Polyarylenes and Poly(arylenevinylene)s, V[1]

Synthesis of Tetraalkyl-Substituted Oligo(1,4-naphthylene)s and Cyclization to Soluble Oligo(*peri*-naphthylene)s[2]

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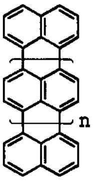
A homologous series of oligo(1,4-naphthylene)s from the binaphthyl **6** to the sexinaphthylene derivative **10** were synthesized successively. The Pd(0)-catalyzed reaction between aryl bromides and arylboronic acids was used as a coupling method. By appropriate choice of the stoichiometry, the method allowed isolation of the intermediates **20** and **21**. Under the influence of potassium in 1,2-dimethoxyethane the 1,4-bridged naphthylenes **6** – **10** were partially cyclized to perylene and terrylene units. This anionic cyclization displayed a high regioselectivity. Complete cyclization to the oligorylenes **3b**, **4b** and **5b** was achieved under the influence of $AlCl_3$ and $CuCl_2$ on the bichromophoric systems **24**, **25** and **28**. The synthetic sequence allowed substitution by *tert*-butyl groups, so that the oligorylenes **2b**, **3b**, **4b** and **5b** were amenable to spectroscopic investigations. The trends in absorption maxima and fluorescence are discussed.

Large polycyclic aromatic hydrocarbons are in general not easily accessible and are often distinguished by a very poor solubility, preventing complete characterization and investigations of their physical properties. Their extremely high melting points and poor solubilities do not allow purification by either zone melting or by chromatography on a preparative scale. Numerous attempts to prepare fully conjugated, organic π systems demonstrate the great demand for these compounds. Until now, poly(*peri*-naphthylene) (PPN, **1**), a representative example of these π systems, has not been available. Previous efforts towards its preparation have included cationic cyclization[3], pyrolytic treatment[4,5] and plasma polymerization[6] of suitable precursors. However, such drastic conditions led to partially graphitized, irregular structures. The number of defects was consequently very large, and structurally well-defined materials could not be obtained. On the other hand, for the polymer **1** a vanishing HOMO-LUMO band gap, indicating the likelihood of intrinsic electrical conductivity, has been theoretically predicted[7,8] but could not be verified due to the synthetic problems indicated above. The synthesis of soluble, structurally well-defined oligomers could allow an examination of the physical properties of this type of polycondensed aromatic hydrocarbon for the first time. The variation of properties such as absorption and fluorescence behavior, electrical conductivity, redox potential, charge density in reduced or oxidized species, etc. in a homologous series enables the extrapolation of these properties to the polymer. Thus, with the use of structurally well-defined oligomers it is possible to determine the effective degree of conjugation and, in addition, to detect structural defects in previously synthesized polymers of the investigated π system[9].

Whereas the physical properties, i.e. fluorescence[10] and scintillation properties[11], hole-burning spectroscopy[12], the photoconductivity[13] of perylene (**2a**) and the electrical conductivity[14,15] of CT complexes of **2a** as the first member in the series of the oligomers of PPN (**1**) have been extensively studied and are still the subject of various investigations, the higher homologues could not be explored. The reasons for this shortcoming are the lack of selective syntheses of these compounds as well as their inprocessibility caused by their poor solubility and high melting points.

Di(*peri*-naphthylene)naphthalene (**3a**) is the second member in the homologous series of the *peri*-condensed naphthalene compounds. This series is termed rylene according to the nomenclature of Clar[16]; the first well-known member has been designated as perylene (**2a**), the second as terrylene (**3a**) and the last known as quaterrylene (**4a**). The synthesis of **3a** or **4a** carried out by Clar required the use of the drastic



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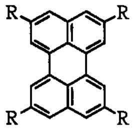
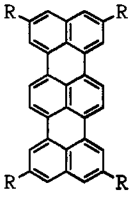


2a: R = H
2b: R = tBu



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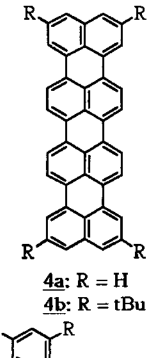
3b: R = tBu



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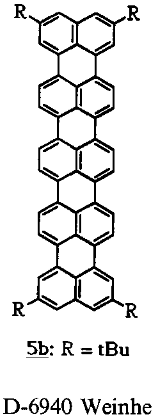
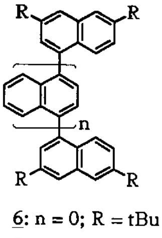
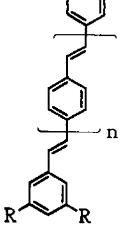
4b: R = tBu



5b: R = tBu



6: n = 0; R = tBu
7: n = 1; R = tBu
8: n = 2; R = tBu
9: n = 3; R = tBu
10: n = 4; R = tBu



11: R = tBu

Scholl reaction by "caking together" ternaphthylene derivatives 7 or perylene 2a, respectively, in an aluminium chloride/sodium chloride melt[17,18]. The compounds formed, **3a** and **4a**, have not been fully characterized and showed insufficient solubility for spectroscopic investigations.

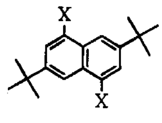
As in the previous synthesis of 2,5,8,11-tetra-*tert*-butylperylene (**2b**) by Friedel-Crafts alkylation of perylene (**2a**)[19,20,21], the required solubility should be attained by substitution of the title compounds in each case by four *tert*-butyl groups in the terminal β positions. The novel synthesis presented here is performed by cyclization of the corresponding substituted oligo(1,4-naphthylene)s **6**, **7**, **8**, **9** and **10**. These compounds have not been prepared before. In the series of the oligo(*p*-phenylenevinylene)s (**11**) it has previously been shown that a fourfold substitution by *tert*-butyl groups in positions comparable to those in the homologues **6**, **7**, **8**, **9** and **10** leads to a sufficient solubility of all compounds **11** containing up to six phenylene moieties (n = 4)[22].

Results and Discussion

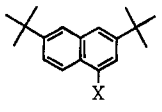
1. Synthesis of the Oligo(1,4-naphthylene)s 6 – 10

The starting material for the synthesis is 2,7-di-*tert*-butylnaphthalene (**13**), which is formed directly by Friedel-Crafts alkylation of napthalene with *tert*-butyl chloride and a catalytic amount of aluminium chloride[23]. Under these reaction conditions a 1:1 mixture of the 2,6 (**12**) and the 2,7 isomer (**13**) is obtained. After optimizing the procedure for the separation of the two isomers via thiourea inclusion complexes, the compounds are now available on a large scale (100 – 150 g). It should be mentioned that the 2,6 isomer **12** can be readily converted into 1,5-dibromo-3,7-di-*tert*-butylnaphthalene (**14**), the substrate for the synthesis of the soluble poly(3,7-di-*tert*-butyl-1,5-naphthylene) (**15**)[24]. In the case of the 2,7 isomer **13** only the monobromo compound is formed by direct bromination. The yield of 1-bromo-3,6-di-*tert*-butylnaphthalene (**16**) amounts to 86% when using tetrachloromethane as solvent and a catalytic amount of iron turnings. Our approach towards the synthesis of the oligo(1,4-naphthylene)s **6 – 10** was stimulated by Suzuki's work on the palladium-catalyzed coupling of arylboronic acids with aryl halides[25]. The efficiency of this method has recently been demonstrated for the preparation of soluble poly(1,4-phenylene)[26] and the above mentioned poly(1,5-naphthylene) derivatives **15**[24]. For that purpose, it is first necessary to transform **16** by treatment with butyllithium at −78°C and reaction with an excess of triisopropoxyborane into its monoboronic acid derivative **17** (76%). The preparation of the *tert*-butylated binaphthyl **6** is achieved by condensing the boronic acid **17** with an equimolar amount of the aryl bromide **16** in boiling toluene under the influence of 3 mol-% of tetrakis(triphenylphosphine)palladium(0) and aqueous potassium carbonate solution (72%). In an analogous fashion, the palladium-catalyzed coupling of **17** with 1,4-dibromonaphthalene (**18**) or 4,4′-dibromo-1,1′-binaphthyl (**19**) in a 2:1 molar ratio leads to the formation of the higher homologues, the ternaphthylene derivative **7** (83%) and the quaternaphthylene **8** (74%), respectively. The specific synthesis of the monocoupling products – the aryl bromides **20** (61%) and **21** (58%) – is successful by coupling equimolar amounts of **17** with 1,4-dibromonaphthalene (**18**) or 4,4′-dibromo-1,1′-binaphthyl (**19**). **20** and **21** are subsequently converted into the corresponding boronic acids **22** and **23** by lithiation and subsequent reaction with triisopropoxyborane. For the preparation of the quinquenaphthylene **9** (60%), compounds **21** and **22** are employed in the boronic acid coupling reaction, whereas for the production of the sexinaphthylene **20** (55%) compounds **21** and **23** are used.

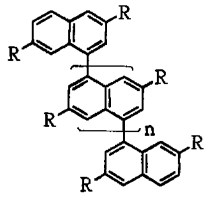
In the series of the prepared oligo(1,4-naphthylene)s **6 – 10** hindered rotation around the connected naphthalene units results in atropisomerism. The existence of the different diastereomers can be detected in the ^{1}H-NMR spectra, where the signals of the *tert*-butyl groups are split into two doublets (see Experimental).



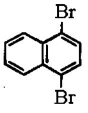
12: X = H
14: X = Br



13: X = H
16: X = Br
17: X = B(OH)$_2$



15: R = tBu



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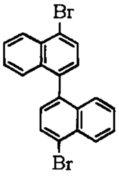

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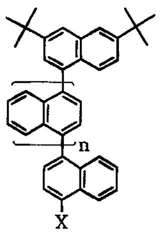


20: n = 0; X = Br
21: n = 1; X = Br
22: n = 0; X = B(OH)$_2$
23: n = 1; X = B(OH)$_2$

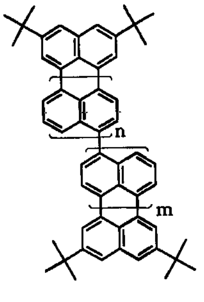
2. Anionic Cyclizations

The key step in the preparation of the oligorylenes **2b – 5b** themselves was inspired by the observation of Solodovnikov[27] that 1,1′-binaphthyl cyclizes spontaneously to perylene (**2a**) upon reduction with alkali metals. According to the reduction conditions described for EPR spectroscopy, the oligo(1,4-naphthylene)s **6 – 9** are reduced by potassium on a preparative scale in 1,2-dimethoxyethane (DME). The solutions are degassed by repeated freeze-and-thaw cycles under vacuum (10^{-3} Torr). In the case of the binaphthyl derivative **6**, a green color appears after several hours indicating its conversion into the radical anion. The spin density in the radical anion is delocalized over the entire π system; detailed results of the EPR investigations of the radical anions of symmetrically substituted biaryles and of the oligorylenes themselves will be published elsewhere[28]. After further 24 hours, the formation of the dianion is complete indicated by a deep red color. In the course of the reaction, the binaphthyl dianion **6**$^{2-}$ is converted by elimination of hydrogen into the dianion of the perylene derivative **2b**$^{2-}$. After approximately 7 days, the mixture shows a purple color caused by the perylene dianion **2b**$^{2-}$ (see Figure 1; ^{1}H-NMR spectra of **2b**$^{2-}$/2 K$^+$). The mixture is then oxidized with freshly sublimed cadmium chloride. Chromatographic purification results in a 40% yield of 2,5,8,11-tetra-*tert*-butylperylene (**2b**). To prevent the formation of byproducts very smooth reaction conditions for the reductive cyclization are chosen. For that reason, a relatively large amount of uncyclized starting compound **6** is recovered.

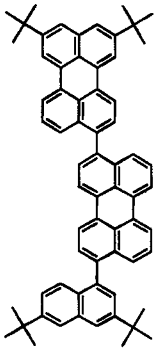
The cyclization of tetra-*tert*-butylternaphthylene **7** leads to the formation of two products, namely the substituted 3-(1′-naphthyl)perylene **24** (42%) in addition to the fully annelated terrylene derivative **3b** (24%) (see Figure 1; ^{1}H-NMR spectra of **3b**$^{2-}$/2 K$^+$). It is remarkable that the potassium-induced cyclization shows a very high regioselectivity; the C–C bond formation occurs only in the *peri* positions of the napthalene units leading to an annelation in positions 1, 8, 1′ and 8′. Condensations at different positions could not be detected. The previously prepared supposed 3-(1′-naphthyl)perylene, which was obtained by the Scholl reaction[17], shows a completely different UV/Vis absorption spectrum. A comparison of the spectra of **24** (λ_{max} = 444 nm) with the published data (λ_{max} = 500, 406 and 329 nm) points towards a structure different from 3-(1′-naphthyl)perylene. Thus, the drastic Scholl reactions possess only a low regioselectivity. Consequently, irregular polycyclic hydrocarbons will be formed, which cannot be separated easily.

Reduction and subsequent oxidation of the quaternaphthylene derivative **8** also result in the formation of perylene and terrylene chromophores. The course of the cyclization evidently depends upon the extent of the redox activity of the π system, since reaction of the substituted quaternaphthylene **8** leads to the 3,3′-biperylenyl **25** rather than to the desired quaterrylene **4b**. The main product of the reaction is the symmetrically substituted 3,3′-biperylenyl derivative **25** (48% yield). Other byproducts are the non-separable binaphthylperylenes (10%) as well as the 3-(1′-naphthyl)terrylene **26** (5%) which could be isolated.

As in the case of **8**, after cyclization of the quinquenaphthylene compound **9**, only perylene and terrylene chromophores are formed by reductive treatment with potassium. After oxidation with anhydrous cadmium chloride and purification on aluminium oxide, the substituted 10-(1″-naphthyl)-3,3′-biperylenyl **27** (52%) as well as the 3-(3′-perylenyl)terrylene **28** (29%) could be isolated. Cyclization to neither quaterrylene nor pentarylene chromophores was observed. With the use of the potassium-induced cyclization method substituted perylene derivatives, which are not easily accessible by other routes, are now available. For example, to our knowledge, all bichromophoric systems mentioned above have previously been unknown. The synthetic route by anionic cyclization of substituted precursors in a highly regioselective process is certainly superior to the classical Scholl reaction. Furthermore, the cleavage of alkyl groups is prevented when employing the reductive method instead of the drastic conditions of an aluminium chloride melt.



24: n = 0; m = 1
25: n = 1; m = 1
26: n = 0; m = 2
28: n = 1; m = 2



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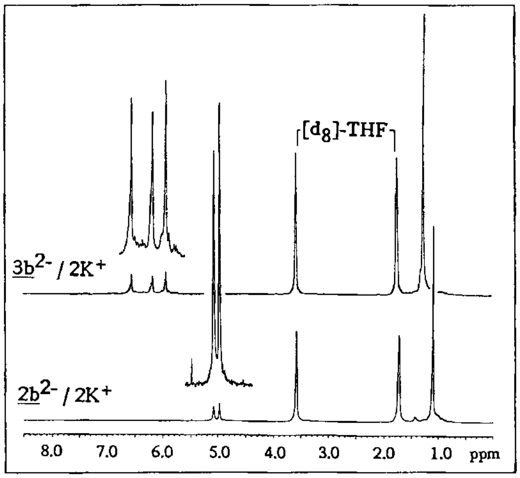

Figure 1. ^{1}H-NMR spectra ([D$_8$]-THF, 200 MHz, −20°C) of the dianion salts **2b**$^{2-}$/2 K$^+$ and **3b**$^{2-}$/2 K$^+$

3. Cationic Cyclizations

To obtain the fully annelated ladder-type structures **3b**, **4b** and **5b** it is necessary to apply more drastic methods of cyclization. The Scholl reactions should not be used, since in addition to their poor regioselectivity, a partial cleavage of the *tert*-butyl groups is expected. Jones[3] made an attempt to synthesize perylene (**2a**) by oxidative treatment of unsubstituted 1,1′-binaphthyl with a mixture of aluminium chloride and copper(II) chloride. The experiments revealed that no perylene (**2a**) is formed; instead, an isomerization to 1,2′- and 2,2′-binaphthyl takes place under these conditions. By employing aromatic π systems in which radical cations are more stabilized than in the case of the oligo(naphthylene)s, i.e. the synthesized perylene derivatives **24**–**28**, this side-reaction should be suppressed.

To obtain larger amounts of 2,5,10,13-tetra-*tert*-butylterrylene (**3b**), the 3-(1′-naphthyl)perylene derivative **24** is allowed to react with aluminium chloride and copper(II) chloride under mild conditions. The reaction is performed in carbon disulfide at room temperature and with exclusion of oxygen. The reaction mixture showed a dark blue color emerging from charge-transfer complexes. After hydrolysis, the formation of the terrylene derivative **3b** (42%) could be easily detected by its purple reddish color and the strong red fluorescence. Whereas the spectroscopic properties of unsubstituted terrylene (**3a**) could not be investigated, the solubility of the substituted derivative **3b** is sufficient to measure, for example, its NMR spectrum (Table 1). As with perylene **2b**, the *peri* protons (3-H) of **3b** show a signal at $\delta = 7.64$. The signal is split into a doublet ($J = 1.5$ Hz) caused by a long-range coupling between 3-H and 1-H. The protons centered in the bay region of **2b** (1-H) and **3b** (1-H and 7-H) are shifted to $\delta = 8.26-8.28$. This is due to an enhanced ring current effect in the pair of napthalene units.

In order to prepare the next higher homologues in the series of the oligorylenes, the 3,3′-biperylenyl derivative **25** is subjected to oxidative coupling. Chromatographic purification of the crude product (aluminium oxide, cyclohexane) results in elution of the byproducts (perylene chromophores) only. The title compound **4b** was recovered from the column packing by repeated extraction with boiling chloroform in a yield of 48%. The solubility of the substituted quaterrylene derivative **4b** is sufficient to measure its ^{1}H-NMR spectrum and therefore allows an unambiguous structure determination (Table 1). Similar to **2b** and **3b**, the aromatic resonance signals for **4b** could be divided into a high-field and a low-field region. The proton signal of 3-H appears at $\delta = 7.62$, whereas the bay protons (1-H, 7-H, 8-H) give rise to a broad peak with a center of gravity at $\delta = 8.22$.

In solution compound **4b** shows a deep blue color; fluorescence is not noticeable. In the solid state the compound possesses a deep black color, and a reddish lustre becomes apparent.

The 3-(3′-perylenyl)terrylene derivative **28** is the precursor of the as yet unknown pentarylene **5b**. In fact, its preparation by oxidative treatment of **28** was successful. The compound **28** was allowed to react with aluminium chloride and copper(II) chloride in 1,2,4-trichlorobenzene at room temperature. The purification of **5b** is performed in a similar fashion as described for the quaterrylene derivative **4b** by adsorption on aluminium oxide. Elution of the byproducts and repeated extractions with boiling chlorobenzene yield 60% of purified pentarylene **5b**. The solubility of the substituted pentarylene **5b** is strongly decreased. The measurement of a ^{1}H-NMR spectrum is prevented by its low solubility.

4. UV/Vis Absorption and Fluorescence Spectra

As a result of the substitution with the *tert*-butyl groups all rylene derivatives **2b**–**5b** prepared are now sufficiently soluble for an investigation of their photophysical properties. The UV/Vis absorption spectra (see Figure 2 and Table 2) demonstrate a strong bathochromic shift of the ^1L_a band lying in the longest wavelength region with increasing degree of annelation. In all cases the absorption band exhibits a similar vibrational structure. The experimentally determined peak positions are in good agreement with the calculated values (PPP-SCF-CI[29]). Remarkable is the small Stoke's shift between the absorption and emission bands in the case of all investigated homologues. As with perylene (**2a**), the fluorescence spectra of the homologues show mirror image symmetry between the longest wavelength absorption band and the corresponding emission band (see Figure 2); thus, in all homologues the geometries of the S_0 and S_1 states are quite similar. Whereas perylene (**2a**), the tetra-*tert*-butylperylene derivative **2b** and also the new terrylene derivative **3b** demonstrate a very intensive fluorescence, the fluorescence intensity of the quaterrylene derivative **4b** is surpris-

Table 1. ^{1}H-NMR data (δ values)[a] of the oligorylenes **2b**, **3b** and **4b**

Compd.	1-H	3-H	7-H	8-H	$C(CH_3)_3$
2b	8.27[b]	7.65[b]	–	–	1.48
3b	8.26[b]	7.64[b]	8.28	–	1.50
4b	8.22[c]	7.62	8.22[c]	8.22[c]	1.50

[a] 200 MHz, $CDCl_3$. – [b] Doublet, $J_{1,3} = 1.5$ Hz. – [c] Center of gravity.

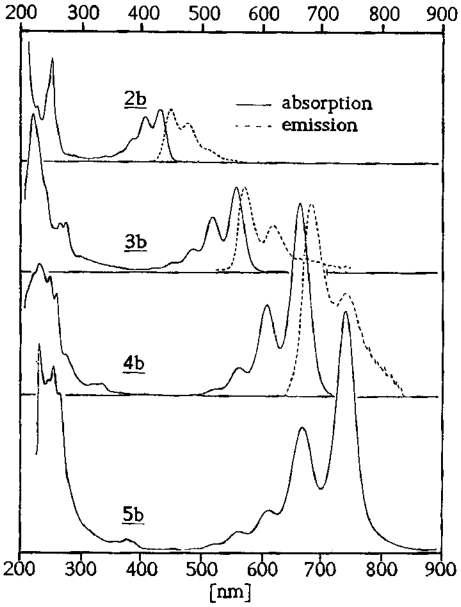

Figure 2. Absorption and fluorescence spectra of the oligorylenes **2b**, **3b**, **4b**, **5b** in 1,4-dioxane
2b: $\lambda_{exc} = 360$ nm. – **3b**: $\lambda_{exc} = 516$ nm. – **4b**: $\lambda_{exc} = 604$ nm.

Table 2. Selected spectroscopic data for compounds **2b**, **3b**, **4b** and **5b**

Compd.	Absorption [nm]			Fluorescence [nm][c]	
	λ_{max}	ε[l/mol·cm][a]	λ_{PPP} (f)[b]	λ_{max}	ϕ_F[d]
2b	439	(28000)	452 (0.91)	446	0.94
3b	560	(65000)	555 (1.54)	573	0.70
4b	660	(138000)	636 (2.19)	678	0.05
5b	748	(–)[e]	703 (2.71)	–	–

[a] Absorption spectra at room temperature in 1,4-dioxane. – [b] Calculated absorptions[29]; f: oscillator strength. – [c] Fluorescence spectra in degassed 1,4-dioxane at room temperature. – [d] Reference materials for fluorescence measurements: **2b**: perylene (**2a**); **3b**: rhodamine 101; **4b**: 3-diethylamino-7-diethyliminophenoxazonium perchlorate (oxazine 1). – [e] Certain determination prevented by low solubility.

ingly weak. The fluorescence quantum yields, Φ_F, amount to 0.94[30], 0.94[21], 0.70[31] and 0.05[31] for the compounds **2a**, **2b**, **3b** and **4b**. It is presently not clear, which mechanism (e.g. an internal-conversion or an intersystem-crossing process) is responsible for quenching of the fluorescence in **4b**.

5. Determination of the Energy Gap ΔE

Sublimation of the 3,3′-biperylenyl **25** as well as the homologous terrylene **3b**, quaterrylene **4b** and pentarylene **5b** onto glass plates in high vacuum leads to thin coatings, which are amorphous and transparent. The thickness of the films is in the range of 100–300 nm. In the case of the tetra-*tert*-butylperylene **2b** only microcrystallites are formed. Figure 3 shows the UV/Vis absorption spectra of the homologues after film formation. The peak positions of the longest wavelength bands undergo no drastic changes compared to those in solution (see Figures 2 and 3).

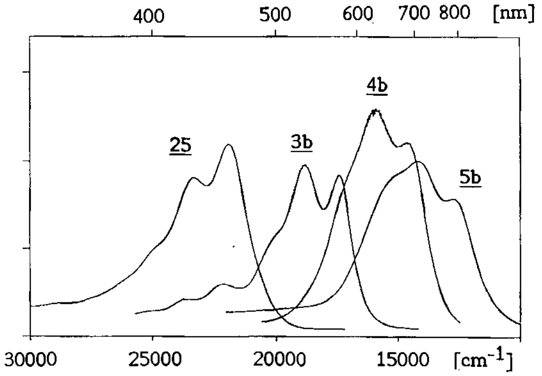

Figure 3. Absorption spectra of **25** and the oligorylenes **3b**, **4b**, **5b** evaporated onto glass plates

Table 3. HOMO-LUMO energy differences ΔE [eV][a] of **2b**, **3b**, **4b** and **5b**

Compd.	Color	Solution[b]	Film[c]
2b	yellow	2.67	–
3b	red	2.14	2.02
4b	blue	1.80	1.58
5b	blue-green	1.56	1.32
1[d]	–	0.98	0.92

[a] Based on the energy of the longest wavelength optical transition, determined at 1/10 of the maximum absorption. – [b] Absorption spectra at room temperature in 1,4-dioxane. – [c] Absorption spectra of the compounds evaporated onto glass plates. – [d] Value extrapolated by using the Padé approximation[34].

The energy gap ΔE of the oligorylenes, i.e. the energy difference between the HOMO and the LUMO, are determined from the UV/Vis/NIR spectra. The successive values in the series of the oligorylenes **2b**–**5b** allow an extrapolation to the value of the structurally related polymer PPN (**1**). The energy differences ΔE are determined at 1/10 of the maximum absorption of the longest wavelength optical transition[32,33] (see Table 3). By using the Padé approximation[34] an odd quantity of no less than 3 ΔE values of successive oligomers (**3b**, **4b** and **5b**) allows the extrapolation to the energy difference ΔE_∞ of the corresponding polymer **1**. Thus, the extrapolated values for ΔE_∞ amount to 0.98 eV in solution and 0.92 eV in the solid, noncrystalline state.

Conclusion

The new synthetic approach described in this paper allows the synthesis of soluble oligorylenes. The accessible homologous series ranges from the perylene derivative **2b** to the pentarylene **5b**. In addition, the intramolecular cyclization of the oligo(1,4-naphthylene)s yields perylene and terrylene chromophors. For instance, the previously unknown 3,3′-biperylenyl derivative **25** is now easily available. Symmetrically substituted biaryls such as **25** are interesting in view of their fluorescence behavior[35]; the 3,3′-biperylenyl is theoretically predicted as a potential "twisted intramolecular charge transfer" (TICT) chromophor[36]. The fluorescence study of **25** will be published separately[37].

The substitution of the oligomers with *tert*-butyl groups is a prerequisite for a series of other spectroscopic investigations. In contrast to unsubstituted quaterrylene (**4a**) prepared by Clar, the UV/Vis absorption spectra of all substituted oligorylenes **2b**–**5b** can be measured in common organic solvents at room temperature. The solubility is also sufficient for the EPR- and ENDOR-spectroscopic studies of the reduced paramagnetic species in the homologous series ranging from the perylene $\mathbf{2b}^{\cdot-}/M^{+}$ to the pentarylene radical anion $\mathbf{5b}^{\cdot-}/M^{+}$ [28].

Quite remarkable is the fact that films of the thermostable aromatic compounds can be easily prepared by evaporation. These films allow the characterization of the nonlinear optical properties of the title compounds[36].

Beyond the first member **2a** of the series of homologues of PPN (**1**), no studies of the physical properties have so far been available. Extrapolation of the properties determined for the compounds synthesized here can lead to estimates for PPN (**1**).

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Experimental

Thin layer chromatography (TLC): Ready-to-use silica gel 60 F_{254} plates (Merck). – Column chromatography: Silica gel or aluminium oxide with the eluents indicated. – Melting points (uncorrected): Reichert Thermovar polarization microscope. – IR: Nicolet 320 FT-IR. – UV/Vis: Perkin-Elmer Lambda 9. – Fluorescence spectra: Perkin-Elmer MPF 44A. – ^{1}H NMR: Bruker AM 300, 300 MHz. – ^{13}C NMR: Bruker AM 300. – MS: Varian MAT CH 7A.

1,4-Dibromonaphthalene (**18**) was commercially available, and 4,4′-dibromo-1,1′-binaphthyl (**19**) was prepared according to the procedure reported[39].

2,7-Di-tert-butylnaphthalene (**13**): To a mixture of naphtalene (200 g, 1.56 mol) and *tert*-butyl chloride (480 g, 5.19 mol) a small amount of aluminium chloride (300 mg) was added. A violent reaction with evolution of gaseous hydrogen chloride occurred. After ca. 30 min, the reaction mixture solidified. To complete the reaction, the mixture was heated on a water bath for further 3 h. After cooling, the mixture was kept at room temperature for 8 h. The solid mixture was dissolved in boiling ethanol (3.3 l), and thiourea (210 g, 2.76 mol) was added. After cooling, the precipitate was filtered and collected. After this separation, the filtrate contained the required 2,7 isomer **13**, whereas the 2,6 isomer **12** was included in the thiourea crystals. The filtrate was treated again, first with 210 g (2.76 mol) and then with 80 g (1.05 mol) of thiourea as described above. After removal of the solvent, the residue was digested with H_2O (300 ml) and extracted three times with $CHCl_3$ (in portions of 300 ml). The combined organic layers were dried with $MgSO_4$ and filtered. Evaporation of the solvent gave 133 g (36% based on naphthalene) of **13**; m.p. 103 °C (ref.[23] 103–104 °C). – IR (KBr): $\tilde{\nu}$ = 3064 cm^{-1}, 2990–2840, 1632, 1512, 1472, 1368, 1280, 1210, 904, 840, 632, 480. – ^1H NMR ($CDCl_3$): δ = 7.75 (br., 2H; 1-, 8-H), 7.73 (d, J = 8 Hz, 2H; 4-, 5-H), 7.52 (dd, J = 8 Hz, 2 Hz, 2H; 3-, 6-H), 1.41 [s, 18H; $C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): δ = 146.00, 130.92, 127.46, 124.56, 121.62, 120.49, 32.34 [$C(CH)_3$], 28.85 [$C(CH_3)$]. – MS (70 eV): m/z (%) = 240 (43) [M^+], 225 (100) [$M^+ - CH_3$], 57 (42) [$C(CH_3)_3^+$].

1-Bromo-3,6-di-tert-butylnaphthalene (**16**): Compound **13** (33.2 g, 0.14 mol) was dissolved in CCl_4 (400 ml), and a catalytic amount of iron filings (300 mg) was added. A solution of bromine (22.4 g, 0.14 mol) in CCl_4 (100 ml) was added at room temperature to the stirred solution by means of a dropping funnel during 1 h. During the reaction light was excluded. After stirring for 8 h, the reaction mixture was hydrolyzed with 300 ml of 0.5 M sodium hydroxide solution. The mixture was stirred for 1 h. Subsequently, the organic layer was separated, dried with $MgSO_4$ and filtered. Evaporation of the solvent and crystallization of the residue from methanol (200 ml) yielded 28.9 g (86%) of **16**; m.p. 58–60 °C. – IR (KBr): $\tilde{\nu}$ = 2990–2855 cm^{-1}, 1634, 1600, 1464, 1360, 1272, 1213, 973, 909, 880, 845, 816, 712, 624. – ^1H NMR ($CDCl_3$): δ = 8.13 (d, J = 8 Hz, 1H; 8-H), 7.84 (d, J = 2 Hz, 1H; 5-H), 7.77 (br., 2H; 2-, 4-H), 7.65 (dd, J = 8 Hz, 2 Hz, 1H; 7-H), 1.43 [s, 9H; $C(CH_3)_3$], 1.41 [s, 9H; $C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): δ = 149.53, 149.39, 134.60, 128.18, 126.52, 125.56, 123.41, 123.20, 34.91 [$C(CH)_3$], 34.82 [$C(CH)_3$], 31.27 [$C(CH_3)$], 31.24 [$C(CH_3)$]. – MS (70 eV): m/z (%) = 320 (20), 318 (20) [M^+], 305 (40), 303 (39) [$M^+ - CH_3$], 57 (100) [$C(CH_3)_3^+$].

$C_{18}H_{23}Br$ (319.3) Calcd. C 67.71 H 7.26 Br 25.03
Found C 67.63 H 7.25 Br 24.70

Preparation of the Boronic Acids. – General Procedure 1: The aryl bromides were dissolved in 250 ml of dry diethyl ether and cooled to −78 °C under nitrogen. Through a syringe, the specified amount of nBuLi solution (in hexane) was injected, the mixture was stirred for 1 h, and subsequently the cooling bath was removed. In a second reaction vessel a 2.8 fold molar amount (based on the aryl bromide) of triisopropoxyborane in 250 ml of dry diethyl ether was cooled to −78 °C under nitrogen. While stirring vigorously the previously prepared lithium organyl was added slowly (1 h) to the mixture by using a metal cannula. After complete addition, the mixture was stirred at low temperature for 1 h and further at room temperature for 8 h. The mixture was subsequently hydrolyzed with 300 ml of 2 M aqueous HCl solution for 30 min. After separation of the layers, the organic layer was dried with $MgSO_4$, filtered and the solvent evaporated. The residue was dissolved in 100 ml of low-boiling petroleum ether, 10 ml of H_2O was added, and the heterogeneous mixture was stirred at room temperature. After ca. 12 h, the product precipitated as fine colorless crystals. The product was filtered with suction, washed with a small amount of petroleum ether and dried in a vacuum desiccator (60 °C, 20 Torr).

3,6-Di-tert-butyl-1-(dihydroxyboryl)naphthalene (**17**): According to the general procedure 1, compound **16** (25 g, 78.3 mmol), 38 ml of butyllithium in hexane (2.5 M) and triisopropoxyborane (44.2 g, 235 mmol) afforded 16.9 g (59.5 mmol) of the colorless monoboronic acid **17** (76%); m.p. 270 °C. – IR (KBr): $\tilde{\nu}$ = 3630–3140 cm^{-1} (br.), 2986–2832, 1496, 1424–1312 (br.), 1277, 1184, 1104, 1056, 912, 848, 664. – ^1H NMR ([D_6]acetone): δ = 8.49 (d, J = 8 Hz, 1H; 7-H), 7.98 (d, J = 2 Hz, 1H), 7.85 (d, J = 2 Hz, 1H), 7.79 (d, J = 2 Hz, 1H), 7.56 (dd, J = 8 Hz, 2 Hz, 1H; 6-H), 1.50 [s, 18H; $C(CH_3)_3$]. – ^{13}C NMR ([D_6]acetone): δ = 205.97, 149.25, 149.11, 136.65, 133.22, 130.55, 128.97, 124.98, 123.89, 123.42, 35.48 [$C(CH)_3$], 35.44 [$C(CH)_3$], 31.39 [$C(CH_3)$]. – Elemental analysis was performed on the cyclic condensation product with ethylene glycol.

$C_{20}H_{27}BO_2$ (415.2) Calcd. C 77.41 H 8.78
Found C 77.68 H 9.03

Palladium-Catalyzed Boronic Acid Coupling Reaction. – General Procedure 2: All boronic acid coupling reactions were carried out under nitrogen and with the exclusion of light. The reaction mixture, consisting of the specified amount of the corresponding boronic acid, 3 mol-% of tetrakis(triphenylphosphine)palladium(0) and the aryl bromide, was suspended in the specified volume of toluene, then aqueous potassium carbonate solution was added. The heterogeneous mixture was refluxed with vigorous stirring for 3 d. After cooling and separation of the layers, the aqueous layer was extracted repeatedly with small portions of $CHCl_3$. The combined organic layers were dried with $MgSO_4$ and filtered, and the solvent was removed. The purification of the crude products is described in detail in the appropriate sections.

3,3′,6,6′-Tetra-tert-butyl-1,1′-binaphthyl (**6**): According to the general procedure 2, **17** (3.0 g, 10.6 mmol), **16** (3.7 g, 11.7 mmol), tetrakis(triphenylphosphine)palladium(0) (340 mg, 0.3 mmol), toluene (20 ml) and 2 M aqueous K_2CO_3 solution (10 ml) afforded the crude product **6**. Pure colorless **6** (3.6 g, 72%) was obtained after chromatography on silica gel (petroleum ether); m.p. 236–238 °C. – IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1}, 2990–2855, 1640, 1614, 1464, 1368, 1272, 1208, 896, 835, 640. – UV (cyclohexane): λ_{max} (lgε) = 293 nm (4.04). – ^1H NMR ($CDCl_3$): δ = 7.90 (br., 4H; 2-, 2′-, 4-, 4′-H), 7.58 (d, J = 2 Hz, 2H; 5-, 5′-H), 7.42 (d, J = 8 Hz, 2H; 8-, 8′-H), 7.36 (dd, J = 8 Hz, 2 Hz, 2H; 7-, 7′-H), 1.50 [s, 18H; $C(CH_3)_3$], 1.46 (s, 18H; *tert*-butyl-H). – ^{13}C NMR ($CDCl_3$): δ = 148.36, 147.95, 138.16, 133.61, 129.48, 126.36, 125.96, 124.13, 123.21, 122.76, 34.92 [$C(CH)_3$], 34.76 [$C(CH)_3$], 31.38 [$C(CH_3)$], 31.32 [$C(CH_3)$]. – MS (70 eV): m/z (%) = 478 (72) [M^+], 57 (100) [$C(CH_3)_3^+$].

$C_{36}H_{46}$ (478.8) Calcd. C 90.32 H 9.68
Found C 90.09 H 8.98

3,3″,6,6″-Tetra-tert-butyl-1,1′:4′,1″-ternaphthylene (**7**): According to the general procedure 2, **17** (3.0 g, 10.6 mmol), **18** (1.37 g, 4.8 mmol), tetrakis(triphenylphosphine)palladium(0) (340 mg, 0.3 mmol), toluene (20 ml) and 2 M aqueous K_2CO_3 solution (10 ml) afforded the crude product **7**. Pure **7** was obtained by precipitation: The residue was dissolved in $CHCl_3$, and **7** (2.67 g, 83%) was precipitated by adding ethanol to the solution. The purity of **7** could be monitored by TLC (petroleum ether). In solution **7** showed as strong blue fluorescence after irradation with UV light; m.p. 275–276 °C. – IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1}, 2990–2855, 1629, 1603, 1472, 1368, 1272, 1216, 960, 893, 829, 768, 648. – UV (cyclohexane): λ_{max} (lgε) = 300 nm (4.20). – ^1H NMR ($CDCl_3$): δ = 7.92–7.28 (m, 16H, arom. H), 1.50 [s, 9H; $C(CH_3)_3$], 1.49 [s, 9H; $C(CH_3)_3$], 1.42 [s, 9H, $C(CH_3)_3$], 1.41 [s, 9H; $C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): δ = 148.63, 148.59, 148.19, 138.90, 138.86, 138.00, 137.96, 133.76, 133.23, 129.69, 127.50, 127.46, 127.07, 126.53, 126.17, 126.10, 125.83, 125.75, 124.44, 124.34, 123.37, 123.12, 35.06 [$C(CH)_3$], 34.88

[*C*(CH)$_3$], 31.51 [C(*C*H$_3$)], 31.41 [C(*C*H$_3$)]. – MS (70 eV): *m/z* (%) = 604 (100) [M$^+$], 589 (16) [M$^+$ − CH$_3$], 57 (79) [C(CH$_3$)$_3^+$].

$C_{46}H_{52}$ (604.4) Calcd. C 91.34 H 8.66
Found C 91.44 H 8.68

4-Bromo-3′,6′-di-tert-butyl-1,1′-binaphthyl (**20**): According to the general procedure 2, **17** (6.0 g, 21.1 mmol), **18** (9.1 g, 31.7 mmol), tetrakis(triphenylphosphine)palladium(0) (480 mg, 0.4 mmol), toluene (80 ml) and 2 M aqueous K_2CO_3 solution (50 ml) afforded the crude product **20**. Pure **20** (5.7 g, 61%) was obtained after column chromatography on silica gel (petroleum ether) and subsequent recrystallization (ethanol). The purity of **20** could be monitored by TLC (petroleum ether); m.p. 168−171 °C. – IR (KBr): $\tilde{\nu}$ = 3072 cm^{-1}, 3008−1248, 1632, 1608, 1512, 1472, 1376, 1256, 1208, 1128, 1032, 968, 944, 912, 888, 832, 768, 672, 640, 496. – ^{1}H NMR (CDCl$_3$): δ = 8.40 (d, *J* = 8 Hz, 1 H, arom. H), 7.89−7.99 (m, 3 H, arom. H), 7.21−7.67 (m, 7 H, arom. H), 1.49 [s, 9 H; C(CH$_3$)$_3$], 1.41 [s, 9 H; C(CH$_3$)$_3$]. – ^{13}C NMR (CDCl$_3$): δ = 148.05, 139.29, 136.74, 134.28, 133.56, 132.03, 129.46, 129.20, 128.17, 127.33, 127.17, 126.66, 126.26, 125.61, 124.40, 123.28, 122.40, 34.89 [*C*(CH)$_3$], 34.76 [*C*(CH)$_3$], 31.32 [C(*C*H$_3$)], 31.25 [C(*C*H$_3$)]. – MS (70 eV): *m/z* (%) = 448 (23), 446 (23) [M$^+$], 433 (6), 431 (6) [M$^+$ − CH$_3$], 57 (100) [C(CH$_3$)$_3^+$].

$C_{28}H_{29}Br$ (445.4) Calcd. C 75.50 H 6.56 Br 17.94
Found C 75.46 H 6.61 Br 18.14

3′,6′-Di-tert-butyl-4-(dihydroxyboryl)-1,1′-binaphthyl (**22**): According to the general procedure 1, **20** (5.0 g, 11.2 mmol), 2 M butyllithium in hexane (6.2 ml) and triisopropoxyborane (5.8 g, 30.9 mmol) afforded 2.4 g (51%) of the colorless monoboronic acid **22**. In the rare cases, where the product did not precipitate, a column chromatography was necessary. For this purpose the nonpolar byproducts were first eluted from silica gel by using petroleum ether as eluent. The product **22** was isolated by choosing a mixture of petroleum ether/acetic ester (1:1, v/v); m.p. 211−213 °C. – IR (KBr): $\tilde{\nu}$ = 3660−3140 cm^{-1} (br.), 3064, 2992−2860, 1632, 1592, 1520, 1472, 1440−1305 (br.), 1267, 1216, 896, 840, 768. – ^{1}H NMR ([D$_6$]acetone): δ = 8.75 (d, *J* = 7 Hz, 1 H, arom. H), 8.03 (d, *J* = 7 Hz, 1 H, arom. H), 7.95 (br. 1 H, arom. H), 7.63 [s, 2 H; B(OH)$_2$], 7.15−7.55 (m, 7 H, arom. H), 1.44 [s, 9 H; C(CH$_3$)$_3$], 1.39 [s, 9 H; C(CH$_3$)$_3$].

3,3‴,6,6‴-Tetra-tert-butyl-1,1′:4′,1″:4″,1‴-quaternaphthylene (**8**): According to the general procedure 2, **17** (3.0 g, 10.6 mmol), **19** (1.98 g, 4.8 mmol), tetrakis(triphenylphosphine)palladium(0) (340 mg, 0.3 mmol), toluene (20 ml) and 2 M aqueous K_2CO_3 solution (10 ml) afforded the crude product **8**. The residue was chromatographed on silica gel by starting with cyclohexane as eluent to which CHCl$_3$ was gradually added [cyclohexane/CHCl$_3$ (5:1, v/v)]. The purity of **8** could be monitored by TLC (petroleum ether). After evaporation of the solvent, compound **8** (2.9 g, 74%) was obtained; m.p. 236−238 °C. – IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1}, 2990 to 2855, 1629, 1603, 1472, 1368, 1272, 1216, 960, 893, 829, 768, 648. – UV (cyclohexane): λ_{max} (lg ε) = 302 nm (4.46). – ^{1}H NMR (CDCl$_3$): δ = 7.30−8.00 (m, 22 H; arom. H), 1.56 [s, 9 H; C(CH$_3$)$_3$], 1.54 [s, 9 H; C(CH$_3$)$_3$], 1.48 [s, 9 H; C(CH$_3$)$_3$], 1.47 [s, 9 H; C(CH$_3$)$_3$]. – ^{13}C NMR (CDCl$_3$): δ = 148.62, 148.22, 148.20, 139.13, 138.46, 138.40, 137.91, 133.75, 133.25, 129.66, 127.56, 127.12, 126.53, 126.11, 125.93, 124.50, 124.40, 123.37, 123.17, 35.08 [*C*(CH)$_3$], 34.88 [*C*(CH)$_3$], 31.52 [C(*C*H$_3$)], 31.41 [C(*C*H$_3$)]. – MS (70 eV): *m/z* (%) = 730 (75) [M$^+$], 715 (9) [M$^+$ − CH$_3$], 350 (29) [M^{2+} − 2 CH$_3$], 57 (100) [C(CH$_3$)$_3^+$].

$C_{56}H_{58}$ (731.1) Calcd. C 92.00 H 8.00
Found C 92.04 H 7.92

4-Bromo-3″,6″-di-tert-butyl-1,1′:4′,1″-ternaphthylene (**21**): According to the general procedure 2, **17** (3.0 g, 10.6 mmol), **19** (6.5 g, 15.8 mmol), tetrakis(triphenylphosphine)palladium(0) (340 mg, 0.3 mmol), toluene (40 ml) and 2 M aqueous K_2CO_3 solution (30 ml) afforded the crude product **21**. The residue was chromatographed on silica gel by using petroleum ether/CHCl$_3$ (5:1, v/v) as eluent. After evaporation of the solvent and subsequent recrystallization of the residue from ethanol, compound **21** (3.5 g, 58%) was obtained; m.p. 176−178 °C. – IR (KBr): $\tilde{\nu}$ = 3072 cm^{-1}, 3000−2840, 1624, 1512, 1464, 1368, 1256, 1200, 960, 944, 928, 888, 824, 752, 640. – ^{1}H NMR (CDCl$_3$): δ = 8.40 (d, *J* = 8 Hz, 2 H, arom. H), 7.96−8.02 (m, 6 H, arom. H), 7.24−7.69 (m, 26 H, arom. H), 1.50 [s, 9 H; C(CH$_3$)$_3$], 1.49 [s, 9 H; C(CH$_3$)$_3$], 1.43 [s, 9 H; C(CH$_3$)$_3$], 1.42 [s, 9 H; C(CH$_3$)$_3$]. – MS (70 eV): *m/z* (%) = 572 (27), 570 (25) [M$^+$], 557 (6), 555 (6) [M$^+$ − CH$_3$], 365 (9) [M$^+$ − C$_{10}$H$_6$Br], 57 (100) [C(CH$_3$)$_3^+$].

$C_{38}H_{35}Br$ (571.6) Calcd. C 79.85 H 6.17 Br 13.98
Found C 80.40 H 6.55 Br 12.02

3″,6″-Di-tert-butyl-4-(dihydroxyboryl)-1,1′:4′,1″-ternaphthylene (**23**): In contrast to the usual preparation of the boronic acids (see general procedure 1), THF was used as solvent, and *tert*-butyllithium was employed instead of *n*-butyllithium. According to the general procedure 1, **21** (3.0 g, 5.2 mmol) in THF (100 ml), 1.6 M *tert*-butyllithium in hexane (12 ml) and triisopropoxyborane (4.8 g, 25.6 mmol) in THF (100 ml) afforded 1.8 g (65%) of the colorless monoboronic acid **23**; m.p. 239−245 °C. – IR (KBr): $\tilde{\nu}$ = 3660−3140 cm^{-1} (br.), 3064, 2992−2860, 1632, 1512, 1464−1280 (br.), 1256, 1216, 1136−936 (br.), 760. – ^{1}H NMR (CDCl$_3$): δ = 8.12−7.38 [m, 38 H; arom. H and B(OH)$_2$], 1.50 [s, 9 H; C(CH$_3$)$_3$], 1.49 [s, 9 H; C(CH$_3$)$_3$], 1.42 [s, 9 H; C(CH$_3$)$_3$], 1.41 [s, 9 H; C(CH$_3$)$_3$].

3,3′′′′,6,6′′′′-Tetra-tert-butyl-1,1′:4′,1″:4″,1‴:4‴,1′′′′-quinquenaphthylene (**9**): According to the general procedure 2, **22** (1.21 g, 2.95 mmol), **21** (1.60 g, 2.8 mmol), tetrakis(triphenylphosphine)palladium(0) (70 mg, 0.06 mmol), toluene (50 ml) and 2 M aqueous K_2CO_3 solution (20 ml) afforded the crude product **9**. The residue was chromatographed on silica gel by starting with cyclohexane as eluent to which CHCl$_3$ was gradually added [cyclohexane/CHCl$_3$ (5:1, v/v)]. The purity of **9** could be monitored by TLC (petroleum ether). After evaporation of the solvent, compound **9** (2.1 g, 60%) was obtained; m.p. 246−248 °C. – IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1}, 2990−2855, 1629, 1603, 1472, 1368, 1272, 1216, 960, 893, 829, 768, 648. – UV (cyclohexane): λ_{max} (lg ε) = 305 nm (4.46). – ^{1}H NMR (CDCl$_3$): δ = 7.93−7.28 (m, 28 H, arom. H), 1.50 [s, 9 H; C(CH$_3$)$_3$], 1.48 [s, 9 H; C(CH$_3$)$_3$], 1.43 [s, 9 H; C(CH$_3$)$_3$], 1.42 [s, 9 H; C(CH$_3$)$_3$]. – ^{13}C NMR (CDCl$_3$): δ = 148.59, 148.19, 139.07, 138.60, 138.30, 138.24, 137.77, 133.58, 133.12, 129.52, 127.60, 127.11, 126.54, 126.01, 124.51, 124.42, 123.29, 123.10, 35.05 [*C*(CH)$_3$], 34.86 [*C*(CH)$_3$], 31.45 [C(*C*H$_3$)], 31.35 [C(*C*H$_3$)]. – MS (70 eV): *m/z* (%) = 856.5 (100) [M$^+$], 428 (10) [M^{2+}], 57 (100) [C(CH$_3$)$_3^+$].

$C_{66}H_{64}$ (857.2) Calcd. C 92.47 H 7.53
Found C 92.24 H 7.62

3,3′′′′′,6,6′′′′′-Tetra-tert-butyl-1,1′:4′,1″:4″,1‴:4‴,1′′′′:4′′′′,1′′′′′-sexinaphthylene (**10**): According to the general procedure 2, **23** (1.58 g, 2.95 mmol), **21** (1.60 g, 2.80 mmol) tetrakis(triphenylphosphine)palladium(0) (70 mg, 0.06 mmol), toluene (50 ml) 2 M aqueous K_2CO_3 solution (20 ml) afforded the crude product **10**. The residue was chromatographed on silica gel by starting with cyclohexane as eluent to which CHCl$_3$ was gradually added [cyclohexane/CHCl$_3$ (5:1, v/v)]. The purity of **10** could be monitored by TLC (petroleum ether). After evaporation of the solvent, the colorless compound **10** (1.51 g, 55%) was obtained; m.p. 267−271 °C. – IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1}, 2990−2855, 1629, 1603, 1472, 1368, 1272, 1216, 960, 893, 829, 768, 648. — UV (cyclohexane): λ_{max} (lg ε) = 306 nm (4.69). — ^{1}H NMR (CDCl$_3$): δ = 7.93–7.28 (m, 34H, arom. H), 1.50 [s, 9H; C(CH$_3$)$_3$], 1.48 [s, 9H; C(CH$_3$)$_3$], 1.43 [s, 9H; C(CH$_3$)$_3$], 1.42 [s, 9H; C(CH$_3$)$_3$]. — MS (70 eV): *m/z* (%) = 982.6 (41) [M$^+$], 745 (100) [M$^+$ − C$_{18}$H$_{23}$], 57 (35) [C(CH$_3$)$_3^+$].

$C_{76}H_{70}$ (983.4) Calcd. C 92.83 H 7.17
Found C 92.86 H 6.99

Anionic Cyclizations. — General Procedure 3: All preparations were carried out under purified argon and with rigorous exclusion of moisture. The oligo(1,4-naphthylene)s were dissolved in dry 1,2-dimethoxyethane in each case. The use of a Schlenk reaction flask allowed us to work under a stream of argon. The potassium, which was separated from its oxide layer and shredded into small pieces, was added. The solutions were degassed by repeated freeze-and-thaw cycles under vacuum (10^{-3} Torr). The flask was sealed off so that the reaction could occur under vacuum. The mixture was stirred at room temperature for 7 d. The degree of reduction could be monitored by the color of the mixture. At the beginning, a green color appeared after several hours (formation of radical monoanions). After some hours, a change to a red color indicated the formation of dianions. At the end of the reaction, the mixture showed a purple or a blue color caused by perylene or terrylene dianion units, respectively. The remaining potassium, which conglomerated to one piece, was removed under argon, and freshly sublimed cadmium chloride was added. Subsequently, the mixture was stirred for 1 d. After filtration, the solid was washed with CHCl$_3$. The collected organic solutions were concentrated, and the residue was chromatographed on aluminium oxide.

2,5,8,11-Tetra-tert-butylperylene (**2b**): According to the general procedure 3, **6** (2.0 g, 4.18 mmol), potassium (1.8 g, 46 mmol), DME (150 ml) and CdCl$_2$ (2.5 g) afforded the crude product **2b**. Pure **2b** (1.1 g, 55%) was obtained after column chromatography (petroleum ether); m.p. 336–338°C (ref.$^{21)}$ 340°C). — IR (KBr): ṽ = 3064 cm^{-1}, 3000–2832, 1616, 1600, 1491, 1469, 1408, 1368, 1264, 1208, 976, 912, 896, 880, 816, 784, 640. — UV (cyclohexane): λ_{max} (lgε) = 436 nm (4.42), 411 (4.36), 258 (4.70), 234 (4.44), 215 (4.77). — ^{1}H NMR (CDCl$_3$): δ = 8.27 (d, *J* = 2 Hz, 4H; 1-, 6-, 7-, 12-H), 7.65 (d, *J* = 2 Hz, 4H; 3-, 4-, 9-, 10-H), 1.48 [s, 36H; C(CH$_3$)$_3$]. — ^{13}C NMR (CDCl$_3$): δ = 148.7, 134.8, 130.7, 125.8 (C-1, -6, -7, -12), 123.2, 117.6 (C-2, -5, -8, -11), 34.9 [*C*(CH)$_3$], 31.3 [C(*C*H$_3$)]. — MS (70 eV): *m/z* (%) = 476 (82) [M$^+$], 153 (100).

2,3′,5,6′-Tetra-tert-butyl-9-(1′-naphthyl)perylene (**24**): According to the general procedure 3, **7** (2.3 g, 3.8 mmol), potassium (1.8 g, 46 mmol), DME (150 ml) and CdCl$_2$ (2.5 g) afforded the crude product **24** besides the reddish terrylene derivative **3b**. Pure **24** (960 mg, 42%) was obtained after column chromatography (petroleum ether). — IR (KBr): ṽ = 3064 cm^{-1}, 3000–2832, 1624, 1600, 1480, 1376, 1264, 880, 840, 768. — UV (cyclohexane): λ_{max} (lgε) = 444 nm (4.54), 418 (4.46), 397 (4.15), 352 (3.30), 326 (3.38), 258 (4.62), 229 (5.05), 205 (5.03). — ^{1}H NMR (CDCl$_3$): δ = 8.35–8.20 (m, 4H; 1-, 6-, 7-, 12-H), 7.85 (br., 2H; 2′-, 4′-H), 7.66 (s, 2H; 3-, 4-H), 7.56 (d, *J* = 2 Hz, 1H; 5′-H), 7.50 (d, *J* = 7 Hz, 1H; 8-H), 7.40 (d, *J* = 8 Hz, 1H; 8′-H), 7.34 (dd, *J* = 8 Hz, 2 Hz, 1H; 7′-H), 7.32–7.28 (m, 2H; 10-, 11-H), 1.51 [s, 9H; C(CH$_3$)$_3$], 1.50 [s, 9H; C(CH$_3$)$_3$], 1.47 [s, 9H; C(CH$_3$)], 1.40 [s, 9H; C(CH$_3$)$_3$]. — MS (70 eV): *m/z* (%) = 602 (100) [M$^+$], 57 (61) [C(CH$_3$)$_3^+$].

$C_{46}H_{50}$ (602.9) Calcd. C 91.64 H 8.36
Found C 91.45 H 8.18

Gradual addition of CHCl$_3$ to the eluent resulting in a mixture petroleum ether/CHCl$_3$ (5:1, v/v) yielded 550 mg (24%) of *2,5,10,13-tetra-tert-butylterrylene* (**3b**). In solution **3b** shows a remarkably strong reddish fluorescence.

8,8′,11,11′-Tetra-tert-butyl-3,3′-biperylenyl (**25**): According to the general procedure 3, **8** (2.3 g, 3.1 mmol), potassium (1.8 g, 46 mmol), DME (150 ml) and CdCl$_2$ (2.5 g) afforded the crude product **25**. Upon chromatography [cyclohexane/CHCl$_3$ (1:0 to 5:1, v/v)] the following fractions were obtained: the nonseparable binaphthylperylenes (290 mg), pure **25** (1.1 g, 48%) and the naphthylterrylene derivative **26**. — **25**: M.p. 252–255°C (dec.). — IR (KBr): ṽ = 3064 cm^{-1}, 3000–2832, 1632, 1600, 1488, 1472, 1376, 1256, 872, 837, 768. — UV (cyclohexane): λ_{max} (lg ε) = 451 nm (4.90), 425 (4.66), 332 (3.40), 317 (3.31), 315 (3.32), 258 (4.83), 208 (5.21). — ^{1}H NMR (CDCl$_3$): δ = 8.40–8.20 (m, 8H; 1-, 1′-, 6-, 6′-, 7-, 7′-, 12-, 12′-H), 7.67 (br., 4H; 3-, 3′-, 4-, 4′-H), 7.55 (d, *J* = 7 Hz, 2H; 8-, 8′-H), 7.34 (m, 4H; 10-, 10′-, 11-, 11′-H), 1.51 [s, 18H; C(CH$_3$)$_3$], 1.49 [s, 18H; C(CH$_3$)$_3$]. — ^{13}C NMR (CDCl$_3$): δ = 149.18, 138.13, 134.84, 134.31, 131.86, 131.51, 130.63, 130.49, 129.37, 128.46, 126.49, 126.39, 125.39, 123.55, 120.01, 119.60, 118.51, 118.32, 34.98 [*C*(CH)$_3$], 31.36 [C(*C*H$_3$)]. — MS (70 eV): *m/z* (%) = 726 (100) [M$^+$], 57 (12) [C(CH$_3$)$_3^+$].

$C_{56}H_{54}$ (727.0) Calcd. C 92.51 H 7.49
Found C 92.04 H 7.92

2,3′,5,6′-Tetra-tert-butyl-11-(1′-naphthyl)terrylene (**26**): The reddish byproduct **26**, which showed the typical terrylene fluorescence in solution, was additionally recrystallized from ethanol. This procedure afforded **26** (114 mg, 5%); m.p. 250–252°C. — UV (cyclohexane): λ_{max} (lgε) = 564 nm (4.72), 523 (4.48), 277 (4.48), 268 (4.47), 204 (4.96). — ^{1}H-NMR (CDCl$_3$): δ = 8.35–8.18 (m, 8H; 1-, 6-, 7-, 8-, 9-, 14-, 15-, 16-H), 7.85 (br., 2H; 2′-, 4′-H), 7.68 (s, 2H; 3-, 4-H), 7.56 (d, *J* = 2 Hz, 1H, 5′-H), 7.52 (d, *J* = 7 Hz, 1H; 10-H), 7.42 (d, *J* = 8 Hz, 1H; 8′-H), 7.36 (dd, *J* = 8 Hz, 2 Hz, 1H; 7′-H), 7.34–7.30 (m, 2H; 12-, 13-H), 1.50 [s, 18H; C(CH$_3$)$_3$], 1.47 [s, 9H; C(CH$_3$)$_3$], 1.40 [s, 9H; C(CH$_3$)$_3$]. — MS (70 eV): *m/z* (%) = 726 (14) [M$^+$], 121 (100), 57 (68) [C(CH$_3$)$_3^+$].

$C_{56}H_{54}$ (727.0) Calcd. C 92.51 H 7.49
Found C 91.24 H 7.63

3″,6″,8,11-Tetra-tert-butyl-10′-(1″-naphthyl)-3,3′-biperylenyl (**27**): According to the general procedure 3, **9** (1.8 g, 2.1 mmol), potassium (2.0 g, 51 mmol), DME (150 ml) and CdCl$_2$ (2.5 g) afforded the crude product **27**. Upon chromatography [cyclohexane/CHCl$_3$ (1:0 to 5:1, v/v)] the following fractions were obtained: yellow, nonseparable ternaphthylperylenes, the 10′-(1″-naphthyl)-3,3′-biperylenyl derivative **27** and the tetra-*tert*-butyl-11-(9′-perylenyl)terrylene derivative **28**. The main products **27** and **28** were separated by repeated column chromatography [cyclohexane/CHCl$_3$ (5:1, v/v)]. This procedure afforded pure **27** (0.9 g, 52%); m.p. 312–316°C. — IR (KBr): ṽ = 3064 cm^{-1}, 3000–2832, 1624, 1600, 1488, 1464, 1376, 1256, 1200, 896, 880, 840, 816, 768. — UV (cyclohexane): λ_{max} (lg ε) = 456 nm (4.93), 430 (4.68), 336 (3.37), 330 (3.37), 258 (4.81), 229 (5.09), 221 (5.13), 208 (5.18). — ^{1}H NMR (CDCl$_3$): δ = 8.42 to 8.18 (m, 8H; 1-, 1′-, 6-, 6′-, 7-, 7′-, 12-, 12′-H), 7.87 (br., 2H; 2″-, 4″-H), 7.68 (br., 2H; 3-, 4-H), 7.62–7.52 (m, 4H; 2′-, 5″-, 11-, 11′-H), 7.47–7.27 (m, 8H; 4′-, 5′-, 7″-, 8-, 8′-, 8″-, 9-, 9′-H), 1.52 [s, 9H; C(CH$_3$)$_3$], 1.50 [s, 9H; C(CH$_3$)$_3$], 1.48 [s, 9H; C(CH$_3$)$_3$], 1.43 und 1.40 [s, 9H; C(CH$_3$)$_3$]. — MS (70 eV): *m/z* (%) = 852.5 (17) [M$^+$], 121 (100), 57 (76) [C(CH$_3$)$_3^+$].

$C_{66}H_{60}$ (853.2) Calcd. C 92.91 H 7.09
Found C 92.94 H 7.17

2,2′,5,5′-Tetra-tert-butyl-11-(9′-perylenyl)terrylene (**28**): The separation described above und subsequent recrystallization from ethanol afforded the perylenylterrylene derivative **28** (0.5 g, 29%) showing a red fluorescence in solution; m.p. >300°C (dec.). — IR (KBr): ṽ = 3064 cm^{-1}, 3000–2832, 1632, 1600, 1472, 1376, 1256, 896, 880, 840, 808, 768. — UV (cyclohexane): λ_{max} (lgε) = 566 nm

(4.83), 524 (4.63), 488 (4.27), 447 (4.39), 419 (4.29), 342 (3.71), 276 (4.56), 257 (4.73), 228 (5.10). – ^1H NMR ($CDCl_3$): δ = 8.39–8.15 (m, 12H; 1-, 1′-, 6-, 6′-, 7-, 7′-, 8-, 9-, 12′-, 14-, 15-, 16-H), 7.67 (br., 4H; 3-, 3′-, 4-, 4′-H), 7.58–7.51 (m, 2H; 8′-, 10-H), 7.41–7.28 (m, 4H; 10′-, 11′-, 12-, 13-H), 1.52 [s, 27H; $C(CH_3)_3$], 1.49 [s, 9H; $C(CH_3)_3$]. – MS (70 eV): *m/z* (%) = 850.5 (14) [M^+], 57 (100) [$C(CH_3)_3^+$].

$C_{66}H_{58}$ (851.2) Calcd. C 93.13 H 6.87
Found C 92.45 H 7.18

2,5,10,13-Tetra-tert-butylterrylene (**3b**): **24** (600 mg, 1.0 mmol), anhydrous $AlCl_3$ (600 mg) and anhydrous $CuCl_2$ (600 mg) in CS_2 (70 ml) were stirred under nitrogen at room temperature for 8 h. At the end of the reaction a dark black-green insoluble precipitate was formed. After decanting the solvent, the solid was hydrolyzed with ice and dilute aqueous ammonia solution. The suspension was extracted repeatedly with small portions of $CHCl_3$ (30 ml) until the organic layer no longer showed a red color caused by the product **3b**. After drying with $MgSO_4$, the combined organic layers were filtered, and the solvent was evaporated.

The residue was dissolved in $CHCl_3$ (20 ml), and aluminium oxide (5 g) was added. Evaporation of the solvent provided aluminium oxide coated with product, which was subjected to column chromatography on aluminium oxide (cyclohexane). By using cyclohexane as eluent only the byproducts (perylene chromophores) were eluted. The terrylene **3b** was recovered from the column packing (dried under nitrogen) by multiple extraction with refluxing $CHCl_3$. After evaporation of the solvent, the residue was recrystallized from ethanol to afford pure **3b** (250 mg, 42%); m.p. 369–370°C. – IR (KBr): ṽ = 3064 cm^{-1}, 3000–2832, 1624, 1600, 1488, 1472, 1376, 1264, 928, 872, 832, 712. – UV (cyclohexane): λ_{max} (lg ε) = 557 nm (4.83), 517 (4.61), 482 (4.19), 448 (3.87), 277 (4.64), 226 (5.07), 203 (4.95). – ^1H NMR ($CDCl_3$): δ = 8.28 (s, 4H; 7-, 8-, 15-, 16-H), 8.26 (d, *J* = 2 Hz, 4H; 1-, 6-, 9-, 14-H), 7.64 (d, *J* = 2 Hz, 4H; 3-, 4-, 11-, 12-H), 1.50 [s, 36H; $C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): δ = 149.22, 134.83, 130.81, 130.59, 125.07, 123.37, 120.83, 118.10, 34.96 [$C(CH)_3$], 31.35 [$C(CH_3)$]. – MS (70 eV): *m/z* (%) = 600 (18) [M^+], 208 (84), 127 (100), 57 (10) [$C(CH_3)_3^+$].

$C_{46}H_{48}$ (600.9) Calcd. C 91.95 H 8.05
Found C 91.63 H 7.35

2,5,12,15-Tetra-tert-butylquaterrylene (**4b**): **25** (500 mg, 0.69 mmol), anhydrous $AlCl_3$ (500 mg) and anhydrous $CuCl_2$ (500 mg) in CS_2 (80 ml) were stirred under nitrogen at room temperature for 8 h. At the end of the reaction a dark black-green insoluble precipitate was formed. After decanting the solvent from the precipitate, the residue was hydrolyzed with ice and diluted aqueous ammonia solution. The suspension was extracted repeatedly with small portions of chlorobenzene (30 ml) until the organic layer failed to show a blue color caused by the product **4b**. After drying with $MgSO_4$, the combined organic phases were filtered, and the solvent was evaporated. The residue was suspended in 60 ml of $CHCl_3$, and aluminium oxide (5 g) was added. Evaporation of the solvent provided aluminium oxide coated with product, which was subjected to column chromatography on aluminium oxide [cyclohexane/$CHCl_3$ (5:1, v/v)]. By using this mixture as eluent only the byproducts (perylene chromophores) were eluted. The quaterrylene **4b** was recovered from the column packing (dried under nitrogen) by multiple extraction with refluxing $CHCl_3$. After reducing the solvent volume, the formed precipitate was filtered off to afford **4b** (240 mg, 48%). The dark blue solid shows a reddish shiny luster. In solution no fluorescence of **4b** was noticeable; m.p. 520–530°C. – IR (KBr): ṽ = 3064 cm^{-1}, 3000–2832, 1624, 1600, 1592, 1475, 1432, 1368, 1259, 1208, 1000, 960, 893, 872, 832, 800, 672. – UV (dioxane): λ_{max} (lg ε) = 660 nm (5.14), 604 (4.81), 558 (4.32), 334 (3.98), 322 (3.95), 235 (4.97). – ^1H NMR ($CDCl_3$): δ = 8.22 (br., 12H; arom. H), 7.62 (d, *J* = 2 Hz; 4H; 3-, 4-, 13-, 14-H), 1.50 [s, 36H; $C(CH_3)_3$]. – MS (70 eV): *m/z* (%) = 724 (14) [M^+], 390 (18), 376 (100), 57 (9) [$C(CH_3)_3^+$].

$C_{56}H_{52}$ (725.03) Calcd. C 92.77 H 7.23
Found C 92.18 H 8.23

2,5,14,17-Tetra-tert-butylpentarylene (**5b**): **28** (400 mg, 0.47 mmol), anhydrous $AlCl_3$ (400 mg) and anhydrous $CuCl_2$ (400 mg) in 1,2,4-trichlorobenzene (50 ml) were stirred under nitrogen at room temperature for 8 h. At the end of the reaction, a dark black-green insoluble precipitate was formed. After reducing the solvent volume under vacuum, the remaining liquor was diluted with ether and the precipitate filtered off. The solid was subsequently hydrolyzed with ice and dilute aqueous ammonia solution. The residue was suspended in $CHCl_3$ (100 ml), and aluminium oxide (5 g) was added. Evaporation of the solvent provided aluminium oxide coated with product, which was subjected to column chromatography on aluminium oxide [cyclohexane/$CHCl_3$ (1:1, v/v)] under nitrogen and with the exclusion of light. By using this mixture as eluent only the byproducts (perylene and terrylene chromophores) were eluted. The green-blue pentarylene **5b** was recovered from the column packing (dried under nitrogen) by multiple extraction with refluxing chlorobenzene. After reducing the solvent volume, the formed precipitate was filtered off to afford **5b** (240 mg, 60%). The dark green solid showed a reddish shiny luster. In solution no fluorescence of **5b** was noticeable; m.p. >540°C. – IR (KBr): ṽ = 3064 cm^{-1}, 3000–2832, 1624, 1600, 1480, 1376, 1256, 1112, 888, 835, 806, 656. – UV ($CHCl_3$): λ_{max} (lgε) = 748 nm (5.0), 676 (4.7), 618 (4.3), 377 (3.7), 359 (3.6), 268 (4.8), 258 (4.9), 234 (5.0). – MS (70 eV): *m/z* (%) = 848.5 (2.5) [M^+], 57 (7) [$C(CH_3)_3^+$].

CAS Registry Numbers

2b: 80663-92-9 / **2b**$^{2-}$ · 2 K^+: 126847-80-1 / **3b**: 126822-83-1 / **3b**$^{2-}$ · 2 K^+: 126847-82-3 / **4b**: 126822-84-2 / **5b**: 133816-33-8 / **6**: 126822-81-9 / 7: 126822-82-0 / **8**: 126847-92-5 / **9**: 133832-35-6 / **10**: 133816-34-9 / **12**: 3905-64-4 / **13**: 10275-58-8 / **16**: 10239-76-6 / **17**: 126822-80-8 / **18**: 83-53-4 / **19**: 49610-35-7 / **20**: 133816-35-0 / **21**: 133816-36-1 / **22**: 133832-36-7 / **23**: 133816-37-2 / **24**: 126822-85-3 / **25**: 126822-86-4 / **26**: 126822-87-5 / **27**: 133816-38-3 / **28**: 133816-39-4 / naphthalene: 91-20-3 / *tert*-butyl chloride: 507-20-0 / triisopropoxyborane: 5419-55-6 / tetrakis(triphenylphosphine)palladium(0): 14221-01-3

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