Towards Highly Fluorescent and Water-Soluble Perylene Dyes

Christopher Kohl, Tanja Weil, Jianqiang Qu, and Klaus Müllen*[a]

Abstract: A systematic approach towards highly fluorescent, water-soluble perylene-3,4:9,10-tetracarboxylic acid diimide chromophores is presented. Water solubility was introduced first through the attachment of four hydrophilic substituents onto the *bay* region of the perylene dye. Positively and negatively charged groups were then applied to the chromophore, and their number and their distance from the aromatic scaffold were systematically varied. To suppress aggregation, the chromophore was further isolated within a dendritic shell. Such variation of structural features and a thorough investigation of the resulting optical properties facilitated the first synthesis of perylene-3,4:9,10-tetracarboxylic acid diimides combining the properties of water solubility and fluorescence quantum yields (FQYs) close to unity, which makes them attractive as high-performance fluorescence probes in aqueous media.

Keywords: aggregation · fluorescence · perylene · polyphenylene dendrimer · water solubility

Introduction

Fluorescence is ideally suited for observation of the location and interaction of biologically active probes in vivo, since it is non-invasive and can be detected with high sensitivity and signal specificity.[1] In particular, in vivo investigations of biological targets require chromophores giving high fluorescence quantum yields (FQYs) in water and displaying absorption and emission maxima in an area that does not interfere with the self-absorption wavelength of the cell: above 500 nm, for example.[2,3] In recent years the investigation of individual biologically active macromolecules such as DNA and proteins has become very popular since it provides better insight into their dynamics and interaction partners than measurements made on ensembles.[4–7] For such measurements, however, the photostability of the chromophore plays a crucial role. Despite the large variety of water-soluble chromophores commercially available today,[8] there are almost no chromophores that meet all the following criteria: i) water solubility, ii) high fluorescence intensities, iii) absorption and emission maxima above 500 nm, iv) no toxicity, and v) high photostability.

In organic solvents, perylene-3,4:9,10-tetracarboxylic acid diimide (PDI) chromophores (Figure 1a) display exceptional chemical, thermal, and photochemical stability with high fluorescence quantum yields close to unity.[8–11] Thanks to these remarkable properties they are used as dye sensitizers in solar cells,[12,13] molecular components of light-emitting diodes,[14] or field effect transistors.[15,16] Recently, their applicability in single-molecule spectroscopy has been successfully demonstrated in investigations of the optical behavior of multichromophoric dendrimers.[17,18] Therefore, thanks to these unique properties, PDI chromophores should also be ideally suited as high-performance fluorescent labels for biologically active probes. Only a few water-soluble perylene monoimide and PDI derivatives have so far been reported, however. Such chromophores carry hydrophilizing substituents, such as sulfonic acid moieties (**1**),[19] quaternized amine groups (**2**),[20] (Figure 1) or crown ethers[21] as part of the imide structure of the chromophore, or polyethylene glycol[22,23] or peptide chains[24] attached to the chromophore scaffold. In all cases these perylene chromophores show almost no fluorescence in water. Until now there has been no synthetic strategy for obtaining PDI chromophores that will retain their exceptional properties in aqueous media.

Herein we introduce different structural concepts for highly fluorescent and water-soluble PDI chromophores.[25] In the course of this work, several hydrophilic groups were attached to the aromatic chromophore scaffold. Furthermore, the distance between such water solubility-inducing groups and the chromophore was increased to suppress fluorescence quenching due to photoinduced electron transfer[26] between the functional group and the chromophore. The chromophore was then encapsulated within a dendritic shell, which is likely to prevent intermolecular chromophore interaction such as aggregation.[27,28] The number of hydrophilic or charged groups was then reduced. Through this systemat-

[a] Dr. C. Kohl, Dr. T. Weil, Dr. J. Qu, Prof. K. Müllen
Max-Planck-Institut für Polymerforschung
Ackermannweg 10, 55128 Mainz (Germany)
Fax: (+49) 6131-379350
E-mail: muellen@mpip-mainz.mpg.de

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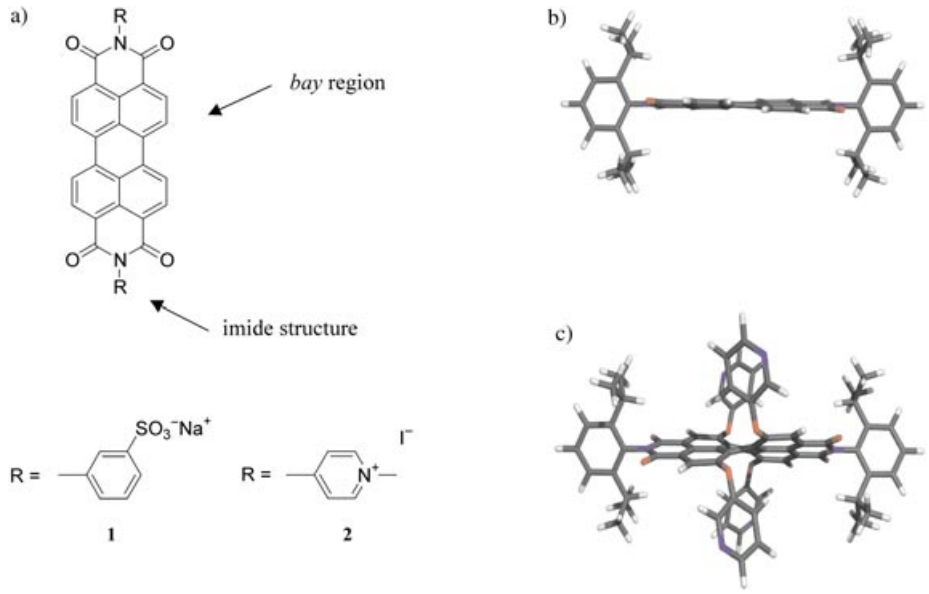


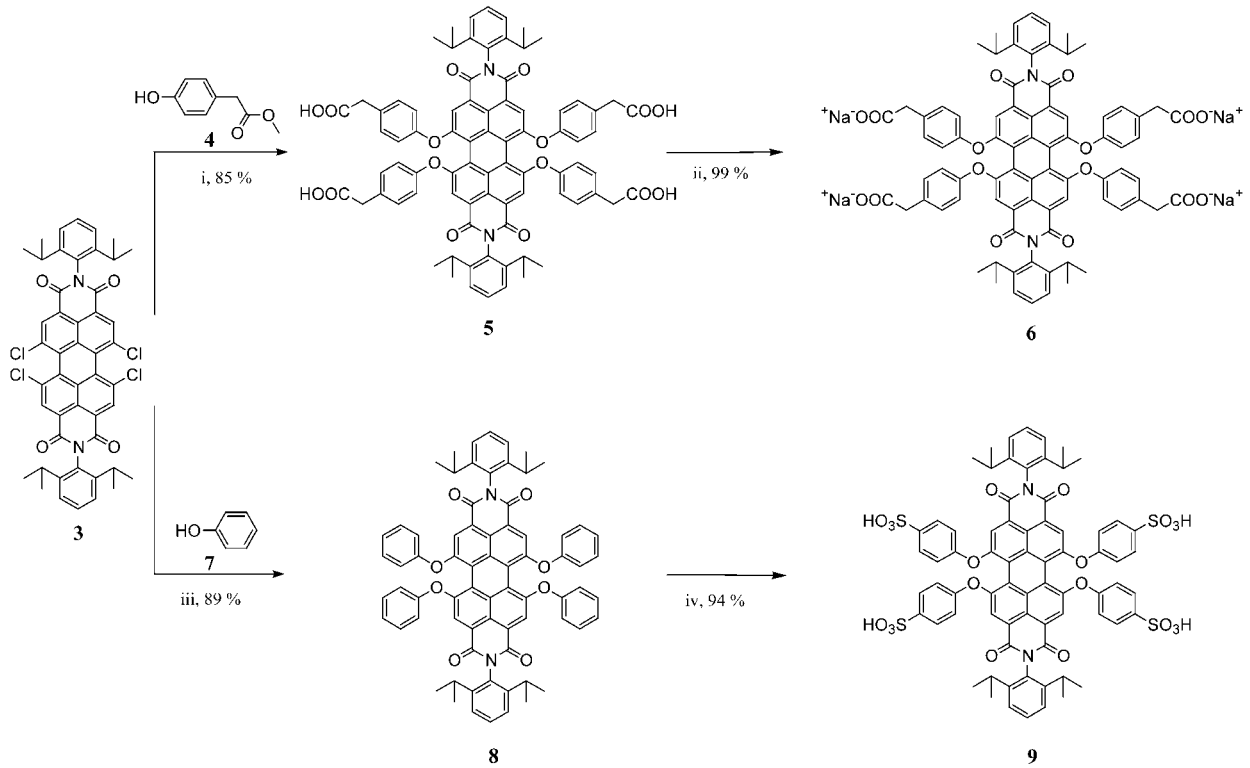
Figure 1. a) PDI bearing substituents attached at the imide structure; b) three-dimensional structure of PDI with no substituents attached at the *bay* region (planar scaffold)—view in the direction of the *bay* region; c) three-dimensional structure with four substituents attached at the *bay* region (twisted scaffold).

ic variation of all available parameters and thorough investigation of the optical properties of all water-soluble chromophores we were able to develop highly fluorescent, water-soluble PDI chromophores.

Results and Discussion

Variation of the hydrophilic group attached at the *bay* region: PDI chromophores bearing hydrophilic substituents attached to the imide structure of the chromophore generally display low FQYs in water.[19–21] We therefore first introduced such groups onto the *bay* region of the chromophore (Figure 1a), which results in a nonplanar, twisted aromatic chromophore scaffold (Figure 1b) that is further shielded by the functional groups.[28]

Based on this concept, the synthesis of **5** with four carboxylic acid substituents attached at the *bay* region was accomplished through treatment of *N,N′*-bis(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid diimide (**3**), which is available on a gram scale,[29] with six equivalents of methyl (4-hyroxyphenyl)acetate (**4**) in 1-methyl-2-pyrrolidone (NMP) (85% yield, Scheme 1). Since this chromophore is not soluble in water, its sodium salt was prepared by addition of sodium hydroxide dissolved in methanol to a concentrated THF so-



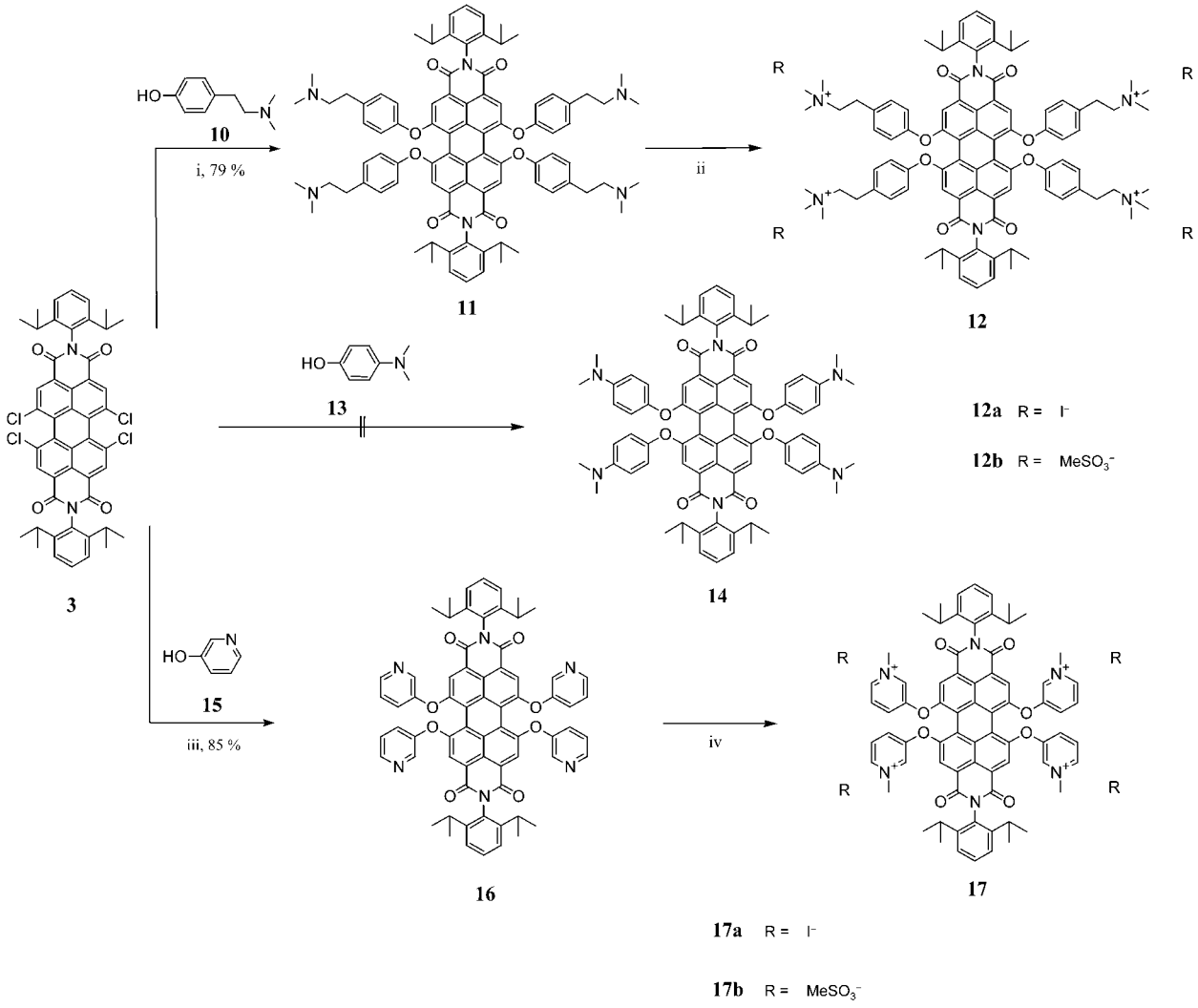
Scheme 1. i) Methyl (4-hydroxyphenyl)acetate (**4**), NMP, K_2CO_3, 100 °C, 15 h, 85%; ii) THF, methanol/sodium hydroxide; iii) phenol, NMP, K_2CO_3, 80 °C, 15 h, 89%; iv) conc. sulfuric acid, RT 15 h, 93%.

lution of **5**. The synthesis of a PDI chromophore with four sulfonic acid substituents (**9**) was performed by a two-step reaction (Scheme 1). The first step involved a phenoxylation of **3** by treatment with phenol (**7**), affording **8** in high yield. Compound **8** was then treated with concentrated sulfuric acid at room temperature for 15 h. The number of sulfonic acid groups and the substitution pattern of the phenyl ring (*para* substitution) were corroborated by NMR experiments (see Experimental Section).

PDI chromophores bearing positively charged branches attached at their *bay* regions were obtained by treatment of **3** with six equivalents of 4-[2-(dimethylamino)ethyl]phenol (**10**) in NMP as shown in Scheme 2. Interestingly, the analogous reaction between **3** and six equivalents of 4-dimethylaminophenol (**13**), which would have given **14** with four dimethylaminophenoxy branches, was not observed. Thereafter, quaternization of the dimethylamino substituents of **11** was carried out by treatment first with an excess of methyl iodide in boiling chloroform for 24 h and then with an additional excess of methyl iodide in boiling methanol for another 24 h. Since the resulting chromophore **12a** was insoluble in water, four equivalents of silver methanesulfonate were applied, the counterion being exchanged from iodide to methanesulfonate to give water-soluble **12b** as a dark red solid.

The synthesis of the pyridinium-substituted PDI chromophores **17a** and **17b** (Scheme 2) involved phenoxylation with 3-pyridinol (**15**) by the same procedure as described above, to yield **16** (85 %). Because of the high solubility of **16** in alcohol, quaternization of **16** was carried out with an excess of methyl iodide in methanol to give **17a**. To increase the solubility in water, four equivalents of silver methanesulfonate were applied, and **17b** was obtained in quantitative yield.

Variation of the distance between the hydrophilic group and the chromophore: To observe the influence on the FQY of the distance separating the hydrophilic groups and the chromophore scaffold, chromophores bearing one additional phenyl ring per side arm as a spacer were synthesized



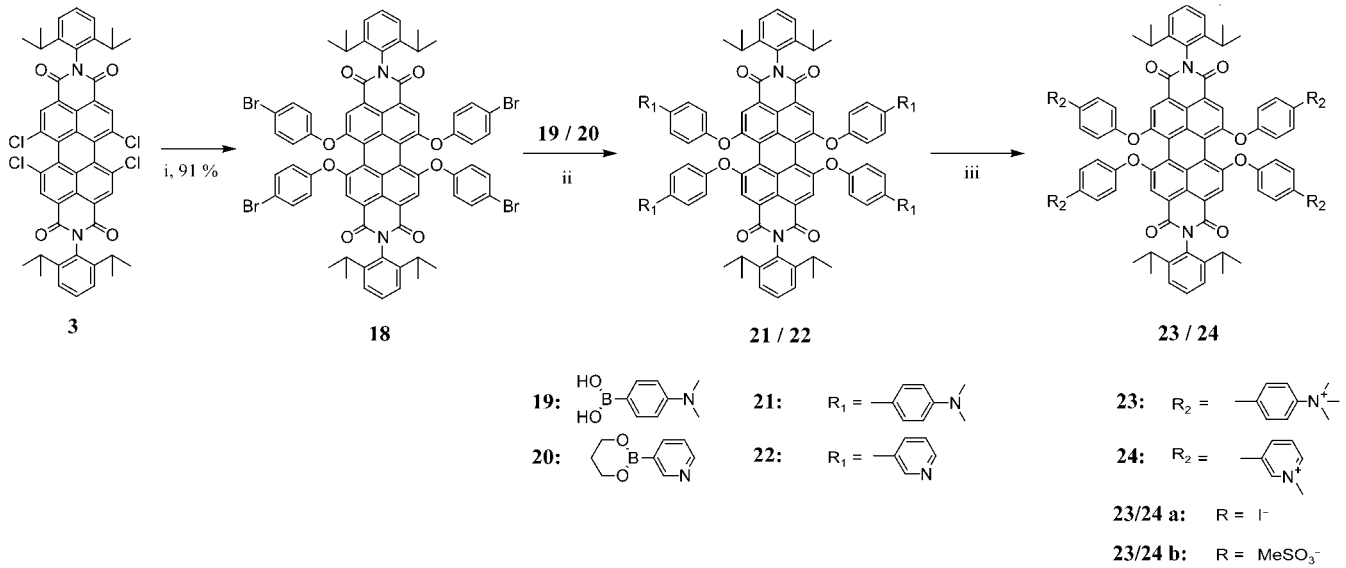
Scheme 2. i) 4-[2-(Dimethylamino)ethyl]phenol (**10**), NMP, K_2CO_3, 80 °C, 15 h, 79 %; ii) **12a**: methyl iodide, methanol, reflux, 24 h, 95 %; **12b**: silver methanesulfonate, methanol, RT, 5 h, 95 %; iii) 3-pyridinol (**15**), NMP, K_2CO_3, 80 °C, 15 h, 85 %; iv) **17a**: methyl iodide, methanol, reflux, 24 h, 95 %; **17b**: silver methanesulfonate, methanol, RT, 5 h, 92 %.

(Scheme 3). First, *N*,*N*′-bis(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid diimide (**3**) was treated with six equivalents of 4-bromophenol to give **18** in high yield (92%). Compound **18** was then subjected to Suzuki reaction conditions[30,31] with either 4-dimethylaminophenylboronic acid (**19**) or pyridine-3-boronic ester (**20**) to give **21** and **22**, respectively, with side arms each containing an additional phenyl ring with respect to the analogous chromophores **12** and **17**. Water-soluble chromophores **23b** and **24b** were obtained in nearly quantitative yield by initial application of methyl iodide in boiling chloroform and subsequent exchange of the counterion for methanesulfonate by treatment with four equivalents of silver methanesulfonate.

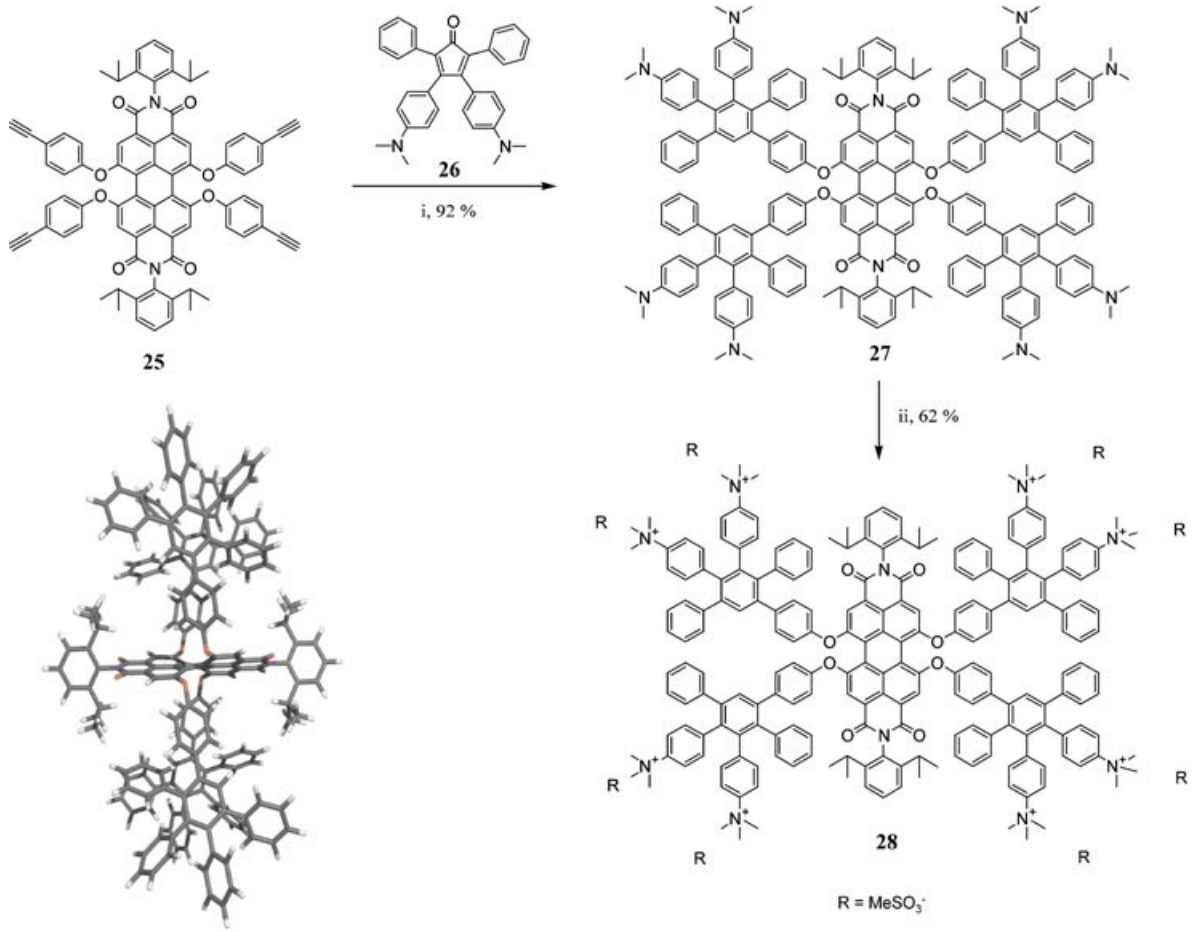
Site isolation of the chromophore: To prevent PDI chromophores from aggregating, bulky substituents such as polyphenylene dendrimer branches attached at the *bay* region of the chromophore were produced by means of successive Diels–Alder reactions.[32,33] Scheme 4 shows the synthesis of a dendronized PDI bearing positively charged groups at the surface, together with the three-dimensional structure of a PDI chromophore surrounded by four bulky polyphenylene branches. The starting point was a PDI core **25** with four free ethynyl functionalities, which were subjected to four Diels–Alder cycloadditions by treatment with a sixfold excess of the tetraphenylcyclopentadienone derivative **26**, bearing two dimethylamino substituents, in *m*-xylene at 140°C.[34] The resulting first-generation dendrimer **27**, with eight dimethylamino groups, was obtained in high yield. Quaternization of **27** was then accomplished with an excess of dimethylsulfate by constant addition of chloroform to a benzene solution. Finally, the complete quaternization succeeded in methanol, to provide **28** in 62% yield.

Polyphenylene dendrimers with PDI cores bearing amino, carboxylic acid, and tetraethylene glycol functions were obtained by the same synthetic sequence. In this way, treatment of **25** with tetraphenylcyclopentadienone **29a** (Scheme 5), bearing two imino groups,[22,35] gave dendrimer **30a** with eight imino groups. After hydrolysis of these imino groups by treatment with hydrochloric acid, compound **31a**, bearing eight amino groups, was isolated (94% yield). The synthesis of **30b**, with eight methyl carboxylate substituents, was achieved by treatment of **25** with tetraphenylcyclopentadienone **29b** at 175°C for 40 h. Subsequent ester cleavage of **30b** with potassium hydroxide in THF at 80°C gave **31b**, with eight carboxylic acid functions. Compound **30c**, bearing 12 tetraethylene glycol chains, was obtained through cycloaddition between **25** and **29c** (56% yield). The synthesis and characterization of the cyclopentadienone building units **26**, **29b**, and **29c** has been described before.[22,35]

Variation of the number of hydrophilic groups: To reduce unwanted quenching processes due to the presence of the solubilizing groups themselves, PDI derivatives with only two charged branches were synthesized. Since the water solubility of the chromophores decreases with a decreasing number of hydrophilic substituents, only groups likely to induce high solubility in water—such as pyridinium and sulfonic acid—were chosen. First, 1,7-dibromoperylenetetracarboxylic acid diimide **32** (Scheme 6) was treated with 2,6-diisopropylaniline in propionic acid to give **33** in high yield (95%). PDI chromophores either with two pyridinium substituents (**34a**) or with two phenoxy groups (**34b**) were then obtained by the same procedure as described for the synthesis of **9** and **16**. First, **33** was treated with 3-pyridinol (**15**) in NMP to afford **34a** in 75% yield. Quaternization of **34a** was carried out by treatment with an excess of methyl iodide in boiling chloroform, which gave **35a** in quantitative yield. Compound **35b** was obtained by application of silver methanesulfonate in methanol. Compound **34b** was produced by phenoxylation of **33** by treatment with phenol in NMP. Subsequently, the sulfonation was carried out by treatment with



Scheme 3. i) 4-Bromophenol, NMP, K_2CO_3, 80°C, 15 h, 91%; ii) a: **19**, [$Pd(Ph_3)_4$], toluene, K_2CO_3/H_2O (1M), 95°C, 12 h, 90%; b: **20**, [$Pd(Ph_3)_4$], toluene, K_2CO_3/H_2O (1M), 95°C, 12 h, 84%; iii) a: methyl iodide, methanol, reflux, 24 h, 94%; b: silver methanesulfonate, methanol, RT, 5 h, 90%.



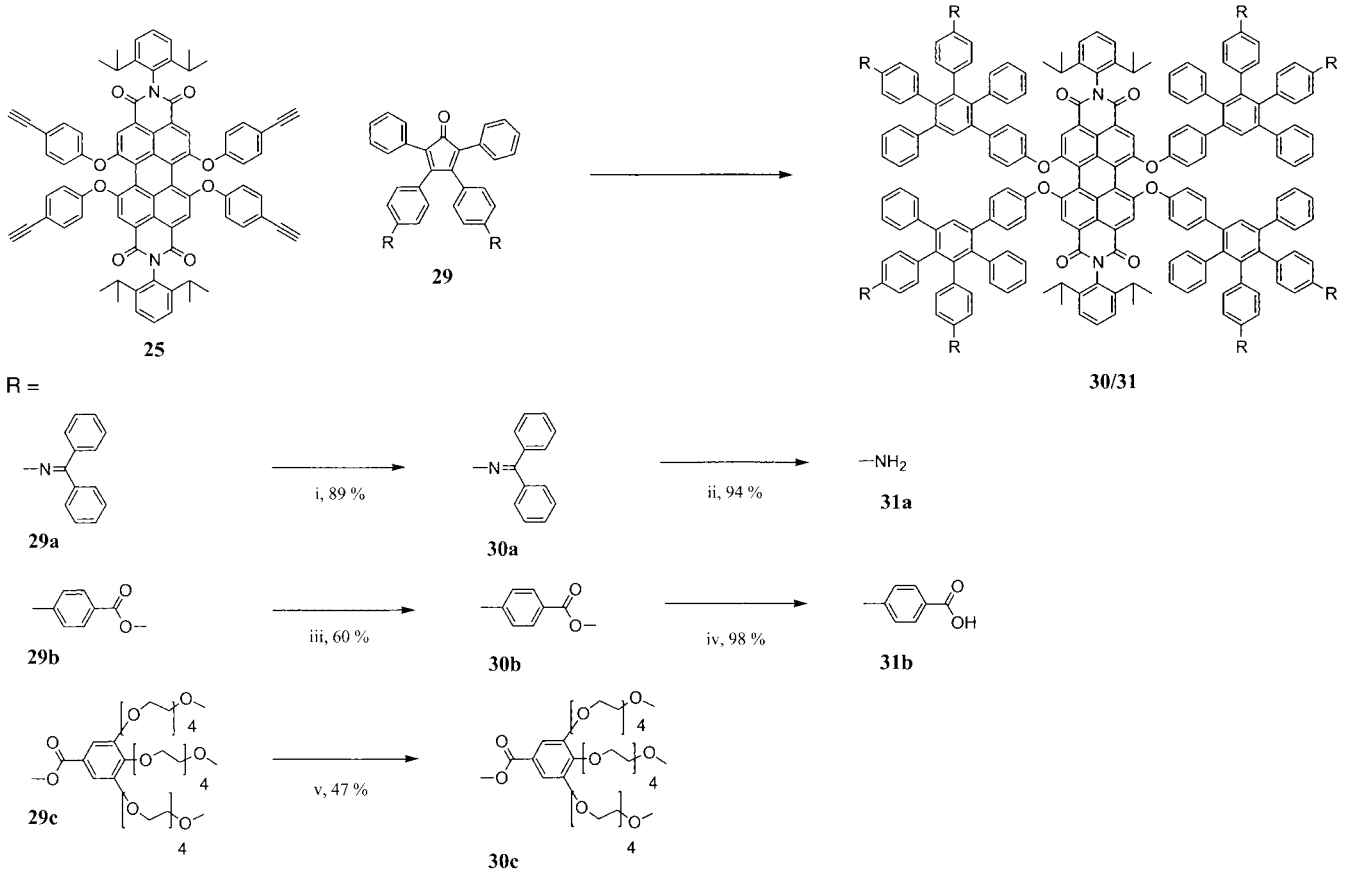
Scheme 4. i) Compound **26**, *m*-xylene, 12 h, reflux, 92 %; ii) a: methyl iodide, benzene, reflux, 4 h, b: silver methanesulfonate, methanol, RT, 5 h, 92 %.

concentrated sulfuric acid at room temperature for 15 h to give **35c** as a red solid in 94 % yield.

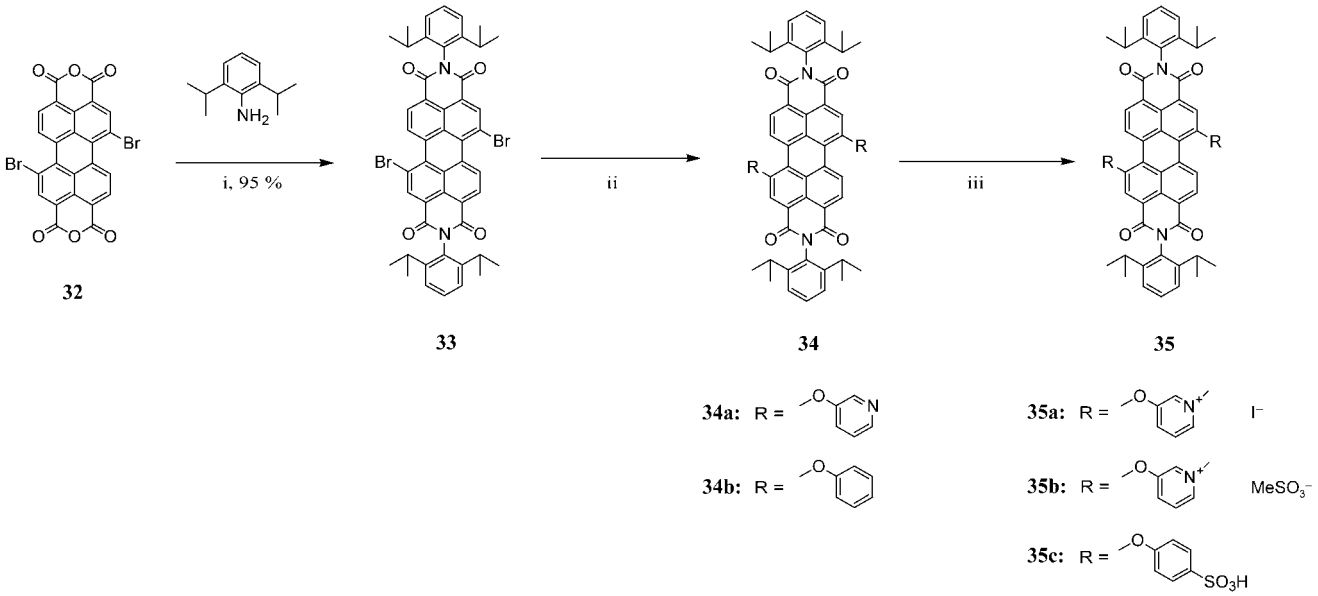
Characterization: All chromophores described here display good thermal stability, with decomposition temperatures above 300 °C. Each structure has been verified by NMR spectroscopy, field desorption (FD) mass spectrometry, and/or matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) spectrometry. In the cases of positively charged chromophores not detected by the mass spectrometry techniques applied here, only ^{1}H NMR and ^{13}C NMR spectroscopy and elementary analysis were applied. The MALDI-TOF mass spectra of all uncharged and negatively charged chromophores reported here each show only a single peak corresponding to the molecular mass of the chromophore. The perfect agreement between the calculated and experimentally determined *m*/*z* ratios confirms the monodispersity of this dendrimer.

Photostability/solubility: The ionic PDI chromophores reported for the first time here display high photostability in aqueous media, comparable to that of PDIs in organic solvents or in the solid state. The UV/Vis absorption and emission spectra of water solutions of these dyes remain almost unchanged under sunlight or after irradiation under UV light (365 nm) for one week. This basic photostability test already offers a good impression of the lightfastness of these novel chromophores.

One of the key features of the ionic PDI chromophores is their outstanding water solubility. Compound **17b** has the highest solubility in water (8.0×10^{-2} mol L^{-1}). The solubility of the other chromophores can be estimated from their calculated log D values[36] (logarithm of the octanol/water partition coefficient as a function of pH) given in Figure 2. In general, water-soluble compounds are characterized by low log D values, whereas high log D values describe lipophilic compounds. Figure 2 shows that chromophores **1**, **2**, **6** (above pH 9), and **9** should be nicely soluble in water, whereas lower water solubility is to be expected in the cases of chromophores **17**, **12**, **35a**, and **35c**. Furthermore, with a decreasing number of hydrophilic groups—from four (**9**, **17**) down to two (**35a**, **35c**)—an increase in the log D value is obtained and so lower water solubility is to be expected. The introduction of a phenyl spacer (chromophores **23** and **24**) gives highly lipophilic compounds in which only very limited water solubility is to be anticipated. However, since neither the distribution of hydrophilic groups in the molecule nor the nature of the charged counter-ion is recognized by log D values, the water solubilities of chromophores **12**, **17**, **23**, **24**, and **35a** are likely to be underestimated.



Scheme 5. i) Compound **29a**, *o*-xylene, 20 h, 170 °C, 89 %; ii) compound **30a**, THF, HCl (5 M), 94 %; iii) compound **29b**, *o*-xylene, diphenyl ether, 40 h, 175 °C, 60 %; iv) compound **30b**, THF, KOH, H_2O, 42 h, 80 °C, 98 %; v) compound **29c**, *o*-xylene, 24 h, 170 °C, 47 %.



Scheme 6. i) 2,6-Diisopropylaniline, propionic acid, 140 °C, 5 h, 95 %; ii) a: compound **33**, 3-pyridinol (**15**), NMP, K_2CO_3, 80 °C, 15 h, 81 %; b: compound **33**, phenol, NMP, K_2CO_3, 80 °C, 15 h, 80 %; iii) a: compound **34a**, methyl iodide, chloroform, reflux, 24 h, b: compound **34a**, methyl iodide, methanol, reflux, 24 h, 94 %; silver methanesulfonate, methanol, RT, 5 h, 90 %; **c**: compound **34b**, conc. sulfuric acid, RT, 15 h, 94 %.

Optical characterization: The absorption and emission maxima of compounds **6**, **9**, **12b**, and **17b** are listed in Table 1. A PDI chromophore bearing phenoxy substituents in the *bay* region displays three absorption maxima at 577, 537, and 444 nm[28] and one emission maximum at 600 nm in toluene. The spectra of chromophores **6**, **9**, **12b**, and **17b** with hydrophilic substituents reveal bathochromic shifts in water relative to toluene, these being very pronounced in

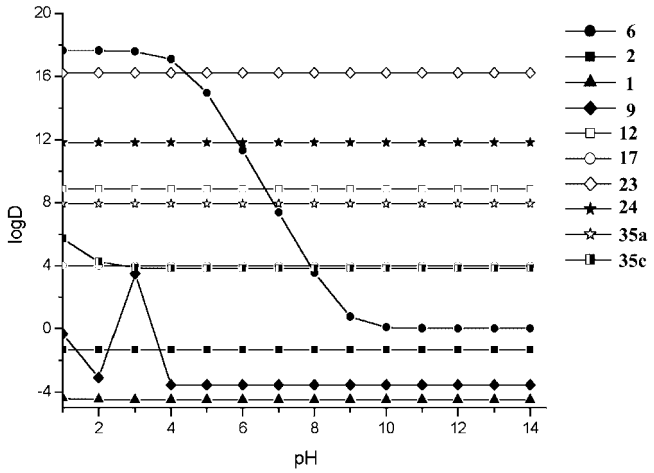


Figure 2. Log D values as a function of pH for selected PDI chromophores.

Table 1. Absorption ($\lambda_{max,\,abs}$) and fluorescence ($\lambda_{max,\,flu}$) maxima and fluorescence quantum yields (FQYs)[a] in water for the water-soluble PDI chromophores.

Compound	$\lambda_{max,\,abs}$ [nm] (extinction coefficient [$M^{-1}cm^{-1}$])	$\lambda_{max,\,flu}$ [nm]	FQY [a]	
PDI-(OPh)$_4$	573(43602)[b]	600	0.96	
6	451, 531, 566	624	0.07	
9	461(10708), 541(21026), 571(27800)	619	0	0.58
12b	460(13537), 551(25342), 586(35436)	627		0.14
17a	518(19300), 550(25700)	594	0.75	
17b	434(9766), 516(24628), 547(33751)	588		0.66
23b	491(17088) 554(24621), 565(27454)	614[c]	0.11[c]	
24b	459(19225), 576(25855)	624	0.23	
35b	400(4535), 503(13640), 536 nm(19022)	573		0.98
35c	411(7565), 523(23196), 554 nm(23718)	594		0.12

[a] Fluorescence quantum yields (FQYs) were measured at room temperature with cresyl violet as reference (the standard value is 0.54 in methanol). [b] Toluene. [c] Compound **23b** has very weak fluorescence in water and its FQY was measured in DMSO.

the cases of **6** and **12b** (36 nm, 39 nm, respectively). The spectrum of **17b**, in contrast to those of **6** and **12b**, shows narrow absorption and emission envelopes that display a higher degree of fine structure (Figure 3) and a hypsochromic shift of the emission maximum (Table 1).

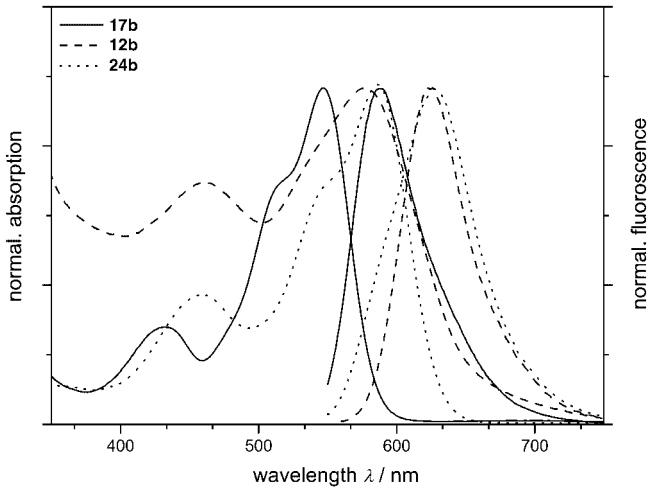


Figure 3. Normalized absorption spectra and emission spectra of **17b** (——), **12b** (•••••), and **24b** (-----) in water.

The FQYs of **9** and **17b** (58%, 66%, Table 1) in water are comparatively high with respect to previously reported analogous chromophores, indicating the value of our approach of attaching the functional groups at the *bay* region of the chromophore instead of at the imide structure.[19,20] However, **6** and **12b** still display low FQYs (7%, 14%, Table 1). Clearly, chromophores bearing hydrophilic groups directly located on the phenyl ring, such as **9** and **17b**, and not at the terminus of a short alkyl chain (**6**, **12b**) show higher FQYs and less spectral broadening. One reason for this behavior might be the alkyl spacers in chromophores **6** and **12b**, the character of the molecule becoming more lipophilic (see Figure 2), which is in accordance with the calculated log D values of **6** and **12b** and leads to a decrease in solubility and, therefore, a higher tendency of these chromophores to form aggregates. Another reason might be that vibrational relaxation becomes more important because of the higher rotational freedom of the hydrophilic groups of **6** and **12b** at the terminus of a short alkyl spacer, leading to a quenching of fluorescence.

However, even **9** and **17b**, with FQYs of 58% and 66%, still display reductions of about 40% in their FQYs with respect to PDI chromophores in organic solvents, in which the FQYs are usually close to unity. In the past, apart from aggregation[23,28] or vibrational relaxation, a reduction of the FQY in polar solvents has also been attributed to the presence of photoinduced electron-transfer (PET) processes.[26] In a case in which triphenylamine groups were attached to a PDI core, it was demonstrated that PET takes place, resulting in a considerable broadening of the emission spectra and a low FQY. Since PET strongly depends on the distance separating the chromophore and the substituent, the role of such processes in the chromophores reported here should be quantifiable by increasing the distance between the hydrophilic group and the chromophore, which should lead to less PET and therefore higher FQYs.

Nevertheless, the emission spectra of **23b** and **24b** (Scheme 3), which each bear one additional phenyl ring per hydrophilic side arm, again reveal considerable bathochromic shifts, of about 14 nm for **23b** in DMSO and 24 nm for **24b** in water, relative to **12b** and **17b** (Figure 4). Furthermore, the FQYs of **23b** and **24b** are very low in both cases (11%, 23%). Despite the longer spacer, which increases the distance between the substituents and the chromophore scaffold by a factor of about two (Figure 5), the FQYs are further reduced relative to the analogous chromophores **12b** and **17b** without spacers. We again attribute this behavior to an increase in the lipophilic character of chromophores **23b** and **24b** due to the additional phenyl ring, which is also supported by very high log D values as shown in Figure 2, thus facilitating aggregation in water.

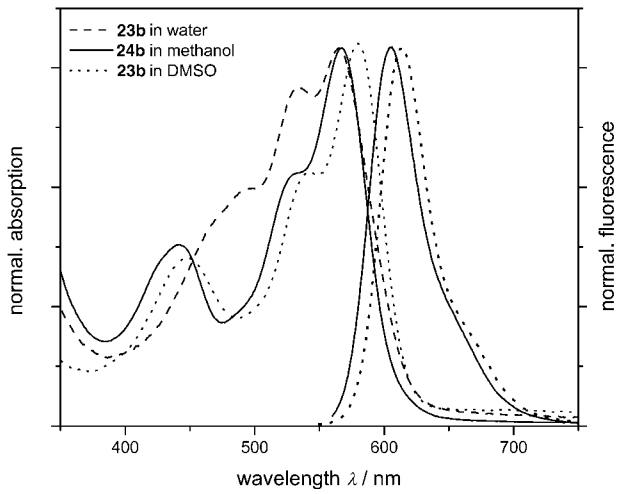


Figure 4. Normalized absorption spectra and emission spectra of **23b** in water (-----), **23b** in DMSO (•••••), and **24b** in methanol (——).

Surprisingly, all the PDI chromophores shielded by polyphenylene shells (Scheme 4), which should in general prevent aggregation, also display low FQYs. Table 2 gives an overview of the optical properties of **18**, **30c**, **31a**, and **31b**. Here, the absorption maxima range between 583 nm and 589 nm, while the emission maxima were found between 615 nm and 620 nm. In toluene, an analogous dendritic chromophore without any substituent **31c**[22] reveals similar absorption maxima, but the emission maximum is shifted by about 10 nm to the blue.

All polyphenylene dendrimers bearing a PDI chromophore in the center reveal low FQYs in polar solvents such as dimethyl sulfoxide (DMSO) and water. The highest FQY—at 19%—was obtained for **30c**, with twelve tetraethylene glycol chains at the periphery. Both ammonia- and carboxylic-acid-terminated dendrimers **28** and **31b** display

Table 2. Absorption ($\lambda_{max,\,abs}$) and fluorescence ($\lambda_{max,\,flu}$) maxima and fluorescence quantum yields (FQYs) of the dendronized PDI chromophores in water[a] or DMSO.

Compound	$\lambda_{max,\,abs}$ [nm] (extinction coefficient [$M^{-1}cm^{-1}$])	$\lambda_{max,\,flu}$ [nm]	FQY[a]
28	463 (17459), 548 (22965), 589 (36113)	620	0.15
30c	582 (water)	615	0.19
31a	585 (DMSO)	617	0.012
31b	584 (DMSO)	619	0.13
31c	583 (toluene)	606	0.9

[a] FQYs were measured at room temperature with cresyl violet as reference (the standard value is 0.54 in methanol).

only low FQYs (15%, 13%) in water and DMSO. A FQY ten times lower is observed for dendrimer **31a**, with eight terminal amino groups, in DMSO; this could be due to the presence of several terminal amino groups capable of acting as electron donors, thus quenching the excited state of the inner PDI chromophore through PET. The low FQY could not be attributable to the formation of aggregates in any of the dendritic PDI cases, since their rigid polyphenylene scaffolds effectively shield the inner chromophores.[28] Therefore, with respect to the large size of the dendritic shell, fluorescence quenching through vibrational relaxation could play a major role. Nevertheless, in the cases of **18**, **30c**, and **31b** we can only speculate as to whether the reduction in FQY is based on insufficient water solubility of the dendrimer, some loss in excitation energy through the dendrimer branches, or both. Additional photophysical investigations will therefore be necessary to understand the low FQYs of these dendritic chromophores, and these are currently underway.

Since the introduction of a large number of hydrophilic substituents into the chromophore scaffold resulted only in weakly fluorescent chromophores, we consequently diminished their number down to a minimum of two, the mini-

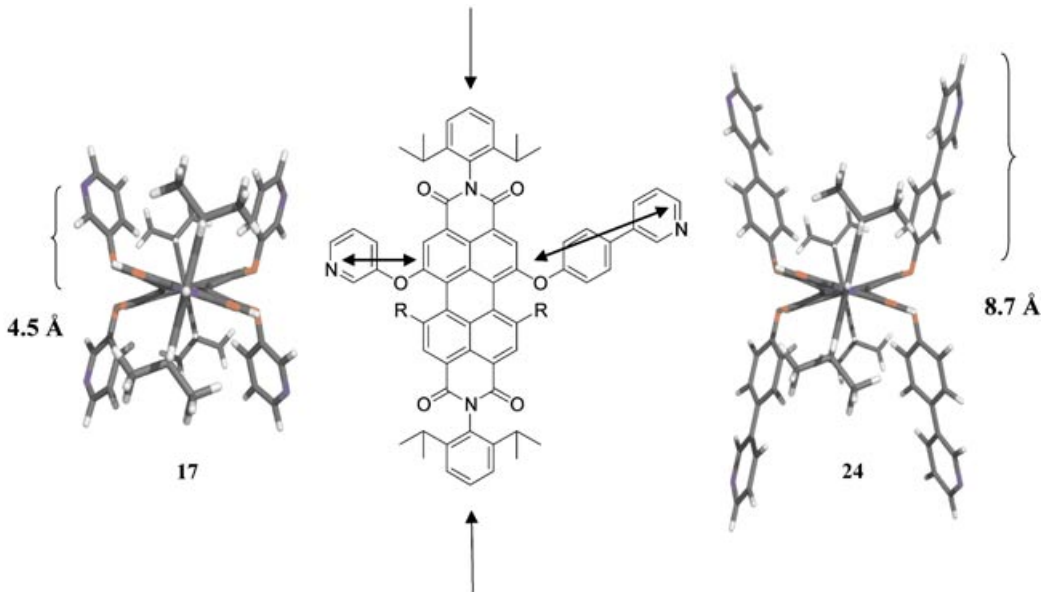


Figure 5. Three-dimensional structure of **17** (left) and **24** (right) with view along the imide structure (middle). Distances from the N heteroatom of the pyridinium group and the PDI scaffold of **17** (4.5 Å, left) and of **24** (12.8 Å, right).

mum number necessary to induce sufficient water solubility. The PDI chromophores **35a** and **35b**, each bearing only two substituents in its *bay* region (Scheme 6), display nearly quantitative FQYs in aqueous media, and their absorption and emission spectra are structured, showing a considerable blue shift with respect to all the chromophores previously discussed (Figure 6). Apparently, the presence of two positively charged pyridinium substituents represents a good compromise for combining sufficient water solubility and a minimum number of functional groups to suppress undesired processes such as PET.

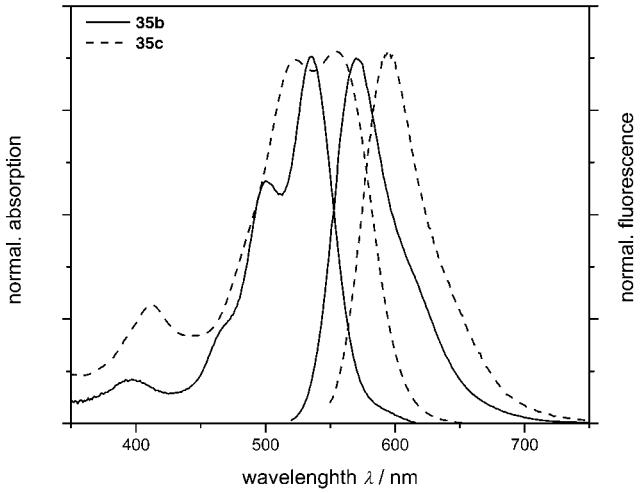


Figure 6. Normalized absorption and emission spectra of two-charge-substituted PDIs **35b** (——) and **35c** (-----) in water.

In the case of **35c**, which bears two sulfonic acid groups (Scheme 6), however, a low FQY (12%) and a smaller hypsochromic shift in the absorption and emission spectra is again found. We attribute this observation to the lower ability of two sulfonic acid groups—relative to four sulfonic acid groups (Figure 2) or to positively charged pyridinium salts—to solubilize the PDI chromophore. In this regard, compound **9** with four sulfonic acid substituents has a higher solubility in water (Figure 2) and, therefore, significantly increased FQYs relative to **35c**, indicating a lower tendency to form aggregates in the case of **9**.

Conclusion

In the course of this work we have presented different synthetic approaches towards fluorescent, water-soluble perylenetetracarboxylic acid diimide chromophores. The introduction of hydrophilic substituents onto the *bay* region of the chromophore results in a loss in planarity of the aromatic scaffold, and water-soluble chromophores displaying low to moderate FQYs (7%–75%) were obtained. The distance between such hydrophilic groups and the chromophore scaffold was then increased to suppress fluorescence quenching due to photoinduced electron-transfer processes. However, attachment of a short alkyl or phenyl spacer was accompanied by a considerable decrease in FQY, which was mainly attributed to the formation of aggregates due to the low solubility of the resulting chromophores. PDI chromophores were then encapsulated within rigid dendritic polyphenylene shells to suppress aggregation completely. Nevertheless, these chromophores displayed only weak FQYs (1% to 19%), which was mainly attributed to energy loss through vibrational relaxation together with photoinduced energy transfer processes between the substituents and the chromophore. The reduction of the number of pyridinium groups down to a minimum of the two groups indispensable for providing sufficient water solubility finally resulted in highly fluorescent chromophores with quantitative FQYs in water. However, analogous chromophores bearing two sulfonic acid functions were again only weakly fluorescent. Such differences were ascribed mainly to the potential of the hydrophilic substituent to solubilize the chromophore sufficiently. Therefore, to obtain water-soluble PDI chromophores with high FQYs, the nature of the hydrophilic substituent, the position at which the substituent is attached to the scaffold, the number of substituents, and the lipophilic character of the chromophore all have to be adjusted carefully.

The PDI chromophore with two pyridinium arms reported here represents the first example of a PDI chromophore combining water solubility with a high FQY in water. Thanks to high photostability and absorption and emission maxima above 500 nm, such chromophores are potential useful, novel, high-performance fluorescence markers in aqueous media.

Experimental Section

Materials: Tetrahydrofuran (Fluka) was distilled over sodium/benzophenone. Tetrabutylammonium fluoride (Fluka), di(triphenylphosphine)dichloropalladium(II) (Strem), trimethylethyne (Aldrich), phenol (Aldrich), 3-pyridiniumboronic acid (Lancaster), copper iodide (Aldrich), *p*-iodophenol (Avocado), and *m*-xylene (Aldrich), were used as obtained. Tetrachloroperylenetetracarboxylic acid diimides and dibromoperylenedianhydride were supplied by BASF AG. Column chromatography was performed with dichloromethane (chromasolv, Riedel) or toluene on silica gel (Geduran Si60, Merck). All the reported yields are isolated yields.

Physical and analytical methods: ^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX 250 and Bruker AC 300 spectrometers with use of the residual proton resonance of the solvent or the carbon signal of the deuterated solvent as the internal standard. Chemical shifts are reported in parts per million. Infrared spectra were obtained on a Nicolet FT IR 320. For ^{13}C j-modulated spin-echo NMR measurements, the abbreviation q represents quaternary C atoms and CH_2, while t denotes CH_3 and CH groups. FD mass spectra were performed with a VG-Instruments ZAB 2-SE-FDP instrument. MALDI-TOF mass spectra were measured with a Bruker Reflex II machine in THF and dithranol as matrix (molar ratio dithranol/sample 250:1). The mass peaks with the lowest isotopic mass are reported. UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 40 spectrophotometer, photoluminescence spectra on a SPEX Fluorolog 3 spectrometer. The quantum yields of polyphenylene-dendronized perylenes were measured against perylene in toluene as a reference. The elemental analyses were carried out at the Microanalytical Laboratory at the University of Mainz (Germany).

***N,N′*-Bis(2,6-diisopropylphenyl)-1,6,7,12-tetra-[4-(acetic acid)phenoxy]-perylene-3,4:9,10-tetracarboxylic acid diimide (5)**: *N,N′*-Bis(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid diimide (**3**, 5 g, 5.9 mmol) was treated with methyl (4-hydroxyphenyl)acetate (5 g, 30 mmol) and K_2CO_3 (4.1 g, 30 mmol) in *N*-methyl-pyrrolidone

(250 mL). The reaction mixture was heated under argon atmosphere for 16 h. The reaction mixture was then allowed to allowed to cool to room temperature, and dilute hydrochloric acid (500 mL) was added. A precipitate was formed and was filtered off, washed with water to neutral pH, and dried under vacuum. The crude product was then purified by column chromatography on silica gel with a dichloromethane/acetone (100:5) solvent mixture. Yield: 6.3 g (82%) as a red solid; m.p. >300°C; ^{1}H NMR (250 MHz, $C_2D_2Cl_4$, 300 K): δ = 8.15 (s, 4H), 7.89 (d, ^3J = 8.8 Hz, 8H), 7.35 (t, ^3J = 8.0 Hz, 2H), 7.19 (d, ^3J = 8.0 Hz, 4H), 6.95 (d, ^3J = 8.8 Hz, 8H), 3.81 (s, 8H), 2.59 (sept, ^3J = 6.9 Hz, 4H), 1.03 (d, ^3J = 6.9 Hz, 24H) ppm; ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 300 K): δ = 166.41 (C=O), 163.07 (C=O), 159.39, 155.32, 145.70, 133.33, 132.23, 130.40, 129.78, 126.65, 124.28, 123.53, 121.44, 121.31, 119.62, 52.66, 29.34, 24.44 ppm; IR (KBr): $\tilde{\nu}$ = 2961, 2361, 2336, 1720, 1674, 1592, 1501, 1435, 1406, 1339, 1310, 1275, 1206, 1162, 1109, 1014, 960, 876, 848, 762 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 529 (33300), 564 nm (50000 M^{-1}cm^{-1}); fluorescence ($CHCl_3$, excitation: 529 nm): λ_{max} = 620 nm; MS (FD 8 kV): *m/z* (%): 1312.9 (100) $[M]^+$; elemental analysis calcd (%) for $C_{80}H_{66}N_2O_{16}$: C 73.27, H 5.07, N 2.14; found: C 73.23, H 5.13, N 2.11.

Compound 9: *N,N′*-Bis(2,6-diisopropylphenyl-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic acid diimide (2 g, 1.8 mmol) was added to concentrated sulfuric acid (5 mL). The flask was sealed, and the mixture was stirred at room temperature for 15 h. Water (7 mL) was slowly added to the flask to form a precipitate, which was filtered under suction. The solid was washed three times with dichloromethane (50 mL), and was then dried at 120°C under vacuum to give a red product (2.4 g, 93%). M.p. >300°C; ^{1}H NMR (300 MHz, CD_3OD, 300 K): δ = 7.91 (s, 4H), 7.59 (d, ^3J = 8.0 Hz, 8H), 7.17 (t, ^3J = 7.5 Hz, 2H), 7.04 (d, ^3J = 8.0 Hz, 4H), 6.88 (d, ^3J = 8.0 Hz, 8H), 2.45 (m, 4H), 0.85 (d, ^3J = 6.75 Hz, 24H) ppm; ^{13}C NMR (75 MHz, CD_3OD, 300 K): δ = 164.1 (C=O), 158.5, 156.9, 147.2, 142.4, 131.8, 129.4, 125.0, 124.4, 122.3, 121.8, 120.7, 30.2 (CH isopropyl), 24.2 (CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 2970, 2361, 1701, 1655, 1588, 1491, 1410, 1340, 1287, 1208, 1180, 1125, 1066, 1032, 1007, 882, 846, 699, 580 cm^{-1}; UV/Vis (H_2O): λ_{max} (ε) = 461 (10708), 541 (21026), 571 nm (27800 M^{-1}cm^{-1}); fluorescence (H_2O, excitation 560 nm): λ_{max} = 619 nm; MS (MALDI-TOF): *m/z* (%): 1401 (%) $[M]^+$ (calcd 1401).

Compound 11: Tetrachloroperylenetetracarboxylic acid diimide (2 g, 2.32 mmol) was stirred under argon with 4-(2-dimethylaminoethyl)phenol hydrochloride acid salt (2.36 g, 11.8 mmol) in NMP (200 mL) in a 500 mL round flask in the presence of powdered anhydrous K_2CO_3 (2 g, 14.4 mmol). The temperature was kept at 100°C under argon overnight. The reaction mixture was allowed to cool to room temperature and was then poured into aqueous hydrochloride acid (2N). The precipitated product was filtered under suction and then washed thoroughly with water and dried at 75°C under vacuum. The product, a red solid, was purified by column chromatography to provide **5** (1.9 g, 62%) as a dark solid. M.p. 208°C; ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K): δ = 8.17 (s, 4H), 7.46 (t, ^3J = 7.5 Hz, 2H), 7.30 (d, ^3J = 7.5 Hz, 4H), 7.30 (d, ^3J = 8.0 Hz, 8H), 6.90 (d, ^3J = 8.0 Hz, 8H), 2.85–2.66 (m, 12H), 2.45 (m, 8H), 2.25 (s, 24H), 1.08 (d, ^3J = 8.0 Hz, 24H; CH_3 isopropyl) ppm; ^{13}C NMR (62.5 MHz, CD_2Cl_2, 300 K): δ = 163.7, 156.3, 153.8, 146.3, 137.5, 133.5, 131.4, 130.5, 129.7, 124.3, 123.1, 121.1, 120.4, 120.1, 61.7, 45.5, 33.7, 29.4 (CH isopropyl), 24.0 (CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 2961, 2864, 2815, 2768, 2361, 1705, 1672, 1587, 1501, 1462, 1406, 1340, 1309, 1284, 1201, 1051, 1015, 958, 877, 825, 737, 675, 537 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 456 (18189), 539 (30196), 577 nm (48744 M^{-1}cm^{-1}); MS (FD 8 kV): *m/z* (%): 1363.2 (%) $[M]^+$ (calcd 1363.7); elemental analysis calcd (%) for $C_{88}H_{94}N_6O_8$: C 77.50, H 6.95, N 6.16; found: C 76.94, H 6.76, N 6.04.

Compound 12a: Perylene derivative **12** (1 g, 0.73 mmol) and methyl iodide (2 mL) in chloroform (100 mL) were placed in a 250 mL round flask. The reaction mixture was heated to 60°C for 1 hour, resulting in the formation of a dark precipitate. After the chloroform had been removed, the residue was dissolved in methanol (20 mL) containing methyl iodide (3 mL). The solution was stirred at 70°C for 24 h. The solvent and the excess methyl iodide were removed under vacuum to give a dark red solid. The product **12a** (1.3 g, 93%) was obtained after drying at 75°C under vacuum. M.p. >300°C; ^{1}H NMR (300 MHz, CD_3CN, 343 K): δ = 8.08 (s, 4H), 7.45 (t, ^3J = 7.5 Hz, 2H), 7.34 (m, 12H), 7.06 (d, ^3J = 7.5 Hz, 8H), 3.62 (m, 8H), 3.20 (s, 36H), 3.13 (m, 8H), 2.75 (m, 4H), 1.09 (d, ^3J = 7.0 Hz, 24H) ppm; ^{13}C NMR (75 MHz, CD_3OD, 328 K): δ = 164.9, 157.6, 155.9, 147.2, 134.5, 133.7, 132.1, 131.9, 129.9, 125.0, 123.9, 122.1, 122.0, 121.3, 120.7, 68.4, 54.1, 40.2, 30.3 (CH isopropyl), 29.8, 24.1 (CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 2961, 2362, 2336, 1698, 1660, 1587, 1501, 1409, 1339, 1285, 1206, 1174, 965, 911, 877, 842, 741, 673, 549 cm^{-1}; UV/Vis (methanol): λ_{max} (ε) = 444 (14216), 539 (24361), 577 nm (29295 M^{-1}cm^{-1}); fluorescence (methanol, excitation: 550 nm): λ_{max} = 613 nm; elemental analysis calcd (%) for $C_{92}H_{106}N_6O_8I_4$: C 57.21, H 5.53, N 4.35; found: C 57.31, H 5.56, N 4.07.

Compound 12b: Ionic perylene derivative **12a** (200 mg, 0.103 mmol) and silver methanesulfonate (83 mg, 0.412 mmol) were added to methanol (50 mL). The reaction mixture was stirred for 3 h at room temperature. The white silver iodide was filtered off under vacuum to give a clear red solution. After the solvent had been removed under vacuum, **12b** (180 mg, 97%) was obtained as a dark red solid. M.p. 280°C; ^{1}H NMR (250 MHz, CD_3CN, 300 K): δ = 8.02 (s, 4H), 7.45 (t, ^3J = 8.0 Hz, 2H), 7.30 (m, 12H), 6.99 (d, ^3J = 8.0 Hz, 8H), 3.64 (m, 8H), 3.15 (s, 36H; CH_3 *N*-methyl) 3.10 (m, 4H), 2.72 (m, 4H; CH isopropyl), 2.43 (s, 12H; S–CH_3), 1.05 (d, ^3J = 7.5 Hz, 24H; CH_3 isopropyl) ppm; ^{13}C NMR (75 MHz, CD_3CN, 343 K): δ = 164.6, 157.1, 155.9, 147.5, 134.5, 133.7, 132.5, 132.0, 130.7, 125.2, 124.5, 121.9, 121.7, 120.9, 68.0, 54.5, 40.2, 30.1 (CH isopropyl), 29.5, 24.3 (CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 2963, 2361, 2336, 1701, 1662, 1589, 1502, 1409, 1340, 1284, 1204, 1052, 912, 877, 781, 672, 558 cm^{-1}; UV/Vis (H_2O): λ_{max} (ε) = 460 (13537), 586 nm (35436 M^{-1}cm^{-1}); fluorescence (H_2O, excitation: 540 nm): λ_{max} = 627 nm; elemental analysis calcd (%) for $C_{96}H_{118}N_6O_{20}S_4$: C 63.91, H 6.59, N 4.66; found: C 63.24, H 6.64, N 4.61.

Compound 16: *N,N′*-Bis(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid diimide (5 g, 5.9 mmol), 3-hydroxypyridine (4.48 g, 47.2 mmol), and anhydrous K_2CO_3 (3.45 g, 25 mmol) were added to NMP (600 mL). The solution was stirred at 100°C under argon for 15 h. The reaction mixture was allowed to cool to room temperature and poured into aqueous hydrochloride acid (1 L, 1M). The precipitated product was filtered under suction and was then washed thoroughly with water and dried at 75°C under vacuum. The product was purified by column chromatography to give **16** (4.7 g, 74%) as a red solid. M.p. >300°C; ^{1}H NMR (250 MHz, $C_2D_2Cl_4$, 300 K): δ = 8.29 (d, ^3J = 6.3 Hz, 4H), 8.28 (s, 4H), 8.14 (s, 4H), 7.35 (t, ^3J = 7.5 Hz, 2H), 7.29 (m, 4H), 7.19 (d, ^3J = 8.0 Hz, 4H), 7.17 (d, ^3J = 8.0 Hz, 4H), 2.58 (m, 4H), 1.03 (d, ^3J = 6.75 Hz, 24H) ppm; ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 300 K): δ = 162.9 (C=O), 155.5, 152.0, 146.3, 145.6, 141.9, 133.5, 130.2, 129.8, 127.3, 124.9, 123.6, 121.4, 121.1, 120.5, 94.2, 29.3 (CH isopropyl), 24.4 (CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 3061, 2963, 2868, 2361, 1707, 1671, 1593, 1508, 1474, 1423, 1407, 1339, 1309, 1279, 1207, 1102, 1019, 958, 875, 808, 738, 705, 581 cm^{-1}; UV/Vis (methanol): λ_{max} (ε) = 526 (30500), 560 nm (44800 M^{-1}cm^{-1}); fluorescence (methanol, excitation: 526 nm): λ_{max} = 610 nm; MS (FD 8 kV): *m/z* (%): 1083.2 (%) $[M]^+$ (calcd 1083.1).

Compound 17a: *N,N′*-Bis(2,6-diisopropylphenyl)-1,6,7,12-tetra(3-pyridoxy)-perylene-3,4:9,10-tetracarboxylic acid diimide (1 g, 0.92 mmol) was dissolved in methanol (100 mL), and the mixture was heated at 80°C. Methyl iodide (655 mg, 4.6 mmol) was then added by syringe with vigorous stirring. After 12 h, the solvent was evaporated under vacuum and the product was dried at 75°C. Yield: 1.5 g (96%) as a dark red solid; M.p. >300°C; ^{1}H NMR (250 MHz, CD_3OD, 300 K): δ = 8.94 (s, 4H), 8.54 (d, ^3J = 6.0 Hz, 4H), 8.38–8.28 (m, 8H), 7.95–7.90 (m, 4H), 7.34 (t, ^3J = 8.2 Hz, 4H), 7.91 (d, ^3J = 8.2 Hz, 4H), 4.30 (s, 12H), 2.73 (sept, ^3J = 6.9 Hz, 4H), 0.97 (d, ^3J = 6.9 Hz, 24H) ppm; ^{13}C NMR (75 MHz, CH_3OH-D_4, 300 K): δ = 164.06 (C=O), 157.02, 154.95, 147.04, 142.99, 139.44, 135.93, 134.19, 131.42, 130.94, 130.29, 126.13, 125.22, 124.53, 124.23, 123.60, 39.54, 30.32, 24.32 ppm; IR (KBr): $\tilde{\nu}$ = 2963, 2361, 2336, 1704, 1665, 1594, 1503, 1473, 1408, 1337, 1309, 1275, 1212, 812, 672 cm^{-1}; UV/Vis (H_2O): λ_{max} (ε) = 520 (19300), 555 nm (25700 M^{-1}cm^{-1}); fluorescence (H_2O, excitation: 520 nm): λ_{max} = 601 nm; elemental analysis calcd (%) for $C_{72}H_{66}I_4N_6O_8$: C 52.38, H 4.03, N 5.09; found: C 52.41, H 4.00, N 5.11.

Compound 17b: Perylene derivative **17** (1 g, 0.92 mmol), methyl iodide (3 mL), and methanol (150 mL) were placed in a 250 mL flask. The reaction mixture was stirred at 80°C for 24 h. After the reaction mixture had been allowed to cool to room temperature, the solvent was removed under vacuum. The residue and silver methanesulfonate (743 mg, 3.68 mmol) were added to methanol (100 mL) to form a white precipitate (silver iodide), which was removed to give a clear red solution. A red

solid (1.4 g, 91 %) was obtained after evaporation of the solvent. M.p. 264 °C; ^{1}H NMR (300 MHz, CD_3OD, 300 K): δ = 8.95 (m, 4H), 8.66 (d, ^3J = 6.0 Hz, 4H), 8.31 (s, 4H), 8.27 (m, 4H), 7.97 (d, ^3J = 7.5 Hz, 2H), 7.94 (d, ^3J = 7.5 Hz, 2H), 7.38 (t, ^3J = 7.5 Hz, 2H), 7.23 (d, ^3J = 7.5 Hz, 4H), 4.34 (s, 12H), 2.61 (m, 2H; CH isopropyl), 2.46 (s, 12H; S–CH_3), 1.08 (d, ^3J = 6.5 Hz, 12H; CH_3 isopropyl) ppm; ^{13}C NMR (75 MHz, CD_3OD, 300 K): δ = 164.0 (C=O), 157.0, 154.9, 127.0, 142.9, 139.4, 135.9, 134.1, 131.4, 130.9, 130.2, 126.1, 125.2, 124.5, 124.2, 123.5, 39.5, 30.3, 24.3 ppm; IR (KBr): $\tilde{\nu}$ = 3432, 2946, 2361, 2336, 1705, 1664, 1595, 1502, 1408, 1335, 1310, 1274, 1200, 1052, 957, 814, 780, 671, 558 cm^{-1}; UV/Vis (H_2O): λ_{max} (ε) = 434 (9766), 516 (24628), 547 nm (33751 M^{-1}cm^{-1}); fluorescence (H_2O, excitation: 540 nm): λ_{max} = 588 nm; elemental analysis calcd (%) for $C_{76}H_{78}N_6O_{20}S_4$: C 59.91, H 5.16, N 5.52; found: C 59.54, H 5.32, N 5.47.

Compound 21: 4-(Dimethylamino)phenylboronic acid **19** (1 g, 6 mmol), tetrabromoperylenediimide **18** (2.8 g, 2 mmol), and toluene (120 mL) were placed in a 250 mL Schlenk flask. Aqueous K_2CO_3 (30 mL, 1 M), ethanol (20 mL), and [$Pd(PPh_3)_4$] (400 mg, 0.25 mmol) were then added to the flask under argon. After 16 h at 80 °C, the reaction mixture was allowed to cool to room temperature. The organic phase was separated and dried under vacuum. The crude material was purified by column chromatography on silica to give **2** (2.86 g, 92 %). M.p. >300 °C; ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K): δ = 8.29 (s, 4H), 7.47 (m, 18H), 7.30 (d, ^3J = 7.5 Hz, 4H), 7.07 (dd, ^3J = 8.0 Hz, 8H), 6.77 (d, ^3J = 8.0 Hz, 8H), 2.97 (s, 24H; CH_3 *N*-methyl) 2.72 (m, 4H; CH isopropyl), 1.09 (d, ^3J = 7.5 Hz, 24H; CH_3 isopropyl) ppm; ^{13}C NMR (62.5 MHz, CD_2Cl_2, 300 K): δ = 164.6, 157.2, 155.0, 151.0, 146.8, 139.1, 134.5, 131.8, 130.7, 129.5, 129.1, 125.3, 123.9, 122.1, 121.7, 121.6, 121.4, 113.9, 41.88, 30.4 (CH isopropyl), 25.5 (CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 2962, 2361, 1701, 1668, 1611, 1585, 1495, 1407, 1338, 1290, 1202, 1166, 946, 884, 808, 733, 525 cm^{-1}; UV/Vis ($CHCl_3$) λ_{max} (ε) = 441 (16085) 553 (33223), 592 nm (38674 M^{-1}cm^{-1}); MS (FD 8 kV): *m*/*z* (%) = 1555.1 (%) $[M]^+$ (calcd 1555.8); elemental analysis calcd (%) for $C_{104}H_{94}N_6O_8$: C 80.28, H 6.09, N 5.40; found: C 79.54, H 5.96, N 5.33.

Compound 22: *N*,*N*′-Bis(2,6-diisopropylphenyl-1,6,7,12-tetra(4-bromophenoxy)perylene-3,4:9,10-tetracarboxylic acid diimide (1.3 g, 1 mmol), 3-pyridinium boronic ester (1 g, 6.2 mmol), and toluene (60 mL) were placed in a 250 mL Schlenk flask. $Pd(PPh_3)_4$ (200 mg, 0.16 mmol), aqueous K_2CO_3 (20 mL, 1 M), and ethanol (10 mL) were then added to the flask under argon. After 16 h at 80 °C, the reaction mixture was allowed to cool to room temperature. The organic phase was separated and dried under vacuum. The crude material was purified by column chromatography on silica to give **22** (1.16 g, 84 %). M.p. 281 °C; ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K): δ = 8.76 (d, ^3J = 1.5 Hz, 4H), 8.53 (dd, ^3J = 5.0 Hz, 4H), 8.35 (s, 4H), 7.82 (t, ^3J = 1.5 Hz, 2H), 7.79 (t, ^3J = 1.5 Hz, 2H), 7.54 (dd, ^3J = 8.0 Hz, 8H), 7.45 (d, ^3J = 7.5 Hz, 2H), 7.32 (m, 8H), 7.14 (d, ^3J = 7.5 Hz, 8H), 2.72 (m, 2H; CH isopropyl), 1.10 (d, ^3J = 6.75 Hz, 12H; CH_3 isopropyl) ppm; ^{13}C NMR (62.5 MHz, CD_2Cl_2, 300 K): δ = 163.6 (q, C=O), 156.0 (q), 148.8 (t), 148.4 (t), 146.3 (q), 135.9 (q), 134.8 (q), 134.4 (t), 133.6 (q), 131.3 (q), 129.9 (t), 129.2 (t), 124.4 (t), 123.9, (t), 123.5 (q), 121.5 (q), 121.2 (q), 121.1 (t), 120.7 (t), 29.5 (t), 24.1 (t) ppm; IR (KBr): $\tilde{\nu}$ = 3031, 2961, 2867, 2361, 2336, 1705, 1669, 1589, 1504, 1472, 1405, 1337, 1307, 1279, 1208, 1172, 1000, 957, 876, 842, 803, 739, 711, 674, 552 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 448 (19864), 534 (30794), 574 nm (50105 M^{-1}cm^{-1}); fluorescence ($CHCl_3$, excitation 540: nm): λ_{max} = 606 nm; MS (FD 8 kV): *m*/*z* (%): 1387.9 (%) $[M]^+$ (calcd 1387.6); elemental analysis calcd (%) for $C_{92}H_{70}N_6O_8$: C 79.63, H 5.08, N 6.06; found: C 79.59, H 5.20, N 6.01.

Compound 23a: Perylene derivative **18** (1 g, 0.64 mmol) and methyl iodide (2 mL) in methanol (100 mL) were placed in a 250 mL round flask. The reaction mixture was heated to 60 °C for 1 hour, resulting in the formation of a dark precipitate. After chloroform had been removed, the residue was dissolved in methanol (20 mL) containing methyl iodide (3 mL). The solution was stirred at 80 °C for 24 h. The solvent and the excess methyl iodide were removed under vacuum. The residue was dried at 75 °C under vacuum to give **23a** (1.2 g, 92 %) as a violet solid. M.p. >300 °C; ^{1}H NMR (250 MHz, CD_3OD, 300 K): δ = 8.16 (s, 4H), 7.90 (d, ^3J = 8.0 Hz, 8H), 7.70 (d, ^3J = 8.0 Hz, 8H), 7.54 (d, ^3J = 8.0 Hz, 8H), 7.29 (t, ^3J = 8.0 Hz, 2H), 7.17 (m, 12H), 3.61 (s, 36H; CH_3 *N*-methyl) 2.60 (m, 4H; CH isopropyl), 0.99 (d, ^3J = 7.5 Hz, 24H; CH_3 isopropyl) ppm; ^{13}C NMR (75 MHz, CD_3OD, 323 K): δ = 164.9, 157.2, 147.5, 147.2, 143.6, 136.6, 134.5, 131.8, 130.7, 129.7, 125.0, 124.1, 122.4, 121.8, 121.7, 121.5, 58.1 (N–CH_3), 30.3 (CH isopropyl), 25.2 (CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 2959, 2361, 2336, 1700, 1660, 1589, 1490, 1406, 1336, 1309, 1278, 1204, 1171, 1119, 1003, 955, 873, 825, 737, 551 cm^{-1}; UV/Vis (methanol): λ_{max} (ε) = 446 (22044), 537 (34082), 575 nm (52404 M^{-1}cm^{-1}); fluorescence (methanol, excitation: 550 nm): λ_{max} = 614 nm; elemental analysis calcd (%) for $C_{108}H_{106}N_6O_8$: C 61.08, H 5.03, N 3.96; found: C 60.69, H 5.26, N 3.73.

Compound 23b: Ionic perylene derivative **23a** (400 mg, 0.188 mmol) and silver methanesulfonate (152 mg, 0.754 mmol) were added to methanol (50 mL). The reaction mixture was stirred for 3 h at room temperature. The white silver iodide was filtered off under vacuum to give a clear red solution. After the solvent had been removed under vacuum, **23b** (345 mg, 92 %) was obtained as a dark red solid. M.p. >350 °C; ^{1}H NMR (250 MHz, CD_3OD, 300 K): δ = 8.16 (s, 4H), 7.86 (d, ^3J = 9.5 Hz, 8H), 7.71 (d, ^3J = 9.0 Hz, 8H), 7.56 (d, ^3J = 8.5 Hz, 8H), 7.30 (t, ^3J = 8.5 Hz, 2H), 7.17 (m, 12H), 3.58 (s, 24H; CH_3 *N*-methyl) 2.60 (m, 4H; CH isopropyl), 2.56 (s, 12H; S–CH_3), 1.09 (d, ^3J = 7.5 Hz, 24H; CH_3 isopropyl) ppm; ^{13}C NMR (75 MHz, CD_3OD, 300 K): δ = 164.8, 157.3, 157.1, 147.5, 147.1, 143.5, 136.6, 134.5, 131.7, 130.7, 130.1, 129.7, 125.1, 124.0, 122.3, 122.0, 121.7, 121.6, 121.2, 57.7 (N–CH_3), 39.5 (S–CH_3), 30.3 (CH isopropyl), 25.2 (CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 2962, 2361, 1701, 1668, 1611, 1585, 1495, 1407, 1338, 1290, 1202, 1166, 946, 884, 808, 733, 525 cm^{-1}; UV/Vis (H_2O): λ_{max} (ε) = 491 (17088) 554 (24621), 565 nm (27454 M^{-1}cm^{-1}); fluorescence (DMSO, excitation: 520 nm): λ_{max} = 614 nm; elemental analysis calcd (%) for $C_{108}H_{106}N_6O_8$: C 67.38, H 5.96, N 4.21; found: C 67.11, H 5.99, N 4.12.

Compound 24a: Perylene derivative **22** (400 mg, 0.28 mmol), methyl iodide (3 mL), acetone (30 mL), and methanol (100 mL) were placed in a 250 mL flask. The reaction mixture was stirred at 70 °C for 20 h. The solvent was removed under vacuum after having been allowed to cool to room temperature. The residue was dissolved in methanol (100 mL), and methyl iodide (2 mL) was added. The solution was stirred at 80 °C for 24 h. The solvent was removed, and the residue was dried under vacuum at 75 °C to give **24a** (380 mg, 91 %) as a brown solid. M.p. 353 °C; ^{1}H NMR (250 MHz, CD_3OD, 300 K): δ = 9.18 (s, 2H), 8.95 (s, 2H), 8.71–8.56 (m, 8H), 8.17 (s, 4H), 7.95 (m, 2H), 7.88 (q, 2H), 7.79–7.68 (m, 8H), 7.33 (t, ^3J = 8.5 Hz, 2H), 7.28–7.18 (m, 12H), 4.36 (s, 6H), 4.34 (s, 6H), 2.61 (m, 4H; CH isopropyl), 1.00 (d, ^3J = 6.75 Hz, 24 H CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 3029, 2961, 2361, 2336, 1695, 1660, 1588, 1492, 1406, 1338, 1283, 1211, 1173, 959, 878, 844, 809, 738, 675, 566, 529 cm^{-1}; UV/Vis (methanol): λ_{max} (ε) = 442 (17257), 529 (24447), 567 nm (37151 M^{-1}cm^{-1}); fluorescence (methanol, excitation: 540 nm): λ_{max} = 606 nm.

Compound 24b: Ionic perylene derivative **24a** (100 mg, 0.051 mmol) and silver methanesulfonate (46 mg, 0.21 mmol) were added to methanol (50 mL). The reaction mixture was stirred for 15 h at room temperature. The white silver iodide was filtered off under vacuum to give a clear red solution. After the solvent had been removed under vacuum, **24b** (85 mg, 94 %) was obtained as a dark red solid. M.p. 243 °C; ^{1}H NMR (250 MHz, CD_3OD, 300 K): δ = 9.16 (s, 4H), 8.73 (d, ^3J = 6.0 Hz, 4H), 8.66 (d, ^3J = 8.2 Hz, 4H), 8.16 (s, 4H), 8.00 (m, 4H), 7.76 (d, ^3J = 8.75 Hz, 8H), 7.34 (t, ^3J = 8.5 Hz, 2H), 7.28 (d, ^3J = 8.5 Hz, 8H), 7.21 (d, ^3J = 7.7 Hz, 4H), 4.35 (s, 12H), 2.61 (m, 4H; CH isopropyl), 2.57 (s, 12H; S–CH_3), 1.00 (d, ^3J = 6.7 Hz, 24H; CH_3 isopropyl) ppm; ^{13}C NMR (62.5 MHz, CD_3OD, 300 K): δ = 164.9 (q, C=O), 159.0 (q), 157.3 (q), 147.4 (q), 145.2 (t), 145.0 (t), 143.9 (t), 141.8 (q),134.8 (q),132.0 (q),131.5 131.1 (t), 129.4 (t), 125.4 (t), (q),124.7 (q), 122.7 (t), 122.4 (q), 121.9 (t), 39.8 (t, S–CH_3), 30.7 (t, CH isopropyl), 24.6 (t, CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 3025, 2923, 2792, 2360, 1707, 1674, 1613, 1522, 1500, 1438, 1403, 1338, 1277, 1199, 1165, 1129, 1069, 1018, 946, 875, 822, 754, 699, 558 cm^{-1}; UV/Vis (H_2O): λ_{max} (ε) = 459 (19225), 578 nm (25855 M^{-1}cm^{-1}); fluorescence (H_2O, excitation: 540 nm): λ_{max} = 624 nm.

Compound 26: 1,3-Diphenylacetone (4.3 g, 20 mmol), 4,4′-bis(dimethylamino)benzyl (6 g, 20 mmol), and EtOH (100 mL) were placed in a 250 mL round flask. The solution was heated to 82 °C, and potassium hydroxide (1.12 g, 20 mmol) in EtOH (20 mL) was then injected into the flask under argon. After the mixture had been stirred at 82 °C for 15 h, it was allowed to cool to room temperature. The solution was filtered to give a yellow solid, which was washed three times with ethanol (100 mL). The product was obtained by column chromatography (2.9 g, 31 %). M.p.

273 °C; ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K): δ = 7.24 (m, 10H), 6.81 (d, ^3J = 8.5 Hz, 4H), 6.50 (d, ^3J = 8.5 Hz, 4H), 2.95 (s, 12H; CH_3) ppm; ^{13}C NMR (62.5 MHz, CD_2Cl_2, 300 K): δ = 200.5 (C=O), 155.2, 150.7, 132.8, 131.5, 130.6, 128.1, 127.0, 124.0, 111.11, 40.2 (CH_3) ppm; IR (KBr): $\tilde{\nu}$ = 2923, 2798, 2361, 1689, 1603, 1517, 1490, 1442, 1355, 1309, 1228, 1197, 1169, 1116, 944, 896, 823, 765, 735, 699, 536 cm^{-1}; MS (FD 8 kV): *m/z* (%): 470.3 (%) $[M]^+$ (calcd 470.6); elemental analysis calcd (%) for $C_{33}H_{30}N_2O$: C 84.22, H 6.43, N 5.95; found: C 84.15, H 6.48, N 6.01.

Compound 27: A mixture of ethynyl-substituted perylenediimide **25** (100 mg, 0.085 mmol) and tetraphenylcyclopentadienone derivative **26** (200 mg, 0.425 mmol) in *m*-xylene (5 mL) was stirred at 140 °C under argon for 15 h. The cooled reaction mixture was poured into methanol (100 mL). The precipitated product was filtered under suction. Finally, the product was dried and purified by column chromatography on silica gel to give a dark red solid. Yield: 230 mg (92 %). M.p. >300 °C; ^{1}H NMR (250 MHz, CD_2Cl_4, 300 K): δ = 8.13 (s, 4H), 7.48 (m, 6H), 7.33 (d, ^3J = 7.5 Hz, 4H), 7.15 (m, 20H), 7.03 (d, ^3J = 8.0 Hz, 8H), 6.94 (m, 8H), 6.83 (m, 12H), 6.71 (d, ^3J = 8.0 Hz, 8H), 6.66 (d, ^3J = 8.0 Hz, 16H), 6.34 (d, ^3J = 8.0 Hz, 8H), 6.30 (d, ^3J = 8.0 Hz, 8H), 2.80 (s, 24H), 2.78 (s, 24H), 2.71 (m, 4H; CH isopropyl), 1.12 (d, ^3J = 8.0 Hz, 24H) ppm; ^{13}C NMR (62.5 MHz, CD_2Cl_2, 300 K): δ = 163.6 (q, C=O), 156.1 (q), 154.1 (q), 148.6 (q), 148.4 (q), 146.4 (q), 142.9 (q), 142.5 (q), 141.6 (q), 141.0 (q), 140.4 (q), 140.1 (q), 139.6 (q), 138.9 (q), 133.2 (q), 132.6 (t), 132.5 (t), 132.0 (t), 131.9 (t), 131.5 (q), 131.2 (t), 130.3 (t), 129.8 (t), 129.1 (q), 128.7 (q), 127.8 (t), 127.2 (t), 126.2 (t), 125.8 (t), 124.4 (t), 123.3 (q), 121.2 (q), 121.1 (t), 120.7 (q), 119.2 (t), 111.3 (t), 111.1 (t), 40.5 (t, CH_3), 29.4 (t, CH isopropyl), 24.1 (p, CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 3030, 2961, 2796, 2361, 2336, 1707, 1673, 1611, 1521, 1500, 1441, 1404, 1338, 1278, 1201, 1167, 1016, 946, 821, 698, 544 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 463 (20661), 545 (27993), 585 nm (43834 M^{-1}cm^{-1}); fluorescence (cyclohexane): λ_{max} = 594 nm (excitation 540 nm); MS (MALDI-TOF 8 kV): *m/z* = 2945 (%) $[M]^+$ (calcd 2945); elemental analysis calcd (%) for $C_{208}H_{178}N_{10}O_8$: C 84.81, H 6.09, N 4.75; found: C 84.51, H 5.88, N 4.90.

Compound 28: Dendronized perylene derivative **27** (200 mg, 0.068 mmol), dimethylsulfate (2 mL), and chloroform (50 mL) were placed in a 100 mL round flask. The reaction mixture was heated to 75 °C for 16 h, resulting in a dark precipitate. After the chloroform had been removed, the residue was dissolved in methanol (50 mL) and dimethylsulfate (1 mL), and the mixture was maintained at 80 °C for 48 h. The solvent was removed under vacuum to give a dark oil. Diethyl ether (100 mL) and dichloromethane (100 mL) were added to the flask to form a precipitate, which was washed three times with dichloromethane (50 mL). The product **28** was obtained after removal of the solvent and drying under vacuum at 100 °C (130 mg, 62 %). M.p. >300 °C; ^{1}H NMR (250 MHz, CD_3OD, 300 K): δ = 7.96 (s, 4H), 7.45 (d, ^3J = 7.5 Hz, 10H), 7.40 (d, ^3J = 7.5 Hz, 10H), 7.25 (d, ^3J = 7.5 Hz, 4H), 7.05 (s, 16H), 7.03 (m, 34H), 6.83 (m, 16H), 6.76 (d, ^3J = 7.5 Hz, 8H), 3.36 (s, 24H), 3.42 (s, 36H), 3.38 (s, 36H), 2.61 (m, 4H), 1.03 (d, ^3J = 6.7 Hz, 24H) ppm; ^{13}C NMR (125 MHz, [D$_4$]DMSO, 306 K): δ = 162.6 (C=O), 155.2, 153.4, 145.5, 145.2, 145.0, 141.5, 141.1, 140.2, 140.1, 139.8, 138.7, 138.6, 137.4, 132.6, 131.4, 131.1, 129.6, 128.0, 127.2, 127.0, 126.3, 123.8, 122.6, 119.9, 119.2, 118.9, 118.5, 56.4 (N–CH_3), 28.4 (CH isopropyl), 23.7 (CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}_{max}$ = 3030, 2962, 2796, 2361, 1696, 1655, 1592, 1485, 1413, 1341, 1285, 1219, 1127, 1033, 842, 625, 574 cm^{-1}; UV/Vis (H_2O): λ_{max} (ε) = 463 (17459), 548 (22965), 589 nm (36113 M^{-1}cm^{-1}); fluorescence (H_2O, excitation 550 nm): λ_{max} = 620 nm; elemental analysis calcd (%) for $C_{224}H_{226}N_{10}O_{40}S_8$: C 68.03, H 5.76, N 3.54; found: C 67.71, H 5.92, N 3.57.

Compound 30a: Compounds **25** (220 mg, 0.187 mmol) and **29a** (834 mg, 1.12 mmol) were dissolved in *o*-xylene (15 mL) and were heated at 170 °C for 20 h under argon atmosphere. The crude mixture was then poured into methanol (100 mL), and the precipitate was filtered, washed several times with methanol, and dried under vacuum. Yield: 670 mg (0.166 mmol, 89 %) as a red solid; m.p. : 262 °C (decomp); ^{1}H NMR (300 MHz, d^8-THF, 298 K): δ = 8.14 (s, 4H; $H_{bay\text{-}p.}$), 7.79–6.22 (m, 178H; arom. H), 2.77 (sept, ^3J = 6.96 Hz, 4H; CH isopropyl), 1.13 (d, ^3J = 6.32 Hz, 24H; CH_3 isopropyl) ppm; ^{13}C NMR (75 MHz, [D$_8$]THF, 298 K): δ = 168.83 (C=N), 163.51 (C=O), 154.98, 153.02, 149.74, 149.40, 142.49, 140.32, 140.19, 137.04, 132.37, 132.21, 131.41, 130.84, 130.59, 130.18, 129.98, 129.87, 129.38, 129.11, 128.76, 128.62, 129.39, 127.60, 125.18, 121.02, 120.54, 120.35, 29.85 (CH isopropyl), 24.21 (CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 3060, 3032, 2967, 2945, 2872, 1708, 1674, 1594, 1501, 1446, 1406, 1338, 1317, 1287, 1206, 1181, 1141, 957, 842, 764, 698 cm^{-1}; UV/Vis (toluene): λ_{max} (ε) = 362 (64807), 543 (22368), 583 nm (33679 M^{-1}cm^{-1}); fluorescence (toluene, excitation: 583 nm): λ_{max} = 607 nm; MS (MALDI-TOF): *m/z* (%): 4036 (%) $[M]^+$, (calcd 4035); elemental analysis calcd (%) for $C_{296}H_{210}N_{10}O_8$: C 88.11, H 5.25, N 3.47; found: C 87.85, H 5.39, N 3.40.

Compound 31a: Compound **30a** (500 mg, 0.124 mmol) was dissolved in THF (7 mL) under argon atmosphere, and degassed hydrochloric acid (5 M, 15 mL) was added. The reaction mixture was stirred under argon at room temperature for 2 h. The precipitate was filtered off and washed with hexane. Yield: 315 mg (0.117 mmol, 94 %) as a violet solid. M.p. >300 °C; ^{1}H NMR (300 MHz, d^8-THF, 298 K): δ = 8.05 (s, 4H; $H_{bay\text{-}p.}$), 7.78–6.79 (m, 98H; arom. H), 2.78 (sept, ^3J = 6.68 Hz, 4H; CH isopropyl), 1.18 (d, ^3J = 6.49 Hz, 24H; CH_3 isopropyl) ppm; ^{13}C NMR (75 MHz, [D$_8$]THF, 298 K): δ = 199.75, 156.42, 155.81, 140.02, 135.55, 134.94, 133.52, 133.12, 132.42, 132.14, 130.67, 130.28, 130.16, 130.09, 130.00, 129.67, 129.18, 128.44, 124.11, 123.86, 123.55, 31.56 (CH isopropyl), 25.53 (CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 3433, 3062, 2881, 3593, 2000, 1704, 1660, 1597, 1504, 1447, 1409, 1339, 1318, 1281, 1207, 1178, 841, 761, 703, 638 cm^{-1}; UV/Vis (methanol): λ_{max} (ε) = 442 (15142), 536 (17016), 572 nm (23069 M^{-1}cm^{-1}); fluorescence (methanol, excitation: 572 nm): λ_{max} = 611 nm; MS (MALDI-TOF): *m/z* (%): 2724 (%) $[M]^+$ (calcd 2721).

Compound 30b: Compounds **25** (150 mg, 0.128 mmol) and **29b** (434 mg, 0.683 mmol) were dissolved in *o*-xylene (9 mL) and diphenyl ether (3 mL), and the mixture was heated at 175 °C under argon atmosphere for 40 h. The solvent was evaporated and the crude product was dried under vacuum. Compound **29b** was separated by column chromatography on silica gel with dichloromethane as eluent, and **25** was eluted from the column with ethyl acetate. The product was then dissolved in dichloromethane and precipitated from pentane, filtered, and dried under vacuum. Yield: 290 mg (0.077 mmol, 60 %) as a red solid; m.p.: >300 °C; ^{1}H NMR (500 MHz, d^8-THF, 323 K): δ = 8.15 (s, 4H), 7.96 (t, ^3J = 7.63 Hz, 12H; arom. H), 7.64 (s, 4H), 7.34–6.79 (m, 114H; arom. H), 4.31 (q, ^3J = 7.12 Hz, 16H; CH_2 ester), 2.80 (sept, ^3J = 6.71 Hz, 4H; CH isopropyl), 1.34 (t, ^3J = 7.32 Hz, 24H; CH_3 ester), 1.16 (d, ^3J = 6.71 Hz, 24H; CH_3 isopropyl) ppm; ^{13}C NMR (125 MHz, d^8-THF, 323 K): δ = 166.48 (C=O ester), 163.85 (C=O PDI), 157.08, 155.25, 147.03, 145.81, 145.76, 142.92, 142.48, 142.40, 141.69, 141.43, 141.33, 141.10, 140.79, 140.14, 139.49, 138.18, 137.94, 134.20, 133.37, 132.74, 130.98, 130.73, 130.49, 130.44, 128.68, 128.27, 127.35, 126.67, 126.41, 124.48, 124.07, 121.51, 120.31, 119.79, 61.38 (CH_2 ester), 30.19 (CH isopropyl), 24.51 (CH_3 isopropyl), 14.78 (CH_3 ester) ppm; UV/Vis (toluene): λ_{max} (ε) = 457 (21429), 542 (31859), 582 nm (50791 M^{-1}cm^{-1}); fluorescence (toluene, excitation: 582 nm): λ_{max} = 604 nm; MS (MALDI-TOF): *m/z* (%): 3787 (100) $[M]^+$; elemental analysis calcd (%) for $C_{264}H_{202}N_2O_{24}$: C 83.74, H 5.38, N 0.74; found: C 82.59, H 5.69, N 0.77.

Compound 31b: Compound **30b** (100 mg, 0.026 mmol) was dissolved in THF (10 mL) under argon atmosphere. Potassium hydroxide (118 mg, 2.113 mmol) dissolved in distilled water (1 mL) was then added, and the mixture was flushed with argon. The reaction mixture was heated at 80 °C for 42 h. After 16 h and 19 h, additional distilled water (1 mL) was added. The reaction mixture was then allowed to cool to room temperature, and the precipitate was poured into hydrochloric acid (2 M, 150 mL). The precipitate was filtered and dried at 80 °C. Yield: 93 mg (0.025 mmol, 98 %) as a dark violet solid. M.p. >300 °C; ^{1}H NMR (500 MHz, [D$_6$]DMSO, 306 K): δ = 12.85 (s, 8H; COOH), 7.94–6.74 (m, 134H; arom. H), 2.71 (m, 4H; CH isopropyl), 1.04 (s, 24H; CH_3 isopropyl) ppm; ^{13}C NMR (125 MHz, [D$_6$]DMSO, 298 K): δ = 168.26 (C=O acid), 163.91 (C=O); 157.89, 156.34, 154.63, 144.44, 142.23, 141.81, 141.32, 140.93, 140.55, 140.36, 139.77, 137.09, 136.79, 133.11, 131.26, 131.09, 130.82, 130.63, 129.00, 127.45, 126.56, 126.19, 124.65, 119.83, 29.64 (CH isopropyl), 24.97 (CH_3 isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 3471, 3049, 2968, 1709, 1609, 1593, 1500, 1409, 1339, 1283, 1207, 1178, 1115, 1007, 842, 752, 702, 567 cm^{-1}; UV/Vis (DMSO): λ_{max} (ε) = 461 (21176), 547 (30013), 584 nm (44408 M^{-1}cm^{-1}); fluorescence (DMSO, excitation: 584 nm): λ_{max} = 620 nm; MS (MALDI-TOF): *m/z* (%): 3562 (%) $[M]^+$, (calcd 3562); elemental analysis calcd (%) for $C_{248}H_{170}N_2O_{24}$: C 83.62, H 4.81, N 0.79; found: C 83.48, H 5.26, N 0.80.

Compound 30c Yield: 87 mg (0.01 mmol, 56%) as a red oil; ^{1}H NMR (500 MHz, [D$_8$]THF, 298 K): δ = 8.03 (s, 4H); 7.42–6.63 (m, 86H); 7.13 (s, 16H); 4.03–4.01 (m, 48H); 3.52–3.39 (m, 36H); 3.32–3.31 (m, 72H); 2.75 (sept, 4H); 1.14 (d, ^3J = 6.79 Hz, 12H) ppm; UV/Vis (H$_2$O): λ_{max} (ε) = 539, 582 nm; fluorescence (H$_2$O, excitation: 582 nm): λ_{max} = 615 nm; MS (MALDI-TOF): *m*/*z* (%): 8545 (100) $[M]^+$ (calcd 8543.80).

Compound 34a: 1,6(7)-Dibromoperylenetetracarboxylic acid diimide (**32**, 2.0 g, 2.3 mmol) was stirred with phenol (1.88 g, 20 mmol) in NMP (150 mL) under argon at 100 °C in a 250 mL round flask in the presence of powdered anhydrous K_2CO_3 (1.38 g, 10 mmol). The temperature was maintained at 100 °C for 20 h under argon. The reaction mixture was allowed to cool to room temperature and poured into aqueous hydrochloric acid (300 mL, 1 M). The precipitated product was filtered under suction, and was then purified by column chromatography to give a red solid **34a** (1.5 g, 75%). M.p. >300 °C; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 300 K): δ = 9.48 (d, ^3J = 8.0 Hz, 2H), 8.64 (d, ^3J = 8.0 Hz, 2H), 8.50 (s, 2H), 8.47 (d, ^3J = 8.0 Hz, 2H), 8.26 (s, 2H), 7.57 (m, 2H), 7.42–7.36 (m, 4H), 7.23 (d, ^3J = 7.5 Hz, 4H), 2.61 (m, 4H), 1.06 (m, 24H) ppm; ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 300 K): δ = 163.4 (C=O), 162.9 (C=O), 154.6, 152.0, 146.6, 145.7, 141.5, 133.5, 131.4, 130.5, 129.9, 129.5, 127.2, 126.4, 125.4, 124.9, 124.5, 124.2, 122.8, 29.2 (CH isopropyl), 24.4 (CH$_3$ isopropyl), 24.3 (CH$_3$ isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 2962, 2869, 2231, 1708, 1667, 1600, 1513, 1472, 1406, 1340, 1258, 1207, 1151, 1020, 971, 909, 810, 737, 702, 576 cm^{-1}; UV/Vis (methanol): λ_{max} (ε) = 504 (15200), 536 nm (21100 M^{-1}cm^{-1}); fluorescence (methanol, excitation: 510 nm): λ_{max} = 575 nm; MS (FD 8 kV): *m*/*z* (%): 896.9 (100) $[M]^+$ (calcd 897.0).

Compound 34b: 1,6(7)-Dibromoperylenetetracarboxylic acid diimide **32** (1.0 g, 1.15 mmol) was stirred under argon with phenol (0.94 g, 10 mmol) in NMP (100 mL) at 100 °C in a 250 mL round flask in the presence of powdered anhydrous K_2CO_3 (690 mg, 5 mmol). The temperature was maintained at 100 °C overnight under argon. The reaction mixture was allowed to cool to room temperature and was poured into aqueous hydrochloride acid (200 mL, 1 M). The precipitated product was filtered under suction, and was then purified by column chromatography to give a red solid (700 mg, 68%). M.p. >300 °C; ^{1}H NMR (250 MHz, CD_2Cl_4, 300 K): δ = 9.56 (d, ^3J = 8.0 Hz, 2H), 8.60 (d, ^3J = 8.0 Hz, 2H), 8.27 (s, 2H), 7.43 (m, 6H), 7.25 (m, 10H), 2.61 (m, 4H), 1.06 (m, 24H) ppm; ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 333 K): δ = 163.5, 163.1, 156.6, 155.5, 155.2, 145.8, 134.0, 130.9, 129.9, 129.6, 129.2, 128.2, 126.0, 125.6, 124.5, 124.3, 124.2, 122.7, 119.9, 119.8, 29.4 (CH isopropyl), 24.3 CH$_3$ isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 2961, 2926, 2867, 2361, 2335, 1708, 1669, 1592, 1511, 1488, 1405, 1337, 1257, 1194, 1072, 970, 909, 865, 837, 812, 743, 685, 574 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 406 (8868), 513 (35046), 545 nm (49387 M^{-1}cm^{-1}); fluorescence ($CHCl_3$, excitation 510 nm): λ_{max} = 575 nm; MS (FD 8 kV): *m*/*z* (%): 895.4 (%) $[M]^+$ (calcd 895.0); elemental analysis calcd (%) for $C_{60}H_{50}N_2O_6$: C 80.51, H 5.63, N 3.13%; found: 80.43, H 5.71, N 3.21.

Compound 35a: *N*,*N*′-Bis(2,6-diisopropylphenyl)-1,7-di(3-pyridoxy)perylene-3,4:9,10-tetracarboxylic acid diimide **34a** (1 g, 1.1 mmol) was treated with methyl iodide (475 mg, 3.3 mmol) according to the procedure described for the synthesis of **12a**. Yield: 1.2 g (93%) as a red solid. M.p. >300 °C; ^{1}H NMR (300 MHz, CH_3OH-D_4, 300 K): δ = 9.42 (d, ^3J = 8.5 Hz, 2H), 9.05 (s, 2H), 8.65 (d, ^3J = 8.5 Hz, 2H), 8.60 (d, ^3J = 6.3 Hz, 2H), 8.53–8.50 (m, 4H), 8.00–7.94 (m, 2H), 7.38 (t, ^3J = 7.9 Hz, 2H), 7.25 (d, ^3J = 7.9 Hz, 4H), 4.32 (s, 6H), 2.64 (sept, ^3J = 6.9 Hz, 4H), 1.02 (d, ^3J = 6.9 Hz, 24H); UV/Vis (H$_2$O): λ_{max} (ε) = 497, 530 nm, fluorescence (H$_2$O, excitation: 500 nm): λ_{max} = 574 nm, elemental analysis calcd (%) for $C_{60}H_{54}N_4O_6$: C 77.73, H 5.87, N 6.04; found: C 77.53, H 5.92, N 6.01.

Compound 35b: Compound **34a** (200 mg, 0.223 mmol), methyl iodide (0.5 mL), and chloroform (50 mL) were placed in a 100 mL flask. The reaction mixture was stirred at 75 °C for 14 h. The solvent was removed under vacuum after the solution of the reaction had been allowed to cool to room temperature. The residue was dissolved in methanol (50 mL) in the present of methyl iodide (0.5 mL). The solution was stirred at 80 °C for 48 h. After evaporation of the solvent, the residue and silver methanesulfonate (177 mg, 0.88 mmol) were added to methanol (50 mL) to form a white precipitate (silver iodide), which was removed to give a clear red solution. The red solid was obtained after evaporation (210 mg, 87%). M.p. 241 °C; ^{1}H NMR (250 MHz, CD_3OD, 300 K): δ = 9.45 (d, ^3J = 8.5 Hz, 2H), 9.08 (s, 2H), 8.67 (d, ^3J = 8.2 Hz, 4H), 8.50 (s, 2H), 8.39 (dd, ^3J = 8.5 Hz, 2H), 8.01 (q, 2H), 7.40 (t, ^3J = 8.2 Hz, 2H), 7.26 (d, ^3J = 7.5 Hz, 4H), 4.35 (s, 6H; N–CH$_3$), 2.66 (m, 4H; CH isopropyl), 2.55 (s, 6H; S–CH$_3$), 1.02 (d, ^3J = 7.0 Hz, 24H; CH$_3$ isopropyl) ppm; ^{13}C NMR (62.5 MHz, CD_3OD, 300 K): δ = 165.1 (q, C=O), 164.4 (q, C=O), 156.8 (q), 153.6 (q), 147.4 (q), 143.0 (t), 138.9 (t), 135.3 (t), 134.7 (q), 133.2 (t), 131.9 (q), 131.5 (q), 131.4 (t), 131.1 (t), 130.6 (t), 128.9 (q), 128.3 (q), 127.2 (t), 126.6 (q), 125.4 (t), 124.6 (q), 49.7 (t), 39.7 (t), 30.7 (t, CH isopropyl), 24.6 (t, CH$_3$ isopropyl), 24.5 (t, CH$_3$ isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 2961, 2361, 2336, 1705, 1664, 1595, 1504, 1468, 1408, 1339, 1200, 1053, 811, 778, 672, 557, 532 cm^{-1} ; UV/Vis (H$_2$O): λ_{max} (ε) = 400 (4535), 503 (13640), 536 nm (19022 M^{-1}cm^{-1}); fluorescence (H$_2$O, excitation: 520 nm): λ_{max} = 573 nm.

Compound 35c: Diphenoxyperylenedicarboxylic acid diimide **34b** (300 mg, 0.335 mmol) was added to concentrated sulfuric acid (1 mL). The flask was sealed, and the mixture was then stirred at room temperature for 15 h. Water (3 mL) was slowly added to the flask to form a precipitate, which was filtered off under suction. The solid was washed three times with dichloromethane (50 mL), and then dried at 75 °C under vacuum to give a red product (330 mg, 94%). M.p. 222 °C; ^{1}H NMR (250 MHz, CD_3OD, 300 K): δ = 8.90 (d, ^3J = 8.0 Hz, 2H), 8.17 (d, ^3J = 8.0 Hz, 2H), 8.02 (s, 2H), 7.58 (d, ^3J = 8.0 Hz, 4H), 7.16 (t, ^3J = 7.5 Hz, 2H), 7.03 (d, ^3J = 8.0 Hz, 4H), 6.94 (d, ^3J = 8.0 Hz, 4H), 2.44 (m, 4H), 0.82 (m, 24H) ppm; ^{13}C NMR (62.5 MHz, CD_3OD, 300 K): δ = 164.6 (q, C=O), 164.2 (q, C=O), 157.8 (q), 155.5 (q), 147.1 (q), 142.9 (q), 134.4 (q), 131.6 (q), 131.5 (t), 130.7 (t), 130.5 (q), 129.7 (t), 129.6 (t), 127.3 (q), 126.7 (t), 126.1 (q), 125.5 (q), 125.1 (t), 123.6 (q), 119.5 (t), 30.4 (t, CH isopropyl), 24.5 (t, CH$_3$ isopropyl), 24.3 (t, CH$_3$ isopropyl) ppm; IR (KBr): $\tilde{\nu}$ = 3432, 2965, 2928, 2361, 2336, 1702, 1657, 1591, 1490, 1464, 1406, 1341, 1260, 1204, 1122, 1060, 1029, 1003, 911, 839, 812, 736, 690, 581 cm^{-1}; UV/Vis (H$_2$O): λ_{max} (ε) = 411 (7565), 523 (23196), 554 nm (23718 M^{-1}cm^{-1}); fluorescence (H$_2$O, excitation 560 nm): λ_{max} = 594 nm; MS (MALDI-TOF): *m*/*z* (%): 1057 (%) $[M]^+$ (calcd 1055); elemental analysis calcd (%) for $C_{60}H_{50}N_2O_{12}S_2$: C 68.30, H 4.78, N 2.65; found: C 68.19, H 4.85, N 2.67.

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[1] P. I. H. Bastiaens, A. Squire, *Trends Cell Biol.* **1999**, *9*, 48–52.
[2] M. Hope-Ross, L. A. Yannuzzi, E. S. Gragoudas, D. R. Guyer, J. S. Slakter, A. Sorenson, *Ophthalmology* **1994**, 101, 529–533.
[3] S. Mordon, J. M. Devoisselle, S. Soulie-Begu, T. Desmettre, *Microvasc. Res.* **1998**, 55, 146–152.
[4] W. E. Moerner, M. Orrit, *Science* **1999**, *283*, 1670.
[5] D. C. Nguyen, R. A. Keller, J. H. Jett, Martin, *J. C. Anal. Chem* **1987**, 59, 2158.
[6] K. Peck, L. Stryer, A. N. Glazer, R. A. Mathies, *Proc. Natl. Acad. Sci. USA* **1989**, *86*, 4087.
[7] G. Seisenberger, M. U. Ried, T. Endress, H. Buning, M. Hallek, C. Bräuchle, *Science* **2001**, *294*, 1929–1932.
[8] R. P. Haugland, *Handbook of Fluorescent Probes and Research Chemicals*, Molecular probes Inc., Eugene, **1989**.
[9] Y. Nagao, T. Misono, *Dyes Pigm.* **1984**, 5, 171.
[10] A. Rademacher, S. Markle, H. Langhals, *Chem. Ber.* **1982**, *115*, 2927.
[11] H. Zollinger, *Color Chemistry*, VCH Verlagsgesellschaft, Weinheim, **1987**.
[12] K. Petritsch, J. J. Dittmer, E. A. Marseglia, R. H. Friend, A. Lux, G. G. Rozenberg, S. C. Moratti, A. B. Holmes, *Sol. Energy Mater. Sol. Cells* **2000**, 61, 63.
[13] J. J. Dittmer, R. Lazzaroni, P. Leclère, P. Moretti, M. Ganström, K. Petritsch, E. A. Marseglia, R. H. Friend, J. L. Brédas, H. Rost, A. B. Holmes, *Sol. Energy Mater. Sol. Cells* **1999**, *61*, 53.

[14] J. Kalinowski, P. D. Marco, V. Fattori, L. Giuletti, M. Cocchi, *J. Appl. Phys.* **1998**, 83, 4242.
[15] P. R. L. Malenfant, C. D. Dimitrakopolous, J. D. Gelorme, L. L. Kosbar, T. O. Graham, A. Curioni, W. Andreoni, *Appl. Phys. Lett.* **2002**, 80, 2517–2519.
[16] Z. J. Chen, M. G. Debije, T. Debaerdemaeker, P. Osswald, F. Würthner, *ChemPhysChem* **2004**, *5*, 137–140.
[17] R. Gronheid, J. Hofkens, F. Köhn, T. Weil, E. Reuther, K. Müllen, F. C. De Schryver, *J. Am. Chem. Soc.* **2002**, *124*, 2418–2419.
[18] T. Vosch, J. Hofkens, M. Cotlet, F. Köhn, H. Fujiwara, R. Gronheid, K. V. D. Best, T. Weil, A. Herrmann, K. Müllen, S. Mukamel, M. v. d. Auweraer, F. C. De Schryver, *Angew. Chem.* **2001**, *113*, 4779–4784; *Angew. Chem. Int. Ed.* **2001**, *40*, 4643–4648.
[19] H. Langhals, DE-3703513: Germany, **1987**.
[20] G. Schnurpfeil, J. Stark, D. Wöhrle, *Dyes Pigm.* **1995**, 27, 339–350.
[21] H. Langhals, W. Jona, F. Einsiedl, S. Wohnlich, *Adv. Mater.* **1998**, *10*, 1022–1024.
[22] T. Weil, T. Ph.D. Thesis, Johannes Gutenberg-Universität Mainz, **2002**.
[23] T. Weil, M. Abdallah, C. Jatzke, J. Hengstler, K. Müllen, *Biomacromolecules* **2004**, unpublished results.
[24] H.-A. Klok, J. R. Hernandez, S. Becker, K. Müllen, *J. Polym. Sci. A* **2001**, *39*, 1572.
[25] J. Qu, C. Kohl, M. Pottek, K. Müllen, *Angew. Chem.* **2004**, *116*, 1554–1557; *Angew. Chem. Int. Ed.* **2004**, *43*, 1528–1531.
[26] M. Lor, J. Thielemans, L. Viaene, M. Cotlet, J. Hofkens, T. Weil, C. Hampel, K. Müllen, M. v. d. Auweraer, F. C. De Schryver, *J. Am. Chem. Soc.* **2002**, *124*, 9918–9925.
[27] H. Quante, P. Schlichting, U. Rohr, Y. Geerts, K. Müllen, *Macromol. Chem. Phys.* **1996**, 197, 4029.
[28] A. Herrmann, T. Weil, V. Sinigersky, U.-M. Wiesler, T. Vosch, J. Hofkens, F. C. D. Schryver, K. Müllen, *Chem. Eur. J.* **2001**, 7, 4854–4862.
[29] G. Seybold, G. Wagenblast, *Dyes Pigm.* **1989**, 11, 303–317.
[30] A. Suzuki, S. Saveda, T. Saegusa, *Macromolecules* **1989**, *22*, 1505.
[31] T. Watanabe, N. Miyaura, A. Suzuki, *Synlett.* **1992**, 3, 207.
[32] F. Morgenroth, K. Müllen, *Tetrahedron* **1997**, *53*, 15349.
[33] U. M. Wiesler, A. J. Berresheim, F. Morgenroth, G. Lieser, K. Müllen, *Macromolecules* **2001**, *34*, 187–199.
[34] Grebel-D. Koehler, T. Weil, C. Hampel, K. Müllen, **2004**, unpublished results .
[35] M. Schlupp, T. Weil, A. J. Berresheim, U.-M. Wiesler, J. Bargon, K. Müllen, *Angew. Chem.* **2001**, *113*, 24, 4779–4784 2001, 113, 4124–4129.
[36] K. L. Bhat, A. Garg, C. W. Bock, *Dyes Pigm.* **2002**, 52, 145–159.

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