Novel Perylene Chromophores Obtained by a Facile Oxidative Cyclodehydrogenation Route

Mike Wehmeier, Manfred Wagner, and Klaus Müllen*[a]

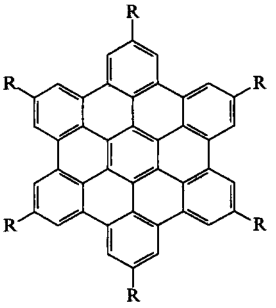
Abstract: New perylene chromophores, phenyl-substituted diindeno[1,2,3-cd:1′,2′,3′-lm]perylenes **5a**,**b** and 4,4′,7,7′-tetraphenyldiacenaphtho[1,2-k:1′,2′,k′]diindeno[1,2,3-cd:1′,2′,3′-me]perylenes **22a,b**, have been synthesized from substituted fluoranthene derivatives **3a**,**b** and **4a**,**b** by means of a surprisingly simple oxidative cyclodehydrogenation reaction. The resulting chromophores, when substituted with alkyl chains at the periphery, show good solubility in organic solvents, and a full characterization of the novel red, green, and blue dyes by field-desorption mass spectrometry, UV/Vis and ^{1}H and ^{13}C NMR spectroscopy becomes possible.

Keywords: chromophores · dehydrogenation · dyes/pigments

Introduction

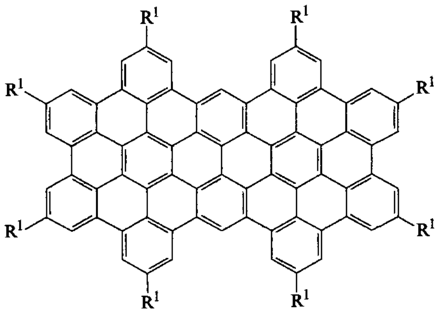
Since the discovery of fullerenes, polycyclic aromatic hydrocarbons (PAHs) have regained considerable interest. From a synthetic point of view, it is challenging to create fullerene subunits[1, 2] and to produce larger and more complex PAHs.[3–5] Furthermore, investigations are stimulated by the useful properties of PAHs in optoelectronics[6] and dyestuff chemistry.[7] Recently, our group established a two-step method to extended polycyclic aromatic hydrocarbons such as **1** and **2**. The synthetic approach for **1** and **2** involves the construction of soluble polyphenylene precursors with a close spatial arrangement of the phenyl rings followed by a planarization of these precursors to the PAHs by *intra*molecular cyclodehydrogenation.[8–10] Compounds such as **1** and **2** are building blocks for supramolecular architectures, for example, **1** shows a stable discotic mesophase over a wide temperature range and forms monomolecular adsorbate layers on suitable substrates.[8, 11]

In this paper, we report the extension of the aforementioned dehydrogenative coupling route to PAHs with five-membered rings, namely 7,8,9,10-tetraphenylfluoranthene (**3a**) and 7,14-diphenylacenaphtho[1,2-k]-fluoranthene (**4a**) as well as their alkyl-substituted derivatives **3b** and **4b**. Molecular orbital calculations[12] suggest that radical cations of **3** and **4** possess the highest spin density mainly on the *peri*-positions. We therefore assumed that oxidation of **3** and **4** to the



1

R = - H, or -$(CH_2)_{11}CH_3$



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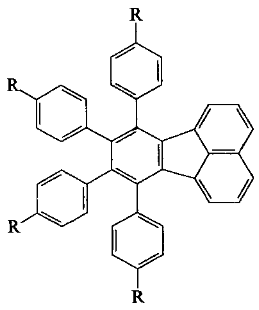
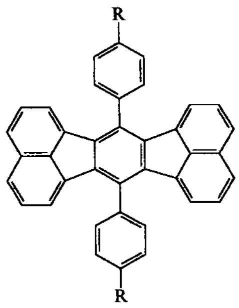
R^1 = -H, or -$C(CH_3)_3$



3

R = **a**: - H, or **b**: -$(CH_2)_{11}CH_3$



4

R = **a**: - H, or **b**: -$(CH_2)_{11}CH_3$

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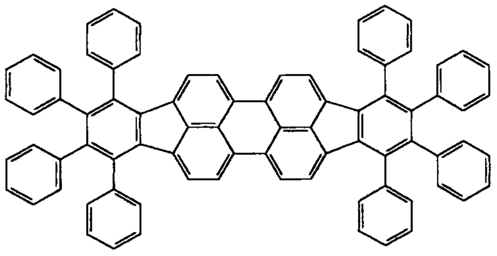
corresponding radical cations could allow not only *intra*molecular cyclodehydrogenation, but also *inter*molecular oxidative coupling, which leads to more complex molecular structures such as the perylene chromophores **5a** and **5b**. Perylenes are important chromophores in dye-stuff chemistry[13–15] due to their excellent thermal, chemical, and photochemical stability and they have recently been applied in photovoltaic cells[16] and optical switches.[17]

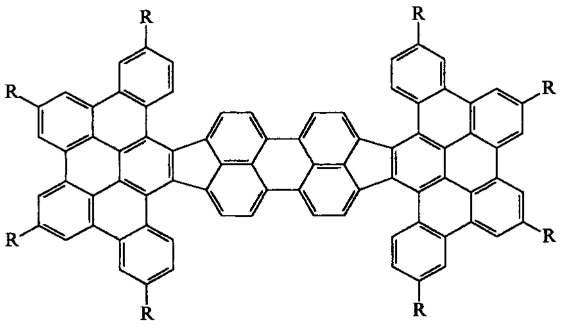
Our group has synthesized terrylene (**7**) and quaterrylene (**8**) dyes, which constitute homologues of the well-known perylenetetracarboxdiimides (**6**).[18–20] The key steps of their synthesis consist of a palladium-catalyzed coupling reaction of suitable precursors followed by a final bond closure to the double-stranded rylene structure. The proposed cyclodehydrogenation route further extends the class of perylene chromophores.

Results and Discussion

Synthesis: Alkyl substitution is a prerequisite for the solubilization of large polycyclic aromatic hydrocarbons and is also important for the formation of liquid crystalline phases. The synthesis of a 7,8,9,10-tetrakis(4-dodecylphenyl)fluoranthene (**3b**) required a new tetra-phenylcyclopentadienone derivative **9b**. This should then be subjected to Diels–Alder cycloaddition with acenaphthylene (**10**) in a similar fashion to the parent, commercially available tetraphenylcyclopentadienone **9a** (see Scheme 1).

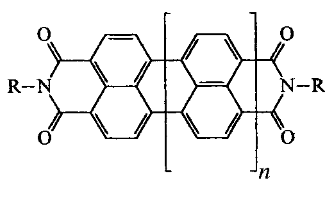


5a



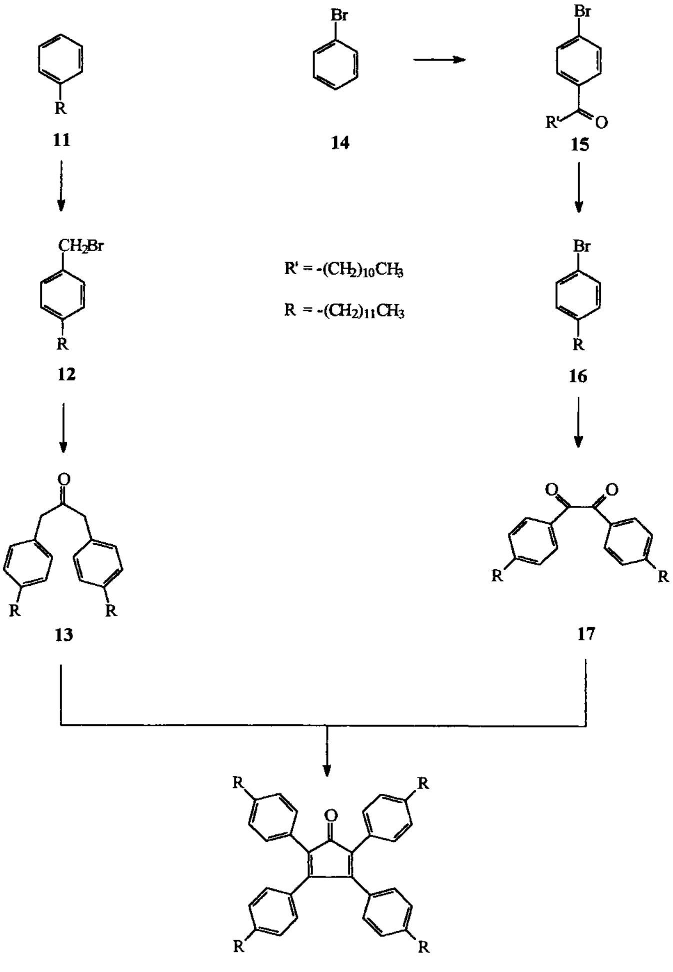
5b

5b: R = -$(CH_2)_{11}CH_3$



6: *n* = 1
7: *n* = 2
8: *n* = 3

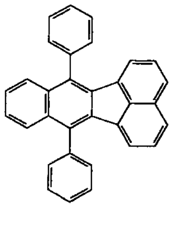
R = -alkyl or -aryl



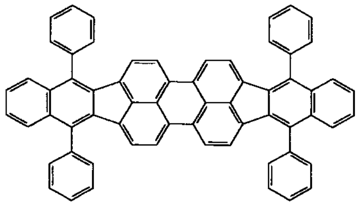
Scheme 1. Synthetic pathway to 2,3,4,5-tetrakis(4-dodecylphenyl)-cyclopentadien-1-one (**9b**) with R = $-(CH_2)_{11}CH_3$.

The tetradodecyl-substituted derivative **9b** had to be synthesized in a twofold aldol condensation reaction of dibenzylketone **13** and diketone **17**; this is a variation of the reaction conditions published by Grummit and Johnson.[21] Alkyl-substituted dibenzylketone **13** was available in a two-step procedure: bromomethylation of dodecylbenzene (**11**) with sodium bromide and *para*-formaldehyde in a mixture of concentrated sulfuric acid and glacial acetic acid yielded 4-bromomethyl dodecylbenzene (**12**). The raw product contained a mixture of *ortho*- and *para*-isomers, and after work-up the desired compound **12** could be isolated in 20% yield only. Afterwards, **12** was converted into the desired compound **13** by a carbonylation reaction with iron pentacarbonyl under phase-transfer conditions following the reports of Otsuji[22] and Thilmont (yield: 67%).[23] The synthesis of the alkyl-substituted diketone **17** was accomplished by using a procedure of Mueller-Westerhoff,[24] which includes lithiation of 4-bromododecylbenzene (**16**) with *sec*-butyllithium in tetrahydrofuran and subsequent treatment with 1,4-dimethylpiperazine-2,3-dione (yield of **17**: 50 %). The aforementioned 4-bromododecylbenzene (**16**) was readily available by Friedel–Crafts acylation of bromobenzene (**14**) with lauroyl chloride (yield: 53 %) followed by a Wolff–Kishner reduction of the resulting ketone **15** (yield: 76%). The Diels–Alder reaction of **9a**,**b** with **10** gave a mixture of **3a**,**b** and the dihydroderivative **3′a**,**b**. Subsequent treatment of this mixture with $KMnO_4$ in refluxing acetone provided **3a**,**b** in essentially quantitative yield.

The key step of the synthetic route was the oxidative coupling reaction of the tetraphenylfluoranthene precursors **3a**,**b**. In the literature, various reaction systems like $AlCl_3$/NaCl (Scholl reaction),[25] $Tl(OCOCF_3)_3$,[26] CoF_3/TFA,[27] $SbCl_5$,[28] or $FeCl_3$[29] are reported for such oxidative cyclodehydrogenation reactions. Recently, Bard[30] synthesized dibenzotetraphenylperiflanthene (**19**) in moderate (56%) yield by treatment of (7,12-diphenyl)benzo[k]fluoranthene (**18**) with CoF_3 in trifluoroacetic acid.



18



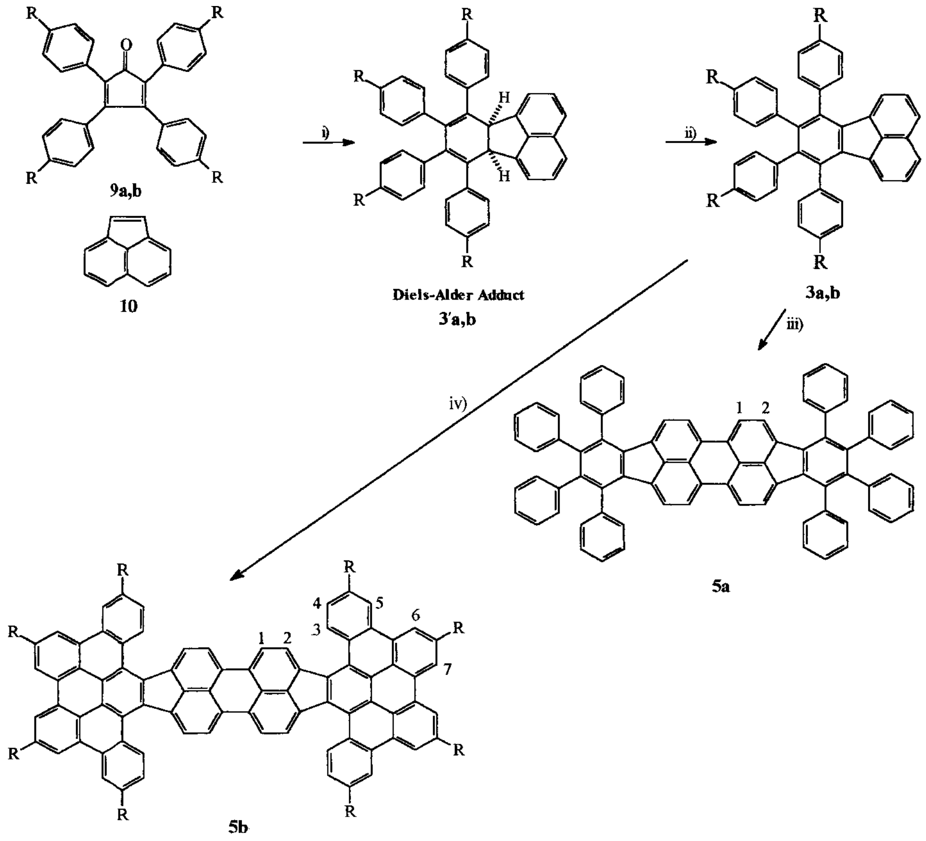
19

Applying this method to **3a**, we found that conversion into 4,4′,5,5′,6,6′,7,7′-tetraphenyldiindeno[1,2,3-cd:1′,2′,3′-lm]perylene (**5a**) was low, and large amounts of the starting material were recovered. We then changed to experimental procedures established in our group for the synthesis of large polycyclic aromatic hydrocarbons: successful cyclodehydrogenation reactions have been performed under Kovacic conditions ($AlCl_3$/Cu triflate/CS_2)[8] or $FeCl_3$ in dichloromethane.[10] However, experiments on **3a**,**b** under these reaction conditions led to undesired multifold chlorination of the fluoranthene derivatives. Therefore, it was necessary to modify the conditions as reported elsewhere for derivatives of **1**.[20] Successful intermolecular coupling of **3a** and **b** in almost quantitative yield was achieved by adding a solution of $FeCl_3$ in nitromethane, rather than solid $FeCl_3$, to a solution of the precursors in dichloromethane, while strongly purging with argon. Predissolving the oxidizing agent in nitromethane speeds up the desired reaction, while bubbling with argon helps to remove evolving HCl, which otherwise facilitates undesired chlorination of the aromatic reactant. Surprisingly, the coupling reaction of tetraphenylfluoranthene **3a** and the alkyl-substituted homologue **3b** using the above-described method afforded different structural motifs (Scheme 2).

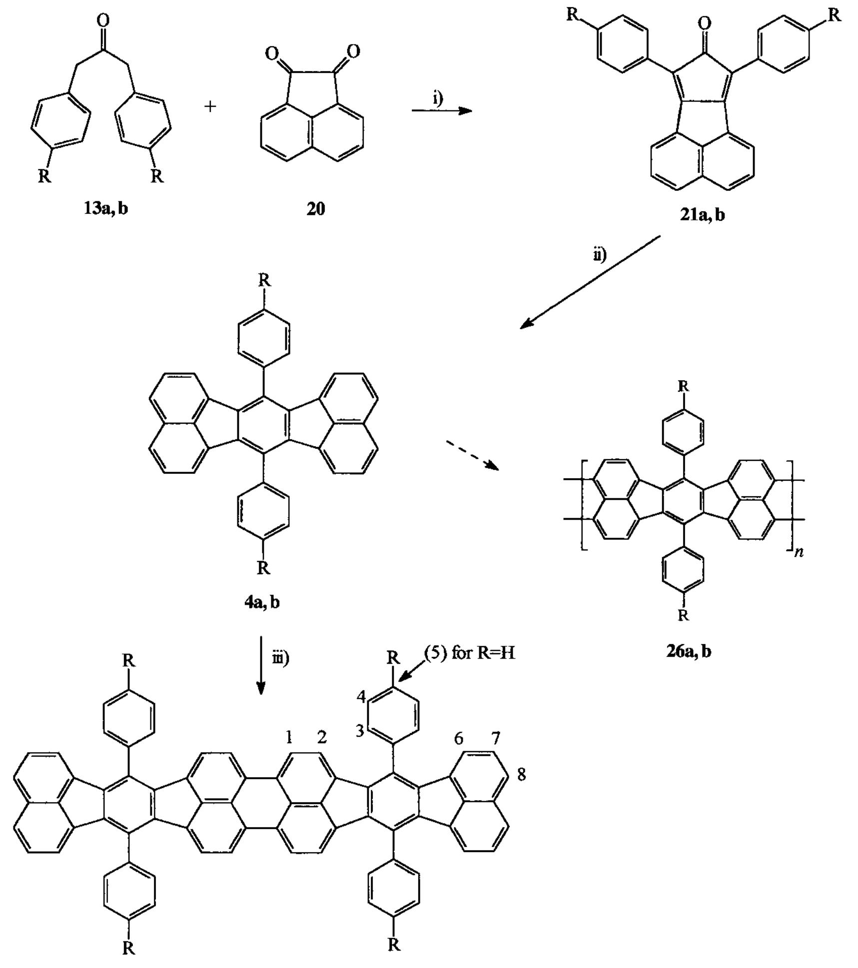
While in the case of **3a** only *inter*molecular coupling to the red chromophore **5a** occurred, the *inter*molecular coupling of **3b** was accompanied by an *intra*molecular reaction of the peripheral phenyl rings that leads to the dark green colored compound **5b** with an extended polyaromatic system. The synthetic results are independent of the amount of oxidizing agent.

The almost quantitative yields of the above-described syntheses gave hope that treatment of **4a**,**b** under the same conditions would allow a polymerization that leads to the ladder-type structures **26a**,**b**. The synthetic pathway to **4a**,**b** is outlined in Scheme 3.

The synthetic buildup of both precursors (**4a**,**b**) proceeded analoguous to compounds **3a**,**b** by a method originally developed by Dilthey.[31] After a twofold aldol condensation of the dibenzyl ketones **13a**,**b** and acenaphthenequinone **20**



Scheme 2. Synthetic pathway to **5a** and **5b** with **a**: R = H and **b**: R = $-(CH_2)_{11}CH_3$. i) ΔT, reflux xylene; ii) $KMnO_4$; iii) $FeCl_3/CH_3NO_2$; iv) $FeCl_3/CH_3NO_2$.



Scheme 3. Synthetic pathway to 7,14-diphenylacenaphtho[1,2-k]-fluoranthenes (**4a**,**b**) and oxidative cyclodehydrogenation of **4a**,**b** to **22a**,**b** with **a**: R = H and **b**: R = $-(CH_2)_{11}CH_3$ i) KOH/EtOH, ΔT; ii) acenaphthylene (**10**), ΔT; iii) $FeCl_3/CH_3NO_2$.

(yield: 86–94%), the resulting 7,9-diphenyl-8H-cyclopenta-[1]acenaphthylen-8-ones (**21a**,**b**) were treated with acenaphthylene (**16**) in a [4+2]-cycloaddition followed by treatment with $KMnO_4$ in acetone to give the desired 7,14-diphenylacenaphtho[1,2-k]-fluoranthenes (**4a**,**b**) (yield: 83–87%). Compounds **4a**,**b** were then subjected to oxidative cyclodehydrogenation under the same reaction conditions as for **3a**,**b** with the aim of constructing an extended ladder-type polymer by means of oxidative coupling at both ends of the molecule. However, work-up of the reaction led exclusively and quantitatively to a blue reaction product that could be unambiguously characterized as 4,4′,7,7′-tetraphenyldiacenaphtho[1,2-k:1′,2′,k′]diindeno-[1,2,3-cd:1′,2′,3′-me]perylenes (**22a**,**b**).

All attempts to obtain higher oligomers under harsher reaction conditions (e.g. use of $SbCl_5$ as oxidizing agent), higher reaction temperatures, and longer reaction times failed.[32]

Structure elucidation: The structures of **5a**, **5b**, **22a**, and **22b** were proven by ^1H NMR spectroscopy, field-desorption mass spectrometry, and UV/Vis spectroscopy. As a result of solubility problems, it was possible to obtain ^{13}C NMR spectroscopic data only for **5a** and **22b**. Planarization of the outer phenyl rings from **3b** to **5b** becomes apparent in the ^1H NMR spectra. In accordance with the extended π-system, resonances occur at considerably lower field than for the non-planarized analogue **5a**. The assignment, based on two-dimensional H,H-correlated NMR analysis of the resonances, is given in Table 1.

As was mentioned before, compound **5b** was expected to be a candidate for thermotropic liquid crystalline phase behavior. However, when **5b** was investigated by means of polarization microscopy, differential scanning calorimetry, and X-ray diffractrometry, no transition into a discotic mesophase could be observed. By means of a polarization microscope, a direct transition of the crystalline solid into the isotropic melt was visible above 300 °C under a nitrogen atmosphere.

Electronic spectra: The three perylene chromophores form deep red (**5a**), green (**5b**), and blue (**22a**,**b**) solutions in common organic solvents like

Table 1. Aromatic ^1H NMR chemical shifts of **5a**, **5b**, **22a**, and **22b** in $C_2D_2Cl_4$ at 135 °C.

	δ	Type	H	Integration
5a	7.8	d	1	4H
	7.30–7.26	m	H phenyl	10H
	6.87–6.78	m	H phenyl	10H
	6.55	d	2	4H
5b	9.42	d	3	4H
	8.87	s	7	4H
	8.84	d	1	4H
	8.76	s	6	4H
	8.68	s	5	4H
	8.08	d	2	4H
	7.65	d	4	4H
22a	7.83	d	1	4H
	7.75–7.71	m	3,4,5,8	24H
	7.3	dd	7	4H
	6.72	d	6	4H
	6.64	d	2	4H
22b	7.83	d	1	4H
	7.66	d	8	4H
	7.58	d	3 or 4	8H
	7.51	d	3 or 4	8H
	7.29	dd	7	4H
	6.81	d	6	4H
	6.64	d	2	4H

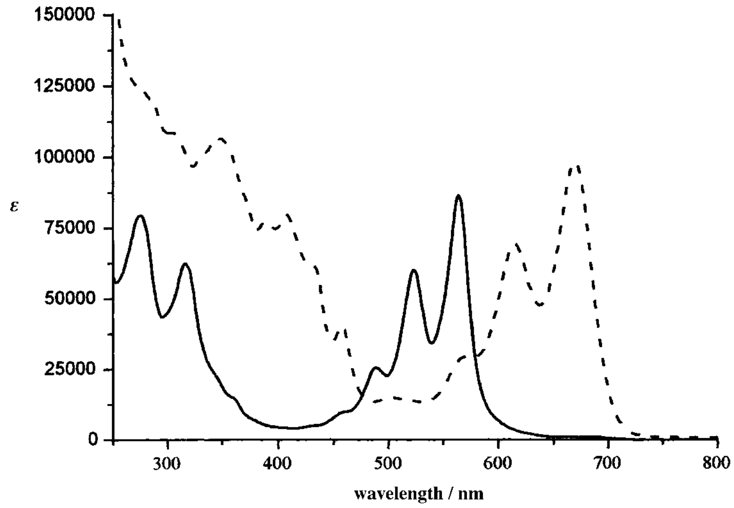


Figure 1. UV/Vis spectra of **5a** (solid line) and **5b** (dotted line) in chloroform.

chloroform or toluene. As can be seen from Figure 1 and Figure 2, absorption of the three chromophores covers a broad range of the visible spectrum. Comparison of **5a** and **5b** shows that, in accordance with the planarization of the outer phenyl rings and the resulting extension of the aromatic π-system, not only a bathochromic shift becomes apparent, but also the absorption coefficient increases. All solutions are highly fluorescent, with a bright fluorescence under UV irradiation and even a pronounced fluorescence under ambient lighting. Figure 2 shows the corresponding UV/Vis absorption and fluorescence spectra measured in chloroform for **5a**.

The Stokes shift is small, which can be explained by the rigid structure of the chromophoric unit. Table 2 summarizes UV/Vis spectroscopic data of the precursor molecules **3** and **4**, chromophores **5a**, **5b**, **22**, parent periflanthene (**23**),[33] dibenzotetraphenyl-periflanthene **19** synthesized by Bard,[30] and a model compound **24** for a ladder polymer of similar structural type reported by

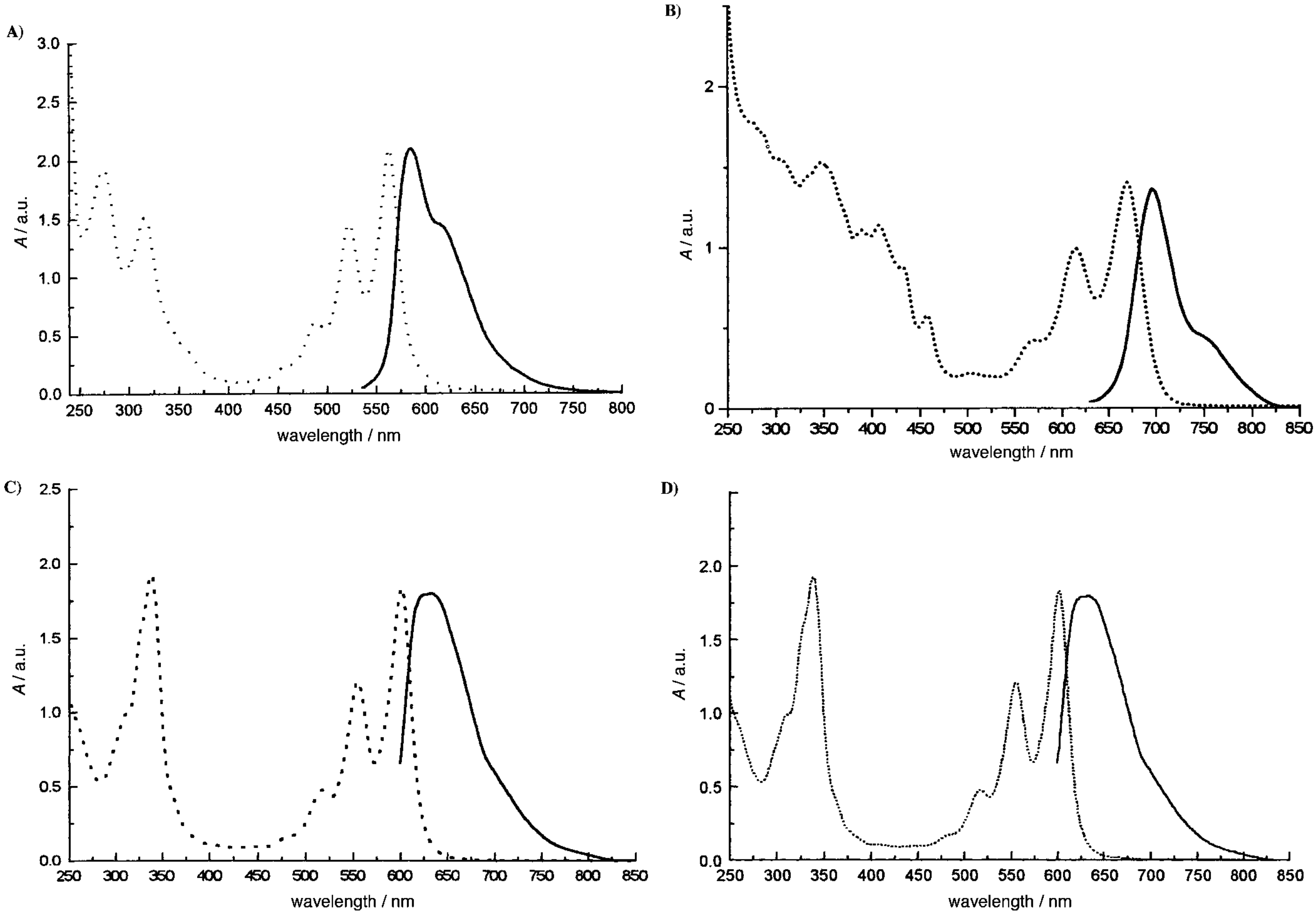
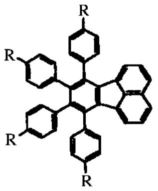
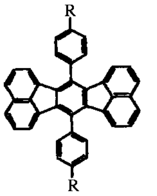
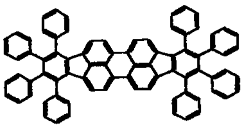
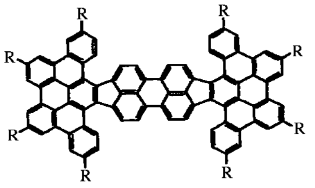
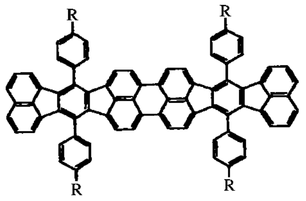
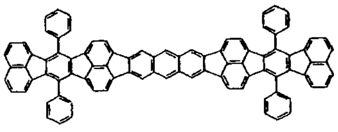
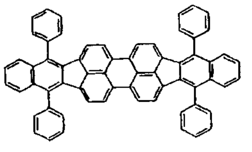
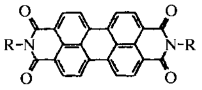
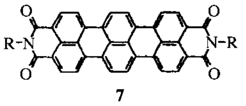


Figure 2. A: UV/Vis absorption (dotted line) and fluorescence (solid line) spectra of **5a** in chloroform. For ε values of compound **5a** see Figure 1; B: UV/Vis absorption (dotted line) and fluorescence (solid line) spectra of **5b** in chloroform. For ε values of compound **5b** see Figure 1; C: UV/Vis absorption (dotted line) and fluorescence (solid line) spectra of **22a** in chloroform. Due to the low solubility of compound **22a** (**a**: R = H), the ε values could not be determined; D: UV/Vis absorption (dotted line) and fluorescence (solid line) spectra of **22b** (**b**: $R = -(CH_2)_{11}CH_3$) in chloroform. For ε values of compound **22b**, see Experimental Section.

Table 2. Summarized UV data (λ_{max}, log ε, and λ_{max} of fluorescence) of compounds **3**, **4**, **5a**, **5b**, **6**, **7**, **19**, **22**, **23**, and **24**.

	λ_{max} [nm]	log ε [L mol^{-1} cm^{-1}]	maximum of fluorescence[a] [nm]
 **3**	375	4.4	[b]
 **4**	427	4.41	[b]
 **23**	540	3.79	[b]
 **5a**	564	4.94	587
 **5b**	670	4.99	696
 **22**	602	5.06	632
 **24**	581	[b]	[b]
 **19**	582	[b]	[b]
 **6**	525	4.67	556
 **7**	664	5.08	707

[a] Excitation in the maximum of absorption. [b] Not available.

Schlüter[34] as well as the rylenetetracarboximides synthesized in our group recently.

Clearly visible is the strong bathochromic shift of roughly 150 nm as a result of the dimerization and the corresponding buildup of a perylene chromophoric subunit of **3** to **5** and **4** to **22**, respectively. Comparing the absorption maxima of the parent polyaromatic unit periflanthene (**23**) with that of octaphenylperiflanthene (**5a**), one observes that only a small bathochromic shift of 25 nm is obtained by attaching eight phenyl rings. The small shift is based on the fact that the outer phenyl rings rotate out of the plane of the aromatic π-system. In contrast, twofold acenaphthoannelation like for compound **22b** or planarization into compound **5b** leads to a strong bathochromic shift due to the extension of the π-system. Compound **24** illustrates that not only simple extension of the π-system is a prerequisite for absorbance at low energies. The ladder structure **24** is by far more extended than those of **22** and **19**, but as a result of their perylene subunit, compound **19** absorbs at a comparable wavelength and **22** even at lower energies. When the spectroscopic data of **5a**, **5b**, and **22b** are compared with the rylene structures **6**, **7**, and **8**, the chromophores presented in this paper can be considered attractive candidates for fluorescent materials. With regard to the ease of the synthetic buildup in relatively few steps from commercially available starting compounds and the absorption maxima between perylene and the terrylenediimide, this holds specially true for the red chromophore (**5a**) and blue chromophore **22**. In contrast, for the synthesis of the green chromophore **5b**, a multistep procedure has to be undertaken. However, with the absorption maxima at lower energies than **7** and only a few known fluorophores absorbing in this region of the visible spectrum, **5b** can also be expected to be an attractive dye.

Conclusion

We present the synthesis of perylene derivatives **5a**, **5b**, and **22** by means of a short and convenient synthetic scheme. They show intense absorptions in the range from 550 nm (**5a**) to 670 nm (**5b**) and, remarkably, strong emissions from 590 nm (**5a**) to 700 nm (**5b**). The ease of the synthetic buildup should make it possible to incorporate functional groups by the buildup of the corresponding tetraphenylcyclopentadienones. Hereby, tailor-made spectroscopic properties could be achieved, which are a prerequisite for applications that require dyes with absorption and emission in a specific region of the visible spectrum. The same synthetic strategy could be used to covalently link the dyes to polymers and therefore obtain migration-stable immobilized dyes. For a more comprehensive assessment of the potential of the synthesized chromophores, a detailed investigation of the photophysical properties is ongoing.

Experimental Section

Spectral data were obtained on Nicolet FT-IR 320 (IR), Perkin Elmer-Lambda 9 and 15 (UV/Vis), Varian Gemini 200, Bruker AC 300, or AMX 500 (NMR). For the 2D-^{1}H-^{1}H NMR experiment, the cosy45 pulseprogram was used with a 90 degree pulse of 16 us and a relaxation delay d1 of 4 s.

Finnigan MAT 312 (FD-MS) instruments were used. The melting points (m.p.) have been reported uncorrected. $FeCl_3$ was purchased from Merck, and all other chemicals were purchased from Aldrich and used as received. Tetrahydrofuran was deionized before use. All other solvents were used as received. KOH/EtOH was prepared by dissolving KOH (3 g) in ethanol (15 mL) at elevated temperature.

4-Bromomethyldodecylbenzene (12): Semi-concentrated sulfuric acid (80 mL) was added to a mixture of dodecylbenzene (75 g, 303 mmol), *para*-formaldehyde (12.5 g, 420 mmol), sodium bromide (51.6 g), and glacial acetic acid (24 mL) over 3 h. The reaction mixture was then stirred for another 12 h at the same temperature. After cooling to room temperature, deionized water (300 mL) was added. The reaction mixture was extracted with dichloromethane, the organic phase was separated, dried over magnesium sulfate, and the solvent was evaporated under vacuum. The resulting precipitate was purified by chromatography on silica gel with petroleum ether as eluent (24 % yield).

M.p. 46 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): $\delta = 7.32$ (d, ^3J(H,H) = 8.2 Hz, 2H; Ar–H), 7.17 (d, ^3J(H,H) = 8.2 Hz, 2H; Ar–H), 4.51 (s, 2H; H-5), 2.62 (t, ^3J(H,H) = 7.6 Hz, 4H; α-CH_2–), 1.70 – 1.20 (m, 20H; –CH_2–), 0.91 (t, ^3J(H,H) = 6.5 Hz, 3H; –CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C): $\delta = 143.9$, 135.4, 129.4, 129.2, 36.4, 36.1, 34.2, 32.3, 31.7, 30.1, 30.0, 29.9, 29.8, 29.7, 23.1, 14.5; MS (FD): *m/z* (%): 340.5 ([*M*]$^+$, 100); elemental analysis calcd (%) for $C_{19}H_{31}Br$ (339.35): C 67.25, H 9.20, Br 23.54; found C 67.16, H 9.26, Br 23.31.

1,3-Bis(4-dodecylphenyl)-propan-2-one (13b): Iron pentacarbonyl (7.3 g, 4.9 mL, 37 mmol) was added to a refluxing mixture of 4-bromomethyldodecylbenzene (24 g, 71 mmol) (**12**), sodium hydroxide (12.3 g), benzyltriethylammonium chloride (0.54 g), deionized water (7 mL), and dichloromethane (170 mL) under a nitrogen atmosphere. The reaction mixture was then refluxed with rigorous stirring overnight. After cooling to room temperature, the reaction mixture was neutralized with HCl (2 N), the organic phase was separated, washed with HCl (2 N) and deionized water, dried over magnesium sulfate, and the solvent was evaporated under vacuum. The resulting solid was purified by chromatography on silica gel with a mixture of dichloromethane and petroleum ether (3:1) as eluent (47 % yield).

M.p. 72 – 74 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): $\delta = 7.15$ (d, ^3J(H,H) = 8.0 Hz, 4H; Ar–H), 7.07 (d, ^3J(H,H) = 8.0 Hz, 4H; Ar–H), 3.69 (s, 4H; H-2), 2.60 (t, ^3J(H,H) = 7.4 Hz, 4H; α-CH_2–), 1.70 – 1.10 (m, 40H; –CH_2–), 0.91 (t, ^3J(H,H) = 6.8 Hz, 6H; –CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C): $\delta = 206.5$, 142.2, 131.7, 129.8, 129.2, 49.2, 36.1, 32.4, 31.9, 30.0, 29.8, 23.2, 14.6; $\tilde{\nu} = 1715$ (C=O), 1677 cm^{-1} (C=O); MS (FD): *m/z* (%): 546.4 ([*M*]$^+$, 100); elemental analysis calcd (%) for $C_{39}H_{62}O$ (546.92): C 85.65, H 11.43; found C 85.17, H 11.40.

4-Bromododecanoylbenzene (15): Dodecanoyl chloride (219 g, 231 mL, 1 mol) was added dropwise to a mixture of bromobenzene (314 g, 2 mol) and aluminum chloride (160 g, 1.2 mol). The reaction mixture was then stirred at 50 °C for 1 h, poured into ice water, and extracted with dichloromethane. The organic phase was washed with HCl solution (2 N) and brine and dried over magnesium sulfate. After removal of the solvent under vacuum, the residue was purified by recrystallization from ethanol to afford 4-bromododecanoylbenzene (**15**) as colorless plates (yield 67 %).

M.p. 64 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): $\delta = 7.73$ (d, $J = 8.0$ Hz, 2H), 7.52 (d, $J = 8.0$ Hz, 2H), 2.83 (t, $J = 7.5$ Hz, 2H), 1.63 (q, $J = 7.5$ Hz, 2H), 1.31 – 1.08 (m, 16H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C): $\delta = 199.8$, 136.2, 132.2, 130.0, 128.3, 39.0, 32.3, 30.0, 29.9, 29.7, 24.7, 23.1, 14.5; $\tilde{\nu} = 1711$ (C=O), 1672 cm^{-1} (C=O); MS (FD): *m/z* (%): 338.5 ([*M*]$^+$, 100).

4-Bromododecylbenzene (16): A mixture of 4-bromododecanoylbenzene (**15**) (200 g, 589 mmol), hydrazine hydrate (98 %, 85.8 mL), and KOH (132 g, 2.36 mol) in triethylene glycol (1 L) was refluxed for 2 h. The mixture was deionized at atmospheric pressure until the temperature of the reaction mixture reached 210 °C. After cooling to room temperature, the resulting mixture was poured into water, acidified with conc. HCl solution (220 mL), and extracted with dichloromethane. The organic phase was washed with water, dried with magnesium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether to afford the benzene **16** as a colorless oil (yield 68 %).

^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): $\delta = 7.40$ (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 8.0$ Hz, 2H), 2.58 (t, $J = 7.5$ Hz, 2H), 1.61 (p, $J = 7.5$ Hz, 2H), 1.36 – 1.18 (m, 18H), 0.92 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C): $\delta = 142.25$, 131.65, 130.56, 119.64, 35.76, 32.33, 31.72, 30.05, 29.98, 29.87, 29.76, 29.60, 23.10, 14.51; MS (FD): *m/z* (%): 324.2 ([*M*]$^+$, 100).

4,4′-Didodecylbenzil (17): *sec*-Butyllithium (0.11 mol) was added to 4-bromododecylbenzene (**16**) (35.8 g, 0.11 mol) in tetrahydrofuran (100 mL) at −78 °C. The reaction mixture was allowed to warm to 0 °C and subsequently added to a suspension of 1,4-dimethylpiperazine-2,3-dione (7.1 g, 0.05 mol) in tetrahydrofuran (180 mL). After stirring overnight, the reaction was quenched with HCl (300 mL, 2 N). Dichloromethane (300 mL) was then added, and the organic phase was separated, washed with HCl (2 N) and deionized water, and dried over magnesium sulfate. The solvent was evaporated under vacuum. The resulting solid was purified by chromatography on silica gel with a mixture of dichloromethane and petroleum ether (3:1) as eluent (yield 57 %).

M.p. 47 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): $\delta = 7.90$ (d, $J = 8.2$ Hz, 4H), 7.30 (d, $J = 8.2$ Hz, 4H), 2.68 (t, $J = 7.4$ Hz, 4H), 1.8 – 1.1 (m, 40H), 0.88 (d, $J = 7.6$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C): $\delta = 194.8$, 151.2, 131.2, 128.8, 129.3, 36.5, 32.2, 31.3, 29.9, 29.8, 29.7, 29.6, 29.5, 23.0, 14.4; $\tilde{\nu} = 1671$ cm^{-1} (C=O); MS (FD): *m/z* (%): 546.3 ([*M*]$^+$, 100); elemental analysis calcd (%) for $C_{38}H_{58}O_2$ (546.87): C 83.46, H 10.69; found C 83.49, H 10.89.

Tetra(4-dodecyl-phen-1-yl)cyclopentadienone (9b): A solution of KOH (1.2 g, 22 mol) in ethanol (6 mL) was added to a refluxing solution of 4,4′-didodecylbenzil (**17**) (12 g, 22 mmol) and 1,3-bis(4-dodecylphenyl)-propan-2-one (**13**) (10.81 g, 20 mmol) in ethanol (36 mL). After five minutes the reaction was cooled to 0 °C, and the resulting purple oil was separated from the solvent. Column chromatography of this viscous oil eluted with petroleum ether/CH_2Cl_2 (4:1) as eluent afforded **9b** as a purple solid (yield 43 %).

M.p. 55 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): $\delta = 7.19$ (d, $J = 8.2$ Hz, 4H), 7.05 (d, $J = 8.2$ Hz, 4H), 6.98 (d, $J = 8.2$ Hz, 4H), 6.83 (d, $J = 8.2$ Hz, 4H), 2.55 (t, $J = 7.5$ Hz, 4H), 1.8 – 1.1 (m, 40H), 0.91 (d, $J = 7.6$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C): $\delta = 154.6$, 143.6, 142.5, 131.2, 130.4, 129.8, 128.9, 128.5, 128.3, 125.2, 36.2, 32.4, 31.7, 31.5, 30.2, 30.0, 29.9, 29.7, 23.2, 14.6; $\tilde{\nu} = 1710$ cm^{-1} (C=O); MS (FD): *m/z* (%): 1057.0 ([*M*]$^+$, 100); elemental analysis calcd (%) for $C_{77}H_{116}O$ (1108.16): C 87.43, H 11.05; found C 87.12, H 11.02.

7,8,9,10-Tetraphenylfluoranthene (3a): A mixture of acenaphthylene (**10**) (1.9 g, 12.5 mmol) and tetraphenylcyclopentadienone (**9a**) (5.11 g, 13.3 mmol) in xylene (40 mL) was refluxed for 16 h under an argon atmosphere. After cooling to room temperature, ethanol (300 mL) was added to the reaction mixture. The precipitated solid was filtered, washed with ethanol, and dried in vacuum. Subsequently, the solid was dissolved in a refluxing mixture of acetone/benzene (1:5, 100 mL) and treated with aliquots of a solution of $KMnO_4$ in acetone until the reaction mixture remained purple. After filtration over a column of silica gel to remove $KMnO_4$, evaporation of the solvent, and drying in vacuum, **3a** was obtained as a yellow, strongly fluorescent solid (yield 85 %).

M.p. > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): $\delta = 7.66$ (d, ^3J(H,H) = 8.0 Hz, 2H), 7.31 – 7.23 (m, 12H), 6.89 – 6.77 (m, 10H), 6.63 (d, ^3J(H,H) = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C): $\delta = 142.3$, 141.4, 138.7, 138.2, 138.0, 132.8, 131.7, 131.3, 129.3, 129.0, 128.1, 127.8, 127.7, 126.6, 124.5; λ_{max} ($CHCl_3$, ε) = 373 (27500), 295 nm (69500); MS (FD): *m/z* (%): 506.6 ([*M*]$^+$, 100); elemental analysis calcd (%) for $C_{40}H_{26}$ (506.64): C 94.83, H 5.17; found C 94.83, H 5.14.

7,8,9,10-Tetrakis(4-dodecylphenyl)fluoranthene (3b): A mixture of acenaphthylene (**10**) (0.4 g, 2.6 mmol) and tetra(4-dodecyl-phen-1-yl)cyclopentadienone (**9b**) (3.0 g, 2.8 mmol) in xylene (20 mL) was refluxed for 16 h under an argon atmosphere. After cooling to room temperature, ethanol (300 mL) was added to the reaction mixture. The precipitated solid was filtered, washed with ethanol, and dried in vacuum. Subsequently, the solid was dissolved in a refluxing mixture of acetone/benzene (1:5, 100 mL) and treated with a solution of $KMnO_4$ in acetone until the reaction mixture remained purple. After filtration over a column of silica gel to remove $KMnO_4$, evaporation of the solvent, and drying in vacuum, **3b** was obtained as a yellow strongly fluorescent solid (yield 77%).

M.p. 57–58 °C. ^1H NMR (300 MHz, $CDCl_3$, 30 °C): $\delta = 7.63$ (d, $^3J(H,H) = 8.0$ Hz, 2H), 7.24 (dd, $^3J(H,H) = 8.0$ Hz, $^3J(H,H) = 6.7$ Hz, 2H), 7.17 (d, $^3J(H,H) = 7.3$ Hz, 4H), 7.06 (d, $^3J(H,H) = 7.3$ Hz, 4H), 6.73 (d, $^3J(H,H) = 8.0$ Hz, 4H), 6.67 (d, $^3J(H,H) = 6.7$ Hz, 2H), 6.63 (d, $^3J(H,H) = 8.0$ Hz, 2H), 2.61 (t, $^3J(H,H) = 7.3$ Hz, 4H; α-CH_2), 2.34 (t, $^3J(H,H) = 7.4$ Hz, 4H; α-CH_2), 1.65–1.15 (m, 80H; $-CH_2-$), 0.89 (t, $^3J(H,H) = 6.7$ Hz, 12H; $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C): $\delta = 142.3$, 142.5, 140.7, 138.9, 138.8, 138.7, 138.6, 137.8, 132.7, 131.5, 131.2, 129.2, 128.9, 127.7, 127.4, 124.4, 36.7, 33.3, 32.5, 31.1, 31.0, 30.9, 30.7, 30.1, 24.1, 15.6; λ_{max} ($CHCl_3$, ε) = 375 (26000), 298 nm (68000); MS (FD): m/z (%): 1179.7 ($[M]^+$, 100); elemental analysis calcd (%) for $C_{88}H_{122}$ (1179.93): C 89.58, H 10.42; found C 89.35, H 10.69.

4,4′,5,5′,6,6′,7,7′-Tetraphenyldiindeno[1,2,3-cd:1′,2′,3′-lm]perylene (5a): A solution of $FeCl_3$ (1.9 g, 11.7 mmol) in nitromethane (3 mL) was added dropwise to a stirred solution of 7,8,9,10-tetraphenylfluoranthene (**3a**) (506 mg, 1 mmol) in CH_2Cl_2 (40 mL). An argon stream was bubbled through the reaction mixture throughout the entire reaction. After stirring for another five minutes, the reaction was quenched with methanol (40 mL). The precipitate was filtered, washed with methanol (40 mL), and dried under reduced pressure. The crude product was purified by column chromatography on silica gel with dichloromethane/petroleum ether (1:1) to afford red **5a** (yield: 90%).

M.p. > 300 °C. ^1H NMR (500 MHz, $C_2D_2Cl_4$, 130 °C): $\delta = 7.80$ (d, $^3J(H,H) = 7.3$ Hz, 4H), 7.30–7.26 (m, 20H), 6.87–6.78 (m, 20H), 6.55 (d, $^3J(H,H) = 7.3$ Hz, 4H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 130 °C): $\delta = 141.3$, 140.2, 137.8, 137.2, 136.8, 134.8, 131.7, 130.5, 128.4, 127.2, 126.9, 125.6, 124.4, 122.2, 121.8; λ_{max} ($CHCl_3$, ε) = 564 (86500), 523 (60150), 480 (25650), 316 (62500), 275 nm (79500); MS (FD): m/z (%): 1008.9 ($[M]^+$, 100); elemental analysis calcd (%) for $C_{80}H_{48}$ (1009.26): C 95.21, H 4.79; found C 95.73, H 4.99.

Compound 5b: A solution of $FeCl_3$ (1.7 g, 10 mmol) in nitromethane (1.7 mL) was added dropwise to a stirred solution of 7,8,9,10-tetrakis(4-dodecylphenyl)fluoranthene (**3b**) (500 mg, 0.4 mmol) in CH_2Cl_2 (40 mL). An argon stream was bubbled through the reaction mixture throughout the entire reaction. After stirring for another 30 min, the reaction was quenched with methanol (50 mL). The precipitate was filtered, washed with methanol (40 mL), and dried under reduced pressure. The crude product was purified by column chromatography on silica gel with dichloromethane/petroleum ether (1:1) to afford dark green **5b** (yield: 45%).

M.p. > 300 °C. ^1H NMR (500 MHz, $[D_4]$*p*-dichlorobenzene, 155 °C): $\delta = 9.42$ (d, $^3J(H,H) = 7.3$ Hz, 4H), 8.87 (s, 4H), 8.84 (d, $^3J(H,H) = 7.8$ Hz, 4H), 8.76 (s, 4H), 8.68 (s, 4H), 8.08 (d, $^3J(H,H) = 7.8$ Hz, 4H), 7.65 (d, $^3J(H,H) = 7.3$ Hz, 4H), 3.28 (t, $^3J(H,H) = 7.7$ Hz, 8H; α-CH_2), 3.18 (t, $^3J(H,H) = 7.7$ Hz, 8H; α-CH_2), 2.20–1.44 (m, 160H; $-CH_2-$), 1.00 (t, $^3J(H,H) = 7.1$ Hz, 24H; $-CH_3$); λ_{max} ($CHCl_3$, ε): 670 (98300), 615 (69500), 571 (29500), 458 (40500), 408 (79800), 346 nm (107100); MS (FD): m/z (%): 2343.5 ($[M]^+$, 100); elemental analysis calcd (%) for $C_{176}H_{228}$ (2343.74): C 90.19, H 9.81; found C 89.88, H 9.67.

7,9-Diphenyl-8H-cyclopenta[l]acenaphthylen-8-one (21a): KOH/EtOH (3 mL) was added to a refluxing solution of acenaphthenequinone (**20**) (1.73 g, 9.5 mmol) and 1,3-diphenylpropane-2-one (**13a**) (2 g, 9.5 mmol) in ethanol (10 mL) and toluene (1 mL). After five minutes, the reaction mixture was cooled to 0 °C, and the precipitated purple solid was filtered, washed with ethanol, and dried in vacuum (yield 94%).

M.p. > 300 °C. ^1H NMR (300 MHz, $CDCl_3$, 30 °C): $\delta = 7.99$ (d, $^3J(H,H) = 7.2$ Hz, 2H), 7.83 (d, $^3J(H,H) = 8.3$ Hz, 2H), 7.75 (d, $^3J(H,H) = 7.2$ Hz, 4H), 7.55 (dd, $^3J(H,H) = 7.2$ Hz, $^3J(H,H) = 8.3$ Hz, 2H), 7.50 (dd, $^3J(H,H) = 7.2$ Hz, $^3J(H,H) = 7.4$ Hz, 4H), 7.39 (t, $^3J(H,H) = 7.4$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C): $\delta = 203.0$, 155.6, 146.1, 133.3, 132.5, 130.3, 130.0, 129.8, 129.7, 129.3, 122.8, 122.3; $\tilde{\nu} = 1699$ cm^{-1} (C=O); MS (FD): m/z (%): 355.9 ($[M]^+$, 100); elemental analysis calcd (%) for $C_{27}H_{16}O$ (356.42): C 90.99, H 4.52; found C 91.06, H 4.53.

7,9-Bis(4-dodecylphenyl)-8H-cyclopenta[l]acenaphthylen-8-one (21b): KOH/EtOH (3.5 mL) was added to a refluxing solution of acenaphthenequinone (**20**) (1.82 g, 10 mmol) and 1,3-bis(4-dodecylphenyl)-propan-2-one (**13b**) (5.46 g, 10 mmol) in ethanol (10 mL) and toluene (1 mL). After five minutes, the reaction mixture was cooled to 0 °C, and the precipitated purple solid was filtered, washed with ethanol, and dried in vacuum (yield 86%).

M.p. 55–56 °C. ^1H NMR (300 MHz, $CDCl_3$, 30 °C): $\delta = 8.06$ (d, $^3J(H,H) = 7.4$ Hz, 2H), 7.89 (d, $^3J(H,H) = 8.6$ Hz, 2H), 7.73 (d, $^3J(H,H) = 8.6$ Hz, 4H), 7.61 (dd, $^3J(H,H) = 7.3$ Hz, $^3J(H,H) = 8.6$ Hz, 2H), 7.35 (d, $^3J(H,H) = 8.6$ Hz, 4H), 2.70 (t, $^3J(H,H) = 7.4$ Hz, 4H; α-CH_2), 1.71–1.29 (m, 40H; $-CH_2-$), 0.88 (t, $^3J(H,H) = 7.4$ Hz, 6H; $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C): $\delta = 203.3$, 154.4, 144.5, 132.6, 129.9, 129.7, 129.5, 129.3, 128.4, 125.8, 122.6, 121.7, 36.8, 32.8, 32.4, 30.6, 30.5, 30.4, 30.3, 30.2, 23.6, 14.8; $\tilde{\nu} = 1699$ cm^{-1} (C=O); MS (FD): m/z (%): 695.3 ($[M]^+$, 100); elemental analysis calcd (%) for $C_{51}H_{64}O$ (693.06): C 88.31, H 9.31; found C 88.12, H 9.67.

7,14-Diphenylacenaphtho[1,2-k]-fluoranthene (4a): A mixture of acenaphthylene (**10**) (1.16 g, 7.6 mmol) and 7,9-diphenyl-8H-cyclopenta[l]acenaphthylen-8-one (**21a**) (3 g, 8.4 mmol) in xylene (20 mL) was refluxed for 16 h under an argon atmosphere. After cooling to room temperature, ethanol (300 mL) was added to the reaction mixture. The precipitated solid was filtered, washed with ethanol, and dried in vacuum. Subsequently, the solid was dissolved in a refluxing mixture of acetone/benzene (1:5, 100 mL) and treated with aliquots of a solution of $KMnO_4$ in acetone until the reaction mixture remained purple. After filtration over a column of silica gel to remove $KMnO_4$, evaporation of the solvent, and drying in vacuum, **4a** was obtained as a yellow, strongly fluorescent solid (yield 87%).

M.p. > 300 °C. ^1H NMR (300 MHz, $CDCl_3$, 30 °C): $\delta = 7.68$–7.60 (m, 14H), 7.30 (dd, $^3J(H,H) = 7.1$ Hz, 4H), 6.67 (d, $^3J(H,H) = 6.9$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C): $\delta = 140.8$, 138.8, 138.3, 135.9, 134.8, 131.5, 131.3, 130.8, 130.1, 129.7, 128.3, 125.1; λ_{max} ($CHCl_3$, ε) = 423 (24900), 400 (18500), 309 nm (76570); MS (FD): m/z (%): 477.9 ($[M]^+$, 100); elemental analysis calcd (%) for $C_{38}H_{22}$ (478.59): C 95.37, H 4.63; found C 95.45, H 4.70.

7,14-Bis[4-dodecylphenyl]acenaphtho[1,2-k]-fluoranthene (4b): A mixture of acenaphthylene (**10**) (807 mg, 5.3 mmol) and 7,9-bis(4-dodecylphenyl)-8H-cyclopenta[l]acenaphthylen-8-one (**21b**) (4 g, 5.8 mmol) in xylene (15 mL) was refluxed for 16 h under an argon atmosphere. After cooling to room temperature, ethanol (300 mL) was added to the reaction mixture. The precipitated solid was filtered, washed with ethanol, and dried in vacuum. Subsequently, the solid was dissolved in a refluxing mixture of acetone/benzene (1:5, 100 mL) and treated with aliquots of a solution of $KMnO_4$ in acetone until the reaction mixture remained purple. After filtration over a column of silica gel to remove $KMnO_4$, evaporation of the solvent, and drying in vacuum, **4b** was obtained as a yellow, strongly fluorescent solid (yield 83%).

M.p. > 300 °C. ^1H NMR (300 MHz, $CDCl_3$, 30 °C): $\delta = 7.74$ (d, $^3J(H,H) = 7.9$ Hz, 4H), 7.58, 7.56 (d, $^3J(H,H) = 8.2$ Hz, 8H), 7.35 (dd, $^3J(H,H) = 7.9$ Hz, $^3J(H,H) = 6.8$ Hz, 4H), 6.79 (d, $^3J(H,H) = 6.8$ Hz, 4H), 2.90 (t, $^3J(H,H) = 9.0$ Hz, 4H; α-CH_2), 1.89–1.30 (m, 40H; $-CH_2-$), 0.89 (t, $^3J(H,H) = 6.7$ Hz, 4H; $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C): $\delta = 143.7$, 137.6, 137.1, 136.8, 134.7, 133.6, 130.2, 130.1, 129.2, 128.1, 126.8, 123.6, 36.3, 32.4, 32.0, 30.2, 30.1, 30.0, 29.8, 29.7, 23.1, 14.3; λ_{max} ($CHCl_3$, ε) = 427 (26100), 403 (17000), 313 nm (73200); MS (FD): m/z (%): 813.7 ($[M]^+$, 100); elemental analysis calcd (%) for $C_{62}H_{70}$ (815.23): C 91.34, H 8.66; found C 91.10, H 8.73.

4,4′,7,7′-Tetraphenyldiacenaphtho[1,2-k:1′,2′,k′]diindeno[1,2,3-cd:1′,2′,3′-lm]-perylene (22a): A solution of $FeCl_3$ (2.04 g, 12.6 mmol) in nitromethane (3 mL) was added dropwise to a stirred solution of 7,14-diphenylacenaphtho[1,2-k]-fluoranthene (**4a**) (1.0 g, 2.1 mmol) in CH_2Cl_2 (20 mL). An argon stream was bubbled through the reaction mixture throughout the entire reaction. After stirring for another ten minutes, the reaction was quenched with methanol (40 mL). The precipitate was filtered, washed with methanol (40 mL), and dried under reduced pressure. The crude product was purified by column chromatography on silica gel with toluene to afford blue **22a** (yield: 85%).

M.p. > 300 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 130 °C): $\delta = 7.83$ (d, ^3J(H,H) = 7.7 Hz, 4H), 7.75–7.71 (m, 24H), 7.30 (dd, ^3J(H,H) = 7.7 Hz, 4H), 6.72 (d, ^3J(H,H) = 7.7 Hz, 4H), 6.64 (d, ^3J(H,H) = 7.7 Hz, 4H); λ_{max} ($CHCl_3$, ε) = 601 (112000), 552 (70000), 513 (28300), 341 nm (116000); MS (FD): m/z (%): 952.2 ($[M]^+$, 100); elemental analysis calcd (%) for $C_{76}H_{40}$ (953.15): C 95.48, H 4.52; found C 95.26, H 4.37.

4,4′,7,7′-Tetrakis(4-dodecylphenyldiacenaphtho) [1,2-k:1′,2′,k′]diindeno-[1,2,3-cd:1′,2′,3′-lm]perylene (22b): A solution of $FeCl_3$ (0.6 g, 3.7 mmol) in nitromethane (1 mL) was added dropwise to a stirred solution of 7,14-bis[4-dodecylphenyl]acenaphtho[1,2-k]-fluoranthene (**4b**) (0.5 g, 0.53 mmol) in CH_2Cl_2 (10 mL). An argon stream was bubbled through the reaction mixture throughout the entire reaction. After stirring for another ten minutes, the reaction was quenched with methanol (40 mL). The precipitate was filtered, washed with methanol (40 mL), and dried under reduced pressure. The crude product was purified by column chromatography on silica gel with toluene to afford blue **22b** (yield: 87%).

M.p. > 300 °C. ^{1}H NMR (500 MHz, $C_2D_2C_{l4}$, 130 °C): $\delta = 7.83$ (d, ^3J(H,H) = 7.7 Hz, 4H), 7.66 (d, ^3J(H,H) = 8.0 Hz, 4H), 7.58, 7.51 (d, ^3J(H,H) = 7.6 Hz, 16H), 7.29 (dd, ^3J(H,H) = 7.6 Hz, ^3J(H,H) = 8.0 Hz, 4H), 6.81 (d, ^3J(H,H) = 7.6 Hz, 4H), 6.64 (d, ^3J(H,H) = 7.7 Hz, 4H), 2.90 (t, ^3J(H,H) = 7.5 Hz, 8H; α-CH_2), 1.88–1.31 (m, 80H; C_{alkyl}), 0.88 (t, ^3J(H,H) = 7.7 Hz, $-CH_3$); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 130 °C): $\delta = 143.5$, 137.9, 137.6, 137.4, 136.9, 134.9, 134.0, 130.9, 129.8, 129.6, 128.1, 126.6, 125.7, 124.5, 123.6, 122.2, 36.1, 32.0, 31.5, 29.9, 29.8, 29.7, 29.5, 29.4, 22.7, 13.9; λ_{max} ($CHCl_3$, ε) = 602 (114000), 555 (75000), 517 (29700), 339 nm (119600); MS (FD): m/z (%): 1624.5 ($[M]^+$, 100); elemental analysis calcd (%) for $C_{124}H_{136}$ (1626.44): C 91.57, H 8.420; found C 91.45, H 8.35.

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