

Anthracene Carboxyimides and Their Dimers

Heinz Langhals,* Gertrud Schönmann, and Kurt Polborn^[a]

Abstract: Soluble anthracenedicarboxyimides have been prepared and undergo a photodimerisation of the anthracene skeleton, which is important for their application as antitumour agents, such as azonafides. Reaction under strongly alkaline conditions causes C–C coupling to form soluble dimeric fluorescent dyes with bathochromic absorption and fluorescence in the NIR region. These dyes are of special interest because of their absorption at longer wavelengths.

Keywords: anthracene derivatives • antitumor agents • dyes/pigments • fluorescence spectroscopy • photochemistry

Introduction

Anthracene-1,9-dicarboxyimides **6** are of special interest as basic structural elements of antitumour agents, such as azonafides.^[1] The chemical behaviour of these substances has not yet attracted interest in spite of their importance in medical applications and neither has their strong fluorescence or photostability. Furthermore, dicarboxyimides **6** are suitable starting materials for the synthesis of Aceanthrene Green dyes (**7** and **8**),^[2] which are used as an emerald-green textile dye (C.I. 71125) and a green pigment.^[3] These dyes are of special interest because of their absorption at longer wavelengths. On the other hand, the poor solubility of anthracene and its dimeric derivatives is an important obstacle to their investigation and application in homogeneous solution. Thus, soluble derivatives would be a significant development.

Results and Discussion

Anthracene (**1**) is a suitable starting material for the synthesis of **6**. The complete synthesis is reported because of some improvements and corrections. We treated anthracene (**1**)

with oxalyl chloride and aluminium chloride in a ratio of 1.0:5.2:2.0 following the procedure of Liebermann and Zsuffa^[4] to prepare aceanthrenequinone^{**} (**2**; Scheme 1). This method proved to give better results than other literature procedures.^[5] The reported sublimation of **2** cannot be recommended for purification.^[4,5a] However, **2** remains as a very pure, bright-orange, shiny and only sparingly soluble solid with an intense solid-state fluorescence if anthroic acid, formed as a byproduct of the synthesis, is completely removed by means of an alkali. Compound **2** is of interest as a fluorescent pigment (for its UV/Vis spectrum, see Figure 1).

Quinone **2** was condensed with hydroxylamine following a reported procedure to give the regioisomeric oximes **4** and **5** as a 45:55 mixture.^[4] The recrystallisation procedure reported for this mixture cannot be recommended for purification.^[4,5f] The regioisomers were used in the subsequent reaction without separation because interconversion was expected with the tautomeric nitroso compounds as intermediates (c.f. ref. [6]). The mixture of **4** and **5** exhibits a strong fluorescence both in solution and in the solid state (see the complicated solid-state fluorescence spectrum in Figure 2). The oximes can be used as fluorescent pigments because of their rather low solubility in the majority of solvents. Beckmann rearrangement of the mixture with concentrated sulfuric acid led to **6a** in a yield of 73% and so separation of the isomeric oximes proved unnecessary.

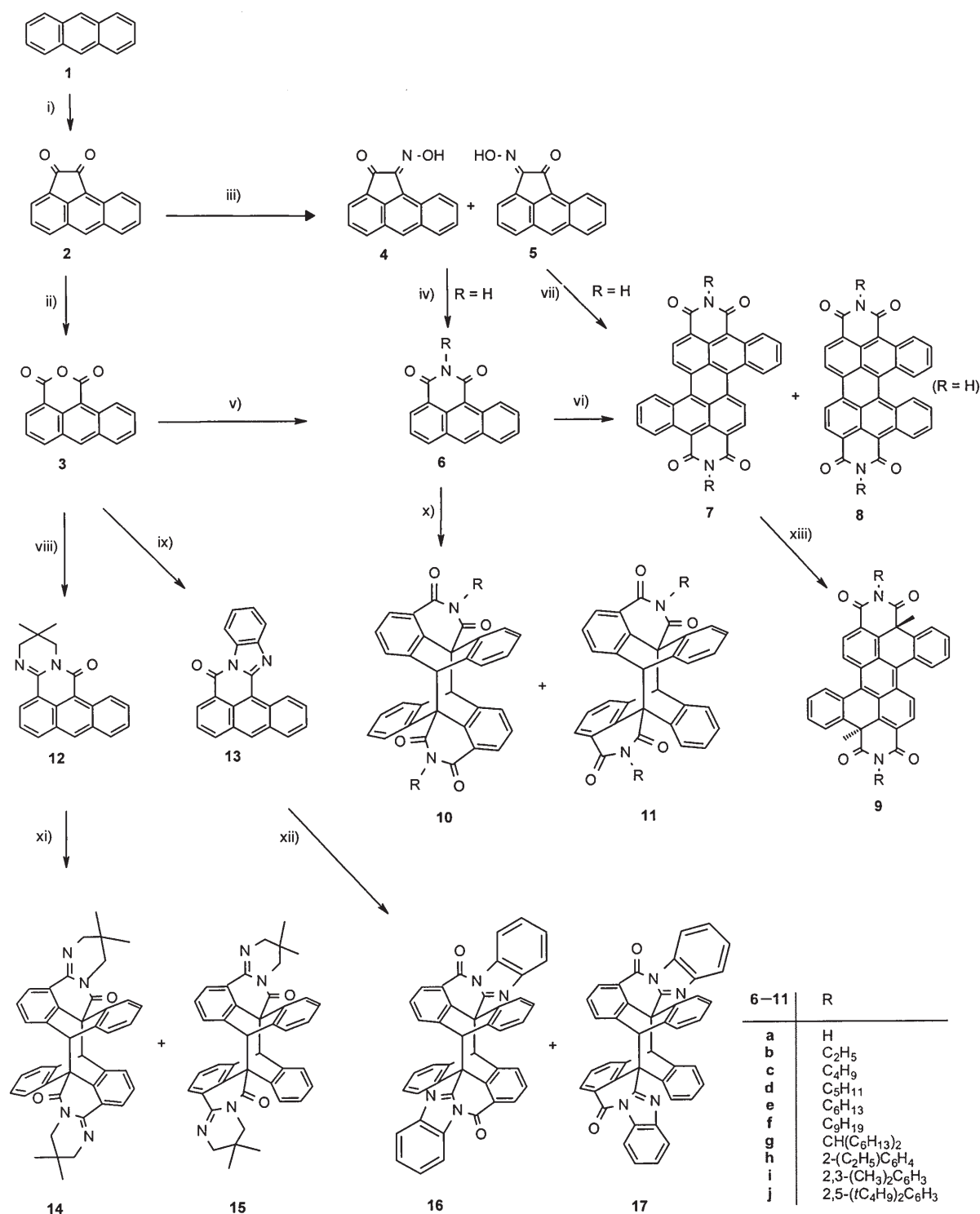
Compound **2** can be oxidised to anhydride **3** as an alternative route for the preparation of the anthracenedicarboxyimides. Anhydride **3** is highly fluorescent both in solution

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[**] The IUPAC name for aceanthrenequinone is aceanthrylene-1,2-dione.



Scheme 1. Synthesis of anthracene and Aceanthrene Green derivatives. Reagents and conditions: i) (COCl)₂, AlCl₃; ii) H₂O₂; iii) NH₂OH; iv) H₂SO₄; v) RNH₂; vi) and vii) KOH; viii) (CH₃)₂C(CH₂NH₂)₂; ix) 1,2-C₆H₄(NH₂)₂; x), xi) and xii) *hν*; xiii) 1. KOH; 2. CH₃I.

(81 % fluorescence quantum yield in chloroform) and in the solid state. The orange fluorescence of the solid has not been reported before and makes the substance of special interest as a fluorescence pigment because of its low solubility and rather high photostability (Figure 3). Dicarboxyimide

6a was prepared by using a modified literature procedure;^[2b,c] anhydride **3** was evaporated several times with concentrated ammonia, however, traces of the starting material were difficult to remove. Thus, the synthesis of **6a** by the Beckmann rearrangement of **4** and **5** is preferred.

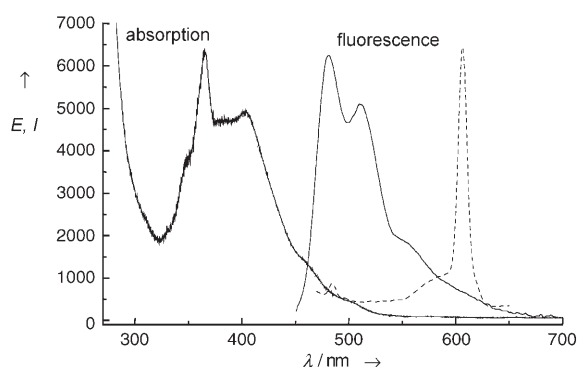


Figure 1. UV/Vis absorption (left) and fluorescence spectra (middle) of **2** in chloroform. Dashed line: solid-state fluorescence spectrum.

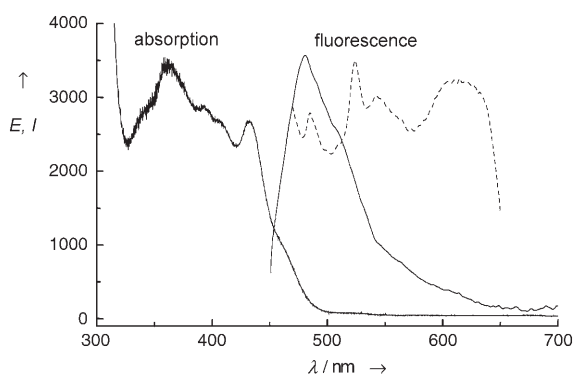


Figure 2. UV/Vis absorption (left) and fluorescence spectra (middle) of the mixture of **4** and **5** in chloroform. Dashed line: Solid-state fluorescence spectrum.

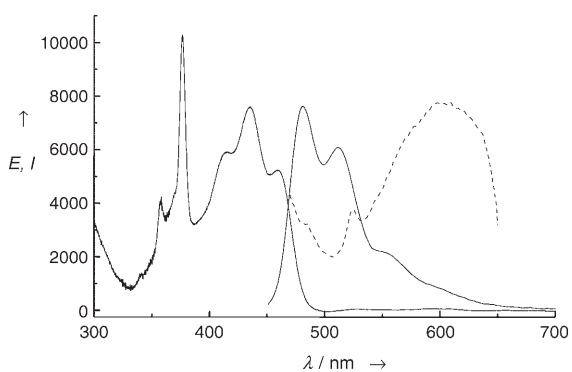


Figure 3. UV/Vis absorption (left) and fluorescence spectra (middle) of **3** in chloroform. Dashed line: Solid-state fluorescence spectrum.

However, anhydride **3** can be used as a starting material for the general preparation of **6** by condensation with primary amines. Ethyl derivative **6b** was prepared from **3** and an aqueous ethylamine solution by a modified procedure;^[2d] the butyl, pentyl and hexyl derivatives (**6c**, **6d** and **6e**, respectively) were also obtained from **3** and the pure amines. The other derivatives of **6** were synthesised from **3** and the corresponding amines in the presence of imidazole.^[7] The dicarboxyimides are more sensitive towards mineral acids

than other six-membered-ring carboxyimides, such as perylene-dicarboxyimides.^[8] Thus, an acidic workup should be avoided. The introduction of solubilising swallow-tail substituents,^[9] such as in **6g** or the 2,5-di-*tert*-butylphenyl substituent in **6j**,^[10] resulted in readily soluble materials, however, even simple long-chain alkyl substituents, such as in **6d**, increase the solubility sufficiently for the majority of applications. X-ray crystal structure analysis was conducted for **6d** (Figure 4). The high tendency for crystallisation of **6d**

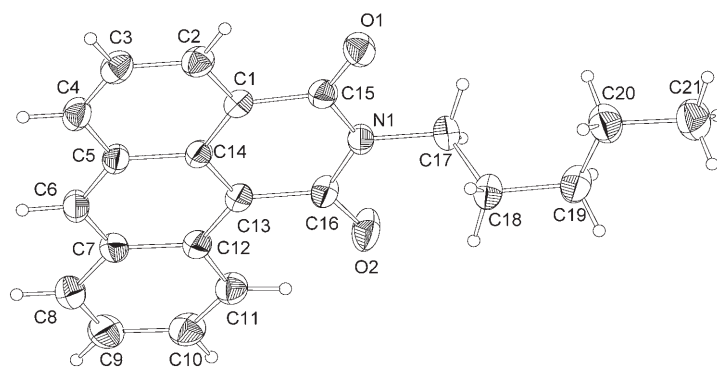


Figure 4. X-ray crystal structure of **6d**.

was necessary because of photodecomposition (see below). The anthracene unit of **6d** forms one plane and the carboxyimide another, twisted at an angle of 5° with respect to the first. The aliphatic substituent is folded downward and forms a third plane beneath the aromatic unit with a zigzag chain.

The anthracenedicarboxyimides are sensitive to daylight and form the hitherto unknown regioisomeric dimers **10** and **11**.^[11–14] Their structures were assigned by NMR spectroscopy; further isomers could not be detected. The conversion of **6** into **10** and **11** in daylight reaches a photostationary equilibrium because of the greater hypsochromic absorption of the latter. A filter solution of naphthalene-1,8-dicarboxylate excludes the hypsochromic UV light (cutoff wavelength 324 nm), and thus allows a complete conversion of **6** into **10** and **11**, as indicated by the disappearance of the fluorescence. Pure dimerisation products were obtained if the solvent was evaporated during irradiation with this filtered light. Dissociation of **10** and **11** to starting material **6** can also proceed thermally, however, this back reaction did not go to completion and typical yields of 90% were obtained.

The derivatives of **6** in homogeneous solution absorb at shorter wavelengths and fluoresce with quantum yields close to 100%. Many derivatives, such as **6b**, exhibit strong fluorescence in the solid state (Figure 5).

The photodimerisation of **6** is important because some of its derivatives are used as tumour static materials.^[1] However, the dimerisation proceeds even with ambient room light. Different tumour static activities are expected for **6**, **10** and **11**, respectively, so care has to be taken in relation to the effect of common daylight.

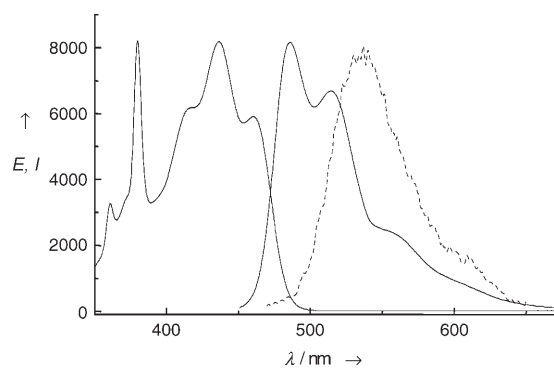


Figure 5. UV/Vis absorption (left) and fluorescence spectra (middle) of **6b** in chloroform. Dashed line: Solid-state fluorescence spectrum.

One of the carbonyl groups in **6** can be replaced with the related imino group when **3** is condensed with neopentanediamine. Only one of the two regioisomers was obtained and its structure was established by X-ray crystal structure analysis (Figure 6). The aromatic core of **12** is planar as one

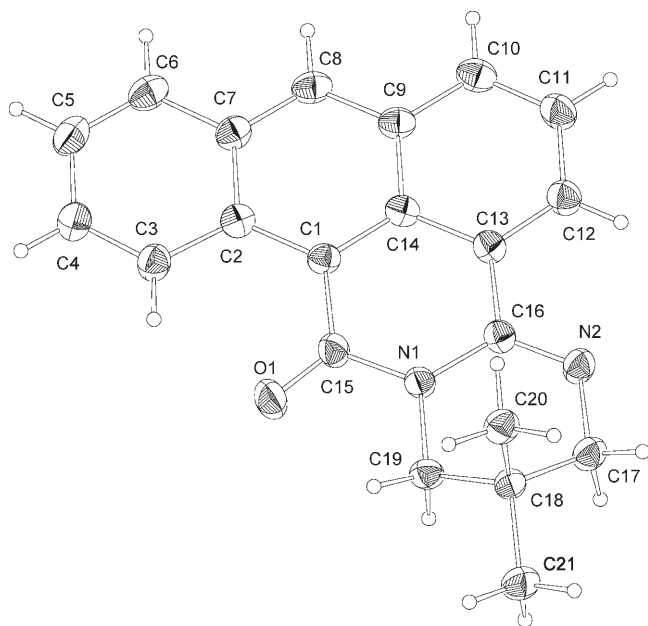


Figure 6. X-ray crystal structure of **12**.

might expect. The dicarboxamidine unit is twisted and the bond lengths to the anthracene core are longer than the corresponding bonds in **6d**. The π system of **6** can be further extended by the condensation of **3** with 1,2-phenylenediamine to obtain **13**, in which the orientation of the amidine unit is opposite to that in **12**, as established by NMR spectroscopy. The amidine from **3** and 1,2-phenylenediamine has already been reported as a maroon powder with a melting point of 234 °C.^[15] A second bright-orange modification of **13** was also found with a melting point of 228 °C and a pronounced solid-state fluorescence. Both modifications can be

interconverted by crystallisation. The maroon modification exhibits a very bathochromic solid-state fluorescence.

The UV/Vis absorption of **6** is successively bathochromically shifted by the replacement of one carbonyl group for an imino group, to form **12**, and by the further extension of the π system in **13** (Figures 7 and 8, respectively). Compound **13** exhibits a fluorescence quantum yield of 48% in solution. Both **12** and **13** form photodimerisation products **14/15** and **16/17**, respectively.

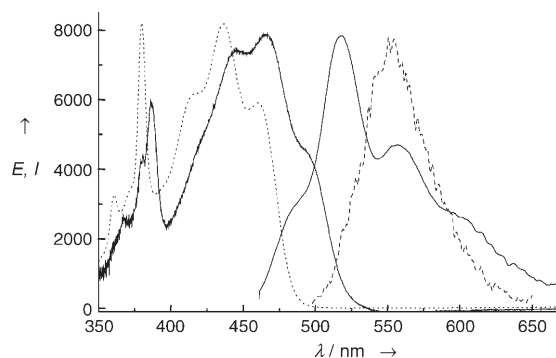


Figure 7. UV/Vis absorption (solid line, left) and fluorescence (solid line, right) spectra of **12** in chloroform. Dashed line: Solid-state fluorescence spectrum. The absorption spectrum of **6b** (dotted line) is shown for comparison.

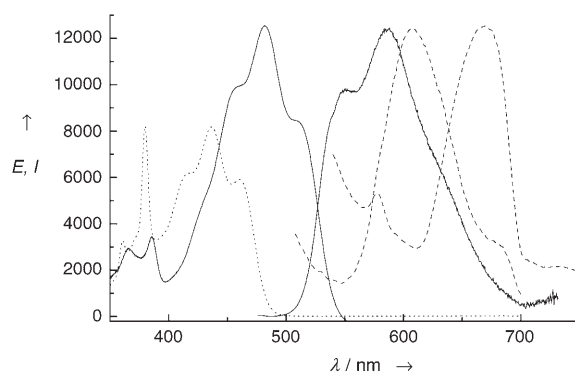


Figure 8. UV/Vis absorption (solid line, left) and fluorescence (solid line, right) spectra of **13** in chloroform. Dashed lines: Solid-state fluorescence spectra of both modifications. The absorption spectrum of **6b** (dotted line) is shown for comparison.

Compounds **6** are starting materials for the synthesis of Aceanthrene Green (**7**) by KOH melt; dicarboxyimide **6a** can be converted into **7a**.^[2a,b,9] Alternatively, the mixture of oximes **4** and **5** can be directly converted into **7a**, although the conditions used for this reaction are strongly alkaline, whereas acidic conditions are commonly used in the Beckmann rearrangement.^[16] The simple interconversion of such oximes^[6] via intermediate nitroso compounds may therefore be of importance. Compound **8a** is formed as a byproduct of the reaction with the alkali melt in a ratio of 1:8 with respect to **7a**. This ratio is higher than that reported in a previous investigation in which **6a** was the starting material.^[15]

Only **7** was detected in the reaction of N-alkylated or N-arylated derivatives of **6** with the alkali melt (monitored by TLC and NMR spectroscopy), in accordance with the earlier investigation.^[15]

The alkali-induced coupling of **6** results first in the formation of a red vat of the green vat dye **7** and is thus completely different from the formation of other carboxyimides, such as perylenetetracarboxydiimides. The vat can be conserved if the alkali melt is allowed to cool and solidify. A dihydroaromatic and electrically neutral structure was previously suggested for this vat,^[15] however, such a structure is not in accordance with the properties of the material. Electrophoresis indicated a quickly migrating anion for the red material, which is readily soluble in water and only sparingly soluble in lipophilic solvents. However, more lipophilic than hydrophilic properties would be expected for the suggested structure. Moreover, the suggested structure contains sp³ centres that would be in electronic isolation and thus a hypsochromic UV/Vis absorption, such as that observed for simple anthracene derivatives would be expected, whereas the red vat exhibits a bathochromic absorption (Figure 9).

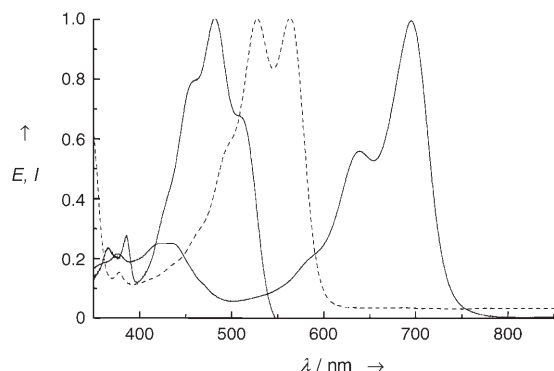


Figure 9. UV/Vis absorption spectra of **6g** (left) in chloroform, the vat from the alkali melt of **6g** (middle, dashed) in water and **7g** in chloroform (right).

The investigation of the structure of the vat is rather complicated because slow oxidation of the vat of **6a** in aqueous solution leads to insoluble **7a** and **8a** and this prevents a precise NMR spectroscopic investigation; acidification or warming results in the formation of starting material **6**. N-Alkylation of **6** renders the vat more lipophilic so that **6g** becomes soluble in organic solvents. However, contact of this vat with chloroform results in the spontaneous formation of the starting material. Oxidation of the vat is delayed by the addition of pyridine as a trap for nucleophilic free radicals, whereas formate as a trap for electrophilic free radicals has no effect. Ascorbic acid prevents the formation of **7** and **8**.

The vat of **6a** can be oxidised by a stream of air,^[2,15] however, several days are required for this to occur and lumps of the insoluble dye are formed that occlude the starting material, thus leading to a reduction in the yield. Better results were obtained in a stirred two-phase system in which

chloroform was used as the lipophilic phase in contact with aqueous 10% hydrogen peroxide. The concentration of H₂O₂ should not exceed this value because at higher concentrations, such as 30%, the material will be destroyed with foaming. This method cannot be applied to **6g** because the contact of the vat with chloroform causes spontaneous decomposition to the starting material. Thus, this vat was oxidised conventionally with air.

The main component Acenanthrene Green **7a** and the minor component **8a** form emerald-green solutions with an intense fluorescence in the visible and NIR regions (Figure 10 for the similar spectra of **7d**). The solid-state

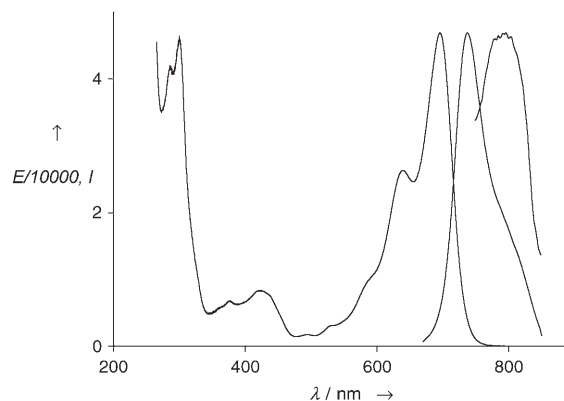


Figure 10. UV/Vis absorption (left) and fluorescence spectra (middle) of **7d** in chloroform, together with the solid-state fluorescence spectrum (right).

fluorescence is bathochromically shifted with respect to that in chloroform. The solubility of **7a** is relatively low and can be appreciably increased by the attachment of long-chain alkyl groups to the nitrogen atoms (**7b–7f**); the solubility of **7e** and **7f** is high enough for the majority of applications. The solubilising effect of the swallow-tail substituent in **7g** is so pronounced that the material was obtained as a green oil.

Perylenetetracarboxydiimides can be partially hydrolysed with KOH in *tert*-butyl alcohol. Derivatives **7** proved to be completely inert towards this reagent and also remained unaffected by acids. However, KOH in *tert*-butyl alcohol induces a reversible colour change in **7** from green to violet. This coloured material can be trapped with methyl iodide to form the methylated derivative **9**; addition of the dipolar aprotic DMSO did not lead to an improvement in the yield. Alkylation of the aromatic nucleus under these simple reaction conditions was unexpected. The novel chromophore **9** forms bright-orange crystals with an intense solid-state fluorescence and a fluorescence quantum yield in solution of 27% (Figure 11).

Conclusion

Compounds **6** have proven to be versatile basic starting materials for developing compounds for pharmaceutical appli-

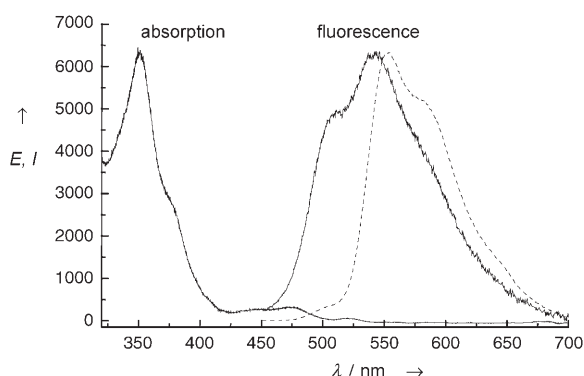


Figure 11. UV/Vis absorption (left) and fluorescence spectra (middle) of **9d** in chloroform. Dashed line: Solid-state fluorescence spectrum.

cations and as switchable and NIR fluorescent dyes. The dyes are formed from **6** by reaction under strongly alkaline conditions, which causes C–C coupling to form soluble dimeric fluorescent dyes with bathochromic absorption and fluorescence in the NIR region. These dyes are of special interest because of their absorption at longer wavelengths.

Experimental Section

General: IR spectra were recorded with a Perkin–Elmer 1420 Ratio Recording Infrared Spectrometer, FT 1000; UV/Vis/NIR spectra were recorded with Bruins Omega 20. Fluorescence spectra were recorded with a Perkin–Elmer FS 3000 spectrophotometer and are totally corrected. NMR spectroscopy was performed by using a Varian Vnmrs 600 spectrometer (600 MHz). Mass spectra were recorded with a Finnigan MAT 95 spectrometer.

Aceanthrenequinone (2):^[4] Anthracene (**1**, 10.00 g, 56.11 mmol), oxalyl chloride (25 mL, 37 g, 0.30 mol; **Caution:** toxic!), carbon disulfide (75 mL) and sublimed anhydrous aluminium chloride (7.93 g, 59.5 mmol) were stirred under argon with ice-cooling for 2 h (black, viscous material), treated with further carbon disulfide (75 mL) and aluminium chloride (7.32 g, 54.9 mmol), stirred for a further 4 h, allowed to stand for 16 h and hydrolysed by the addition of aqueous 2 N HCl (200 mL). Carbon disulfide was removed by distillation (b.p. 42°C, bath temperature = 50–70°C; **Caution!** Highly inflammable) and the residue collected by vacuum filtration (G4 glass filter, orange powder), twice extracted with a 2.5% aqueous solution of potassium carbonate (100 mL each at 70°C and 30 min, vacuum filtration, G4 glass filter), washed with distilled water (100 mL) and a small amount of methanol and dried at 115°C in air to give an orange, electrostatically charging powder with a strong solid-state fluorescence (9.74 g, 75%; lit.^[4] 9.00 g, 69%). M.p. 263–265°C (lit.^[4] 270°C); R_f (silica gel; CHCl_3) = 0.58; $^1\text{H NMR}$ ($[\text{D}_6]\text{DMSO}/\text{CDCl}_3$, 10:1): δ = 7.78 (m, 1H; aromatic H), 7.90 (m, 2H; aromatic H), 8.07 (d, J = 6.7 Hz, 1H; aromatic H), 8.38 (d, J = 8.5 Hz, 1H; aromatic H), 8.52 (d, J = 8.4 Hz, 1H; aromatic H), 9.01 (d, J = 8.5 Hz, 1H; aromatic H), 9.17 ppm (s, 1H; aromatic H); $^{13}\text{C NMR}$ ($[\text{D}_6]\text{DMSO}/\text{CDCl}_3$, 10:1): δ = 121.2, 122.9, 123.5, 126.5, 127.1, 127.4, 127.9, 128.0, 129.8, 130.3, 132.2, 132.4, 134.0, 145.7, 187.4 (C=O), 188.3 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 3051 (w), 1735 (s, C=O), 1707 (s, C=O), 1626 (w, C=C), 1576 (s, C=C), 1529 (w, C=C), 1454 (w), 1436 (w), 1339 (w), 1282 (w), 1226 (w), 1152 (w), 1086 (m), 1016 (w), 919 (w), 883 (w), 752 (m), 741 (m), 700 (w), 483 (w), 411 cm^{-1} (w); UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$) = 348 (sh) (3.558), 365 (3.804), 382 (sh) (3.678), 404 (3.695), 462 (sh) (3.122), 502 nm (sh) (2.648); fluorescence (CHCl_3): λ_{max} (I_{rel}) = 481 (1), 512 (0.81), 557 nm (sh) (0.28); solid-state fluorescence: λ_{max} = 485, 575 (sh), 606 nm; MS (70 eV): m/z (%): 233 (9), 232 (55) $[\text{M}]^+$, 205 (16), 204 (100) $[\text{M}-\text{CO}]^+$, 178 (3),

177 (11), 176 (73) $[\text{M}-2\text{CO}]^+$, 175 (12), 174 (10), 150 (11) $[\text{M}-2\text{CO}-\text{C}_2\text{H}_2]^+$, 149 (3), 116 (4), 98 (2), 88 (24), 87 (6), 75 (8); elemental analysis calcd (%) for $\text{C}_{16}\text{H}_8\text{O}_2$: C 82.75, H 3.47; found: C 80.60, H 3.50.

Aceanthrenequinone oxime, mixture of isomers 4 and 5:^[2] Anhydrous sodium carbonate (2.20 g, 20.8 mmol) was added to a suspension of aceanthrenequinone (**2**, 4.82 g, 20.8 mmol) and hydroxylamine hydrochloride (1.44 g, 20.7 mmol) in ethanol (50 mL, 96%). The mixture was heated at reflux with stirring for 30 min (colour change from orange to ochre-yellow), collected by vacuum filtration (G4 glass filter), washed with distilled water and dried over calcium chloride to give an ochre electrostatically charging powder. (4.66 g, 91%; lit.^[2] 100%). M.p. 251°C decomp (lit.^[2] 251°C); R_f (silica gel; CHCl_3) = 0.03; $^1\text{H NMR}$ (CDCl_3 , 600 MHz): isomer **4** (C=O in *p*-position of proton 10-H): δ = 7.68 (m, 2H; aromatic H), 7.84 (m, 1H; aromatic H), 7.93 (d, J = 6.6 Hz, 1H; aromatic H), 8.10 (d, J = 8.7 Hz, 1H; aromatic H), 8.20 (d, J = 8.5 Hz, 1H; aromatic H), 8.83 (s, 1H; aromatic H), 9.06 ppm (d, J = 8.5 Hz, 1H; aromatic H); isomer **5** (C=NOH in *p*-position of proton 10-H): $^1\text{H NMR}$ (CDCl_3): δ = 7.68 (m, 2H; aromatic H), 7.78 (m, 1H; aromatic H), 8.10 (d, J = 8.7 Hz, 1H; aromatic H), 8.16 (d, J = 8.5 Hz, 1H; aromatic H), 8.35 (d, J = 6.6 Hz, 1H; aromatic H), 8.73 (s, 1H; aromatic H), 9.19 ppm (d, J = 8.7 Hz, 1H; aromatic H); IR (KBr): $\tilde{\nu}$ = 3248 (m, OH), 3050 (w), 2850 (w), 1705 (s, C=O), 1635 (m, C=N), 1619 (m, C=C), 1576 (m, C=C), 1530 (w, C=C), 1456 (s, OH), 1394 (w), 1225 (w), 1178 (w), 1158 (w), 1079 (w), 1021 (m), 999 (m), 877 (s), 793 (m), 738 (m), 630 (w), 561 (w), 491 cm^{-1} (w); UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$) = 342 (sh) (3.457), 361 (3.548), 393 (3.461), 407 (sh) (3.429), 432 (3.428), 463 nm (sh) (2.979); fluorescence (CHCl_3): λ_{max} = 481 nm; solid-state fluorescence: λ_{max} = 485, 524, 543, 614 nm; MS (70 eV): m/z (%): 248 (12), 247 (63) $[\text{M}]^+$, 233 (2), 232 (16), 231 (69), 230 (99) $[\text{M}-\text{OH}]^+$, 205 (3), 204 (26), 203 (100) $[\text{M}-\text{OH}-\text{HCN}]^+$, 202 (59) $[\text{M}-\text{OH}-\text{CO}]^+$, 201 (30), 200 (2), 190 (3), 187 (4), 178 (3), 177 (8), 176 (27), 175 (22) $[\text{M}-\text{CO}]^+$, 174 (12), 151 (4), 150 (7), 149 (5), 115 (7), 101 (16), 88 (21), 87 (15), 75 (7), 74 (4).

Anthracene-1,9-dicarboxylic anhydride (3):^[5a] An aqueous hydrogen peroxide solution (46.3 mL, 30%) was slowly added with stirring to aceanthrenequinone (**2**, 9.25 g, 39.8 mmol) in 1,4-dioxane (200 mL) and 2 N aqueous NaOH (55.5 mL) at reflux. The free anthracene-1,9-dicarboxylic acid was precipitated by the addition of distilled water (200 mL) and 2 N sulfuric acid (400 mL), and was allowed to stand for 16 h. The light-yellow precipitate was transformed into the orange anhydride, which was collected by vacuum filtration (G4 glass filter), dissolved in 2 N aqueous KOH, separated from insoluble material by filtration (G4 glass filter), precipitated by the dropwise addition of concentrated hydrochloric acid, collected by vacuum filtration (D4 glass filter), repeatedly washed with distilled water and dried in air at 115°C to give an orange electrostatically charging powder (10.15 g, 97%; lit.^[5a] 100% crude material). M.p. 285–290°C (lit.^[5a] 290°C); R_f (silica gel; CHCl_3) = 0.40; $^1\text{H NMR}$ (CDCl_3): δ = 7.72 (m, 1H; aromatic H), 7.80 (m, 1H; aromatic H), 7.92 (m, 1H; aromatic H), 8.19 (d, J = 8.4 Hz, 1H; aromatic H), 8.48 (d, J = 8.4 Hz, 1H; aromatic H), 8.78 (d, J = 7.0 Hz, 1H; aromatic H), 8.97 (s, 1H; aromatic H), 9.75 ppm (d, J = 9.1 Hz, 1H; aromatic H); $^{13}\text{C NMR}$ (CDCl_3): δ = 125.8, 126.3, 127.2, 129.9, 132.3, 135.7, 136.4, 137.9 ppm; IR (KBr): $\tilde{\nu}$ = 3050 (w), 1760 (s, C=O), 1720 (s, C=O), 1622 (w, C=C), 1561 (s, C=C), 1535 (m, C=C), 1432 (w), 1365 (w), 1285 (w), 1268 (w), 1249 (w), 1160 (w), 1139 (m, C–O), 1086 (m, C–O), 1054 (w), 1010 (m), 940 (w), 863 (w), 794 (m), 745 (m), 733 (m), 511 cm^{-1} (w); UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$) = 269 (4.704), 358 (3.657), 376 (4.037), 414 (3.848), 435 (3.913), 459 nm (3.784); fluorescence (CHCl_3): λ_{max} (I_{rel}) = 481 (1), 513 (0.80), 553 nm (sh) (0.28); fluorescence quantum yield (CHCl_3 , reference perylene-3,4,9,10-tetracarboxylic tetramethyl ester^[17] with $\Phi = 1.0$): 81%; solid-state fluorescence: λ_{max} = 485, 525, 605 nm; MS (70 eV): m/z (%): 249 (17), 248 (100) $[\text{M}]^+$, 205 (8), 204 (52) $[\text{M}-\text{CO}_2]^+$, 177 (7), 176 (50) $[\text{M}-\text{CO}_2-\text{CO}]^+$, 175 (8), 174 (7), 150 (8), 124 (3), 88 (18), 87 (5), 75 (7).

Anthracene-1,9-dicarboxyimide (6a)^[5b,c] from anthracene-1,9-dicarboxylic anhydride (**3**):^[5b] Anthracene-1,9-dicarboxylic anhydride (3520 mg, 2.09 mmol) was heated with aqueous concentrated ammonia (50 mL) for 1 h and then evaporated three times with concentrated ammonia to complete the reaction. The reaction mixture was suspended in distilled water,

collected by vacuum filtration (G4 glass filter), washed with distilled water and dried in air at 130 °C to give an ochre electrostatically charging powder (440 mg, 85%). M.p. 288–294 °C (lit.:^[5b] 293–294 °C); R_f (silica gel; CHCl_3)=0.16; $^1\text{H NMR}$ ($[\text{D}_6]\text{DMSO}/\text{CDCl}_3$, 10:1): δ =7.71 (m, 1H; aromatic H), 7.86 (m, 2H; aromatic H), 8.30 (d, J =9.0 Hz, 1H; aromatic H), 8.62 (2d, J =7.0 Hz, 2H; aromatic H), 9.21 (s, 1H; aromatic H), 9.94 (d, J =9.3 Hz, 1H; aromatic H), 11.70 ppm (s, 1H; NH); $^{13}\text{C NMR}$ ($[\text{D}_6]\text{DMSO}/\text{CDCl}_3$, 10:1): δ =114.9, 122.6, 125.5, 125.9, 126.3, 129.0, 129.3, 129.9, 131.1, 131.9, 132.4, 132.6, 135.6, 136.9, 163.4 (C=O), 165.6 ppm (C=O); IR (KBr): $\tilde{\nu}$ =3185 (m), 3067 (m), 2922 (w), 2850 (w), 1687 (s, C=O), 1678 (s, C=O), 1653 (w), 1622 (w, C=C), 1563 (s, C=C), 1532 (m, C=C), 1435 (m), 1397 (m), 1368 (m), 1313 (m), 1281 (m), 1251 (w), 1235 (m), 1153 (w), 909 (w), 858 (w), 799 (w), 746 (w), 733 (m), 677 (w), 625 (w), 505 (w), 416 cm^{-1} (w); UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$)=360 (3.570), 379 (3.928), 416 (3.785), 437 (3.900), 462 nm (3.752); fluorescence (CHCl_3): λ_{max} (I_{rel})=494 (1), 518 nm (0.91); solid-state fluorescence: λ_{max} =485 (sh), 524, 597, 633 nm (sh); MS (70 eV): m/z (%): 248 (17), 247 (100) $[\text{M}]^+$, 246 (6), 219 (10) $[\text{M}-\text{CO}]^+$, 204 (4), 203 (13), 202 (3), 191 (3), 190 (8), 177 (3), 176 (10), 175 (3), 163 (3), 150 (3), 124 (3), 110 (4), 88 (7), 87 (3), 75 (3).

Anthracene-1,9-dicarboxyimide (6a) from aceanthrenequinone oxime (4 and 5):^[2d] Finely powdered aceanthrenequinone oxime (4 and 5, 450 mg, 1.82 mmol) was heated with concentrated sulfuric acid (3 mL, 30 min) at 100 °C (colour change from brown to cherry-red), allowed to cool, diluted with distilled water, collected by vacuum filtration (G4 glass filter), washed with distilled water and dried in air at 130 °C to give an ochre electrostatically charging powder (330 mg, 73%; lit.:^[2d] nearly quantitative). M.p. 285–292 °C (lit.:^[2d] 293–294 °C); R_f (silica gel; CHCl_3)=0.16; for further spectroscopic data see above.

N-Ethylanthracene-1,9-dicarboxyimide (6b): Compound 3 (1.94 g, 7.82 mmol) in aqueous ethylamine solution (75 mL, 70%) was heated at reflux for 1.5 h (bath 150 °C), treated with further ethylamine solution (25 mL, 70%), heated at reflux for 3.5 h, and cautiously acidified with concentrated HCl. The product was collected by vacuum filtration (G4 glass filter), thoroughly washed with small amounts of distilled water, dried in air at 115 °C, purified by column chromatography (silica gel, chloroform, exclusion of light because otherwise dimers would be formed), rapidly evaporated, dried in an argon gas stream and then in a medium vacuum and stored in the dark under argon. The product was obtained as a bright golden-yellow powder with lemon-yellow solid-state fluorescence (1.63 g, 76%). M.p. 184–186 °C; R_f (silica gel; CHCl_3)=0.30; $^1\text{H NMR}$ ($[\text{D}_6]\text{DMSO}/\text{CDCl}_3$, 10:1): δ =1.31 (t, J =7.0 Hz, 3H; CH_3), 4.23 (q, J =6.9 Hz, 2H; NCH_2CH_3), 7.72 (t, J =7.1 Hz, 1H; aromatic H), 7.88 (m, 2H; aromatic H), 8.31 (d, J =8.0 Hz, 1H; aromatic H), 8.61 (d, J =8.5 Hz, 1H; aromatic H), 8.69 (d, J =7.0 Hz, 1H; aromatic H), 9.22 (s, 1H; aromatic H), 9.95 ppm (d, J =9.1 Hz, 1H; aromatic H); $^{13}\text{C NMR}$ ($[\text{D}_6]\text{DMSO}/\text{CDCl}_3$, 10:1): δ =13.1 (CH_3), 34.9 (CH_2), 118.5, 121.9, 125.6, 126.0, 126.2, 127.8, 128.6, 130.0, 131.2, 132.0, 132.7, 133.2, 135.5, 136.9, 162.7 (C=O), 164.3 ppm (C=O); IR (KBr): $\tilde{\nu}$ =3050 (w), 2980 (w), 2935 (w), 1685 (s, C=O), 1653 (s, C=O), 1640 (s, C=O), 1621 (w, C=C), 1560 (s, C=C), 1533 (m, C=C), 1456 (m), 1437 (m), 1400 (m), 1368 (m), 1351 (m), 1312 (s), 1247 (m), 1231 (m), 1146 (w), 1103 (m), 900 (w), 875 (w), 855 (w), 795 (m), 747 (m), 732 (s), 539 cm^{-1} (m); UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$)=361 (3.514), 380 (3.914), 416 (3.790), 437 (3.913), 460 nm (3.771); fluorescence (CHCl_3): λ_{max} (I_{rel})=486 (1), 516 (0.81), 556 nm (sh) (0.29); fluorescence quantum yield (CHCl_3 , reference perylene-3,4,9,10-tetracarboxylic tetramethyl ester^[17] with Φ =100%): 44%; solid-state fluorescence: λ_{max} =537, 606 nm (sh); MS (70 eV): m/z (%): 276 (20), 275 (94) $[\text{M}]^+$, 274 (9), 260 (17) $[\text{M}-\text{CH}_3]^+$, 259 (5), 248 (19), 247 (100) $[\text{M}-\text{C}_2\text{H}_4]^+$, 246 (7), 233 (8), 231 (9), 230 (4) $[\text{247}-\text{OH}]^+$, 219 (7), 205 (11), 204 (9) $[\text{M}-\text{C}_2\text{H}_5\text{NCO}]^+$, 203 (22) $[\text{204}-\text{H}]^+$, 202 (9), 190 (9), 177 (19), 176 (27) $[\text{204}-\text{CO}]^+$, 175 (9), 174 (6), 150 (7), 116 (7), 88 (29) $[\text{176}-\text{C}_7\text{H}_4]^+$, 75 (6); elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{13}\text{NO}_2$: C 78.53, H 4.76, N 5.09; found: C 78.62, H 4.86, N 4.83.

N-Butylanthracene-1,9-dicarboxyimide (6c): Compound 3 (3.96 g, 16.0 mmol) in *n*-butylamine (100 mL, 1.01 mol) and toluene (10 mL) was heated at reflux under argon for 2.5 h. The mixture was evaporated at normal pressure (dark-red residue) and the residue was suspended in

chloroform (250 mL), shaken with 2N HCl and distilled water, evaporated, purified by column chromatography (silica gel, chloroform, exclusion of light because otherwise dimers would be formed), rapidly evaporated, dried in an argon gas stream and then in a medium vacuum and stored under argon in the dark. The product was obtained as a bright golden-yellow powder with yellow solid-state fluorescence (3.53 g, 73%). M.p. 140–142 °C; R_f (silica gel, CHCl_3)=0.39; $^1\text{H NMR}$ (CDCl_3): δ =1.01 (m, 3H; CH_3), 1.49 (m, 2H; CH_2CH_3), 1.76 (m, 2H; NCH_2CH_2), 4.24 (m, 2H; NCH_2), 7.58 (m, 1H; aromatic H), 7.67 (m, 1H; aromatic H), 7.78 (m, 1H; aromatic H), 8.05 (d, J =8.5 Hz, 1H; aromatic H), 8.27 (d, J =8.4 Hz, 1H; aromatic H), 8.69 (d, J =7.1 Hz, 1H; aromatic H), 8.73 (s, 1H; aromatic H), 9.95 ppm (d, J =9.2 Hz, 1H; aromatic H); $^{13}\text{C NMR}$ (CDCl_3): δ =14.3 (CH_3), 20.9 (CH_2), 30.7 (CH_2), 40.9 (NCH_2), 115.8, 123.0, 125.8, 126.8, 127.2, 128.5, 129.2, 130.1, 131.6, 132.8, 133.8, 134.0, 135.4, 136.6, 164.1 (C=O), 165.6 ppm (C=O); IR (KBr): $\tilde{\nu}$ =3067 (w), 3040 (w), 2951 (m), 2935 (m), 2872 (m), 1689 (s, C=O), 1642 (s, C=O), 1621 (m, C=C), 1563 (s, C=C), 1533 (m, C=C), 1433 (m), 1401 (m), 1370 (m), 1354 (m), 1313 (m), 1279 (m), 1220 (m), 1204 (m), 1150 (m), 1111 (s), 903 (m), 861 (m), 828 (m), 797 (m), 750 (s), 741 (s), 662 (w), 625 (w), 544 (w), 516 cm^{-1} (w); UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$)=361 (3.196), 380 (3.616), 416 (3.505), 436 (3.631), 459 nm (3.486); fluorescence (CHCl_3): λ_{max} (I_{rel})=484 (1), 514 (0.79), 556 nm (sh) (0.23); fluorescence quantum yield (CHCl_3 , reference perylene-3,4,9,10-tetracarboxylic tetramethyl ester^[17] with Φ =100%): 100%; solid-state fluorescence: λ_{max} =535 nm; MS (70 eV): m/z (%): 304 (19), 303 (87) $[\text{M}]^+$, 286 (16) $[\text{M}-\text{OH}]^+$, 274 (6), 262 (6), 261 (36), 260 (16) $[\text{M}-\text{C}_2\text{H}_5]^+$, 259 (8), 248 (22), 247 (100) $[\text{M}-\text{C}_4\text{H}_9]^+$, 231 (6), 230 (7) $[\text{247}-\text{OH}]^+$, 219 (5), 204 (5) $[\text{M}-\text{C}_4\text{H}_9\text{NCO}]^+$, 203 (11) $[\text{204}-\text{H}]^+$, 202 (8), 190 (5), 177 (9), 176 (14) $[\text{204}-\text{CO}]^+$, 150 (2), 88 (4) $[\text{176}-\text{C}_7\text{H}_4]^+$; elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{17}\text{NO}_2$: C 79.19, H 5.65, N 4.62; found: C 79.45, H 5.67, N 4.53.

N-Pentylanthracene-1,9-dicarboxyimide (6d): Compound 3 (4.00 g, 16.1 mmol) and *n*-pentylamine (65 mL, 0.56 mol) were heated at reflux under argon for 3 h, evaporated and further treated as described 6c. The product was obtained as bright-orange, analytically pure crystals with a strong solid-state fluorescence (2.60 g 51%). M.p. 133–135 °C; R_f (silica gel; CHCl_3)=0.57; $^1\text{H NMR}$ (CDCl_3): δ =0.93 (m, 3H; CH_3), 1.45 (m, 4H; $(\text{CH}_2)_2\text{CH}_3$), 1.76 (m, 2H; $\text{CH}_2\text{CH}_2\text{N}$), 4.22 (m, 2H; CH_2N), 7.62 (m, 1H; aromatic H), 7.71 (m, 1H; aromatic H), 7.80 (m, 1H; aromatic H), 8.08 (d, J =6.3 Hz, 1H; aromatic H), 8.33 (d, J =7.6 Hz, 1H; aromatic H), 8.74 (d, J =5.8 Hz, 1H; aromatic H), 8.80 (s, 1H; aromatic H), 10.01 ppm (d, J =8.0 Hz, 1H; aromatic H); $^{13}\text{C NMR}$ (CDCl_3): δ =14.1 (CH_3), 22.4, 27.9, 29.3, 40.5 (CH_2N), 116.0, 123.3, 125.9, 126.9, 127.3, 128.7, 129.3, 130.1, 131.7, 132.5, 132.9, 133.8, 135.4, 136.6, 164.2 (C=O), 165.7 ppm (C=O); IR (KBr): $\tilde{\nu}$ =3063 (w), 2950 (s), 2936 (m), 2872 (m), 2849 (m), 1685 (s, C=O), 1644 (s, C=O), 1619 (s, C=C), 1561 (s, C=C), 1533 (s, C=C), 1431 (s), 1400 (s), 1371 (s), 1348 (s), 1310 (s), 1279 (m), 1268 (m), 1221 (m), 1193 (m), 1150 (s), 1109 (s), 964 (w), 915 (m), 883 (m), 864 (m), 797 (s), 750 (s), 737 (s), 664 (m), 626 (m), 528 (m), 435 cm^{-1} (m); UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$)=361 (3.433), 380 (3.889), 416 (3.778), 436 (3.910), 460 nm (3.760); fluorescence (CHCl_3): λ_{max} (I_{rel})=484 (1), 513 (0.77), 559 nm (sh) (0.21); solid-state fluorescence: λ_{max} =474, 505, 523, 610 nm; MS (70 eV): m/z (%): 318 (23), 317 (100) $[\text{M}]^+$, 300 (11) $[\text{M}-\text{OH}]^+$, 274 (5), 261 (33), 260 (15) $[\text{M}-\text{C}_4\text{H}_9]^+$, 248 (24), 247 (90) $[\text{M}-\text{C}_5\text{H}_{10}]^+$, 230 (6) $[\text{247}-\text{OH}]^+$, 219 (4), 204 (4) $[\text{M}-\text{C}_5\text{H}_9\text{NCO}]^+$, 203 (9), 202 (7), 190 (4), 177 (8), 176 (11) $[\text{204}-\text{CO}]^+$, 88 (3) $[\text{176}-\text{C}_7\text{H}_4]^+$; elemental analysis calcd (%) for $\text{C}_{21}\text{H}_{19}\text{NO}_2$: C 79.47, H 6.03, N 4.41; found: C 79.43, H 5.93, N 4.32.

Crystal data for 6d: The crystal structure was determined with an Enraf-Nonius CAD4 diffractometer with $\text{MoK}\alpha$ radiation and a highly oriented graphite crystal as monochromator. $\text{C}_{21}\text{H}_{19}\text{NO}_2$, M_r =317.37, a =11.525(5), b =15.794(6), c =9.563(4) Å, β =113.16(2)°, volume=1600.4(11) Å³, Z =4, ρ_{calcd} =1.317 g cm⁻³, μ =0.084 mm⁻¹, monoclinic, space group $P2_1/c$ (Nr. 14). Data collection: single crystal 0.40×0.47×0.53 mm³ (orange block); ω data collection, scan width 0.80+0.35tan θ ; maximal collection time 90 s for each reflex, number of reflections: 2344 (collected), 2223 (independent), 1739 (observed) [$I > 2\sigma(I)$], no correction for absorption, structure solution with SHELXS86, refinement with SHELXL93,^[18] 218 parameters, R_1 =0.0499($2\sigma(I)$), wR_2 =0.1386($2\sigma(I)$),

weighing $w = 1/[\sigma_2 F_0^2 + 0.0693]$, GOF = 1.080, max. and min. residual electron density 0.310/−0.182 e Å^{−3}.

CCDC 679419 contains the supplementary crystallographic data for **6d**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

N-Hexylanthracene-1,9-dicarboxyimide (6e): Compound **3** (4.10 g, 16.5 mmol) and *n*-hexylamine (120 mL, 0.908 mol) were allowed to react as described for **6d** for 1 h 45 min. The product was obtained as bright-yellow crystals with an intense solid-state fluorescence (4.42 g, 81%). M.p. 109–110 °C; *R*_f (silica gel; CHCl₃) = 0.56; ¹H NMR (CDCl₃): δ = 0.89 (m, 3H; CH₃), 1.40 (m, 6H; (CH₂)₃CH₃), 1.78 (m, 2H; CH₂CH₂N), 4.25 (m, 2H; CH₂N), 7.61 (m, 1H; aromatic H), 7.71 (m, 1H; aromatic H), 7.81 (m, 1H; aromatic H), 8.10 (d, *J* = 7.8 Hz, 1H; aromatic H), 8.33 (d, *J* = 8.4 Hz, 1H; aromatic H), 8.74 (d, *J* = 7.1 Hz, 1H; aromatic H), 8.81 (s, 1H; aromatic H), 10.01 ppm (d, *J* = 9.2 Hz, 1H; aromatic H); ¹³C NMR (CDCl₃): δ = 14.1 (CH₃), 22.6, 26.8, 28.1, 31.6, 40.7 (CH₂N), 115.6, 122.7, 125.5, 126.4, 126.9, 128.4, 128.9, 129.7, 131.2, 132.5, 133.4, 133.6, 135.0, 136.2, 163.7 (C=O), 165.2 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 3120 (w), 3060 (w), 2957 (s), 2925 (s), 2853 (s), 1685 (s, C=O), 1644 (s, C=O), 1620 (m, C=C), 1561 (s, C=C), 1532 (s, C=C), 1452 (m), 1431 (s), 1402 (m), 1370 (m), 1353 (s), 1312 (s), 1279 (m), 1253 (m), 1219 (m), 1190 (m), 1149 (m), 1111 (s), 914 (m), 862 (m), 798 (s), 752 (s), 737 (s), 660 (w), 621 (w), 559 (w), 528 cm^{−1} (w); UV/Vis (CHCl₃): λ_{\max} (log ϵ) = 361 (3.269), 380 (3.591), 416 (3.484), 436 (3.596), 460 nm (3.464); fluorescence (CHCl₃): λ_{\max} (*I*_{rel}) = 481 (1), 512 nm (0.77); solid-state fluorescence: λ_{\max} = 560 nm; MS (70 eV): *m/z* (%): 332 (23), 331 (100) [M]⁺, 314 (9) [M−OH]⁺, 274 (4), 262 (6), 261 (31), 260 (15), 259 (6), 248 (24), 247 (81) [M−C₆H₁₂]⁺, 230 (6) [247−OH]⁺, 219 (4), 204 (4) [M−C₆H₁₃NCO]⁺, 203 (8), 202 (6), 190 (4), 177 (6), 176 (9) [204−CO]⁺; elemental analysis calcd (%) for C₂₉H₃₅NO₂: C 79.73, H 6.39, N 4.23; found: C 79.30, H 6.28, N 4.33.

N-Nonylanthracene-1,9-dicarboxyimide (6f): Compound **3** (2.03 g, 8.18 mmol), *n*-nonylamine (2.07 g, 14.4 mmol) and zinc acetate dihydrate (350 mg) in imidazole (9 g) were heated under argon at 150 °C for 4 h. The resulting mixture was treated dropwise with concentrated HCl whilst still warm and then added to chloroform, separated from the red HCl phase, extracted with a small amount of 2 N HCl, dried, evaporated and purified by fast pressure-induced column chromatography (silica gel, chloroform, exclusion of light), rapidly evaporated, dried in a stream of argon and then in a medium vacuum and stored in the dark. The product was obtained as a bright-yellow powder with a strong solid-state fluorescence (2.00 g, 65%). M.p. 141–143 °C; *R*_f (silica gel; CHCl₃) = 0.67; ¹H NMR (CDCl₃): δ = 0.85 (m, 3H; CH₃), 1.38 (m, 12H; (CH₂)₆CH₃), 1.77 (m, 2H; NCH₂CH₂), 4.26 (m, 2H; NCH₂), 7.63 (m, 1H; aromatic H), 7.72 (m, 1H; aromatic H), 7.81 (m, 1H; aromatic H), 8.11 (d, *J* = 8.4 Hz, 1H; aromatic H), 8.35 (d, *J* = 8.4 Hz, 1H; aromatic H), 8.75 (d, *J* = 7.1 Hz, 1H; aromatic H), 8.82 (s, 1H; aromatic H), 10.02 ppm (d, *J* = 9.2 Hz, 1H; aromatic H); ¹³C NMR (CDCl₃): δ = 14.0 (CH₃), 22.6, 27.2, 28.1, 29.2, 29.4, 29.5, 31.8, 40.6 (CH₂N), 122.6, 125.4, 126.4, 126.8, 128.3, 128.6, 129.6, 131.2, 132.2, 132.8, 133.4, 134.9, 136.1, 162.3 (C=O), 165.1 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 3068 (w), 2957 (m), 2926 (s), 2854 (m), 1685 (s, C=O), 1660 (s, C=O), 1601 (w, C=C), 1560 (m, C=C), 1534 (w, C=C), 1462 (w), 1452 (w), 1394 (w), 1355 (s), 1311 (w), 1280 (w), 1243 (w), 1170 (w), 1109 (w), 902 (w), 820 (w), 778 (w), 750 (m), 712 (w), 605 cm^{−1} (w); UV/Vis (CHCl₃): λ_{\max} (log ϵ) = 361 (3.457), 380 (3.722), 416 (3.590), 437 (3.696), 461 nm (3.555); fluorescence (CHCl₃): λ_{\max} (*I*_{rel}) = 485 (1), 513 nm (0.77); solid-state fluorescence: λ_{\max} = 536, 635 nm (sh); MS (70 eV): *m/z* (%): 374 (26), 373 (100) [M]⁺, 356 (7) [M−OH]⁺, 261 (29), 260 (17) [M−C₈H₁₇]⁺, 248 (29), 247 (72) [M−C₉H₁₈]⁺, 230 (7) [247−OH]⁺, 205 (5), 204 (5) [M−C₉H₁₉NCO]⁺, 203 (10), 202 (7), 177 (9), 176 (10) [204−CO]⁺; elemental analysis calcd (%) for C₂₅H₂₇NO₂: C 80.40, H 7.29, N 3.75; found: C 80.41, H 7.30, N 3.79.

N-(1-Hexylheptyl)anthracene-1,9-dicarboxyimide (6g): Compound **3** (1.94 g, 7.82 mmol), 1-hexylheptylamine (2.22 g, 11.1 mmol), zinc acetate dihydrate (350 mg) and imidazole (10 g) were allowed to react (4 h) as described for **6f**. The product was obtained as yellow crystals with a brightly shining yellow solid-state fluorescence (2.15 g, 64%). M.p. 245 °C, *R*_f (silica gel, toluene) = 0.80; ¹H NMR (CDCl₃): δ = 0.79 (t, *J* = 6.8 Hz, 6H; CH₃), 1.26 (m, 16H; (CH₂)₄), 1.88 (m, 2H; (CH₂)CHN), 2.28

(m, 2H; (CH₂)CHN), 5.27 (m, 1H; (CH₂)₂CHN), 7.61 (m, 1H; aromatic H), 7.72 (m, 1H; aromatic H), 7.81 (m, 1H; aromatic H), 8.10 (d, *J* = 8.4 Hz, 1H; aromatic H), 8.33 (d, *J* = 8.4 Hz, 1H; aromatic H), 8.72 (d, *J* = 6.9 Hz, 1H; aromatic H), 8.81 (s, 1H; aromatic H), 9.96 ppm (d, *J* = 9.1 Hz, 1H; aromatic H); ¹³C NMR (CDCl₃): δ = 14.0 (CH₃), 22.6, 27.0, 29.3, 31.8, 32.6, 54.6 (NCHR₂), 125.5, 126.4, 127.0, 128.5, 128.8, 129.7, 131.0, 132.6, 134.6, 135.8 ppm; IR (KBr): $\tilde{\nu}$ = 3050 (w), 2955 (m), 2925 (s), 2855 (m), 1689 (s, C=O), 1653 (s, C=O), 1617 (w, C=C), 1563 (m, C=C), 1533 (m, C=C), 1457 (m), 1430 (m), 1399 (m), 1369 (m), 1309 (m), 1280 (m), 1243 (m), 1212 (m), 1191 (m), 1150 (w), 1114 (m), 895 (w), 793 (w), 750 (w), 730 (m), 624 (w), 610 cm^{−1} (w); UV/Vis (CHCl₃): λ_{\max} (log ϵ) = 361 (2.628), 380 (3.016), 415 (2.929), 435 (3.051), 459 nm (2.898); fluorescence (CHCl₃): λ_{\max} (*I*_{rel}) = 481 (1), 512 nm (0.78); solid-state fluorescence: λ_{\max} = 485, 524, 632 nm; MS (70 eV): *m/z* (%): 430 (10), 429 (33) [M]⁺, 344 (3) [M−C₆H₁₃]⁺, 260 (6), 248 (45), 247 (100) [M−C₁₃H₂₆]⁺, 230 (7) [247−OH]⁺, 205 (4), 204 (2) [M−C₁₅H₂₇NCO]⁺, 203 (4), 202 (5), 177 (3), 176 (3) [204−CO]⁺; elemental analysis calcd (%) for C₂₉H₃₅NO₂: C 81.08, H 8.21, N 3.29; found: C 80.90, H 8.29, N 3.14.

N-(2-Ethylphenyl)anthracene-1,9-dicarboxyimide (6h): Compound **3** (2.06 g, 8.30 mmol), 2-ethylaniiline (2.01 g, 16.6 mmol), zinc acetate dihydrate (330 mg) and imidazole (10 g) were allowed to react (4 h) as described for **6f**. The product was obtained as a brightly shining yellowish-orange powder with a strong solid-state fluorescence (1.31 g, 45%). M.p. 175–176 °C; *R*_f (silica gel, CHCl₃) = 0.21; ¹H NMR (CDCl₃): δ = 1.18 (t, *J* = 7.7 Hz, 3H; CH₃), 2.57 (q, *J* = 7.5 Hz, 2H; CH₂CH₃), 7.27 (d, *J* = 7.4 Hz, 1H; aromatic H), 7.41 (m, 1H; aromatic H), 7.49 (m, 2H; aromatic H), 7.65 (m, 1H; aromatic H), 7.81 (m, 2H; aromatic H), 8.17 (d, *J* = 8.4 Hz, 1H; aromatic H), 8.45 (d, *J* = 7.6 Hz, 1H; aromatic H), 8.83 (d, *J* = 7.0 Hz, 1H; aromatic H), 8.93 (s, 1H; aromatic H), 9.98 ppm (d, *J* = 9.1 Hz, 1H; aromatic H); ¹³C NMR (CDCl₃): δ = 13.9 (CH₃), 24.1 (CH₂), 115.5, 122.8, 125.6 (CH), 126.7 (CH), 127.0 (CH), 127.1 (CH), 127.2, 128.8 (CH), 129.18 (CH), 129.11, 129.2 (CH), 129.7 (CH), 131.6 (CH), 132.6, 133.9, 134.9 (CH), 134.8, 135.5 (CH), 136.8 (CH), 141.4, 163.8 (C=O), 165.4 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 3060 (w), 2970 (w), 2935 (w), 2875 (w), 1695 (s, C=O), 1658 (s, C=O), 1623 (m, C=C), 1563 (s, C=C), 1532 (m, C=C), 1493 (m), 1454 (m), 1430 (m), 1392 (m), 1370 (m), 1320 (m), 1254 (m), 1214 (s), 1197 (m), 1148 (m), 1054 (w), 888 (m), 860 (w), 795 (m), 751 (s), 735 (s), 659 (m), 493 cm^{−1} (w); UV/Vis (CHCl₃): λ_{\max} (log ϵ) = 361 (3.294), 380 (3.623), 418 (3.538), 438 (3.651), 462 nm (3.521); fluorescence (CHCl₃): λ_{\max} (*I*_{rel}) = 481 (1), 512 nm (0.77); solid-state fluorescence: λ_{\max} = 486, 524, 544 (sh), 600, 630 nm (sh); MS (70 eV): *m/z* (%): 352 (16), 351 (66) [M]⁺, 335 (24), 334 (91) [M−OH]⁺, 323 (17), 322 (71) [M−C₂H₅]⁺, 319 (24), 306 (12), 291 (16), 247 (11), 204 (5) [M−C₂H₅−C₆H₄−NCO]⁺, 203 (9), 202 (12), 177 (11), 176 (24) [204−CO]⁺, 175 (11), 150 (10) [176−C₂H₅]⁺, 121 (43), 106 (100), 101 (13); elemental analysis calcd (%) for C₂₄H₁₇NO₂: C 82.03, H 4.88, N 3.99; found: C 82.47, H 5.17, N 4.15.

N-(2,3-Dimethylphenyl)anthracene-1,9-dicarboxyimide (6i): Compound **3** (1.99 g, 8.02 mmol), 2,3-dimethylaniline (1.98 g, 16.3 mmol), zinc acetate dihydrate (370 mg) and imidazole (10 g) were allowed to react (4 h) as described for **6f**. The product was obtained as orange crystals with yellow solid-state fluorescence (1.57 g, 56%). M.p. 290–291 °C; *R*_f (silica gel; CHCl₃) = 0.24; ¹H NMR (CDCl₃): δ = 2.11 (s, 3H; CH₃), 2.48 (s, 3H; CH₃), 7.36 (m, 2H; aromatic H), 7.65 (m, 1H; aromatic H), 7.80 (m, 2H; aromatic H), 7.89 (m, 1H; aromatic H), 8.16 (d, *J* = 7.7 Hz, 1H; aromatic H), 8.44 (d, *J* = 8.3 Hz, 1H; aromatic H), 8.82 (d, *J* = 7.1 Hz, 1H; aromatic H), 8.93 (s, 1H; aromatic H), 9.98 ppm (d, *J* = 9.1 Hz, 1H; aromatic H); ¹³C NMR (CDCl₃): δ = 14.6 (CH₃), 20.9 (CH₃), 113.6, 123.2, 126.0, 126.3, 126.5, 126.9, 127.1, 127.4, 127.5, 127.8, 129.5, 130.2, 130.9, 131.3, 132.0, 133.0, 134.4, 135.9, 137.2, 138.6, 163.0 (C=O), 163.5 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 3070 (w), 2920 (w), 1718 (m), 1695 (w), 1680 (s, C=O), 1660 (s, C=O), 1602 (w, C=C), 1565 (m, C=C), 1535 (w, C=C), 1472 (m), 1452 (w), 1392 (w), 1366 (s), 1321 (m), 1267 (m), 1239 (m), 1215 (m), 1200 (w), 1152 (w), 884 (w), 777 (m), 753 (m), 738 (m), 710 (m), 610 (w), 557 cm^{−1} (w); UV/Vis (CHCl₃): λ_{\max} (log ϵ) = 361 (3.539), 380 (3.946), 418 (3.857), 438 (3.986), 463 nm (3.839); fluorescence (CHCl₃): λ_{\max} (*I*_{rel}) = 483 (1), 513 nm (0.76); solid-state fluorescence: λ_{\max} = 484, 523, 540 (sh), 631 nm; MS (70 eV): *m/z* (%): 352 (11), 351 (46) [M]⁺, 337 (8), 336 (36), 335 (25), 334 (100) [M−OH]⁺, 319 (11), 306 (6) [334−CO]⁺, 291 (8), 230

(3), 202 (4), 176 (14), 175 (3), 168 (3); elemental analysis calcd (%) for $C_{24}H_{17}NO_2$: C 82.03, H 4.88, N 3.99; found: C 82.23, H 5.07, N 3.99.

N-(2,5-Di-*tert*-butylphenyl)anthracene-1,9-dicarboxyimide (6j): Compound **3** (1.98 g, 7.98 mmol), 2,5-di-*tert*-butylaniline (2.37 g, 11.5 mmol), zinc acetate dihydrate (350 mg) and imidazole (10 g) were allowed to react (4 h) as described for **6f**. The product was obtained as bright golden-yellow crystals with a strong solid-state fluorescence (2.22 g, 64%). M.p. 335–337 °C; R_f (silica gel; $CHCl_3$)=0.73; 1H NMR ($CDCl_3$): δ =1.31 (s, 9H; $C(CH_3)_3$), 1.34 (s, 9H; $C(CH_3)_3$), 7.07 (d, J =2.2 Hz, 1H; aromatic H), 7.47 (dd, J_1 =8.4, J_2 =2.2 Hz, 1H; aromatic H), 7.61 (d, J =8.5 Hz, 1H; aromatic H), 7.66 (m, 1H; aromatic H), 7.83 (m, 2H; aromatic H), 8.17 (d, J =8.6 Hz, 1H; aromatic H), 8.45 (d, J =8.4 Hz, 1H; aromatic H), 8.84 (d, J =7.2 Hz, 1H; aromatic H), 8.93 (s, 1H; aromatic H), 9.97 (d, J =9.3 Hz, 1H; aromatic H); ^{13}C NMR ($CDCl_3$): δ =31.3 (CH_3), 31.7 (CH_3), 34.3 ($C(CH_3)_3$), 35.5 ($C(CH_3)_3$), 113.4, 123.1, 125.6, 126.1, 126.6, 127.0, 128.1, 128.7, 129.0, 129.2, 129.7, 131.5, 132.6, 133.5, 133.85, 133.92, 135.3, 136.6, 143.7, 150.0, 164.7 (C=O), 166.5 ppm (C=O); IR (KBr): $\tilde{\nu}$ =3050 (w), 2963 (m), 2910 (w), 2875 (w), 1700 (s, C=O), 1662 (s, C=O), 1621 (w, C=C), 1563 (s, C=C), 1532 (m, C=C), 1430 (m), 1398 (m), 1372 (m), 1318 (m), 1279 (w), 1251 (w), 1213 (m), 1185 (w), 1176 (w), 1145 (w), 1055 (w), 895 (w), 840 (w), 796 (w), 752 (w), 736 (m), 722 (w), 667 (w), 625 cm^{-1} (w); UV/Vis ($CHCl_3$): λ_{max} (log ϵ)=361 (3.583), 379 (3.868), 416 (3.753), 436 (3.873), 462 nm (3.731); fluorescence ($CHCl_3$): λ_{max} (I_{rel})=481 (1), 512 nm (0.77); fluorescence quantum yield ($CHCl_3$, reference perylene-3,4,9,10-tetracarboxylic tetramethyl ester¹⁷¹ with Φ =100%): 92%; solid-state fluorescence: λ_{max} =529, 559 nm (sh); MS (70 eV): m/z (%): 435 (2) [M]⁺, 380 (5), 379 (28), 378 (100) [$M-C_4H_9$]⁺, 363 (5), 362 (12), 346 (3), 279 (5), 167 (10), 149 (33), 112 (4), 111 (5), 109 (3), 105 (3), 97 (7), 95 (5), 91 (4), 85 (10), 83 (17), 81 (6), 71 (11), 69 (11), 57 (18), 55 (12); elemental analysis calcd (%) for $C_{30}H_{29}NO_2$: C 82.73, H 6.71, N 3.22; found: C 82.77, H 6.66, N 3.22.

Dimerisation of the anthracene-1,9-dicarboxyimides—preparation of the optical filter solution and apparatus for irradiation: A solution was prepared with naphthalene-1,8-dicarboxylic anhydride and KOH pellets (efficient exclusion of carbonate) in distilled water so that an extinction of 4–5 cm^{-1} was obtained between 250 and 320 nm; cutoff wavelength=324 nm and absorptivity $E=1$ per cm at 329 nm. The extinction must be low for $\lambda > 360$ nm. The anthracene-1,9-dicarboxyimides to be dimerised were dissolved in chloroform in standard NMR tubes (5 mm diameter), placed in the centre of the beaker and irradiated from the side through the filter solution by using a 150 W tungsten wire bulb lamp.

Photoreaction of anthracene-1,9-dicarboxyimides to form 10 and 11—general procedure: Compounds **6** (200 mg, about 0.5–0.7 mmol depending on the substituents on the nitrogen atoms of **6**) to be dimerised were dissolved in chloroform (1 mL or more) in a standard NMR tube (inner diameter 4 mm). The tube was sealed and irradiated through the filter solution of dipotassium naphthalene-1,8-dicarboxylate for several days until fluorescence had completely disappeared. The NMR tube was then opened and irradiation was continued until complete evaporation.

N-Ethylanthracene-1,9-dicarboxyimide dimers 10b and 11b: Compound **6b** (200 mg, 7.3 mmol) was allowed to react according to the general procedure for photodimerisation. The product was obtained as a pale-yellow powder (200 mg, $\approx 100\%$). M.p. 173–175 °C; R_f (silica gel; $CHCl_3$)=0.34; 1H NMR ($CDCl_3$): δ =0.90 (m, 6H; CH_3), 4.23 (m, 2H; NCH_2CH_3), 4.33 (m, 2H; NCH_2CH_3), 4.81 (s, 1H), 4.83 (s, 1H), 6.78 (m, 1H; aromatic H), 6.86 (m, 1H; aromatic H), 7.00 (m, 5H; aromatic H), 7.12 (m, 1H; aromatic H), 7.51 (m, 3H; aromatic H), 7.72 (m, 1H; aromatic H), 7.81 (m, 1H; aromatic H), 7.83 ppm (m, 1H; aromatic H); ^{13}C NMR ($CDCl_3$): δ =13.9 (CH_3), 36.1 (CH_2), 58.2, 62.4 (CH), 123.6, 125.96, 126.04, 127.4, 127.6, 128.0, 129.2, 130.0, 131.3, 132.5, 132.8, 135.5, 140.2, 140.7, 141.2, 143.2, 144.0, 165.3 (C=O), 173.7 ppm (C=O); IR (KBr): $\tilde{\nu}$ =3079 (w), 2980 (w), 2936 (w), 1707 (m, C=O), 1666 (s, C=O), 1603 (w, C=C), 1560 (w), 1482 (w, C=C), 1452 (w), 1437 (w), 1388 (w), 1371 (w), 1356 (m), 1312 (w), 1250 (m), 1231 (w), 1138 (w), 1096 (m), 824 (w), 796 (w), 780 (w), 751 (w), 732 (w), 708 (w), 670 (w), 609 cm^{-1} (w); UV/Vis ($CHCl_3$): λ_{max} (log ϵ)=264 (4.026) (sh), 300 (3.366), 313 nm (3.280); MS (70 eV): m/z (%): 276 (20), 275 (94) [M]⁺, 274 (9), 260 (17) [$M-CH_3$]⁺, 259 (5), 248 (19), 247 (100) [$M-C_2H_5$]⁺, 246 (7), 233 (8), 231 (9), 230 (4)

[247–OH]⁺, 219 (7), 205 (11), 204 (9) [$M-C_3H_5NCO$]⁺, 203 (22) [204–H]⁺, 202 (9), 190 (9), 177 (19), 176 (27) [204–CO]⁺, 175 (9), 174 (6), 150 (7), 116 (7), 88 (29) [176– C_7H_4]⁺, 75 (6).

N-Butylanthracene-1,9-dicarboxyimide dimers 10c and 11c: Compound **6c** (200 mg, 6.6 mmol) was allowed to react according to the general procedure for photodimerisation. The product was obtained as a pale-yellow powder (200 mg, $\approx 100\%$). M.p. 170–172 °C; R_f (silica gel; $CHCl_3$)=0.50; 1H NMR ($CDCl_3$): δ =1.03 (t, J =7.3 Hz, 6H; CH_3), 1.49 (m, 4H; CH_2CH_3), 1.76 (q, J =7.1 Hz, 4H; NCH_2CH_2), 4.24 (m, 4H; NCH_2), 4.79 (s, 1H), 4.80 (s, 1H), 6.77 (m, 1H; aromatic H), 6.84 (m, 1H; aromatic H), 6.98 (m, 5H; aromatic H), 7.10 (m, 1H; aromatic H), 7.25 (m, 1H; aromatic H), 7.48 (m, 3H; aromatic H), 7.78 (m, 1H; aromatic H), 7.81 ppm (m, 1H; aromatic H); ^{13}C NMR ($CDCl_3$): δ =14.3 (CH_3), 20.8 (CH_2), 30.8 (CH_2), 40.7 (NCH_2), 58.3, 62.4 (CH), 62.5 (CH), 123.3, 123.5, 126.0, 126.2, 127.1, 127.3, 127.4, 127.57, 127.63, 127.8, 128.0, 128.7, 130.0, 132.5, 133.9, 140.2, 140.5, 140.7, 141.1, 141.4, 142.2, 142.7, 163.7 (C=O), 163.8 (C=O), 173.9 (C=O), 174.1 ppm (C=O); IR (KBr): $\tilde{\nu}$ =3068 (w), 2960 (m), 2932 (m), 2872 (w), 1709 (s, C=O), 1667 (s, C=O), 1602 (w, C=C), 1481 (w, C=C), 1462 (m), 1452 (m), 1433 (w), 1390 (m), 1355 (s), 1322 (w), 1275 (w), 1239 (m), 1190 (w), 1139 (w), 1099 (m), 939 (w), 819 (w), 779 (w), 755 (m), 708 (m), 671 (w), 610 cm^{-1} (m); UV/Vis ($CHCl_3$): λ_{max} (log ϵ)=264 (4.123) (sh), 302 (3.512), 313 nm (3.466); MS (70 eV): m/z (%): 304 (19), 303 (87) [M]⁺, 286 (16) [$M-OH$]⁺, 274 (6), 262 (6), 261 (36), 260 (16) [$M-C_3H_7$]⁺, 259 (8), 248 (22), 247 (100) [$M-C_4H_9$]⁺, 231 (6), 230 (7) [247–OH]⁺, 219 (5), 204 (5) [$M-C_4H_9NCO$]⁺, 203 (11) [204–H]⁺, 202 (8), 190 (5), 177 (9), 176 (14) [204–CO]⁺, 150 (2), 88 (4) [176– C_7H_4]⁺.

N-Pentylanthracene-1,9-dicarboxyimide dimers 10d and 11d: Compound **6d** (200 mg, 6.3 mmol) was allowed to react according to the general procedure for photodimerisation. The product was obtained as a pale-yellow powder (200 mg, $\approx 100\%$). M.p. 159–162 °C; R_f (silica gel; $CHCl_3$)=0.62; 1H NMR ($CDCl_3$): δ =0.96 (m, 6H; CH_3), 1.45 (m, 8H; $(CH_2)_2CH_3$), 1.79 (m, 4H; CH_2CH_2N), 4.25 (m, 4H; CH_2N), 4.81 (s, 1H), 4.82 (s, 1H), 6.79 (m, 1H; aromatic H), 6.86 (m, 1H; aromatic H), 7.01 (m, 5H; aromatic H), 7.11 (m, 1H; aromatic H), 7.27 (m, 1H; aromatic H), 7.45 (m, 3H; aromatic H), 7.80 (m, 1H; aromatic H), 7.83 ppm (m, 1H; aromatic H); ^{13}C NMR ($CDCl_3$): δ =12.2 (CH_3), 20.5, 26.0, 27.4, 38.6 (CH_2N), 55.9, 60.1 (CH), 60.2 (CH), 121.0, 121.2, 123.6, 123.9, 124.8, 125.1, 125.1, 125.3, 125.3, 125.4, 125.7, 126.4, 127.7, 130.2, 131.6, 137.9, 138.2, 138.4, 138.8, 139.1, 139.9, 140.4, 161.3 (C=O), 161.4 (C=O), 171.6 (C=O), 171.8 ppm (C=O); IR (KBr): $\tilde{\nu}$ =3069 (w), 2957 (m), 2930 (m), 2860 (w), 1709 (s, C=O), 1668 (s, C=O), 1602 (w, C=C), 1481 (w, C=C), 1462 (w), 1452 (w), 1434 (w), 1390 (w), 1355 (m), 1309 (w), 1262 (w), 1241 (w), 1187 (w), 1141 (w), 1102 (m), 1073 (w), 819 (w), 779 (w), 756 (w), 709 (w), 670 (w), 610 cm^{-1} (w); UV/Vis ($CHCl_3$): λ_{max} (log ϵ)=266 (4.733), 300 (3.619), 313 (3.591), 360 (3.233), 380 (3.584), 415 (3.466), 437 (3.595), 461 nm (3.446); MS (70 eV): m/z (%): 318 (23), 317 (100) [M]⁺, 300 (11) [$M-OH$]⁺, 274 (5), 261 (33), 260 (15) [$M-C_4H_9$]⁺, 248 (24), 247 (90) [$M-C_5H_{10}$]⁺, 230 (6) [247–OH]⁺, 219 (4), 204 (4) [$M-C_5H_{10}NCO$]⁺, 203 (9), 202 (7), 190 (4), 177 (8), 176 (11) [204–CO]⁺, 88 (3) [176– C_7H_4]⁺.

N-Hexylanthracene-1,9-dicarboxyimide dimers 10e and 11e: Compound **6e** (200 mg, 6.0 mmol) was allowed to react according to the general procedure for photodimerisation. The product was obtained as a pale-yellow powder (200 mg, $\approx 100\%$). M.p. 165–166 °C; R_f (silica gel; $CHCl_3$)=0.89; 1H NMR ($CDCl_3$): δ =0.91 (m, 6H; CH_3), 1.40 (m, 12H; $(CH_2)_3CH_3$), 1.78 (m, 4H; CH_2CH_2N), 4.25 (m, 4H; CH_2N), 4.80 (s, 1H), 4.82 (s, 1H), 6.77 (m, 1H; aromatic H), 6.85 (t, J =7.1 Hz, 1H; aromatic H), 6.98 (m, 5H; aromatic H), 7.10 (t, J =7.7 Hz, 1H; aromatic H), 7.27 (m, 1H; aromatic H), 7.48 (m, 3H; aromatic H), 7.79 (m, 1H; aromatic H), 7.81 ppm (m, 1H; aromatic H); ^{13}C NMR ($CDCl_3$): δ =14.5 (CH_3), 23.1, 27.2, 28.7, 32.0, 40.9 (CH_2N), 58.3, 62.4 (CH), 62.6 (CH), 123.3, 123.5, 126.0, 126.2, 127.2, 127.3, 127.4, 127.6, 127.6, 127.8, 128.0, 128.7, 130.0, 132.5, 133.9, 140.2, 140.5, 140.67, 140.70, 141.2, 141.4, 142.2, 142.7, 163.6 (C=O), 163.8 (C=O), 173.9 (C=O), 174.1 ppm (C=O); IR (KBr): $\tilde{\nu}$ =2957 (m), 2930 (s), 2858 (m), 1708 (s, C=O), 1667 (s, C=O), 1602 (w, C=C), 1462 (w, C=C), 1434 (w), 1390 (w), 1355 (s), 1250 (w), 1182 (w), 1140 (w), 1101 (w), 1073 (w), 820 (w), 779 (w), 757 (w), 709 (w), 671 (w), 610 cm^{-1} (m); UV/Vis ($CHCl_3$): λ_{max} (log ϵ)=265 (4.418), 301 (3.302), 313 nm (3.154); MS (FAB,

3-nitrobenzyl alcohol): m/z : 685 [$M+Na$] $^+$, 663 [M] $^+$; MS (70 eV): m/z (%): 332 (23), 331 (100) [M] $^+$, 314 (9) [$M-OH$] $^+$, 274 (4), 262 (6), 261 (31), 260 (15), 259 (6), 248 (24), 247 (81) [$M-C_6H_5$] $^+$, 230 (6) [$247-OH$] $^+$, 219 (4), 204 (4) [$M-C_6H_5NCO$] $^+$, 203 (8), 202 (6), 190 (4), 177 (6), 176 (9) [$204-CO$] $^+$.

N-Nonylanthracene-1,9-dicarboxyimide dimers 10f and 11f: Compound **6f** (200 mg, 5.4 mmol) was allowed to react according to the general procedure for photodimerisation. The product was obtained as a pale-yellow powder (200 mg, $\approx 100\%$). M.p. 151–153 °C; R_f (silica gel; $CHCl_3$)=0.76; 1H NMR ($CDCl_3$): δ =0.86 (m, 6H; CH_3), 1.26–1.42 (m, 24H; $(CH_2)_6CH_3$), 1.76 (m, 4H; NCH_2CH_3), 4.23 (m, 4H; NCH_2), 4.79 (s, 1H), 4.80 (s, 1H), 6.75 (m, 1H; aromatic H), 6.84 (m, 1H; aromatic H), 6.92–7.01 (m, 5H; aromatic H), 7.09 (m, 1H; aromatic H), 7.26 (m, 1H; aromatic H), 7.45 (m, 3H; aromatic H), 7.79 (m, 1H; aromatic H), 7.81 ppm (m, 1H; aromatic H); ^{13}C NMR ($CDCl_3$): δ =13.5 (CH_3), 22.1, 26.6, 27.7, 28.7, 28.8, 29.0, 31.3, 40.0 (CH_2N), 57.3, 61.4 (CH), 61.6 (CH), 122.3, 125.0, 125.2, 126.2, 126.3, 126.6, 126.8, 127.0, 127.7, 129.0, 131.5, 132.9, 139.5, 139.7, 140.2, 140.4, 162.8 (C=O), 172.9 (C=O), 173.1 ppm (C=O); IR (KBr): $\tilde{\nu}$ =2927 (m), 2856 (m), 1707 (s, C=O), 1663 (s, C=O), 1462 (w, C=C), 1391 (w), 1356 (m), 1242 (w), 1170 (w), 1102 (w), 820 (w), 778 (w), 752 (w), 710 (w), 606 cm^{-1} (m); UV/Vis ($CHCl_3$): λ_{max} ($\log \epsilon$)=266 (sh) (4.214), 303 (3.059), 313 nm (3.068); MS (70 eV): m/z (%): 374 (26), 373 (100) [M] $^+$, 356 (7) [$M-OH$] $^+$, 261 (29), 260 (17) [$M-C_8H_{17}$] $^+$, 248 (29), 247 (72) [$M-C_9H_{19}$] $^+$, 230 (7) [$247-OH$] $^+$, 205 (5), 204 (5) [$M-C_9H_{19}NCO$] $^+$, 203 (10), 202 (7), 177 (9), 176 (10) [$204-CO$] $^+$.

N-(1-Hexylheptyl)anthracene-1,9-dicarboxyimide dimers 10g and 11g: Compound **6g** (200 mg, 4.7 mmol) was allowed to react according to the general procedure for photodimerisation. The product was obtained as a pale-yellow powder (200 mg, $\approx 100\%$). M.p. 142–144 °C; R_f (silica gel; toluene)=0.90; 1H NMR ($CDCl_3$): δ =0.84 (m, 12H; CH_3), 1.20–1.45 (m, 32H; $(CH_2)_4$), 1.88 (m, 8H; $(CH_2)CHN$), 2.34 (m, 8H; $(CH_2)CHN$), 4.82 (s, 2H), 5.18–5.32 (m, 2H; $(CH_2)_2CHN$), 6.77 (m, 1H; aromatic H), 6.84 (m, 1H; aromatic H), 6.90–7.04 (m, 5H; aromatic H), 7.08 (m, 1H; aromatic H), 7.27 (m, 1H; aromatic H), 7.38 (m, 2H; aromatic H), 7.47 (m, 1H; aromatic H), 7.77 (s, 1H; aromatic H), 7.79 ppm (s, 1H; aromatic H); ^{13}C NMR ($CDCl_3$): δ =14.5 (CH_3), 23.0, 27.4, 29.6, 32.3, 42.5, 54.7 ($NCHR_2$), 58.5, 62.7 (CH), 123.8, 124.1, 125.1, 125.7, 126.0, 127.2, 127.4, 127.4, 127.6, 127.8, 128.8, 130.1, 132.3, 133.7, 140.7, 140.9, 141.1, 141.4, 143.4, 143.6 ppm; IR (KBr): $\tilde{\nu}$ =2955 (m), 2926 (s), 2856 (m), 1708 (s, C=O), 1666 (s, C=O), 1462 (s, C=C), 1402 (w), 1353 (m), 1320 (w), 1245 (m), 1180 (w), 1105 (w), 1072 (w), 881 (w), 819 (w), 778 (w), 752 (w), 710 (w), 670 (w), 612 cm^{-1} (m); UV/Vis ($CHCl_3$): λ_{max} ($\log \epsilon$)=266 (4.647), 301 (3.622), 314 (3.585), 380 (3.518), 410 (3.395), 434 (3.556), 458 (3.492), 489 (3.262), 526 nm (3.474); MS (70 eV): m/z (%): 430 (10), 429 (33) [M] $^+$, 344 (3) [$M-C_6H_{13}$] $^+$, 260 (6), 248 (45), 247 (100) [$M-C_{13}H_{26}$] $^+$, 230 (7) [$247-OH$] $^+$, 205 (4), 204 (2) [$M-C_{13}H_{27}NCO$] $^+$, 203 (4), 202 (5), 177 (3), 176 (3) [$204-CO$] $^+$.

N-(2-Ethylphenyl)anthracene-1,9-dicarboxyimide dimers 10h and 11h: Compound **6h** (200 mg, 5.7 mmol) was allowed to react according to the general procedure for photodimerisation. The product was obtained as a pale-yellow powder (200 mg, $\approx 100\%$). M.p. 148–150 °C; R_f (silica gel; $CHCl_3$)=0.30; 1H NMR ($CDCl_3$): δ =1.13 (m, 3H; CH_3), 1.47 (m, 3H; CH_3), 2.41 (m, 2H; CH_2CH_3), 2.81 (m, 2H; CH_2CH_3), 5.01 (m, 1H), 5.03 (m, 1H), 6.95–7.02 (m, 7H; aromatic H), 7.10–7.18 (m, 3H; aromatic H), 7.41 (m, 3H; aromatic H), 7.50–7.56 (m, 7H; aromatic H), 7.84–7.86 ppm (m, 2H; aromatic H); ^{13}C NMR ($CDCl_3$): δ =14.4 (CH_3), 14.5 (CH_3), 24.3 (CH_2), 24.7 (CH_2), 59.7, 60.0, 63.1 (CH), 63.6 (CH), 124.2, 124.9, 127.3, 127.4, 127.6, 127.9, 128.0, 128.3, 129.0, 129.6, 130.0, 134.3, 134.5, 141.3, 141.9, 142.7, 143.4 ppm; IR (KBr): $\tilde{\nu}$ =3066 (w), 3034 (w), 2968 (w), 2932 (w), 2875 (w), 1718 (s, C=O), 1679 (s, C=O), 1600 (w, C=C), 1491 (w, C=C), 1452 (m), 1363 (s), 1321 (w), 1264 (m), 1234 (w), 1208 (w), 1145 (w), 1055 (w), 910 (w), 852 (w), 779 (w), 757 (m), 735 (m), 707 (w), 615 cm^{-1} (m); UV/Vis ($CHCl_3$): λ_{max} ($\log \epsilon$)=262 (4.294), 301 (3.610), 316 (3.594), 380 (2.913), 412 (2.726), 437 (2.898), 463 nm (2.700); MS (70 eV): m/z (%): 352 (16), 351 (66) [M] $^+$, 335 (24), 334 (91) [$M-OH$] $^+$, 323 (17), 322 (71) [$M-C_2H_5$] $^+$, 319 (24), 306 (12), 291 (16), 247 (11), 204 (5) [$M-C_2H_5-C_6H_4-NCO$] $^+$, 203 (9), 202 (12), 177 (11), 176 (24) [$204-CO$] $^+$, 175 (11), 150 (10) [$176-C_2H_5$] $^+$, 121 (43), 106 (100), 101 (13).

N-(2,3-Dimethylphenyl)anthracene-1,9-dicarboxyimide dimers 10i and 11i: Compound **6i** (200 mg, 5.7 mmol) was allowed to react according to the general procedure for photodimerisation. The product was obtained as a pale-yellow powder (200 mg, $\approx 100\%$). M.p. 290–292 °C; R_f (silica gel; $CHCl_3$)=0.29; 1H NMR ($CDCl_3$): δ =2.00 (s, 3H; CH_3), 2.40 (s, 6H; CH_3), 2.49 (s, 3H; CH_3), 5.03 (m, 2H), 6.95–7.52 (m, 18H; aromatic H), 7.87 ppm (m, 2H; aromatic H); ^{13}C NMR ($CDCl_3$): δ =14.5 (CH_3), 14.9 (CH_3), 20.9 (CH_3), 58.9, 62.5 (CH), 62.9 (CH), 123.2, 126.3, 127.1, 127.2, 127.6, 128.0, 128.3, 128.9, 131.3, 133.0, 134.5, 134.7, 138.7, 139.0, 140.5, 141.5, 142.5, 164.5 (C=O), 165.1 (C=O), 174.6 (C=O), 175.3 ppm (C=O); IR (KBr): $\tilde{\nu}$ =3071 (w), 2924 (w), 1718 (s, C=O), 1681 (s, C=O), 1602 (w, C=C), 1472 (m, C=C), 1453 (w), 1365 (s), 1322 (w), 1267 (m), 1239 (m), 1153 (w), 1048 (w), 912 (w), 884 (w), 835 (w), 818 (w), 777 (m), 756 (m), 738 (w), 708 (w), 610 (w), 558 cm^{-1} (w); UV/Vis ($CHCl_3$): λ_{max} ($\log \epsilon$)=264 (4.525), 301 (3.639), 312 (3.628), 379 (3.415), 414 (3.314), 437 (3.446), 462 nm (3.296); MS (70 eV): m/z (%): 352 (11), 351 (46) [M] $^+$, 337 (8), 336 (36), 335 (25), 334 (100) [$M-OH$] $^+$, 319 (11), 306 (6) [$334-CO$] $^+$, 291 (8), 230 (3), 202 (4), 176 (14), 175 (3), 168 (3).

N-(2,5-Di-*tert*-butylphenyl)anthracene-1,9-dicarboxyimide dimers 10j and 11j: Compound **6j** (200 mg, 4.6 mmol) was allowed to react according to the general procedure for photodimerisation. The product was obtained as a pale-yellow powder (200 mg, $\approx 100\%$). M.p. >300 °C; R_f (silica gel; $CHCl_3$)=0.83; 1H NMR ($CDCl_3$): δ =1.24 (m, 20H), 1.44 (s, 6H), 1.61 (m, 10H), 4.94 (m, 1H), 5.11 (m, 1H), 6.75 ppm (m, 1H; aromatic H); ^{13}C NMR ($CDCl_3$): δ =31.6 (CH_3), 31.7 (CH_3), 32.3 (CH_3), 32.6 (CH_3), 36.5 ($C(CH_3)_3$), 58.4, 63.8 (CH), 64.2 (CH), 125.1, 125.1, 125.97, 126.01, 127.2, 127.6, 127.8, 128.7, 129.1, 129.6, 130.1, 135.0 ppm; IR (KBr): $\tilde{\nu}$ =3069 (w), 2963 (m), 2869 (w), 1719 (s, C=O), 1679 (s, C=O), 1601 (w, C=C), 1481 (w, C=C), 1462 (w), 1394 (w), 1360 (s), 1321 (w), 1251 (m), 1204 (w), 1158 (w), 1054 (w), 910 (w), 836 (m), 778 (w), 755 (w), 735 (w), 709 (w), 674 (w), 616 cm^{-1} (w); UV/Vis ($CHCl_3$): λ_{max} ($\log \epsilon$)=265 (4.460), 303 (3.701), 315 (3.664), 379 (3.370), 416 (3.283), 436 (3.386), 460 nm (3.253); MS (70 eV): m/z (%): 435 (2) [M] $^+$, 380 (5), 379 (28), 378 (100) [$M-C_4H_9$] $^+$, 363 (5), 362 (12), 346 (3), 279 (5), 167 (10), 149 (33), 112 (4), 111 (5), 109 (3), 105 (3), 97 (7), 95 (5), 91 (4), 85 (10), 83 (17), 81 (6), 71 (11), 69 (11), 57 (18), 55 (12).

Amidine 12 from anthracene-1,9-dicarboxylic anhydride and neopentane-diamine: Compound **3** (1.27 g, 5.12 mmol), neopentanediamine (5 mL, 48.9 mmol) and distilled water (30 mL) were stirred at room temperature under argon for 1 h and then heated at reflux with stirring for 3 h (bath temperature 170 °C, orange material). The mixture was allowed to cool, collected by vacuum filtration (G4 glass filter), washed with small amounts of distilled water and purified by pressure-induced flash chromatography in the dark (silica gel, chloroform). The yellow fluorescent main fraction was rapidly evaporated, dried in a stream of argon, then in a medium vacuum and stored in the dark; dimers **14** and **15** would be formed in daylight. The product was obtained as a bright-yellow powder with a strong solid-state fluorescence (1.77 g, 79%). M.p. 175–177 °C; R_f (silica gel; $CHCl_3$)=0.10; 1H NMR ($CDCl_3$): δ =1.10 (s, 6H; CH_3), 3.49 (s, 2H; CH_2N), 3.82 (s, 2H; CH_2N), 7.59 (m, 2H; aromatic H), 7.72 (m, 1H; aromatic H), 8.04 (d, J =7.9 Hz, 1H; aromatic H), 8.16 (d, J =8.2 Hz, 1H; aromatic H), 8.69 (d, J =7.4 Hz, 1H; aromatic H), 8.72 (s, 1H; aromatic H), 10.00 ppm (d, J =9.2 Hz, 1H; aromatic H); ^{13}C NMR ($CDCl_3$): δ =24.8 (CH_3), 27.7 (CH_2N), 50.9 (CH_2N), 57.8 ($C(CH_3)_2$), 113.3, 116.1, 125.1, 125.5, 126.0, 127.1, 127.5, 128.9, 129.3, 129.9, 131.5, 132.3, 132.7, 134.9, 146.4 (C=N), 163.9 ppm (C=O); IR (KBr): $\tilde{\nu}$ =3125 (w), 3060 (w), 2960 (w), 2950 (w), 2847 (w), 1661 (s, C=O), 1631 (s, C=N), 1603 (s, C=C), 1562 (m, C=C), 1533 (w, C=C), 1428 (m), 1369 (m), 1355 (w), 1330 (w), 1298 (m), 1261 (s), 1196 (m), 1169 (m), 1144 (m), 1091 (w), 1023 (w), 895 (m), 790 (m), 731 (m), 668 (m), 532 cm^{-1} (w); UV/Vis ($CHCl_3$): λ_{max} ($\log \epsilon$)=253 (4.476), 271 (4.795), 368 (3.408), 381 (3.643), 387 (3.773), 419 (sh) (3.666), 445 (3.870), 466 (3.895), 497 nm (sh) (3.633); fluorescence ($CHCl_3$): λ_{max} (I_{rel})=518 (1), 558 (0.59), 601 nm (sh) (0.32); solid-state fluorescence: λ_{max} =555 nm; MS (70 eV): m/z (%): 316 (3), 315 (23), 314 (100) [M] $^+$, 313 (12), 300 (7), 299 (33) [$M-CH_3$] $^+$, 284 (9), 271 (10) [$99-CO$] $^+$, 259 (10), 258 (27) [$M-C_4H_8$] $^+$, 246 (9), 231 (19), 230 (59) [$258-CO$] $^+$, 203 (15), 202 (32) [$M-C_5H_{10}NCO$] $^+$, 201 (13), 176 (6) [$202-CN$] $^+$, 175 (7); elemental analysis calcd (%) for $C_{21}H_{18}N_2O$: C 80.23, H 5.77, N 8.91; found: C 79.96, H 5.80, N 8.95.

Crystal data for 12: The crystal structure was determined with an Enraf-Nonius CAD4 diffractometer with $\text{MoK}\alpha$ radiation and a highly oriented graphite crystal as monochromator. $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}$; $M_r = 314.37$; $a = 9.134(3)$, $b = 10.189(2)$, $c = 16.816(4)$ Å; $\beta = 101.22(3)^\circ$; $V = 1535.1(7)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.360$ g cm⁻³; $\mu = 0.085$ mm⁻¹; monoclinic; space group $P2_1/c$ (Nr. 14). Data collection: single crystal $0.10 \times 0.40 \times 0.47$ mm³ (yellow plate); ω data collection, scan width $0.50 + 0.35 \tan \theta$; maximal collection time 90 s for each reflex, number of reflections: 2275 (collected), 2120 (independent), 1641 (observed) [$I > 2\sigma(I)$], minimal correction for absorption, structure solution with SHELXS86, refinement with SHELXL93,^[18] 219 parameters, $R_1 = 0.0462(2\sigma(I))$, $wR_2 = 0.1293(2\sigma(I))$, weighing $w = 1/[\sigma_2 F_o^2 + 0.0621]$, GOF = 1.108, max. and min. residual electron density $0.170/-0.168$ e Å⁻³.

CCDC 204452 contains the supplementary crystallographic data for **12**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Amidine 13 from anthracene-1,9-dicarboxylic anhydride and *o*-phenylenediamine: Compound **3** (560 mg, 2.26 mmol) and *o*-phenylenediamine (1.56 g, 14.4 mmol) in acetic acid (100 mL) were heated at reflux under argon for 3 h (dark-red solution). The mixture was then evaporated in vacuo and purified by pressure-induced flash chromatography in the dark (silica gel, chloroform). The reddish-orange fluorescent main fraction was rapidly evaporated, dried in a stream of argon and then in a medium vacuum and stored in the dark; dimers **16** and **17** would be formed in daylight. The product was obtained as a bright-red, analytically pure powder with a reddish-orange solid-state fluorescence (260 mg, 36%). Recrystallisation from chloroform gave reddish-brown needles. M.p. 228°C; R_f (silica gel, CHCl_3) = 0.75; ¹H NMR (CDCl_3): $\delta = 7.51$ (m, 2H; aromatic H), 7.64 (m, 1H; aromatic H), 7.76 (m, 1H; aromatic H), 7.89 (m, 1H; aromatic H), 7.97 (m, 1H; aromatic H), 8.09 (d, $J = 8.4$ Hz, 1H; aromatic H), 8.40 (d, $J = 8.4$ Hz, 1H; aromatic H), 8.63 (m, 1H; aromatic H), 8.69 (s, 1H; aromatic H), 8.91 (d, $J = 7.1$ Hz, 1H; aromatic H), 10.64 ppm (d, $J = 9.1$ Hz, 1H; aromatic H); ¹³C NMR (CDCl_3): $\delta = 114.9$, 116.0 (CH), 120.2 (CH), 123.1, 125.3 (CH), 125.5 (CH), 125.7 (CH), 126.4, 126.7 (CH), 128.0 (CH), 129.5 (CH), 129.6, 130.5 (CH), 131.0, 131.5, 132.5, 133.4 (CH), 133.7 (CH), 136.5 (CH), 144.1, 150.1 (C=N), 160.8 ppm (C=O); IR (KBr): $\tilde{\nu} = 3050$ (w), 2930 (w), 1690 (s, C=O), 1622 (m, C=N), 1559 (m, C=C), 1532 (m, C=C), 1522 (m, C=C), 1450 (m), 1403 (s), 1371 (w), 1362 (m), 1331 (m), 1299 (w), 1272 (m), 1214 (m), 1157 (w), 1058 (w), 878 (w), 748 (s), 714 (m), 442 cm⁻¹ m; UV/Vis (CHCl_3): λ_{max} (log ϵ) = 366 (3.469), 385 (3.535), 461 (3.998), 482 (4.098), 508 nm (3.927); fluorescence (CHCl_3): λ_{max} (I_{rel}) = 554 (0.79), 589 nm (1); fluorescence quantum yield (CHCl_3 , reference perylene-3,4,9,10-tetracarboxylic tetramethyl ester^[17] with $\Phi = 100\%$): 48%; solid-state fluorescence (bright-red powder): $\lambda_{\text{max}} = 607$, 680 nm (sh); solid-state fluorescence (reddish-brown needles): $\lambda_{\text{max}} = 578$, 670 nm; MS (70 eV): m/z (%): 322 (2), 321 (20), 320 (100) [M]⁺, 319 (12), 292 (3) [$M - \text{CO}$]⁺, 291 (8), 290 (3), 289 (1), 265 (1), 264 (1), 160 (6) [M]²⁺, 146 (10) [$M - \text{CO}$]²⁺, 145 (10), 133 (1), 132 (2), 131 (2), 118 (2); elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{12}\text{N}_2\text{O}$: C 82.49, H 3.78, N 8.75; found: C 82.52, H 4.08, N 8.66.

Synthesis of the dimers **7** and **8**:

Aceanthrene Green (7a and 8a): Solid 85% KOH (30.01 g, 454.7 mmol) was heated in a nickel crucible at 150–155°C (temperature control of the melt by a thermocouple). Aceanthrenequinone oxime (**4** and **5**, 6.01 g, 24.3 mmol) was then added in portions with efficient stirring (stainless steel stirrer) and allowed to react for 15 min. The mixture was then cooled to room temperature, treated with distilled water (150 mL), transferred to a large vessel because of the formation of foam, treated with 30% acetic acid (63 mL) and 30% hydrogen peroxide (200 mL) and allowed to stand in air for 6 d. The product was collected by vacuum filtration (G4 glass filter), washed with a small amount of distilled water, dried in air at 115°C, finely pulverised, extracted with ethanol for 2 d (the extract turned from red to colourless) and dried in air at 115°C (5.89 g, 99%; lit.^[2] 90%). M.p. > 300°C; R_f (silica gel, CHCl_3) = 0.00 for the main product **7a**; R_f (silica gel, CHCl_3) = 0.03 for the byproduct **8a**; ¹H NMR ($\text{CDCl}_3/\text{F}_3\text{CCOOD}$): $\delta = 7.49$ (t, $J = 6.06$ Hz, 2H; 6-H, 6'-H, *cis* isomer **8a**), 7.63 (d, $J = 6.74$ Hz, 2H; 5-H, 5'-H, *cis* isomer **8a**), 7.86 (t, $J = 8.08$ Hz, 2H; 6-H, 6'-H, *trans* isomer **7a**), 7.94 (t, $J = 6.74$ Hz, 2H; 7-

H, 7'-H, *cis* isomer **8a**), 8.05 (t, $J = 6.74$ Hz, 2H; 7-H, 7'-H, *trans* isomer **7a**), 8.63 (m, 4H; 3-H, 3'-H, 5-H, 5'-H, *trans* isomer **7a**), 8.90 (m, 4H; 2-H, 2'-H, *trans* isomer **7a**; 3-H, 3'-H, *cis* isomer **8a**), 9.03 (d, $J = 8.76$ Hz, 2H; 2-H, 2'-H, *cis* isomer **8a**), 9.87 (d, $J = 8.08$ Hz, 2H; 8-H, 8'-H, *cis* isomer **8a**), 9.99 ppm (d, $J = 9.43$ Hz, 2H; 8-H, 8'-H, *trans* isomer **7a**); IR (KBr): $\tilde{\nu} = 3067$ (w), 2850 (w), 1674 (s, C=O), 1655 (m, C=O), 1583 (w), 1565 (m), 1534 (m), 1426 (m), 1394 (w), 1371 (w), 1331 (w), 1282 (w), 1259 (w), 1236 (w), 1164 (w), 813 (w), 775 (w), 745 (w), 651 (w), 591 (w), 574 (w), 518 (w), 420 cm⁻¹ (w); UV/Vis (DMSO): λ_{max} (log ϵ) = 285 (4.556), 300 (sh) (4.497), 419 (3.940), 442 (sh) (3.901), 578 (sh) (3.807), 635 (4.100), 691 nm (4.269); fluorescence (DMSO): $\lambda_{\text{max}} = 750$ nm; solid-state fluorescence: $\lambda_{\text{max}} = 796$ nm; MS (70 eV): m/z (%): 491 (22), 490 (61) [M]⁺, 422 (18), 421 (56), 420 (12), 419 (13), 373 (10), 352 (11), 350 (13), 349 (10), 348 (11), 247 (22), 222 (12), 217 (11), 194 (24), 178 (13), 176 (18), 175 (15), 174 (22), 173 (20), 172 (10), 168 (10), 167 (10), 165 (19), 161 (12), 63 (11), 44 (100), 32 (17), 28 (88); MS: m/z calcd for $\text{C}_{32}\text{H}_{14}\text{N}_2\text{O}_4$: 490.0953; found: 490.0967 (MS).

Dimer 7b: Solid 85% KOH (3.90 g, 59.1 mmol) and compound **6b** (750 mg, 2.72 mmol) were allowed to react as was described for **7a** and **8a** (225–235°C, 10 min). The melt was treated with distilled water (400 mL) and oxidised by passing air over it for 1 d. The product was collected by vacuum filtration (G4 glass filter), washed with distilled water, dried at 115°C, purified by flash chromatography (silica gel, starting with a concentrated solution of **7b** in chloroform, elution with toluene and collection by the addition of *tert*-butyl methyl ether to the chloroform), evaporated and extracted with ethanol for one week to give the product as a dark-green powder and violet crystals (210 mg, 28%). M.p. > 350°C; R_f (silica gel; CHCl_3) = 0.01; R_f (silica gel; CHCl_3/n -butanol 40:1) = 0.32; ¹H NMR (CDCl_3): $\delta = 1.46$ (t, $J = 6.8$ Hz, 6H; CH_3), 4.37 (q, $J = 6.9$ Hz, 4H; CH_2N), 7.58 (m, 2H; aromatic H), 7.80 (m, 2H; aromatic H), 8.18 (d, $J = 7.2$ Hz, 2H; aromatic H), 8.32 (d, $J = 8.2$ Hz, 2H; aromatic H), 8.56 (d, $J = 7.3$ Hz, 2H; aromatic H), 9.95 ppm (d, $J = 8.8$ Hz, 2H; aromatic H); ¹³C NMR (CDCl_3): $\delta = 13.9$ (CH_3), 36.5 (CH_2), 116.3, 124.4, 126.3, 127.4, 127.7, 127.9, 129.2, 130.3, 130.9, 131.6, 133.6, 134.5, 163.0 (C=O), 164.5 ppm (C=O); IR (KBr): $\tilde{\nu} = 3125$ (w), 2978 (w), 2934 (w), 2875 (w), 2854 (w), 1685 (s, C=O), 1648 (s, C=O), 1583 (w, C=C), 1565 (m, C=C), 1539 (w, C=C), 1436 (m), 1432 (w), 1399 (w), 1387 (w), 1375 (w), 1355 (w), 1323 (m), 1279 (w), 1254 (w), 1238 (w), 1106 (m), 962 (w), 813 (m), 774 (m), 630 cm⁻¹ (w); UV/Vis (CHCl_3): λ_{max} (log ϵ) = 257 (4.750), 285 (4.562), 299 (4.608), 376 (3.718), 424 (3.847), 543 (sh) (3.409), 586 (sh) (3.904), 639 (4.349), 696 nm (4.601); fluorescence (CHCl_3): $\lambda_{\text{max}} = 730$ nm; MS (70 eV): m/z (%): 548 (7); 547 (37), 546 (100) [M]⁺, 531 (6), 519 (8), 518 (22) [$M - \text{C}_2\text{H}_4$]⁺, 504 (5), 503 (6), 491 (6), 490 (19) [$M - 2\text{C}_2\text{H}_4$]⁺, 476 (10), 475 (8), 474 (4), 448 (8), 447 (11), 446 (8), 433 (5), 420 (11), 419 (5), 377 (5), 376 (5), 375 (7), 374 (4), 373 (4), 364 (5), 362 (7), 349 (6), 348 (6), 188 (4), 187 (8), 174 (9), 85 (25), 83 (40), 47 (7); MS: m/z calcd for $\text{C}_{36}\text{H}_{22}\text{N}_2\text{O}_4$: 546.1580; found: 546.1580; elemental analysis calcd (%) for $\text{C}_{36}\text{H}_{22}\text{N}_2\text{O}_4$: C 79.11, H 4.06, N 5.13; found: C 78.00, H 4.61, N 5.05.

Dimer 7c: Solid 85% KOH (4.05 g, 61.4 mmol) and *N*-butylanthracene-1,9-dicarboxyimide (**6c**, 1.00 g, 3.30 mmol) were allowed to react as was described for **7a** and **8a** (225–235°C, 14 min). The melt was cautiously treated with 10% hydrogen peroxide (120 mL), treated with chloroform (200 mL) to form a lower layer and weakly stirred for 20 min so that the phase separation between the cherry-red aqueous phase and the dark-green chloroform phase remained visible. The chloroform phase was collected and the aqueous phase was treated a further two times with chloroform in the same manner. The combined organic phases were washed with distilled water, evaporated and the residue extracted with methanol until the extract remained colourless. The extracting solvent was changed to chloroform to collect **7c**, evaporated, purified by flash column chromatography (silica gel, chloroform for elution and ethyl acetate for collection), evaporated and extracted with methanol for 2 d to give the product as an analytically pure, dark-green powder (110 mg, 11%). M.p. > 350°C; R_f (silica gel, CHCl_3) = 0.16; ¹H NMR (CDCl_3): $\delta = 1.06$ (t, $J = 7.3$ Hz, 6H; CH_3), 1.53 (m, 4H; CH_2CH_3), 1.83 (m, 4H; $\text{CH}_2\text{CH}_2\text{N}$), 4.28 (m, 4H; CH_2N), 7.56 (m, 2H; aromatic H), 7.77 (m, 2H; aromatic H), 8.14 (d, $J = 7.8$ Hz, 2H; aromatic H), 8.28 (d, $J = 8.6$ Hz, 2H; aromatic H), 8.54 (d, $J = 7.8$ Hz, 2H; aromatic H), 9.92 ppm

(d, $J=8.8$ Hz, 2H; aromatic H); ^{13}C NMR (CDCl_3): $\delta=14.3$ (CH_3), 21.0 (CH_2), 30.7 (CH_2), 41.2 (CH_2N), 116.2, 122.4, 124.3, 127.1, 127.5, 127.9, 129.2, 130.0, 130.8, 130.9, 131.5, 133.4, 133.5, 134.2, 163.1 ($\text{C}=\text{O}$), 164.5 ppm ($\text{C}=\text{O}$); IR (KBr): $\tilde{\nu}=2962$ (m), 2932 (w), 2871 (w), 1683 (s, $\text{C}=\text{O}$), 1644 (s, $\text{C}=\text{O}$), 1583 (m, $\text{C}=\text{C}$), 1567 (s, $\text{C}=\text{C}$), 1538 (m, $\text{C}=\text{C}$), 1438 (w), 1435 (m), 1401 (w), 1389 (m), 1344 (w), 1326 (m), 1198 (w), 1112 (m), 812 (m), 773 (m), 730 (w), 574 cm^{-1} (w); UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$) = 258 (4.807), 287 (4.610), 300 (4.666), 372 (sh) (3.719), 423 (3.875), 583 (sh) (3.928), 640 (4.426), 696 nm (4.678); fluorescence (CHCl_3): $\lambda_{\text{max}}=740$ nm; MS (70 eV): m/z (%): 604 (10), 603 (44), 602 (100) $[\text{M}]^+$, 586 (9), 585 (20) $[\text{M}-\text{OH}]^+$, 547 (9), 546 (10) $[\text{M}-\text{C}_6\text{H}_8]^+$, 529 (8) $[\text{M}-\text{OH}]^+$, 505 (5), 504 (12), 503 (3) $[\text{M}-\text{C}_6\text{H}_9\text{NCO}]^+$, 491 (12), 490 (20) $[\text{M}-2\text{C}_6\text{H}_8]^+$, 420 (7), 419 (7), 374 (5), 373 (5), 348 (5); elemental analysis calcd (%) for $\text{C}_{40}\text{H}_{30}\text{N}_2\text{O}_4$: C 79.72, H 5.02, N 4.65; found: C 79.86, H 5.08, N 4.79.

Dimer 7d: Solid 85% KOH (21.12 g, 340 mmol) and compound **6d** (4.92 g, 15.5 mmol) were allowed to react as was described for **7c**. The product was obtained as an analytically pure, turquoise powder (1.09 g, 22%). M.p. 345–348 °C; R_f (silica gel; CHCl_3) = 0.18; ^1H NMR (CDCl_3): $\delta=0.97$ (t, $J=7.0$ Hz, 6H; CH_3), 1.47 [m, 8H; $(\text{CH}_2)_2\text{CH}_3$], 1.84 (quintet, $J=7.3$ Hz, 4H; $\text{CH}_2\text{CH}_2\text{N}$), 4.29 (m, 4H; CH_2N), 7.59 (m, 2H; aromatic H), 7.79 (m, 2H; aromatic H), 8.19 (d, $J=7.8$ Hz, 2H; aromatic H), 8.34 (d, $J=8.6$ Hz, 2H; aromatic H), 8.58 (d, $J=7.8$ Hz, 2H; aromatic H), 9.94 ppm (d, $J=8.7$ Hz, 2H; aromatic H); ^{13}C NMR (CDCl_3): $\delta=14.1$ (CH_3), 22.5 (CH_2), 27.9 (CH_2), 29.5 (CH_2), 41.0 (CH_2N), 115.9, 122.1, 124.1, 126.9, 127.3, 127.5, 128.8, 129.8, 130.5, 130.6, 131.2, 133.1, 133.3, 134.0, 162.8 ($\text{C}=\text{O}$), 164.2 ppm ($\text{C}=\text{O}$); IR (KBr): $\tilde{\nu}=3070$ (w), 2957 (m), 2931 (w), 2870 (w), 1685 (s, $\text{C}=\text{O}$), 1647 (s, $\text{C}=\text{O}$), 1583 (w, $\text{C}=\text{C}$), 1568 (m, $\text{C}=\text{C}$), 1539 (m, $\text{C}=\text{C}$), 1434 (m), 1421 (w), 1388 (m), 1343 (w), 1326 (m), 1256 (w), 1238 (w), 1192 (w), 1111 (m), 812 (m), 773 (m), 730 (w), 575 (w), 430 cm^{-1} (w); UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$) = 256 (4.805), 286 (4.624), 300 (4.662), 361 (sh) (3.791), 376 (3.851), 422 (3.937), 495 (3.323), 532 (3.541), 585 (sh) (3.995), 639 (4.423), 696 nm (4.672); fluorescence (CHCl_3): $\lambda_{\text{max}}=738$ nm; solid-state fluorescence: $\lambda_{\text{max}}=791$ nm; MS (70 eV): m/z (%): 632 (11), 631 (45), 630 (100) $[\text{M}]^+$, 614 (5), 613 (11) $[\text{M}-\text{OH}]^+$, 562 (5), 561 (13), 560 (8) $[\text{M}-\text{C}_5\text{H}_{10}]^+$, 543 (3) $[\text{M}-\text{OH}]^+$, 505 (5), 504 (10), 492 (6), 491 (13), 490 (17) $[\text{M}-2\text{C}_5\text{H}_{10}]^+$, 445 (3) $[\text{M}-\text{CO}-\text{OH}]^+$, 420 (6), 419 (5) $[\text{M}-\text{C}_5\text{H}_{11}\text{NCO}-\text{CO}]^+$, 376 (2) $[\text{M}-2\text{C}_5\text{H}_{11}\text{NCO}-\text{CO}]^+$, 375 (4), 374 (4), 373 (4), 362 (3), 349 (4), 348 (3); elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{34}\text{N}_2\text{O}_4$: C 79.98, H 5.43, N 4.44; found: C 80.07, H 5.52, N 4.28.

Dimer 7e: Solid 85% KOH (5.00 g, 75.7 mmol) and compound **6e** (1.26 g, 3.80 mmol) were allowed to react as was described for **7c**. The product was obtained as an analytically pure, green powder (200 mg, 16%). M.p. 325–327 °C; R_f (silica gel; CHCl_3) = 0.19; R_f (silica gel; $\text{CHCl}_3/1\text{-butanol}$, 40:1) = 0.66; ^1H NMR (CDCl_3): $\delta=0.94$ (t, $J=6.9$ Hz, 6H; CH_3), 1.46 (m, 12H; $(\text{CH}_2)_2\text{CH}_3$), 1.82 (m, 4H; $\text{CH}_2\text{CH}_2\text{N}$), 4.22 (t, $J=7.6$ Hz, 4H; CH_2N), 7.42 (m, 2H; aromatic H), 7.69 (m, 2H; aromatic H), 7.90 (d, $J=7.8$ Hz, 2H; aromatic H), 8.03 (d, $J=8.6$ Hz, 2H; aromatic H), 8.34 (d, $J=7.8$ Hz, 2H; aromatic H), 9.81 ppm (d, $J=8.8$ Hz, 2H; aromatic H); ^{13}C NMR (CDCl_3): $\delta=14.5$ (CH_3), 23.1 (CH_2), 27.4 (CH_2), 28.5 (CH_2), 32.1 (CH_2), 41.5 (CH_2N), 115.9, 122.2, 124.0, 126.8, 127.2, 127.8, 129.1, 129.6, 130.6, 130.7, 131.2, 133.0, 134.0, 162.9 ($\text{C}=\text{O}$), 164.3 ppm ($\text{C}=\text{O}$); IR (KBr): $\tilde{\nu}=3122$ (w), 3045 (w), 2955 (m), 2929 (m), 2857 (m), 1685 (s, $\text{C}=\text{O}$), 1647 (s, $\text{C}=\text{O}$), 1583 (m, $\text{C}=\text{C}$), 1565 (s, $\text{C}=\text{C}$), 1539 (m, $\text{C}=\text{C}$), 1433 (m), 1420 (m), 1400 (w), 1386 (m), 1343 (m), 1325 (m), 1255 (w), 1236 (w), 1187 (w), 1112 (m), 883 (w), 812 (m), 773 (m), 728 (m), 574 cm^{-1} (m); UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$) = 257 (4.790), 286 (4.593), 300 (4.651), 360 (sh) (3.649), 376 (3.652), 422 (3.836), 585 (sh) (3.933), 639 (4.421), 696 nm (4.676); fluorescence (CHCl_3): $\lambda_{\text{max}}=736$ nm; MS (70 eV): m/z (%): 660 (13), 659 (48), 658 (100) $[\text{M}]^+$, 642 (9), 641 (10) $[\text{M}-\text{OH}]^+$, 588 (4), 576 (8), 575 (19), 574 (8) $[\text{M}-\text{C}_6\text{H}_{12}]^+$, 505 (7), 504 (11), 492 (8), 491 (16), 490 (17) $[\text{M}-2\text{C}_6\text{H}_{12}]^+$, 446 (3), 445 (4), 432 (4), 421 (4), 420 (7), 419 (6), 375 (4), 374 (5), 373 (4), 349 (4), 348 (4), 174 (3); elemental analysis calcd (%) for $\text{C}_{44}\text{H}_{38}\text{N}_2\text{O}_4$: C 80.22, H 5.81, N 4.25; found: C 80.41, H 6.03, N 4.31.

Dimer 7f: Solid 85% KOH (6.00 g, 90.0 mmol) and compound **6f** (250 mg, 0.67 mmol) were allowed to react (225–235 °C) as described for

7c and further purified by column chromatography (silica gel, chloroform) and extracted with methanol until a colourless extract was given. The product was obtained as an analytically pure, dark-green powder (17.8 mg, 7%). M.p. 293–295 °C; R_f (silica gel; CHCl_3) = 0.32; R_f (silica gel; $\text{CHCl}_3/1\text{-butanol}$, 40:1) = 0.75; ^1H NMR (CDCl_3): $\delta=0.88$ (t, $J=6.4$ Hz, 6H; CH_3), 1.36 (m, 24H; $(\text{CH}_2)_6\text{CH}_3$), 1.83 (quintet, $J=7.0$ Hz, 4H; $\text{CH}_2\text{CH}_2\text{N}$), 4.24 (t, $J=7.4$ Hz, 4H; CH_2N), 7.47 (m, 2H; aromatic H), 7.72 (m, 2H; aromatic H), 7.98 (d, $J=7.8$ Hz, 2H; aromatic H), 8.11 (d, $J=8.6$ Hz, 2H; aromatic H), 8.40 (d, $J=7.8$ Hz, 2H; aromatic H), 9.84 ppm (d, $J=8.9$ Hz, 2H; aromatic H); ^{13}C NMR (CDCl_3): $\delta=14.5$ (CH_3), 23.1 (CH_2), 27.8 (CH_2), 28.6 (CH_2), 29.7 (CH_2), 29.9 (CH_2), 30.1 (CH_2), 32.3 (CH_2), 41.5 (CH_2N), 116.0, 122.3, 124.1, 126.9, 127.3, 127.8, 129.1, 129.8, 130.7, 131.3, 133.2, 134.1, 163.0 ($\text{C}=\text{O}$), 164.4 ppm ($\text{C}=\text{O}$); IR (KBr): $\tilde{\nu}=3122$ (w), 3084 (w), 3040 (w), 2955 (m), 2923 (s), 2854 (s), 1687 (s, $\text{C}=\text{O}$), 1644 (s, $\text{C}=\text{O}$), 1583 (m, $\text{C}=\text{C}$), 1567 (s, $\text{C}=\text{C}$), 1538 (m, $\text{C}=\text{C}$), 1467 (m), 1433 (s), 1400 (m), 1388 (m), 1356 (m), 1341 (m), 1326 (m), 1278 (m), 1252 (m), 1234 (m), 1183 (w), 1154 (w), 1114 (s), 1077 (w), 880 (w), 812 (s), 772 (s), 725 (m), 655 (w), 637 (w), 573 cm^{-1} (w); UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$) = 258 (4.783), 287 (4.582), 301 (4.633), 371 (sh) (3.660), 425 (3.834), 584 (sh) (3.905), 640 (4.404), 696 nm (4.660); fluorescence (CHCl_3): $\lambda_{\text{max}}=736$ nm; MS (70 eV): m/z (%): 745 (3), 744 (15), 743 (58), 742 (100) $[\text{M}]^+$, 726 (5), 725 (10) $[\text{M}-\text{OH}]^+$, 630 (4), 629 (4), 618 (11), 617 (22), 616 (6) $[\text{M}-\text{C}_6\text{H}_{18}]^+$, 599 (2), 505 (6), 504 (9), 503 (4), 493 (3), 492 (9), 491 (18), 490 (13) $[\text{M}-2\text{C}_6\text{H}_{18}]^+$, 446 (3), 445 (3), 432 (4), 421 (4), 420 (7), 419 (5), 375 (3), 374 (4), 349 (3), 174 (4), 173 (5), 83 (3), 57 (3), 55 (6); elemental analysis calcd (%) for $\text{C}_{50}\text{H}_{50}\text{N}_2\text{O}_4$: C 80.83, H 6.78, N 3.77; found: C 81.07, H 7.03, N 3.75.

Dimer 7g: Solid 85% KOH (10.25 g, 155.3 mmol) and compound **6g** (70 mg, 0.16 mmol) were allowed to react (238–240 °C, 1 h 50 min) as described for **7c**. The cold melt was cautiously dissolved in a 1:1:1 mixture of water, methanol and ethanol and oxidised by a stream of air bubbles (1 d). The precipitate was collected by vacuum filtration (D4 glass filter) and dissolved in a mixture of petroleum ether and methanol. The green phase of petroleum ether was collected, extracted with methanol, evaporated and purified by column chromatography (silica gel, *n*-hexane/toluene, 1:1) to give the product as a bright-green, highly viscous oil (3.2 mg, 5%). R_f (silica gel; toluene/*n*-hexane, 1:1) = 0.42; ^1H NMR (CDCl_3): $\delta=0.81$ (t, $J=7.0$ Hz, 12H; CH_3), 1.30 (m, 32H; $(\text{CH}_2)_4\text{CH}_3$), 1.94 [m, 4H; $(\text{CH}_2)\text{CHN}$], 2.35 (m, 4H; $(\text{CH}_2)\text{CHN}$), 5.33 (m, 2H; $(\text{CH}_2)_2\text{CHN}$), 7.79 (m, 2H; aromatic H), 7.90 (m, 2H; aromatic H), 8.55 (d, $J=7.8$ Hz, 2H; aromatic H), 8.77 (d, $J=8.9$ Hz, 2H; aromatic H), 8.86 (d, $J=7.8$ Hz, 2H; aromatic H), 10.00 ppm (d, $J=9.1$ Hz, 2H; aromatic H); ^{13}C NMR (CDCl_3): $\delta=14.0$ (CH_3), 22.6 (CH_2), 27.0 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 32.6 (CH_2), 45.8 (NCHR₂), 113.4, 124.7, 127.6, 127.8, 128.0, 128.8, 130.5, 130.8, 131.0, 132.8, 133.6, 134.5 ppm; IR (film): $\tilde{\nu}=2955$ (m), 2925 (s), 2856 (m), 1691 (s, $\text{C}=\text{O}$), 1652 (s, $\text{C}=\text{O}$), 1567 (m, $\text{C}=\text{C}$), 1539 (m, $\text{C}=\text{C}$), 1456 (w), 1421 (m), 1388 (w), 1377 (w), 1344 (w), 1323 (m), 1279 (w), 1227 (w), 1162 (w), 1117 (w), 884 (w), 813 (m), 774 (m), 730 (m), 668 cm^{-1} (w); UV/Vis (CHCl_3): $\lambda_{\text{max}}=257$, 286, 301, 364 (sh), 385 (sh), 423, 580 (sh), 638, 694 nm; fluorescence (CHCl_3): $\lambda_{\text{max}}=729$ nm; MS (70 eV): m/z (%): 857 (5), 856 (21), 855 (64), 854 (100) $[\text{M}]^+$, 838 (3), 837 (4) $[\text{M}-\text{OH}]^+$, 769 (2), 675 (4), 674 (13), 673 (22), 672 (17) $[\text{M}-\text{C}_{13}\text{H}_{26}]^+$, 656 (3), 655 (4), 588 (3), 504 (4), 503 (6), 494 (3), 493 (11), 492 (33), 491 (55), 490 (57) $[\text{M}-2\text{C}_{13}\text{H}_{26}]^+$, 489 (3), 475 (4), 474 (6), 473 (5), 446 (6), 445 (10), 444 (3), 421 (7), 420 (14), 419 (7), 375 (4), 374 (6), 373 (5), 349 (3), 173 (3), 167 (3), 149 (8), 125 (3), 111 (6), 97 (11), 83 (13), 71 (12), 69 (19), 57 (20), 56 (11), 55 (27); MS: m/z calcd for $\text{C}_{58}\text{H}_{66}\text{N}_2\text{O}_4$: 854.5023; found: 854.5046.

Tests for the hydrolysis of dimers 7 and 8: *Test for the acid hydrolysis of Aceanthrene Green (7a and 8a):* Aceanthrene Green (**7a** and **8a**, 160 mg, 0.33 mmol) was treated with concentrated sulfuric acid (30 mL), heated with stirring at (120 °C, 3 h), allowed to cool, diluted with distilled water (200 mL), collected by vacuum filtration (G5 glass filter), washed with a small amount of distilled water and dried at 115 °C. TLC analysis (silica gel, chloroform) indicated a complete decomposition of the starting material (no green spot).

Test for alkaline hydrolysis of Aceanthrene Green (7a and 8a): Aceanthrene Green (**7a** and **8a**, 170 mg, 0.35 mmol) was suspended in *tert*-butyl

alcohol (50 mL) with heating, treated with 85% solid KOH (1.06 g, 16.0 mmol), heated at reflux for 2 h, hydrolysed by the addition of a 1:1 mixture of acetic acid and concentrated HCl, diluted to a volume of 100 mL with distilled water, collected by vacuum filtration (G4 glass filter) and dried at 115°C. The material proved to be identical to the starting material according to IR, MS and UV/Vis spectroscopic analyses.

Test for the N-alkylation of the Aceanthrene Green (7a and 8a): Aceanthrene Green (7a and 8a, 110 mg, 0.22 mmol), potassium carbonate (1.00 g, 5.64 mmol) and 1-bromoheptane (1.06 mL, 6.72 mmol) were heated at reflux in anhydrous DMF (10 mL) for 24 h. The mixture was allowed to cool, poured into distilled water (10 mL), acidified with 2 N HCl, stirred for 45 min and collected by vacuum filtration. Only traces of an emerald-green material could be detected (R_f (silica gel; CHCl_3) = 0.47). More than 14 byproducts were detected.

Reaction of dimers 7 with alkali: Reaction of 7 with KOH in *tert*-butyl alcohol: Dimers 7b–e (3 mg, ca. 0.05 mmol) under argon was dispersed in *tert*-butyl alcohol (60 mL), heated at reflux for 2 h, treated with 85% solid KOH (1.00 g, 15.2 mmol; spontaneous colour change from green to violet), heated at reflux for a further 50 min, quenched by acidification with a mixture of acetic acid/2 N HCl (2:1), collected by vacuum filtration (G4 glass filter), washed with distilled water and dried at 115°C in air. The unchanged starting material was obtained in all cases according to IR, TLC and MS analyses.

Reaction of 7 with KOH in *tert*-butyl alcohol/DMSO: Dimers 7b–e (100 mg, ca. 0.16 mmol) was dispersed in a mixture of DMSO (15 mL) and *tert*-butanol (15 mL) under argon. The mixture was heated at reflux for 2 h, treated with 85% solid KOH (120 mg, 1.82 mmol; spontaneous colour change from dark-green to violet), and further treated as was described before. The unchanged starting material was obtained in all cases according to IR, TLC and MS analyses.

Methylation of the violet intermediate of the reaction of 7d with KOH in *tert*-butyl alcohol/DMSO to form 9d: Dimer 7d (160 mg, 0.25 mmol) was dissolved in a mixture of DMSO (25 mL) and *tert*-butyl alcohol (25 mL) at 130°C (bath temperature), treated with 85% solid KOH (170 mg, 2.57 mmol; spontaneous colour change from dark-green to violet), heated at reflux for 1 h, evaporated in vacuo, treated with iodomethane (13 mL, 208 mmol), stirred at room temperature for 16 h, evaporated (reddish-brown residue), evaporated in vacuo and purified by flash chromatography (silica gel, chloroform). The product was obtained as bright-orange crystals with a strong solid-state fluorescence (14 mg, 9%). M.p. 132–135°C; R_f (silica gel; CHCl_3) = 0.65; $^1\text{H NMR}$ (CDCl_3): δ = 0.90 (t, J = 6.9 Hz, 6H; CH_3), 1.37 (m, 8H; $(\text{CH}_2)_2$), 1.66 (m, 4H; $\text{CH}_2\text{CH}_2\text{N}$), 1.72 (s, 6H; CH_3), 4.03 (m, 4H; CH_2N), 7.19 (d, J = 7.9 Hz, 2H; aromatic H), 7.59 (dt, J_1 = 7.4, J_2 = 1.3 Hz, 2H; aromatic H), 7.71 (m, 2H; aromatic H), 7.79 (dd, J_1 = 7.7, J_2 = 1.5 Hz, 2H; aromatic H), 8.14 (d, J = 7.7 Hz, 2H; aromatic H), 8.75 ppm (dd, J_1 = 8.2, J_2 = 1.0 Hz, 2H; aromatic H); $^{13}\text{C NMR}$ (CDCl_3): δ = 14.0 (CH_3), 22.4 (CH_2), 27.8 (CH_2), 29.2 (CH_2), 40.7 (CH_3), 41.7 (CH_2N), 45.3 (C_q), 122.6 (CH), 124.3, 125.0, 128.0 (CH), 129.3 (CH), 130.4 (CH), 130.6 (CH), 130.7 (CH), 133.8, 134.8, 137.6, 144.4, 163.5 (C=O), 174.0 ppm (C=O); IR (KBr): $\tilde{\nu}$ = 2958 (m), 2929 (m), 2859 (w), 1723 (s, C=O), 1678 (s, C=O), 1626 (m, C=C), 1449 (m), 1432 (m), 1386 (m), 1360 (s), 1334 (m), 1291 (w), 1258 (w), 1229 (w), 1207 (w), 1178 (w), 1107 (m), 1079 (w), 851 (w), 766 (m), 745 cm^{-1} ; UV/Vis (CHCl_3): λ_{max} ($\log \epsilon$) = 256 (4.504), 267 (sh) (4.495), 351 (3.802), 378 (sh) (3.436), 447 (2.433), 474 nm (2.509); fluorescence (CHCl_3): λ_{max} (I_{rel}) = 511 (sh) (0.80), 543 nm (1); fluorescence quantum yield (CHCl_3 , reference perylene-3,4,9,10-tetracarboxylic tetramethyl ester^[17] with Φ = 100%): 27%; solid-state fluorescence: λ_{max} (I_{rel}) = 555 (1), 584 nm (sh) (0.83); MS (70 eV): m/z (%): 662 (13), 661 (46), 660 (92) $[M]^+$, 647 (11), 646 (46), 645 (100) $[M-\text{CH}_3]^+$, 631 (6), 630 (13), 548 (6), 547 (14) $[M-\text{C}_5\text{H}_{11}\text{NCO}]^+$, 534 (6), 533 (26), 532 (65) $[M-\text{C}_5\text{H}_{11}\text{NCO}-\text{CH}_3]^+$, 505 (8), 504 (19) $[532-\text{CO}]^+$, 435 (13), 434 (14) $[M-2\text{C}_5\text{H}_{11}\text{NCO}]^+$, 363 (6), 217 (49) $[434-217]^+$, 189 (27), 182 (20), 181 (16); MS: m/z calcd for $\text{C}_{44}\text{H}_{40}\text{N}_2\text{O}_4$: 660.2988; found: 660.2991; elemental analysis calcd (%) for $\text{C}_{44}\text{H}_{40}\text{N}_2\text{O}_4$: C 79.98, H 6.10; found: C 76.84, H 6.17.

Methylation of the violet intermediate of the reaction of 7d with KOH in DMSO to form 9d: Dimer 7d (160 mg, 0.25 mmol) under argon was heated at reflux in DMSO (25 mL) for 1 h (complete dissolution), treated

with 85% solid KOH (170 mg, 2.57 mmol, colour change from green to violet), stirred for further 10 min (bath temperature 150°C), evaporated in vacuo, treated with iodomethane (13 mL, 208 mmol), allowed to stand for 24 h and purified by flash chromatography (silica gel, chloroform). The TLC R_f value and the mass spectrum of the orange red material obtained were identical to the above mentioned reaction in *tert*-butyl alcohol/DMSO. For further characterisation see above.

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