}\text{N}_5\text{O}_8$ : %C 57.14; %H 5.18; %N 13.33. Found: %C 56.95; %H 5.20; %N 13.18.

IR:  $\nu(\text{cm}^{-1})$  2961 ( $\nu_{\text{a}} \text{CH}_3$ ), 2927 ( $\nu_{\text{a}} \text{CH}_2$ ), 2878 ( $\nu_{\text{s}} \text{CH}_3$ ), 2855 ( $\nu_{\text{s}} \text{CH}_2$ ), 2146 ( $\nu \text{C}\equiv\text{N}$ ),

1738 ( $\nu$  C<sub>aliph.</sub>=O), 1599 ( $\delta$  C=C, aromatic ring), 1536 ( $\nu$ <sub>a</sub> NO<sub>2</sub>), 1516 ( $\delta$  C=C, aromatic ring), 1383 ( $\delta$ <sub>s</sub> CH<sub>3</sub>).

<sup>1</sup>H NMR (200 MHz):  $\delta$  1.50 (d,3H), 2.05 (s,6H), 3.75 (t,4H), 4.10 (m,1H), 4.30 (t,4H), 4.40 (m,2H), 6.85 (d,2H), 7.75 (d,1H), 7.85 (d,2H), 8.25 (dd,1H), 8.50 (d,1H). <sup>13</sup>C NMR:  $\delta$  18.2 (q,1C), 20.8 (q,2C), 48.6 (d,1C), 49.8 (t,2C), 60.8 (t,2C), 66.6 (t,1C), 111.8 (d,2C), 118.8 (d,2C), 125.6 (d,1C), 126.6 (d,1C), 129.0 (s,1C), 133.6 (d,1C), 144.6 (s,1C), 147.0 (s,1C), 148.2 (s,1C), 151.6 (s,1C), 157.5 (s,1C), 163.6 (s,1C), 170.4 (s,2C).

#### **Poly[(S)-1-(4-(4-(N,N-di(acetoxyethyl)amino)phenylazo)-3-nitrobenzoyloxymethyl)-ethylisocyanide] (11d)**

Isocyanide **11c** (0.96 g, 1.8 mmol) was polymerized following the procedure as described for **8d**, using [Ni<sup>2+</sup>]/[**11c**]=9.6·10<sup>-3</sup>. For the final purification, the polymer was dissolved in a minimum amount of chloroform and precipitated in vigorously stirred ethyl acetate. Yield: 0.60 g (63%) of **11d**.

Elem. anal. calcd. for (C<sub>25</sub>H<sub>27</sub>N<sub>5</sub>O<sub>8</sub>)<sub>n</sub>: %C 57.14; %H 5.18; %N 13.33. Found: %C 56.73; %H 5.28; %N 13.07.

IR:  $\nu$  (cm<sup>-1</sup>) 2973 ( $\nu$ <sub>a</sub> CH<sub>3</sub>), 2960 ( $\nu$ <sub>s</sub> CH<sub>3</sub>), 2894 ( $\nu$ <sub>s</sub> CH<sub>2</sub>), 1738 ( $\nu$  C<sub>aliph.</sub>=O), 1634 ( $\nu$  C=N), 1601 ( $\delta$  C=C, aromatic ring), 1536 ( $\nu$ <sub>a</sub> NO<sub>2</sub>), 1516 ( $\delta$  C=C, aromatic ring), 1385 ( $\delta$ <sub>s</sub> CH<sub>3</sub>).

<sup>1</sup>H NMR (200 MHz):  $\delta$  1.50 (d,3H), 2.05 (s,6H), 3.75 (t,4H), 4.10 (m,1H), 4.30 (t,4H), 4.40 (m,2H), 6.85 (d,2H), 7.75 (d,1H), 7.85 (d,2H), 8.25 (dd,1H), 8.50 (d,1H).

Molecular weight:  $\bar{M}_n = 51 \cdot 10^3$  D.

#### **4-[4-N-Morpholinophenylazo]-3-nitrobenzoic acid (12a)**

4-Amino-3-nitrobenzoic acid (2.00 g, 11 mmol) was added to 0.77 g (11.2 mmol) of NaNO<sub>2</sub> and 4.45 ml of conc. H<sub>2</sub>SO<sub>4</sub> at 0°C. To this solution was subsequently added 44 ml of DMSO. The resulting solution was then added to a mixture of 1.8 g (11 mmol) of N-phenylmorpholine, 4.7 g (57.2 mmol) of sodium acetate, 31.45 g (0.5 mol) of acetic acid and 40 ml of DMSO, and stirred for 24 h. The red mixture was added slowly to a twenty fold excess of icewater and the precipitated product was collected by filtration. After extraction of the precipitate with hot acetone, **12a** was obtained as a red solid. Yield: 1.96 g (5.5 mmol, 50%) of product.

Elem. anal. calcd. for  $C_{17}H_{16}N_4O_5$ : %C 57.30; %H 4.52; %N 15.72. Found: %C 57.18; %H 4.59; %N 15.73.

IR:  $\nu$  ( $cm^{-1}$ ) 2924 ( $\nu_a$   $CH_2$ ), 2871 ( $\nu_s$   $CH_2$ ), 1711 ( $\nu$   $C=O$ ), 1599 ( $\delta$   $C=C$ , aromatic ring), 1532 ( $\nu_a$   $NO_2$ ), 1516 ( $\delta$   $C=C$ , aromatic ring), 1377 ( $\nu_s$   $NO_2$ ), 1349 ( $\nu$   $C_{arom.}-N$ ).

$^1H$  NMR (200 MHz,  $DMSO-d_6$ ):  $\delta$  3.4 (t,4H), 3.75 (t,4H), 7.1 (d,2H), 7.8 (m,3H), 8.25 (d,1H), 8.42 (d,1H).

#### **(*R,S*)-2-*N*-Formylaminopropyl 4-[4-*N*-morpholinophenylazo]-3-nitrobenzoate (12b)**

A mixture of 2.00 g (5.6 mmol) of acid **12a**, 0.75 g (6.7 mmol) of (*R,S*)-2-*N*-formylamino-1-propanol, and 1.6 g (5.6 mmol) of 4-*N,N*-diaminopyridinetoluene sulphonate (DPTS)<sup>7</sup> were refluxed in 100 ml of  $CH_2Cl_2$  for 30 min. Subsequently 1.4 g (6.7 mmol) of dicyclohexylcarbodiimide was added at 0°C and the mixture was stirred overnight. The mixture was refluxed for 24 h and the solvent was removed under reduced pressure. The crude product was dissolved in  $CHCl_3$ , washed with water (3x), dried ( $MgSO_4$ ), and purified with column chromatography ( $SiO_2$ , eluent acetone-pet. ether 50:50 v/v). Yield: 1.48 g (3.36 mmol, 60%) of **12b**.

Elem. anal. calcd. for  $C_{21}H_{23}N_5O_6$ : %C 57.14; %H 5.25; %N 15.87. Found: %C 57.15; %H 5.37; %N 15.72.

IR:  $\nu$  ( $cm^{-1}$ ) 2975 ( $\nu_a$   $CH_3$ ), 2937 ( $\nu_a$   $CH_2$ ), 2878 ( $\nu_s$   $CH_3$ ), 1722 ( $\nu$   $C_{arom.}=O$ ), 1654 (amide I), 1601 ( $\delta$   $C=C$ , aromatic ring), 1533 ( $\nu_a$   $NO_2$ ), 1379 ( $\nu_s$   $NO_2$ ).

$^1H$  NMR (200 MHz):  $\delta$  1.35 (d,3H), 3.4 (t,4H), 3.75 (t,4H), 4.4 (d,2H), 4.5 (m,1H), 5.85 (d,1H), 6.95 (d,2H), 7.8 (m,3H), 8.2 (s,1H), 8.25 (dd,1H), 8.45 (s,1H).

#### **(*R,S*)-2-Isocyanopropyl 4-[4-*N*-morpholinophenylazo]-3-nitrobenzoate (12c)**

This compound was prepared from 3.1 g (7.0 mmol) of **12b** as described for **8c**. The crude product was purified by column chromatography ( $SiO_2$ , eluent  $CH_2Cl_2$ -ethyl acetate, 20:1 v/v). Yield: 2.07 g (4.9 mmol, 70%) of **12c**.

Elem. anal. calcd. for  $C_{21}H_{21}N_5O_5$ : %C 59.57; %H 5.00; %N 16.54. Found: %C 59.80; %H 5.28; %N 15.73.

IR:  $\nu$  ( $cm^{-1}$ ) 2975 ( $\nu_a$   $CH_3$ ), 2937 ( $\nu_a$   $CH_2$ ), 2878 ( $\nu_s$   $CH_3$ ), 2145 ( $\nu$   $C\equiv N$ ), 1728 ( $\nu$   $C=O$ ), 1599 ( $\delta$   $C=C$ , aromatic ring), 1534 ( $\nu_a$   $NO_2$ ), 1377 ( $\nu_s$   $NO_2$ ).

$^1H$  NMR (200 MHz):  $\delta$  1.25 (d,3H), 3.4 (t,4H), 3.75 (t,4H), 4.4 (d,2H), 4.5 (m,1H), 6.95 (d,2H),

7.8 (m,3H), 8.25 (dd,1H), 8.45 (s,1H).

**Poly[(*R,S*)-1-(4-(4-*N*-morpholinophenylazo)-3-nitrobenzoyloxymethyl)ethylisocyanide]  
(12d)**

Isocyanide **12c** (0.53 g, 125 mmol) was polymerized following the procedure described for **8d**, using  $[\text{Ni}^{2+}]/[\mathbf{13c}]=9.9\cdot 10^{-3}$ . For the final purification step polymer was dissolved in a minimum amount of chloroform and precipitated in vigorously stirred ethyl acetate. Yield: 0.37 g (70%) of **12d**.

Elem. anal. calcd. for  $(\text{C}_{21}\text{H}_{21}\text{N}_5\text{O}_5)_n$ : %C 59.57; %H 5.00; %N 16.54. Found: %C 60.15; %H 5.18; %N 15.65.

IR:  $\nu$  ( $\text{cm}^{-1}$ ) 2975 ( $\nu_a$  CH<sub>3</sub>), 2937 ( $\nu_a$  CH<sub>2</sub>), 2878 ( $\nu_s$  CH<sub>3</sub>), 1726 ( $\nu$  C=O), 1600 ( $\delta$  C=C, aromatic ring), 1534 ( $\nu_a$  NO<sub>2</sub>), 1379 ( $\nu_s$  NO<sub>2</sub>).

<sup>1</sup>H NMR (200 MHz)  $\delta$  1.25 (d,3H), 3.4 (t,4H), 3.75 (t,4H), 4.4 (d,2H), 4.5 (m,1H), 6.95 (d,2H), 7.8 (m,3H), 8.25 (dd,1H), 8.45 (s,1H).

Molecular weight:  $\bar{M}_n=40\cdot 10^3$  D.