

## Donor–Acceptor-Substituted Oligo(1,4-phenylene)s

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Oligo(*para*-phenylene)s (DAOPPs) **2a–2d** ( $n = 1–4$ ) with terminal donor–acceptor substitution ( $D = C_6H_{13}O$ ,  $A = NO_2$ ) were prepared by applying *Suzuki* cross-couplings for chain extension and end capping. The push–pull effect induces short-reaching polarizations of the chain consisting of conjugated but twisted benzene rings, which was studied by NMR measurements. Electron excitation from the ground-state  $S_0$  to the more planar first-excited singlet state  $S_1$  is combined with a strong intramolecular charge transfer (ICT), which is documented by the red shift of the long-wavelength absorption (charge-transfer band) for short chains (one or two repeat units,  $n = 1$  or  $2$ ). The opposite influence of decreasing ICT and increasing conjugation length leads to a bathochromic series ( $\lambda_{max}(n+1) \geq \lambda_{max}(n)$ ) with a fast saturation of  $\lambda_{max}(n)$ . The effective conjugation length  $n_{ECL} = 4$  corresponds to  $\lambda_{\infty}$  349 nm. These results are discussed in the context of other oligo(*para*-phenylene)s (OPPs).

**Introduction.** – Conjugated oligomers with terminal donor–acceptor substitution ( $D-\pi-A$ ) represent an interesting class of compounds since their unusual linear and nonlinear optical and optoelectronic properties distinguish them as target compounds in materials science [1].

The 1,4-phenylene (*para*-phenylene) building blocks are simple repeat units for oligo- and poly(*para*-phenylene)s (OPPs and PPPs) **1** (Fig. 1), which belong to the class of conjugated oligo- and poly(arylene)s [2–5]. Unsubstituted OPPs and PPPs **1** ( $R = H$ ) have a very low solubility and, therefore, a difficult process ability. *Kern et al.* [6] and *Heitz and Ullrich* [7] were the first who improved the solubility by the introduction of alkyl side chains. A drawback, caused by these side chains, is due to the fact, that the conjugation of the main chain is impaired by such substituents. As already realized in 1,1'-biphenyl, the OPPs and PPPs are nonplanar. The average torsion angle  $\theta$  of  $23^\circ$  in the parent, unsubstituted chain is a compromise between the ideal conjugation ( $\theta = 0^\circ$ ) and the lowest steric interaction of neighboring benzene rings ( $\theta = 90^\circ$ ). From perturbation theory, the decrease of resonance energy is well described by

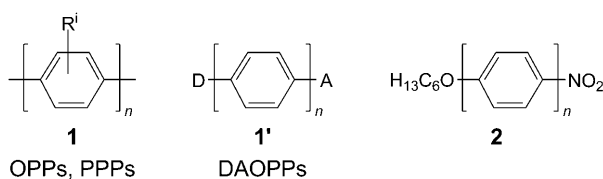


Fig. 1. Oligo- and poly(*para*-phenylene)s **1**, the corresponding oligomers with terminal donor–acceptor substitution **1'**, and the special target systems **2** ( $D = C_6H_{13}O$ ,  $A = NO_2$ )

$\cos^2\theta$  for each torsion angle  $\theta$  [8]. An OPP chain of  $n$  benzene rings has therefore a factor of  $(\cos^2\theta)^{n-1}$ . Thus, the average torsion angle  $\theta$  of  $23^\circ$  reduces the resonance energy in a  $p$ -sexiphenyl segment ( $n=6$ ) to 50%. Moreover, a  $\theta$  of  $55.7^\circ$  would implicate a 90% decrease of the resonance energy already in a substituted  $p$ -terphenyl ( $n=3$ ).

Alkyl side chains can enhance the twist angle to  $50\text{--}90^\circ$ , so that the conjugation effect disappears more and more. When the substitution with alkyl chains is confined to the terminal benzene rings [9] or to few selected benzene rings in the chain [10], the solubilizing effect is limited and yet the conjugation effect impaired. Therefore, we disclaimed alkyl side chains in our concept of DAOPPs (donor–acceptor OPPs) **1'** and decided to use hexyloxy ( $\text{C}_6\text{H}_{13}\text{O}$ ) as electron-donating (D) and solubilizing substituents. Moreover, we assumed that the effective conjugation length of such DAOPPs **2** with  $\text{D} = \text{C}_6\text{H}_{13}\text{O}$  and  $\text{A} = \text{NO}_2$  should be low, so that it is not necessary to synthesize long conjugated chains with many repeat units.

**Results and Discussion.** – The 1-(hexyloxy)-4-nitrobenzene (**2a**) can be easily prepared from 4-nitrophenol (**3**) and 1-bromohexane (**4**) [11]. The higher members **2b–2d** ( $n = 2\text{--}4$ ) of the DAOPP series were obtained by applying the *Suzuki* cross-coupling method [12–17] (*Scheme*). Due to the better solubility of the donor part, we

Scheme. Preparation of the OPPs **2a–2d**

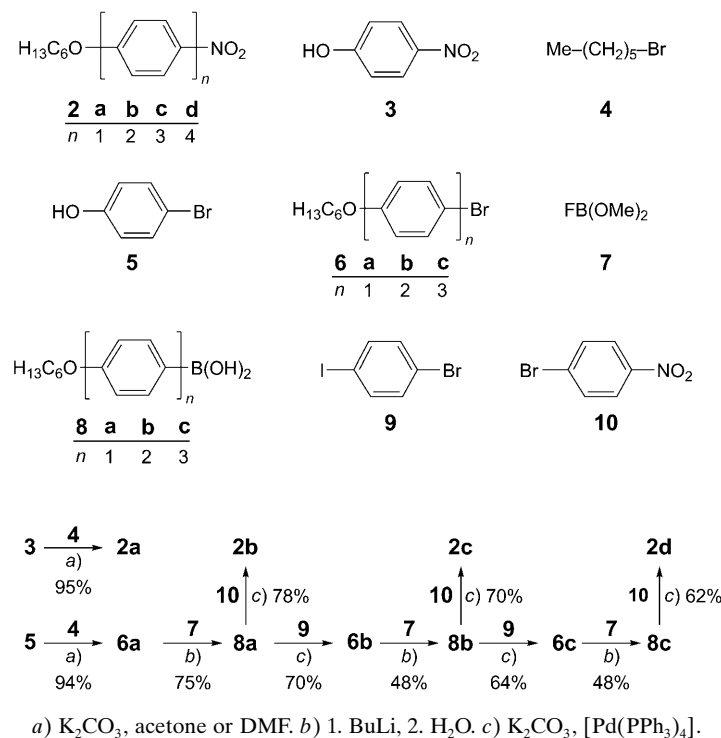


Table. <sup>1</sup>H- and <sup>13</sup>C-NMR Data of **6a–6c**. δ Values in CDCl<sub>3</sub> rel. to Me<sub>4</sub>Si as internal standard.

<i>n</i>	δ (arom. H)		δ (aliph. H)							
	AA'BB'		CH <sub>2</sub> O ( <i>t</i> , <i>J</i> = 6.6 Hz)							
			CH <sub>2</sub> (m)	CH <sub>2</sub> (m)	CH <sub>2</sub> (m)	(CH <sub>2</sub> ) <sub>2</sub> (m)	Me ( <i>r</i> <sup>a</sup> )			
<b>6a</b>	1	7.33, 6.74			3.89	1.68–1.72	1.38–1.45	1.30–1.35	0.88	
<b>6b</b>	2	7.50, 7.39	7.45, 6.94		3.97	1.75–1.81	1.42–1.48	1.31–1.35	0.90	
<b>6c</b>	3	7.61, 7.55	7.60, 7.48	7.55, 6.97	3.99	1.78–1.82	1.44–1.50	1.31–1.37	0.90	
<i>n</i>	δ (C–O) <sup>b</sup>	δ (C–Br) <sup>b</sup>	δ (C) <sup>b</sup>	δ (CH)	δ (CH <sub>2</sub> O)	δ (CH <sub>2</sub> )	δ (CH <sub>2</sub> )	δ (CH <sub>2</sub> )	δ (CH <sub>2</sub> )	δ (Me)
<b>6a</b>	1	158.3	112.6	132.2, 116.3	68.3	29.1	25.6	31.6	22.6	14.0
<b>6b</b>	2	159.2	120.8	139.9, 132.3	68.2	29.3	25.7	31.6	22.6	14.0
<b>6c</b>	3	159.0	121.5	140.3, 139.8, 138.2, 132.8	68.2	29.3	25.7	31.6	22.6	14.0

<sup>a</sup>) Not well resolved. <sup>b</sup>) Quaternary C-atoms.

performed the chain extension with OPPs **6**, which contain the hexyloxy group at one end and a bromo substituent at the other terminal position.

The starting compound **6a** was obtained by alkylation of phenol **5** with **4**. Lithiation of **6** and reaction with fluorodimethoxyborane (**7**) [18] (see also [19]) yielded the boronic acids **8** (48–75%). Regardless of their self-condensation, they were transformed to the higher ‘phenylogues’ (**6a** → **8a** → **6b** → **8b** → **6c** → **8c**) by alternate reactions with 1-bromo-4-iodobenzene (**9**) and fluorodimethoxyborane (**7**). Hensel and co-workers found that the iodo side of **9** is much more reactive than the bromo side [20]. Thus, a chemoselective coupling is possible under certain reaction conditions. Therefore, a protection/deprotection technique could be avoided. The bromo substituent can then be used subsequently for the transformation to the higher boronic acid **8**. The final step, the end capping with 1-bromo-4-nitrobenzene (**10**), furnished the target DAOPPs **2b–2d** ( $n = 2–4$ ). The total yields amounted to 55% (**5** → **2b**, three steps), 17% (**5** → **2c**, five steps), and 5% (**5** → **2d**, seven steps). We stopped the chain extension at the quaterphenyl **2d** ( $n = 4$ ) because the effective conjugation length was reached there, and the solubility became rather low. Further chain extensions ( $n = 5, 6, \dots$ ) are certainly feasible on this route when branched, that means better solubilizing alkoxy groups are applied.

The purity of the intermediates **6a–6c** was checked by NMR spectroscopy. Their  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data are summarized in the *Table*. The target compounds **2a–2d** were characterized by their UV, NMR, and MS data and by their elemental analyses (*Exper. Part*).

Polarization of the conjugated chain by terminal donor–acceptor substitution is a typical property of D– $\pi$ –A systems. Such a push–pull effect is often described by zwitterionic resonance structures – as shown in *Fig. 2* for DAOPPs and the related oligo(1,4-phenylenevinylene)s (DAOPVs). Apart from this characterization in the valence-bond theory (VB), a quadrupolar description according to MO theory is often more appropriate – in particular for longer chains. The donor group D enhances the electron density at one end of the  $\pi$  chain, and the acceptor group A decreases the electron density at the other end [1]. Strength of D and A and the nature of the  $\pi$  linker decide how ‘deep’ the change of electron density ‘grabs’ into the chain.

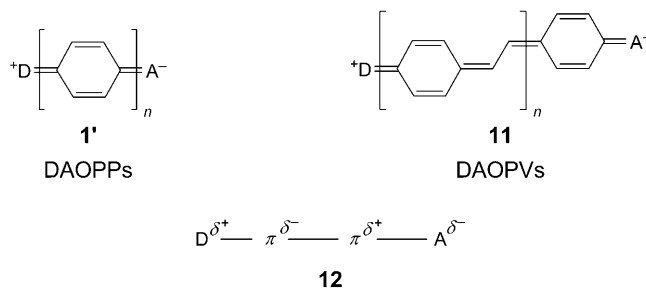


Fig. 2. Zwitterionic resonance structures of donor–acceptor substituted oligo(1,4-phenylene)s (DAOPPs) **1'** and oligo(1,4-phenylenevinylene)s (DAOPVs) **11** in the VB theory and quadrupolar counterpart **12** for both in MO theory

Whereas OPVs are essentially planar (in a flat well of the potential energy related to torsions), unsymmetrical OPPs **1'** with  $n \geq 2$  repeat units exist in  $2^{n-1}$  nonplanar conformations [21]. Torsions along the chain diminish certainly the mesomeric push–pull effect and the extra resonance energy. Fig. 3 illustrates the  $^1\text{H-NMR}$  data of **2a–2d** ( $n=1–4$ ). Each benzene ring represents an  $AA'BB'$  spin system with a certain  $\Delta\delta$  difference. The  $\Delta\delta$  values are high for the ‘outer’ benzene rings and very low for the ‘inner’ benzene rings. On the whole, all chemical shifts  $\delta(\text{H})$  increase with increasing  $n$  values. This is, however, an anisotropy effect. The anisotropy cone of the aromatic region increases with increasing number of rings.

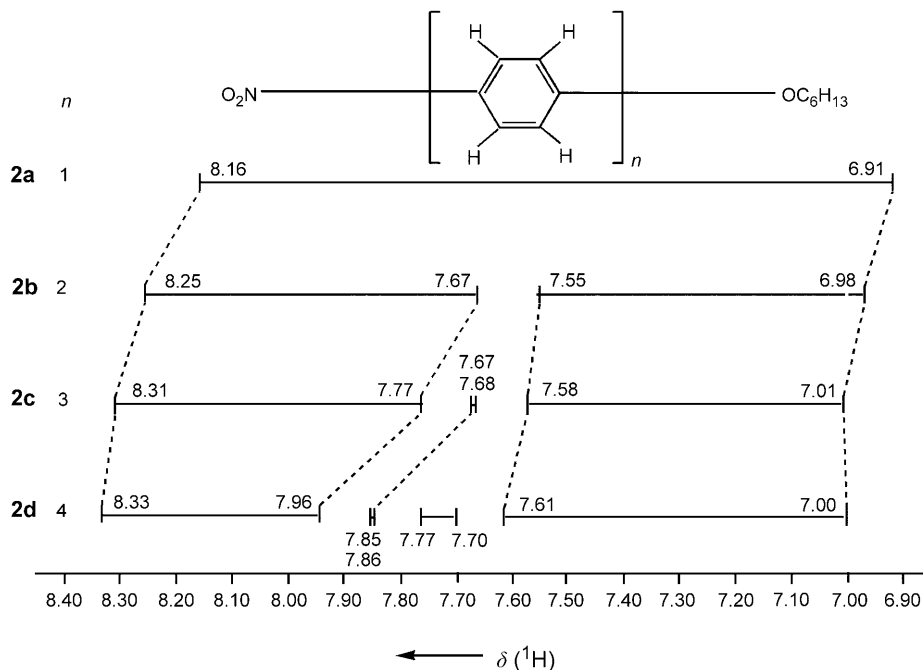


Fig. 3.  $AA'BB'$  Spin systems of the benzene rings in the  $^1\text{H-NMR}$  spectra of **2a–2d** ( $n=1–4$ ). Measurement in  $\text{CDCl}_3$ , except **2d**, which was measured in  $(\text{D}_8)\text{THF}$ .

The superposition of anisotropy and electron-density effects plays a minor role in  $^{13}\text{C-NMR}$  spectroscopy, so that the  $\delta(\text{C})$  values permit a reliable statement about charge densities. Fig. 4 summarizes the  $\delta(\text{C})$  values of 1,1'-biphenyl (**13**), the merely acceptor- or donor-substituted model compounds **14** and **15**, and the push–pull compounds **2b** and **2c**. The  $\delta(\text{C})$  values of **13–15** reveal that the electron-withdrawing  $\text{NO}_2$  group and the electron releasing  $\text{C}_6\text{H}_{13}\text{O}$  group have a strong effect on their own benzene ring, each, but only a minor effect on the next benzene ring. The polarization of the  $\pi$  chain by the push–pull substitution is much higher in the DAOPV series **11** [22][23] than here in the DAOPP series **1'**. The torsion of the benzene rings in **1'** reduces the charge transfer. Nevertheless, a certain push–pull effect is present in series **2**. The ‘inner’ quaternary C-atoms of **2b** and **2c** have – compared to **13** ( $\delta(\text{C})$  141.1) – alternately high and low  $\delta$  values, *i.e.*,  $\delta(\text{C})$  147.2 and 130.7 in the case of **2b**, and  $\delta(\text{C})$

147.3, 136.8, 141.6, and 132.4 in the case of **2c**. The same effect should be valid for **2d**. The solubility of **2d** in  $\text{CDCl}_3$  is, however, too low to obtain reliable  $\delta$  values of the quaternary C-atoms.

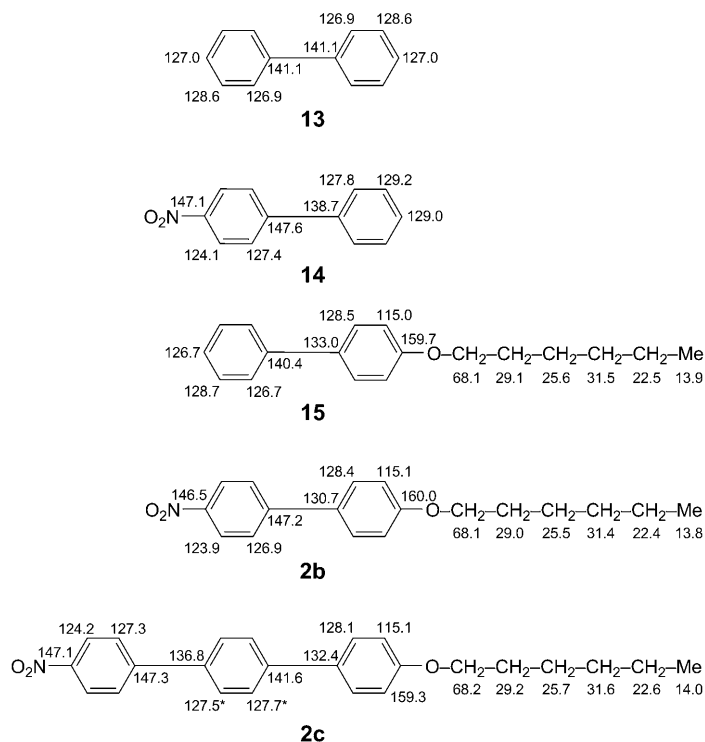


Fig. 4.  $^{13}\text{C}$ -NMR Chemical shifts  $\delta$  [ppm] of *1,1'*-biphenyl (**13**), *4-nitro-1,1'*-biphenyl (**14**), *4-(hexyloxy)-1,1'*-biphenyl (**15**), *4-(hexyloxy)-4'-nitro-1,1'*-biphenyl (**2b**), and *4-(hexyloxy)-4'-nitro-1,1':4',1''-terphenyl* (**2c**). Measurement in  $\text{CDCl}_3$ , with  $\text{Me}_4\text{Si}$  as internal standard.

After the polarization of the DAOPPs in the ground-state  $S_0$ , the charge distribution in the more planar first-excited singlet state  $S_1$  shall be discussed here. The band of the allowed long-wavelength electron excitation  $S_0 \rightarrow S_1$  is called a charge-transfer band because it is based on an intramolecular charge transfer (ICT). The shift of electron density from the donor to the acceptor leads in the majority of  $\text{D}-\pi-\text{A}$  compounds to very high dipole moments  $\mu$  ( $S_1$ ) [1]. The ICT lowers the transition energy  $\Delta E$  ( $S_0 \rightarrow S_1$ ) by reducing the electron-correlation energy. However, when the distance between D and A increases, the ICT decreases. Increasing length of the  $\pi$  chain effects, on the other hand, a decreasing HOMO–LUMO gap. Consequently, the increasing number  $n$  of repeat units has two opposite effects, and the crucial question is, which of the two effects will prevail. Fig. 5 puts the  $\lambda_{\text{max}}$  values, obtained for the series **2a–2d** ( $n = 1–4$ ) in the context of other OPPs. The parent OPP series **13a–13f** [24] as well as series **16a–16d** [9] with *tert*-butyl groups at the terminal rings are ‘normal’ series of conjugated oligomers. That means, their  $\lambda_{\text{max}}$  values increase monotonously with

increasing  $n$  values and approach to a limiting value  $\lambda_{\infty}$ . The curves shown in Fig. 5 correspond to empirical exponential functions [26], which proved to be much better for intra- and extrapolations of the transition energy  $\Delta E$  than earlier used hyperbolic functions ( $\Delta E = f(1/n)$ ) [1][21][26] or trigonometric functions ( $\Delta E = f(\cos \pi/n + 1)$ ) [27]. Recently Gierschner and co-workers [28] and Bednarz and co-workers [29]

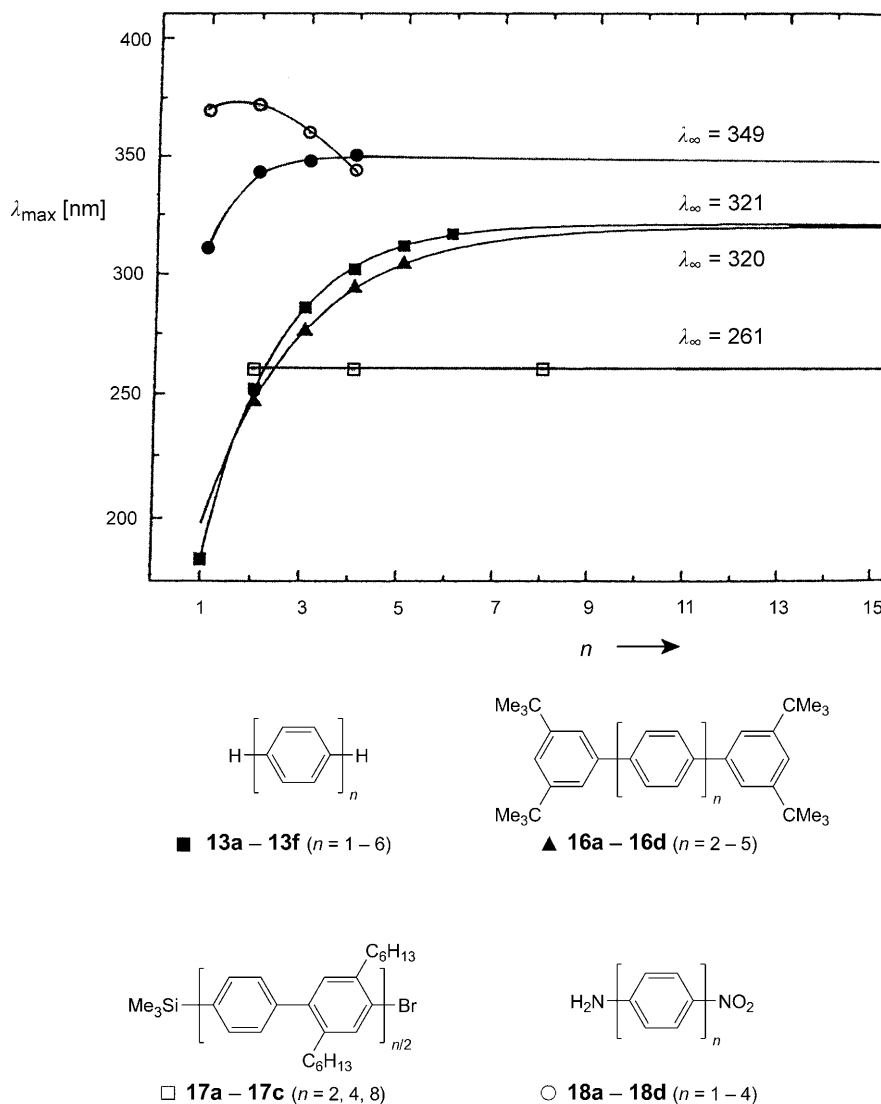


Fig. 5. Long-wavelength absorption maxima of **2a–2d** in  $\text{CHCl}_3$  ( $\bullet$ ) in comparison to other OPP series: **13a–13f** in THF [24], **16a–16d** in THF [9], **17a–17d** in octane [20], and **18a–18d** in 1-methylpyrrolidin-2-one [25]

proposed semi- to nonempirical equations for the dependence of  $\lambda$  or  $\Delta E$  on the number  $n$  of repeat units.

The effective conjugation length [30] of **13** and **16** amounts to  $n_{\text{ECL}} = 9$  and 11, respectively. These numbers  $n_{\text{ECL}}$ , as well as  $\lambda_{\infty}$ , characterize the saturation phenomenon of conjugated oligomers. Series **17** [20] gave the remarkable result that the  $\lambda_{\text{max}}$  values do not depend on  $n$ , that means on the length of the chain. Two hexyl groups at every second benzene ring are obviously sufficient for the total loss of conjugation.

The push–pull series **2a–2d** is a bathochromic series:  $\lambda_{\text{max}}$  311, 344, 346, and 348 nm (in  $\text{CHCl}_3$ ) for  $n = 1, 2, 3$ , and 4, respectively, but the convergence limit ( $\lambda_{\infty} \pm 1$ ) nm [1] is already reached at  $n_{\text{ECL}} = 4$  (Fig. 5). The  $S_0 \rightarrow S_2$  transition approaches, with increasing chain length, the  $S_0 \rightarrow S_1$  transition. Both bands are still separate for  $n = 3$  but have to be separated for  $n = 4$ . A slightly unsymmetrical *Gauss* function proved to be successful for this purpose [31]. The ICT effects a very strong red shift for  $n = 1$  and 2, but then it decreases fast for higher  $n$  values. The bathochromic effect ( $\lambda_{\text{max}}(n+1) \geq \lambda_{\text{max}}(n)$ ) caused by the increased conjugation is almost cancelled by the decreasing ICT effect. Series **18** [25] has – compared to **2** – an even stronger push–pull character (Fig. 5). Increasing conjugation can no more compensate the decreasing ICT for  $n > 2$ . Thus  $\lambda_{\text{max}}$  of series **18** reaches a maximum for  $n = 2$ . The extrapolation to  $\lambda_{\infty}$  in such a case would require some higher  $n$  values ( $n > 4$ ) [1].

**Conclusion and Outlook.** – Oligo(*para*-phenylene)s **2a–2d** with terminal donor–acceptor substitution (RO/NO<sub>2</sub>) can be easily prepared by applying the *Suzuki–Miyaura* protocol. A protecting/deprotecting technique can be avoided, when the different reactivity of 1-bromo-4-iodobenzene is used for the chain-extension steps.

Although the polarization of such D– $\pi$ –A chains is rather low in the ground-state  $S_0$  (NMR measurements), the intramolecular charge transfer (ICT) on electronic excitation ( $S_0 \rightarrow S_1$ ) is high, that means the long-wavelength absorption is considerably red-shifted for small numbers of repeat units ( $n = 1$  and 2). Higher  $n$  values ( $n = 3$  and 4) lead very fast to a saturation ( $n_{\text{ECL}} = 4$ ) in the UV region ( $\lambda_{\infty}$  349 nm). The calculations of DAOPPs **1'** on the CNDOVSB basis [32] or DFT basis [33] do not completely satisfy, in this respect, but together with the results discussed here, one can predict, that longer DAOPPs ( $n = 5, 6, \dots$ ) with strong push–pull effects will have high dipole moments  $\mu$  and first-order hyperpolarizabilities  $\beta$ , but will still have a very good transparency in the VIS region. Their preparation and process ability should be facilitated by well solubilizing, strong donor groups such as bis(2-hexyloctyl)amino [ $(\text{C}_6\text{H}_{13})_2\text{CHCH}_2\text{N}$ ] or (2-hexyloctyl)oxy groups [ $(\text{C}_6\text{H}_{13})_2\text{CHCH}_2\text{O}$ ].

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### Experimental Part

1. *General.* The starting compounds **3–5**, **9**, and **10** and the model compounds **13** and **14** are commercially available. M.p. (uncorrected): *Büchi* apparatus. UV/VIS Spectra: *Zeiss-MCS-320/340* diode array;  $\text{CHCl}_3$  solns.;  $\lambda_{\text{max}}$  in nm. <sup>1</sup>H- and <sup>13</sup>C-NMR Spectra: *Bruker AM 400* and *AMX 400*;  $\text{CDCl}_3$  solns.;  $\delta$  in ppm, rel. to  $\text{Me}_4\text{Si}$  as internal standard,  $J$  in Hz. FD-MS: *Finnigan MAT-95*; in  $m/z$  (rel. %).



2. Alkylation of 4-Nitrophenol (**3**) and 4-Bromophenol (**5**) with 1-Bromohexane (**4**). Preparations according to [11][34][35].

1-(Hexyloxy)-4-nitrobenzene (**2a**): Yield 95%. M.p. 26° (EtOH) ([34]: 25.5°). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 0.89 (t, *J* = 6.1, Me(6'')), 1.28–1.37 (m, CH<sub>2</sub>(4'), CH<sub>2</sub>(5'')); 1.40–1.48 (m, CH<sub>2</sub>(3'')); 1.75–1.83 (m, CH<sub>2</sub>(2'')); 4.02 (t, *J* = 6.4, CH<sub>2</sub>(1'')); 6.91, 8.16 (AA'BB', H–C(2,6), H–C(3,5)). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 13.9 (Me(6'')); 22.4 (CH<sub>2</sub>(5'')); 25.6 (CH<sub>2</sub>(3'')); 28.9 (CH<sub>2</sub>(2'')); 31.4 (CH<sub>2</sub>(4'')); 68.9 (CH<sub>2</sub>(1'')); 114.4 (C(3)); 125.8 (C(2)); 141.4 (C(1)); 164.3 (C(4)). The product corresponds to an authentic sample [34].

1-Bromo-4-(hexyloxy)benzene (**6a**): Colorless viscous oil. Yield 94%. The product corresponds to an authentic sample [35].

3. Chain Extension **6a** → **8a** → **6b** → **8b** → **6c** → **8c**. 3.1. Steps **6** → **8**: General Procedure. A soln. of the corresponding bromo compound **6a–6c** (20.0 mmol) in Et<sub>2</sub>O (60–100 ml) was purged with a stream of Ar, before 2.5M BuLi in hexane (8.4 ml, 21.0 mmol) was added at –78° with a syringe. After 2 h stirring, the soln. was slowly added at –78° to fluorodimethoxyborane (**7**; 368 g, 40.0 mmol) [18][19]. The cooling was stopped and the soln. allowed to come to r.t. After 12–24 h, H<sub>2</sub>O (50 ml) was added. The aq. layer was extracted with Et<sub>2</sub>O (2 × 30 ml), and the combined org. phase was washed with H<sub>2</sub>O (20 ml), dried (MgSO<sub>4</sub>), and purified by column filtration (SiO<sub>2</sub>, 15 × 8 cm, hexane/Et<sub>2</sub>O 100:0 → 0:100). Evaporation yielded the crude boronic acids **8a** (75%), **8b** (48%), or **8c** (48%), which could be directly used for the Suzuki reaction with 1-bromo-4-iodobenzene (**9**) or for the end capping with 1-bromo-4-nitrobenzene (**10**).

3.2. Steps **8** → **6**: General Procedure. A soln. of the boronic acid **8a,b** (6.0 mmol) and iodo component **9** (1.70 g, 6.0 mmol) in toluene/THF 1:1 (200 ml) was degassed and purged with a slow stream of Ar. Aq. 2M K<sub>2</sub>CO<sub>3</sub> (100 ml) and [Pd(PPh<sub>3</sub>)<sub>4</sub>] (115 mg, 0.1 mmol) were added. The mixture was vigorously stirred and refluxed under Ar for 2–3 d. The H<sub>2</sub>O phase was extracted with toluene (2 × 20 ml), and the combined org. phase was washed with sat. NaCl soln. (20 ml), dried (MgSO<sub>4</sub>), and purified by column filtration (SiO<sub>2</sub>, 15 × 8 cm, toluene). The crude products **6b** (70%) or **6c** (64%) could be directly used for the next step. A purity control was based on the NMR data: Table.

4. End Capping **8a–8c** → **2b–2d**: General Procedure. A soln. of crude boronic acid **8a–8c** (1.0 mmol) and 1-bromo-4-nitrobenzene (**10**) in toluene/THF 1:1 (30–40 ml) was degassed and purged with Ar. Aq. 2M K<sub>2</sub>CO<sub>3</sub> (15–20 ml) and [Pd(PPh<sub>3</sub>)<sub>4</sub>] (20 mg, 17.4 · 10<sup>–3</sup> mmol) were added. The mixture was vigorously stirred and heated under reflux for 2–4 d. The H<sub>2</sub>O phase was extracted with toluene (2 × 20 ml), and the combined org. phase was washed with sat. NaCl soln. (20 ml), dried (MgSO<sub>4</sub>), and evaporated. The crude DAOPPs **2a–2d** were purified by crystallization.

4-(Hexyloxy)-4'-nitro-1,1'-biphenyl (**2b**): Yield 78%. Colorless solid. M.p. 60° (PrOH). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 0.90 (t, *J* = 6.1, Me(6'')); 1.32–1.38 (m, CH<sub>2</sub>(4''), CH<sub>2</sub>(5'')); 1.42–1.48 (m, CH<sub>2</sub>(3'')); 1.75–1.85 (m, CH<sub>2</sub>(2'')); 4.00 (t, *J* = 6.4, CH<sub>2</sub>(1'')); 6.98, 7.55 (AA'BB', H–C(2,6), H–C(3,5)); 7.67, 8.25 (AA'BB', H–C(2',6'), H–C(3',5')). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 13.8 (Me); 22.4 (CH<sub>2</sub>(5'')); 25.5 (CH<sub>2</sub>(3'')); 29.0 (CH<sub>2</sub>(2'')); 31.4 (CH<sub>2</sub>(4'')); 68.1 (CH<sub>2</sub>(1'')); 115.1 (C(3)); 123.9 (C(3')); 126.9 (C(2')); 128.4 (C(2)); 130.7 (C(1)); 146.5 (C(4'')); 147.2 (C(1'')); 160.0 (C(4)). FD-MS: 300 (100, [M + H]<sup>+</sup>). Anal. calc. for C<sub>18</sub>H<sub>21</sub>NO<sub>3</sub> (299.4): C 72.22, H 7.07, N 4.68; found: C 71.98, H 7.26, N 4.88.

4-(Hexyloxy)-4'-nitro-1,1':4',1''-terphenyl (**2c**): Yield 70%. Light yellow solid. M.p. 198–200° (PrOH/1,2-dichlorobenzene). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 0.93 (t, *J* = 6.1, Me(6''')); 1.32–1.40 (m, CH<sub>2</sub>(4'''), CH<sub>2</sub>(5''')); 1.43–1.53 (m, CH<sub>2</sub>(3''')); 1.77–1.89 (m, CH<sub>2</sub>(2''')); 4.01 (t, *J* = 6.5, CH<sub>2</sub>(1''')); 7.01, 7.58 (AA'BB', H–C(2,6), H–C(3,5)); 7.67, 7.68 (AA'BB', H–C(2',6'), H–C(3',5')); 7.77, 8.31 (AA'BB', H–C(2'',6''), H–C(3'',5'')). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 14.0 (Me(6''')); 22.6 (CH<sub>2</sub>(5''')); 25.7 (CH<sub>2</sub>(3''')); 29.2 (CH<sub>2</sub>(2''')); 31.6 (CH<sub>2</sub>(4''')); 68.2 (CH<sub>2</sub>(1''')); 115.1 (C(3)); 124.2 (C(3'')); 127.3 (C(2'')); 127.5, 127.7 (C(2'), C(3')); 128.1 (C(3)); 132.4 (C(1)); 136.8 (C(4'')); 141.6 (C(1'')); 147.3 (C(1'')); 147.1 (C(4'')); 159.3 (C(4)). FD-MS: 376 (100, [M + H]<sup>+</sup>). Anal. calc. for C<sub>24</sub>H<sub>25</sub>NO<sub>3</sub> (375.5): C 76.77, H 6.71, N 3.73; found: C 76.99, H 7.01, N 3.75.

4-(Hexyloxy)-4''-nitro-1,1':4',1'':4'',1'''-quaterphenyl (**2d**): Yield 62%. Light yellow solid. M.p. > 200° (dec.; PrOH/1,2-dichlorobenzene). <sup>1</sup>H-NMR ((D<sub>8</sub>)THF): 0.94 (t, *J* = 6.1, Me); 1.34–1.41 (m, CH<sub>2</sub>(4'''), CH<sub>2</sub>(5''')); 1.45–1.54 (m, CH<sub>2</sub>(3''')); 1.76–1.85 (m, CH<sub>2</sub>(2''')); 4.01 (t, *J* = 6.4, CH<sub>2</sub>(1''')); 7.00, 7.61 (AA'BB', H–C(2,6), H–C(3,5)); 7.70, 7.77 (AA'BB', H–C(2',6'), H–C(3',5')); 7.85, 7.86 (AA'BB', H–C(2'',6''), H–C(3'',5'')); 7.96, 8.33 (AA'BB', H–C(2''',6'''), H–C(3''',5''')). <sup>13</sup>C-NMR: Solubility

unsufficient for reliable data. FD-MS: 452 (100,  $[M + H]^+$ ). Anal. calc. for  $C_{30}H_{29}NO_3$  (451.6): C 79.80, H 6.47, N 3.10; found: C 80.08, H 6.33, N 2.90.

5. 4-(Hexyloxy)-1,1'-biphenyl (**15**). Preparation according to [36] and analogously to **3** + **4** → **2a**. Yield 93%. M.p. 68° ([36]: 63–63.5°).

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