

# Quaterrylenebis(dicarboximide)s: near infrared absorbing and emitting dyes

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New ladder-type chromophores, the quaterrylenebis(dicarboximide)s **2**, **18** and **23**, have been synthesised which, despite their extended  $\pi$ -system, exhibit good solubility in organic solvents and film forming properties when adequately substituted. These unprecedented dyes, which absorb and even emit light in the NIR window, are also characterized by outstanding chemical, thermal and photochemical stability with regard to their absorption range. The potential formation of J-aggregates in strongly acidic media has been investigated and has been ruled out by combined <sup>1</sup>H NMR and UV–VIS–NIR spectroscopy experiments. In addition, their photophysical and electrochemical characteristics have been explored and are discussed.

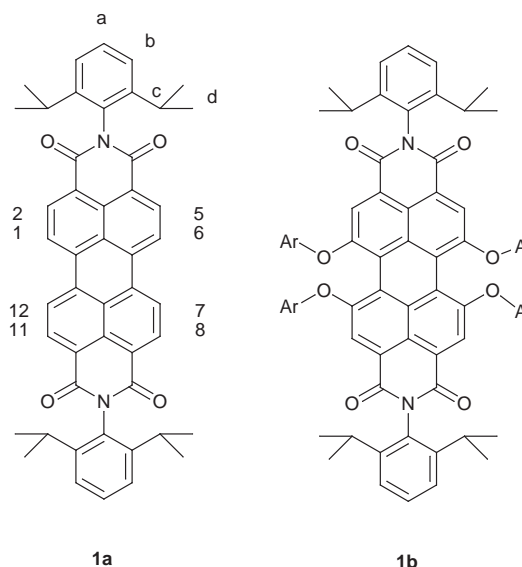
## Introduction

The search for novel, near infrared (NIR) absorbing and emitting dyes is a challenge in dyestuff chemistry, mainly because of the potential high-technology applications in optical recording, thermally written displays, laser printers, laser filters, infrared photography and medicine.<sup>1</sup> Despite the high demand, only a few NIR dyes, such as cyanine dyes, are effectively used in practice. A prerequisite in the design of chromophores is the consideration of their chemical, thermal and photochemical stability.<sup>2</sup> Perylene derivatives and, in particular, perylenebis(dicarboximide)s **1**, are well-known for their outstanding chemical, thermal and photochemical inertness.<sup>3,4</sup> Their uses range from paints and varnishes to high-technology applications such as tracers in fluorescence analytical assays,<sup>5</sup> charge-transport in Langmuir–Blodgett films,<sup>6</sup> photovoltaic cells,<sup>7</sup> xerography,<sup>8</sup> optical switches,<sup>9</sup> laser-dyes<sup>10</sup> and fluorescent collectors.<sup>11</sup> Clearly, new chromophores such as quaterrylenebis(dicarboximide)s **2**, which combine the outstanding properties of perylenebis(dicarboximide)s **1** with NIR absorption, are highly desirable.

The first attempts at extending the  $\pi$ -system of perylene **3** to higher rylenes, namely terrylene **4** and quaterrylene **5**, were carried out by Clar.<sup>12</sup> However, due to the lack of adequate alkyl substitution, resulting in extreme insolubility, the purification and characterization of terrylene **4** and quaterrylene **5** were not possible.<sup>13</sup>

More recently, we synthesized the first soluble oligorylene series **6**.<sup>14</sup> The introduction of *tert*-butyl groups at the periphery of the rigid aromatic structure drastically improved their solubility in common organic solvents. Remarkably enough, terrylene, quaterrylene and even pentarylene were fully characterized and their photophysical behavior correlated with their structure.<sup>14b</sup>

We have also reported some new fluorescent dyes emitting at long wavelengths ( $600 < \lambda < 750$  nm) and even in the NIR range ( $\lambda > 750$  nm), which are structurally related to quaterrylenebis(dicarboximide)s, namely the terryleneimides **7,8**<sup>15</sup> and



the perylenebisamidine **9**.<sup>16</sup> These NIR dyes are characterized by high photochemical and thermal stability. Moreover terryleneimides **7** and **8** exhibit outstanding quantum fluorescence yields of  $0.9 \pm 0.1$  and  $0.6 \pm 0.1$ , respectively.

In this paper, we report the detailed synthesis and the characterization of quaterrylenebis(dicarboximide)s **2**, **18** and **23**, which are higher homologues of perylenebis(dicarboximide)s **1**<sup>17</sup> and of terrylenebis(dicarboximide)s **7**.<sup>15</sup> In addition, the photophysical, thermal and electrochemical properties of quaterrylenebis(dicarboximide)s **2**, **18** and **23** are compared to those of perylenebis(dicarboximide)s **1** and to terrylenebis(dicarboximide)s **7** and discussed in the light of their structures.

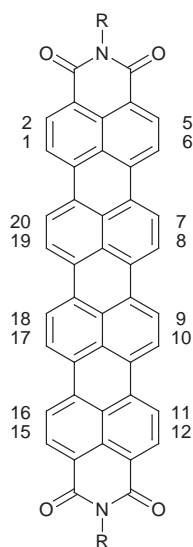
## Results and discussion

### Synthesis

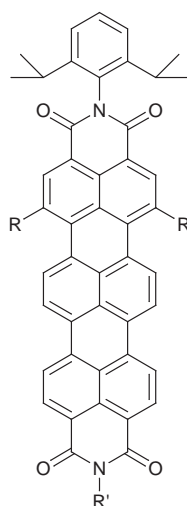
The synthetic pathway to quaterrylenebis(dicarboximide)s **2a,b** is illustrated in Scheme 1. The key building block for the synthesis of quaterrylenebis(dicarboximide)s is the *N*-substituted perylene-3,4-dicarboximides **11a,b** which are obtained *via* the partial

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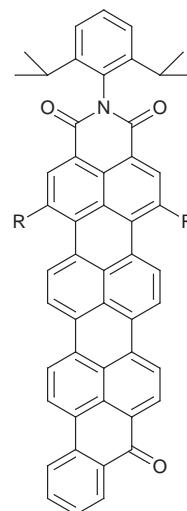
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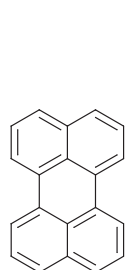
- 2a R = C<sub>12</sub>H<sub>25</sub>  
 b R = C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sub>2</sub>  
 c R = Bu



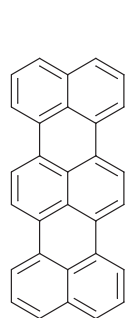
7a,b



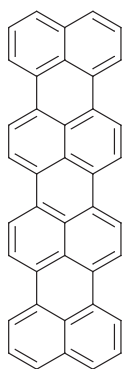
8a,b



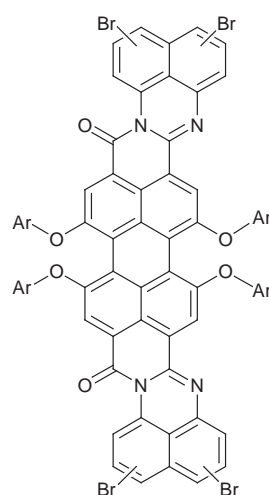
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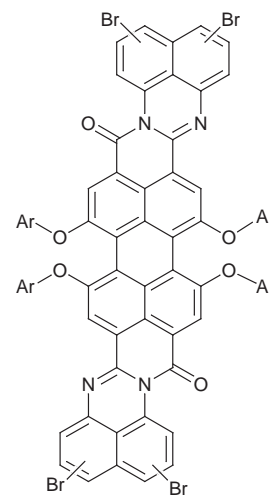
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5



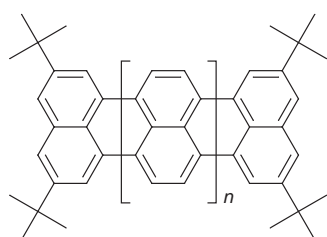
9-syn



9-anti

a R = H, b R = OAr

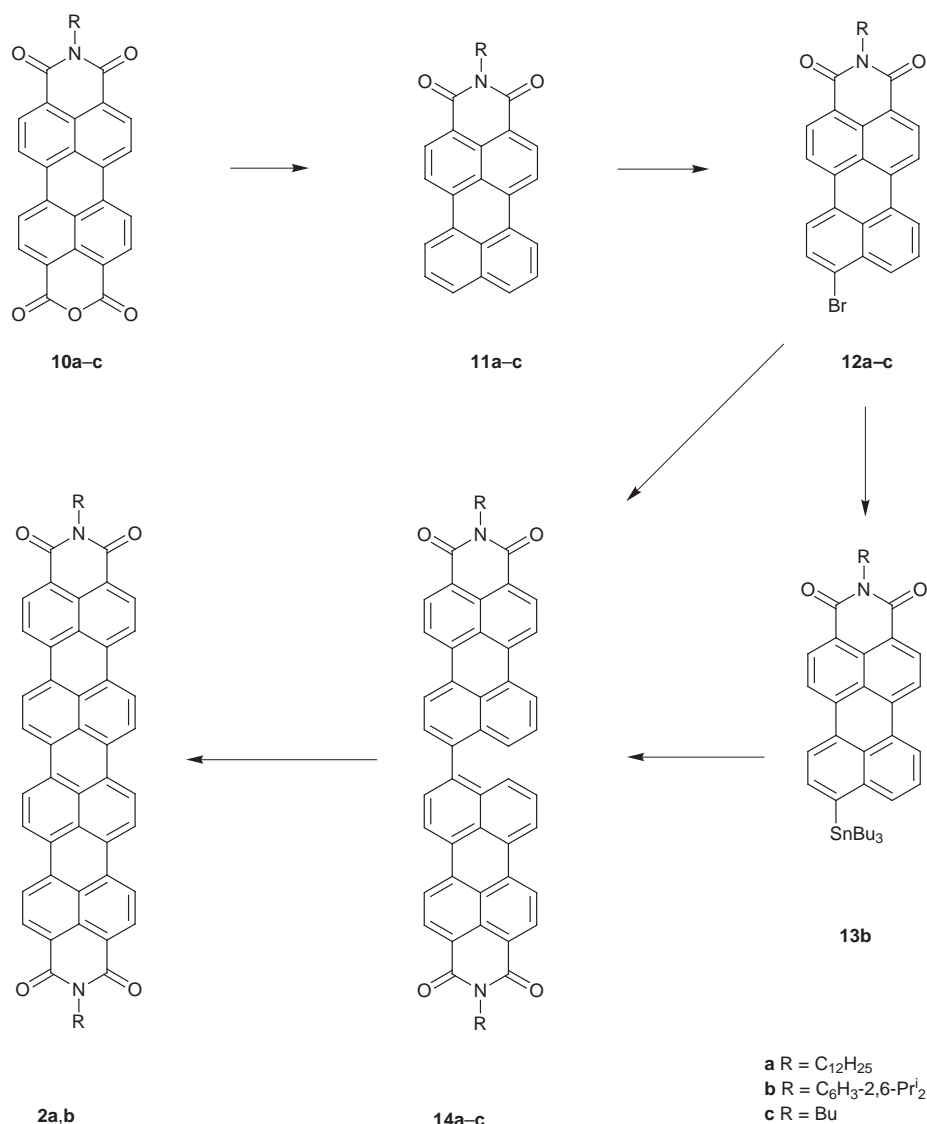
R' = C<sub>8</sub>H<sub>17</sub>, C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sub>2</sub>



6	a	b	c	d
n	0	1	2	3

decarboxylation of perylenedicarboxylic anhydrides **10a,b**.<sup>18,19</sup> The bromination of the *N*-substituted perylene-3,4-dicarboximides **11a,b** at position 9 leads to the monobromo *N*-substituted perylene-3,4-dicarboximides **12a,b** in 94–98% yield. Misono and Nagao have synthesized the biperylene **14c** via an Ullmann coupling of the 9-bromo-*N*-butylperylene-3,4-dicarboximide **12c** in low yield.<sup>18,19</sup> The low yield has been attributed to the large amount of side products rendering the purification difficult and to the inadequate alkyl substitution at the imide position resulting in low solubility of the biperylene **14c**.

However, we recently reported some developments in the field of organometallic aryl–aryl coupling which allows the synthesis of **14a,b** in higher yields.<sup>15,17</sup> Specifically, two organometallic synthetic pathways from the monobromo *N*-substituted perylene-3,4-dicarboximide **12a,b** to the biperylene **14a,b** have been attempted. The first synthetic route, a one step Yamamoto homocoupling<sup>20</sup> with the zero-valent nickel catalyst bis(cycloocta-1,5-diene)nickel(0) [Ni(cod)<sub>2</sub>] has successfully been applied and afforded the biperylenes **14a,b** in excellent yields (83–89%). The second synthetic route to the biperylene **14b** is based on the Stille heterocoupling of monobromo *N*-substituted perylene-3,4-dicarboximide **12b** with its stannylated analogue **13b** in the presence of the zero-valent tetrakis(triphenylphosphine)palladium catalyst [Pd(PPh<sub>3</sub>)<sub>4</sub>].<sup>15,21</sup> This route requires an additional step, but presents the advantage of replacing the relatively toxic, air-sensitive and expensive Ni(cod)<sub>2</sub> by the more conventional Pd(PPh<sub>3</sub>)<sub>4</sub>. Moreover, the coupling of two differently substituted perylene derivatives, resulting in non-symmetrically *N*-substituted quaterylenebis(dicarboximide)s, is therefore possible. This significantly widens the scope of applications of the quaterylenebis(dicarboximide)s which could be introduced as side chain functions in polymers to combine the processability



**Scheme 1** Synthetic pathway to quaterrylenebis(dicarboximide) **2a**.

and good film-forming properties of polymers with the intrinsic properties of quaterrylenebis(dicarboximide)s. One could also selectively introduce another functional group, *e.g.* an electron donor for photoinduced electron transfer or a biologically active molecule for NIR fluorescence analytical assays.<sup>5</sup>

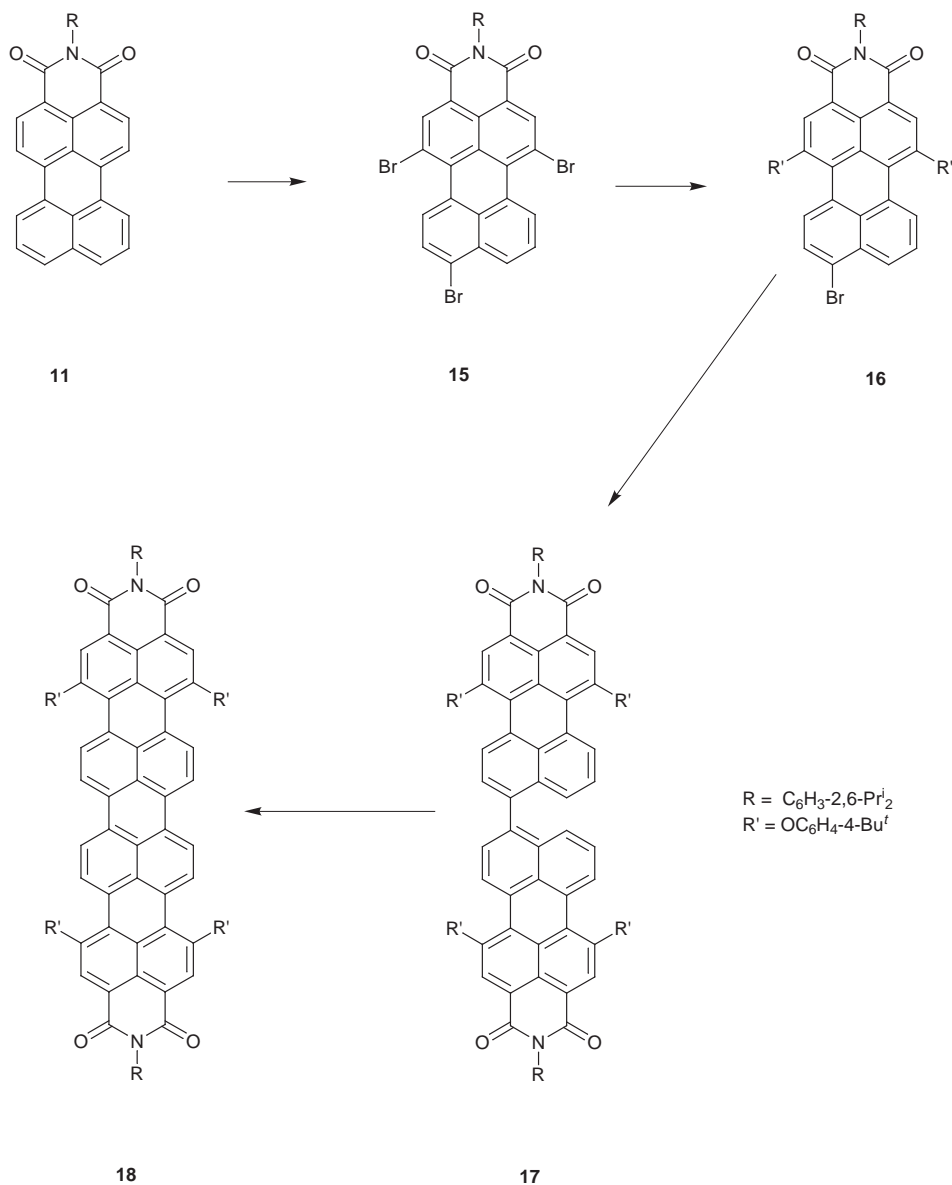
The last synthetic step of Scheme 1 involves the cyclization of the biperylenes **14a,b** into quaterrylenebis(dicarboximide)s **2a,b** in the presence of a base and an oxidizing agent.<sup>23,24</sup> Specifically, the cyclization reaction has been carried out in a KOH/ethanol melt containing glucose as oxidizing agent at 120 °C.<sup>24</sup> The resulting quaterrylenebis(dicarboximide) **2b** was readily purified by recrystallization, affording the desired product **2b** in 83% yield, whereas the less soluble quaterrylenebis(dicarboximide) **2a** was obtained in lower yield (37%) and was purified by extraction of the by-products with chloroform. In the case of quaterrylenebis(dicarboximide) **2b**, further purification by column chromatography was only performed for the preparation of analytical samples.

The quaterrylenebis(dicarboximide) **2a** is only slightly soluble in organic solvents (typically  $<10^{-5}$  M) at room temperature and is better viewed as a pigment than a dye. However for numerous applications, good processability, *i.e.* high solubility in organic media and good film-forming properties, is required. As previously mentioned, one way to achieve processability is to introduce quaterrylenebis(dicarboximide) **2a** as a pendant group on a polymer chain. Another method,

which consists of introducing phenoxy substituents into the *bay*-regions of the aromatic core, is well-known in the case of the perylenebis(dicarboximide) **1b**.<sup>15,16,25</sup> The introduction of substituents in the *bay*-region of the perylenebis(dicarboximide) **1b** presents the additional advantage of further extending the absorption maxima to longer wavelength. In analogy to perylenebis(dicarboximide) **1b**, we have attempted the synthesis of tetraphenoxy substituted quaterrylenebis(dicarboximide) **18**. The synthetic pathway to the tetraphenoxy substituted quaterrylenebis(dicarboximide) **18** is given in Scheme 2 and shares many similarities with that of the unsubstituted quaterrylenebis(dicarboximide)s **2a,b**.

The three-fold bromination of **11** under drastic conditions gives the perylene tribromide **15** in excellent yield (91%). The selective nucleophilic substitution under basic conditions of the two bromine atoms in the *bay*-regions with phenol derivatives affords **16** in a yield of 33%. The moderate yield is due to side reactions, namely the substitution of all three bromine atoms by phenoxy groups and dehalogenation.

Comparable to the synthesis of the biperylenes **14a,b**, the Yamamoto coupling affords the biperylene **17** in a yield of 88%. The cyclization of **17** to the tetraphenoxy substituted quaterrylenebis(dicarboximide) **18**, in a yield of 85%, has been carried out as described for the unsubstituted perylene **14**. As expected, the solubility of quaterrylenebis(dicarboximide) **18** is much higher than that of **2** and reaches  $\sim 10^{-2}$  M in



**Scheme 2** Synthetic pathway to quaterrylenebis(dicarboximide) **18**.

chlorinated solvents. These encouraging results suggest that an additional increase of solubility should result from an eight-fold substitution by phenoxy groups of the quaterrylenebis(dicarboximide) core. Therefore, we have embarked on the synthesis of octaphenoxy substituted quaterrylenebis(dicarboximide) **23** (Scheme 3).

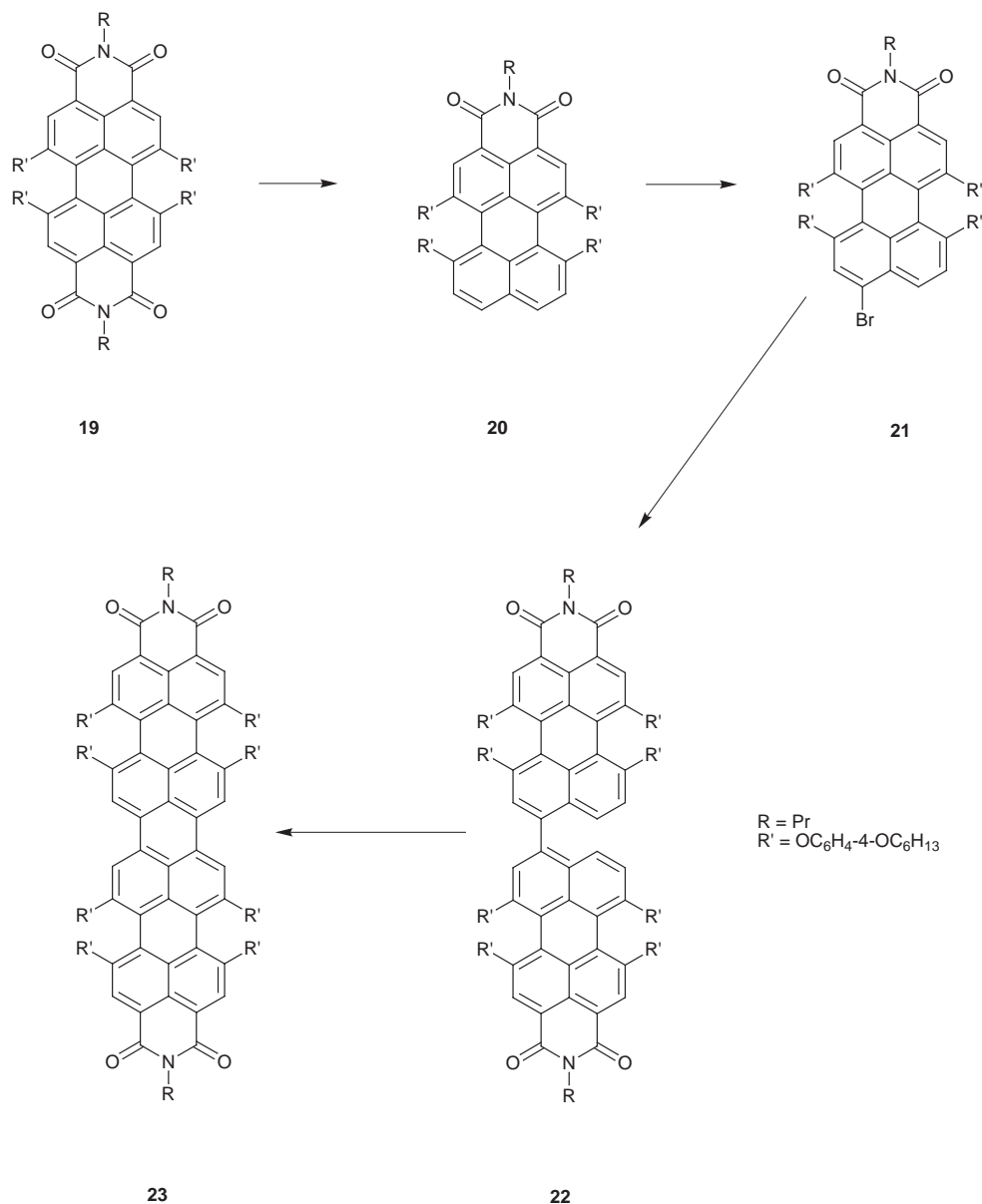
The entry point to the synthetic scheme is the perylene-dicarboximide **20** carrying four phenoxy substituents, which has been synthesized by hydrolysis of one imide function of perylenebis(dicarboximide) **19** under basic conditions, followed by decarboxylation with copper(I) oxide under vacuum. Purification by chromatography and recrystallisation affords tetraphenoxyperylene-dicarboximide **20** in 53% yield. The monobromination of **20** under the mild conditions described by Mitchell<sup>26</sup> with *N*-bromosuccinimide in dimethylformamide leads selectively to bromoperylene-dicarboximide **21** in high yield (98%). Surprisingly enough, the Yamamoto coupling of the bromoperylene-dicarboximide **21** under the conditions previously described for the bromoperylene-dicarboximides **13** and **16** resulted mainly in the cleavage of the phenoxy substituents. The reason for this unexpected side reaction remains enigmatic and could not be explained by simple mechanistic considerations. However, this forced us to use another coupling reaction reported by Sontheimer<sup>27</sup> and modified by Iyoda

and Oda<sup>28</sup> where the catalyst, tetrakis(triphenylphosphine)-nickel(0), is generated *in situ*.<sup>29</sup> The biperylene **22** was then obtained in 79% yield.

The reaction conditions used for the cyclization of biperylenes **14** and **17** resulted, in the case of **22**, also in the partial cleavage of the phenoxy groups of the resulting octasubstituted quaterrylenebis(dicarboximide) **23**. Consequently, milder reaction conditions have been applied to afford the octaphenoxy substituted quaterrylenebis(dicarboximide) **24** in very low yield (0.3%). The separation of octaphenoxy substituted quaterrylenebis(dicarboximide) **24** from numerous side products was conducted by gel permeation chromatography (GPC) on polystyrene as stationary phase with chloroform as eluent.

#### Structure elucidation

The structures of quaterrylenebis(dicarboximide)s were proven by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, field desorption mass spectroscopy (FD-MS), FT-IR spectroscopy and UV-VIS spectroscopy. Due to a plane of symmetry, the <sup>1</sup>H NMR spectra of quaterrylenebis(dicarboximide)s **2b**, **18** and **23** have a simpler appearance than those of their synthetic precursors, the biperylene diimides **14**, **17** and **22**. The aromatic region of the <sup>1</sup>H NMR spectrum of quaterrylenebis(dicarboximide) **2b** exhibits



**Scheme 3** Synthetic pathway to quaterylenebis(dicarboximide) **23**.

six resonances, as expected from the structure. The assignment, based on  $^1\text{H}$ ,  $^1\text{H}$  correlated NMR analysis, of the resonances of **2b** is given in Table 1. The chemical shifts for H-7,10,17,20 are almost identical to those of H-8,9,18,19 and no unambiguous assignment of these protons has been achieved.

The  $^{13}\text{C}$  NMR spectrum of the tetraphenoxy substituted quaterylenebis(dicarboximide) **18** exhibits thirteen quaternary and seven tertiary aromatic C-atoms, in accordance with the proposed structure. However, a comprehensive assignment of the resonances to the carbon atoms has been hindered by the lack of

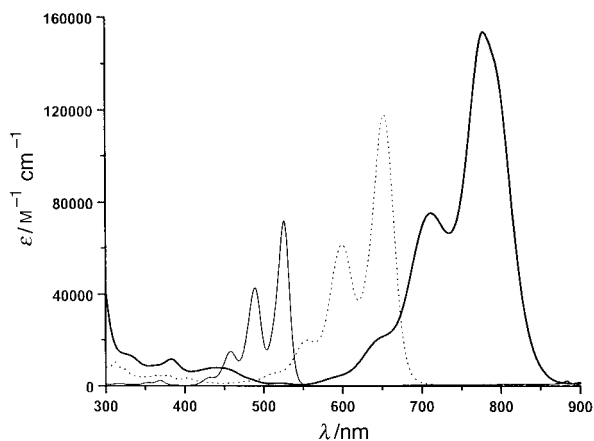
appropriate reference compounds. The parent ions of the quaterylenebis(dicarboximide)s **2a,b**, **18** and **23** are in good agreement with the calculated masses and isotopic distributions corroborating, therefore, the proposed chemical structures. The FT-IR spectra of the quaterylenebis(dicarboximide)s **2a,b**, **18** and **23** confirm the presence of the characteristic carbonyl bands, which appear between  $1700$  and  $1670\text{ cm}^{-1}$ , depending on the substitution at the nitrogen atoms.

The comparison of the UV-VIS-NIR spectra of perylenebis(dicarboximide) **1a** and terylenebis(dicarboximide) **7a** with the spectrum of quaterylenebis(dicarboximide) **2b**, given in Fig. 1, is very instructive. Specifically, a bathochromic shift of the absorption maxima from  $526\text{ nm}$  for **1a**, to  $650\text{ nm}$  for **7a** and extending to  $764\text{ nm}$  for **2b** is clearly observed. The extinction coefficient increases from  $\epsilon = 80\,000\text{ M}^{-1}\text{ cm}^{-1}$  for the perylenebis(dicarboximide) **1a** to  $\epsilon = 120\,000\text{ M}^{-1}\text{ cm}^{-1}$  for terylenebis(dicarboximide) **7a** and up to  $\epsilon = 162\,000\text{ M}^{-1}\text{ cm}^{-1}$  for the quaterylenebis(dicarboximide) **2b**.

A comparison with the absorption maximum of the previously reported tetra-*tert*-butylquaterylene **6c**,<sup>14</sup> shows that the two dicarboximide functions at the *peri*-position of the quaterylenebis(dicarboximide) **2b** are responsible for a bathochromic shift of more than  $100\text{ nm}$ , as expected from the comparison of the

**Table 1**  $^1\text{H}$  NMR Chemical shifts of quaterylene **2b** ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $500\text{ MHz}$ ,  $135^\circ\text{C}$ )

$\delta$ (ppm)	Type	H	Integration
8.68	d	2, 5, 12, 15	4 H
8.68, 8.63	d, d	7, 10, 17, 20, 8, 9, 18, 19	8 H
8.56	d	1, 6, 11, 16	4 H
7.42	dd	a	2 H
7.29	d	b	4 H
2.80	q	c	4 H
1.19	d	d	24 H



**Fig. 1** UV-VIS-NIR spectra of perylenebis(dicarboximide) **1a** (solid line) terylenebis(dicarboximide) **7a** (dotted line) and quaterrylenebis(dicarboximide) **2b** (solid bold line) in  $\text{CH}_2\text{Cl}_2$ .

UV-VIS spectrum of perylene **3** with the one of perylenebis(dicarboximide) **1a**. The UV-VIS-NIR spectrum of quaterrylenebis(dicarboximide) **2b** appears less structured than those of the reference chromophores: the quaterrylene **6c**, the perylenebis(dicarboximide) **1b**, and the terylenebis(dicarboximide) **7a**. We attribute this feature to the enlarged  $\pi$ -system of quaterrylenebis(dicarboximide) **2b** in regards to **1b** and **7a**.

### Properties

**Solubility.** The solubility of the quaterrylenebis(dicarboximide)s **2a,b, 18** and **23**, which is the key to their processability, has been investigated in chlorinated solvents at room and elevated temperatures. The results are collected in Table 2.

The low solubility of quaterrylenebis(dicarboximide) **2a** compared to the much higher solubility of **2b** is striking. Despite the presence of two long dodecyl chains, quaterrylenebis(dicarboximide) **2a** remains poorly soluble. The improved solubility of quaterrylenebis(dicarboximide) **2b** is due to facially encumbering substituents,<sup>31</sup> *i.e.* the two 2,6-diisopropylphenyl groups at the imide position, which decrease the tendency of the quaterrylenebis(dicarboximide) core to form  $\pi$ -stacks. The solubility of the quaterrylenebis(dicarboximide) core is further increased by the introduction of four substituents in the *bay*-region, as shown by the good solubility of **18** at room temperature. Note as well that either the introduction of eight substituents in the *bay*-regions or four substituents in the *bay*-region and the additional effect of 2,6-diisopropylphenyl groups give rise to similar solubilities.

**Absorption behavior.** From a practical aspect, it is worth mentioning the almost colorless solutions, which are only slightly blue, of quaterrylenebis(dicarboximide) **2b**. This weak absorption in the visible window strictly contrasts with the deeply orange-red and blue colored solutions of perylene **1a** and terylene **7a**, respectively, observed for comparable concentrations. As hitherto mentioned, the substitution of the quaterrylenebis(dicarboximide) in the *bay*-regions offers not only a way to increase the solubility, but also to finely tune the absorption maximum. For instance, comparison of the absorp-

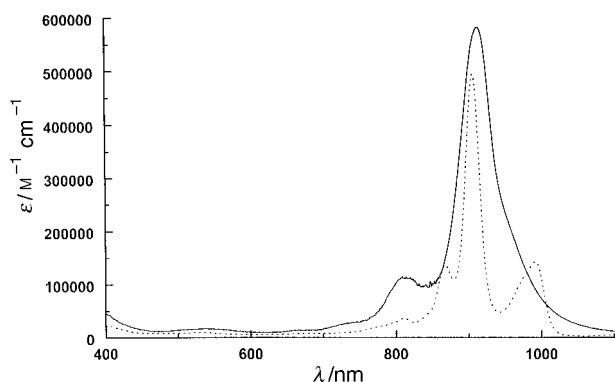
tion maxima of the quaterrylenebis(dicarboximide) **2b** with that of the tetraphenoxy substituted quaterrylenebis(dicarboximide) **18** and tetraphenoxy substituted perylenebis(dicarboximide)s **23** indicates a bathochromic shift of 19 ( $\lambda_{\text{max}} = 762$  nm) and 28 nm ( $\lambda_{\text{max}} = 790$  nm), respectively. The observed bathochromic shifts are due to the electron donating effect of the phenoxy groups, and the effect has already been observed in the case of tetraphenoxy substituted perylenebis(dicarboximide)s.<sup>16,17</sup> Also of practical relevance, films of good optical quality are easily cast from a solution of the tetraphenoxy substituted quaterrylenebis(dicarboximide) **18**. The VIS-NIR spectra of **18**, both in solution and as a film, show different aspects. Instead of the sharp absorption maximum at 781 nm accompanied by a shoulder at 709 nm observed in solution, as a film **18** displays two absorption maxima of nearly equal intensity at 724 and 795 nm. The high extinction coefficients of quaterrylenebis(dicarboximide)s **2a,b, 18** and **23**, which are only equalled in the NIR range by a few squarylium dyes,<sup>1</sup> suggest their use in optical data storage, where an excellent signal to noise ratio could be reached.<sup>31</sup>

**J-Aggregates and absorption behavior in strongly acidic media.** A totally new situation arises when the quaterrylenebis(dicarboximide) **2b** is dissolved in strongly acidic media. Characteristically enough, a bathochromic shift of 112 nm is obtained when **2b** is dissolved in a mixture of sulfuric acid and oleum (57%) (4:1) instead of chlorinated solvents. Specifically, two peaks are observed, one at  $\lambda = 813$  nm with an  $\epsilon$  of  $111\,000\text{ M}^{-1}\text{ cm}^{-1}$ , while the  $\lambda$  of the second reaches a value as high as 912 nm with an  $\epsilon$  of  $581\,000\text{ M}^{-1}\text{ cm}^{-1}$ . The value of  $\lambda_{\text{max}}$  is slightly higher than those reported earlier.<sup>17</sup> This is due, we believe, to traces of water in the sulfuric acid/oleum mixture, inducing differences in the oleum/sulfuric ratio (see below). After dilution with water, the quaterrylenebis(dicarboximide) **2b** can be recovered, which indicates that the chromophore is chemically stable even in the presence of strong acids and oxidizing agents. The fact that **2b** remains chemically unaltered also indicates that the large bathochromic shift and the sharp increase of  $\epsilon$  are presumably due to the protonation of the carboximide functions. The role of the protonation of this group on the NIR spectrum of quaterrylenebis(dicarboximide) **2b** was further confirmed by slightly changing the nature of the acidic medium. A dramatic change of the spectrum of **2b** in concentrated sulfuric acid, in comparison to chlorinated solvents, is also observed. However, the NIR spectrum of quaterrylenebis(dicarboximide) **2b** in concentrated sulfuric acid and in a sulfuric acid/oleum mixture are not superimposable (Fig. 2). Specifically, in concentrated sulfuric acid, three absorption maxima are present at 868, 907 and 992 nm, with  $\epsilon$  of 137 000, 493 000 and  $143\,000\text{ M}^{-1}\text{ cm}^{-1}$ , respectively, whereas only two absorption maxima are observed in the sulfuric acid/oleum mixture.

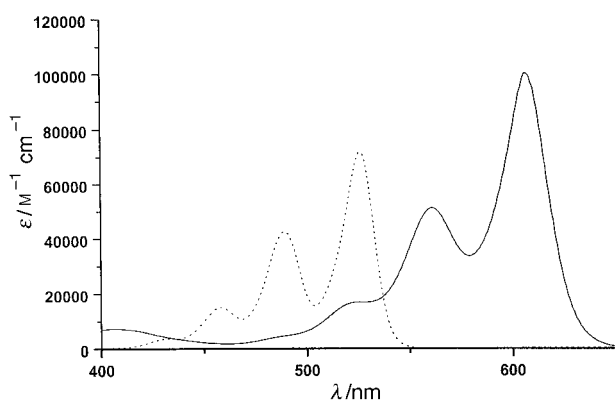
Similarly, a large bathochromic shift and a dramatic increase of  $\epsilon$ , by a factor 5.4, have also been observed for terylenebis(dicarboximide) **7a** in sulfuric acid as compared to a chloroform solution.<sup>15</sup> Together, the large bathochromic shift and the dramatic increase of  $\epsilon$  could suggest for both the quaterrylenebis(dicarboximide) **2b** and terylenebis(dicarboximide) **7a** the formation of a J-aggregate.<sup>32</sup> J-Aggregates are supramol-

**Table 2** Solubility and colors in solution of quaterrylenebis(dicarboximide)s

Compound	Solubility in $\text{CH}_2\text{Cl}_2$ at r.t./mg ml <sup>-1</sup>	Solubility in $\text{C}_2\text{H}_2\text{Cl}_4$ at 135 °C/mg ml <sup>-1</sup>	Color in chlorinated solvents
<b>2a</b>	—	—	purple-green
<b>2b</b>	< 0.2	~ 2	green
<b>15</b>	~ 30	> 80	green
<b>20</b>	~ 40	> 80	green



**Fig. 2** UV-VIS-NIR spectra of quaterylenebis(dicarboximide) **2b** in a mixture of sulfuric acid and oleum (57% (4:1)) (solid line) and in concentrated sulfuric acid (96%) (dotted line).



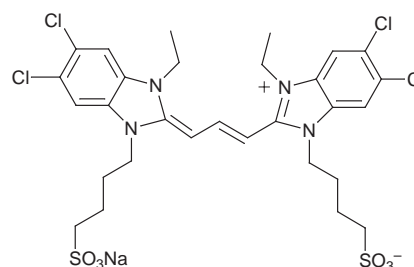
**Fig. 3** UV-VIS spectra of perylenebis(dicarboximide) **1a** in  $\text{CH}_2\text{Cl}_2$  (dotted line) and in concentrated sulfuric acid (96%) (solid line).

ecular assemblies of chromophores in which head-to-tail arrangement of transition dipole moments results in a sharp, intense and bathochromically shifted absorption band compared to the isolated chromophore.<sup>32</sup>

After discussing the absorption spectra of terrylenebis(dicarboximide) **7a** and quaterylenebis(dicarboximide) **2b** in strongly acidic media, it is important to consider also that of perylenebis(dicarboximide) **1a**. Three observations are easily made from the comparison between Fig. 2 and 3. Firstly, a large bathochromic shift of all the visible spectrum occurs also for perylenebis(dicarboximide) **1a** in concentrated sulfuric acid in comparison to chloroform solution. Secondly, the absorption peaks of **1a** in concentrated sulfuric acid are not sharper and are only slightly more intense than their corresponding peaks in chloroform solution. The increase in intensity for the absorption maxima of **1a** in concentrated sulfuric acid in comparison to chloroform solution, *i.e.* by a factor 1.4, is significantly less pronounced than for terrylenebis(dicarboximide) **7a** and quaterylenebis(dicarboximide) **2b**, *i.e.* by a factor 5.4 and 3.0, respectively. Thirdly, the shape of the absorption curve of **1a** in concentrated sulfuric acid remains somewhat similar to the one in chloroform solution (Fig. 3). This observation contrasts with the very different shapes of the absorption curves of the quaterylenebis(dicarboximide) **2b** in concentrated sulfuric acid and in chloroform solution. It should be concluded for the perylenebis(dicarboximide) **1a** that, despite the large bathochromic shift observed, the absence of a sharp and intense absorption in concentrated sulfuric acid seems not to indicate the formation of J-aggregates.<sup>32</sup>

It is well documented that temperature and concentration dependent  $^1\text{H}$  NMR experiments are particularly suited to the investigation of the presence of aggregates in solution.<sup>33</sup> Therefore, to elucidate the nature of the species present in

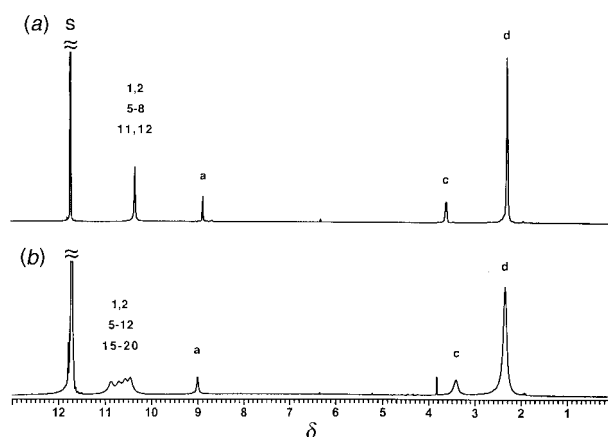
strongly acidic solutions, *i.e.* tightly packed aggregates or individual molecules,  $^1\text{H}$  NMR experiments in  $\text{D}_2\text{SO}_4$  were conducted on the oligomeric series: perylenebis(dicarboximide) **1a**, terrylenebis(dicarboximide) **7a** and quaterylenebis(dicarboximide) **2b**. Since the three members of this oligomeric series behave similarly, and for the sake of clarity, only the  $^1\text{H}$  NMR spectra of the perylenebis(dicarboximide) **1a** and the quaterylenebis(dicarboximide) **2b** are presented in Fig. 4.



**24**

Three observations are made: Firstly, the  $^1\text{H}$  NMR spectra of **1a**, **7a** and **2b** are sufficiently resolved in a viscous solvent such as  $\text{D}_2\text{SO}_4$ . Secondly, the  $^1\text{H}$  NMR spectra of **1a**, **7a**, and **2b** are independent of concentration in the range  $10^{-2}$ – $10^{-3}$  M. Thirdly, the chemical shifts of the protons of **1a**, **7a**, and **2b**, located on the N-substituent and on the aromatic core, are comparable within the oligomeric series. It also follows from the  $^1\text{H}$  NMR spectra of **1a**, **7a** and **2b** that the protons adjacent to the isopropyl groups on the phenyl substituents at the imide positions undergo rapid exchange with deuterium in  $\text{D}_2\text{SO}_4$ . This has also been confirmed by FD-MS analysis. Clearly, the well-resolved and concentration independent spectra of **1a**, **7a** and **2b** are inconsistent with the formation of any aggregates in solution. Moreover,  $^1\text{H}$  NMR spectra of a commercially available dye forming J-aggregates in  $\text{D}_2\text{O}$ , namely the benzimidocyanine **24**, have been recorded at 30 and 80 °C. Beside the characteristic peak of the solvent, the expected peaks of the dye were so broad that they could not be detected, indicating the formation of tightly packed aggregates. This last finding corroborates the view that no J-aggregates are formed in the case of the oligomeric series **1a**, **7a** and **2b** in concentrated sulfuric acid.

Therefore, the exact nature of the species present in strongly acidic solutions of perylenebis(dicarboximide) **1a**, terrylenebis(dicarboximide) **7a** and quaterylenebis(dicarboximide) **2b** remains unknown. One can only conclude that the different behavior of **1a**, **7a** and **2b** in chlorinated solvents and strongly acidic media must be related to the protonation

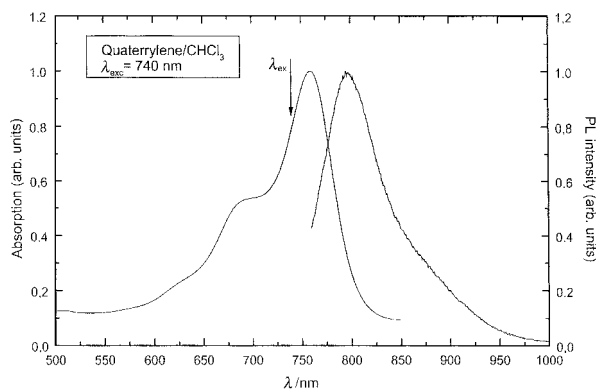


**Fig. 4**  $^1\text{H}$  NMR Spectra of (a) perylenebis(dicarboximide) **1a** and (b) quaterylenebis(dicarboximide) **2b** [ $\text{D}_2\text{SO}_4$  (96%), 500 MHz, 30 °C].

of the carboximide functions, and do not result from chemical modification or from aggregation of the chromophores.

**Photophysical behavior.** Based on the remarkably large quantum yield of fluorescence ( $\phi_f$ ) of perylene **1a** and terylene **7a** approaching unity in solution,<sup>15,34</sup> one would have expected that quaterrylenebis(dicarboximide) **2b** will, to some degree, emit light in the NIR window. However, no luminescence could be detected for quaterrylenebis(dicarboximide) **2b** in dilute solutions. Similarly, a dramatic decrease of  $\phi_f$  has been observed for quaterrylenebis(dicarboximide) **6c** ( $\phi_f=0.05$ ) in comparison with perylene **6a** and terylene **6b**.<sup>14</sup> Remarkably enough, it was recently discovered that the lack of emission of **2b** is related to traces of unknown impurities. Normally, samples of quaterrylenebis(dicarboximide) **2b** purified by column chromatography on silica gel with methylene chloride as eluent and precipitation in methanol, do not emit in chloroform solution, even though no impurities were observed by <sup>1</sup>H NMR and UV–VIS–NIR spectroscopy, FD-MS, and thin layer chromatography. Nevertheless if quaterrylenebis(dicarboximide) **2b** is further purified by several extractions in ethyl acetate, an emission centered at 797 nm in chloroform solution is observed (Fig. 5). Characteristically, the emission maxima [ $\lambda_{\text{max}}$  (nm)] of quaterrylenebis(dicarboximide) **2b** extends to even longer wavelength in the NIR window than those of terylenebis(dicarboximide) **7a** [ $\lambda_{\text{max}}$  (nm)=673 nm], benzoylteryleneimide **8a** [ $\lambda_{\text{max}}$  (nm)=701 nm] and perylenebis-amidine **9** [ $\lambda_{\text{max}}$  (nm)=768 nm].<sup>15,16</sup>

In Fig. 5 the absorption as well as the steady state photoluminescence (PL) are shown for the sake of comparison. The ground state absorption spectrum shows a strong inhomogeneously broadened  $S_0-S_1$  (0–0) transition centered at 763 nm followed by inhomogeneously broadened vibronic satellites centered at 695 and 626 nm, respectively. Deconvolution of the ground state absorption spectrum with Gaussian profiles allows the estimation of the absorption coefficient  $\epsilon$  as well as the oscillator strength  $f$  of the observed transitions. The molar extinction coefficients for the optical transitions are  $\epsilon=90000 \text{ cm}^2 \text{ mol}^{-1}$ , corresponding to an oscillator strength of about  $f=0.9$ , and  $\epsilon=51700 \text{ cm}^2 \text{ mol}^{-1}$ , relating to  $f=0.67$ , for the pure electronic (0–0) and the dominant vibronic (0–1) transitions, respectively. The dominant vibrational mode is energetically offset by about  $1300 \text{ cm}^{-1}$ , indicating a ring breathing mode. Comparing the transition intensities of the pure electronic transition with the ones of the vibronic transitions, it becomes evident that the quaterrylenebis(dicarboximide) **2b** is a very rigid material showing a slight distortion in the excited state only. Furthermore, the slight deviations from mirror symmetry indicate only minor differences in the nuclear configurations of the ground and the excited state. Therefore, we conclude that the large Stokes shift (about 35 nm) observed in emission is mainly due to solvation effects.



**Fig. 5** Absorption and emission spectra of quaterrylenebis(dicarboximide) **2b** in  $\text{CHCl}_3$ . The photoluminescence excitation is at 740 nm.

In a semiquantitative analysis, the radiative lifetime  $\tau_{\text{FM}}$ , defined as the reciprocal of the radiative transition probability, can be estimated from the Strickler–Berg<sup>35</sup> equation, which for dilute solutions becomes eqn. (1),

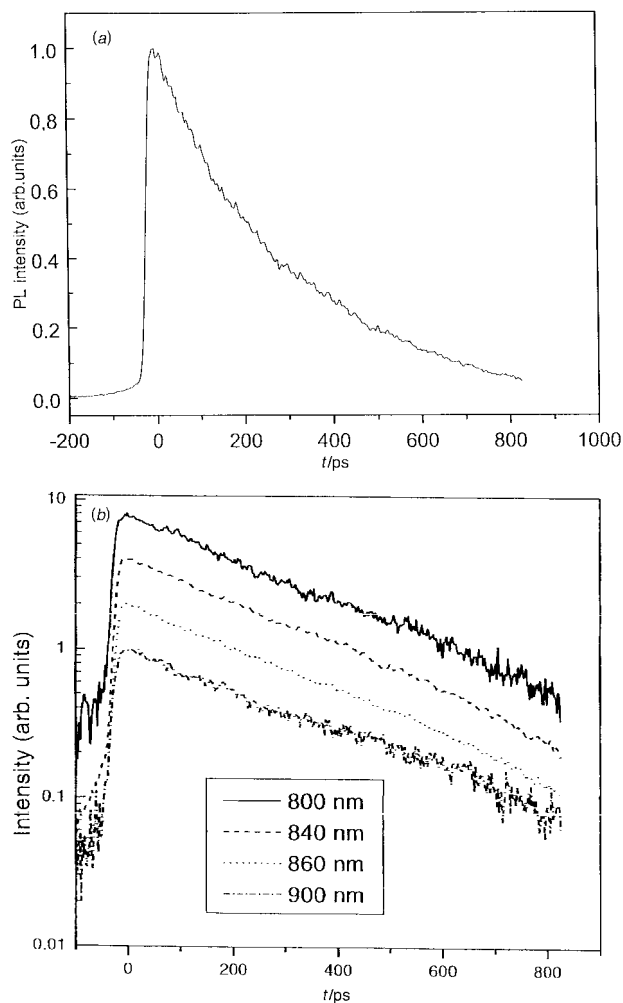
$$\frac{1}{\tau_{\text{FM}}} = 2.88 \times 10^{-9} n^2 \langle \tilde{\nu}^{-3} \rangle^{-1} \int \frac{\epsilon(\tilde{\nu})}{\tilde{\nu}} d\tilde{\nu} \quad (1)$$

where  $n$  is the refractive index and  $\langle \tilde{\nu}^{-3} \rangle^{-1}$  is the reciprocal of an appropriate average over the fluorescence spectrum defined in eqn. (2).

$$\langle \tilde{\nu}^{-3} \rangle^{-1} = \frac{\int F(\nu) d\nu}{\int \frac{F(\nu) d\nu}{\nu^3}} \quad (2)$$

The essential values needed eqn. (1) and (2) can be inferred from the absorption spectrum as well as from the steady state PL spectrum. Insertion of these parameters then leads to a radiative lifetime of about  $\tau_{\text{FM}}=65 \text{ ns}$ .

Further information about the photophysical properties of quaterrylenebis(dicarboximide) **2b** are given by time resolved photoluminescence measurements. In Fig. 6(a) a transient of the PL detected at the PL maximum at 800 nm is displayed. The measurement shows a monoexponential decay with a surprisingly short fluorescence decay time of about 320 ps. All transients taken at different wavelength of the PL spectrum exhibit exactly the same time dependence, as can be seen from



**Fig. 6** (a) Time dependence behaviour of the emission detected at 800 nm after excitation with 100 fs pulses. (b) Semilogarithmic plot of PL decays monitored at different detection energies.



Fig. 6(b), in which the transients are displayed on a semi-logarithmic scale.

This proves that no time and energy dependent rate, *e.g.* filling process, is involved in the radiative transition. However, the decay time seems to be surprisingly short compared to other members of this molecular family. Following the work on radiationless transitions in molecules one can roughly estimate that the probability of nonradiative transitions increases exponentially with decreasing energy gap  $\Delta E$  between the potential minima for the state involved [eqn. (3)],<sup>36</sup>

$$k_{\text{nr}} \propto \exp\left(-\frac{\gamma\Delta E}{2\pi\hbar\omega}\right) \quad (3)$$

where  $\omega$  is the vibrational frequency and  $\gamma$  is a quantity expressible in terms of molecular parameters. By comparing quaterrylenebis(dicarboximide) with perylene on the basis of this expression and taking into account that the main excess energy is dissipated through C–H vibrational modes (*ca.* 300 cm<sup>-1</sup>) an increase of the nonradiative transition probability of roughly a factor 25 can be estimated, which concurs fairly well with the PL decay time of  $\tau_{\text{FM}} = 320$  ps measured. Moreover, by insertion of the values obtained throughout the analysis above the quantum efficiency expressed as  $Q = \tau/\tau_{\text{FM}}$  can be estimated to approximately 5%.

**Electrochemical behavior.** The reduction potentials of substituted perylenebis(dicarboximide) **1b** and quaterrylenebis(dicarboximide) **18** are collected in Table 3. The cyclic voltammogram (CV) shows a four-fold reduction of the quaterrylenebis(dicarboximide)s **18**. The first two electrons are localized on the carbonyl groups because only a small difference is observed for the first (–0.74 V) and second reduction potentials (–1.10 V) of quaterrylenebis(dicarboximide) **18** as compared to the smaller homologue, perylenebis(dicarboximide) **1b**, at –0.85 and –1.11 V, respectively. This suggests that the two first reduction potentials are independent of the size of the conjugated  $\pi$ -system, indicating that the electrons go in to the quaterrylenebis(dicarboximide) **18** and the perylenebis(dicarboximide) **1b** in two different locations, presumably at the two imide functions, without appreciable interaction.<sup>37</sup>

In contrast, a definite charge stabilization, due to the extension of the  $\pi$ -system of the quaterrylenebis(dicarboximide) **18** in comparison to the perylene **1b**, is observed for the reduction to the tri- and tetra-anion. The third reduction potential of the quaterrylenebis(dicarboximide) **18** (–1.97 V) has a much lower absolute value than the one of the corresponding perylenebis(dicarboximide) **1b** (–2.64 V). Remarkably enough, a fourth reduction is observed for the quaterrylenebis(dicarboximide) **18**. Moreover, this fourth reduction potential lies at –2.26 V, *i.e.* 0.38 V lower than the third reduction potential of perylenebis(dicarboximide) **1b**.

**Thermal stability.** Thermogravimetric analyses (TGA) conducted under nitrogen atmosphere show that quaterrylenebis(dicarboximide) **18** possesses a high thermal stability. The first weight loss is observed between 485 and 500 °C and corresponds to the cleavage of the isopropyl groups. In this respect,

**Table 3** Reduction potentials *versus* saturated calomel electrode of perylenebis(dicarboximide) **1b** and quaterrylenebis(dicarboximide) **18** in tetrahydrofuran at 0 °C

Charge	<i>E/V vs. SCE</i>	
	Perylene <b>1b</b>	Quaterrylene <b>18</b>
–1	–0.85	–0.74
–2	–1.11	–1.10
–3	–2.64	–1.97
–4	—	–2.26

the perylenebis(dicarboximide) **1b**, the terrylenebis(dicarboximide) **7b**, and the quaterrylenebis(dicarboximide) **18** do not differ significantly.

**Photochemical stability.** The photostability of quaterrylenebis(dicarboximide) **2b** has been estimated by exposing under air a polystyrene film of roughly 10  $\mu\text{m}$  containing 0.5 wt% of dyes to UV light ( $\lambda = 366$  nm) for a prolonged period of time.<sup>15</sup> After 10 days of irradiation, no significant alteration of the absorption spectrum could be observed, demonstrating the photochemical inertness of quaterrylenebis(dicarboximide) **2b** in a polymer matrix.

## Conclusions

The synthesis of three quaterrylenebis(dicarboximide)s **2a,b**, **18** and **23** differing by their substitution pattern has been achieved. The extension of the  $\pi$ -system of the quaterrylenebis(dicarboximide)s **2a,b**, **18** and **23**, in comparison to the perylenebis(dicarboximide)s **1**, has several intriguing consequences for their photophysical and electrochemical properties. Firstly, the quaterrylenebis(dicarboximide)s **2a,b**, **18** and **23** are characterized by an intense absorption in the NIR, between 750 and 800 nm in chlorinated solvents, whereas the absorption of perylenebis(dicarboximide)s **1** ranges between 520 and 590 nm. Secondly, the quaterrylenebis(dicarboximide) **2b** presents an emission centered at 797 nm with a quantum efficiency estimated at 5%, which is significantly lower than those of perylenebis(dicarboximide)s **1** which approach one. Thirdly, a definite stabilization of the tri- and tetra-anion of the quaterrylenebis(dicarboximide) **18** occurs, whereas little difference is observed between the two first reduction potentials of **18** and **1b**. Fourthly, the quaterrylenebis(dicarboximide) **2b** exhibits, in strongly acidic solvents, an extremely intense absorption around 900 nm. However, this intense absorption cannot be explained by the formation of J-aggregates in solution, and is more likely caused by the protonation of the carboximide functions.

In addition to these new photophysical and electrochemical properties the quaterrylenebis(dicarboximide)s **2a,b**, **18** and **23** also display good chemical, photochemical and thermal stability. Clearly, this unusual ensemble of properties qualifies the quaterrylenebis(dicarboximide)s **2a,b** and **18** as functional NIR materials and suggests the synthesis of even larger rylenebis(dicarboximides) dyes.

We gratefully acknowledge the financial support of BASF AG and the Bundesministerium für Forschung und Technologie.

## Experimental

Spectral data were obtained on Nicolet FT-IR 320 (IR), Perkin-Elmer Lambda 9 and 15 (UV–VIS), Varian Gemini 200, Bruker AC 300 or AMX 500 (NMR), Potentiostat/Galvanostat PAR Model 173 (CV), Finnigan MAT 312 (FD-MS) and Mettler TG 50 (TGA) instruments. For the cyclic voltammetric experiments with **18** (in THF, with Bu<sub>4</sub>NPF<sub>6</sub> added) a Potentiostat/Galvanostat PAR Model 173 was used. The setup for photoluminescence consisted of an XeCl excimer pumped dye laser system (15 Hz rep. rate and 10 ns pulse width) running at 740 nm. The emission from the sample was collected and focussed into the entrance slit of a 270 cm grating monochromator fitted with a charge coupled device (CCD) array for detection. Fluorescence lifetime measurements were performed with an Kerr-lens mode-locked Ti:sapphire laser operating at 740 nm and producing 100 fs pulses at a repetition rate of 80 MHz. Here, as in the time integrated experiments, the emission was dispersed in a monochromator and monitored by a streak camera to follow the photoluminescence decay with a time resolution of about 6 ps. All measurements were performed at room temperature. The photostability tests were

conducted with a UV lamp (Camag, 0.25 A, 220 V), placing the polystyrene films 12 cm away from the lamp. The melting points (mp) are reported uncorrected. All solvents for reactions were distilled before use. Ni(cod)<sub>2</sub> was purchased from Strem Chemicals, all other chemicals were purchased from Aldrich and used as received. 3,4,9,10-Perylenetetracarboxylic dianhydride and *N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (**11b**) were obtained from BASF AG. The *N*-propyl-1,6:7,12-tetra(4-hexyloxyphenoxy)perylene-3,4:9,10-bis(dicarboximide) (**19**) has been previously described in the literature.<sup>17,25</sup>

#### ***N*-Dodecylperylene-3,4,9,10-tetracarboxylic acid 3,4-anhydride 9,10-dicarboximide§**

15.0 g (38 mmol) 3,4,9,10-Perylenetetracarboxylic dianhydride and 84.0 g (0.45 mmol) dodecylamine were added to a mixture of 1 L propan-1-ol and 0.5 L water. The reaction mixture was stirred at 65 °C for 7 h. After cooling to room temperature, 150 mL of concentrated HCl were added to the reaction mixture and 1 L of water was added. The precipitate was separated from the liquid phase by centrifugation and dried under vacuum, affording 20 g of the title compound as an orange powder (94% yield). *N*-Dodecylperylene-3,4,9,10-tetracarboxylic acid 3,4-anhydride 9,10-dicarboximide **10a** was used directly for the next reaction without further purification. For characterization purposes, a small amount was purified by chromatography on silica gel with chloroform as eluent.

$\delta_{\text{H}}$  (300 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 135 °C) 8.68 (d, 2H, H-8,11), 8.66 (d, 2H, H-2,5), 8.60 (d, 2H, H-7,12), 8.59 (d, 2H, H-1,6), 4.20 (t, 2H,  $\alpha$ -CH<sub>2</sub>), 1.79 (m, 2H,  $\beta$ -CH<sub>2</sub>), 1.41 (m, 2H,  $\gamma$ -CH<sub>2</sub>), 1.28 [br, 16H, (CH<sub>2</sub>)<sub>8</sub>], 0.87 (t, 3H, CH<sub>3</sub>);  $\nu_{\text{max}}/\text{cm}^{-1}$  2954, 2924, 2850, 1765 (C=O), 1743, 1724 (C=O), 1697 (C=O), 1656 (C=O), 1616, 1595, 1580, 1508, 1434, 1407, 1350, 1340, 1324, 1297, 1274, 1253, 1241, 1153, 1127, 1033, 1018, 866, 810, 739;  $\lambda_{\text{max}}$ (H<sub>2</sub>SO<sub>4</sub>)/nm ( $\epsilon$ ) (absorption) 390 (8170), 544 (42800), 581 (60440);  $m/z$  (EI) 559.3 (M<sup>+</sup>, 86%), 405.2 (M<sup>+</sup> - C<sub>11</sub>H<sub>22</sub>, 24%), 392.2 (M<sup>+</sup> - C<sub>12</sub>H<sub>24</sub>, 100%), 248.2 (perylene<sup>+</sup>, 60%) (calc. M<sup>+</sup>, 558.7); mp > 300 °C.

#### ***N*-Dodecylperylene-3,4-dicarboximide 11a**

5.0 g (8.9 mmol) **10a** and 200 mL of a 12 wt% KOH solution were introduced into a 250 mL autoclave. The temperature was raised to 230 °C for 18 h. After cooling to room temperature, the resulting precipitate was filtered off, washed with plenty of water and dried under vacuum. The resulting solid was extracted with diethyl ether and precipitated in a large volume of methanol. Then the red powder was dried under vacuum to afford 3.25 g of the title compound (75% yield). *N*-Dodecylperylene-3,4-dicarboximide **11a** was used directly for the next reaction without further purification. For characterization purposes a small amount (500 mg) was purified by column chromatography on silica gel with toluene as eluent.

$\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, 30 °C) 8.49 (d, 2H, H-2,5), 8.32 (d, 2H, H-7,12), 8.29 (d, 2H, H-1,6), 7.83 (d, 2H, H-9,10), 7.55 (dd, 2H, H-8,11), 4.16 (t, 2H,  $\alpha$ -CH<sub>2</sub>), 1.77 (m, 2H,  $\beta$ -CH<sub>2</sub>), 1.42 (m, 2H,  $\gamma$ -CH<sub>2</sub>), 1.28 [br, 16H, (CH<sub>2</sub>)<sub>8</sub>], 0.87 (t, 3H, CH<sub>3</sub>);  $\delta_{\text{C}}$  (75.5 MHz, CDCl<sub>3</sub>, 30 °C) 163.89 (C=O), 137.25, 134.74, 131.45, 130.85, 129.68, 128.37, 127.21, 123.72, 121.71, 120.36, 40.74, 32.00, 29.73, 29.70, 29.52, 29.36, 28.45, 27.43, 22.67, 13.96;  $\nu_{\text{max}}/\text{cm}^{-1}$  2956, 2916, 2850, 1691 (C=O), 1652 (C=O), 1595, 1571, 1469, 1381, 1354, 1295, 1262, 1249, 1105, 1079, 1032, 1022, 813, 762, 753;  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) (absorption) 263 (33100), 480 (28810), 502 (28330);  $m/z$  (FD) 489.3 (M<sup>+</sup>, 100%), 978.3 (M<sup>2+</sup>, 77%) [C<sub>34</sub>H<sub>35</sub>NO<sub>2</sub> (489.66 g mol<sup>-1</sup>) calc.: C, 83.40; H, 7.21; N, 2.86. Found: C, 82.87; H, 7.04; N, 2.71%]; mp 179 °C.

§IUPAC name: *N*-dodecyl-13,15-dioxo-9,10-(methanoepiminomethano)perylene-3,4-dicarboxylic anhydride

#### ***N*-Dodecyl-9-bromoperylene-3,4-dicarboximide 12a**

2.5 g (5.1 mmol) *N*-Dodecylperylene-3,4-dicarboximide **11a** were dissolved in 750 ml methylene chloride and a catalytic amount of iron powder was added. After 15 min, 8 g (50 mmol) of bromine in 50 ml methylene chloride were added to the reaction mixture. The temperature was slowly increased and the reaction mixture was refluxed for 3 h. After cooling to room temperature, the excess bromine and most of the methylene chloride were evaporated under vacuum. The resulting concentrated solution was poured into a large volume of methanol and this solution was stored at -20 °C for 1 h. The resulting precipitate was filtered and washed with plenty of methanol. Drying under vacuum afforded 2.73 g of the title compound **12a** as a red powder (94% yield).

$\delta_{\text{H}}$  (500 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 135 °C) 8.6–8.5 (m, 2H, H-2,5), 8.5–8.3 (m, 4H, H-12,7,1,6), 8.15 (d, 1H, H-10), 7.90 (d, 1H, H-8), 7.71 (dd, 1H, H-11), 4.23 (t, 2H,  $\alpha$ -CH<sub>2</sub>), 1.84 (m, 2H,  $\beta$ -CH<sub>2</sub>), 1.48 (m, 2H,  $\gamma$ -CH<sub>2</sub>), 1.35 [br, 16H, (CH<sub>2</sub>)<sub>8</sub>], 0.94 (t, 3H, CH<sub>3</sub>);  $\nu_{\text{max}}/\text{cm}^{-1}$  2954, 2921, 2870, 2851, 1694 (C=O), 1651 (C=O), 1616, 1594, 1562, 1497, 1467, 1455, 1383, 1359, 1333, 1296, 1244, 812, 805, 751;  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) (absorption) 255 (18930), 263 (34690), 480 (31240), 504 (32090);  $m/z$  (FD) 569.4 (M<sup>+</sup>, 100%) [C<sub>34</sub>H<sub>34</sub>NO<sub>2</sub>Br (568.55 g mol<sup>-1</sup>) calc.: C, 71.83; H, 6.03; N, 2.46; Br, 14.05. Found: C, 70.59; H, 5.71; N, 2.40; Br, 14.21%]; mp 231 °C.

#### ***N*-(2,6-Diisopropylphenyl)-9-bromoperylene-3,4-dicarboximide 12b**

10 g (21 mmol) *N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide **11b** were dissolved under slight heating in 1 L chlorobenzene. Bromine (15 g, 95 mmol) was added and the reaction mixture was stirred for 4.5 h at 50 °C. Chlorobenzene and unreacted bromine were removed under vacuum. The resulting solid was recrystallised from methylene chloride–methanol, yielding 11.4 g (98%) of the title compound **12b**.

$\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, 30 °C) 8.64 (d, 1H, H-2), 8.62 (d, 1H, H-5), 8.45 (d, 1H, H-1), 8.42 (d, 1H, H-6), 8.37 (d, 1H, H-12), 8.27 (d, 1H, H-7), 8.20 (d, 1H, H-10), 7.87 (d, 1H, H-8), 7.69 (t, 1H, H-11), 7.47 (dd, 1H, H-16), 7.33 (d, 2H, H-15), 2.77 [m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.18 [d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>];  $\delta_{\text{C}}$  (125.5 MHz, CDCl<sub>3</sub>, 30 °C) 163.85, 145.69, 136.90, 136.77, 133.02, 132.09, 132.02, 131.31, 130.94, 130.43, 130.08, 129.66, 129.44, 129.21, 129.11, 128.21, 126.69, 126.20, 124.47, 123.98, 123.81, 121.43, 120.75, 120.48, 29.13, 23.96;  $\nu_{\text{max}}/\text{cm}^{-1}$  1701 (C=O), 1660 (C=O);  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) (absorption) 263 (34056), 355 (3065), 484 (34762), 509 (35319); (fluorescence) 540;  $m/z$  (FD) 561.1 (M<sup>+</sup>, 100%) [C<sub>34</sub>H<sub>26</sub>NOBr (560.49 g mol<sup>-1</sup>) calc.: C, 72.86; H, 4.68; N, 2.50; Br, 14.26. Found: C, 71.93; H, 4.71; N, 2.50; Br, 13.77%]; mp > 300 °C. R<sub>f</sub> (silica gel) 0.45 (CH<sub>2</sub>Cl<sub>2</sub>), 0.09 (toluene).

#### ***N*-(2,6-Diisopropylphenyl)-9-(tributylstannyl)perylene-3,4-dicarboximide 13b**

13.5 g (24 mmol) of the monobromoperylene **12b**, 26.3 g (45 mmol) hexabutylditin and 0.1 g (0.1 mmol, 0.3 mol%) Pd(PPh<sub>3</sub>)<sub>4</sub> were refluxed in 700 ml toluene for 4 days. The solvent was removed under vacuum. Purification was carried out by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub> as eluent, affording 16 g of the title compound as a red solid (88% yield).

$\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>, 30 °C) 8.66 (d, 1H), 8.65 (d, 1H), 8.50 (d, 1H), 8.47 (d, 1H), 8.46 (d, 1H), 8.40 (d, 1H), 7.88 (d, 1H), 7.84 (d, 1H), 7.69 (t, 1H), 7.49 (t, 1H), 7.35 (d, 2H), 2.79 (h, 2H), 1.69–1.56 (m, 6H), 1.44–1.33 (m, 6H), 1.31–1.27 (m, 6H), 1.20 (d, 12H), 0.92 (t, 9H);  $\delta_{\text{C}}$  (125.5 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 30 °C) 164.0, 149.7, 145.7, 140.1, 138.0, 137.7, 136.3, 133.4, 132.0, 131.1, 130.5, 129.8, 129.4, 129.2, 127.0, 126.8, 124.0, 123.7, 122.7, 120.8, 120.0, 119.9, 29.3, 29.2, 27.3, 24.0, 13.6, 10.8;  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 1699 (C=O), 1663 (C=O);

$\lambda_{\max}$ (CHCl<sub>3</sub>)/nm ( $\epsilon$ ) (absorption) 267 (4.45), 496 (4.56), 521 (4.54);  $m/z$  (FD) 772.5 (M<sup>+</sup>, 100%) calc. M<sup>+</sup>, 772.5; mp 158–159 °C.

#### *N,N'*-Bis(dodecyl)-9,9'-biperylene-3,4:3',4'-bis(dicarboximide) 14a

Ni(cod)<sub>2</sub> (180 mg, 0.67 mmol), cyclooctadiene (600 mg, 5.6 mmol) and 2,2'-bipyridyl (105 mg, 0.67 mmol) were added to 80 ml DMF in a 100 ml Schlenk flask under argon. The mixture was stirred at room temperature for 1 h and bromoperylenedicarboximide **12a** (382 mg, 0.67 mmol) was added to the purple solution. After 36 h at 65 °C, the reaction mixture was cooled to room temperature and poured into 120 mL water–hydrochloric acid–methanol (1:1:2). The resulting precipitate was filtered off, washed with water and dried under vacuum, yielding 293 mg (89%) of the title compound **14a** as a deep red powder.

$\delta_{\text{H}}$  (500 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 135 °C) 8.53 (2d, 4H, H-5,2), 8.38 (d, 2H, H-7), 8.32 (d, 2H, H-6), 8.28 (2d, 4H, H-1,12), 8.12 (d, 2H, H-8), 7.88 (d, 2H, H-10), 7.69 (t, 4H, H-11), 4.22 (t, 4H,  $\alpha$ -CH<sub>2</sub>), 1.81 (m, 4H,  $\beta$ -CH<sub>2</sub>), 1.48 (m, 4H,  $\gamma$ -CH<sub>2</sub>), 1.34 [br, 32H, (CH<sub>2</sub>)<sub>8</sub>], 0.94 (t, 6H, CH<sub>3</sub>);  $\delta_{\text{C}}$  (125.5 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 135 °C) 164.85, 164.84, 137.58, 137.45, 134.40, 132.59, 132.56, 132.53, 131.10, 131.08, 130.94, 130.52, 130.50, 129.41, 127.71, 127.23, 125.44, 124.75, 123.12, 123.10, 121.94, 121.66, 41.91, 33.14, 30.87, 30.84, 30.82, 30.65, 30.50, 29.55, 28.55, 23.83, 15.16;  $\nu_{\max}/\text{cm}^{-1}$  2955, 2923, 2852, 1696, 1651, 1594, 1563, 1497, 1384, 1359, 1245, 805, 750;  $\lambda_{\max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) (absorption) 263 (56150), 481 (51030), 504 (53160);  $m/z$  (FD) 977.3 (M<sup>+</sup>, 100%) [C<sub>68</sub>H<sub>68</sub>N<sub>2</sub>O<sub>4</sub> (977.30 g mol<sup>-1</sup>) calc.: C, 83.57; H, 7.01; N, 2.87. Found: C, 83.09; H, 7.11; N, 2.92%]; mp 204 °C.

#### *N,N'*-Bis(2,6-diisopropylphenyl)-9,9'-biperylene-3,4:3',4'-bis(dicarboximide) 14b

Ni(cod)<sub>2</sub> (496 mg, 1.78 mmol), cod (161 mg, 1.48 mmol) and 2,2'-bipyridyl (278 mg, 1.78 mmol) were added to 80 ml DMF in a 100 ml Schlenk flask under argon. The mixture was stirred at room temperature for 1 h and bromoperylenedicarboximide (1 g, 1.78 mmol) was added to the purple solution. After two days at 70 °C, the reaction mixture was cooled to room temperature and poured into 1 L water–hydrochloric acid (5:1). The precipitate was filtered off, washed with water, dried under vacuum and purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as eluent. Solvent was evaporated under vacuum, then the resulting solid was redissolved in a minimum of CH<sub>2</sub>Cl<sub>2</sub> and a large excess of methanol was added. The green precipitate was filtered, washed with methanol and dried under vacuum, yielding 710 mg (83%) of the title compound **14b**.

$\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, 30 °C) 8.72 (d, 2H, H-5), 8.70 (d, 2H, H-2), 8.65 (d, 2H, H-7), 8.58 (d, 2H, H-6), 8.50–8.55 (m, 4H, H-12,1), 7.74 (d, 2H, H-8), 7.62 (d, 2H, H-10), 7.55 (d, 2H, H-11), 7.48 (dd, 2H, Ph-H-16), 7.34 (d, 4H, Ph-H-15), 2.78 [m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.18 [d, 24H, CH(CH<sub>3</sub>)<sub>2</sub>];  $\delta_{\text{C}}$  (125.5 MHz, CDCl<sub>3</sub>, 30 °C) 163.95, 145.74, 145.71, 140.53, 137.44, 137.23, 135.30, 133.71, 132.13, 130.99, 130.57, 129.65, 129.59, 129.48, 129.37, 129.27, 128.32, 127.47, 127.01, 124.08, 124.04, 123.40, 121.34, 121.29, 120.61, 120.47, 29.17, 24.03;  $\nu_{\max}/\text{cm}^{-1}$  1702 (C=O), 1662 (C=O);  $\lambda_{\max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) (absorption) 264 (57790), 355 (6503), 499 (66477), 528 (83055); (fluorescence) 597;  $m/z$  (FD) 480.8 (M<sup>2+</sup>, 29%), 960.8 (M<sup>+</sup>, 100%) [C<sub>68</sub>H<sub>52</sub>N<sub>2</sub>O<sub>4</sub> (961.17 g mol<sup>-1</sup>) calc.: C, 84.97; H, 5.45; N, 2.91. Found: C, 84.02; H, 5.39; N, 2.70%]; mp > 300 °C;  $R_f$  (silica gel) 0.12 (CH<sub>2</sub>Cl<sub>2</sub>), 0.84 (THF).

#### *N,N'*-Bis(dodecyl)quaterrylene-3,4:13,14-bis(dicarboximide) 2a

*N,N'*-Bis(dodecyl)-9,9'-biperylene-3,4:3',4'-bis(dicarboximide) (977 mg, 1 mmol), 100 g KOH, 4 g glucose and 100 mL were

added in a 250 ml Schlenk flask under argon. The reaction mixture was vigorously stirred at 120 °C for 2.5 h. After cooling to room temperature, the solidified solution was dissolved in water and poured into 500 mL water–hydrochloric acid (5:1). The resulting precipitate was filtered and dried under vacuum. Purification was carried out by extraction using CHCl<sub>3</sub> as solvent until no colored side product could be extracted. Drying the resulting dark blue powder afforded 369 mg of the title compound (83% yield).

$\delta_{\text{C}}$ (CP MAS TOSS, 4.5 kHz) 161.54 (C=O), 140–115 (C, aromatic), 40.60, 30.75, 23.43, 14.42;  $\lambda_{\max}/\text{cm}^{-1}$  2921, 2851, 1690 (C=O), 1650 (C=O), 1594, 1575, 1548, 1502, 1455, 1430, 1404, 1382, 1354, 1288, 1244, 1126, 1115, 810;  $\lambda_{\max}$ (H<sub>2</sub>SO<sub>4</sub>)/nm ( $\epsilon$ ) 208 (0.375), 374 (0.055), 622 (0.170), 858 (0.219), 896 (0.419), 989 (0.469), 1134 (0.021);  $\lambda_{\max}$  [H<sub>2</sub>SO<sub>4</sub>-oleum (57%) (4:1)]/nm ( $\epsilon$ ) 281 (524300), 323 (57700), 784 (34400), 876 (337000);  $m/z$  (FD) 974.2 (M<sup>+</sup>, 100%) (calc. M<sup>+</sup>, 975.3); mp > 300 °C.

#### *N,N'*-(2,6-Diisopropylphenyl)quaterrylene-3,4:13,14-bis(dicarboximide) 2b

*N,N'*-Bis(2,6-diisopropylphenyl)-9,9'-biperylene-3,4:3',4'-bis(dicarboximide) (750 mg, 0.78 mmol), 80 g KOH and 6 g glucose, were added in a 250 ml Schlenk flask under argon. The reaction mixture was vigorously stirred at 120 °C for 2.5 h. After cooling to room temperature, the solidified solution was dissolved in water and poured into 500 mL water–hydrochloric acid (5:1). The resulting precipitate was filtered and dried under vacuum. Purification was carried out by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent. Precipitation from CH<sub>2</sub>Cl<sub>2</sub> in methanol afforded 620 mg of the title compound as a green powder (83% yield).

$\delta_{\text{H}}$ (300 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 135 °C) 8.68 (d, 4H, H-2, 5, 12, 15), 8.68, 8.63 (d, 4H, H-7, 10, 17, 20, 8, 9, 18, 19), 8.56 (d, 4H, H-1, 6, 11, 16), 7.42 (dd, 2H, Ph-H-24), 7.29 (d, 4H, Ph-H-23), 2.80 [m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.19 [d, 24H, CH(CH<sub>3</sub>)<sub>2</sub>];  $\nu_{\max}/\text{cm}^{-1}$  1702 (C=O), 1659 (C=O);  $\lambda_{\max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) 264 (97377), 274 (100124), 317 (9195), 375 (14689), 764 (162024);  $\lambda_{\max}$  [H<sub>2</sub>SO<sub>4</sub>-oleum (59%) (4:1)]/nm ( $\epsilon$ ) 281 (698994), 326 (58801), 783 (83173), 876 (654705);  $m/z$  (FD) 479.2 (M<sup>2+</sup>, 37%), 958.5 (M<sup>+</sup>, 100%), (calc. M<sup>+</sup>, 959.1); mp > 300 °C;  $R_f$  (silica gel) 0.02 (CH<sub>2</sub>Cl<sub>2</sub>), 0.81 (THF).

#### *N*-(2,6-Diisopropylphenyl)-1,6,9-tribromoperylene-3,4-dicarboximide 15

To a solution of *N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide **11** (12 g, 25 mmol) in 1.5 L chloroform, 70 mL of bromine were added and the reaction mixture was refluxed for 6 h. After cooling to room temperature, the reaction mixture was washed with a solution of 15 g KOH and 10 g sodium sulfite in 2 L water. The organic layer was separated and dried on magnesium sulfate. Removing the solvent under vacuum afforded 19.5 g of the title compound as an orange solid. The purity was found to be sufficient for the next reaction. For analytical purposes, 2 g of the orange solid were purified by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent. Precipitation from CH<sub>2</sub>Cl<sub>2</sub> in methanol afforded 1.67 g of the title compound (91% yield).

$\delta_{\text{H}}$ (500 MHz, CDCl<sub>3</sub>, 30 °C) 9.33 (d, 1H, H-12), 9.11 (d, 1H, H-7), 8.94 (s, 1H, H-2), 8.93 (s, 1H, H-5), 8.45 (d, 1H, H-10), 7.99 (d, 1H, H-8), 7.80 (t, 1H, H-11), 7.51 (t, 1H, Ph-H-16), 7.36 (d, 2H, Ph-H-15), 2.73 [heptet, 2H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.20 [d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>];  $\delta_{\text{C}}$ (125.5 MHz, CDCl<sub>3</sub>, 30 °C) 162.54, 145.63, 135.37, 135.15, 134.56, 131.62, 130.92, 130.69, 130.33, 130.28, 129.82, 129.78, 129.58, 128.86, 128.75, 127.53, 126.94, 126.91, 126.74, 126.50, 124.14, 120.94, 120.89, 119.24, 119.02, 29.25, 23.98;  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 1711 (C=O), 1672 (C=O);  $\lambda_{\max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) 228 (78697), 281 (28194), 379 (3116), 401 (3398), 513 (33013);  $m/z$  (FD) 719.0 (M<sup>+</sup>, 100%) [C<sub>34</sub>H<sub>24</sub>NO<sub>2</sub>Br<sub>3</sub> (718.27 g mol<sup>-1</sup>) calc.: C, 56.86; H, 3.37; N,

1.95; Br, 33.37. Found: C, 56.49; H, 3.42; N, 1.72; Br, 32.01%; mp >300 °C;  $R_f$  (silica gel) 0.77 (CH<sub>2</sub>Cl<sub>2</sub>), 0.48 (toluene).

#### ***N*-(2,6-Diisopropylphenyl)-1,6-bis(4-*tert*-butylphenoxy)-9-bromoperylene-3,4-dicarboximide 16**

*N*-(2,6-Diisopropylphenyl)-1,6,9-tribromoperylene-3,4-dicarboximide **15** (16 g, 22 mmol), 4-*tert*-butylphenol (6.6 g, 0.044 mol) and potassium carbonate (6.9 g, 0.05 mol) were stirred in 500 ml NMP at 120 °C for 6 h. After cooling to room temperature, the reaction mixture was poured into 2 l water–HCl (5:1). The resulting precipitate was filtered, washed with water and dried under vacuum. The desired product was purified by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent. Precipitation from CH<sub>2</sub>Cl<sub>2</sub> into methanol afforded 6.28 g of the title compound as a red powder (33% yield).

$\delta_H$ (300 MHz, CDCl<sub>3</sub>, 30 °C) 9.40 (d, 1H, H-12), 9.16 (d, 1H, H-7), 8.35 (d, 1H, H-10), 8.34 (s, 1H, H-2), 8.32 (s, 1H, H-5), 7.88 (d, 1H, H-8), 7.69 (t, 1H, H-11), 7.4–7.5 (m, 5H, Ph-H-16,3,3'), 7.30 (d, 2H, Ph-H-15), 7.08 (m, 4H, Ph-H-2,2'), 2.72 [m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.35 (s, 18H, *tert*-butyl), 1.15 [d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>];  $\delta_C$ (125.5 MHz, CDCl<sub>3</sub>, 30 °C) 163.14, 153.80, 153.69, 153.17, 153.10, 147.35, 147.33, 145.64, 132.00, 131.54, 131.01, 130.87, 130.67, 129.42, 129.32, 129.29, 128.68, 128.05, 127.83, 127.55, 127.18, 126.63, 126.54, 125.35, 124.36, 124.30, 123.91, 123.02, 121.89, 121.87, 118.43, 118.36, 34.43, 31.45, 29.09, 23.99;  $\nu_{max}$ (KBr)/cm<sup>-1</sup> 1706 (C=O), 1670 (C=O);  $\lambda_{max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) 274 (40081), 420 (9949), 513 (41553);  $m/z$  (FD) 855.2 (M<sup>+</sup>, 100%) [C<sub>54</sub>H<sub>50</sub>NO<sub>4</sub>Br (856.90 g mol<sup>-1</sup>): calc.: C, 75.69; H, 5.88; N, 1.63; Br, 9.32. Found: C, 75.27; H, 5.92; N, 1.41; Br, 8.69%]; mp 297 °C;  $R_f$  0.86 (CH<sub>2</sub>Cl<sub>2</sub>), 0.56 (toluene).

#### ***N,N'*-Bis(2,6-diisopropylphenyl)-1,1',6,6'-tetra(4-*tert*-butylphenoxy)-9,9'-biperylene-3,4:3',4'-bis(dicarboximide) 17**

770 mg (2.8 mmol) Ni(cod)<sub>2</sub>, 252 mg (2.34 mmol) cod, 440 mg (2.8 mmol) 2,2'-bipyridyl and 2 g (2.33 mmol) *N*-(2,6-diisopropylphenyl)-1,6-bis(4-*tert*-butylphenoxy)-9-bromoperylene-3,4-dicarboximide **13** were reacted as described for the preparation of **14**. Purification was carried out by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>–toluene as eluent. Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>–methanol afforded 1.55 g of the title compound as a red powder (86% yield).

$\delta_H$ (500 MHz, CDCl<sub>3</sub>, 30 °C) 9.46 (d, 2H, H-7,7'), 9.36 (d, 2H, H-12,12'), 8.36 (s, 2H, H-5,5'), 8.34 (s, 2H, H-2,2'), 7.64 (d, 2H, H-8,8'), 7.60 (d, 2H, H-10,10'), 7.4–7.5 (m, 12H, H-11,11', Ph-H-3,3',16,16'), 7.29 (d, 4H, Ph-H-15,15'), 7.09, 7.13 (d, 4H, Ph-H-2,2'), 2.73 [m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.34 (s, 36H, *tert*-butyl), 1.15 [d, 24H, CH(CH<sub>3</sub>)<sub>2</sub>];  $\delta_C$ (125.5 MHz, CDCl<sub>3</sub>, 30 °C) 163.2, 153.8, 153.7, 153.3, 147.3, 147.2, 145.7, 145.7, 140.1, 132.8, 131.9, 130.7, 129.7, 129.4, 128.9, 128.3, 127.9, 127.9, 127.2, 127.2, 127.0, 126.9, 124.3, 124.2, 123.9, 123.1, 121.6, 118.6, 118.5, 34.4, 31.5, 29.1, 24.0;  $\nu_{max}$ (KBr)/cm<sup>-1</sup> 1709 (C=O), 1672 (C=O);  $\lambda_{max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) 275 (66307), 417 (15681), 534 (91474);  $m/z$  (FD) 777.1 (M<sup>2+</sup>, 6%), 1554.1 (M<sup>+</sup>, 100%) [C<sub>108</sub>H<sub>100</sub>N<sub>2</sub>O<sub>8</sub> (1553.99 g mol<sup>-1</sup>): calc.: C, 83.47; H, 6.49; N, 1.80. Found: C, 83.31; H, 6.33; N, 1.62%]; mp 259 °C;  $R_f$  0.84 (CH<sub>2</sub>Cl<sub>2</sub>), 0.26 (toluene).

#### ***N,N'*-Bis(2,6-diisopropylphenyl)-1,6,11,16-tetra(4-*tert*-butylphenoxy)quaterrylene-3,4:13,14-bis(dicarboximide) 18**

The synthesis was performed as described for **2**. Modifications: 500 mg (0.32 mmol) *N,N'*-bis(2,6-diisopropylphenyl)-1,1',6,6'-tetra(4-*tert*-butylphenoxy)-9,9'-biperylene-3,4:3',4'-bis(dicarboximide) **17**, 80 g KOH and 6 g glucose. The desired product was purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>–toluene as eluent. Precipitation from CH<sub>2</sub>Cl<sub>2</sub> into

methanol afforded 421 mg of quaterrylenebis(dicarboximides) **18** as a green powder (85% yield).

$\delta_H$ (500 MHz, CDCl<sub>3</sub>, 30 °C) 9.09 (d, 4H, H-7, 10, 17, 20), 8.32 (s, 4H, H-2, 5, 12, 15), 7.76 (d, 4H, H-8, 9, 18, 19), 7.41 (t, 2H, Ph-H-24), 7.34 (d, 8H, Ph-H-24), 7.28 (d, 4H, Ph-H-23), 7.00 (d, 8H, Ph-H-2), 2.76 [m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.26 (s, 36H, *tert*-butyl), 1.13 [d, 24H, CH(CH<sub>3</sub>)<sub>2</sub>];  $\delta_C$ (125.5 MHz, CDCl<sub>3</sub>, 30 °C) 162.99, 153.55, 152.93, 147.00, 145.75, 131.24, 130.85, 130.80, 129.40, 129.19, 128.87, 127.73, 127.47, 127.17, 126.42, 125.24, 124.32, 123.94, 122.53, 121.63, 117.39, 34.37, 31.44, 29.23, 24.10;  $\nu_{max}$ (KBr)/cm<sup>-1</sup> 1707 (C=O), 1669 (C=O);  $\lambda_{max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) (absorption) 262 (95819), 271 (97645), 382 (12895), 709 (71931), 781 (166571); (fluorescence) 806;  $m/z$  (FD) 775.2 (M<sup>2+</sup>, 38%), 1551.3 (M<sup>+</sup>, 100%) (calc. M<sup>+</sup>, 1552.0); mp >300 °C;  $R_f$  0.43 (CH<sub>2</sub>Cl<sub>2</sub>), 0.03 (toluene).

#### ***N*-Propyl-1,6,7,12-tetra(4-hexyloxyphenoxy)perylene-3,4-dicarboximide 20**

*N*-Propyl-1,6,7,12-tetra(4-hexyloxyphenoxy)perylene-3,4:9,10-bis(dicarboximide) **19** (15 g, 12 mmol) and 150 g KOH were added to 1 L of propan-2-ol. The reaction mixture was refluxed for 105 min. After cooling to room temperature, 2.5 L water and 250 ml of concentrated hydrochloric acid were added. The resulting precipitate was filtered, washed with water and dried under vacuum. The crude product was then dissolved in a suspension of 25 g Cu<sub>2</sub>O in 800 ml quinoline. The temperature was raised to 240 °C under vacuum and 500 ml quinoline were distilled over a period of 6 h. The reaction mixture was cooled to room temperature, and 2.5 L water and 150 mL concentrated hydrochloric acid were added. The resulting precipitate was filtered, washed with water and dried under vacuum. Purification was carried out by chromatography on silica gel with toluene as eluent. The second fraction was identified as the title compound. Precipitation in methanol afforded 5.70 g of the title compound as a red–orange powder (42% yield).

$\delta_H$ (300 MHz, CDCl<sub>3</sub>, 30 °C) 8.10 (s, 2H, H-2, 5), 7.72 (d, 2H, H-9, 10), 7.09 (d, 2H, H-8, 11), 6.7–7.0 (m, 16H, Ph-H), 4.08 (t, 2H, -CH<sub>2</sub>), 3.93 [t, 8H, -CH<sub>2</sub> (hexyl)], 2.75 [m, 8H, -CH<sub>2</sub> (hexyl)], 1.1–1.6 [m, 26H, (CH<sub>2</sub>)<sub>3</sub> (hexyl), -CH<sub>2</sub> (propyl)], 0.96 [m, 15H, CH<sub>3</sub> (hexyl), CH<sub>3</sub> (propyl)];  $\lambda_{max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) (absorption) 277 (1.23), 414 (0.27), 538 (0.55);  $m/z$  (FD) 1132.8 (M<sup>+</sup>, 100%) (calc. M<sup>+</sup>, 1132.5).

#### ***N*-Propyl-1,6,7,12-tetra(4-hexyloxyphenoxy)-9-bromoperylene-3,4-dicarboximide 21**

5 g (4.4 mmol) *N*-Propyl-1,6,7,12-tetra(4-hexyloxyphenoxy)perylene-3,4-dicarboximide **20** and 2 g (11 mmol) NBS were dissolved in 600 mL of DMF. The reaction mixture was reacted for 12 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into 3 L water–HCl (5:1). The resulting precipitate was filtered, washed with water and dried under vacuum. Precipitation from CH<sub>2</sub>Cl<sub>2</sub> into methanol afforded 4.68 g of the title compound **21** as a red powder (93% yield).

$\delta_H$ (500 MHz, CDCl<sub>3</sub>, 30 °C) 8.12 (s, 1H, H-2), 8.10 (s, 1H, h-5), 8.09 (d, 1H, H-10), 7.38 (s, 1H, H-8), 7.18 (d, 1H, H-11), 6.7–7.0 (m, 16H, Ph-H), 4.05 (t, 2H, -CH<sub>2</sub>); 3.92 [t, 8H, -CH<sub>2</sub> (hexyl)]; 1.77 [m, 10H, -CH<sub>2</sub> (hexyl)], 1.2–1.6 [m, 24H, (CH<sub>2</sub>)<sub>3</sub>], 0.94 [m, 15H, CH<sub>3</sub>/CH<sub>3</sub> (hexyl)];  $m/z$  (FD) 1211.6 (M<sup>+</sup>, 100%) (calc. M<sup>+</sup>, 1211.4).

#### ***N,N'*-Dipropyl-1,1',6,6',7,7',12,12'-octa(4-hexyloxyphenoxy)-9,9'-biperylene-3,4:3',4'-bis(dicarboximide) 22**

654 mg (1 mmol) Bis(triphenylphosphine)nickel(II) chloride, 450 mg activated zinc and 131 mg (1 mmol) tetraethylammonium iodide were poured into a 100 mL Schlenk flask under

argon containing 80 mL of THF. After stirring for 4 h at room temperature, 1.2 g (1.06 mmol) *N*-propyl-1,6,7,12-tetra(4-hexyloxyphenoxy)-9-bromoperylene-3,4-dicarboximide **21** were added. Then, the reaction mixture was stirred for 12 h at room temperature. The reaction mixture was filtered through Al<sub>2</sub>O<sub>3</sub> and washed with CH<sub>2</sub>Cl<sub>2</sub>. Precipitation from CH<sub>2</sub>Cl<sub>2</sub> into methanol afforded 3.45 g of the title compound as a red powder (75% yield). The purity was sufficient for the next reactions. For analytical purposes, 100 mg were purified by column chromatography on silica gel with toluene as eluent.

$\delta_{\text{H}}$ (300 MHz, CDCl<sub>3</sub>, 30 °C) 8.11 (s, 2H, H-2,2'), 8.09 (s, 2H, H-5,5'), 7.42 (d, 2H, H-10,10'), 7.1–7.2 (m, 20H, Ph-H-3,3',3'',3''', H-8,8',11,11'), 6.7–6.9 (m, 16H, Ph-H-2,2',2'',2'''), 4.05 (t, 4H, N-CH<sub>2</sub>-), 1.68 (t, 4H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.26 (3s, 72H, *tert*-butyl), 0.93 (t, 24H, CH<sub>3</sub>); *m/z* (FD) 1909.2 (M<sup>+</sup>, 100%), 955 (M<sup>2+</sup>, 92%) (calc. M<sup>+</sup>, 1910.4).

$\delta_{\text{H}}$ (300 MHz, CDCl<sub>3</sub>, 30 °C) 8.12 (s, 2H, H-2,2'), 8.11 (s, 2H, H-5,5'), 7.42 (d, 2H, H-10,10'), 7.08 (s, 2H, H-8,8'), 6.7–7.0 (m, 34H, H-11,11', Ph-H-2,2',2'',2''', Ph-H-3,3',3'',3'''), 4.06 (t, 4H, -CH<sub>2</sub>), 3.93 [t, 16H, -CH<sub>2</sub> (hexyl)], 1.76 [m, 20H, -CH<sub>2</sub>/-CH<sub>2</sub> (hexyl)], 1.3–1.7 [m, 48H, (CH<sub>2</sub>)<sub>3</sub>], 0.93 [m, 30H, CH<sub>3</sub>/CH<sub>3</sub> (hexyl)]; *m/z* (FD) 1131.6 (M<sup>2+</sup>, 100%), 2263.1 (M<sup>+</sup>, 62%) (calc. M<sup>+</sup>, 2262.9).

### *N,N'*-Dipropyl-1,6,7,10,11,16,17,20-octa(4-hexyloxyphenoxy)quaterrylenebis(dicarboximide) **23**

500 mg (0.22 mmol) *N,N'*-dipropyl-1,1',6,6',7,7',12,12'-octa(4-hexyloxyphenoxy)-9,9'-biperylene-3,4:3',4'-bis(dicarboximide) **22**, 30 g KOH and 4 g glucose, dissolved in 30 mL of ethanol, were reacted as described for the preparation of **2**. Purification was carried out by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub> as eluent. Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>–methanol afforded 119 mg of a green powder containing the title compound and some degradation products, *i.e.* loss of hexyloxyphenoxy side groups. The title compound was finally purified by gel permeation chromatography in chloroform on polystyrene as stationary phase, affording 15 mg (0.3% yield).

$\delta_{\text{H}}$ (500 MHz, CDCl<sub>3</sub>, 30 °C) 8.08 (s, 4H, H-2,5,12,15), 8.06 (s, 4H, H-8, 9, 18, 19), 6.93 (d, 4H, Ph-H-3,3'), 6.92 (d, 4H, Ph-H-3'',3'''), 6.84 (d, 4H, Ph-H-2,2'), 6.82 (d, 4H, Ph-H-2'',2'''), 4.04 [t, 4H, -CH<sub>2</sub> (propyl)], 3.94 [m, 8H, -CH<sub>2</sub> (Ph)], 1.77 [m, 8H, -CH<sub>2</sub> (Ph)], 1.68 [m, 4H, -CH<sub>2</sub> (propyl)], 1.47 [m, 8H, -CH<sub>2</sub> (Ph)], 1.37 [m, 16H, (CH<sub>2</sub>)<sub>2</sub> (Ph)], 0.93 [m, 18H, CH<sub>2</sub> (Ph), CH<sub>2</sub> (propyl)];  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon$ ) 258 (1.27), 271 (1.28), 790 (1.45); *m/z* (FD) 2260.7 (M<sup>+</sup>, 100%), 2066.8 ([M–Ph]<sup>+</sup>, 54%), 1874.8 ([M–2Ph]<sup>+</sup>, 66%), 1681.6 (M–3Ph)<sup>+</sup>, 49%) (calc. M<sup>+</sup>, 2261.1).

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