New Thermotropic Dyes Based on Amino-Substituted Perylendicarboximides

Stefan Becker,[a] Arno Böhm,[b] and Klaus Müllen*[a]

Abstract: We report on an facile multigram synthesis of novel thermotropic dyes. When these dyes are heated they undergo an irreversible change from a photostable primary color to a photostable secondary color. Our concept is based on thermally initiated fragmentation to afford a chromophore with a donor and an acceptor substituent. We used thermally unstable alkoxycarbonyl substituents as masking groups for the strong electron-donating primary amino group attached to a perylenedicarboximide chromophore. On heating the alkoxycarbonylated dyes, the parent primary amino-functionalized dyes are regenerated in almost quantitative yield by elimination of an alkene and carbon dioxide. This process is accompanied by a large bathochromic shift in the absorption spectrum. Variations in the alkoxycarbonyl substitution lead to different reaction temperatures for the color change in this class of materials. The synthetic route used for the amino-functionalized perylene imide dyes involves the palladium-catalyzed amination of bromo-substituted precursors.

Keywords: chromophores · donor–acceptor systems · dyes · perylenes · synthetic methods · thermotropy

Introduction

Thermotropic dyes find applications in the technically important field of thermographical processes. In particular, they can be used for laser marking of polymers with an NIR laser as a heat source for the imprinting of the laser marks.[1] Until now, no academic contribution has been published concerning the development of laser marking systems. Nevertheless, there is a growing industrial interest in laser-marking because this technology eliminates costs and environmental complications associated with inks, masks and other printing or hot-stamping expendables, which are used for printing on polymers.[2]

Hence, within the last few years, much effort has been made towards new suitable materials for laser marking.[2, 3] In spite of this, most of the commercially available systems for this process show only color changes between one real color and black or white.[2, 3] In contrast to this, our concept of thermotropic systems, based on the formation of a donor- and acceptor-substituted chromophore by thermally initiated fragmentation, may provide colors that cover the whole range of the visible spectrum.

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Our idea of designing thermotropic dyes stems from a striking bathochromic color change that occurs if an electron-donating group, for example amino or hydroxy, is attached to a chromophore with an electron-withdrawing substituent.[4] The donor ability of the electron-donating substituent may be drastically diminished by a masking group (MG), such as acyl. Furthermore, if one uses masking groups that may be thermally cleaved, a thermotropic system results which exhibits a bathochromic absorption shift upon heating (Figure 1).

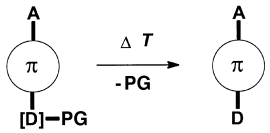

Figure 1. Irreversible thermal cleavage of the protecting groups (PG) affords a dye with a donor (D) group and an acceptor (A) group. This process is accompanied by a color change.

Heat-sensitive masking of NH_2 groups can be achieved by *tert*-butoxy-carbonylation (Boc protection), as the Boc groups decompose upon heating to afford the parent amino compound along with CO_2 and isobutene.[5] This thermal cleavage of Boc groups is part of conventional protective-group chemistry and has recently been used in pigment chemistry after Iqbal and co-workers found it to be a powerful tool for the reversible transformation of insoluble organic pigments into soluble "latent pigments".[6]

We decided to test the usefulness of our concept for thermotropic dyes with a perylene-3,4-dicarboximide, because these are well-known chromophores that combine high extinction coefficients with outstanding light fastness and thermal stability.[7] Moreover, they are well established as colorants for polymers.

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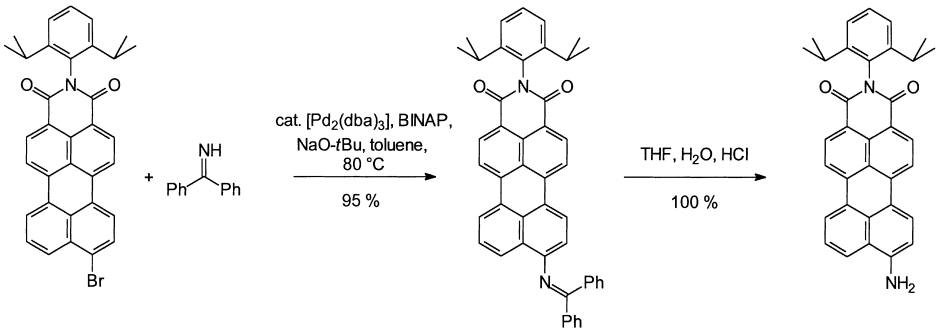
Amino-substituted perylenedicarboximides derivatives have rarely been studied as they are difficult to synthesize. To the best of our knowledge, only two syntheses for these compounds have been published until now: Polborn et al. used a conventional synthetic route to prepare a primary amino-substituted perylendicarboximide, namely the nitration of perylene-3,4-dicarboximide with nitrogen dioxide and reduction of the product with iron powder and HCl.[8] This method has certain disadvantages: the corrosive and very toxic nitrogen dioxide is difficult to handle, the yield of the recommended 9-nitro-perylene is only modest, and a mixture of two different nitro-substituted isomers is obtained by this reaction. The second route to the amino-substituted perylenedicarboximides was developed by Wasielewski et al. who introduced a pyrrolidino-substituent into perylenedicarboximide by nucleophilic displacement of bromine.[9]



1 2 3

Scheme 1. Synthesis of 9-amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (**3**).

Results and Discussion

Synthesis and properties of 9-aminosubstituted perylene-3,4-dicarboximide (2): Palladium-catalyzed *N*-aryl-coupling reactions are reliable synthetic tools, as proven by several articles.[10] Therefore, in our new synthetic approach, the bromo precursor (**1**), which is readily prepared and purified by precipitation in 90% yield, is treated with benzophenone imine as an ammonia equivalent and a palladium catalyst.[11, 12] The 9-(diphenylmethylenimino)-*N*-(2,6-diisopropylphenyl)-perylene-3,4-dicarboximide (**2**) is obtained from 9-bromo-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (**1**), in 95% yield, even with a catalyst loading of BINAP-ligated palladium as low as 0.12 mol% palladium (Scheme 1). The ketimine **2** is cleaved quantitatively by hydrolysis with a catalytic amount of HCl in wet THF to afford the corresponding amino compound 9-amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (**3**).[11]

The absorption band of the amino-substituted dye **3** is broad and almost structureless, as is to be expected for a charge-transfer transition (Figure 2). These properties of **3** are analogous to these of 4-amino-substituted 1,8-naphthalimides (see below, Figure 6).[13]

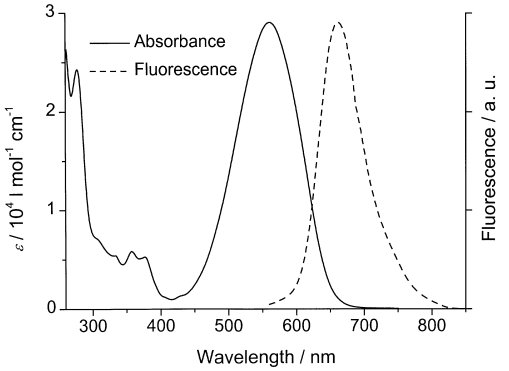


Figure 2. UV/Vis absorption spectrum of 9-amino-*N*-(2,6-diisopropylphenyl)-perylene-3,4-dicarboximide (**3**) in chloroform (10^{-5} M).

The spectra of **3** in solvents of varying polarity indicate a positive solvatochromism of both the absorption and the fluorescence peaks; this is characteristic for a charge-transfer transition (Table 1).

Table 1. Absorbance and fluorescence maxima of 9-amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (**3**) in different solvents.

Solvent	Absorbance λmax [nm]	Fluorescence λ_{max} [nm]
benzene	554	641
chloroform	561	661
acetonitrile	581	700
methanol	605	724

Abstract in German: *Wir berichten über eine einfache Synthese neuer thermotroper Farbstoffe, deren Farbe beim Erhitzen irreversibel von einer photostabilen Primärfarbe zu einer ebenfalls photostabilen Sekundärfarbe umschlägt. Unser Konzept basiert auf der Bildung sowohl donor- als auch akzeptorsubstituierter Chromophore durch thermisch induzierte Fragmentierung. Wir verwenden dazu thermisch instabile Alkoxycarbonylsubstituenten als Maskierungsgruppen für eine primäre Aminogruppe, die als kräftiger Donor an einem Perylendicarboximidchromophor fungiert. Durch Erhitzen der alkoxycarbonylsubstituierten Farbstoffe erhält man die aminosubstituierten Farbstoffe unter quantitativer Eliminierung eines Alkens und von Kohlendioxid. Dieser Prozess wird von einer deutlichen bathochromen Verschiebung im Vis-Absorptionsspektrum begleitet. Variation der Alkoxycarbonylsubstituenten führt zu verschiedenen Temperaturen für den Farbwechsel bei diesen Materialien. Der entscheidende Schritt in der Synthese der aminofunktionalisierten Perylendicarboximidfarbstoffe ist die palladiumkatalysierte Aminierung einer bromsubstituierten Ausgangsverbindung.*

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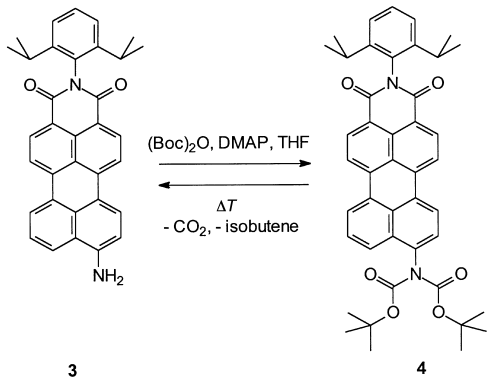
Synthesis and properties of thermotropic dyes: *N*,*N*-Di-(*tert*-butoxycarbonyl)-9-amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (**4**) is obtained in high yield under mild conditions by simply stirring a solution of the amino compound **3** in dry THF with two equivalents of a di-*tert*-butyl dicarbonate at room temperature (Scheme 2).[14] A small amount of 4-dimethylaminopyridine is used as a catalyst for nucleophilic acylation.



3 4

Scheme 2. Synthesis and fragmentation of the thermotropic dye **4**.

As expected, the alkoxycarbonylation is accompanied by an eye-catching hypsochromic shift in the absorption spectrum from blue to orange-red. A chloroform solution of alkoxycarbonylated dye **4** exhibits an absorption maximum at $\lambda =$ 510 nm (Figure 3).

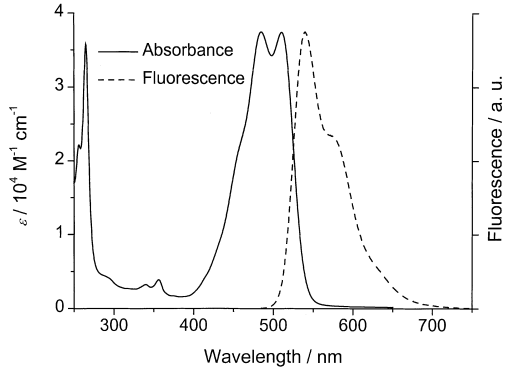
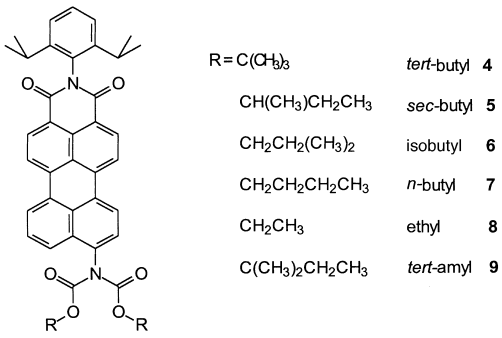


Figure 3. Absorption spectrum of 9-(di-*tert*-butoxycarbonyl)amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (**4**).

Dye **4** undergoes a thermal elimination of the Boc protecting groups at about 200 °C (Figure 4). The weight loss determined by thermogravimetry, TLC, and NMR monitoring of the elimination process prove that the reaction is quantitative, as defined by the limits of these analytical and spectroscopic methods.

Unfortunately, for the use of this compound in polymer laser marking, the fragmentation temperature of the Boc-protected dye **4** is not high enough as the manufacturing of polymers by extrusion and other technical processes is often performed at temperatures over 200 °C. Thus the color change would already occur during the manufacturing process. In order to explore the evident potential of 9-(dialkoxycarbonyl)amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximides as thermotropic dyes, we searched for alternative substitution patterns that would lead to higher temperatures for the fragmentation reaction.

Hence, we synthesized a series of alkoxycarbonylated derivatives (Scheme 3) that bear different alkyl substituents. For this purpose we used other dialkoxydicarbonates instead of di-*tert*-butyl-dicarbonate.



Scheme 3. Thermotropic dyes **4**–**9** which bear different alkyl substituents.

Table 2 gives the halfstep temperature, defined as the temperature at which half of the total weight loss for the fragmentation process occurs. The comparison between the different substituted compounds clearly indicates that the fragmentation temperature depends on the degree of branching of the alkyl groups. The highest fragmentation temperatures were measured for the isobutyl-substituted (**6**) and *n*-butyl-substituted (**7**) compounds. A lower temperature was observed for the *sec*Bu group (**5**), and the lowest for the *tert*-butyl group (**4**). Nevertheless, the length of the alkyl chain did not significantly affect the fragmentation temperature. The values found for the ethyl-substituted dye (**8**) and for the *n*-butyl-substituted dye (**7**)are very similar. Likewise, similarity is found for the *tert*-butyl and the *tert*-amyl-substituted compounds.

Table 2. Halfstep temperature for the fragmentation process of the thermotropic dyes **4**, **5**, **6**, **7**, **8**, and **9**.

No.	Substituent	Reaction temperature [°C]
7	*n*-butyl	340
6	isobutyl	355
5	*sec*-butyl (mixture of isomers)	289
4	*tert*-butyl	213
8	ethyl	340
9	*tert*-amyl	216

Figure 4 illustrates the results of the TGA analysis of these thermotropic dyes. The temperature requirements specified above for a laser marking material are met perfectly by **6**, **7**, and **8**.

The parent amino-substituted dye **3** is thermally very stable (like most perylene dyes) and further thermal treatment ($\leq$400 °C) did not lead to any decomposition process.

The UV/Vis spectra and the fluorescence spectra of the alkoxycarbonylated dyes **4**, **5**, **6**, **7**, **8**, and **9** are all very similar.

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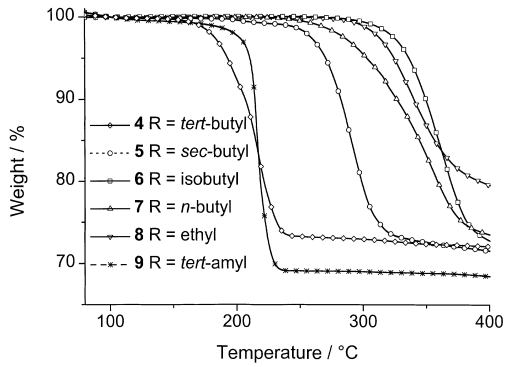

Figure 4. TGA analysis of thermotropic dyes **4**–**9** as a function of the temperature (heating rate: 10 °C min^{-1}).

Depending on the substituents, the maximum of the longest wavelength absorption ranges from $\lambda_{max} = 507$ to 511 nm, the maximum of the fluorescence from $\lambda_{max} = 535$ to 540 nm.

We used spin coating to prepare thin orange-red films of polystyrene that contained 10% of the thermotropic dye **4**. Upon heating these films to 180 °C, the color changed to violet-blue (Figure 5).

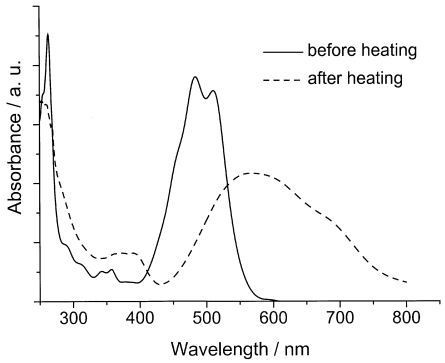

Figure 5. Spectra of polystyrene films that contain 9-(di-*tert*-butoxycarbonyl)amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (**4**) before and after heating (180 °C, 3 min).

Associated with the change in the absorption wavelength upon thermal cleavage of the Boc groups is a change in the intensity and the wavelength of the fluorescence. Therefore, 9-(dialkoxycarbonyl)amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximides can be used as a heat-sensitive fluorescence or absorption probe. Especially when included in a polymer film, this dye promises a high practical potential for thermographical processes and also for applications, such as optical data storage.

Conclusions

We have described a short and efficient method for the synthesis of multigram quantities of 9-amino-substituted perylene-3,4-dicarboximides and of a new class of thermotropic perylenedicarboximide dyes. We are able to control the reaction temperature for the color change of these thermotropic dyes by means of suitable substituents.

Investigation of masked donor–acceptor chromophores, other than perylenedicarboximides, as thermotropic dyes are currently in progress. By the use of different chromophores it should be possible to design thermotropic materials which exhibit any desired color.

Additionally, we believe that the aminoperylenedicarboximide, which is now readily available in multigram quantities, should show similar versatility for different applications as the well-known 4-aminonaphthalene-1,8-dicarboximides. These dicarboximides (Figure 6) are well-established in the literature for their versatility in a wide range of applications. They have received considerable attention on account of their use as antitumor agents,[15] fluorescent cell markers and stains,[16] laser dyes,[17] dyes for synthetic polymers,[18] solar collectors,[19] fluorescent flaw detectors,[20] models for PET processes,[21] electroluminescent devices,[22] and very recently as fluorescent pH sensors.[23]

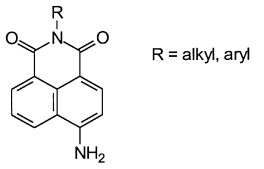

Figure 6. 4-Aminonaphthalene-1,8-dicarboximides.

However, 9-amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide seems an especially promising starting material for further synthetic dye chemistry, for example, the preparation of new azo dyes.

Experimental Section

Materials: Tetrahydrofuran (Fluka) was distilled over sodium/benzophenone. Toluene (Riedel) was distilled over potassium/sodium alloy. Benzophenone imine (Fluka), sodium *tert*-butoxide (Aldrich), di-*tert*-butyl dicarbonate (Fluka), diethyl dicarbonate (Fluka), di-*tert*-amyl dicarbonate (Fluka), 4-dimethylaminopyridine (Aldrich), racemic-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) (Strem), 25% aqueous ammonia (Riedel), tris(dibenzylideneacetone)dipalladium(0) ([$Pd_2(dba)_3$]) (Strem), pyridine (Riedel), benzyltriethylammonium chloride (Aldrich), toluene-4-sulfonyl chloride (Fluka), and chloroform (Riedel, Chromasolv) were used as obtained from commercial sources. Diisobutyl dicarbonate and di-*n*-butyl dicarbonate were prepared by reported procedures.[24] All the reported yields are isolated yields unless otherwise indicated.

Physical and analytical methods: ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AMX250, a Bruker AC300, and a Bruker AMX500 NMR spectrometer. The residual proton resonance of the solvent or the carbon signal of the deuterated solvent was used as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; h, heptet; dd, doublet of doublets; m, multiplet; br, broad. Infrared spectra were obtained on a Nicolet FT-IR320. FD mass spectra were performed with a VG-Instruments ZAB2-SE-FDP. MALDI-TOF mass spectra were measured with a Bruker Reflex II in a THF and dithranol matrix (molar ratio dithranol/sample: 250:1). The mass peaks with the lowest isotopic mass are reported. UV/Vis absorption spectra were recorded on a Perkin–Elmer Lambda 9, fluorescence spectra on a SPEX Fluorolog 2. The elemental analyses were carried out by the Microanalytical Laboratory of the Universität Mainz (Germany). Thermogravimetry was performed on a Mettler TG 50 thermobalance.

9-(Diphenylmethylenimino)-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (2): An oven-dried 2 L Schlenck flask was charged with [$Pd_2(dba)_3$] (73.0 mg, 0.24 mmol) and BINAP (149.5 mg, 0.00375 mmol) and then purged with argon. Toluene (1.5 L), 9-bromo-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (**1**, 10.0 g, 18 mmol), benzophenone imine (6.52 g, 36 mmol), and *t*BuONa (3.46 g, 36 mmol) were added. The mixture was heated to 80 °C with stirring for 15 h, cooled to room

temperature, filtered, and the solvent removed under reduced pressure. To obtain the ketimine in analytical purity the product was chromatographed (silica gel, chloroform). The first colored fraction contained the desired product as a dark violet powder (11.30 g, 95%). M.p. = 230 °C; R_f ($CHCl_3$/silica gel) = 0.54; UV/Vis ($CHCl_3$): λ_{max} (ε) = 535 (40480), 356 (4632), 258 nm (44100 $M^{-1}cm^{-1}$); fluorescence ($CHCl_3$, excitation: 480 nm): λ_{max} (I_{rel}) = 540 (1), 588 nm (0.92); ^1H NMR (500 MHz, $C_2D_2Cl_4$, 140 °C): δ = 8.63 (d, J = 8.0 Hz, 1H), 8.57 (d, J = 8.0 Hz, 1H), 8.50 (d, J = 7.30 Hz, 1H), 8.44 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 8.22 (d, J = 8.5 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.66 (dd, 1H), 7.59 (m, 4H), 7.46 (t, J = 8.0 Hz, 1H), 7.43 (m, 6H), 7.32 (d, J = 8.0 Hz, 2H), 6.72 (d, J = 8.0 Hz, 1H), 2.81 (h, J = 6.7 Hz, 2H, 2CH (*i*Pr)), 1.22 (d, J = 6.7 Hz, 12H, $4CH_3$ (*i*Pr)); ^{13}C NMR (j-modulated spinecho, 125 MHz, $C_2D_2Cl_4$, 140 °C): δ = 170.03 (C=N), 164.13 (C=O), 164.10 (C=O), 151.51 (q), 145.83 (q), 138.19 (q), 137.99 (q), 132.93 (t), 132.14 (t), 132.01 (t), 131.64 (q), 130.79 (q), 130.33 (t), 129.37 (t), 129.23 (q), 128.69 (t), 128.38 (q), 128.17 (q), 127.68 (t), 126.98 (t), 126.74 (q), 125.18 (t), 124.74 (t), 124.45 (q), 124.21 (t), 120.80 (q), 120.11 (t), 119.83 (q), 119.29 (t), 116.56 (t), 29.35(CH (*i*Pr)), 24.35 (CH_3 (*i*Pr)); IR (KBr): $\tilde{\nu}$ = 2961 (m, CH_3), 2926 (w), 2866 (w), 1696 (s, C=O), 1657 (s, C=O), 1630 (m), 1592 (s), 1564 (s), 1497 (m), 1445 (m), 1407 (m), 1356 (s), 1267 (m), 1239 (m), 1187 (w), 1177 (w), 1148 (w), 1125 (w), 1063 (w), 1053 (w), 950 (m), 907 (m), 855 (m), 754 cm^{-1} (w); MS (FD, 8 kV): m/z (%): 660.3 (100) $[M]^+$; anal. calcd for $C_{47}H_{36}N_2O_2$: C 85.43, H 5.49, N 4.24; found C 85.11, H 5.61, N 4.14.

9-Amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (3): Ketimine **2** (10.0 g, 15.1 mmol) was dissolved in THF and 2 M HCl (50 mL) was added. After 45 min of hydrogenolysis, the acid was neutralized with 25% aqueous ammonia and the THF was evaporated. Water (1 L) and aqueous ammonia (50 mL) were added and the blue dye powder collected by filtration. To remove inorganic impurities, the product was suspended twice in hot aqueous ammonia (20%, 1 L) and filtered. Benzophenone and other organic impurities were removed by extraction of the blue powder with petrol ether in a Soxhlett apparatus, since **3** is almost insoluble in this solvent, to yield a dark blue powder (7.30 g, 98%). M.p. = 212 °C; R_f ($CHCl_3$/silica gel) = 0.18; UV/Vis ($CHCl_3$): λ_{max} (ε) = 561 (29070), 377 (5270), 357 (5840), 277 nm (24270 $M^{-1}cm^{-1}$); fluorescence ($CHCl_3$, excitation: 550 nm): λ_{max} = 661 nm; ^1H NMR (500 MHz, $(CD_3)_2SO$), 25 °C): δ = 8.75 (d, J = 7.8 Hz, 1H), 8.59 (d, J = 8.3 Hz, 1H), 8.49 (d, J = 8.4 Hz, 1H), 8.43 (d, J = 8.3 Hz, 1H), 8.38 (d, J = 7.8 Hz, 1H), 8.36 (d, J = 8.3 Hz, 1H), 8.29 (d, J = 8.3 Hz, 1H), 7.64 (dd, 1H), 7.42 (t, J = 7.8 Hz, 1H), 7.31 (d, J = 7.8 Hz, 2H), 7.14 (s, 2H, NH_2), 6.91 (d, J = 8.4 Hz, 1H), 2.62 (h, J = 6.6 Hz, 2H, 2CH (*i*Pr)), 1.08 (d, 12H, J = 6.6 Hz, $4CH_3$ (*i*Pr)); H,H COSY NMR (500 MHz, $(CD_3)_2SO$, 25 °C): coupling of δ = (7.64, 8.75, 8.38), (8.59, 8.43), (8.49, 6.91), (8.29, 8.36), (7.42, 7.31), (2.62, 1.08); NOE NMR (500 MHz, $(CD_3)_2SO$, 25 °C) coupling of δ = (8.75, 8.59), (8.28, 8.49); ^{13}C (j-modulated spinecho NMR, 125 MHz, $(CD_3)_2SO$, 25 °C): δ = 163.41 (C=O), 163.28 (C=O), 150.45 (q), 145.37 (q), 139.66 (q), 138.30 (q), 131.95 (t), 131.73 (q), 131.28 (t), 130.70 (q), 128.94 (t), 128.72 (t), 128.21 (q), 128.12 (q), 126.38 (t), 126.02 (t), 125.87 (q), 124.95 (t), 123.50 (t), 121.74 (q), 119.19 (t), 118.65 (q), 116.66 (t), 115.31 (q), 115.27 (q), 109.87 (t), 28.46 (CH (*i*Pr)), 23.55 (CH_3 (*i*Pr)); IR (KBr): $\tilde{\nu}$ = 348 (m, NH_2), 3237 (w, NH_2), 2959 (m), 2866 (w), 1686 (s, C=O), 1641 (s), 1595 (w), 1559 (m), 1504 (m), 1455 (w), 1352 (s), 1277 (s), 1191 (w), 1174 (w), 1135 (w), 1024 (w), 909,9 (w), 803 (m), 753 (m), 739 cm^{-1} (w); MS (FD, 8 kV): m/z (%): 496.2 (100) $[M]^+$; anal. calcd for $C_{34}H_{28}N_2O_2$: C 82.23, H 5.68, N 5.64; found C 81.89, H 5.68, N 5.54.

General procedure for the preparation of alkoxycarbonylated dyes: In a typical procedure, dialkyl dicarbonate (8 mmol) was added to a stirred solution of 4-dimethylaminopyridine (49 mg, 0.4 mmol), triethylamine (408 mg, 0.8 mmol), and 9-amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (1.00 g, 2.02 mmol) in anhydrous THF (100 mL) under argon. The reaction mixture was stirred at 45 °C for 6 h. During this time, the color of the solution changed from dark blue to orange-red. Thereafter, the volume of the solvent was reduced in vacuo to 20 mL. The product was precipitated by the slow addition of methanol (50 mL). Crystallization was completed by cooling the mixture in a refrigerator. Further purification by column chromatography (silica, chloroform) is optional; however, it is usually not necessary.

9-(Di-*tert*-butoxycarbonyl)amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (4): According to the general procedure, the amino-substituted dye **3** (1.00 g, 2.02 mmol), 4-dimethylaminopyridine (49 mg, 0.40 mmol), triethylamine (408 mg, 0.80 mmol), and di-*tert*-butyl dicarbonate (1.75 g, 8.0 mmol) were allowed to react in anhydrous THF to yield an orange powder (1.07 g, 76%). M.p. > 180 °C (decomp.); R_f ($CHCl_3$/silica gel) = 0.21; UV/Vis ($CHCl_3$): λ_{max} (ε) = 510 (37430), 485 (37500), 356 (3910), 346 (3257), 265 nm (35600 $M^{-1}cm^{-1}$); fluorescence ($CHCl_3$, excitation: 480 nm): λ_{max} = 540 nm; ^1H NMR (500 MHz, $C_2D_2Cl_4$, 25 °C): δ = 8.54 (m, 2H), 8.41 (m, 4H), 7.81 (d, J = 8.5 Hz, 1H), 7.65 (dd, 1H), 7.40 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 2.64 (h, J = 6.7 Hz, 2H, 2CH (*i*Pr)), 1.29 (s, 18H, $6CH_3$ (*t*Bu)), 1.08 (d, J = 6.7 Hz, 12H, $4CH_3$ (*i*Pr)); ^{13}C NMR (j-modulated spinecho; 125 MHz, $C_2D_2Cl_4$, 25 °C): δ = 164.03 (C=O), 151,69 (C=O), 145,86 (q), 138.53 (q), 137.61 (q), 137.31 (q), 132.26 (t), 132.23 (t), 131.84 (q), 131.44 (q), 130.66 (q), 129.82 (q), 129.45 (t), 129.38 (q), 128.90 (q), 128.14 (t), 127.41 (t), 127.05 (q), 125.26 (t), 124.33 (t), 124.23 (t), 123.97 (t), 121.46 (q), 121.43 (q), 121.00 (t), 121.06 (t), 83.60 (q), 29.38 (CH (*i*Pr)), 28.13 (CH_3 (*t*Bu)), 24.33 (CH_3 (*i*Pr)); IR (KBr): $\tilde{\nu}$ = 2966 (m), 2931 (m), 2870 (w), 1788 (m), 1750(s), 1703 (s), 1665 (s), 1592 (s), 1577 (s), 1457 (m), 1359 (s), 1293 (m), 1245 (m), 1153 (m), 1115 (m), 1030 (w), 937 (w), 847 (m), 811 (m), 753 cm^{-1} (m); MS (MALDI-TOF): m/z: 696.3 $[M]^+$; anal. calcd for $C_{44}H_{44}N_2O_6$: C 75.84, H 6.36, N 4.02; found: C 75.58, H 6.38, N 3.93.

Di-*sec*-butyl dicarbonate: Sodium hydride (60%, 21 g, 0.55 mol) was slowly added to a solution of racemic 2-butanol (37.06 g, 0.50 mol) in anhydrous toluene (400 mL) cooled to 0 °C, under an argon atmosphere. Then dry CO_2 (26.4 g, 0.60 mol) was introduced in such a manner that the temperature of the reaction mixture remained between 5–10 °C. The suspension which formed was heated to 15 °C and benzyltriethylammonium chloride (1.59 g, 7 mmol), pyridine (1.34 g, 17 mmol), and *p*-toluenesulfonyl chloride (40 g, 0.21 mol) were added. After stirring for 15 h at room temperature, the reaction mixture was cooled to 5 °C and aqueous sulfuric acid (5%, 180 mL) was added dropwise in such a manner that the temperature did not exceed 10 °C. The organic phase was separated, washed (5% aqueous sodium hydrogen carbonate solution (500 mL) and twice with water (500 mL)), and then dried over sodium sulfate. The toluene was removed under reduced pressure and the residue was fractionated on a 15 cm Vigreux column to yield a colorless liquid (40.2 g, 74%). B.p. 63 °C, 1×10^{-2} Torr); ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 4.68 (m, 2H), 1.54 (m, 4H), 1.22 (d, 6H, J = 6.3 Hz), 0.84 (t, 6H J = 7.5 Hz); ^{13}C NMR (inverse gated, 75 MHz, 100 mg sample, $[Cr(acac)_3]$ (70 mg), $CDCl_3$ (1 mL), 25 °C): δ = 147.98 (2C, C=O), 79.20 (2C, CH), 28.24 (2C, CH_3), 18.82 (2C, CH_2), 9.25 (2C, CH_3); IR (neat): $\tilde{\nu}$ = 2978 (m), 2941 (m), 2883 (w), 1819 (s, OC=O), 1759 (s), 1458 (w), 1383 (m), 1293 (m), 1178 (s), 1126 (m), 1079 (s), 1023 (w), 992 (w), 965 (m), 871 (m), 772 (w), 655 cm^{-1} (w); anal. calcd for $C_{10}H_{18}O_5$: C 55.03, H 8.31; found C 55.06, H 8.30.

9-(Di-*sec*-butoxycarbonyl)amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (5) (mixture of stereoisomers): According to the general procedure, the amino-substituted dye **3** (1.00 g, 2.02 mmol), 4-dimethylaminopyridine (49 mg, 0.4 mmol), triethylamine (408 mg, 0.8 mmol), and di-*sec*-butyl dicarbonate (1.75 g, 8 mmol) were allowed to react in anhydrous THF to yield an orange powder (1.08 g, 77%). M.p. = 230 °C (decomp.); R_f ($CHCl_3$/silica gel) = 0.14; UV/Vis ($CHCl_3$): λ_{max} (ε) = 509 (36780), 483 (36500), 356 (3737), 340 (3667), 265 nm (34990 $M^{-1}cm^{-1}$); fluorescence ($CHCl_3$, excitation: 480 nm): λ_{max} = 537 nm; ^1H NMR (500 MHz, $C_2D_2Cl_4$, 25 °C): δ = 8.55 (d, J = 8.0 Hz, 1H), 8.54 (d, J = 8.0 Hz, 1H), 8.40 (m, 4H), 7.80 (d, J = 8.5 Hz, 1H), 7.64 (dd, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 4.78 (m, 2H, 2CH *sec*Bu), 2.65 (h, J = 6.7 Hz, 2H, 2CH (*i*Pr)), 1.38 (m, 2H, CH_2 *sec*Bu), 1.31 (m, 2H, CH_2 *sec*Bu), 1.13 (d, J = 6.1 Hz, 3H, CH_3 *sec*Bu), 1.09 (d, J = 6.7 Hz, 12H, $4CH_3$ (*i*Pr)), 1.04 (d, J = 6.1 Hz, 3H, CH_3 (*i*Pr)), 0.70 (t, J = 6.7 Hz, 3H, CH_3 *sec*Bu), 0.52 (t, J = 6.7 Hz, 3H, CH_3 *sec*Bu); ^{13}C NMR (j-modulated spinecho, 125 MHz, $C_2D_2Cl_4$, 25 °C): δ = 163.91 (C=O), 152.5 (C=O), 145.75 (q), 137.53 (q), 137.40 (q), 137.05 (q), 132.17 (t), 132.15 (t), 132.10 (t), 131.76 (q), 131.31 (q), 130.52 (q), 129.76 (q), 129.67 (q), 129.38 (t), 128.85 (q), 128.22 (t), 127.41 (t), 126.93 (q), 124.33 (t), 124.15 (t), 123.77 (t), 121.46 (q), 121.37 (q), 121.05 (t), 120.98 (t), 76.29 (CH *sec*Bu), 76.23 (CH *sec*Bu), 29.29 (CH (*i*Pr)), 28.65 (CH_2 *sec*Bu), 28.60 (CH_2 *sec*Bu), 24.23 (CH_3 (*i*Pr)), 19.48 (CH_3 *sec*Bu), 19.32 (CH_3 *sec*Bu), 9.65 (CH_3 *sec*Bu), 9.44 (CH_3 *sec*Bu); IR: $\tilde{\nu}$ = 2962 (m), 2931 (m), 2870 (w), 1780 (m), 1754 (m), 1702 (s), 1665 (s), 1593 (m), 1577 (m), 1458 (w), 1357 (s), 1291 (m), 1246 (m), 1199 (s), 1102 (m), 812 (m), 754 cm^{-1} (w); MS (MALDI-TOF): m/z: 696.3 $[M]^+$; anal. calcd for $C_{44}H_{44}N_2O_6$: C 75.84, H 6.36, N 4.02; found C 75.49, H 6.38, N 3.96.

9-(Diisobutoxycarbonyl)amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (6): According to the general procedure, the amino-substituted dye **3** (1.00 g, 2.02 mmol), 4-dimethylaminopyridine (49 mg,

0947-6539/00/0621-3988 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 21

0.4 mmol), triethylamine (408 mg, 0.8 mmol), and diisobutyl dicarbonate (1.75 g, 8 mmol) were allowed to react in anhydrous THF to yield an orange powder (1.10 g, 78 %). M.p. = 215 °C; R_f ($CHCl_3$/silica gel) = 0.18; UV/Vis ($CHCl_3$): λ_{max} (ε) = 508 (38490), 481 (37700), 356 (3577), 340 (2855), 264 nm (37530 $M^{-1}cm^{-1}$); fluorescence ($CHCl_3$, excitation: 480 nm): λ_{max} = 535 nm; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 25 °C): δ = 8.55 (d, J = 8.0 Hz, 1H), 8.42 (m, 4H), 7.81 (d, J = 8.5 Hz, 1H), 7.65 (dd, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 3.86 (d, J = 6.7 Hz, 4H, 2 CH_2 (*i*Bu)), 2.63 (h, 6.7 Hz, 2H, 2 CH (*i*Pr)), 1.65 (m, 2H, 2 CH (*i*Bu)), 1.08 (d, J = 6.7 Hz, 12H, 4 CH_3 (*i*Bu)), 0.57 (d, J = 6.7 Hz, 12H, 4 CH_3 (*i*Pr)); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 25 °C): δ = 163.99 (C=O), 152.73 (C=O), 145.80 (q), 137.47 (q), 137.25 (q), 137.08 (q), 132.29 (t), 132.22 (t), 131.73 (q), 131.35 (q), 130.61 (q), 129.91 (q), 129.87 (q), 129.49 (t), 128.91 (q), 128.46 (t), 127.43 (t), 127.05 (q), 124.97 (t), 124.49 (t), 124.26 (t), 123.78 (t), 121.61 (q), 121.49 (q), 121.23 (t), 121.17 (t), 73.56 (CH_2 (*i*Bu)), 29.37 (CH (*i*Pr)), 27.80 (CH (*i*Bu)), 24.35 (CH_3 (*i*Pr)), 19.0 (CH_3 (*i*Bu)); IR (KBr): $\tilde{\nu}$ = 2962 (m), 2932 (s), 2871 (s), 1797 (m), 1757 (m), 1703 (s), 1664 (s), 1592 (s), 1578 (m), 1469 (m), 1359 (s), 1291 (m), 1245 (s), 1105 (m), 1032 (w), 810 (m), 752 cm^{-1} (m); MS (MALDI-TOF): m/z: 696.3 $[M]^+$; anal. calcd for $C_{44}H_{44}N_2O_6$: C 75.84, H 6.36, N 4.02; found C 75.58, H 6.37, N 3.94.

9-(Di-*n*-butoxycarbonyl)amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (7): According to the general procedure, the amino-substituted dye **3** (1.00 g, 2.02 mmol), 4-dimethylaminopyridine (49 mg, 0.4 mmol), triethylamine (408 mg, 0.8 mmol), and di-*n*-butyl dicarbonate (1.75 g, 8 mmol) were allowed to react in anhydrous THF to yield an orange powder (1.13 g, 80 %). M.p. = 174 °C; R_f ($CHCl_3$/silica gel) = 0.15; UV/Vis ($CHCl_3$): λ_{max} (ε) = 508 (37180), 481 (37700), 356 (3448), 340 (2744), 264 nm (36060 $M^{-1}cm^{-1}$); fluorescence ($CHCl_3$, excitation: 480 nm): λ_{max} = 535 nm; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 25 °C): δ = 8.54 (d, J = 8.0 Hz, 1H), 8.53 (d, J = 8.0 Hz, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.39 (m, 3H), 7.79 (d, J = 8.0 Hz, 1H), 7.64 (dd, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 4.10 (t, J = 6.4 Hz, 4H, 2 CH_2 (Bu)), 2.65 (h, J = 6.7 Hz, 2H, 2 CH (*i*Pr)), 1.41 (m, 4H, 2 CH_2 (Bu)), 1.09 (d, J = 6.7 Hz, 12H, 4 CH_3 (*i*Pr)), 1.03 (m, 4H, 2 CH_2 (Bu)), 0.67 (t, 6H, J = 7.3 Hz, 2 CH_3 (Bu)); ^{13}C NMR (j-modulated spinecho, 125 MHz, $C_2D_2Cl_4$, 25 °C): δ = 164.00 (C=O), 152.96 (C=O), 145.82 (q), 137.40 (q), 137.27 (q), 137.03 (q), 132.27 (t), 132.20 (t), 131.76 (q), 131.37 (q), 130.59 (q), 129.94 (q), 129.91 (q), 129.48 (t), 128.99 (q), 128.42 (t), 127.56 (t), 127.00 (q), 124.91 (t), 124.40 (t), 124.27 (t), 123.86 (t), 121.61 (q), 121.50 (q), 121.18 (t), 121.12 (t), 67.61 (CH_2 (*n*Bu)), 30.58 (CH_2 (*n*Bu)), 29.39 (CH (*i*Pr)), 24.35 (CH_3 (*i*Pr)), 19.08 (CH_2 (*n*Bu)), 13.80 (CH_3 (*n*Bu)); IR (KBr): $\tilde{\nu}$ = 2961 (m), 2832 (m), 2871 (w), 1795 (m), 1758 (m), 1703 (s), 1664 (s), 1592 (m), 1578 (m), 1460 (s), 1369 (s), 1292 (m), 1247 (s), 1183 (m), 816 (m), 752 cm^{-1} (m); MS (MALDI-TOF): m/z: 696.3 $[M]^+$; anal. calcd for $C_{44}H_{44}N_2O_6$: C 75.84, H 6.36, N 4.02; found C 75.75, H 6.40, N 3.99.

9-(Diethoxycarbonyl)amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (8): According to the general procedure, the amino-substituted dye **3** (1.00 g, 2.02 mmol), 4-dimethylaminopyridine (49 mg, 0.4 mmol), triethylamine (408 mg, 0.8 mmol), and diethyl dicarbonate (1.30 g, 8 mmol) were allowed to react in anhydrous THF to yield an orange powder (1.05 g, 81 %). M.p. > 277 °C (decomp.); R_f ($CHCl_3$/silica gel) = 0.16; UV/Vis ($CHCl_3$): λ_{max} (ε) = 507 (37620), 481 (36780), 356 (3650), 340 (2950), 255 nm (21870 $M^{-1}cm^{-1}$); fluorescence ($CHCl_3$, excitation: 480 nm): λ_{max} = 535 nm; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 25 °C): δ = 8.52 (d, J = 8.0 Hz, 1H) 8.51 (d, J = 8.0 Hz, 1H), 8.39 (m, 3H), 8.35 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.5 Hz, 1H), 7.64 (dd, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 4.16 (q, J = 6.9 Hz, 4H, 2 CH_2 (Et)), 2.65 (h, J = 6.7 Hz, 2H, 2 CH (*i*Pr)), 1.09 (m, J not resolved because of overlap, 18H, 4 CH_3 (*i*Pr), 2 CH_3 (Et)); ^{13}C NMR (j-modulated spinecho; 125 MHz, $C_2D_2Cl_4$, 25 °C): δ = 163.91 (C=O), 152.89 (C=O), 145.70 (q), 137.25 (q), 137.09 (q), 136.88 (q), 132.17 (t), 132.10 (t), 131.62 (q), 131.26 (q), 130.45 (q), 129.86 (q), 129.82 (q), 129.40 (t), 128.92 (q), 128.35 (t), 127.55 (t), 126.85 (q), 124.80 (t), 124.32 (t), 124.18 (t), 123.84 (t), 121.47 (q), 121.35 (q), 121.05 (t), 120.99 (t), 63.90 (CH_2 (Et)), 29.28 (CH (*i*Pr)), 24.27 (CH_3 (*i*Pr)), 14.36 (CH_3 (Et)); IR (KBr): $\tilde{\nu}$ = 2963 (m), 2930 (w), 2870 (w), 1794 (w), 1759 (m), 1702 (s), 1664 (s), 1592 (s), 1578 (m), 1359 (s), 1245 (s), 1098 (m), 1035 (w), 817 (m), 753 cm^{-1} (m); MS (MALDI-TOF): m/z: 640.3 $[M]^+$; anal. calcd for $C_{40}H_{36}N_2O_6$: C 74.98, H 5.66, N 4.37; found C 74.82, H 5.64, N 4.23.

9-(Di-*tert*-amoxycarbonyl)amino-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (9): According to the general procedure, the amino-substituted dye **3** (1.00 g, 2.02 mmol), 4-dimethylaminopyridine (49 mg, 0.4 mmol), triethylamine (408 mg, 0.8 mmol), and di-*tert*-amyl dicarbonate (1.97 g, 8 mmol) were allowed to react in anhydrous THF to yield an orange powder (1.08 g, 74 %). M.p. > 180 °C (decomp.); R_f ($CHCl_3$/silica gel) = 0.17; UV/Vis ($CHCl_3$): λ_{max} (ε) = 511 (36680), 485 (36770), 356 (3681), 340 (3041), 265 nm (34100 $M^{-1}cm^{-1}$); fluorescence ($CHCl_3$, excitation: 480 nm): λ_{max} = 540 nm; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 25 °C): δ = 8.64 (m, 2H), 8.50 (m, 3H), 8.48 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.72 (dd, 1H), 7.47 (m, 2H), 7.32 (d, J = 8.0 Hz, 1H), 2.71 (h, J = 6.7 Hz, 2H, 2 CH (*i*Pr)), 1.52 (q, J = 7.3 Hz, 2H, CH_2 *tert*-amyl), 1.47 (q, J = 7.3 Hz, 2H, CH_2 (*tert*-amyl)), 1.38 (s, 6H, 2 CH_3 (*tert*-amyl)), 1.32 (s, 6H, 2 CH_3 (*tert*-amyl)), 1.15 (d, J = 6.7, 12H, 4 CH_3 (*i*Pr)), 0.49 (t, J = 7.3 2, 6H, CH_3 (*tert*-amyl)); ^{13}C NMR (j-modulated spinecho, 125 MHz, $C_2D_2Cl_4$, 25 °C,): δ = 164.03 (C=O), 151.28 (C=O), 145.86 (q), 138.56 (q), 137.66 (q), 137.34 (q), 132.26 (t), 132.24 (t), 131.86 (q), 131.43 (q), 130.70 (q), 129.75 (q), 129.46 (t), 129.31 (q), 128.86 (q), 128.15 (t), 127.18 (t), 127.10 (q), 125.31 (t), 124.40 (t), 124.24 (t), 123.90 (t), 121.49 (q), 121.45 (q), 121.05 (t), 121.00 (t), 85.91 (q (*tert*-amyl)), 34.13 (CH_2 (*tert*-amyl)), 29.37 (CH (*i*Pr)), 25.58 (CH_3 (*tert*-amyl)), 25.29 (CH_3 (*tert*-amyl)), 24.32 (CH_3 (*i*Pr)), 8.10 (CH_3 (*tert*-amyl)); IR (KBr): $\tilde{\nu}$ = 2966 (m), 2930 (w), 2870 (w), 1784 (s), 1753 (m), 1703 (s), 1687 (s), 1592 (m), 1577 (m), 1468 (w), 1358 (s), 1292 (m), 1245 (m), 1153 (m), 1112 (m), 842 (m), 812 (m), 754.5 cm^{-1} (w); MS (MALDI-TOF): m/z: 724.4 $[M]^+$; $C_{46}H_{48}N_2O_6$:. C76.22, H 6.67, N 3.86; found C 75.89, H 6.69, N 3.80.

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