A Bichromophore Based on Perylene and Terrylene for Energy Transfer Studies at the Single-Molecule Level

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Abstract: A functionalized dialkylperylene and a modified *t*errylene*t*etra*c*arbox*dii*mide (TTCDI) were joined together by a hexanediyl spacer. The resulting bichromophoric molecule **4** is a suitable model system for donor–acceptor energy transfer studies at the single-molecule level. With its absorption and fluorescence maximum at shorter wavelengths ($\lambda_{max} = 450$ nm, $\lambda_{fl} = 458$ nm) the dialkylperylene acts as the donor, while the TTCDI with $\lambda_{max} = 665$ nm and $\lambda_{fl} = 705$ nm is the acceptor molecule. The synthetic route to the new bichromophoric molecule and its optical properties (UV/Vis, fluorescence spectroscopy) are presented herein. Energy transfer from the perlyene to the terrylene moiety was confirmed by conventional ensemble fluorescence excitation and emission spectroscopy. Single bichromophores **4** embedded in polyvinylbutyral were imaged with a scanning confocal optical microscope at room temperature by selectively exciting the perylene chromophore and detecting the terrylene emission.

Keywords: bichromophores · donor–acceptor systems · dyes · fluorescence spectroscopy · UV/Vis spectroscopy

Introduction

The transfer of electronic excitation energy from a donor to an acceptor chromophore by the Förster mechanism is a well-known technique used to measure distances in the range of nanometers.[1, 2] Recent studies have shown that this process can also be observed at the level of a single donor–acceptor pair thereby entering the area of single-molecule spectroscopy.[3, 4] The goal of the present work was to design and synthesize a bichromophore in which the donor and acceptor parts are covalently linked; this should serve as a versatile model system for single-molecule energy transfer.

In a typical energy transfer couple the excited donor molecule besides deexcitation by fluorescence emission can transfer its energy to a nearby acceptor molecule. The acceptor then releases the energy through fluorescence radiation and nonradiative internal conversion. Depending on the donor–acceptor distance, the electronic energy transfer takes place through dipole–dipole or exchange interactions.[5]

Over the past few years a number of microscopic and frequency selective techniques have been employed to isolate and detect the fluorescence of a single chromophore in the condensed phase.[6, 7] While the extension of single-molecule fluorescence imaging at room temperature to single-pair energy transfer studies is straightforward, low-temperature frequency-selective single-molecule detection is more demanding with respect to the properties of the molecular system to be investigated. As the bichromophore described in this paper was designed for general purpose single-molecule studies without restriction to specific experimental conditions, the system selected had to strictly combine the following properties, such as a strong absorption, a fairly high fluorescence quantum yield, a high chemical and photochemical stability, a low photobleaching efficiency at room temperature, a weak electron–phonon coupling at low temperature, and a negligible population of bottleneck states.[8] Especially the electron–phonon coupling part, which is imperative for the observation of strong and sharp zero-phonon lines at low temperatures, dramatically limits the number of suitable donor–acceptor combinations. After careful consideration we decided to focus on a perylene–terrylene pair where both chromophores meet the above requirements, and the spectral characteristics would allow energy transfer. Because it proved to be very difficult to connect the pure unsubstituted aromatic

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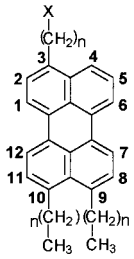
hydrocarbons by a spacer molecule, extensive synthetic efforts were necessary to first appropriately modify and then chemically link the modified chromophores.

The bichromophore was finally assembled from a dialkylperylene **1** (X = -CN, -COOH, -OH; R = 4-*tert*-butylphenoxy) and the recently synthesized terrylenetetracarboxdiimide (TTCDI) **2** with an alkanediyl spacer.[9, 10] Both chromophores proved to be excellently suitable for single-molecule spectroscopy under various conditions.[8] As the TTCDI absorption



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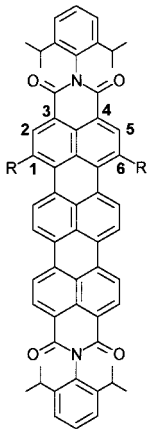

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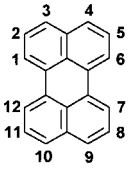

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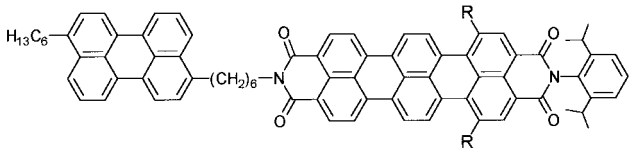
has virtually no overlap with the perlyene **1** absorption, the latter can be excited selectively in the bichromophore. Besides the synthetic route to the novel bichromphoric molecule, we also present the results of absorption and fluorescence spectroscopy that verify the occurrence of efficient energy transfer. Additionally, the first successful attempts to image the energy transfer of a single bichromophore will be discussed.

Results and Discussion

Synthesis of the bichromophore: The synthesis of bichromophore **4** (R = 4-*tert*-butylphenoxy) was based on the recent discovery of a new way to functionalize perylene (**3**) and to link this functionalized dialkylperylene **1** to terrylenetetracarboxdiimide (TTCDI) **2** (R = 4-*tert*-butylphenoxy).[9, 10] In particular, the bichromophore which contains a hexanediyl chain as



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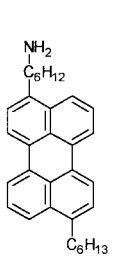
a spacer was obtained by connecting three key molecules, namely 3-(6-aminohexyl)-9(10)-hexylperylene (**5**), *N*-(2,6-diisopropylphenyl)-1,6-di(4-*tert*-butylphenoxy)-9-(tributyltin)-perylene-4,5-dicarboximide (**6**; R = 4-*tert*-butylphenoxy), and the commercially available 1-bromonaphthalene-4,5-dicarboximide (**7**).



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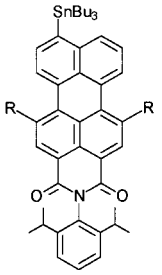

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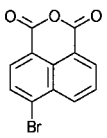

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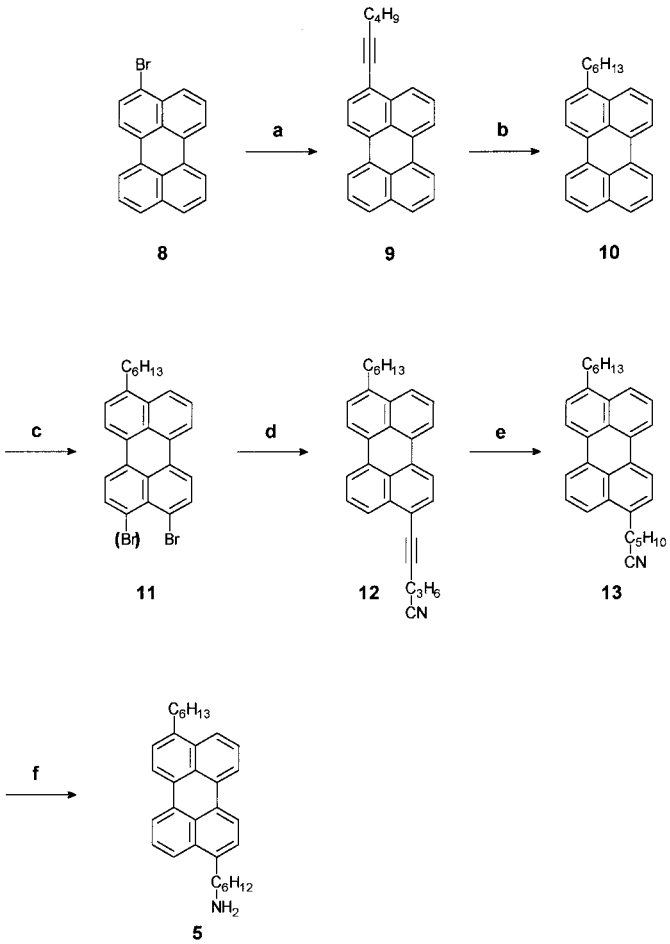
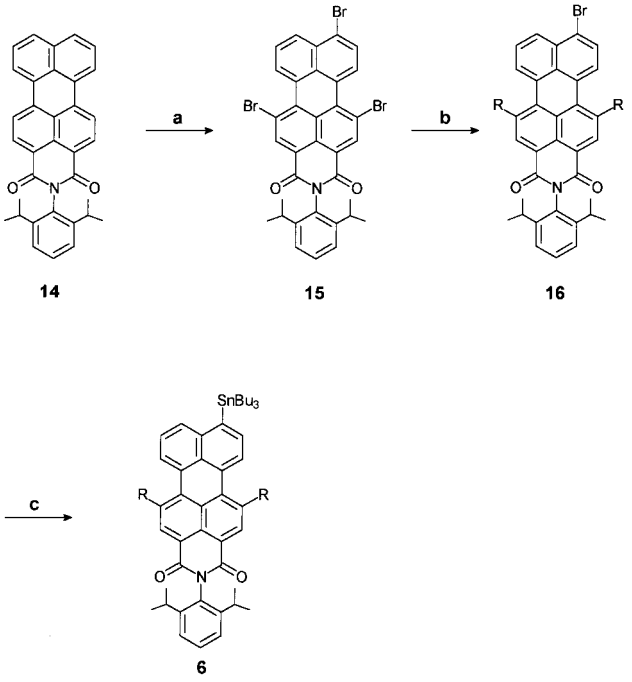
As the starting material for the synthesis of **5** we used 3-bromoperylene (**8**), which was isolated in 92% yield after a NBS (*N*-bromosuccinimide) bromination of perylene (**3**) in DMF.[11, 12] We then treated the bromoperylene **8** with 1-hexyne under Hagihara coupling conditions followed by a catalytic hydrogenation of the triple bond of 1-hexynylperylene (**9**), which gave 3-hexylperylene (**10**) in an overall yield of 100% (Scheme 1). Further bromination of **10** produced a 1:1 isomeric mixture of 3-bromo-9-hexyl- and 3-bromo-10-hexyl-substituted perylene **11**, which could not be separated by chromatographic methods. In earlier experiments, however, a



Scheme 1. Synthesis of aminoperylene **5**: a) 1-hexyne, piperidine/THF, CuI, $[Pd(PPh_3)_4]$, 80 °C, 14 h, 98%; b) H_2, THF, Pd/C (10%), room temperature, 2–3 h, 100%; c) NBS, DMF, room temperature, 24 h, 80%; d) 5-cyano-1-pentynyl, piperidine/THF, CuI, $[Pd(PPh_3)_4]$, 80 °C, 14 h, 98%; e) H_2, THF, Pd/C (10%), room temperature, 2–3 h, 100%; f) $B_2H_6 \cdot$ THF, THF, reflux, 5 h, 80%.

mixture of these isomers showed no significant differences in solubility, absorption, and reactivity compared with the pure 3,10-substituted isomers.[9] Although 3,9- and 3,10-isomers are present, only the 3,9-isomers are shown in the following schemes for the sake of simplicity. This refers to all schemes in this paper. The hexylmonobromide **11** was again subjected to a Hagihara coupling with 5-hexynonitrile followed by a catalytic hydrogenation of the alkyne **12** to give 3-(5-pentylnitrile)-9(10)hexylperylene (**13**) in almost quantitative yield. In the last step towards the generation of a monofunctionalized dialkylperylene, the nitrile **13** was reduced with a $B_2H_6 \cdot THF$ complex quantitatively to yield 3-(6-aminohexyl)-9(10)-hexylperylene (**5**).

The second key molecule was the tributyltin perylene derivative **6**. This compound was produced in a three-step synthesis starting from the perylenedicarboximide **14**, which was supplied by BASF AG. The first reaction step was a threefold bromination of the perylene core of **14**, which afforded the perylene-1,6,9-tribromodicarboximide **15** in 96% yield (Scheme 2).[13] Note that compound **15** is not an isomeric

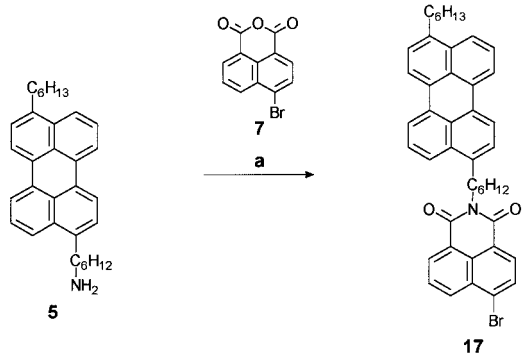


Scheme 2. Synthesis of tin compound **6** (R = 4-*tert*-butylphenoxy): a) Br_2, $CHCl_3$, reflux, 6 h, 96%; b) 4-*tert*-butylphenol, K_2CO_3, NMP, 120 °C, 6 h, 32%; c) hexabutylditin, $[Pd(PPh_3)_4]$, toluene, reflux, 2 d, 73%.

mixture. As a result of the different reactivities of the three bromine atoms in **15**, it was possible to synthesize the diphenoxyperylene **16** by selective substitution of the two bromine atoms in the bay-region of the perylene **15**. The red diphenoxy-substituted compound **16** was isolated in 32% yield.[13]

It is very important to note that the etherfication took place without affecting the bromine atom in the 9-position, as this should be converted into the stannane **6** in a subsequent step. The two *tert*-butyl-phenoxy side groups were introduced to ensure that the bichromophore **4** and the other precursors would be soluble for the various chromatographic purifications. The stannylation of the monobrominated compound **16** was the crucial reaction step in the overall synthesis of the bichromophoric system **4**. Usually aromatic stannyl compounds are generated by metalation of the aromatic halide and subsequent nucleophilic attack on the trialkylstannyl chloride.[14, 15] In this particular case it was obvious that we could not use any metalation reactions in the presence of the highly reactive carboxy groups. As an alternative to this type of stannylation, we focused on a palladium-catalyzed stannylation that was first reported by A. Pidcock and already successfully utilized by us on perylene systems.[10, 16] In this stannylation reaction, the aryl bromide or iodide is directly converted to the aryl tributylstannane with hexabutylditin in the presence of palladium(0) and palladium(II) catalysts. We subjected our monobromoperylene **16** to these reaction conditions and were able to obtain the stannyl compound **6** after chromatography in 73% yield.

For the final assembly of the bichromophore, the aminoperylene **5** was first connected in an imidization reaction with the commercially available 4-bromo-1,8-naphthyldicarboxanhydride (**7**) (Scheme 3). The coupling product **17** offered the



Scheme 3. Synthesis of **17**: a) NMP, glacial acetic acid, 85 °C, 6 h, 80%.

opportunity to link the dialkyperylene **5** to the functionalized perylenedicarboximide **6**, which could then be converted into the terrylentetracarboxdimide (TTCDI) core.

The molecules **6** and **17** were linked by means of a Stille coupling to give the red coupling product **18** in 45% yield after chromatography (Scheme 4). The last step in this synthesis was the generation of the terrylene core of the bichromophoric molecule **4** by oxidative cyclization of the naphthalene and the perylene dicarboximide of **18** in a KOH melt.[17] This reaction was already successfully applied for the synthesis of several quaterrylene and terrylenediimides.[13] During the cyclization the color of the mixture turned from bright red to black. After chromatographic purification on preparative silica-gel glass plates, target molecule **4** was obtained in 40% yield as a deep green, almost black amorphous powder. The bichromophore **4** shows a good solubility in most organic solvents, while giving a strong green color as the spectral sum of the yellow perylene and the blue terrylenediimide building blocks. This color was a first qualitative proof for the existence of bichromophoric molecule **4**.

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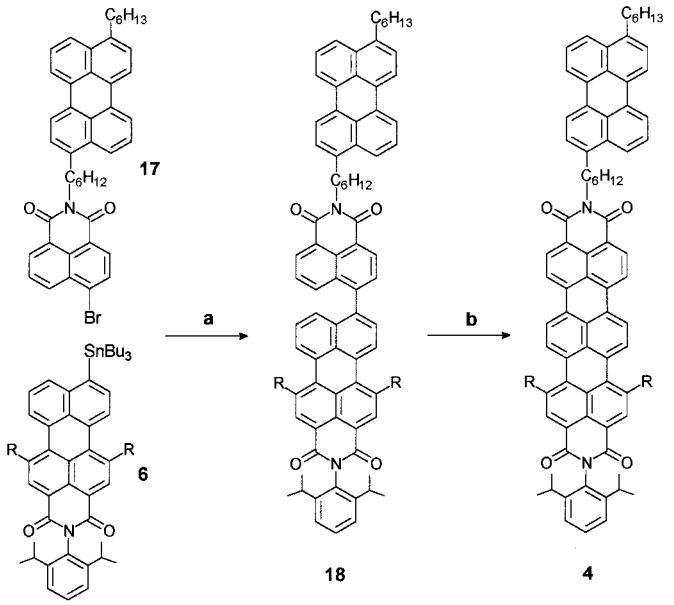

Scheme 4. Synthesis of bichromophore **4** (R = 4-*tert*-butylphenoxy): a) [$Pd(PPh_3)_4$], toluene, reflux, 4 d, 45%; b) KOH/glucose, EtOH, 60–90 °C, 8 h, 40%.

All compounds were characterized by elemental analysis, FD-mass spectrometry, NMR, IR, and UV/Vis spectroscopy. Figure 1 shows the field desorption mass spectrum of the target compound **4**. Besides the molecular $[M]^+$ signal at 1389.3 g mol^{-1} the signal of the two times cluster $[M_2]^+$ with 2778.6 g mol^{-1} and the double charged species of **4** with half the molecular mass at 694.6 g mol^{-1} could be detected.

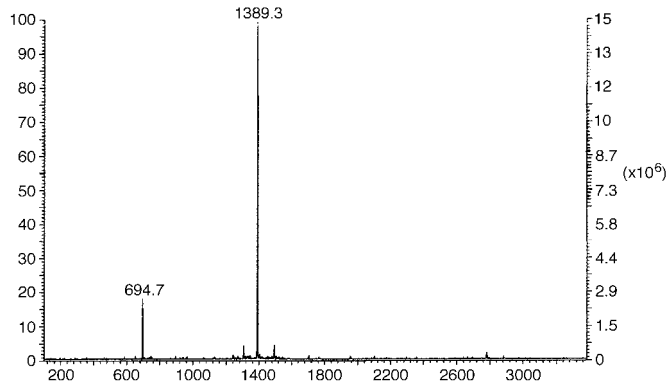

Figure 1. Field desorption mass spectrum of the bichromophore **4**.

Optical spectroscopy of the bichromophore: The most vivid method to confirm the existence of the molecules **17**, **18**, and **4** is based on UV/Vis absorption spectroscopy because each molecule we used to build the bichromophore **4** exhibits its own specific UV/Vis pattern. Compound **17**, which consists of a 3,9(10)-dialkylperylene and an alkyl-substituted naphthalenedicarboximide, shows the absorption bands of both molecules. While the naphthalene derivative of **17** exhibits its longest absorption wavelength between 320 nm and 360 nm, the perylene component of **17** shows the typical fine structure in the range of 390 nm to 460 nm (Figure 2). An analogous behavior can be observed in the UV/Vis spectra of **18** and the

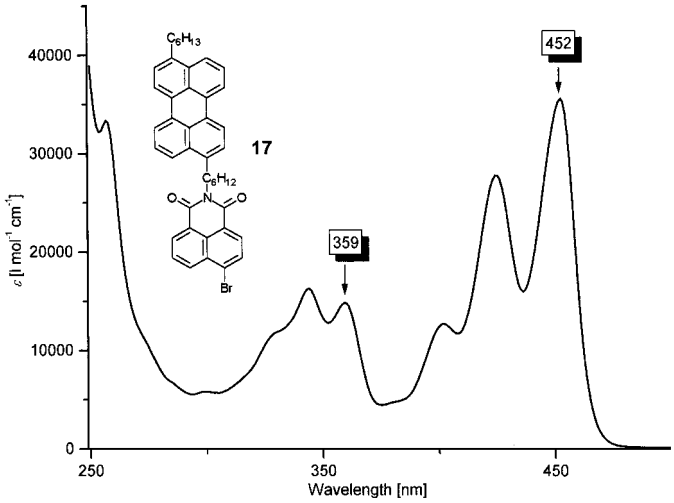

Figure 2. UV/Vis absorption spectrum of **17** ($CHCl_3$).

target molecule **4** (Figures 3 and 4). The spectrum of **18** exhibits the absorption of a naphthalenedicarboximide ($\lambda_{max} = 340$ nm), a dialkylperylene ($\lambda_{max} = 424$ nm, 453 nm) and a perylenedicarboximide derivative ($\lambda_{max} = 520$ nm). Although the absorptions of the dialkylperylene and the perylenedicarboximide show some overlap, it is still possible to distinguish the contributions of both molecules (Figure 3).

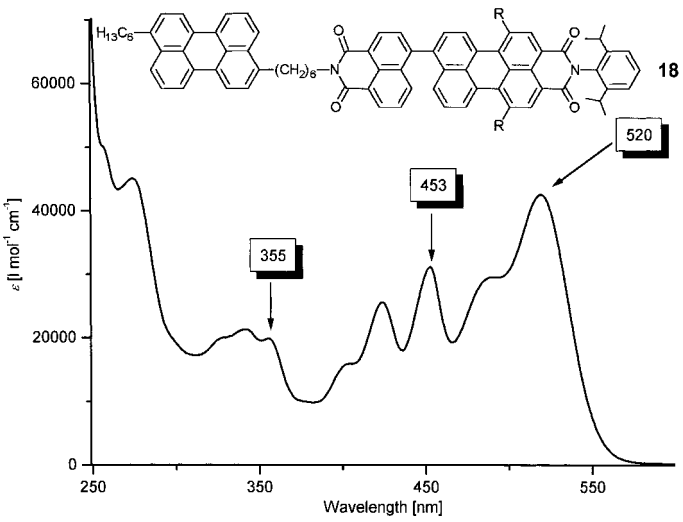

Figure 3. UV/Vis absorption spectrum of **18** ($CHCl_3$); R = 4-*tert*-butylphenoxy.

In comparison with the uncyclized molecule **18** the UV/Vis spectrum of the bichromophore **4** (Figure 4) displays the absorption only of the dialkylperylene and the terrylenediimide unit. As a result of the extended π system the absorption of the terrylene component in **4** ($\lambda_{max} = 665$ nm) is bathochromically shifted compared with the perylenecarboximide unit in **18** ($\lambda_{max} = 520$ nm) (Figure 3) and shows only very weak overlap with the dialkylperylene part ($\lambda_{max} = 452$ nm) of the bichromophore **4**. The overall absorption spectrum of **4** can be approximated by the sum of the spectra of the constituent perylene and terrylene moieties. The only difference relates to

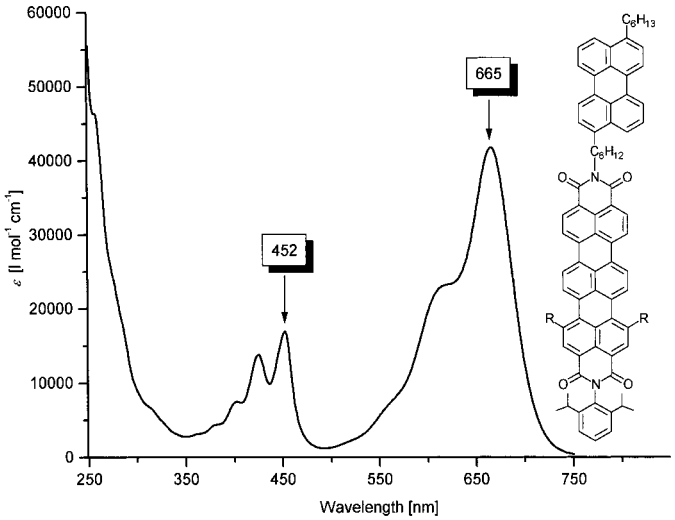

Figure 4. UV/Vis absorption spectrum of **4** ($CHCl_3$); R = 4-*tert*-butylphenoxy.

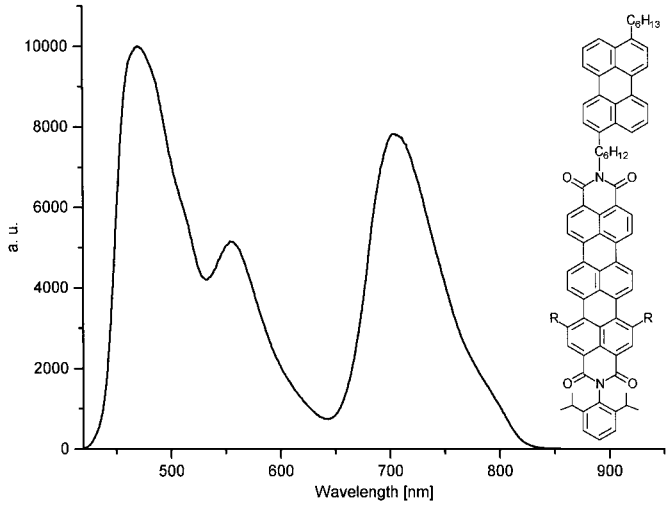

Figure 5. Fluorescence emission spectrum of **4**; $\lambda_{exc.} = 410$ nm (CH_2Cl_2); R = 4-*tert*-butylphenoxy.

the vibronic progressions, which are less resolved in the bichromophoric molecule. A possible explanation invokes a slightly hindered rotation between the two chromophores which may result in low frequency torsional motions smearing out the vibronic structure of the absorption spectrum.

In the next step we addressed the energy transfer between the two chromophores. Inserting the overlap integral of the fluorescence spectrum of the perylene unit and the absorption spectrum of the terrylene unit into the standard formula given in the literature we estimated the Förster radius R_0 to be approximately 33 Å for the bichromophore **4**.[1, 2, 5]

The Förster radius R_0 denotes the donor–acceptor distance at which 50% of the energy is transferred. κ^2 which is related to the relative orientation between the transition dipoles was set to ⅔; this accounts for a statistical distribution of the dipoles. The hexanediyl chain linking the two chromophores is clearly shorter than the Förster radius R_0. Additionally, because of the flexibility of the alkanediyl chain, numerous configurations exist in solution with varying distances and orientations of the interacting dipoles. For very short distances even exchange coupling may be possible. Based on these arguments, we expect efficient energy transfer in the bichromophore after selective excitation of the perylene donor moiety.

A fluorescence spectrum recorded after excitation at $\lambda_{exc} =$ 410 nm is shown in Figure 5. As expected, the spectrum consists of perylene as well as terrylene emissions. If no absorption of terrylene in the range of the excitation wavelength is considered (see Figure 4), the only possible explanation for the terrylene fluorescence is the occurrence of an electronic energy transfer from the perylene to the terrylene unit. The existence of an intense perylene emission indicates that only part of the electronic excitation energy is transferred which is probably related to orientational factors influencing the transfer efficiency.[2] We also recorded emission spectra with an excitation wavelength of $\lambda_{exc.} = 665$ nm. In this case only terrylene emission was observed.

The bichromophore **4** was further investigated by fluorescence excitation spectroscopy, which confirmed the transfer of electronic energy. The shape of the excitation spectrum in Figure 6 is very similar to that of the absorption spectrum of **4**

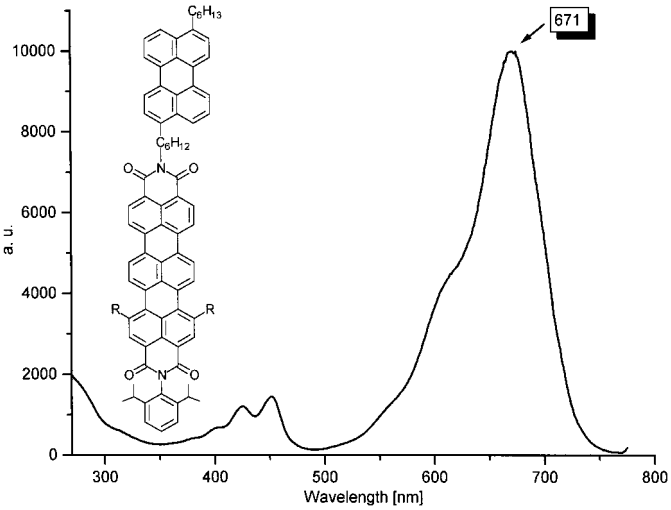

Figure 6. Excitation spectrum of **4** (CH_2Cl_2); R = 4-*tert*-butylphenoxy.

(see Figure 4). The main difference between both spectra is the relative intensity ratio of the perylene and terrylene parts. To record an excitation spectrum, the fluorescence intensity was measured at a fixed emission wavelength as a function of the excitation wavelength. In the present case the emission was detected at a wavelength of 780 nm. In this spectral region no perylene emission is expected at all because it is restricted to shorter wavelengths. Therefore, without interaction between the covalently linked chromophores no perylene absorption could be monitored in the excitation spectrum under the given conditions. The appearance of the perylene part in the excitation spectrum in Figure 6 (370–470 nm) is again indicative of energy transfer between the two moieties of the bichromophore. If the excitation energy would be

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transferred completely from perylene to terrylene the relative spectral intensities of the chromophores should be similar in the absorption and excitation spectra.

One possible explanation for the terrylene emission after excitation of the perylene moiety is the trivial process of reabsorption. The strongest evidence against this assumption follows from the observation of single-pair energy transfer. In these experiments extremely small sample volumes containing only a single bichromophore are investigated. Under these conditions the only mechanism to create the terrylene emission is the interaction between two transition dipoles in their optical near-field.

Single-molecule experiments: After the electronic energy transfer had been established by conventional excitation and emission spectroscopy we proceeded to experiments at the single-molecule level. For this purpose we prepared thin films of polyvinylbutyral (PVB) by the spin-coating technique, which were doped at very low concentration with the bichromophore **4**. The samples were mounted in a scanning-confocal microscope operated at room temperature. The details of the microscope can be found elsewhere.[18] The sample was excited with a He-Cd-laser at 442 nm and the emission light was detected with an avalanche photodiode after it had been passed through a 442 nm notch-filter to reject the excitation light and an RG 610 long-pass filter to reject any emission from the perylene part of the bichromophore. Consequently the perylene moiety was excited and only terrylene emission was detected.

A fluorescence image of the dye-doped polymer film is shown in Figure 7. The data was gathered by line scanning of the sample from botton to top through the focus of the microscope objective. Each of the bright spots corresponds to the emission of a single bichromophore. Specifically, as we excite the donor (perylene) part and detect the acceptor (terrylene) emission, we observe only those bichromophores where energy transfer takes place. As checked in separate experiments, most of the molecules also emit in the blue. However, this emission does not contribute to the signals in Figure 7 as a result of filtering.

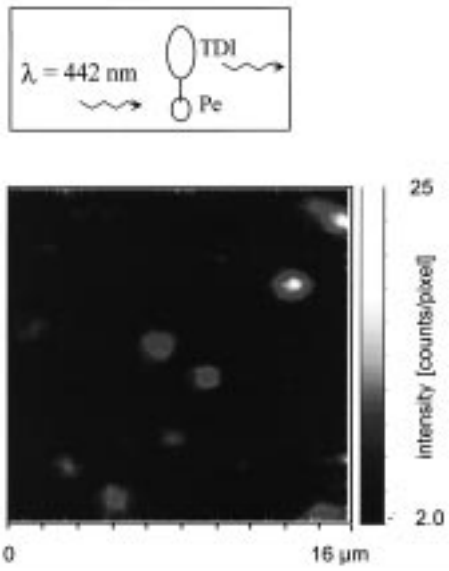

Figure 7. Fluorescence image of single donor–acceptor pairs of the bichromophore **4** in PVB at room temperature. The data was gathered by exciting the perylene moiety of the bichromophore at 422 nm and detecting the terrylene fluorescence emission at wavelengths > 610 nm.

To prove that we are indeed looking at a single molecule, common testing procedures were applied and these were found to also be valid for the bichromophore investigated here. First, the signal could be lowered to the background level by rotating the polarization of the laser light. This behavior is expected only for the observation of a single molecule with a well-defined transition dipole. Second, after prolonged irradiation the fluorescence signal at a given spot ceased abruptly indicating discrete photo-bleaching. According to these observations, we have succeeded in utilizing energy transfer to image single donor–acceptor pairs of the bichromophore **4**. The intensity differences between the various spots seen in Figure 7 may be caused by a number of reasons which in terms of the energy transfer process include variations in donor–acceptor distance or their relative orientation.

Conclusion

We have described the synthesis of a novel bichromophoric molecule that is tailor-made to study electronic energy transfer at the single-molecule level. The design of the molecule was defined by the stringent requirements to achieve single-molecule sensitivity under various experimental conditions. An appropriate solution was found by linking a dialkylperylene and a terrylenetetracarboxdiimide with a hexanediyl spacer. The assembly of the bichromophore **4** relied on recently developed novel synthetic approaches for the modification of rylene chromophores.[10] The energy transfer from the perylene donor to the terrylene acceptor was observed unambiguously by fluorescence excitation and emission spectroscopy. Subsequently, confocal microscopy at room temperature was employed to image single donor–acceptor couples through the energy transfer process.

The results presented in this paper indicate a number of promising future research directions. With regard to the bichromophore itself, synthetic efforts will focus on the implementation of longer and more rigid spacers. On the other hand some flexibility in the interconnecting chain is quite desirable, because it will offer the possibility to study changes in distance or orientation between the two chromophores. Such alterations can be extracted from the relative intensity changes of the perlyene and terrylene emission spectra, respectively. Thus single-molecule donor–acceptor energy transfer experiments might allow to monitor molecular motions in the nanometer range. Additionally, since the chromophores were selected by their ability to exhibit narrow zero-phonon lines at low temperature, optical high resolution studies of the interacting pair will be possible in the future.

Experimental Section

All commercially available reagents and solvents were used without further purification unless otherwise stated. THF, DMF, and piperidine were purified and dried according to standard procedures.[19] The argon used was passed through an oxygen scavenger (BTS catalyst, BASF AG), silica gel, and then KOH pellets. Hydrogen gas was purchased from Linde and used without further purification; hexynonitrile, 1-hexyne, bromine (Br_2), [$Pd(PPh_3)_4$], *N*-bromsuccinimide, palladium on charcoal (10% palladium), *p-tert*-butylphenol, hexabutylditin, and borane/THF complex (1M solution stabilized with <0.005 M $NaBH_4$) were purchased from Aldrich and used without further purification; 3-bromoperylene was prepared as described in the literature;[11, 12] ^{1}H NMR: Varian Gemini 200 (200 MHz), Bruker AC 300 (300 MHz), Bruker AMX 500 (500 MHz); ^{13}C NMR: Varian Gemini 200 (50.32 MHz), Bruker AC 300 (75.48 MHz), Bruker AMX 500 (125.80 MHz); UV/Vis: Perkin–Elmer Lambda 9, Perkin–Elmer Lambda 15 (peak assignment: S = shoulder); FD-MS: ZAB2-SE-FPD (VG Instruments); IR: Nicolet FT-IR 320; melting points (uncorrected): Büchi melting point apparatus; thin-layer chromatography (TLC): ready-to-use silica gel 60 F_{254} plates (Merck); column chromatography: silica gel, particle size 70–230 mesh (Merck, Geduran Si 60) and aluminum oxide (Merck, Geduran AL 90) with the eluents indicated; elemental analyses were performed by BASF AG and by the Department of Chemistry and Pharmacy of the University of Mainz. 3-(1-Hexynyl)perylene (**9**), 3-hexylperylene (**10**), 3-bromo-10(11)-hexylperylene (**11**), 3-(6-cyano-1-pentynyl)-10(11)-hexylperylene (**12**), 3-(6-cyanopentyl)-10(11)-hexylperylene (**13**), and 3-(7-aminohexyl)-10(11)-hexylperylene (**5**) were prepared as described in the literature.[9]

***N*-(2,7-Diisopropylphenyl)-1,7,10-tribromoperylene-3,4-dicarboximide** (**15**): *N*-(2,6-Diisopropylphenyl)perylene-3,4-dicarboximide (**14**) (10 g, 21 mmol) was dissolved in chloroform (1.5 L), and bromine (60 mL) was added under vigorous stirring and finally refluxed for 6 h. After completion of the bromination the mixture was allowed to cool down to room temperature and poured into a solution of water (2 L), KOH (15 g), and sodium sulfite (10 g) under vigorous stirring. To destroy the remaining bromine the addition of KOH and sodium sulfite was continued until the color changed from dark red-brown to a strong orange. The organic layer was dried over magnesium sulfate and the chloroform evaporated. The orange product **15** (14.5 g, 96%) was used for further reactions without any purifications. For characterization analytical amounts were purified by column chromatography on silica gel (1×17 cm, CH_2Cl_2). M.p. $>300\,^\circ$C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 9.34-9.32$ (d, 1H, $J = 7.5$ Hz; Ar-H), 9.13–9.10 (d, 1H, $J = 8$ Hz; Ar-H), 8.94 (s, 1H; Ar-H), 8.93 (s, 1H; Ar-H), 8.46–8.44 (d, 1H, $J = 8$ Hz; Ar-H), 7.99–7.97 (d, 1H, $J = 8$ Hz; Ar-H), 7.82–7.79 (t, 1H, $J = 8$ Hz; Ar-H), 7.53–7.50 (t, 1H, $J = 7$ Hz; Ph-H), 7.36–7.34 (d, 2H, $J = 7$ Hz; 2 Ph-H), 2.75–2.71(m, 2H; $2CH(CH_3)_2$), 1.21–1.19 (d, 12H, $J = 6$ Hz; $2CH(CH_3)_2$); **^{13}C NMR** (125 MHz, [D_8]THF): $\delta = 162.54$ (C=O), 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; UV/Vis (dioxane): λ_{max} (ε) = 513 (33 013), 401 (3398), 379 nm (3116); MS (8 kV, FD): *m*/*z* (%): 719.0 (100) $[M]^+$; $C_{34}H_{24}NO_2Br_3$ (718.28): calcd C 56.85, H 3.37, N 1.95, Br 33.37; found C 56.56, H 3.50, N 1.92, Br 32.75.

***N*-(2,7-Diisopropylphenyl)-1,7-bis(4-*tert*-butylphenoxy)-10-bromoperylene-3,4-dicarboximide** (**16**): Tribromoperylene **15** (15 g, 20.6 mmol), 4-*tert*-butylphenol (6.2 g, 41.3 mmol), and K_2CO_3 (6.5 g, 46.9 mmol) were dissolved in *N*-methyl-2-pyrrolidinone (NMP) (500 mL). After 6 h at 120 °C the reaction mixture was allowed to cool to room temperature and then poured while stirring into aqueous HCl (2 L; pH 1). The precipitate was filtered, washed with water, dried under vacuum, and purified by column chromatography on silica gel (12×120 cm, toluene). The product was dissolved in CH_2Cl_2 and precipitated with MeOH. After filtering and drying, the red product **16** (5.80 g, 32%) was obtained. M.p. 297 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 9.41-9.40$ (d, $J = 8$ Hz, 1H; Ar-H), 9.16–9.15 (d, $J = 8.5$ Hz, 1H; Ar-H), 8.36–8.35 (d, $J = 7.5$ Hz, 1H; Ar-H), 8.34 (s, 1H; Ar-H), 8.32 (s, 1H; Ar-H-5), 7.88–7.86 (d, $J = 8.5$ Hz, 1H; Ar-H), 7.70–7.68 (t, $J = 8$ Hz, 1H; Ar-H), 7.50–7.40 (m, 5H; 5Ph-H), 7.30–7.28 (d, $J = 7$ Hz, 2H; Ph-H), 7.10–7.07 (m, 4H; 4Ph-H), 2.75–2.72 (m, 2H; $2CH(CH_3)_2$), 1.35 (s, 18H; 2*t*Butyl), 1.15–1.13 (d, 12H, $J = 6$ Hz; $2CH(CH_3)_2$; ^{13}C NMR (125 MHz, [D_8]THF) $\delta = 163.14$, 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 ($C(CH_3)_3$), 31.45 ($C(CH_3)_3$), 29.09 ($CH(CH_3)_2$), 23.99 ($CH(CH_3)_2$); UV/Vis (dioxane): λ_{max} (ε) = 513 (41 553), 420 (9949), 274 nm (40 081); MS (8 kV, FD): *m*/*z* (%): 855.2 (100) $[M]^+$; $C_{54}H_{50}NO_4Br$ (856.90): calcd 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.

***N*-(2,7-Diisopropylphenyl)-1,7-bis(4-*tert*-butylphenoxy)-10-(tri-*n*-butyltin)-perylene-3,4-dicarboximide** (**6**): A solution of bromodiphenoxydicarboximide **16** (1 g, 1.7 mmol), hexabutylditin (1 g, 1.8 mmol), and [$Pd(PPh_3)_4$] (7 mol%; 137 mg, 0.119 mmol) in toluene (100 mL) was refluxed for 2 d in a Schlenk flask. After complete conversion of the starting material the solvent was evaporated and the residue was dried in vacuo, and finally purified by column chromatography (silica gel, 40×7 cm, CH_2Cl_2) to yield the intensively red product **6** (1.32 g, 73%). M.p. 265 °C; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): $\delta = 9.30-9.28$ (d, 1H, $J = 7.7$ Hz; Ar-H), 9.19–9.18 (d, 1H, $J = 7.7$ Hz; Ar-H), 8.20 (s, 1H; Ar-H), 8.17 (s, 1H; Ar-H), 7.80–7.79 (d, 1H, $J = 7.5$ Hz; Ar-H), 7.76–7.75 (d, 1H, $J = 7.7$ Hz; Ar-H), 7.62–7.58 (t, 1H, $J = 8$ Hz; Ar-H), 7.40–7.37 (m, 4H; 4Ar-H), 7.36–7.33 (t, 1H, $J = 8$ Hz; Ar-H), 7.20–7.19 (d, 1H, $J = 7.8$ Hz; Ar-H), 7.11–7.07 (m, 4H; 4Ar-H), 2.62–2.57 (m, 2H; $2CH(CH_3)_2$), 1.56–1.50 (m, 6H; $3CH_2$), 1.36–1.26 (m, 6H; $3CH_2$), 1.29 (s, 18H; $2C(CH_3)_3$), 1.21–1.12 (m, 6H; $3CH_2$), 1.05–1.04 (d, 12H, $J = 7$ Hz; $2CH(CH_3)_2$), 0.84–0.81 (t, 9H, $J = 7$ Hz; $3CH_3$); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): $\delta = 163.54$, 163.50, 154.06, 153.74, 153.24, 153.17, 149.15, 147.85, 147.73, 145.67, 139.30, 137.07, 135.90, 132.13, 131.01, 129.84, 128.89, 128.41, 128.08, 127.86, 127.71, 127.43, 127.24, 127.21, 126.80, 124.79, 124.22, 123.86, 123.62, 122.90, 121.28, 121.17, 119.90, 119.69, 119.32, 119.11, 118.72, 118.54, 34.65, 32.16, 31.76, 31.37, 30.86, 29.92, 29.42, 29.27, 28.35, 27.93, 27.73, 27.62, 24.69, 24.34, 24.01, 14.02, 11.00, 10.29; IR (KBr): $\tilde{\nu} = 2958$, 2925, 1708 (C=O), 1597, 1506, 1334, 1282, 1210 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 524 (33 985), 494 (23 611) S, 416 (7090), 276 nm (27 767); MS (8 kV, FD): *m*/*z* (%): 1067.5 (100) $[M]^+$; $C_{66}H_{77}NO_4Sn$ (1067.04): calcd C 74.29, H 7.27, N 1.31; found C 74.37 H 7.48, N 1.20.

3-(*N*-ω-Hexyl-4-bromonaphthalene-1,9-dicarboximide)-10(11)-hexylperylene (**17**): Glacial acetic acid (120 mg) and 3-hexyl-9(10)-(6-aminohexyl)-perylene (**5**) (250 mg, 0.57 mmol) were added to a stirred solution of 4-bromonaphthalene-1,8-dicarboxanhydride (**7**) (100 mg, 0.36 mmol) in NMP (100 mL). The reaction was stirred under argon at 85 °C for 6 h. After cooling to room temperature the mixture was poured into ice-cold dilute HCl, and extracted with CH_2Cl_2. The organic layer was dried over magnesium sulfate, the solvent was evaporated, and the product purified with column chromatography (20×2 cm, CH_2Cl_2) to yield the orange product **17** (315 mg, 80%). M.p. 136 °C; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): $\delta =$ 8.56–8.54 (dd, 1H, $J_1 = 7$ Hz, $J_2 = 1$ Hz; Naph-H), 8.48–8.46 (dd, 1H, $J_1 =$ 7 Hz, $J_2 = 1$ Hz; Naph-H), 8.31–8.29 (d, 1H, $J = 8$ Hz; Ar-H), 8.12–8.08 (m, 2H; 2Per-H), 8.04–7.99 (m, 2H; 2Per-H), 7.98–7.96 (d, 1H, $J = 8$ Hz; Naph-H), 7.82–7.75 (m, 3H; 2Per-H, 1Naph-H), 7.46–7.43 (t, 2H, $J =$ 8 Hz; 2Per-H), 7.28–7.26 (m, 2H; 2Per-H), 4.10–4.07 (t, 2H, $J = 7.5$ Hz; CH_2-N), 2.96–2.92 (m, 4H; $2CH_2$-Ar), 1.72–1.67 (m, 2H; CH_2-CH_2-N), 1.48–1.19 (m, 14H; $7CH_2$), 0.87–0.84 (t, 3H, $J = 7$ Hz; CH_3); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): $\delta = 163.93$, 138.99, 138.72, 133.63, 133.24, 133.07, 132.94, 132.38, 132.17, 131.56, 131.51, 130.96, 130.92, 130.86, 130.67, 129.81, 129.76, 129.51, 129.26, 129.14, 129.01, 128.51, 127.87, 127.51, 127.35, 127.30, 127.15, 126.75, 126.70, 126.15, 124.80, 124.75, 124.40, 123.40, 122.50, 121.10, 121.04, 120.65, 120.46, 120.03, 119.88, 119.48, 40.96, 33.68, 33.57, 32.15, 30.89, 30.73, 29.92, 28.44, 27.44, 23.10, 15.10; UV ($CHCl_3$): λ_{max} (ε) = 452 (35 587), 425 (27 745), 402 (12 675), 381 (4781) S, 359 (14 837), 344 (16 260), 328 (11 529) S, 299 (5798), 257 nm (33 370); MS (8 kV, FD): *m*/*z* (%): 693.4 (100) $[M]^+$; $C_{44}H_{40}NO_2Br$ (694.71): calcd C 76.07, H 5.80, N 2.02, Br 11.50; found C 75.97, H 5.84, N 2.14, Br 11.73.

***N*-(2,7-Diisopropylphenyl)-1,6-di(4-*tert*-butylphenoxy)-10-{1-[*N*-ω-hexyl-(10(11)-hexyl-perylene-3-yl)]naphthalene-4,6-dicarboximide}perylene-3,4-dicarboximide** (**18**): A solution of **17** (100 mg, 0.14 mmol), stannylmonoimide **6** (180 mg, 0.168 mmol), and [$Pd(PPh_3)_4$] (13 mg, 0.01 mmol) in toluene (20 mL) was refluxed for 4 d. The solvent was evaporated and the residue purified by column chromatography on silica gel (20×1 cm, CH_2Cl_2) to yield **18** (87 mg, 45%) as a bright red solid. M.p 285 °C (decomp); ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 90 °C): $\delta = 9.48-9.46$ (d, 1H, $J =$ 8 Hz; Per-H), 9.37–9.36 (d, 1H, $J = 7$ Hz; Per-H), 8.69–8.68 (d, 1H, $J =$ 7 Hz; Ar-H), 8.59–8.57 (d, 1H, $J = 7$ Hz; Ar-H), 8.31–8.29 (m, 2H; Ar-H), 8.16–8.14 (m, 2H; Ar-H), 8.06–8.04 (m, 2H; Ar-H), 7.86–7.80 (m, 3H; Ar-H), 7.68–7.10 (m, 20H; Ar-H), 4.20–4.16 (t, 2H, $J = 6$ Hz; -CH_2-N), 3.03–

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3.00 (m, 4H; -CH_2-Ar), 2.71–2.69 (m, 2H; CH(CH_3)$_2$), 1.82–1.26 (m, 34H; -CH_2-, -C(CH_3)$_3$), 1.12–1.11 (m, 12H; -CH(CH_3)$_2$), 0.88–0.86 (t, 3H, J = 7 H; -CH_3); UV ($CHCl_3$): λ_{max} (ε) = 520 (42504), 488 (29468), 453 (31148), 424 (25596), 403 (15846) S, 356 (19842), 342 (21257), 327 (19904), 274 nm (45081); MS (8 kV, FD): m/z (%): 1390.2 (100) $[M]^+$; $C_{98}H_{90}N_2O_6$ (1391.80): calcd. C 84.57, H 6.52, N 1.81.

***N*-(2,7-Diisopropylphenyl)-*N*′-[ω-hexyl-(10(11)-hexylperylene-3-yl)]-1,6-di(4-*tert*-butyl-phenoxy)terrylene-3,4:12,13-tetracarboxdiimide** (**4**): Compound **18** (55 mg, 0.04 mmol), glucose (0.5 g), finely grounded KOH (2 g, 0.035 mol), and ethanol (6 mL) were mixed together in a round-bottom flask. The flask was flooded with argon, equipped with a reflux condenser, and heated to 60 °C. After 2 h, glucose (0.5 g) was added to the reaction mixture and the temperature was increased to 90 °C for another 6 h. The black melt was poured onto 2 M HCl (80 mL), extracted with CH_2Cl_2, washed twice with water and the organic layer dried over magnesium sulfate. The solvent was evaporated and the residue purified by column chromatography on silica gel (20 × 1 cm, toluene). The purified material was again subjected to a preparative thin-layer chromatography on silica gel (20 × 20 cm glass plate, toluene) to give the target compound **4** (22 mg, 40%) as a dark green to black solid. M.p. > 300 °C; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ = 9.52–9.50 (d, 2H, J = 8.5 Hz; 2Ar-H), 8.56–8.55 (d, 4H, J = 7.5 Hz; 4Ar-H), 8.44–8.42 (d, 2H, J = 8 Hz; 2Ar-H), 8.32 (s, 2H; 2Ar-H), 8.10–8.07 (m, 2H; 2Ar-H), 8.03–7.98 (m, 2H; 2Ar-H), 7.83–7.77 (m, 2H; 2Ar-H), 7.46–7.36 (m, 3H; 3Ar-H), 7.28–7.23 (m, 4H; 4Ar-H), 7.16–7.15 (d, 4H, J = 8.5 Hz; 4Ar-H), 4.21–4.19 (t, 2H, J = 7 Hz; CH_2-NR_2), 3.00–2.93 (m, 4H; 2CH_2-Ar), 2.71–2.66 (m, 2H; 2CH(CH_3)$_3$), 1.82–1.70 (m, 6H; 3CH_2), 1.55–1.22 (m, 2H; CH_2, C(CH_3)$_3$), 0.86–0.84 (t, 3H, J = 7 Hz; CH_3); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): δ = 163.62, 163.28, 163.10, 154.98, 153.13, 148.23, 146.20, 145.58, 139.42, 138.75, 136.49, 133.61, 133.48, 132.42, 132.38, 131.64, 130.85, 130.45, 130.27, 130.15, 129.95, 129.75, 129.29, 129.19, 127.88, 127.34, 127.22, 127.18, 126.69, 126.58, 125.45, 124.70, 124.22, 123.92, 123.88, 123.79, 123.69, 123.58, 123.00, 122.53, 122.29, 121.55, 121.19, 120.43, 120.08, 119.88, 118.79, 107.04, 40.96, 34.61, 33.76, 33.59, 32.08, 31.56, 31.01, 30.78, 29.99, 29.31, 28.39, 27.51, 24.03, 23.01, 14.89; IR (KBr): $\tilde{\nu}$ = 3074, 3042, 3014, 3007, 2961, 2949, 2927, 2916, 2855, 2848, 1693 (C=O), 1657 (C=O), 1590, 1583, 1506, 1466, 1370, 1357, 1331, 1304, 1248, 1186, 842, 810, 751, 721 cm^{-1}; UV ($CHCl_3$): λ_{max} (ε) = 665 (41746), 615 (23052), 558 (6957) S, 452 (16947), 425 (13807), 403 (7497), 380 (4357) S, 257 nm (46368); MS (8 kV, FD): m/z (%): 1389.3 (100) $[M]^+$, 694.7 (20) $[M]^{2+}$; $C_{98}H_{88}N_2O_6$ (1389.78): calcd C 84.69, H 6.38, N 2.02; found C 84.08, H 6.22 N 1.94.

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[1] L. Stryer, *Annu. Rev. Biochem*. **1978**, 47, 819–846.
[2] R. M. Clegg, in *Fluorescence Imaging Spectroscopy and Microscopy* (Eds.: X. F. Wang, B. Herman), Wiley, New York **1996**.
[3] T. Ha, T. Enderle, D. F. Ogletree, D. S. Chemla, P. R. Selvin, S. Weiss, *Proc. Natl. Acad. Sci. USA* **1996**, *93*, 6264–6268.
[4] G. J. Schütz, W. Trabesinger, T. Schmidt, *Biophys. J.* **1998**, *74*, 2223–2226.
[5] T. Förster, *Discuss. Faraday Soc.* **1959**, *27*, 7–17.
[6] *Single-Molecule Optical Detection, Imaging and Spectroscopy* (Eds.: T. Basché, W. E. Moerner, M. Orrit, U. P. Wild), VCH, Weinheim **1996**.
[7] D. Chiu, R. N. Zare, *Chem. Eur. J.* **1997**, *3*, 335–339.
[8] S. Mais, J. Tittel, T. Basché, C. Bräuchle, W. Göhde, H. Fuchs, G. Müller, K. Müllen, *J. Phys. Chem.* **1997**, *A101*, 8345–8440.
[9] P. Schlichting, U. Rohr, K. Müllen, *Liebigs Ann./Recueil* **1997**, 395–407.
[10] F. O. Holtrup, G. R. J. Müller, H. Quante, S. De Feyter, F. C. De Schryver, K. Müllen, *Chem. Eur. J.* **1997**, *3*, 219–225.
[11] R. H. Mitchell, Y.-H. Lai, R. V. Williams, *J. Org. Chem*. **1979**, *44*, 4733–4735.
[12] R. Lapuyade, J. Pereyre, P. Garrigues, *C. R. Acad. Sci. Ser. II* **1986**, *303*, 903–906.
[13] H. Quante, K. Müllen, *Angew. Chem*. **1995**, *107*, 1487–1489; *Angew. Chem. Int. Ed. Engl*. **1995**, 34, 1323–1325.
[14] C. Eaborn, A. R. Thompson, D. R. M. Walton, *J. Chem. Soc. C* **1967**, 1364–1366.
[15] J. A. Söderquist, G. J.-H. Hsu, *Organometallics* **1982**, *1*, 830–834.
[16] H. Azizian, C. Eaborn, A. Pidcock, *J. Organomet. Chem*. **1981**, *215*, 49–58.
[17] W. Bradley, F. W. Pexton, *J. Chem. Soc*. **1954**, 4432–4435.
[18] W. Göhde, J. Tittel, T. Basché, C. Bräuchle, U. C. Fischer, H. Fuchs, *Rev. Sci. Instrum*. **1997**, *68*, 2466–2474.
[19] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, in *Purification of Laboratory Chemicals*, 2nd ed., Pergamon, Frankfurt, **1987**.

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