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Benzoylperylenedicarboximides: Functional Dyes with Attractive Optical and Electronic Properties

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Abstract: Little is known about benzoylperyleneimides **3**. Two new syntheses of **3** have been worked out, based on boronic acid and organotin intermediates, respectively. These mild methods allow the isolation of the uncyclized precursor **10** and the introduction of various groups R. The purple benzoylperyleneimides **3** are fluorescent dyes and exhibit a high thermal and photochemical stability. The electrochemical properties have been investigated showing that **3** can take up 2 electrons while **10** accepts 4 electrons due to the existence of two weakly interacting aryl units

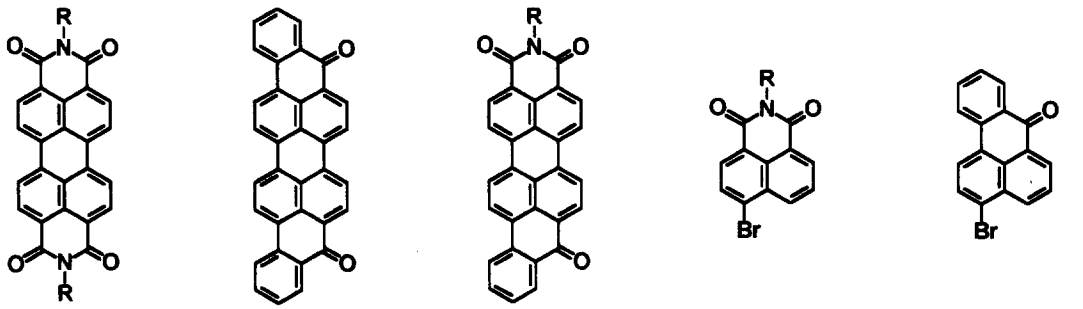
INTRODUCTION

Perylene-3,4:9,10-tetracarboxdiimides (**1**) and violanthrone (**2**) have for long been appreciated due to their outstanding chemical and optical properties.[1] They are characterized by a brilliant color, strong fluorescence and thermal, chemical and photochemical stability.[2] Perylenediimides **1** absorb in the visible range at 525 nm and show a fluorescence quantum yield of nearly 100 %.[3] Besides their application as commercial dyes and pigments, they are used in reprographical processes,[4] in fluorescence solar collectors,[5] in photovoltaic devices,[6] in dye lasers[7] and in molecular switches.[8] Violanthrone (**2**) has been known since the beginning of this century and is frequently used for dyeing cotton fibers. It is generated by potash fusion of benzanthrone and has an intense blue color, showing a maximum absorption at 600 nm and a fluorescence quantum yield of 95 %.[3]

Benzoylperyleneimides **3** can be regarded as a hybrid structure consisting of half a molecule of perylenediimide and half a molecule of violanthrone. Perylenediimides **1** are bright red and well soluble in organic solvents, while violanthrones **2** are dark blue and almost insoluble in common solvents. Benzoylperyleneimides **3** fulfill an important function because their physical and chemical properties should lie between those of **1** and **2**. The combination of two well known fluorescent dyes (perylenediimide and violanthrone) should yield dyes absorbing in a new wavelength range and exhibiting a high fluorescence quantum yield and high stability which makes them promising candidates for various applications.[9]

Benzoylperyleneimides **3** have already been synthesized previously by condensation of chloronaphthalimides and benzanthrone in the presence of sodium alcoholates (125 °C, 4-5 h).[10] Under these conditions, however, only *N*-alkyl-benzoylperyleneimides could be obtained while no *N*-aryl compouds were formed. Moreover, the yields of the *N*-alkyl derivatives were low (R = Me: 47 %; Et: 35 %) and decreased further for larger alkyl groups (R = *cyclo*-C_6H_{11}: 5 %).[10f] Nothing about the properties has been reported except for a UV/Vis spectrum of an impure compound (the given values were λ_{max} = 692 nm, 554 nm). Also, the intermediate coupling product **10** has never been isolated before.

The major purpose of this work was to improve the synthesis of **3** and investigate the optical and electronic properties of this class of dyes. Instead of carrying out the condensation of naphthylimide and benzanthrone under drastic conditions in one step, we first coupled the two aromatic molecules by organometallic coupling reactions and then carried out the cyclization under mild conditions in a separate step. The new syntheses tolerate many different residues at the imide group and enable the synthesis of *N*-aryl-benzoylperyleneimides. The shape of *N*-aryl substituents does not allow for a coplanar arrangement with the rest of the molecule, leading to an increased solubility (by a factor of 5 to 10 in most organic solvents, compared to *N*-alkyl derivatives)[1] and a better processability. Through the present two-step-method we were also able to compare the coupled molecules **10** and the cyclized, ladder type molecules **3** with respect to their optical and electrochemical properties.



1 **2** **3** **4a: X = Br** **4b: X = H** **5a: X = Br** **5b: X = H**

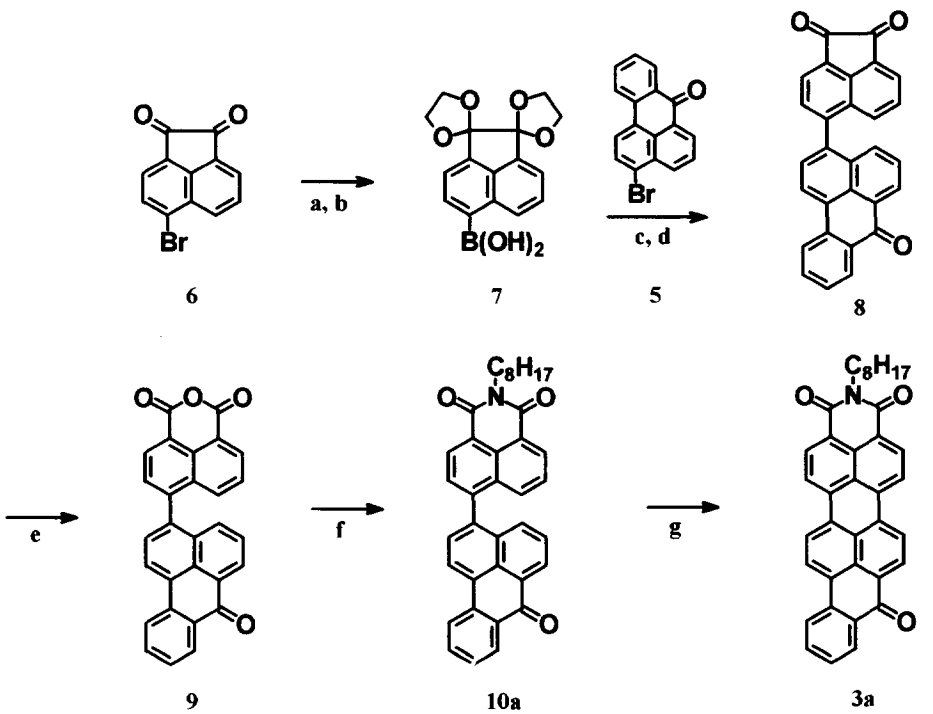
R = Alkyl, Aryl

Fig.1: Formulae of perylenediimide **1**, violanthrone **2**, benzoylperyeleneimide **3**, 4-bromonaphthylimide **4a**, naphthylimide **4b**, 3-bromobenzanthrone **5a**, benzanthrone **5b**.

RESULTS AND DISCUSSION

Suitable starting compounds for the synthesis of **3** are bromonaphthylimide **4a** and bromobenzanthrone **5a**. Not surprisingly, the coupling of the two bromides **4a** and **5a** with a Ni(0) complex[11] led to a mixture of the

three possible coupling products (**4-4**, **4-5** and **5-5**), lowering the yield of the desired mixed product **10**. This non-selective method also required a chromatographic purification of the mixture. In order to improve the selectivity of the synthesis, one would need to establish a heterocoupling method that avoids a mixture of products. The synthesis of **3** via a heterocoupling would first require the transformation of one of the bromides **4** or **5** into the corresponding boronic acid (or another organometallic compound), which is usually done by lithiation or via the Grignard compound. Attempted metallation of **4** or **5** with butyllithium or magnesium, however, resulted in the reduction of the imide structure (**4**) or carbonyl group (**5**) without affecting the bromine. Therefore, we chose a synthetic route with protecting groups (Scheme 1). In this synthetic route, we started from 5-bromoacenaphthenequinone (**6**)[12] and protected the carbonyl groups against nucleophilic attack by forming the ketal with ethyleneglycol (82 %).[13] The resulting ketal was then transformed into the boronic acid **7** (60 %), which was condensed in the following Suzuki coupling[14] with **5** (80 %) and hydrolyzed quantitatively to **8**. Compound **8** was oxidized by air under basic conditions, giving the anhydride **9** (95 %), which was reacted with octyl amine, giving the respective imide **10a** (79 %) and cyclized in a KOH melt to the final compound **3a** (64 %).[15]



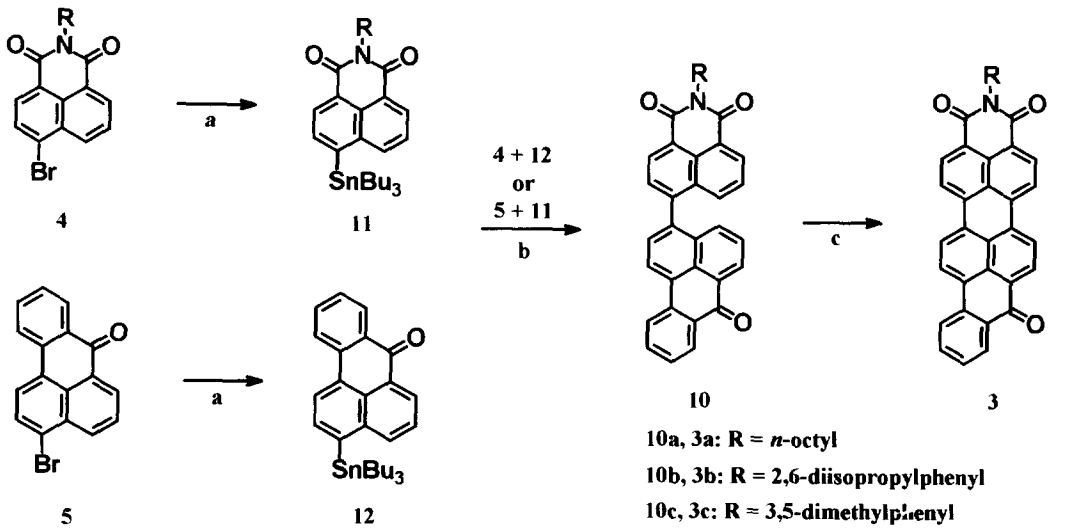
6 7 5 8

9 10a 3a

Scheme 1. Synthesis of benzoylperyleneimide **3a**: reagents, conditions, yields: a) ethyleneglycol, conc. H_2SO_4/ m-xylene, reflux, 4 d/ 82 %; b) 1. *n*-butyllithium/THF, -78 °C; 2. triisopropylborate/THF, -78 °C; 3. H_2O/ 60 %; c) [$Pd(PPh_3)_4$], 2M K_2CO_3/ toluene, reflux, 20 h/ 80 %; d) H_2SO_4, H_2O/ 1-PrOH, reflux, 4 d/ 95 %; e)

KOH, O_2/ 1-PrOH, 60 °C, 4 h/ >95 %; f) *n*-octylamine/ 2-PrOH, reflux, 10 h/ 79 %; g) KOH, ox./ EtOH, 70 °C, 15 min/ 64 %.

While this heterocoupling via a boronic acid is much more selective than the Ni(0) induced mixed homocoupling reaction, it is tedious and involves many steps. Therefore, we continued to search for a short, selective and widely applicable approach to benzoylperyleneimides **3**. We succeeded in transforming the bromide **4** into a stannyl compound that can be condensed with the bromide **5** (Scheme 2). In this synthetic route, 4-bromonaphthyl-1,8-dicarboximide (**4**) is transformed into the tin compound **11** by means of hexabutylditin under Pd(0) catalysis (88 %).[16] Since there are no nucleophilic organometallics employed in this mild method, a protection of the imide group is unnecessary. The tin group was also introduced into bromide **5**, showing the great tolerance of this reaction to functional and electronic variations (imide group in **4**, carbonyl group in **5**). The resulting tin compound can be reacted with a variety of aromatic bromides according to Stille.[17] The coupling of **11** with 3-bromobenzanthrone (**5**) yields **10** (73 %), minor side reactions are the homocoupling of the stannane and the bromides and destannylation (altogether 20 %). The following cyclization to the final compound **3** is achieved again by an oxidative alkali melt.



Scheme 2. Synthesis of **3b**, **3c**: reagents, conditions, yields: a) $Sn_2(Bu)_6$, $[Pd(PPh_3)_4]$/ toluene, reflux, 4 d/ 97-99 %; b) $[Pd(PPh_3)_4]$/ DMF, 90 °C, 4 d/ 77-78 %; c) KOH, ox./ EtOH, 70 °C, 15 min/ **3a**: 64 %, **3b**: 78 %, **3c**: 27 %;

The advantage of the stannane route is that the mild stannylation eliminates the necessity for the protection of the sensitive carbonyl groups and for inert conditions. Both the ketal and the stannane route make

it possible to prepare **3** with different groups (alkyl, aryl) at the imide. This enables subsequent reactions such as hydrolysis and decarboxylation. Furthermore, the ready availability of tin compound **11** permits the coupling with many other chromophoric units.[18]

The FD mass spectra and the ^{1}H and ^{13}C NMR spectra prove the structure of the dark purple compounds **3** unequivocally. The thermal stabilities of **3** are very high — decomposition sets in only above 490 °C, starting at the *N*-bonded groups. The photostability of **3** was estimated by exposing a non-degassed chloroform solution of **3** in quartz cuvettes to UV light (λ = 366 nm) for one week. No significant change in the extinction of **3** was observed after that time, indicating as high a photostability as an equally treated sample of perylenetetracarboxdiimide **1** known for its excellent photochemical stability.[3]

The UV/Vis spectra of the benzoylperyleneimides show absorption bands at 566 nm, lying between those of perylenediimide **1** (525 nm) and violanthrone **2** (600 nm), as expected. The fine structures of the absorption spectra of **1** and **3** are very similar, showing the close structural relationship of the two compounds (Fig. 2). The extinction coefficients of **3** (ε = 47000-69000) are in the same range as those of **1** (ε = 84000) and **2** (ε = 60000).

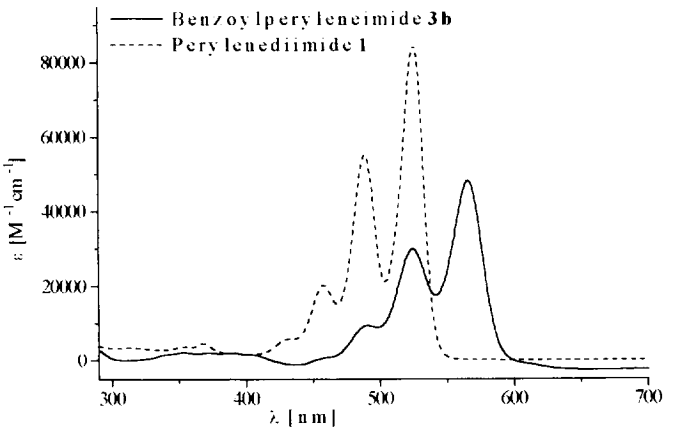


Fig.2. Absorption spectra of **3b** and **1** ($CHCl_3$)

In concentrated sulfuric acid, **3** dissolves with a dark blue color. The absorption bands are very broad and shifted bathochromically by 130 nm (**3b**: λ_{max} = 698 nm) (Fig. 3). The extinction coefficients in sulfuric acid are lower (**3b**: ε = 37000 $M^{-1}cm^{-1}$) than in the chloroform solution (ε = 47000 $M^{-1}cm^{-1}$). The bathochromic shift can be explained by protonation of the carbonyl or imide groups. Besides the band at 698 nm, absorptions at 566 nm and 524 nm can be observed which are due to non-protonated species also present in the equilibrium. After

dilution with water, the benzoylperyleneimides can be recovered unchanged, indicating their high stability to acids and oxidizing agents.

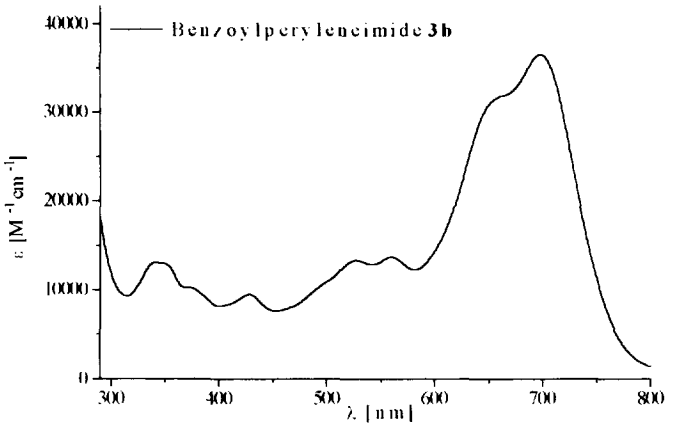


Fig. 3. Absorption spectrum of **3b** in conc. H_2SO_4 (96 %)

In fluorescence spectroscopy (excitation wavelength: λ_{exc} = 520 nm) the emission bands of **3** are shifted bathochromically by 16 nm compared to the absorption bands (**3a**: λ_{em} = 582 nm) (Fig. 4). The small Stokes shift indicates that the geometry of the transition state differs only slightly from that of the ground state. This is due to the rigid structure of the planar molecules.

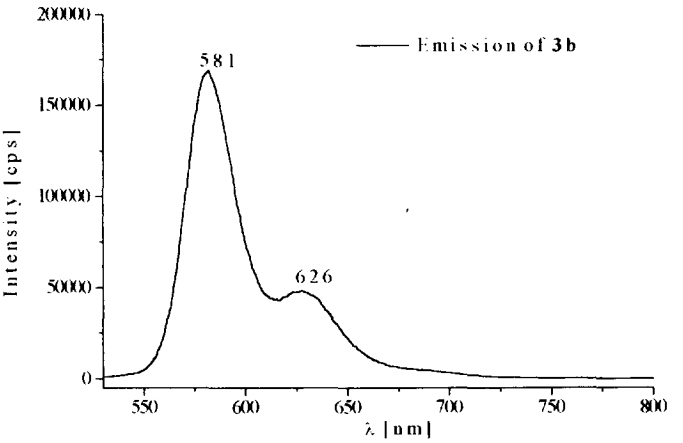


Fig. 4. Emission spectrum of **3b** ($CHCl_3$, excitation wavelength λ_{exc} = 520 nm)

The reduction potentials of **1**, **3b**, **4b**, **5b**, **10b** were examined in order to compare the conjugation in the cyclized species **3** and its precursor **10**. Cyclovoltammetric measurements were performed in dry, degassed THF under an argon atmosphere at -10 °C using a Au electrode as working electrode. The potentials $E_{1/2}$ are given in V vs. ferrocene (Fc), the accuracy is ± 5 mV (table 1).

Table 1: Reduction Potentials of Compounds **10b**, **3b**, **1**, **5b** and **4b**.

	$E_{1/2}^{I}$ [V]	$E_{1/2}^{II}$ [V]	$E_{1/2}^{III}$ [V]
Benzanthronyl-naphthylimide **10b**	-1.67	-1.82	-2.61
Benzoylperyleneimide **3b**	-1.05	-1.29	
Perylenediimide **1**	-1.00	-1.35	
Benzanthrone **5b**	-1.78	-2.48	
Naphthylimide **4b**	-1.86		

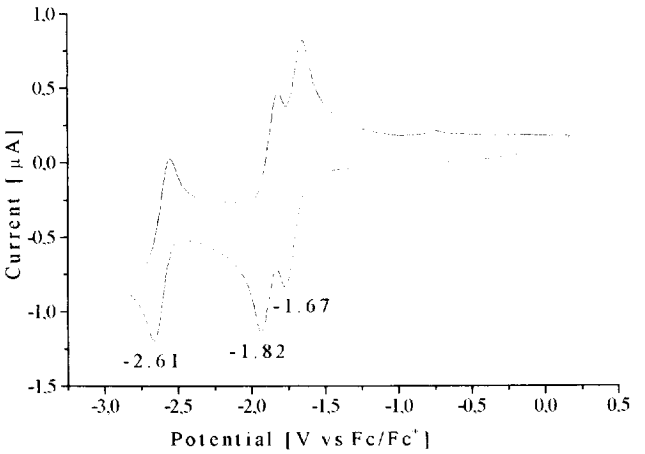


Fig. 5. Cyclic voltammogram of the reduction of **10b** in THF, 100 mV/s

The most striking result is that benzanthronylperyleneimide **10b** can accept three electrons reversibly ($E_{1/2}$ = -1.67, -1.82, -2.61 V) (Fig. 5) and a fourth electron that gives rise to subsequent reactions (E_P = -2.84 V). This extraordinary high concentration of negative charges on such a small molecule indicates that the two subunits of the molecule act as more or less independant redox centers. This observation is in complete agreement with our recent redox studies on oligonaphthylenes and related oligomers.[19]

The reduction properties of benzanthrone **5b** and naphthylimide **4b** support this conclusion and help to assign the potentials of **10b**. Benzanthrone **5b** takes up two electrons reversibly ($E_{1/2}$ = -1.78, -2.48 V) while naphtylimide **4b** accepts only one electron reversibly ($E_{1/2}$ = -1.86 V) and the second one irreversibly (E_P = -2.62 V). Since the first reduction of benzanthrone **5b** ($E_{1/2}$ = -1.78 V) occurs at a higher potential than that of **4b** ($E_{1/2}$ = -1.86 V), the first electron transfer of **10b** ($E_{1/2}$ = -1.67 V) occurs into the benzanthrone subunit while the second reduction affects the naphthylimide subunit ($E_{1/2}$ = -1.86 V). The second reduction of benzanthrone **5b** ($E_{1/2}$ = -2.48 V) corresponds to the third reduction step of **10b** ($E_{1/2}$ = -2.61 V), while the second irreversible reduction of naphthylimide **4b** (E_P = -2.62 V) corresponds to the fourth reduction step of **10b** (E_P = -2.84 V).

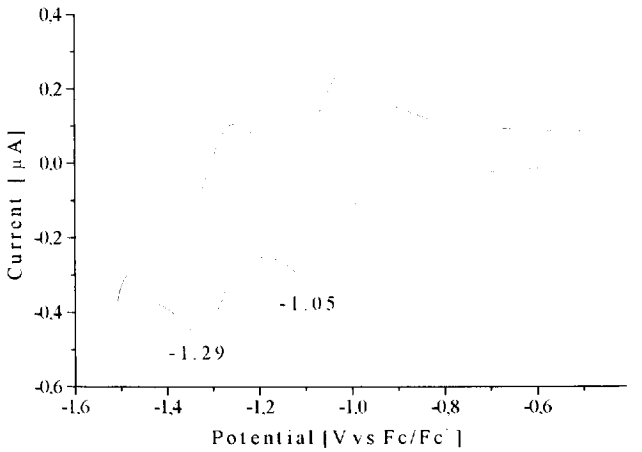


Fig. 6. Cyclic voltammogram of the reduction of **3b** in THF, 100 mV/s

The cyclised benzoylperyleneimide **3b**, on the other hand, exhibits only two reduction steps at a much lower potential than **10b** ($E_{1/2}$ = -1.05, 1.29 V), since the two charges can strongly interact in the planar extended π-system (Fig. 6). The reduction properties of **3b** can be compared to those of perylenediimide **1** (R = 2,6-Diisopropylphenyl), which also shows two reversible reduction steps ($E_{1/2}$ = -1.00, -1.35 V). The potentials of both compounds **1** and **3b** have roughly the same value due to the similar perylene-based structure. The difference between the first and the second potential, however, is smaller for **3b** ($\Delta E_{1/2}$ = -0.24 V) than for **1** ($\Delta E_{1/2}$ = -0.35 V), indicating that the two charges can be better stabilized in case of **3b** than in case of **1**.

We have described two new selective routes to benzoylperyleneimides **3** that allow us to introduce various substituents (alkyl and aryl) for improving on the solubility of the chromophores. Benzoylperyleneimides **3** are very stable, dark purple compounds exhibiting a maximum absorption band at 566 nm in the UV/Vis spectra. The spectroscopic properties of **3** lie in the spectral range between the

perylenediimides **1** (red) and violanthrone **2** (blue). The reduction of **3** and its uncyclized precursor **10** did not only reveal information about the charging mechanism and its relationship to the molecular structure in solution, but also showed the strong charge storing capacity of **10**.

EXPERIMENTAL

All commercially available reagents and solvents were used without further purification unless otherwise stated. THF was distilled from potassium, DMF from calcium hydride. Column chromatography was performed on silica gel (Merck, Geduran Si 60), mesh size 70-230. IR spectra (KBr method) were recorded on a Nicolet FT-IR 320 spectrometer, UV visible spectra were taken on a Perkin-Elmer Lambda 9 spectrometer. NMR spectra were recorded on AMX 500, Bruker AC 300 and Varian Gemini 200 spectrometers (at room temperature, unless otherwise noted), the operating frequencies being given with the data. FD mass spectra were recorded on a VG ZAB 2-SE-FDP spectrometer. For the cyclovoltammetric examination of **3b** (in THF, with Bu_4NPF_6 added) a Potentiostat/Galvanostat PAR Model 173 was used. Elemental analyses were performed by the Department of Chemistry and Pharmacy of the University of Mainz.

4-(3-Benzanthronyl)-acenaphthenequinone (**8**). A solution of 4-bromoacenaphthenequinone (**6**) (15.0 g, 57 mmol), ethyleneglycol (30.0 g, 480 mmol) and p-toluenesulfonic acid (200 mg, 1 mmol) in m-xylene (700 ml) was refluxed for 4 days. The resulting water was removed from the reaction by means of molecular sieve (4A). Every 12 h more ethyleneglycol (20 g, 322 mmol) and p-toluenesulfonic acid (200 mg, 1 mmol) were added to the mixture. After cooling, the solution was washed three times with aqueous $NaHCO_3$ (1 M). The solvent was evaporated and the residue recrystallized from 800 ml petroleum ether to give white ketal (16.4 g, 82 %). (The resulting ketal is a mixture of two isomers that can both be used in the subsequent reaction. For reasons of simplicity only one form is shown).

To a solution of the ketal (3.0 g, 8.6 mmol) in THF (80 ml) at -78 °C was added butyllithium (6.5 ml, 10.4 mmol, 1.6 M in hexane). After stirring for 2 h the solution was transferred to a solution of triisopropylborate (8.1 g, 43.0 mmol) in THF (200 ml) at -78 °C. After 3 h at this temperature, the solution was allowed to warm to room temperature, the solvent evaporated and the residue dissolved in methylene chloride and washed with water. The solvent was evaporated again and the residue recrystallized from toluene (20 ml) to give the boronic acid **7** (1.6 g, 60 %). Due to the ease of hydrolysis of the ketal function, the product was not purified further and used in the following coupling.

3-Bromobenzanthrone (**5a**) (0.56 g, 1.8 mmol), the boronic acid **7** and $Pd(PPh_3)_4$ (55 mg, 3 mol%) were refluxed in a mixture of toluene (70 ml) and aqueous K_2CO_3 solution (2 N, 20 ml) for 15 h. The organic phase was seperated, the toluene evaporated and the residue purified by column chromatography (silica gel,

methylene chloride) to give the coupled ketal (960 mg, 80 %). The ketal was hydrolyzed by refluxing it (0.5 g, 1.0 mmol) in a mixture of 1-propanol (100 ml), water (10 ml) and sulfuric acid (0.3 ml) for 4 days. The solution was poured onto 300 ml of water containing $NaHCO_3$ (3.0 g) and the precipitate removed by filtration to give 4-(3-benzanthronyl)-acenaphthenequinone (**8**). It was further purified by recrystallization from ethanol to give pure **8** (390 mg, 95 %). — m.p. 170 °C (dec.). — IR (KBr): ν = 2960, 2926, 1730 (C=O), 1701 (C=O), 1662, 1606, 1592, 1577, 1359, 1246, 812 cm^{-1}. — UV/Vis ($CHCl_3$): λ_{max} (ε) = 397 nm (21100), 313 (20200). — ^1H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): δ = 9.73 (d, J = 7.2 Hz, 1 H), 8.59 (d, J = 7.6 Hz, 1 H), 8.46 (d, J = 7.8 Hz, 1 H), 8.41 (d, J = 8.0 Hz, 1 H), 8.23 (d, J = 7.1 Hz, 1 H), 8.10 (d, J = 7.0 Hz, 1 H), 7.92 (d, J = 7.0 Hz, 1 H), 7.86-7.75 (m, 4 H), 7.69 (t, J = 7.6 Hz, 1 H), 7.61 (m, 2 H).— ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 120 °C): δ = 188.1, 179.8, 183.3, 146.1, 143.9, 137.9, 135.8, 134.0, 133.0, 131.8, 131.6, 131.0, 130.8, 130.6, 130.3, 129.1, 129.0, 128.9, 128.8, 128.6, 128.5, 128.2, 128.1, 127.9, 127.4, 123.9, 123.5, 122.6, 122.1. — FD-MS (8 kV): m/z: 410.0 (100 %) [M^+]. — $C_{29}H_{14}O_3$ (661.77): calcd. C 84.87, H 3.44; found C 84.48, H 3.80.

N-Octyl-4-(3-benzanthronyl)-naphthalene-1,8-dicarboximide (**10a**). A solution of **8** (300 mg, 0.7 mmol) and KOH (5.0 g) in 1-propanol (200 ml) was heated in the presence of air to 60 °C for 4 h. The solution was poured onto HCl (600 ml, 1 N) and the precipitate removed by filtration to give **9**.

A solution of **9** (300 mg, 0.7 mmol) and *n*-octylamine (0.3 g, 2.2 mmol) in isopropanol (50 ml) was refluxed for 6 h. The yellow solution was poured onto 200 ml of 1 M HCl and the precipitate removed by filtration and recrystallized from ethanol (150 ml) to give **10a** (310 mg, 79 %). — m.p. 175 °C (dec.). — IR (KBr): ν = 2958, 2922, 1699 (C=O), 1660 (C=O), 1590, 1577, 1356, 1245, 1234, 812, 787, 757 cm^{-1}. — UV/Vis ($CHCl_3$): λ_{max} (ε) = 394 nm (37700), 343 (32400), 319 (29800). — ^1H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): δ = 8.68 (dd, J = 7 Hz, 1 H), 8.62 (d, 2 H), 8.54 (m, 2 H), 8.44 (dd, 1 H), 8.37 (d, 1 H), 7.80-7.63 (m, 5 H), 7.59-7.51 (m, 3 H), 4.11 (m, 2 H), 1.30 (m, 12 H), 0.79 (m, 3 H). — ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 120 °C): δ = 184.0, 164.4, 164.2, 144.3, 139.0, 136.1, 134.1, 133.5, 132.8, 132.2, 131.7, 131.5, 131.2, 130.9, 130.4, 129.5, 129.2, 129.0, 128.9, 128.6, 128.4, 128.3, 127.8, 127.6, 127.5, 127.3, 124.0, 123.6, 123.2, 123.0, 41.0, 32.1, 30.0, 29.7, 28.5, 27.6, 27.1, 23.0, 14.5. — FD-MS (8 kV): m/z: 537.3 (100 %) [M^+]. — $C_{37}H_{31}NO_3$ (537.00): calcd. C 82.66, H 5.81, N 2.60; found C 82.27, H 5.99, N 2.30.

N-Octyl-9-oxo-9H-dibenzo[de,rst]pentaphene-3,4-dicarboximide or N-Octyl-9(C'O),10-benzoylperylene-3,4-dicarboximide (**3a**). Compound **10a** (250 mg), KOH (15.0 g) and ethanol (40 ml) were heated to 70 °C for 30 min. The brown melt was poured onto 2 M HCl (300 ml), the precipitate removed by filtration, washed twice with water and extracted twice with boiling ethanol (100 ml) and once with chloroform (30 ml) to dissolve the impurities to give **3a** (160 mg, 64 %). — m.p. > 360 °C; — IR (KBr): ν = 2959, 1702 (C=O), 1656 (C=O), 1585, 1378, 1357, 1330, 1304, 1248, 841, 809, 751 cm^{-1}. — UV/Vis ($CHCl_3$): 564 nm (69200),

522 (44100), 487 (17100); — fluorescence emission (exc.: 520 nm): 582 nm. — ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 120 °C): δ = 8.60 (d, J = 7.0 Hz, 1 H), 8.50-8.30 (m, 8 H), 8.13 (d, J = 7.0 Hz, 1 H), 7.66 (m, 1 H), 7.50 (m, 1 H), 4.12 (m, 2 H), 1.75 (m, 2 H), 1.44-1.27 (m, 10 H), 0.86 (t, 3 H); — Due to the low solubility of **3a** no ^{13}C NMR spectrum was recorded. — FD-MS (8 kV): m/z: 535.0 (100 %) [M$^+$]. — $C_{37}H_{29}NO_3$ (535.00): calcd. C 82.97, H 5.46, N 2.61; found C 82.57, H 5.55, N 2.20.

N-(2,6-Diisopropylphenyl)-4-(tributyltin)naphthalene-1,8-dicarboximide (**11b**). A solution of **4b** (5.0 g, 11.46 mmol), hexabutylditin (13.10 g, 22.58 mmol) and $Pd(PPh_3)_4$ (0.05 g, 0.05 mmol, 0.3 mol%) in toluene (250 ml) was refluxed for 4 days. The solvent was evaporated and the residue purified by column chromatography (silica gel, methylene chloride) to give **11b** as a yellow oil (7.19 g, 97 %). — IR (KBr): ν = 2958, 1699 (C=O), 1663 (C=O), 1590, 1463, 1355, 1292, 1245, 838, 814, 804, 750 cm^{-1}. — UV/Vis ($CHCl_3$): 346 nm (18800), 362 (16500); —^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.66 (d, J = 7.4 Hz, 1 H), 8.55 (d, J = 7.2 Hz, 1 H), 8.25 (d, J = 7.2 Hz, 1 H), 7.88 (d, J = 7.4 Hz, 1 H), 7.84 (d, J = 7.8 Hz, 1 H), 7.49 (t, J = 7.8 Hz, 1 H), 7.35 (d, J = 7.8 Hz, 2 H), 2.79 (h, J = 7 Hz, 2 H), 1.69-1.56 (m, 6 H), 1.44-1.33 (m, 6 H), 1.31-1.27 (m, 6 H), 1.20 (d, J = 7 Hz, 12 H), 0.92 (t, J = 7 Hz, 9 H); — ^{13}C NMR (50 MHz, $C_2D_2Cl_2$): δ = 165.2, 164.7, 155.1, 140.1, 138.0, 137.7, 136.3, 135.7, 132.0, 131.1, 130.5, 127.0, 126.8, 126.7, 124.0, 123.7, 29.3, 29.2, 27.3, 24.0, 13.6, 10.8; — FD-MS (8 kV): m/z: 647.5 (100 %) [M$^+$]. — $C_{36}H_{49}NO_2Sn$ (646.48): calcd. C 66.88, H 7.64, N 2.17; found C 69.05, H 7.68, N 2.20.

N-(3,5-Dimethylphenyl)-4-(tributyltin)naphthalene-1,8-dicarboximide (**11c**). A solution of **4c** (4.13 g, 10.86 mmol), hexabutylditin (13.11 g, 22.60 mmol) and $Pd(PPh_3)_4$ (0.05 g, 0.05 mmol, 0.3 mol%) in toluene (250 ml) was refluxed for 4 days. The solvent was evaporated and the residue purified by column chromatography (silica gel, methylene chloride) to give **11c** as a yellow oil (6.38 g, 99 %). — IR (KBr): ν = 2958, 1699 (C=O), 1663 (C=O), 1590, 1463, 1355, 1292, 1245, 838, 814, 804, 750 cm^{-1}. — UV/Vis ($CHCl_3$): 364 nm (17000), 348 (18400); —^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.68 (d, J = 7.3 Hz, 1 H), 8.57 (d, J = 7.0 Hz, 1 H), 8.23 (d, J = 7.2 Hz, 1 H), 7.99 (d, J = 7.0 Hz, 1 H), 7.81 (d, J = 7.8 Hz, 1 H), 7.13 (s, 1 H), 6.97 (s, 2 H), 2.42 (s, 6 H, Ar-CH_3), 1.69-1.55 (m, 6 H), 1.48-1.29 (m, 12 H), 0.92 (t, J = 7.2 Hz, 9 H); — ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.3, 164.9, 155.3, 139.5, 138.2, 136.9, 136.5, 135.9, 131.6, 131.0, 130.3, 127.1, 126.7 (2C), 124.2, 123.3, 29.6, 27.8, 21.8 (Ar-CH_3), 14.1, 11.4; — FD-MS (8 kV): m/z: 589.4 (100 %) [M$^+$]. — $C_{32}H_{41}NO_2Sn$ (590.40): calcd. C 65.10, H 7.00, N 2.37; found C 65.05, H 6.68, N 2.20.

3-(Tributyltin)benzanthrone (**12**). A solution of **5a** (4.50 g, 14.60 mmol), hexabutylditin (16.80 g, 28.96 mmol) and $Pd(PPh_3)_4$ (0.05 g, 0.05 mmol, 0.3 mol%) in toluene (200 ml) was refluxed for 2 days. The solvent was evaporated and the residue purified by column chromatography (silica gel, methylene chloride) to give **12**

as a yellow oil (7.55 g, 99 %). — UV/Vis ($CHCl_3$): 423 nm (9800), 402 (11800); — ^1H NMR (200 MHz, $CDCl_3$): δ = 8.80 (dd, J = 7.5 Hz, J = 1.1 Hz, 1 H), 8.52 (dd, J = 7.8 Hz, J = 1.4 Hz, 1 H), 8.40 (d, J = 7.3 Hz, 1 H), 8.38 (d, J = 8.1 Hz, 1 H), 8.17 (dd, J = 8.1 Hz, J = 1.1 Hz, 1 H), 7.89-7.70 (m, 3 H), 7.55 (t, J = 7.5 Hz, 1 H), 1.69-1.52 (m, 6 H), 1.46-1.22 (m, 12 H), 0.88 (t, J = 7.3 Hz, 9 H); — ^{13}C NMR (50 MHz, $CDCl_3$): δ = 184.3, 148.6, 139.3, 137.9, 137.1, 136.3, 133.8, 131.6, 129.9, 129.8, 128.9, 128.6, 128.5, 127.3, 126.7, 123.6, 123.4, 29.6, 27.8, 14.1, 11.3; — FD-MS (8 kV): m/z: 520.6 (100 %) [M^+]. — $C_{29}H_{36}OSn$ (519.32): calcd. C 67.07, H 6.99; found C 67.25, H 6.65.

N-(2,6-Diisopropylphenyl)-4-(3-benzanthronyl)naphthalene-1,8-dicarboximide (**10b**). A solution of **4b** (1.19 g, 2.7 mmol), 3-(tributyltin)benzanthrone (**12**) (1.72 g, 3.3 mmol) and $Pd(PPh_3)_4$ (20 mg, 0.02 mmol, 1 mol%) in DMF (130 ml) was heated to 120 °C for 15 h. The solvent was evaporated, the residue taken up in methylene chloride, washed with 6 M HCl and purified by column chromatography on silica gel (methylene chloride) to give **10b** as a yellow solid (1.17 g, 77 %). — m.p. > 360 °C; — IR (KBr): ν = 2962, 1698 (C=O), 1655 (C=O), 1592, 1575, 1358 cm^{-1}. — UV/Vis ($CHCl_3$): 396 nm (20600), 357 (15900), 343 (16800), 322 (15500); — fluorescence emission (exc.: 396 nm): 466 nm. — ^1H NMR (500 MHz, $CDCl_3$): δ = 8.85 (d, J = 6.5 Hz, 1 H), 8.84 (d, J = 7.4 Hz, 1 H), 8.72 (d, J = 7.1 Hz, 1 H), 8.66 (d, J = 7.7 Hz, 1 H), 8.59 (dd, J = 7.7 Hz, J = 0.8 Hz, 1 H), 8.47 (d, J = 8.1 Hz, 1 H), 7.91 (m, 2 H), 7.85 (m, 2 H), 7.78 (d, J = 7.5 Hz, 1 H), 7.67 (m, 3 H), 7.52 (t, J = 7.7 Hz, 1 H), 7.38 (m, 2 H), 2.85 (m, 2 H), 1.23 (m, 12 H); — ^{13}C NMR (125 MHz, $CDCl_3$): δ = 184.0, 164.4, 164.2, 146.0, 145.9, 144.7, 138.9, 136.1, 134.0, 133.4, 133.1, 132.4, 132.2, 131.8, 131.4, 131.3, 131.0, 130.4, 129.8, 129.5, 129.3, 129.2, 129.1, 128.8, 128.6, 128.4, 128.1, 127.6, 127.5, 124.3, 123.7, 123.5, 123.3, 123.1, 29.5 (CH), 24.3 (CH_3); — FD-MS (8 kV): m/z: 585.2 (100 %) [M^+]. — $C_{41}H_{31}NO_3$ (585.70): calcd. C 84.08, H 5.34, N 2.39; found C 84.41, H 5.20, N 2.31.

N-(3,5-Dimethylphenyl)-4-(3-benzanthronyl)naphthalene-1,8-dicarboximide (**10c**). A solution of **11c** (2.10 g, 3.55 mmol), 3-bromobenzanthrone (**5a**) (1.10 g, 3.55 mmol) and $Pd(PPh_3)_4$ (20 mg, 0.02 mmol, 1 mol%) in DMF (100 ml) was heated to 90 °C for 5 days. The solvent was evaporated, the residue taken up in methylene chloride, washed with 6 M HCl and purified by column chromatography on silica gel (methylene chloride) to give **10c** as a yellow solid (1.46 g, 78 %). — m.p. 345 °C (dec.); — IR (KBr): ν = 2960, 1699 (C=O), 1657 (C=O), 1591, 1576, 1357 cm^{-1}. — UV/Vis ($CHCl_3$): 397 nm (21700), 358 (16500), 343 (17000), 322 (16100); — ^1H NMR (200 MHz, $CDCl_3$): δ = 8.85-8.77 (m, 2 H), 8.71-8.55 (m, 3 H), 8.46 (d, J = 7.9 Hz, 1 H), 7.90-7.74 (m, 5 H), 7.70-7.59 (m, 3 H), 7.14 (s, 1 H), 6.99 (s, 2 H), 2.42 (s, 6 H, CH_3); — ^{13}C NMR (50 MHz, $CDCl_3$): δ = 184.2, 164.8, 164.7, 144.9, 139.7, 139.0, 136.3, 135.6, 134.2, 134.1, 133.5, 133.3, 132.6, 132.3, 132.0, 131.6, 131.4, 131.2, 130.6, 130.5, 129.7, 129.3, 129.0, 128.8, 128.6, 128.3, 127.8, 127.6, 126.6

(2 C), 123.9, 123.7, 123.5, 21.8 (CH_3); — FD-MS (8 kV): m/z: 529.5 (100 %) [M^+]. — $C_{37}H_{23}NO_3$ (529.60): calcd. C 83.91, H 4.38, N 2.64; found C 84.21, H 4.62, N 2.35.

N-(2,6-Diisopropylphenyl)-9-oxo-9H-dibenzo[de,rst]pentaphene-3,4-dicarboximide or N-(2,6-Diisopropylphenyl)-9(10),10-benzoylperylene-3,4-dicarboximide (**3b**). Compound **10b** (508 mg, 0.87 mmol), KOH (6.9 g) and ethanol (14 ml) were heated to 70 °C for 20 min. The brown melt was poured onto water, acidified with 2 M HCl, the precipitate removed by filtration, washed twice with water and twice with boiling ethanol and purified by column chromatography on silica gel, eluting the unchanged material with methylene chloride and then switching to THF to elute **3b** (396 mg, 78 %). — m.p. > 360 °C; — IR (KBr): ν = 2959, 1702 (C=O), 1656 (C=O), 1585, 1378, 1357, 1330, 1304, 1248, 841, 809, 751 cm^{-1}. — UV/Vis ($CHCl_3$): 566 nm (47400), 524 (36200), 490 (14300); — fluorescence emission (exc.: 520 nm): 581 nm. — ^1H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): δ = 8.83 (d, J = 8.0 Hz, 1 H), 8.72-8.68 (m, 3 H), 8.66-8.55 (m, 3 H), 8.51 (d, J = 7.9 Hz, 1 H), 7.79 (t, J = 7.6 Hz, 1 H), 7.72-7.60 (m, 2 H), 7.44 (t, J = 7.8 Hz, 1 H), 7.30 (d, J = 7.9 Hz, 2 H), 2.77 (m, J = 6.8 Hz, 2 H), 1.18 (d, J = 6.8 Hz, 12 H); — ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 120 °C): δ = 183.1, 164.0, 163.9, 146.0, 136.3, 136.0, 135.5, 135.3, 134.1, 132.4, 132.2, 131.3, 130.9, 130.8, 130.4, 130.3, 129.7, 129.5, 129.4, 129.2, 129.0, 128.4, 127.9, 126.5, 125.3, 124.4, 124.2, 124.0, 123.8, 123.3, 123.2, 122.4, 122.3, 29.5 (CH), 24.5 (CH_3); — FD-MS (8 kV): m/z: 583.5 (100 %) [M^+]. — $C_{41}H_{29}NO_3$ (583.69): calcd. C 84.37, H 4.66, N 2.40; found C 84.77, H 4.43, N 2.28.

N-(3,5-Dimethylphenyl)-9-oxo-9H-dibenzo[de,rst]pentaphene-3,4-dicarboximide or N-(3,5-Dimethylphenyl)-9(10),10-benzoylperylene-3,4-dicarboximide (**3c**). Compound **10c** (270 mg, 0.51 mmol), KOH (5.0 g) and ethanol (10 ml) were heated to 70 °C for 10 min. The brown melt was poured onto water, acidified with 2 M HCl, the precipitate removed by filtration, washed twice with water and twice with boiling ethanol and purified by column chromatography on silica gel, eluting the unreacted educt with methylene chloride and then switching to THF to elute **3c** (71 mg, 27 %). — m.p. > 360 °C; — IR (KBr): ν = 2959, 1702 (C=O), 1656 (C=O), 1585, 1378, 1357, 1330, 1304, 1248, 841, 809, 751 cm^{-1}. — UV/Vis ($CHCl_3$): 566 nm (53100), 525 (40200), 491 (16500); — fluorescence emission (exc.: 520 nm): 583 nm. — ^1H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): δ = 8.85 (d, J = 7.9 Hz, 1 H), 8.76-8.50 (m, 6 H), 8.38 (d, J = 7.8 Hz, 1 H), 7.91-7.56 (m, 4 H), 7.13 (s, 1 H), 6.95 (s, 2 H), 2.42 (s, 6 H, CH_3); — Due to the low solubility of **3c** no ^{13}C NMR spectrum was recorded. — FD-MS (8 kV): m/z: 527.3 (100 %) [M^+]. — $C_{37}H_{21}NO_3$ (527.58): calcd. C 84.23, H 4.01, N 2.65; found C 84.57, H 4.38, N 2.30.

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