Perylene-Derived Dyes

Synthesis, Photophysical Properties, and Nanocrystal Formation of a New Class of Tetra-N-Substituted Perylenes**

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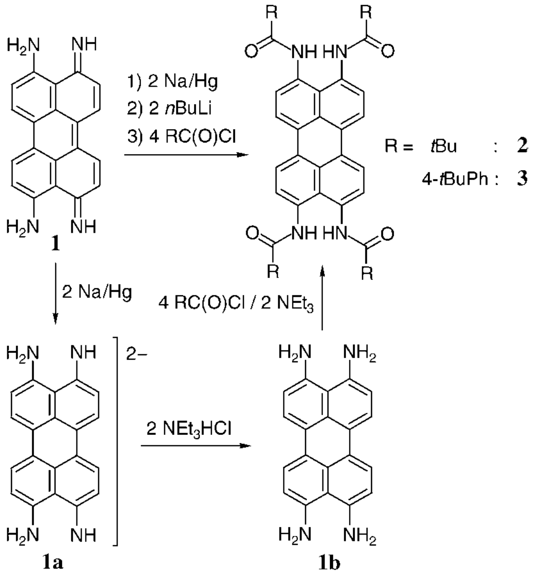
Perylenes as pigments and fluorescent dyes have found wide ranging applications in very diverse fields of current research.[1–3] There are very few examples of tetra-N-substituted perylenes to be found in the literature to date which is because of the cumbersome nature of the established preparative methods.[4] We recently discovered a novel and efficient route to 4,9-diaminoperylenequinone-3,10-diimines[5] and showed that it is possible to convert these quinoidal systems to the reduced 3,4,9,10-tetraaminoperylenes,[6] a class of compounds which has very recently been cited in the patent literature of photovoltaic devices.[7]

However, these tetraaminoperylenes have extremely negative redox potentials, which leads to their instantaneous reoxidation when exposed to air and makes them impossible to manipulate under the conditions normally encountered in dye chemistry. Herein we report the first successful stabilization of such derivatives in the form of their carboxamides. In a sense, these compounds are perylene derivatives that are inversely functionalized with respect to the ubiquitous perylenebisimides.[8,9] Furthermore we show that these compounds can form very interesting rod-shaped structures that are promising candidates as building blocks in self-assembled functional nanostructures.

The treatment of 4,9-diaminoperylenequinone-3,10-diimine (**1**)[5a,6] with two molar equivalents of sodium amalgam or potassium metal in THF and subsequent deprotonation of the dianion **1a** with two equivalents of *n*-butyllithium gave a nonisolable tetraanionic intermediate. The addition of four molar equivalents of pivalyl chloride and 4-*tert*-butylbenzoyl chloride to this intermediate gave the corresponding carboxamides 3,4,9,10-[*t*BuC(O)NH]$_4$C$_{20}$H$_8$ (**2**) and 3,4,9,10-[(4′-*t*BuPh)C(O)NH]$_4$C$_{20}$H$_8$ (**3**) with a high yield. (Scheme 1). An equally efficient preparative route involves the neutral tetraaminoperylene **1b** obtained by controlled protonation of **1a** and subsequent coupling with the carboxyl chlorides.



Scheme 1. Synthesis of the tetra(carboxamido)perylenes **2** and **3**.

Whereas compound **2** is readily soluble in polar solvents, such as CH$_2$Cl$_2$, THF, or dimethyl sulfoxide, the 4-*tert*-butylphenyl substituted derivative **3** is much less so and only dissolves readily in DMSO. Both compounds were characterized by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy, and infrared spectroscopy.

Crystals of compound **2** suitable for an X-ray diffraction study were grown from dimethyl sulfoxide at room temperature. The molecule of **2** has exact crystallographic C_i symmetry (Figure 1a) with two dimethyl sulfoxide solvent molecules hydrogen bonded to two centrosymmetrically related carboxamido hydrogen atoms of **2** through their oxygen atoms (O1s···H1N 2.30 Å).[10] There is evidence of hydrogen bonding between the two adjacent independent carboxamido groups (N(1)···H(2N) 2.06 Å).

The most remarkable feature of the molecular structure of **2** is the lack of coplanarity of the perylene core and its carboxamido substituents (Figure 1b). The aromatic hydrocarbon core shows a slight twisting (maximum deviation from planarity 0.15 Å for C(1)) but the two independent carboxamido groups are markedly rotated relative to this plane

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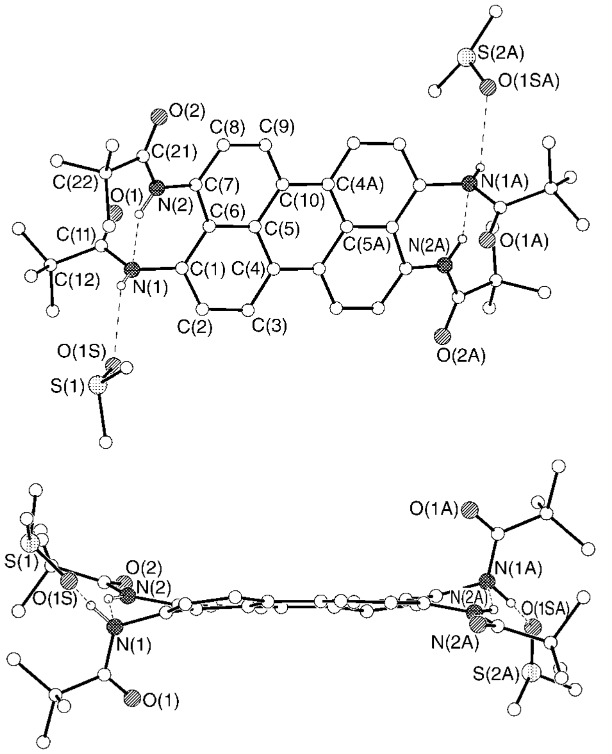

Figure 1. Molecular structure of compound **2**. Views orthogonally to the polyaromatic plane (a) and along a bisecting vector in the perylene unit (b) showing the distortion of the four carboxamido groups out of the molecular plane.

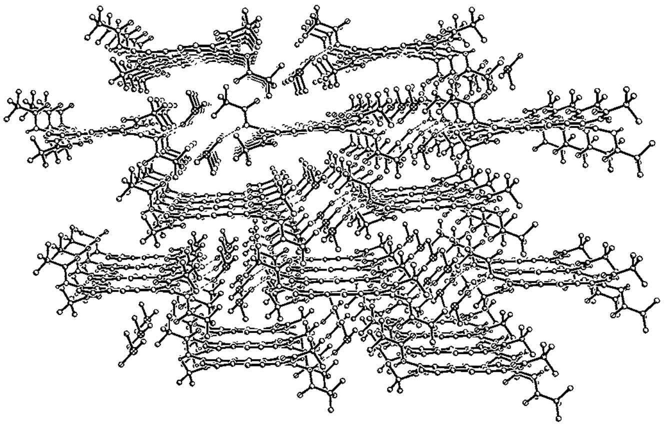

Figure 2. The packing of the perylene layers in the crystal.

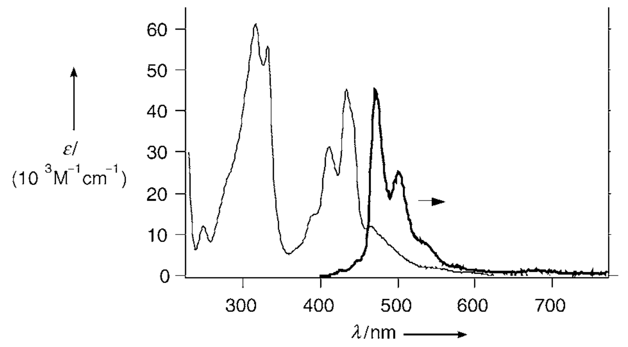

Figure 3. UV/Vis absorption and emission spectra of compound **3** in dichloromethane. The emission was recorded upon 392 nm excitation of 7×10^{-6} M solution by using a 400 nm cutoff filter. I = intensity, λ = wavelength.

(dihedral angles N(1)-O(1)-C(11)-C(12) 86.2°; N(2)-O(2)-C(21)-C(22) 22.8°). This marked overall twisting of the molecule may be attributed to mutual repulsion between the bulky pivalyl substituents. We note that deviations from planarity of perylene units were reported and studied previously.[11]

The carbon–carbon bond lengths C(2)–C(3), C(8)–C(9), and C(4)–C(10A) of 1.386(4), 1.394(5), and 1.469(4) Å, respectively, are similar to the corresponding interatomic distances in the unsubstituted parent perylene (1.394(3) and 1.476(3) Å)[12] as well as those established for a large number of perylene tetracarboximides.[13]

The molecules in the crystal are all parallel and arranged in approximately planar layers, each consisting of rows of molecules running along the *b* axes of the unit cells (Figure 2a); adjacent rows are separated by the hydrogen-bonded solvent DMSO molecules. The parallel layers aggregate in an "AB pattern" (Figure 2) with alternate layers lying above each other, and adjacent layers staggered. This arrangement appears to be unique in perylene chemistry.

Both **2** and **3** are dark orange-red in the solid state, and yellow to red, depending on the concentration, in dichloromethane solution. Although the composition and structures of the two compounds appear to be very similar, their absorption and emission characteristics differ significantly.[14,15] The UV/Vis apsorption and emission spectra of compound **3**, recorded in CH_2Cl_2, are shown in Figure 3. The symmetry observed in the relation between the absorption and emission spectra of this derivative is a clear indication of its monomeric nature at the concentration chosen in this study (7×10^{-6} M). The fluorescence quantum yield is $\Phi_{fl} = 0.092$ with a lifetime of $\tau_{fl} = 1.77$ ns for compound **3**. From the overlap of the spectra of the two compounds, the singlet state energies are determined to be 460 and 507 nm ($^1E_{00} = 2.7$ and 2.45 eV) for **3** and **2**, respectively.

The UV/Vis absorption spectra of compound **2** in dichloromethane turned out to be virtually concentration independent. However, whereas compound **3** is only sparingly soluble in dichloromethane, its behavior in DMSO is very different and at high concentrations (10^{-2} M) gives rise to magenta solutions. Upon dilution, compound **3** display significantly altered photophysics (Figure 4) indicating aggregation. The absorption is strongly red-shifted and broadened relative to the monomer, with a maximum at 574 nm ($\varepsilon = 3\times10^4$ mol^{-1}cm^{-1}), while the emission of the aggregated form is located at 690 nm, and has much lower quantum yield (10^{-2}).

A fresh magenta solution of the compound at high concentration (10^{-3} M) was studied with scanning probe microscopy (AFM-tapping mode; AFM = atomic force microscopy) (Figure 5).[16] The sample consists of long rod-type structures with a length between 100 and 400 nm, a width of approximately 40 nm and a height of only 2 nm. The observed structures can best be described as nanocrystals.[17] Related structures have been studied,[17a–b] which were made

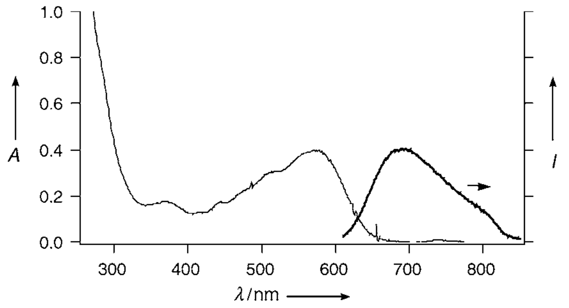

Figure 4. UV/Vis absorption ($l = 1$ mm) and emission spectra of the magenta aggregated form of compound **3** in DMSO. Concentration is 1.3×10^{-4} M; the emission was recorded upon 500 nm excitation by using a 550 nm cutoff filter. A = Absorbance.

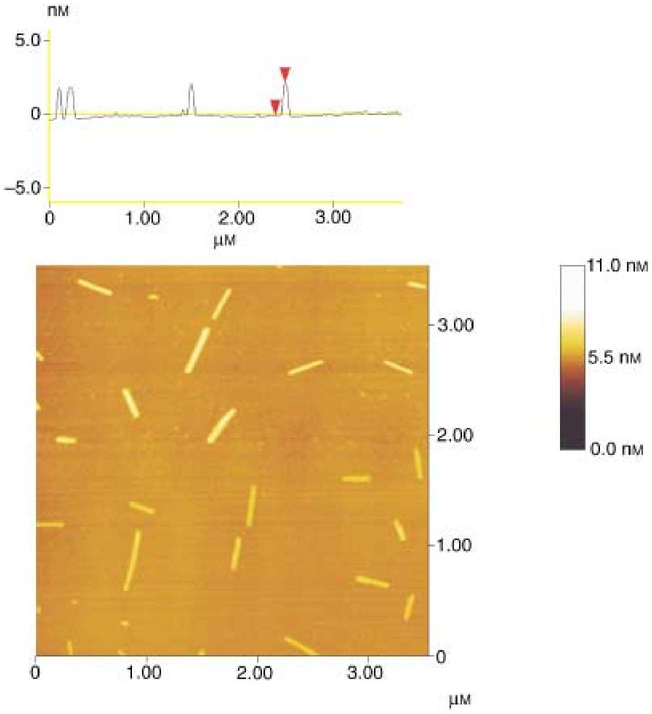

Figure 5. AFM image obtained with a purple solution of compound **3** in DMSO (10^{-3} M) on mica by using the tapping mode. The top section shows a height profile, which indicates a very narrow height distribution.

by the reprecipitation method (involving injection of perylene solutions into hot water).[17c] They can be considered a special form of "Scheibe" or J aggregates[17d–g] because of their linear rod-type shape even though we do not have a direct spectroscopic evidence of their nature. Noteably, the solvent, DMSO, plays a major role in the formation of the rods, and it is the only solvent in which it was possible to grow such nanocrystals.

From the assumption that the molecular network in the crystallites of **3** is similar to that established for compound **2** by single-crystal X-ray diffraction, an interesting picture of these Scheibe polymers emerges. Since the unit cell, which in the case of **2** contains one perylene molecule, has dimensions in the order of 1 nm, the nanocrystal rods generated by the stacking of molecular units would contain two molecules in one dimension. We observed that the length of the rods is sensitive to the concentration of the solution from which they are obtained (maximum lengths of several microns). A coalescence effect was observed with AFM, by adjusting the concentration of the solution, although the thickness of the aggregates remained essentially unchanged.

Given the proposed molecular stacking, the transition dipole moment (along the long axis of the molecule) is most likely to be perpendicular to the long axis of the nanocrystal, a notion which we plan to establish in a future systematic structural study of related derivatives. The possibility of assembling nanosize rods is essential for the construction of nanoelectronic devices, and the molecular assembly of conducting self-assembled wires remains a challenge in this field.

In this first investigation into a new class of perylene-derived dyes we have shown that the chosen synthetic approach to the tetra-N-substituted derivatives opens up the possibility of a wide range of further modifications of the chromophores, in particular their use in extended functional supramolecular arrays based on well-defined building principles, such as nanoscopic rods. We are currently aiming to construct a more rigid auxochromic periphery, which is thought to increase the emission quantum yields of these fluorescent dyes, thus bringing them closer to potential applications.

Experimental Section

Preparation of 3,4,9,10-[RC(O)NH]$_4$C$_{20}$H$_8$: A solution of compound **1** (310 mg = 1.00 mmol) in THF (30 mL) was slowly added at ambient temperature to freshly prepared sodium amalgam (Na: 2.00 mmol). After stirring the deep blue solution for 3 days, a 2.5 M solution of n-butyllithium in n-hexane (1.00 mL = 2.50 mmol) was added. After the reaction mixture was stirred for another 18 h at ambient temperature the blue-violet solution was decanted from the metallic mercury by using canula–septa techniques. The solution of the tetraanion, thus obtained, was slowly added to a solution of 4.10 mmol of the acid chloride dissolved in cooled THF (−30 °C, 40 mL). After the product mixture was stirred for 48 h at ambient temperature the solvent was removed in vacuo and the residue washed with water (100 mL), acetone (20 mL) and, finally, n-pentane (30 mL). After recrystallization from DMSO, compounds **2** and **3** were obtained as air stable, orange microcrystalline solids, which were washed with diethyl ether and then dried in vacuo.

3,4,9,10-[tBuC(O)NH]$_4$C$_{20}$H$_8$ (**2**): Yield: 78 %. M.p.: 268 °C. ^{1}H NMR (400.13 MHz, (CD$_3$)$_2$SO, 295 K): $\delta = 1.29$ (s, 36 H, C(CH$_3$)$_3$), 7.73 (d, 4 H, $^3J_{\mathrm{HaHb}} = 8.4$ Hz, H^a, C$_{20}$H$_8$), 8.31 (d, 4 H, H^b, C$_{20}$H$_8$), 9.64 ppm (s, 4 H, NH). {^{1}H}^{13}C NMR (100.61 MHz, (CD$_3$)$_2$SO, 295 K): $\delta = 27.3$ (C(CH$_3$)$_3$), 39.6 (C(CH$_3$)$_3$), 121.1 (CH, C$_{20}$H$_8$), 124.1 (CH, C$_{20}$H$_8$), 124.5 (C, C$_{20}$H$_8$), 128.2 (C, C$_{20}$H$_8$), 129.2 (C, C$_{20}$H$_8$), 134.3 (CN, C$_{20}$H$_8$), 178.3 ppm (CO). IR (KBr): $\tilde{\nu} = 3340$ (vbr m), 3119 (vw), 2965 (s), 2932 (m), 2906 (m), 2870 (m), 1680 (s), 1623 (s), 1591 (s), 1519 (br vs), 1479 (s), 1430 (m), 1398 (m), 1366 (m), 1285 (vs), 1202 (s), 1172 (s), 1138 (vs), 1104 (s), 1050 (m), 1015 (m), 931 (m), 819 (m), 629 (w), 571 cm^{-1}(w); elemental analysis calcd. for C$_{40}$H$_{48}$N$_4$O$_4$ ($M_r = 648.85$): C 74.05, H 7.46, N 8.63; found: C 73.99, H 7.32, N 8.45.

3,4,9,10-[(4′-tBuPh)C(O)NH]$_4$C$_{20}$H$_8$ (**3**): Yield: 66 %, M.p.: 286 °C (dec.); ^{1}H NMR (200.13 MHz, (CD$_3$)$_2$SO, 295 K): $\delta = 1.26$ (s, 36 H, C(CH$_3$)$_3$), 7.27 (d, 8 H, $^3J_{\mathrm{H2H3}} = 8.4$ Hz, H^3, C$_6$H$_4$), 7.71 (d, 4 H, $^3J_{\mathrm{HaHb}} = 8.3$ Hz, H^a, C$_{20}$H$_8$), 7.83 (d, 8 H, H^2, C$_6$H$_4$), 8.42 (d, 4 H, H^b, C$_{20}$H$_8$), 10.74 ppm (s, 4 H, NH); {^{1}H}^{13}C NMR (100.61 MHz, (CD$_3$)$_2$SO, 295 K): $\delta = 31.3$ (C(CH$_3$)$_3$), 34.9 (C(CH$_3$)$_3$), 118.8 (C, C$_{20}$H$_8$), 121.3

(CH, $C_{20}H_8$), 125.0 (CH, C_6H_4), 125.1 (CH, $C_{20}H_8$), 127.1 (C, $C_{20}H_8$), 128.1 (CH, C_6H_4), 129.1 (C, $C_{20}H_8$), 131.6 (C, C_6H_4), 133.7 (CN, $C_{20}H_8$), 154.6 (C, C_6H_4), 165.9 ppm (CO); IR (KBr): $\tilde{\nu} = 3385$ (vbr m), 3274 (vbr m), 3058 (w), 2963 (vs), 2906 (m), 2869 (m), 1655 (s), 1611 (m), 1593 (m), 1524 (vs), 1497 (vs), 1461 (s), 1409 (s), 1363 (m), 1301 (s), 1265 (vs), 1106 (br s), 1020 (s), 848 (m), 816 (s), 703 cm^{-1} (m); elemental analysis calcd. for $C_{64}H_{64}N_4O_4$ ($M_r = 953.24$): C 80.64, H 6.77, N 5.88; found: C 80.37, H 6.61, N 5.86. UV/Vis data. **2**: $\lambda_{max}(\varepsilon) = 271$ (33690), 382 (14960), 442 (36020), 465 nm (45980 $M^{-1}cm^{-1}$); **3**: $\lambda_{max}(\varepsilon) = 248$ (11860), 316 (61154), 332 (55497), 390 (sh) (14560), 412 (31155), 434 (45010), 466 nm (sh) (11859 $M^{-1}cm^{-1}$).

X-ray Crystallographic Study of **2**: X-ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer. Formula $C_{40}H_{48}N_4O_4 \cdot 2(C_2H_6OS)$, Crystal size $0.4 \times 0.2 \times 0.1$ mm, $M = 808.08$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.0280(16)$, $b = 10.213(2)$, $c = 11.504(2)$ Å, $\alpha = 84.843(13)$, $\beta = 72.388(15)$, $\gamma = 74.140(15)°$, $V = 1080.2(3)$ Å^3, $Z = 1$, $\rho_{calc} = 1.238\ g\,cm^{-3}$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 0.174\ mm^{-1}$, $F(000) = 432$. Reflections collected: 5832, Data/restraints/parameters = 2188/0/287, GOF = 1.100, $R_1 = 0.0634$, $wR_2 = 0.1752$, max and min $\Delta\rho = +0.644/-0.467\ e$ Å^{-3}. The structure was solved using direct methods (SHELXL 97).[18] The asymmetric unit only contains one half of a perylene molecule and a DMSO molecule, the other half being generated by the symmetry operation $-x+2, -y, -z+2$). The amino hydrogen atoms were directly located and their positions refined. All other hydrogen atoms were placed in calculated positions with displacement parameters set equal 1.2 U_{eq} (or 1.5 U_{eq} for methyl groups) of the parent carbon atoms. The DMSO molecule in the asymmetric unit was disordered in a 50:50 ratio between two sites. In the final cycles of full-matrix least-squares refinement the non-hydrogen atoms (except for the disordered carbon atom C3S of the DMSO molecule) were assigned anisotropic displacement parameters. CCDC 205348 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[14] Emission spectra were recorded on a SPEX Fluorolog I (1681) instrument equipped with an R928 photomultiplier (Products for Research) and were measured on dilute solutions by using a 395 nm (emission-path) cut-off filter. Corrections for the photomultiplier sensitivity were applied to the emission spectra. For determination of the emission quantum yields, using the "optical dilute relative method",[13a] bis(di-*tert*-butylphenyl)perylenebisi-

mide in air-saturated dichloromethane ($\Phi_{em} = 0.99$)[13b] was used as a standard. Quantum yields and lifetimes are reported or air saturated dichloromethane solutions. The excitation wavelength was 392 nm, and the optical density of both the reference and the sample was adjusted to 0.1 (1 cm) at this wavelength. Absorption spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer, using 1 nm bandwidth. Time resolved emission was recorded with a Hamamatsu C-5680 streak camera equipped with an M 5677 sweep unit. Excitation was performed with a LTB, MGS 450 TD nitrogen laser (337 nm, 600 ps) operating at 10 Hz. a) J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991; b) W. E. Ford, P. V. Kamat, *J. Phys. Chem.* **1987**, *91*, 6373.

[15] Compound **2** displays rather sharp absorption features, with maxima observed at 271, 382, 442, 466 nm (see also Experimental Section) and a tailing band, with the last maximum at 572 nm, which is significantly beyond the emission maximum at 530 nm (the typical wavelength for the first emission maximum for perylenebisimides). The position of the absorption band maximum at 466 nm and symmetrically featured emission band at 530 nm indicates a rather large stokes shift of 2591 cm^{-1}. The emission at 530 nm, which we attribute to single, nonaggregated dye molecules, displays a moderate quantum yield of emission ($\Phi_{fl} = 0.091$) with a normal fluorescence lifetime ($\tau_{fl} = 4.4$ ns). Remarkably both the absorption and emission maxima of 3,4,9,10-$[(4'\text{-}t\text{BuPh})C(O)NH]_4C_{20}H_8$ (**3**) are blue-shifted with respect to the pivalyl-substituted compound **2**. It appears that the larger amide substituents introduce steric crowding at the N-amido functions, making them turn out of the plane of the aromatic ring system, thus canceling the enhanced conjugation and red shift (auxochromic effect) as observed with **2**, and making the absorption and emission characteristics much more like perylene itself. Absorption maxima are observed at 248, 316, 323, 390 (sh), 411, 434, and 465 nm, and vibrationally resolved emission is displayed at 471, 501, and 537 nm (sh). The Stokes shift based on the 434 and 471 nm maxima is 1810 cm^{-1}.

[16] For scanning force microscopy (SFM) investigations, the substance was dissolved in DMSO and dropped onto freshly cleaved mica surfaces and dried in vacuo. SFM inspections were performed with a commercial instrument (Digital Instruments, Nanoscope IIIa, Dimension 3000, Santa Barbara, CA) running in the tapping mode. Silicon cantilevers (Nanosensors) with a resonant frequency of 250–350 kHz were used for the experiments. AFM images obtained under identical conditions with compound **3** from a saturated dichloromethane only displayed a featureless aggregation, which indicates that this phenomenon is directly associated with the incorporation of the solvent.

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