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Room-Temperature Columnar Liquid-Crystalline Perylene Imido-Diesters by a Homogeneous One-Pot Imidification–Esterification of Perylene-3,4,9,10-tetracarboxylic Dianhydride

Julien Kelber,[a] Harald Bock,*[a] Olivier Thiebaut,[a] Eric Grelet,[a] and Heinz Langhals[b]

Dedicated to the memory of Dr. Marc Julia

Keywords: Liquid crystals / Heterocycles / Fluorescence spectroscopy / Self-assembly

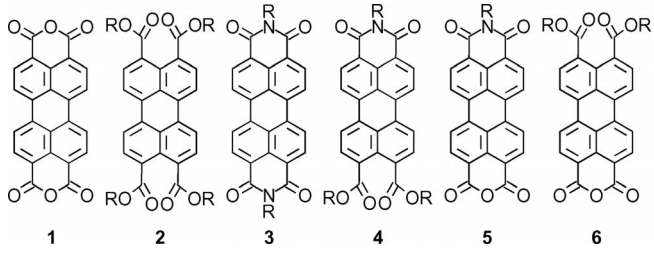
The reaction of PTCDA (perylene-3,4,9,10-tetracarboxylic dianhydride) with an alcohol, a bromoalkane, and an alkylamine in the presence of DBU in DMF yields imido-diester-substituted perylenes. The reaction is limited to polar alcohols such as propanol, but longer alkyl chains are efficiently introduced in a second step by alkyl group exchange by using selective acidic ester hydrolysis that leaves the imide group intact. This amine-efficient approach to imido-diesters is used to obtain acceptor-type self-assembling dyes that form a hexagonal columnar liquid crystalline phase at room temperature.

Introduction

Derivatives of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA, **1**) constitute an extraordinarily successful class of functional dyes and pigments whose applications range from car paints to photoreceptors in photocopiers.[1] They have been incorporated in organic solar cells starting with Tang's seminal bilayer cell in 1986,[2] and liquid crystalline derivatives have been discussed as self-assembling electron acceptor layers with superior charge transport properties.[3]

Tetraalkyl esters **2** show large hexagonal columnar liquid crystalline temperature ranges, and this mesophase can be stabilized at room temperature by the incorporation of racemically branched alkyl chains.[4] The face-on (homeotropic) alignment needed in photovoltaic devices, where the columnar charge transport pathways are aligned perpendicular to the substrate, has been conveniently obtained by thermal annealing (Scheme 1) with room-temperature columnar ester and imido-ester materials.[5]

Tetraesters **2** contain moderate electron density in the aromatic core as expressed by their lowest unoccupied and highest occupied molecular orbital energy (E_{LUMO} and E_{HOMO}) values of –3.5 and –5.8 eV, respectively.[6] This quality makes these materials potential electron-acceptor and electron-donor layers depending on what type of material they are paired with at a donor–acceptor interface; more pronounced acceptor-type behavior is observed with their dialkyl diimide analogues **3**, with a E_{LUMO} value of about –4.2 eV.[7] Contrary to tetraesters **2**, diimides **3** do not possess a sufficient number of alkyl substituents to induce a stable hexagonal columnar mesophase at room temperature.[8] However, imido-diesters **4**[9] possess an enhanced acceptor-type behavior compared to esters **2** and display a sufficient number of alkyl substituents to suggest the possibility of a stable room-temperature mesophase, together with accessible clearing temperatures (i.e., moderate transition temperatures to the isotropic liquid state) to allow controlled growth and alignment of columnar liquid crystalline samples.



Scheme 1. PTCDA and its symmetrically and dissymmetrically substituted ester and carboxylic imide derivatives.

Yang et al.[10] recently synthesized perylene imido-diesters **4** with three identical nonbranched *n*-alkyl substituents and found pronounced chromophore aggregation in amorphous sublimed films. No evidence of a columnar mesophase or a transition to the liquid state at accessible tem-

[a] CRPP: Centre de Recherche Paul Pascal, CNRS 115, Avenue Schweitzer, 33600 Pessac – Bordeaux, France
Fax: +33-5-56845600
E-mail: bock@crpp-bordeaux.cnrs.fr
[b] Department of Chemistry, LMU University of Munich, Butenandtstr. 13, 81377 Munich, Germany

peratures could be found. They did, however, find E_{LUMO} values of about –4.0 eV, confirming a good acceptor-type electronic structure. Their synthetic approach involved the low-yield formation and isolation of unsubstituted perylenetetracarboxylic monoimido-monoanydride **5** (R = H), followed by phase-transfer trialkylation of its dipotassium salt with an excess amount of the alkyl bromide. Although useful, this approach is limited to providing perylenes with identical substituents on both the carboxylic imide and ester groups and, more importantly, to easily accessible primary alkyl bromides.

A common approach to alkyl-substituted **5** starts with diimidification of PTCDA with an alkylamine, followed by its delicate monohydrolysis.[9,11] Such alkylimidoanhydrides can then be esterified, or, as is frequently the case, imidated with another amine to which shall be grafted a strongly fluorescent or electronically interacting perylenetetracarboxdiimide (PTCDI) moiety.[12,13]

Perylenetetracarboxylic dialkylimides **3** are known to be highly soluble and low melting only if the alkyl substituent is secondary, that is, derived from an α-branched alkylamine such as 7-aminotridecane.[14] Such amines can be obtained in two efficient steps from the corresponding ketone through the oxime.[13,14]

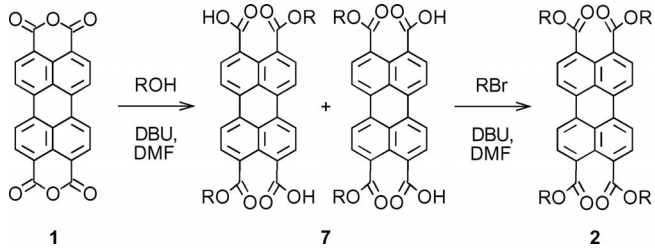
Both aforementioned synthetic procedures necessitate the selective formation and isolation of monoimido-monoanhydride **5** and are not economical with respect to the alkyl substituent on the imide function. Given that long α-branched alkylamines are not commercially available and that even the ketone starting materials can be expensive, we envisioned a synthetic procedure for the direct monoalkylimidation of PTCDA that is more efficient with respect to the amine, does not involve kinetically controlled half reactions or separations based on differential solubilities,[11] is not limited to primary alkyl substituents,[10] and, ideally, only creates soluble side products of strongly different polarity that are easily separated by column chromatography.

The main difficulty in the monoimidation of PTCDA with an alkylamine is that the former is an insoluble pigment, which dissolves in an organic solvent only upon reaction with the amine. Monoimidated molecules therefore dissolve readily and react a second time more quickly than the initial pigment. This undesired disubstitution explains why the most common procedure for monoimidation entails initial carboxylic diimide formation followed by monohydrolysis.

A similar approach that relies on controlled monohydrolysis of a symmetrically substituted PTCDA derivative to create a monoanhydride while maintaining soluble alkyl chains on the other side of the perylene moiety was recently described by Xue and co-workers.[15] This approach uses tetraester **2** as starting material, thus avoiding the excessive use of the branched amine; anhydride-diester **6** results following acid-catalyzed monohydrolysis. The anhydride-diester can be converted subsequently with an equimolar amount of the amine into imido-diester **4** in three steps from PTCDA (**1**, which may be hydrolyzed to yield imido-anhydride **5** through a fourth step).

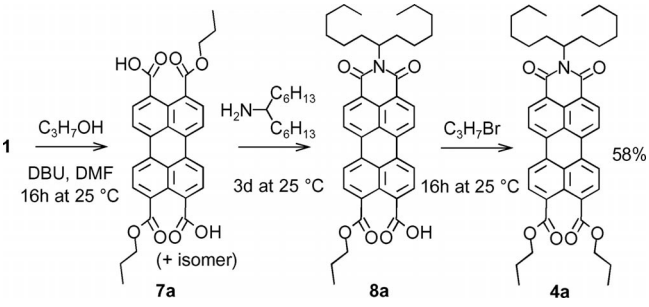
Results and Discussion

It occurred to us during our syntheses of perylene tetracarboxylic tetraesters from PTCDA with an alkanol and a bromoalkane that, in the presence of a strong lipophilic base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and with DMF as polar aprotic solvent, the pigment quickly dissolved even if the bromoalkane was initially omitted. In this ester synthesis, base-catalyzed ring opening of each anhydride moiety by the alcohol first produces a carboxylic ester-acid, which can then react with the bromoalkane to form the diester (Scheme 2). If the bromoalkane is omitted, the pigment dissolves with formation of perylenetetracarboxylic diester **7**, and a homogeneous solution is obtained.



Scheme 2. Esterification of PTCDA with alkanol and alkyl halide in homogeneous solution (3 h at 60 °C or 24 h at 25 °C, yield >80% for R = ethyl, propyl, or butyl).

We envisioned that the vicinal ester-acid groups could be labile to attack by various amines leading to expulsion of alcohol. Indeed it was found that if the addition order is alcohol, alkylamine, and then bromoalkane, with sufficient time between additions and using excess amounts of all components relative to the amine, a yield of carboxylic imido-diester of more than 50% with respect to the amine could be obtained at room temperature in a single step from PTCDA (**1**) (Scheme 3). After initial formation of diester-diacid **7**, addition of alkylamine led to the formation of imido-ester-acid **8**, which was finally treated with the bromoalkane to give imido-diester **4**.



Scheme 3. One-pot formation of imido-diester in homogeneous solution by sequential addition of alcohol, alkylamine, and alkyl halide (R_f = 0.45 in DCM on silica). Side products are the much less polar diimide [**3** with R = $CH(C_6H_{13})_2$, R_f = 0.8] and the much more polar tetraester (**2** with R = C_3H_7, R_f = 0.23). Yields are calculated with respect to the amine, using **1** in twofold excess.

As the reaction depends on the good initial dissolution of the pigment by incorporation of alcohol, the scope is limited to polar alcohols such as methanol, ethanol, or pro-

panol that quickly and efficiently achieve this dissolution. Longer chain alcohols such as 2-ethylhexan-1-ol (yielding flexible alkyl chain substituents that are efficient in stabilizing the liquid crystalline state) are inefficient at inducing solubilization. The main side product of the reaction is tetraester **2**, along with small quantities of carboxylic diimide **3**. Because an alkylimide group is intrinsically more lipophilic than two vicinal alkyl ester groups, the carboxylic diimide is more lipophilic than the tetraester, and the imido-diester has intermediate lipophilicity, as long as all alkyl groups are of similar size. Separation of the three products by column chromatography is possible as long as the combined size of the ester alkyl groups is similar to the size of the carboxylic imide alkyl group, and separation becomes trivial if the carboxylic imide alkyl group is much bigger than the combined ester alkyl groups: Trace amounts of carboxylic diimide are eluted with a lipophilic solvent that does not elute the targeted imido-diester. The latter can be eluted with a solvent of medium polarity leaving the tetraester on the column.

In order to freely choose the alkyl substituents on the ester groups, we then looked for a selective way to hydrolyze the initial short-chain esters without affecting the imide group. We found that this can be cleanly achieved by heating at reflux with sulfuric acid in acetic acid for a couple of hours – no trace of dianhydride was observed and the ester groups were quantitatively reverted to the corresponding anhydride.

Reaction of 7-aminotridecane, a long α-branched amine, a twofold excess of PTCDA (**1**) to minimize the formation of diimide, and an excess amount of propanol and 1-bromopropane as short alkyl reagents for esterification proceeded to give 58% yield of imido-diester **4a** in addition to 15% of the carboxylic diimide (73% combined yield with respect to the amine). Analytically pure imido-anhydride **5a** (R = 1-hexylheptyl) was obtained by acidic hydrolysis of **4a**. Esterification of **5a** with 2-ethylhexanol, 2-butyloctanol, or 2-hexyldecanol together with the corresponding 2-alkyl-1-bromoalkanes yielded the series of imido-diesters **4b**–**d** as brilliant red waxes. The UV/Vis absorption and fluorescence spectra of **4a**–**d** corresponded well to previously described spectra of the methyl ester,[9] and consequently were found to be independent of the esterifying alkyl groups. The spectra for **4a**–**d** were found to be about 10 nm more hypsochromic than those of diimides **3** (Figure 1). The fluorescence spectra were found to mirror the absorption spectra. The materials are highly fluorescent, with fluorescence quantum yields of 93, 98, 90, and 93% for **4a**–**d**, respectively, in chloroform.

The electronic system of **4** was further analyzed by quantum chemical DFT calculations of the N and O methyl analogues (Figure 2). The chromophore of **4** is found to be planar with the ester groups twisted out of the plane by about 30° (steric interactions are somewhat underestimated[16] by the DFT method; the AM1 method gave a twist of some 60°, and the real value may lie between these values). As a consequence, the ester groups are weakly coupled electronically to the chromophore, as can be seen by

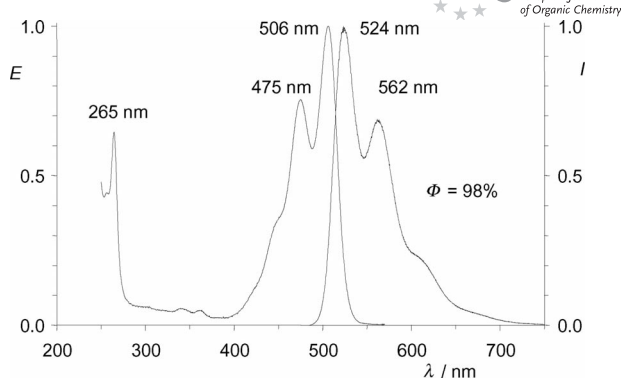


Figure 1. Absorption (left) and fluorescence (right) spectra of **4b** in chloroform.

the very slight contribution to the HOMO and LUMO. Light absorption in the visible region is estimated to be attributable to a pure π–π* transition according to the calculated orbitals in Figure 2. The central nodal planes in the HOMO and LUMO correspond to the analogous nodal planes in **3**[17] and are of special interest for labeling with **4** because the chromophore remains essentially unaffected by substituents at the nitrogen atom.

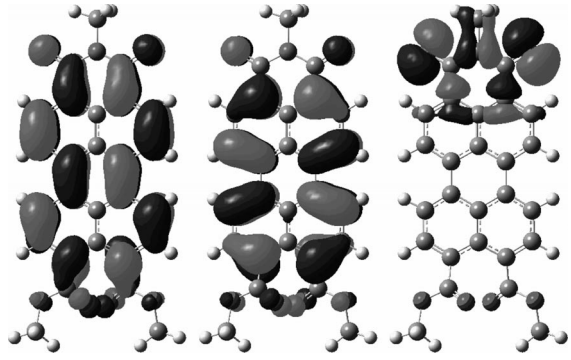
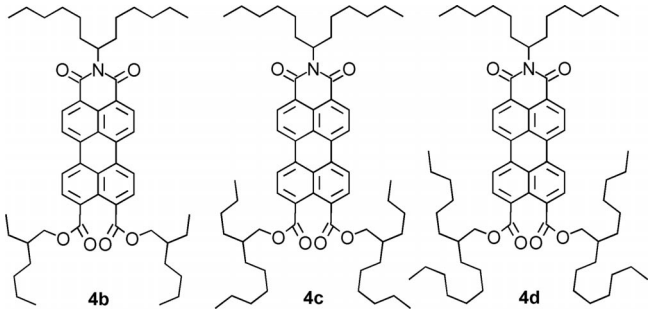


Figure 2. Quantum chemical calculated orbitals (DFT B3LYP) of the trimethyl derivative of **4**. From left to right: LUMO, HOMO, HOMO – 1 (second-highest occupied molecular orbital).

Mesogens **4b**–**d** form large hexagonal columnar mesophase ranges. Although 2-ethylhexyl derivative **4b** was, like propyl derivative **4a**, crystalline at room temperature with a single mesophase at higher temperature, higher homologues **4c** and **4d** were found to be liquid crystalline at room temperature (Scheme 4).

Differential scanning calorimetry was performed on all four homologues **4a**–**d** (Figure 3). Derivative **4a** showed a crystal to mesophase transition (melting point characterized by its large transition enthalpy and its appearance only on first heating) at 118 °C and a mesophase to isotropic liquid transition (clearing point) at 199 °C. Compound **4b** was found to melt at 69 °C and cleared at 252 °C. Both **4a** and **4b** showed no other (LC to LC) phase transitions between melting and clearing. Compound **4c** showed no large enthalpy melting, but a nonhysteretic small enthalpy transition at 8 °C that may be a mesophase to meso-



Scheme 4. Hexagonal columnar liquid crystalline imido-diesters with racemic alkyl ester substituents obtained by selective hydrolysis to the imido-anhydride.

phase transition, which was not characterized further given the low temperature; a clearing point of 192 °C was found for **4c**. Derivative **4d** showed no other transition above our lower limit of –30 °C other than clearing at 131 °C. The textures of all four homologues between glass plates by polarizing optical microscopy upon cooling through the clearing point consisted of homeotropic domains of hexagonal symmetry (Figure 4, left). Powder X-ray diffraction on **4d** at room temperature confirmed the hexagonal nature of the columnar mesophase with the presence of the characteristic (100), (110), and (210) reflections (Figure 4, right). The liquid crystalline feature was evidenced by the presence of a broad peak at about 1.8 $Å^{-1}$, characteristic of liquid-like order between the disk-shaped molecules within the columns.

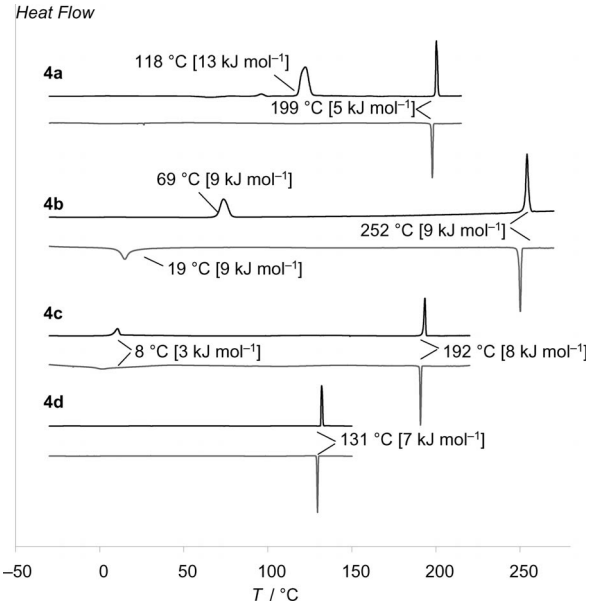


Figure 3. Differential calorimetry scans (heating in black, cooling in gray) of **4a**–**d** (5 K/min for **4a** and **4b**, 3 K/min for **4c** and **4d**). The temperatures given are onset temperatures. Transition enthalpies are given in brackets.

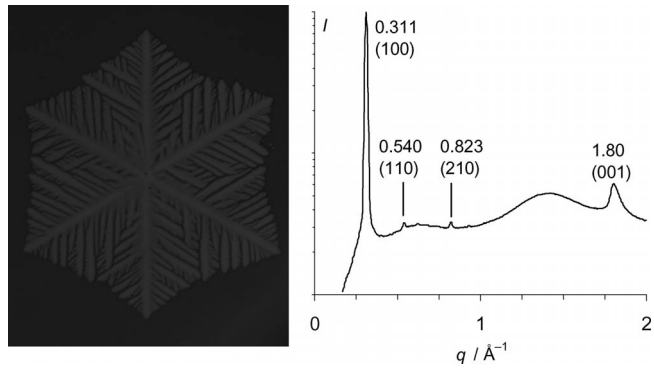


Figure 4. Left: homeotropic mesophase domain growing from the isotropic liquid between glass plates at cooling through the liquid to mesophase transition of **4c** (polarizing optical microscopy with slightly uncrossed polarizers, 0.5 mm × 0.6 mm). Right: powder X-ray diffraction spectrum of **4d** at room temperature (logarithmic intensity scaling). The indicated Miller indices correspond to a column lattice of hexagonal symmetry.

Conclusions

In summary, imido-diesters **4** with long branched alkyl chains are hexagonal columnar liquid crystals at room temperature. Combined with their known acceptor-type character and good absorption, this property makes them potentially interesting materials for use in organic electronic devices based on the unidirectional columnar self-assembly of energy pathways. The fluorescence quantum efficiency of **4** in dilute solution is close to unity. Imido-anhydrides **5**, from which the mesogens are obtained by esterification and which constitute versatile and important chromophore building blocks, are accessible by a novel and convenient two-step procedure involving the one-pot imidification–esterification of alkylamines with an excess amount of PTCDA, alcohol, and bromoalkane.

Experimental Section

General: IR spectra were recorded with a Perkin–Elmer 1420 Ratio Recording Infrared Spectrometer, FT 1000. UV/Vis spectra were recorded with a Varian Cary 5000 and a Bruins Omega 20. Fluorescence spectra were recorded with a Varian Eclipse. NMR spectra were recorded with a Bruker Advance 400 and a JEOL ECS 400 (400 MHz). Mass spectra were obtained with a Finnigan MAT 95. Fluorescence quantum yields were determined according to ref.[18]

***N*-(1-Hexylheptyl)-9,10-bis(propyloxycarbonyl)perylene-3,4-dicarboximide (4a):** A mixture of PTCDA (9.8 g, 25 mmol), DBU (15.2 g, 100 mmol), 1-propanol (13.6 g, 200 mmol), and DMF (100mL) was stirred at room temperature with the exclusion of moisture for 16 h (homogeneous solution was formed within the first hour). The mixture was treated with 7-aminotridecane (2.49 g, 12.5 mmol) and further stirred for 3 d. The mixture was then treated with 1-bromopropane (23 g, 200 mmol, beginning precipitation), stirred for another 16 h, and then treated with dichloromethane (DCM, 500 mL) and 5% aqueous HCl (500 mL). The organic phase was separated, and the aqueous phase was extracted with DCM (3 × 100 mL). The combined organic phases were evaporated, and the crude residue was subjected to column chromatography [silica gel; DCM/*n*-pentane, 2:1; for elution of the tetracarb-

oxylic bis(imide), 690 mg (from 1-butanol and completed with methanol), 15%; R_f (silica gel, DCM) = 0.8; then DCM for elution of **4a**; the tetraester remained on the column; R_f (silica gel, DCM) = 0.23]. Yield: 4.93 g (58% from ethanol and competed with methanol); bright red, shiny wax. R_f (silica gel, DCM) = 0.45. IR (ATR): $\tilde{\nu}$ = 3386 (w), 2954 (s), 2922 (s), 2854 (s), 2348 (w), 1921 (w), 1720 (m)1693 (s), 1655 (s), 1614 (s), 1591 (s), 1579 (m), 1511 (w), 1456 (m), 1415 (m), 1397 (w), 1350 (m), 1310 (m), 1292 (m), 1257 (m), 1200 (m), 1173 (m), 1156 (m), 1129 (w), 1097 (w), 1071 (m), 1038 (w), 930 (w), 845 (w), 826 (w), 805 (m) 745 (w), 699 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.57 (br., 2 H, ArH next to imide), 8.41 (d, J = 8 Hz, 2 H, ArH), 8.38 (d, J = 8 Hz, 2 H, ArH), 8.07 (d, J = 8 Hz, 2 H, ArH), 5.18 (tt, J = 9, 8 Hz, 1 H, NCH), 4.31 (t, J = 7 Hz, 4 H, OCH_2), 2.25 (m, 2 H, one H of CH_2 next to NCH), 1.85 (m, 2 H, other H of CH_2 next to NCH), 1.83 (sext., J = 7 Hz, 4 H, propyl-CH_2), 1.39–1.17 (m, 16 H, CH_2), 1.05 (t, J = 7 Hz, 6 H, propyl-CH_3), 0.82 (t, J = 7 Hz, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 164.7 & 163.7 (two broad peaks of the imide carbonyls[17]); 134.8, 131.8, 131.7, 131.6 & 130.8 (br.[17]); 130.1, 129.1, 129.0, 128.8, 125.6, 122.7 & 121.9 (br.[17]); 122.1, 121.6, 67.2, 54.6, 32.4, 31.8, 29.2, 27.0, 22.6, 22.0, 14.0, 10.5 ppm. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 474.2 (0.75), 505.8 nm (1.00). Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 523.0 (1.00), 562.3 nm (0.68). Fluorescence quantum yield ($CHCl_3$, λ_{ex} = 474 nm, $E_{474\ nm/1\ cm}$ = 0.0143, ref.[16] **1** with Φ = 1.00): 0.93 ppm. MS (70 eV): m/z (%) = 364.06 (21.06), 392.06 (53.73), 493.16 (100.00), 494.16 (51.44), 675.36 (99.65), 676.36 (49.43). $C_{43}H_{49}NO_6$ (675.9): calcd. C 76.42, H 7.31, N 2.07; found C 76.39, H 7.46, N 2.01.

***N*-(1-Hexylheptyl)perylene-3,4-dicarboximide-9,10-dicarboxylic Anhydride (5a):**[19] Imido-diester **4a** (3.5 g, 51.8 mmol) was suspended in a mixture of concentrated sulfuric acid (3.5 g) and glacial acetic acid (100 g). The mixture was heated at reflux for 2 h, allowed to cool to room temperature, and poured into water (100 mL). The solid was collected by vacuum filtration, washed with distilled water, and dried in vacuo. Yield: 2.95 g (99%, 51.4 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.69 (br., 2 H, ArH next to imide), 8.65 (d, J = 8 Hz, 2 H, ArH), 8.63 (d, J = 8 Hz, 2 H, ArH), 8.61 (d, J = 8 Hz, 2 H, ArH), 5.17 (tt, J = 9, 8 Hz, 1 H, NCH), 2.23 (m, 2 H, CH_2), 1.92–1.82 (m, 2 H, CH_2), 1.38–1.17 (m, 16 H, CH_2), 0.82 (t, J = 7 Hz, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4 & 163.3 (br.[17]) 159.9, 136.4, 133.6 (2 C), 132.0 & 131.2 (br.), 131.8, 129.5, 126.7, 126.5, 124.7 & 123.9 (br.), 124.1, 123.1, 119.0, 54.9, 32.4, 31.8, 29.2, 26.9, 22.6, 14.0 ppm. $C_{37}H_{35}NO_5$ (573.7): calcd. C 77.46, H 6.15, N 2.44; found C 77.23, H 6.15, N 2.43.

9,10-Bis(2-hexyldecyloxycarbonyl)-*N*-(1-hexylheptyl)perylene-3,4-dicarboximide (4d): A solution of imido-anhydride **5a** (2.5 g, 43.6 mmol), DBU (5 g), 1-bromo-2-hexyldecane (10 g), and 2-hexyldecan-1-ol (10 g) in ethyl acetate (200 mL) was stirred at 60 °C for 16 h under exclusion of moisture and treated with DCM (500 mL) and 5% aqueous HCl (500 mL). The organic layer was collected, and the aqueous layer was extracted with DCM (3 × 100 mL). The combined organic phases were evaporated, dissolved in a small amount of DCM, precipitated with methanol, collected by vacuum filtration, purified by column separation (silica gel, DCM), dissolved in DCM and recrystallized from 2-propanol; the product precipitates not in the crystalline state, but in the columnar liquid crystalline state. Yield: 3.45 g (76%); brilliant red wax. IR (ATR): $\tilde{\nu}$ = 2953 (s), 2921 (s), 2853 (s), 1709 (s), 1694 (s), 1656 (s), 1594 (s), 1524 (w), 1511 (m), 1465 (m), 1457 (m), 1415 (m), 1397 (w), 1377 (w), 1351 (s), 1308 (w), 1292 (s), 1262 (s), 1200 (m), 1168 (s), 1104 (m), 1070 (m), 1035 (w), 1001 (w), 947 (w), 844 (m), 825 (w), 805 (m), 745 (m), 723 (w), 700 (w), 641 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.60 (br., 2 H, ArH), 8.45 (d, J = 8 Hz, 2 H, ArH), 8.43 (d, J = 8 Hz, 2 H, ArH), 8.07 (d, J = 8 Hz, 2 H, ArH), 5.18 (tt, J = 9, 6 Hz, 1 H, NCH), 4.25 (d, J = 6 Hz, 4 H, OCH_2), 2.25 (m, 2 H, CH_2), 1.91–1.78 (m, 4 H, CH & CH_2), 1.49–1.17 (m, 64 H, CH_2), 0.87 (t, J = 7 Hz, 6 H, CH_3), 0.86 (t, J = 7 Hz, 6 H, CH_3), 0.82 (t, J = 7 Hz, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 164.8 & 163.7 (br.[17]), 135.1, 132.0, 131.9, 131.7 & 131.0 (br.), 130.0, 129.3, 129.2, 129.0, 125.8, 122.7 & 122.0 (br.), 122.4, 121.6, 68.5, 54.5, 37.4, 32.4, 32.0, 31.9, 31.8, 31.4 (2×), 30.1, 29.71, 29.66, 29.4, 29.3, 27.0, 26.8, 26.7, 22.7 (2×), 22.6, 14.1 (2×), 14.0 ppm. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 474.8 (0.76), 506.6 nm (1.00). Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 523.6 (1.00), 562.4 nm (0.68). Fluorescence quantum yield ($CHCl_3$, λ_{ex} = 475 nm, $E_{475\ nm/1\ cm}$ = 0.0136, ref.[16] **1** with Φ = 1.00): 0.93 ppm. MS (70 eV): m/z (%) = 392.05 (29.65), 574.25 (22.21), 1039.76 (100.00), 1040.77 (74.17), 1041.77 (27.19). $C_{69}H_{101}NO_6$ (1040.9): calcd. C 79.64, H 9.78, N 1.35; found C 79.80, H 10.00, N 1.17.

9,10-Bis(2-butyloctyloxycarbonyl)-*N*-(1-hexylheptyl)perylene-3,4-dicarboximide (4c): Imido-anhydride **5a** (1.0 g, 1.74 mmol), DBU (2 g, 13 mmol), 1-bromo-2-butyloctane (4.0 g, 16 mmol), 2-butyloctan-1-ol (4 g, 21 mmol), and ethyl acetate (100 mL) were allowed to react in a fashion analogous to that of **4d**. Yield: 1.24 g (77%); red wax. IR (ATR): $\tilde{\nu}$ = 2953 (s), 2922 (s), 2855 (s), 1710 (s), 1694 (s), 1656 (s), 1593 (s), 1524 (w), 1511 (m), 1466 (m), 1456 (m), 1416 (m), 1397 (w), 1378 (w), 1350 (s), 1308 (w), 1292 (s), 1260 (s), 1200 (s), 1168 (s), 1104 (m), 1070 (m), 1036 (w), 948 (w), 844 (m), 825 (w), 805 (m), 773 (w), 746 (m), 725 (w), 700 (w), 641 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.61 (br., 2 H, ArH), 8.49 (d, J = 8 Hz, 2 H, ArH), 8.46 (d, J = 8 Hz, 2 H, ArH), 8.08 (d, J = 8 Hz, 2 H, ArH), 5.19 (tt, J = 9, 6 Hz, 1 H, NCH), 4.26 (d, J = 6 Hz, 4 H, OCH_2), 2.25 (m, 2 H, CH_2), 1.91–1.77 (m, 4 H, CH & CH_2), 1.51–1.16 (m, 48 H, CH_2), 0.92 (t, J = 7 Hz, 6 H, CH_3), 0.88 (t, J = 7 Hz, 6 H, CH_3), 0.82 (t, J = 7 Hz, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 164.9 & 163.8 (br.[17]), 135.4, 132.2, 132.0, 131.9 & 131.1 (br.), 130.1, 129.5, 129.4, 129.3, 126.0, 122.8 & 122.1 (br.), 122.5, 121.8, 68.5, 54.6, 37.4, 32.4, 31.9, 31.8, 31.4, 31.0, 29.7, 29.2, 29.0, 26.9, 26.7, 23.0, 22.7, 22.6, 14.1 (2×), 14.0 ppm. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 474.8 (0.76), 506.6 nm (1.00). Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 523.4 (1.00), 562.2 nm (0.69). Fluorescence quantum yield (λ_{ex} = 475 nm, $E_{475\ nm/1\ cm}$ = 0.0150, $CHCl_3$, ref.[16] **1** with Φ = 1.00): 0.90 ppm. MS (70 eV): m/z (%) = 392.05 (28.06), 927.64 (100.00), 928.64 (62.77). $C_{61}H_{85}NO_6$ (928.4): calcd. C 78.92, H 9.23, N 1.51; found C 79.18, H 9.32, N 1.44.

9,10-Bis(2-ethylhexyloxycarbonyl)-*N*-(1-hexylheptyl)perylene-3,4-dicarboximide (4b): Imido-anhydride **5a** (500 mg, 0.87 mmol), DBU (1.0 g, 7 mmol), 1-bromo-2-ethylhexane (2.0 g, 10 mmol), 2-ethylhexan-1-ol (2.0 g, 15 mmol), and ethyl acetate (50 mL) were allowed to react in a fashion analogous to that of **4d**. Yield: 570 mg (80%); red wax. IR (ATR): $\tilde{\nu}$ = 2955 (s), 2922 (s), 2855 (s), 1709 (s), 1692 (s), 1654 (s), 1614 (w), 1594 (s), 1524 (w), 1512 (m), 1458 (m), 1416 (m), 1400 (w), 1378 (w), 1351 (s), 1292 (s), 1259 (s), 1199 (s), 1169 (s), 1104 (s), 1070 (m), 1036 (m), 948 (w), 856 (w), 843 (m), 825 (w), 805 (m), 773 (w), 746 (m), 726 (w), 700 (w), 682 (w), 671 (w), 639 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.63 (br., 2 H, ArH), 8.52 (d, J = 8 Hz, 2 H, ArH), 8.49 (d, J = 8 Hz, 2 H, ArH), 8.10 (d, J = 8 Hz, 2 H, ArH), 5.19 (tt, J = 9, 6 Hz, 1 H, NCH), 4.29 (dd, J = 10, 6 Hz, 2 H, OCH_2), 4.25 (dd, J = 10, 6 Hz, 2 H, OCH_2), 2.24 (m, 2 H, 1 H of CH_2 next to NCH), 1.90–1.75 (m, 4 H, CH & 1 H of CH_2 next to NCH), 1.53–1.17 (m, 32 H, CH_2), 0.97 (t, J = 7 Hz, 6 H, CH_3), 0.91 (t, J = 7 Hz, 6 H, CH_3), 0.82 (t, J = 7 Hz, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 164.9 & 163.8 (br.[17]), 135.4, 132.2, 132.0, 131.9 & 131.1 (br.), 130.1, 129.5, 129.3, 129.3, 126.1, 122.8 & 122.1 (br.), 122.6,

121.9, 68.1, 54.6, 38.8, 32.4, 31.8, 30.5, 29.3, 29.0, 26.9, 23.9, 23.0, 22.6, 14.1 (2×), 11.0 ppm. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 474.6 (0.75), 506.0 nm (1.00). Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 524.3 (1.00), 561.6 nm (0.69). Fluorescence quantum yield ($CHCl_3$, λ_{ex} = 475 nm, $E_{475\ nm/1\ cm}$ = 0.0153, ref.[16] **1** with Φ = 1.00): 0.98 ppm. MS (70 eV): *m/z* (%) = 392.06 (31.07), 633.30 (19.97), 815.51 (100.00), 816.51 (53.48). $C_{53}H_{69}NO_6$ (816.13): calcd. C 78.00, H 8.52, N 1.72; found C 78.31, H 8.76, N 1.64.

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[8] Note that carboxylic diimides **3** with one or both of the branched chains being 2,5,8,12,15,18-hexaoxanonadec-10-yl or 2,5,8,11,15,18,21,24-octaoxapentacos-13-yl have been reported to come close to room-temperature stability, with melting points between 50 and 80 °C and clearing points between 100 and 160 °C (see ref.[3c]).

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