

Functionalized Nanoparticles

Grafting Perylenes to ZnO Nanoparticles

Jörg Schönamsgruber, Lukas Zeininger, and Andreas Hirsch^{*[a]}

Abstract: A new prototype of dendritic perylenes suitable for the chemical functionalization of inorganic nanoparticles was synthesized and characterized. The bay-functionalized perylene core of these molecular architectures was coupled to a catechol moiety, which serves as an anchor group for the functionalization of metal oxides, in particular ZnO. To increase the solubility of both the perylene and the targeted hybrid nanostructures, a Newkome-type dendron bearing nine positive charges was introduced. This charge was also

Introduction

Perylene-3,4,9,10-tetracarboxylic acid diimides (bis-imides; PDI, PBI; Figure 1) are widely investigated and used in scientific studies.^[1] They are also produced as excellent stable pigments in the chemical industry. A well-known example is the deep red dye Pigment Red 179 (Figure 1, PDI: R=methyl), which was first reported in 1913.^[2] As mother compound for PDIs, perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA) is used. Solubility can be controlled by synthesizing PDIs with dif-



benzimidazole derivative

Figure 1. Perylene-3,4,9,10-tetracarboxylic acid diimide (PDI), perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA), and benzimidazole derivative.

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employed to stabilize the nanoparticles and further protect them from Ostwald ripening through Coulombic repulsion. ZnO quantum dots with an average diameter of 5 nm were synthesized and functionalized with the perylene derivative. Successful functionalization was clearly demonstrated by dynamic light scattering, zeta-potential measurements, thermogravimetric analysis/MS, and UV/Vis and fluorescence spectroscopy. The generated particle dispersions were stable against agglomeration for more than eight weeks.

ferent substituents in the imide position. By introducing polar groups, even water-soluble perylene derivatives could be obtained.^[3-5] In recent years we have synthesized a family of such polar, even amphiphilic, PDIs by integrating dendrons bearing multiple negative and positive charges.^[3,4,5a] Moreover, the steric hindrance of the imide substituents can control self-aggregation due to π - π stacking. The perylene moiety can be substituted directly in the so-called bay region (1,6,7,12-positions)^[6] and in the recently exploited ortho positions (2,5,8,11positions).^[7] By introducing different substituents in these positions, electronic and optical properties can be tuned, and selfaggregation can be hampered. In our study, another substitution pattern at PTCDA was also used. A benzimidazole-like bridge was created by condensing an ortho-phenylenediamine to the anhydride moiety of a perylene compound (Figure 1, bottom).^[8] The π system of perylene is extended along the longer axis of the molecule. This evokes a bathochromic shift in the absorption spectra, and solutions of such compounds appear violet, blue, or green.

Perylenes are also widely investigated in hybrid systems. Especially the generation of organic hybrid systems by linkage to carbon allotropes such as C_{60} , carbon nanotubes, and graphene is well studied, among others by us.^[9] We showed that carbon nanotubes and graphene could be noncovalently functionalized with amphiphilic PDI derivatives (through π – π interaction) to individualize, solubilize, and investigate them. For generating mixed hybrid systems consisting of perylene linked to inorganic metal oxides such as ZnO, TiO₂, and indium tin oxide, the perylene core must be covalently functionalized with a suitable anchor group.

Zinc oxide quantum dots (QDs), as an established member of aforementioned metal oxides family, have attracted considerable attention owing to their promising electronic, optical, and piezoelectric properties. ZnO is a direct-bandgap semiconductor (3.37 eV) that absorbs in the near-UV region of the opti-

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cal spectrum with a large free exciton binding energy of 60 meV at room temperature.^[10] Meulenkamp et al.^[11a] reported in 1989 the synthesis and characterization of ZnO QDs. Since then, many studies on their biological behavior and toxicity,^[12] physical properties,^[13] and functionalization of the particle surface,^[14-16] which is the main topic of this report, were published. Moreover, ZnO is an interesting material for thin solid films with optoelectronic applications.^[15a,17] In the functionalization of inorganic nanoparticles, the colloidal stability of the target systems must always be taken into account, which can be achieved by means of charges on the surface of the QDs.^[15b]

Herein, we report on the synthesis of perylene derivative 1, which is suitable for the functionalization of ZnO nanoparticles and simultaneously provides colloidal stability of resulting particle dispersions through Coulombic repulsions. Compound 1 is composed of three subunits (Figure 2). Subunit **A** of the



Figure 2. Cationic perylene compound 1 with a catechol as anchoring group for ZnO QDs.

molecule is a second-generation dendrimer of the Newkome type. The exterior branches carry quaternized pyridinium groups, generating nine positive charges. This pattern was already used in our previous studies on the synthesis of watersoluble PDIs. In this case, the dendron is intended to provide solubility in alcohols, which are utilized as solvents for targeted functionalization of the ZnO nanoparticles. Moreover, the ionic dendron is expected to guarantee stability of the nanoparticles in a colloidal dispersion due to electrostatic stabilization (Coulombic repulsion). The dendron section is linked to the perylene core (B) by an imide bond and a small spacer unit. For the functionalization step, self-aggregation of the compound induced by $\pi-\pi$ stacking should be minimized. Hence, a 1,6,7,12-substituted (bay-functionalized) PTCDA derivative was employed. The slight twisting of the perylene plane and the sterically large substituents hamper close approach of the molecules, in addition to the electrostatic hindrance provided by the dendron. As anchoring group for ZnO binding, a catechol unit was chosen, annulated directly to perylene through an imidazole-like bridge (C). Catechol is well established as a good anchor group to ZnO. We confirmed successful functionalization using dynamic light scattering (DLS), zeta-potential measurements, thermogravimetric analysis (TGA), and UV/ Vis, fluorescence, and IR spectroscopy. The resulting perylene/ QD hybrid system was stable against aggregation and sedimentation and showed electronic communication between chromophore and semiconductor.

Results and Discussion

We first describe the synthesis and characterization of perylene derivative **1** (Scheme 1). Preparation of the anchoring building block started with veratrole (**2**), which was twofold nitrated



Scheme 1. Synthesis of protected catechol 6.

and subsequently deprotected with hydrobromic acid to obtain 4,5-dinitrocatechol (3). Heating 3 with dichloro compound 4 gave diphenylmethyl-protected catechol 5 in 52% yield.^[18] For condensation to the perylene anhydride, *ortho*-diamino compound 6 was required. It was synthesized by reducing dinitro compound 5 with hydrogen at 50 bar in an autoclave with the aid of a Pd catalyst.

Perylene precursor **7**, synthesized according to a literature procedure,^[19] was then condensed with protected catechol **6** at 180° C in quinoline to give mono-benzimidazolide **8** (Scheme 2). Formation of the undesired bis-benzimidazolide was prevented by using an almost equimolar ratio of **7** and **6**.

The Newkome-type dendron $9^{[3,4]}$ was subsequently attached to the perylene platform through a condensation reaction with the remaining anhydride position of perylene **8** to generate imide **10** (Scheme 3). Treating **10** with trifluoroacetic acid (TFA) at 60 °C deprotected the carboxyl groups and the

25

 $+28.1\pm1.2$



Scheme 2. Synthesis of protected perylene catechol 8.

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catechol subunit to give **11**. The cationic charges of **1** were introduced by a ninefold amide coupling reaction with cationic building block **12** in the presence of *N*,*N'*-dicyclohexylcarbodiimide (DCC) and *N*-hydroxybenzotriazole (HOBt) according to a procedure that we reported earlier.^[4]

The ZnO quantum dots were synthesized according to previous reports^[11, 14] by hydrolysis of zinc acetate. The average diameter of the nanoparticles was determined to be 5 nm by DLS and from the UV/Vis absorption spectra by means of an algorithm.^[20] For functionalization, equal volumes of a solution of **1** in methanol (1×10^{-4} M) and ZnO QDs (washed and redispersed in methanol, ca. 10 wt %) were mixed and ultrasonicated for 15 min at room temperature. The resulting blue-green solution remained stable for more than eight weeks until slight precipitation occurred.

Table 1 lists particle sizes measured by DLS and zeta potentials of the unwashed, washed, and functionalized QDs. Where-

tial measurements.	eters of the QDs	measured by DL	.5 and zeta poten-
	Unwashed	Washed	Functionalized

5

 -16.8 ± 1.0

5

 -8.1 ± 0.5

DLS diameter [nm]

zeta potential [mV]

as the particle size did not change during the washing process, a pronounced increase of the hydrodynamic diameter from 5 to 25 nm was observed after the addition of **1**. The size distribution of the washed and functionalized particles is shown in Figure 3 (for details, see the Supporting Information). After treatment with **1**, only particles with an average diameter of 25 nm could be found. This could be explained not only by bonding of perylene compound **1** to the surface of the nanoparticles, but also by the great influence of the cationic charges at the periphery of the particles, which affect the solvate shell of the QDs and thereby increase the hydrodynamic diameter.

The zeta potential decreased during the washing process from -8.1 to -16.8 mV, owing to removal of residual acetate molecules in solution and at the surface of the particle,^[11b] which results in enhanced stability. For the functionalized QDs, a zeta potential of +28.1 mV was measured. Values near to or above 30 mV are regarded as an indication for a stable dispersion.^[21] The particles gain stability due to the cationic charges on the surface.

For further characterization, UV/Vis absorption spectra of 1, washed QDs, and functionalized QDs in methanol were record-



Scheme 3. Synthesis of target compound 1.

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Figure 3. Number size distribution of washed and functionalized ZnO nanoparticles, determined by algorithm from UV/Vis spectra and by DLS. The difference between the solid and dashed curves is due to the hydrodynamic diameter, which is measured in DLS.

Figure 4. UV/Vis absorption spectra of functionalized ZnO nanoparticles and references in MeOH.

ed (Figure 4). The spectrum of 1 shows a broad absorption band at 588 nm. Broadening and bathochromic shifting of the absorption bands compared to unsubstituted PBIs is caused by bay substituents and enhancement of the π system by the benzimidazole-bridged catechol. The absorption spectra of the ZnO nanoparticles showed a typical absorption edge at 350 nm. In the spectrum of the functionalized nanoparticles, both characteristic elements (absorption edge and perylene bands) are combined. The only difference is a hypsochromic shift of the perylene band to 582 nm, which can be attributed to electronic interaction between QDs and 1. An effect of growth of the ZnO particle during functionalization could be excluded, because the ZnO edge in the spectrum of functionalized particles has the same slope and width as that of the reference. Any agglomeration would lead to increased absorption beyond the bandgap absorption due to light-scattering effects. Hence, the aforementioned increase in hydrodynamic diameter

Figure 5. Fluorescence spectra of perylene compound 1 and ZnO nanoparticles in MeOH. The asterisk indicates a peak due to direct scattering at the excitation wavelength in the spectrometer.

revealed by DLS measurements is generated merely by functionalization and not by any growth of ZnO.

Figure 5 shows the fluorescence spectra of **1** and washed ZnO QDs. The perylene compound has a strong fluorescence peak at 649 nm. The spectrum of the ZnO QDs shows the two typical fluorescence bands: the exciton emission (bandgap fluorescence) at 361 nm in the UV region and the broad, green fluorescence band in the visible region, which appears with much higher intensity at 525 nm.^[16,22]

When the emission of the functionalized QDs was measured with excitation at 330 nm (ZnO edge), the broad fluorescence in the visible region appeared to be quenched almost completely (Figure 6). Only a very weak and broad peak with a maximum at 510 nm remained. This decrease can be attributed to charge transfer (fluorescence resonance energy transfer, FRET) between **1** and the QDs, because the radiation of free particles is caused by excited electrons in the region of trapped holes

Figure 6. Fluorescence spectra of functionalized nanoparticles. The asterisks indicate peaks due to direct and second-order scattering at the excitation wavelength in the spectrometer.

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on the surface of the QDs.^[14,22] FRET should be possible owing to the short distance between perylene and nanoparticle and overlap of QD emission and perylene absorption.^[23] The exciton peak of the QDs in the UV region remains constant. The perylene fluorescence (excitation at 600 nm) shows a maximum fluorescence at 653 nm (dashed line). A slight bathochromic shift of the maximum compared to free perylene 1 again indicated interaction of the electronic states of perylene and ZnO. Interchromophoric interaction, arising from densely functionalized particles, could also cause changes in absorption and fluorescence spectra. To prevent this, a low concentration of 1 compared to the number of QDs was used during the functionalization step. Thus, the surface should be covered only sparsely.

To confirm that surface binding of cationic perylene **1** occurred through the catechol anchor group and not just by Coulombic interactions, we performed a reverse-phase (RP) TLC experiment (Figure 7). Whereas a spot of **1** was eluted in

Figure 7. RP TLC plate (RP-18, eluent: THF/water 2/1). a) 1. b) 13. c) Functionalized QDs. d) Mixture of 13 and QDs.

a long band on the plate (Figure 7 a), the functionalized particles stayed on the baseline (Figure 7 c). Thus, complete functionalization is shown, assuming that the particles are too large to be eluted. In a reference experiment, cationic perylene compound $13^{[4]}$ (Figure 8), which bears the same cationic den-

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drons as 1, and a mixture of ZnO QDs with 13 were eluted at the same time (Figure 7b and d). In contrast to the 1-functionalized particles (Figure 7c), 13 could be eluted from the mixture with ZnO (Figure 7d). Hence, the linkage of ZnO to 1 must be stronger than the Coulombic interaction with 13, and this confirms covalent linkage of 1 through the catechol anchor group.

Figure 9 shows TGA and TGA-MS curves of pure perylene 1, washed ZnO QDs, and dried functionalized particles. Compound 1 showed a significant weight loss of 60% from 220 to

Figure 9. TGA and TGA-MS curves of perylene 1, washed ZnO QDs, and functionalized QDs. The ion currents belong to the TGA curve of the functionalized QDs.

500 °C. The washed ZnO particles showed an overall weight loss of 15%, which conforms to the literature.^[11b] The decrease resulted from loss of weakly bound lithium acetate and, above 250 °C, of covalently bound acetate molecules. The weight loss of the functionalized particles is related to the aforementioned processes. Moreover, the simultaneously measured mass spectra showed ion current for three m/z values in the temperature range of covalent weight loss. The ions with m/z=92, 120, and 135, which are fragment ions of 1 (pyridinium head group), gives evidence for successful functionalization of the ZnO nanoparticles. Larger fragment ions of 1 could not be observed.

Functionalization of ZnO particles deposited on a glass slide was investigated. The glass slide was first spin-coated with a solution of ZnO QDs and then annealed on a hot plate to dry the surface. Subsequently, it was dipped in a solution of 1, rinsed with methanol, and dried. Figure 10 shows the UV/Vis absorption spectrum of the functionalized slide. The absorption band of the ZnO QDs could be detected at 350 nm, and the maximum absorption of the perylene moiety appeared at 582 nm, as in the case of the particle solution. Thus, it could be determined that 1 was directly bound to the nanoparticles, because it could not be washed away by rinsing with methanol. An equilibrium at the surface between adsorbed and free perylene compound 1 was not observed. In this case, the absorption of 1 should have been decreased over several washing steps.

Figure 10. UV/Vis absorption spectra of functionalized ZnO nanoparticles on an object slide.

Conclusion

A bay-functionalized perylene derivative was connected through an imidazole-like bridge to a catechol anchor group for binding to metal oxide surfaces. This construction motif significantly extends the conjugated π system of the perylene chromophore and, after functionalization, links the surface atoms of the particle to the perylene core in a conjugative manner. The particle dispersions showed pronounced stability against agglomeration due to Coulombic repulsion provided by the positive charges of the attached Newkome-type dendrons of perylene derivative 1. The zeta potential of about +30 mV clearly reflects the stability of the dispersions. Size measurements by DLS confirmed functionalization of the particle surface, which resulted in an increase in hydrodynamic diameter. Solutions of the perylene-functionalized ZnO nanoparticles were also investigated by UV/Vis absorption and fluorescence measurements. Moreover, TGA-MS analysis proved that 1 is attached to the surface, due to the detection of characteristic mass fragments of 1 generated by thermal cleavage reactions and subsequent release from the surface into the gas phase. To provide additional proof for the covalent binding of 1 to ZnO, an RP TLC experiment was carried out. Compound 1, covalently bound to the nanoparticles, could not be eluted on a TLC plate, whereas a comparable compound without an anchoring group was easily eluted. Furthermore, ZnO nanoparticles were deposited on glass slides by spin-coating and subsequently functionalized with 1. Here, the direct binding mode of 1 to the surface was proven, because it was not possible to remove 1 by washing. Such new prototypes of functionalized nanoparticles open interesting possibilities for the construction of optoelectronic devices by layer-by-layer deposition techniques, especially alternating ligation with suitable negatively charged counterparts. Investigations along these lines are currently under way.

Experimental Section

Materials and methods

The ZnO QDs were prepared according to procedures reported earlier.^[11,14] In brief, $Zn(OAc)_2$ dihydrate (550 mg) was dissolved in boiling ethanol (25 mL) and the solution cooled to 35 °C. LiOH (60 mg) was dissolved in ethanol (25 mL) and the solution brought to synthesis temperature, too. Then LiOH solution was added dropwise to zinc acetate solution with vigorous stirring. After 19 h of aging at 35 °C, the ZnO nanoparticles were washed to remove by-products by addition of *n*-heptane. White ZnO flocculates precipitated. The supernatant was separated by centrifugation at 3500 rpm for 10 min. For characterization and functionalization the ZnO QDs were redispersed in MeOH. Converting the absorption spectra to the particle size distribution with an algorithm developed by Segets et al.^[20] gave an average particle size of approximately 5 nm.

The ZnO thin-layer films were generated by spin coating of object slides with washed ZnO QDs (5 nm) in 0.1 M ethanolic solution. After spin coating for 60 s at 1200 rpm and then 5 min at 8000 rpm, the object slides were annealed at 90 °C on a hot plate for 30 min. The resulting ZnO thin-layer films were stable against washing and immersion in alcoholic solution for at least 48 h. For functionalization the object slides were immersed in a methanolic solution of perylene derivative 1 (6 × 10⁻¹⁰ M) for 40 min and subsequently dried on a hot plate (75 °C) for 10 min.

4,5-Dinitrocatechol (3) was prepared from veratrole in two steps, as reported earlier.^[24] The tetrasubstituted perylene 7 was synthesized according to a literature procedure.^[8] Synthesis of dendrimer 9 and its precursors was described previously by us.^[3,4] Preparation of cationic building block 12 was reported before.^[4] Quinoline was freshly distilled, degassed with argon, and handled under inert atmosphere. DMF was used in HPLC grade. All other solvents and chemicals were used as received. NMR spectra were recorded with Bruker Avance 300 (300 MHz), Bruker Avance 400 (400 MHz), and Jeol EX 400 (400 MHz) spectrometers. IR spectra were recorded on a Bruker Tensor 27 (ATR or ZnSe plate) spectrometer. A Varian Cary 5000 was used for UV/Vis measurements. Fluorescence spectra were obtained from a Shimadzu RF-5301 PC. Mass spectrometry was carried out with a Shimadzu AXIMA Confidence (MALDI-TOF, matrices: 2,5-dihydroxybenzoic acid (DHB), trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)). High-resolution mass spectrometry (HRMS) was performed on a Bruker microTOF II focus and a Bruker maXis 4G. For DLS measurements and determination of the zeta potentials, a Zetasizer Nano series ZEN3600 (Malvern Instruments) was used. The device uses a red laser for measurements. Compound 1 also absorbs and emits light in this region, but we observed no interaction between the laser beam and 1, which could result in low-quality measurements. Detailed DLS studies on free compound 1 and functionalized QDs are given in the Supporting Information. Solutions of 1 in methanol showed DLS signals above 100 nm, which could result from surfactantlike aggregation of the molecules. The centrifuge was a Heraeus Multifuge X1R (Thermo Scientific). The crystal structure of 5 (see Supporting Information) was obtained by a SuperNova Dual Atlas (Mo, Agilent Technology GmbH). TGA and TGA-MS experiments were carried out on a TGA/SDTA 851e (Mettler Toledo) and a Skimmer STA 409 CD (Netzsch).

Synthesis

1,2-Diphenylmethylenedioxy-4,5-dinitrobenzene (5): 4,5-Dinitrocatechol (2.150 g, 10.74 mmol) was mixed with α , α -dichlorodiphe-

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nylmethane (2.546 g, 10.74 mmol), and the reaction mixture heated to 170 °C in a preheated oil bath under a steady flow of nitrogen. Orange foaming was observed. After 30 min the reaction was completed and the mixture was cooled to room temperature. The crude product was recrystallized from hot ethanol to give **5** as light yellow crystals (2.049 g, 5.62 mmol, 52%). ¹H NMR (300 MHz, RT, CDCl₃): δ = 7.35 (s, 2H, CH), 7.43 (m, 6H, CH), 7.52 ppm (m, 4H, CH); ¹³C NMR (75 MHz, RT, CDCl₃): δ = 105.1 (CH), 122.4 (C), 126.0, 128.6, 130.2 (CH) 137.6, 138.9, 150.1 ppm (C); IR (ATR): $\tilde{\nu}_{max}$ =624, 637, 669, 697, 725, 753, 766, 794, 816, 70, 918, 938, 1016, 1034, 1077, 1158, 1176, 1213, 1258, 1279, 1306, 1323, 1333, 1352, 1377, 1447, 1471, 1496, 1525, 1544, 1576, 1593, 1633, 1652, 3069, 3276, 3465 cm⁻¹; MS (MALDI-TOF, DCTB): m/z =365 [*M*+H]⁺.

1,2-Diphenylmethylenedioxy-4,5-diaminobenzene (6): Compound 5 (1.244 g, 3.42 mmol) was dissolved in ethyl acetate (50 mL). After addition of 100 mg of catalyst (20% Pd(OH)₂ on charcoal), the mixture was hydrogenated in an autoclave at 50 bar H₂ pressure for 16 h. The catalyst was filtered off by using Celite as filter aid. The solvent was evaporated and the resulting solid was dried under vacuum to afford light yellow 6 (1.007 g, 3.31 mmol, 97%). ¹H NMR (300 MHz, RT, CDCl₃): $\delta = 3.16$ (br s, 4 H, NH₂), 6.36 (s, 2H, CH), 7.33 (m, 6H, CH), 7.53 ppm (m, 4H, CH); ¹³C NMR (75 MHz, RT, CDCl₃): $\delta = 99.6$ (CH), 115.9 (C), 126.4, 128.1, 128.8 (CH) 140.6, 140.7 ppm (C); IR (ATR): $\tilde{\nu}_{max} = 624,637, 669, 696, 725, 753, 795,$ 816, 870, 918, 938, 1016, 1034, 1077, 1176, 1214, 1257, 1279, 1306, 1324, 1334, 1353, 1377, 1447, 1471, 1496, 1525, 1544, 1576, 1594, 1633, 1652, 3069, 3277, 3466 cm^{-1;} MS (MALDI-TOF, DCTB): m/z =304 $[M]^+$; HRMS (ESI-TOF, acetonitrile/methylene chloride) found: *m*/*z* = 304.12061; calcd: 304.12063 [*M*]⁺.

Perylene compound 8: 1,6,7,12-Tetrakis(4-tert-butylphenoxy)pery-(1000 ma, lene-3,4:9,10-tetracarboxylic acid dianhvdride 1.015 mmol, 1.0 equiv), 6 (309 mg, 1.015 mmol, 1.0 equiv), and zinc chloride (166 mg, 1.218 mmol, 1.2 equiv) were dissolved in 10 mL of degassed and freshly distilled quinoline. The mixture was stirred at 180°C for 4 h under argon atmosphere. After cooling to room temperature quinoline was distilled off with a kugelrohr. The dark residue was dissolved in 25 mL of dichloromethane, washed with water, and dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (dichloromethane/hexane 1/1). After evaporation of the solvent, 8 was obtained as a dark green solid (493 mg, 0.393 mmol, 39%). ¹H NMR (300 MHz, RT, CDCl₃): $\delta = 1.30$ (m, 36H, CH₃), 6.84 (m, 8H, CH), 7.17 (s, 1H, CH), 7.23 (m, 8H, CH), 7.32 (m, 6H, CH), 7.55 (m, 4H, CH), 7.90 (s, 1H, CH), 7.95, 8.13, 8.16, 8.37 ppm (s, 4H, perylene-H); ¹³C NMR (100.5 MHz, RT, CDCl₃): $\delta =$ 31.4, 31.4, 31.4, 31.5 (CH₃), 34.3, 34.3, 34.3, 34.4 (C), 96.7, 96.8, 99.7, 99.8 (CH), 114.8, 115.4, 117.3, 117.8, 117.8, 118.2, 118.2, 118.3, 118.7 (perylene-C), 119.0, 119.1, 119.2, 119.3, 119.4, 119.4, 119.5, 119.5 (CH), 120.0, 121.1, 121.2, 121.3, 121.6, 121.7, 121.9, 122.1, 122.2, 122.4, 123.0, 123.4 (perylene-C), 126.2, 126.3, 126.4, 126.6, 126.7, 126.7, 126.8, 126.8, 126.8, 126.9, 126.9, 128.3, 129.2 (CH), 132.3, 132.8, 132.8, 133.9, 139.1, 139.1, 139.8, 139.9, 143.3 (perylene-C), 146.8, 146.9, 147.0, 147.2, 147.3, 147.4, 147.6, 147.7, 147.8, 152.6, 152.6, 152.9, 153.1, 153.2, 153.4, 153.4, 153.5, 155.5, 155.6, 155.8, 155.9, 156.0, 156.2, 156.3, 156.7, 159.6, 159.9, 160.1, 160.2 ppm (C); IR (ATR): $\tilde{\nu}_{max} = 613, 641, 696, 727, 746, 765, 796, 828, 849, 888, 949,$ 977, 1014, 1043, 1091, 1110, 1137, 1171, 1209, 1281, 1341, 1377, 1408, 1457, 1497, 1548, 1588, 1697, 1739, 1768, 1980, 2049, 2361, 2586 2867, 2958, 3059 cm⁻¹; UV/Vis (CH₂Cl₂): $\lambda = 450$, 632 nm; fluorescence (CH₂Cl₂): $\lambda = 694$ nm; HRMS (ESI-TOF, acetonitrile/methylene chloride) found: *m/z*=1252.494061; calcd: 1252.486848 [*M*]⁺.

 0.118 mmol, 0.3 equiv) and imidazole (1070 mg, 15.720 mmol, 40 equiv) were heated to 100 $^\circ\text{C}$ for 2 h. After cooling down to room temperature the mixture was dissolved in CHCl_3 and purified by column chromatography (CHCl₃/MeOH 200/1). 10 was obtained as a dark green solid (135 mg, 0.048 mmol, 12%). ¹H NMR (400 MHz, RT, CDCl₃): δ = 1.21 (m, 2 H, CH₂), 1.28 (m, 36 H, CH₃), 1.39 (s, 27 H, CH₃), 1.39 (s, 81 H, CH₃), 1.64 (m, 4 H, CH₂), 1.91 (m, 24 H, CH₂), 2.16 (m, 26 H, CH₂), 4.08 (t, J=7.3 Hz, 2 H, CH₂), 6.05 (m, 4 H, NH), 6.81 (m, 8H, CH), 7.24 (m, 8H, CH and 1H, CH), 7.34 (m, 6H, CH), 7.58 (m, 4H, CH), 7.98 (s, 1H, CH), 8.16, 8.18, 8.37, 8.38 ppm (s, 4 H, perylene-H); ¹³C NMR (100.5 MHz, RT, CDCl₃): $\delta = 25.4$, 26.9 (CH2), 28.0 (CH3), 29.7, 29.8 (CH2), 31.4 (CH3), 31.7, 31.9 (CH2), 34.3 (C), 37.1 (CH₂), 57.4, 80.5 (C), 96.8, 99.7 (CH), 115.6, 117.8, 118.4, 118.5, 119.0 (perylene-C), 119.3, 119.4, 119.4, 119.5 (CH), 119.7, 119.9, 120.2, 120.3, 120.8, 121.2, 121.8, 121.8, 122.0, 122.8, 122.9 (perylene-C), 126.3, 126.6, 126.7, 126.8, 128.4, 129.3 (CH), 132.2, 133.6, 139.2, 139.9 (perylene-C), 146.7, 146.8 (CH), 147.0 (perylene-C), 147.3, 147.4 152.9, 153.0, 153.1, 153.4, 155.7, 155.9, 156.1, 156.1, 159.9, 163.4 (C), 172.8, 172.9, 173.2 ppm (COO); IR (ZnSe): $\tilde{\nu}_{max} =$ 849, 1018, 1153, 1215, 1291, 1367, 1459, 1508, 1542, 1590, 1656, 1698, 1732, 2362, 2854, 2925, 3356 cm⁻¹; UV/Vis (CH₂Cl₂): $\lambda = 377$, 449, 585, 625 nm; fluorescence (CH₂Cl₂): $\lambda = 675$ nm; MS (MALDI-TOF, DCTB): $m/z = 2788 [M]^+$; HRMS (ESI-TOF, acetonitrile/methanol) found: m/z = 1416.2497; calcd: 1416.2467 $[M+2Na]^{2+}$.

Perylene compound 11: Compound 10 (135 mg, 0.048 mmol) was dissolved in 5 mL of trifluoroacetic acid (TFA) and the solution was heated to 60 °C for 2 h. TFA was distilled off on a rotary evaporator and the residue was suspended in toluene and the solvent evaporated again. The procedure of distilling toluene was repeated three times to fully remove the TFA by codistillation. The crude dark solid was dissolved in a small amount of THF and precipitated with pentane. After two additional reprecipitation steps, 10 was filtered off and dried in vacuum to obtain a dark green solid (100 mg, 0.048 mmol, 98%). ¹H NMR (400 MHz, RT, CDCl₃ + [D]TFA): δ = 1.29 (m, 48H, CH₃), 1.32 (m, 2H, CH₂), 1.64 (m, 4H, CH₂), 2.12 (m, 26H, CH2), 2.40 (m, 24 H, CH2), 4.10 (m, 2 H, CH2), 6.50 (m, 4H NH), 7.32 (m, 9H, CH), 8.20, 8.22, 8.23, 8.48, 8.57 (s, 5H, CH); $^{13}\mathrm{C}\;\mathrm{NMR}$ (100.5 MHz, RT, CDCl₃ + [D]TFA): δ = 28.1, 29.0 (CH₂), 28.0 (CH₃), 31.0 (CH₃), 31.7, 31.9 (CH₂), 34.4 (C), 36.5 (CH₂), 59.2 (C), 99.3, 102.8 (CH), 117.9, 119.3, 119.7, 122.5 (perylene-C), 127.3 (CH), 131.7 (perylene-C), 149.0 (CH), 147.0 (perylene-C), 152.3 (C), 176.5 (COO), 180.3 ppm (COOH); IR (ATR): $\tilde{\nu}_{max}\!=\!611,~703,~720,~748,~800,~834,$ 878, 892, 918, 989, 1014, 1034, 1093, 1173, 1284, 1346, 1407, 1457, 1505, 1543, 1587, 1655, 1694, 1980, 2049, 2162, 2322, 2954, 3064, 3306 cm⁻¹; UV/Vis (THF): $\lambda = 377$, 437, 583, 610 nm; fluorescence (THF): $\lambda = 655$ nm; MS (MALDI-TOF, DHB): $m/z = 2120 [M]^+$, 2143 $[M+Na]^+$.

Perylene compound 1: Compound 11 (50 mg, 0.024 mmol, 1 equiv) and HOBt (58 mg, 0.432 mmol, 18 equiv) were dissolved in 3 mL of DMF under N_2 atmosphere and the solution cooled to 0 °C. A solution of DCC (89 mg, 0.432 mmol, 18 equiv) in 1 mL of DMF was added and the solution stirred at 0°C. 12 (472 mg, 1.728 mmol, 72 equiv) in 1 mL of DMF was added dropwise and the mixture was stirred for 48 h at room temperature. DMF was distilled off under reduced pressure and the residue was dissolved in a small amount of methanol. A red solid was precipitated by addition of a larger quantity of acetone. The suspension was centrifuged and the precipitation repeated twice. After drying in vacuum, 1 was obtained as a dark blue solid (36 mg, 0.009 mmol, 38%). ¹H NMR (400 MHz, RT, CD₃OD): $\delta = 1.26$ (m, 81 H, CH₃), 1.40 (m, 40H, CH₃+CH₂), 1.95, 2.20 (m, 74H, CH₂), 3.23 (m, 18H, CH₂), 4.62 (m, 18H, $\rm CH_2),~7.26$ (m, 8H, CH), 7.67 (m, 8H, CH), 8.12 (m, 18H, CH), 8.93 ppm (m, 18H, CH), perylene protons could not be

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observed due to line broadening; ¹³C NMR (100.5 MHz, RT, CD₃OD): δ = 30.5, 32.3 (CH₃), 35.4, 36.9 (^qC tBu), 37.7, 55.0, 59.1, 59.9 (CH₂), 118.1–132.6 (br, per-C), 126.9, 145.9 (py-CH), 172.9 (py-C), 182.0 ppm (COO), not all signals could be observed due to line broadening; IR (ATR): $\tilde{\nu}_{max}$ = 622, 658, 800, 813, 836, 877, 891, 962, 1015, 1041, 1113, 1152, 1175, 1214, 1281, 1341, 1396, 1457, 1506, 1556, 1643, 1691, 1980, 2015, 2148, 2162, 2321, 2360, 2960, 3056, 3274 cm⁻¹; UV/Vis (MeOH): λ = 396, 448, 588 nm; fluorescence (MeOH): λ = 648 nm.

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