Synthesis and Modification of Terrylenediimides as High-Performance Fluorescent Dyes

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Abstract: Two new synthetic approaches to terrylenediimides, highly photostable fluorescent dyes, are described. For the first time terrylenediimide has been synthesised in a straightforward procedure that makes large quantities available. The second route includes an efficient cross-coupling reaction followed by a cyclodehydrogenation. Monofunctionalisation of the imide structure allows terrylenediimides now to be coupled with a variety of compounds, for example, by Suzuki cross-coupling, which can lead to an array of terrylenediimides with new functional groups such as hydroxy, amino, or carboxy groups needed to link up with other molecules. The functionalisation in the bay region is used to tune the properties of terrylenediimides and extend the range of applications, for example, by introducing water solubility. These tetrasubstituted terrylenediimides offer, depending on the substituents used, exciting features such as good solubility in common organic solvents, water solubility, or NIR absorption.

Keywords: C–C coupling · dyes/pigments · fluorescence · terrylenediimides

Introduction

Stable, highly fluorescent perylene-3,4:9,10-tetracarboxdiimides of type **1** are widely used as dyes or pigments, depending on the substituent R at the *N*-imide position (Scheme 1). They are suitable for demanding applications such as modern reprographics,[1] fluorescence light collectors,[2] photovoltaic devices,[3] dye lasers,[4] light-emitting diodes (LEDs)[5] and molecular switches.[6] By extending the core π-conjugated system, we have synthesised the higher homologues of perylenediimide **2**, that is, terrylenediimide **3**[7] and quaterrylenediimide **4**.[8] The absorption maxima of the deep blue terrylenediimides **3** are shifted bathochromically in comparison to perylenediimide **2**. Terrylenediimides **3** exhibit brilliant colour, high extinction coefficients, high fluorescence quantum yields of 90%,[7] and high thermal, chemical, and photochemical stabilities, which are generally required for practical use.[9] The number of organic compounds showing intense fluorescence like terrylenediimide in the red and deep red spectral region of the electromagnetic spectrum is rather limited.[10] A great advantage of this spectral region is that inexpensive and effective excitation sources such as the HeNe laser (633 nm), krypton-ion laser (647, 676 nm) and common diode lasers are available, which is important for fluorescent labels.[11] In addition to the photophysical properties such as high extinction coefficients and photochemical stability, the negligible population of the triplet bottleneck, low photobleaching efficiency at room temperature, and weak electron–phonon coupling at low temperature qualify terrylenediimide **3** as an ideal chromophore for single-molecule spectroscopy.[12] With single-molecule spectroscopy experiments, it is also possible to excite and detect the zero-phonon line of single terrylenediimide molecules, which is only possible with exceptionally photostable systems.[13] Terryleneimides have been used in biomimetic models of plant photosystems,[14] bichromophores,[15] and light-harvesting dyads[16] and triads.[17]

Our previously published synthesis of terryleneimide, however, suffered from the following problems:[7] 1) the use of toxic stannyl compounds as intermediates, 2) long reaction times (three days for transformation of bromide **7** into stannyl derivative **6**; four days for the subsequent Stille coupling), 3) the use of molten KOH as base in the final cyclodehydrogenation, which excludes the synthesis of terryleneimides with base-labile substituents at the *N*-imide position and causes corrosion of the reaction vessel, 4) limited access

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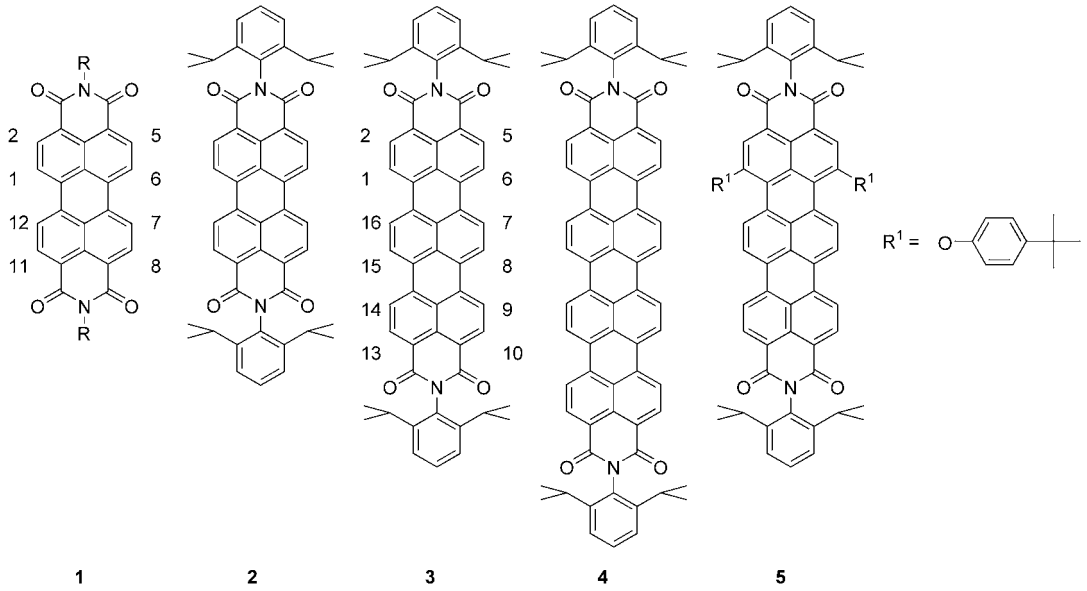


Scheme 1. Chemical structures of rylenediimides.

to the soluble disubstituted terrylenediimide **5**, and 5) the unavailability of functional groups for further reactions.

Two new strategies are now available to improve the established synthesis of symmetrical and unsymmetrical terrylenediimides[7,18] that avoid the use of toxic organostannanes and provide higher overall yields.[19] Both routes also offer the important possibility of controlled monofunctionalisation of the imide structure of terrylenediimides. Although many monofunctionalised perylenediimides have been described, monofunctionalisation methods for the higher homologues, terrylenediimides, are hithertho unknown. By starting from tetrabromoterrylenedicarboximide **19**, the synthesis of a series of terrylenediimides in which it is possible to significantly increase the solubility (Table 1), to introduce water solubility or to obtain NIR-absorbing dye is accomplished.

Table 1. Solubility of terrylenediimides **3**, **19** and **20a** in CH_2Cl_2 at room temperature.

Compound	**3**	**19**	**20a**
Solubility [mg mL^{-1}]	1.5	18	> 180

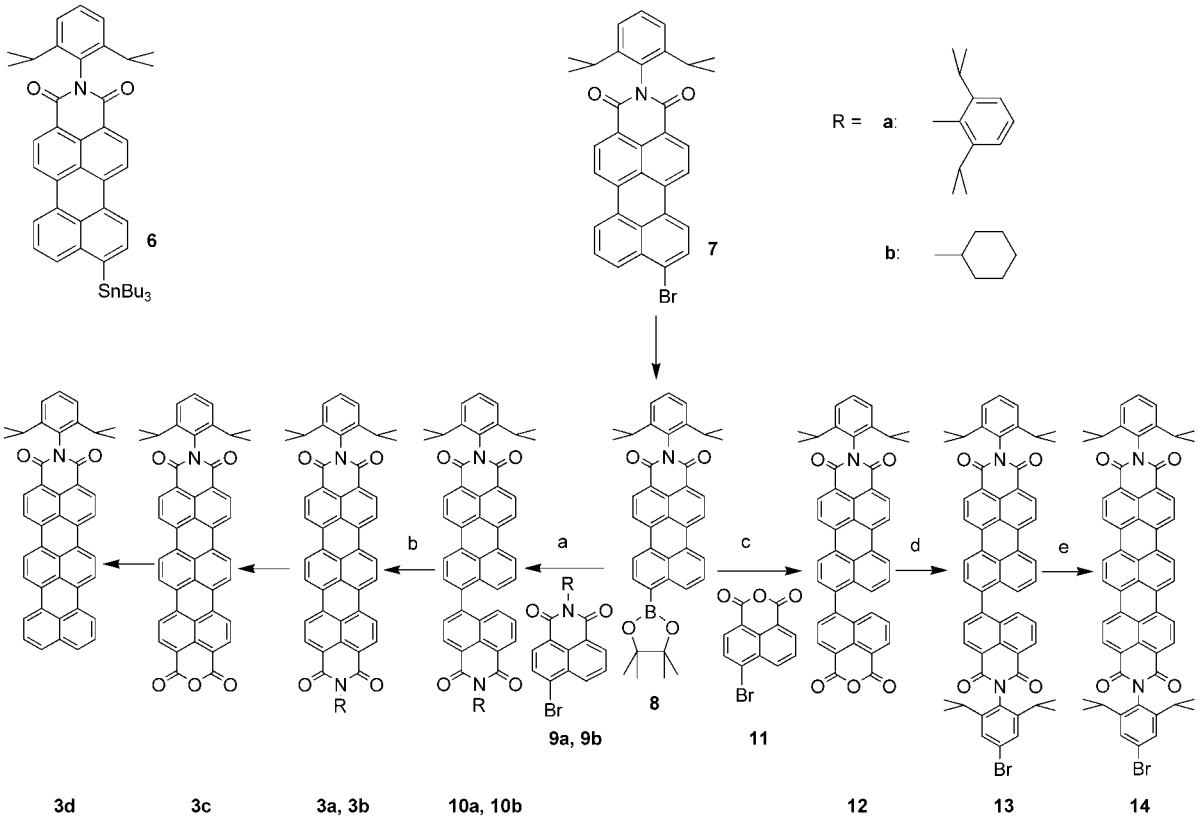
Results and Discussion

The first new synthetic route (Scheme 2) to terrylenediimides is similar to the previous one, but in all three steps major improvements were made. Here, the toxic stannyl derivative **6** is replaced with a boronic ester **8**, whose synthesis has recently been described.[20] With bis(pinacolato)diboron and [$PdCl_2$(dppf)] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) it is possible to convert 9-bromoperylenedicarboximide **7** to the corresponding boronic ester **8** in 75% yield. In a Pd-catalysed Suzuki reaction,[21] coupling of boronic ester **8** with 4-bromonaphthalenedicarboximide **9a** and **9b** gives the naphthylperylene derivatives **10a** and **10b** in good yields (**10a** 85%, **10b** 90%). Terrylenediimide precursors **10a** and **10b** are then cyclised by using K_2CO_3 as base in ethanolamine. After isolation and purification by column chromatography, **3a** and **3b** are both obtained in 95% yield.

The synthesis of boronic acids or esters normally involves the reaction of organolithium reagents with trialkyl borates. This method is not applicable here, since the imide structure is sensitive to organolithium compounds. We therefore used the method reported by Miyaura et al., which transforms aryl halides directly into boronic esters even in the presence of functional groups such as esters, ketones and nitro groups.[22] Under these conditions, debrominated and homocoupled derivates of **7** are obtained as minor by-products, and hence column chromatography is required for purification.

Another advantage of Suzuki cross-coupling of boronic ester **8** and **9a** is that it proceeds considerably faster (16 h) than the previous palladium-catalysed Stille coupling of organostannane **6** and **9a** (96 h). The synthesis of the terrylenediimide precursors **10a** and **10b** can also be carried out by using the analogous boronic ester of 4-bromonaphthalenedicarboximides **9a** and **9b** and 9-bromo-perylenedicarboximide **7**.

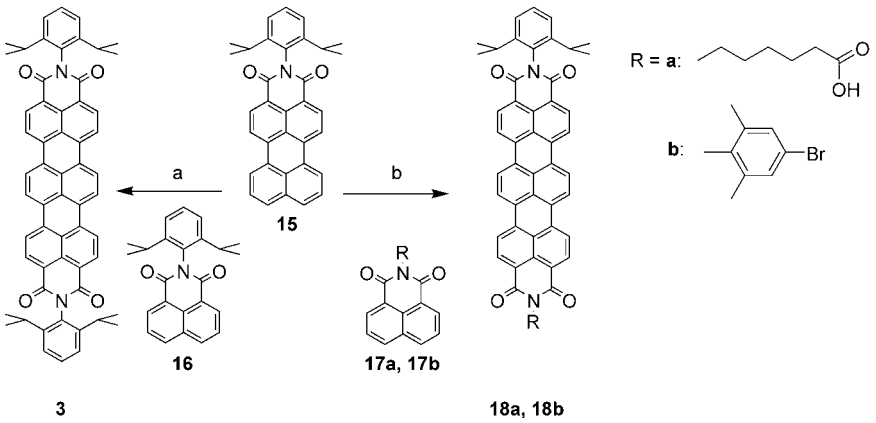
The final cyclodehydrogenation step of this protocol is carried out under very mild conditions.[23,24] In contrast to the cyclisation with molten KOH, the cyclisation of **10a** and **10b** with K_2CO_3 as base in ethanolamine gives almost quantitative yields. The use of an oxidative alkali melt has another drawback, because unlike the bulky N-substituents of naphthylperylene derivative **10a**, the cyclohexyl substituent of **10b** can be saponified with such a strong base. The formation of terrylenediimides with base-labile N-substituents can therefore be accomplished only under very mild condi-



Scheme 2. Synthesis of **3a**, **3b** and **14**. a) $[Pd(PPh_3)_4]$, K_2CO_3/H_2O, toluene, 80 °C, 16 h (**10a** 85 %, **10b** 90 %); b) ethanolamine, K_2CO_3, 120 °C, 3 h, 95 %; c) $[Pd(PPh_3)_4]$, K_2CO_3/H_2O, toluene, 80 °C, 15 h, 80 %; d) 4-bromo-2,6-diisopropylaniline, propionic acid, 150 °C, 16 h, 38 %; e) ethanolamine, K_2CO_3, 160 °C, 3 h, 90 %.

tions. It is now possible to perform the saponification of the cyclohexyl substituent of **3b**, which is unwanted in the final cyclodehydrogenation, with a strong base like KOH to gain terrylenemonoanhydridemonoimide **3c**, which provides terrylenemonoimide **3d** after decarboxylation.[25] This has potential as a starting material for the synthesis of the higher homologues of **2**–**4** with even larger π systems.

After isolation and purification by column chromatography, **3a** is obtained in an overall yield of 63 %. This new synthetic route (Scheme 2) thus gives a 13 % increase in overall yield compared to the previous procedures and avoids toxic organostannanes like **6**.



Scheme 3. Synthesis of **3** and **18a**. a) Diazabicyclo[4.3.0]non-5-ene, *t*BuONa, diglyme, 130 °C, 3 h, 42 %; b) diazabicyclo[4.3.0]non-5-ene, *t*BuONa, diglyme, 130 °C, 2 h, 36 %.

The second route (Scheme 3) for terrylenediimide **3** is even simpler because it utilizes a one-pot procedure which is reminiscent of the direct coupling reactions of 1,8-naphthalenedicarboximides affording the corresponding perylenediimide dyes.[19,26,27] Heating a mixture of perylenedicarboximide **15**, naphthalenedicarboximide **16**, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and *t*BuONa in diglyme delivers terrylenediimide **3**.

In addition to the enhanced multistep synthesis involving column chromatography we are looking for a short route usable on a very large scale. Perylenediimides[19] and quaterrylenediimides,[28] the lower and higher homologues of terrylenediimides, can be synthesised by base-promoted homocoupling of naphthalenedicarboximide or perylenedicarboximide, respectively. The obvious synthesis of symmetric ter-

rylenediimide **3** in this kind of one-pot base-promoted reaction would depend on heterocoupling of perylenedicarboximide **15** and naphthalenedicarboximide **16**. In principle, under these reaction conditions three combinations—two homocouplings and the desired heterocoupling—could readily form diimides. To favour the heterocoupling and suppress the formation of the homocoupling product quaterrylenediimide **4**, which can not be easily separated, a fourfold excess of naphthalenedicarboximide **16** is used to provide terrylenediimide **3**.

By using KOH/glucose/ethanol in the heterocoupling only perylenediimide **2** is obtained. The improved cyclodehydrogenation conditions of the multistep route (K_2CO_3, ethanolamine; Scheme 2) give terrylenediimide **3** and the unwanted byproduct quaterrylenediimide **4**. Owing to the low yield of terrylenediimide **3** and the formation of quaterrylenediimide **4**, these conditions are not suitable. The *t*BuONa/DBN pair gives rise to terrylenediimide **3** without the formation of quaterrylenediimide **4** after 3 h at 130 °C in diglyme under argon. The only byproduct, perylenediimide **2**, and the remaining starting materials can be removed by washing with ethanol because of their good solubility. Terrylenediimide **3** is finally recrystallised from ethanol/chloroform to give an overall yield of 42 % with >95 % purity. The time-consuming chromatographic purification and bromination of perylenemonoimide **15** characteristic of the multistep route can now be avoided and scale-up (>100 g) becomes easily possible.

The base-promoted one-pot reaction is also the simplest monofunctionalisation method for terrylenediimides. The use of a perylenedicarboximide and a naphthalenedicarboximide with different substituents in the imide structures afford an asymmetric terrylenediimide in the one-pot synthesis (Scheme 3). Monocarboxy-functionalised terrylenediimide **18a** was synthesised by using *N*-(5-carboxypentyl)-naphthalenedicarboximide **17a** in place of nonfunctionalised naphthalenedicarboximide **16** under the same conditions (*t*BuONa/DBN, diglyme) used in the one-pot synthesis of terrylenediimide **2**. The reaction mixture of the coupling reaction is poured into a small amount of water to obtain the sodium salt of monocarboxyl-substituted terrylenediimide **18a**. A very convenient way of purifying the sodium salt is by washing away all by-products and all starting materials with chloroform. The sodium salt is insoluble in nonpolar solvents (e.g., chloroform, as used here). The dark blue precipitate is then redissolved in methanol and acidified with hydrochloric acid to give the desired pure monocarboxy-functionalised terrylenediimide **18a** in 36 % yield.

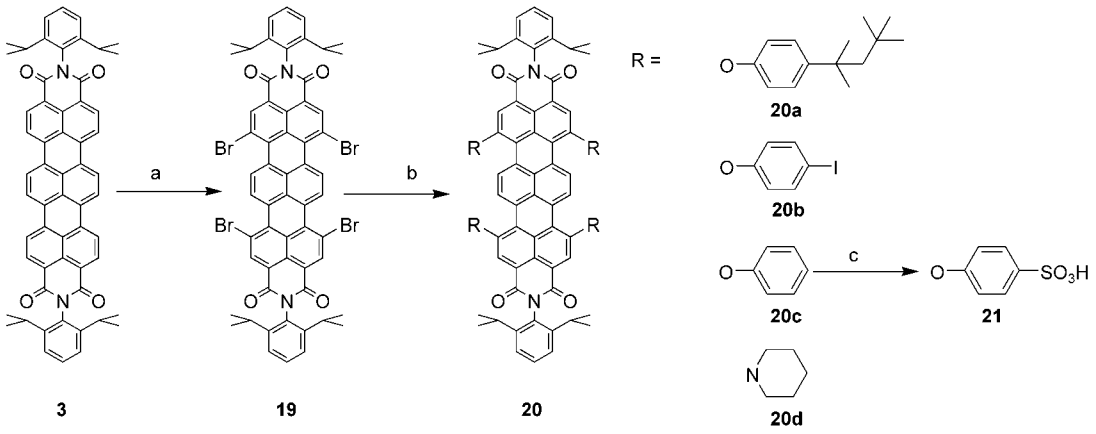
The use of palladium-catalysed C–C coupling reactions (Stille, Suzuki etc.) makes a halogen-functionalised terrylenediimide an important intermediate (Scheme 3). The yield of the monobrominated terrylenediimide derivative **18b** is, however, very low (<5 %), since the bromo substituent does not survive the strongly basic conditions of the base-promoted one-pot reaction. Therefore, the synthetic route via the boronic ester **8** was chosen to synthesise monobromo-functionalised terrylenediimide **17b** (Scheme 2). Under Suzuki conditions boronic ester **8** couples with 4-bromonaphthalenedicarboxanhydride **11** to give anhydride **12** in 80 % yield. The naphthylperylene derivative **13** is obtained by condensation of **12** with a monobromo-functionalised amine in 38 % yield. The ring closure of **13**, which is carried out with K_2CO_3 in ethanolamine, affords terrylenediimide **14** under mild conditions in 90 % yield.

Selective cross-coupling of boronic ester **8** with a 4-bromonaphthalenedicarboximide with a bromo substituent on the aryl group at the *N*-imide position is not possible. Hence, the bromo substituent must be introduced later. With 4-bromonaphthalenedicarboxanhydride **11** and catalysis by $[Pd(PPh_3)_4]$, boronic ester **8** is coupled to the naphthylperylene derivative **12**, which allows the introduction of a bromo-functionalised aniline or other secondary amines in the imide structure. Monofunctionalisation is achieved by imidisation of anhydride **12** with a bromo-containing amino substituent. 4-Bromo-2,6-diisopropylaniline was used to also improve the solubility and stability of naphthylperylene derivative **13**, due to the bulky *ortho*-alkyl substituents. The reason for the moderate yield is decomposition of anhydride **12** at 150 °C.[29] With K_2CO_3 as base in ethanolamine, the cyclodehydrogenation of **13** completes the synthesis of the corresponding terrylenediimide with one *para*-bromo substituent **14** in excellent yield.

Tetrabromoterrylenediimide **19**, whose synthesis has recently been described,[20] creates numerous possibilities for the functionalization of terrylenediimide (Scheme 4), since **19** is susceptible to reactions with nucleophiles at the brominated positions.[2] The phenoxylation of **19** with *tert*-octylphenol gives the corresponding tetrasubstituted terrylenedicarboximide **20a** in 86 % yield. The substitution under basic conditions of the four bromine atoms of **19** with phenol produces **20c** in 90 % yield. Further, this terrylenediimide can be sulfonated with concentrated sulfuric acid at room temperature to afford **21**. The reaction of piperidine with **19** at 85 °C forms the terrylenediimide with four piperidyl substituents **20d** in 34 % yield.

Perylenediimides can be halogenated in the bay region,[2,8] and perylenemonoimides can be selectively brominated in the 9-position.[8,30] Bromination of terrylenediimide **3** with elemental bromine in chloroform at 60 °C with exclusion of light gives the tetrabrominated terrylenediimide **19** as the main product[20,25] No catalyst is required for this reaction. The directing effect of the imide structures leads to selective fourfold bromination in the 1-, 6-, 9- and 14-positions. However, bromination does not stop at tetrabromination, and penta- and hexabrominated terrylenediimides are obtained as minor by-products. Fortunately, penta- and hexabromination occur in the *meta*-positions of the imide phenyl rings and not in the bay region or in the aliphatic side chains. These by-products can be removed by column chromatography with toluene or chloroform/ethanol.

The introduction of bromine atoms leads to a significant increase in solubility (Table 1), because of the distortion of the terrylene skeletal structure of **19**, and also changes the spectral properties.[2] While the maxima of the absorption



Scheme 4. Synthesis of **20a**, **20d** and **21**. a) Br_2, chloroform, reflux, 12 h, 75%; b) **20a**: *tert*-octylphenol, K_2CO_3, *N*-methylpyrrolidone, 80°C, 8 h, 86%; **20c**: phenol, K_2CO_3, *N*-methylpyrrolidone, 80°C, 15 h, 90%; **20d**: piperidine, 85°C, 5 d, 34%; c) conc. H_2SO_4, RT, 15 h, 94%.

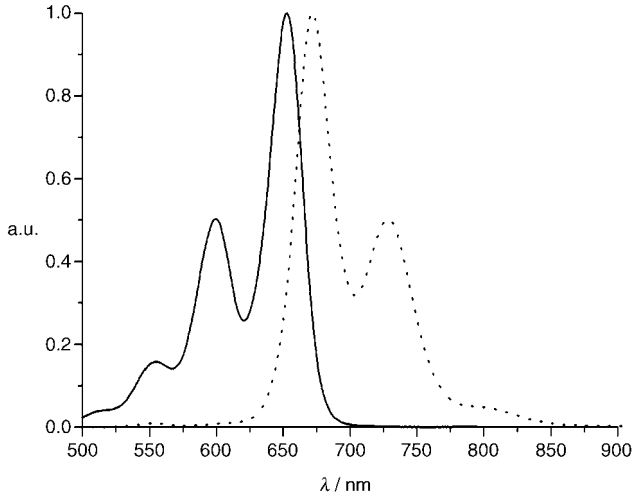


Figure 1. Absorption (continuous line) and emission spectra (dotted line) of **3** in toluene.

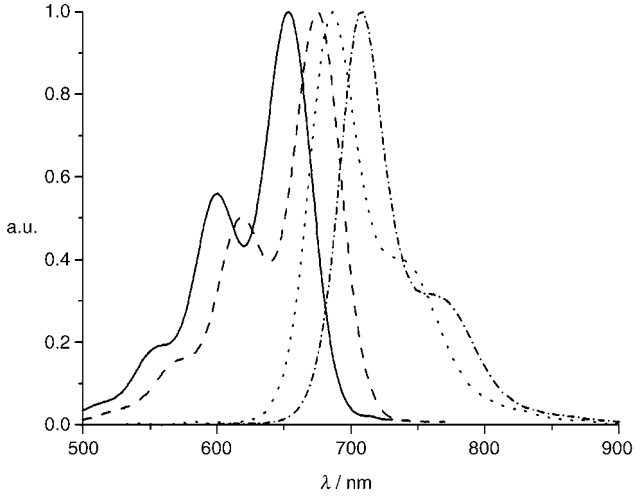


Figure 2. Absorption spectra of **19** (continuous line) and **20a** (dashed line) in toluene, and emission spectra of **19** (dotted line) and **20a** (dash dot line) in toluene.

bands remain unaffected, the most intense emission band is shifted bathochromically by 13 nm to 686 nm (Figure 1). The bands in the emission spectrum of **19** are also broader than the bands in the emission spectrum of **3**.

Several strategies are available to improve the solubility of the ryleneimides. One option is the introduction of bulky substituents such as 2,6-diisopropyl groups in the imide structure. Phenoxyl substituents in the bay regions of the π system also can be used to improve the solubility. The limited access to the soluble diphenoxy-substituted terrylenediimide **5** is clearly an issue, since for many applications good solubility in organic solvents is required.[31] The obvious way to synthesise tetraphenoxy-substituted terrylenediimides, which absorb and emit at longer wavelengths, is to phenoxylate tetrabrominated terrylenediimide **19**. The bulky *tert*-octylphenoxy substituents of terrylenediimide **20a** increase the solubility dramatically (Table 1). The absorption bands and emission band are shifted bathochromically because of substitution with four phenoxyl substituents (Figure 2), which also affords bluish green products instead of the blue terrylenediimides **3** and **19**. The absorption wavelength depends on the number of phenoxyl substituents. The maximum of the diphenoxyl-substituted terrylenediimide **5** at 664 nm is shifted hypsochromically compared to that of tetrasubstituted **20a** by 11 nm. By varying the number of phenoxyl substituents on the terrylenediimides, it is possible to cover the whole red and deep-red spectral region. The fluorescence quantum yields of terrylenediimides **19** and **20a** were determined relative to tetraphenylporphine, which has a known fluorescence quantum yield ($\varphi_F = 0.10$)[32] and absorbs at similar wavelength. Compound **19** has a quantum yield of 64% ($\varphi_F = 0.64 \pm 0.1$), and **20a** one of 53% ($\varphi_F = 0.53 \pm 0.1$). The bromine atoms of terrylenediimide **19** can also be substituted by functional phenols like 4-iodophenol.[20] After this tetrafunctionalisation, **20b** can serve as a multifunctional core molecule for the synthesis of dendritic multichromophores.

Even though terrylenediimides with four phenoxyl substituents such as **20a** have good solubility in common organic solvents, they are insoluble in water and only slightly soluble in polar solvents. For certain applications and environmentally benign processes, good processability in water or polar solvents is needed. One strategy to obtain solubility in water is to introduce charged groups. Water-soluble perylenediimides with four phenoxyl substituents bearing negatively charged sulfonyl groups were reported recently.[33] The same concept is used to obtain water-soluble terrylenediimides. The *para* positions of the phenol substituents of **20d** are the expected the sites of sulfonation with sulfuric acid, and indeed complete and selective conversion is obtained. The purification of **21** is accomplished by slowly adding a small amount of water to the reaction mixture, which directly induces precipitation of the product. After washing with dichloromethane, water-soluble terrylenediimide **21**, bearing four sulfonyl groups, is isolated in 93% yield.

Direct substitution of the perylenediimide core can change the chemical and optical properties.[34] Wasielewski et al. reported that introduction of dialkylamino groups into the bay regions leads to a large bathochromic shift of the absorption bands.[35] The reaction of tetrabromoterrylenediimide **19** with the electron-rich secondary cyclic amine piperidine gives the first ever NIR-absorbing terrylenediimide **20d**. The absorption maximum of the longest wavelength absorption band of tetrapiperidinyl-substituted terrylenediimide **20d** at 819 nm is shifted bathochromically compared to that of **19** by 168 nm (Figure 3), due the electron-donating effect of the piperidinyl groups.[36] The charge transfer also causes broadening and loss of the fine structure of the absorption bands of **20d** as compared to unsubstituted terrylenediimide **3**. Compound **20d** has a light violet colour in solution, as opposed to the blue colour of terrylenediimide **3**. In concentrated sulfuric acid, the colour of **20d** changes to bright blue. The absorption maximum of protonated **20d** is shifted hypsochromically by 197 nm (Figure 3). This solvent effect on the charge transfer bands can be explained by protonation of the piperidinyl groups.[37]

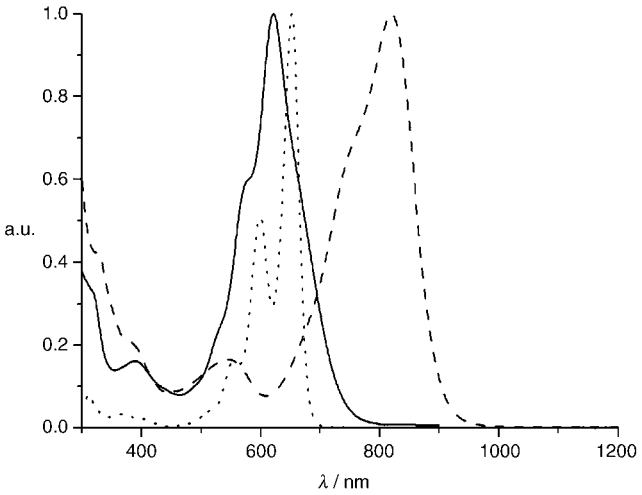


Figure 3. Absorption spectra of **20d** in chloroform (dashed line) and in sulfuric acid (continuous line), and absorption spectrum of **3** (dotted line) in chloroform.

Conclusion

With the current synthetic strategies—monofunctionalisation of the imide structure and additional functionalisation in the bay region—the toolbox of terrylenediimide chemistry is notably enlarged. The nontoxic boronic ester **8** is a valuable intermediate in the new multistep synthesis of terrylenediimides. It provides access to monobromo-functionalised terrylenediimide **14**, which will be a useful in a broad variety of palladium-catalysed cross-coupling reactions. Tetrabromoterrylenediimide **19** is used as a versatile building block for the synthesis of a series of new terrylenediimides. To dramatically improve the handling of the dyes, terrylenediimide **20a** with four phenoxyl substituents and good solubility in common organic solvents and water-soluble terrylenediimide **21** were synthesised. Substitution of the bromine atoms of **19** with a cyclic amine afforded the first NIR-absorbing terrylenediimide **20d**. Owing to the excellent redox properties of the rylene dyes and NIR absorption, these dyes could be candidates for organic photovoltaic cells and field effect transistor (FET) devices. Furthermore the one-pot synthesis of terrylenediimide offers an easy and attractive access to terrylene substrates from a commercial point of view.

Experimental Section

General: The solvents used were of commercial grade. Perylenemonoimide **15** was supplied by BASF AG. Compounds **8**, **9a** and **19** were prepared as described in the literature.[7,20] Column chromathography was preformed on silica gel (Geduran Si60, Merck). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avanche 250, Bruker AMX 300, Bruker DRX 500 and Bruker Avanche 700. Infrared spectra were obtained on a Nicolet FT IR 320. FD mass spectra were recorded with a VG-Instruments ZAB 2-SE-FDP instrument. MALDI-TOF mass spectra were recorded on a Bruker MALDI-TOF spectrometer. UV/Vis spectra were recorded on a Perkin-Elmer Lambda 9, and fluorescence spectra on a SPEX Fluorolog 3 spectrometer. The quantum yields were measured relative to tetraphenylporhine. Elemental analyses were preformed by the Department of Chemistry and Pharmacy of the University of Mainz.

***N*-(Cyclohexyl)-4-bromonaphthalene-1,8-dicarboxiimide (9b)**: 4-Bromo-1,8-naphthalic anhydride (35.0 g, 0.13 mol) and cyclohexylamine (28.0 g, 0.29 mol) were refluxed in ethanol (1 L) for 12 h. The reaction mixture was cooled to room temperature. The resulting **9b** was removed by filtration, washed with ethanol and dried under vacuum (45 g, 96%). M.p. 265 °C; ^{1}H NMR (250 MHz, $C_2D_2Cl_4$, 25 °C): δ = 8.51 (d, J = 8.47 Hz, 1H), 8.44 (d, J = 8.47 Hz, 1H), 8.26 (d, J = 8.17 Hz, 1H), 7.94 (d, J = 7.82 Hz, 1H), 7.75 (t, J = 7.8 Hz, 1H), 4.88 (m, 1H), 2.40 (m, 2H), 1.79 (m, 2H), 1.65 (m, 3H), 1.26 ppm (m, 3H); ^{13}C NMR (62.5 MHz, $C_2D_2Cl_4$, 25 °C): δ = 165.07, 165.05, 133.99, 133.00, 132.20, 131.40, 130.99, 129.91, 129.25, 124.59, 123.74, 55.04, 30.21, 27.68, 26.58 ppm; IR (KBr pellet): $\tilde{\nu}$ = 2919, 2846, 1703, 1655, 1585, 1362, 1258, 1233, 1186, 1109, 983, 910, 855, 779, 748 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 359 (13244), 344 nm (15247 M^{-1}cm^{-1}); MS (FD, 8 kV): m/z (%): 357.2 (100) [M^+]; elemental

analysis calcd (%) for $C_{12}H_{18}NO_2Br$: C 60.35, H 4.50, N 3.91; found: C 60.36, H 4.79, N 3.95.

***N*-(2,6-Diisopropylphenyl)-9-(4-*N*-(2,6-diisopropylphenyl)naphthalene-1,8-dicarboximide)perylene-3,4-dicarboximide (10a)**: Compounds **8** (5.0 g, 8.2 mmol) and **9a** (7.2 g, 16.5 mmol) were dissolved in toluene (380 mL). A solution of Na_2CO_3 in water (20 mL, 1 M) and ethanol (13 mL) were added, and the mixture was flushed with argon. $[Pd(PPh_3)_4]$ catalyst (400 mg, 0.3 mmol) was added, and the reaction mixture stirred under argon for 16 h at 80 °C. The reaction mixture was cooled to room temperature. The organic phase was separated, and the solvent evaporated under reduced pressure. The crude material was purified by column chromatography on silica (CH_2Cl_2) to give **10a** (6.19 g, 90 %). The analytical data corresponded to those in the literature.[7]

***N*-(2,6-Diisopropylphenyl)-9-(4-*N*-cyclohexylnaphthalene-1,8-dicarboximide)perylene-3,4-dicarboximide (10b)**: **8** (1.9 g, 3.1 mmol) and **9b** (0.74 g, 2.0 mmol) were dissolved in toluene (200 mL). A solution of K_2CO_3 in water (40 mL, 1 M) was added, and the mixture flushed with argon. $[Pd(PPh_3)_4]$ catalyst (300 mg, 0.25 mmol) was added, and the reaction mixture stirred under argon for 16 h at 80 °C. The reaction mixture was cooled to room temperature. The organic phase was separated, and the solvent evaporated under reduced pressure. The crude material was purified by column chromatography on silica (CH_2Cl_2) to give **10b** (2.1 g, 90 %). M.p. >286 °C; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 25 °C): δ = 8.67 (d, J = 7.4 Hz, 1H), 8.63 (m, 2H), 8.53 (d, J = 8.3 Hz, 1H), 8.48 (m, 2H), 7.81 (m, 2H), 7.64 (d, J = 7.7 Hz, 1H), 7.59 (m, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.42 (m, 2H), 7.28 (d, J = 7.8 Hz, 2H), 2.71 (d, J = 6.8 Hz, 2H), 2.56 (m, 2H), 1.89 (m, 2H), 1.74 (m, 4H), 1,44 (m, 2H), 1.14 ppm (d, J = 6.8 Hz, 12H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 25 °C): δ = 163.6, 163.4, 163.0, 144.8, 143.9, 138.6, 138.2, 136.6, 136.3, 134.3, 132.5, 130.4, 130.3, 129.6, 129.1, 128.8, 128.0, 127.4, 126.1, 123.3, 122.2, 122.0, 120.6, 120.4, 28.3, 23.3 ppm; IR (KBr pellet) $\tilde{\nu}$ = 2958, 2930, 2860, 1701, 1662, 1590, 1576, 1465, 1357, 1235, 1180, 813, 783, 754 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 264 (25703), 336 (12882), 484 (35481), 512 nm (36307 M^{-1}cm^{-1}); MS (FD, 8 kV): m/z (%): 757.8 (100) [M^+]; elemental analysis calcd (%) for $C_{52}H_{42}NO_4$: C 82.3, H 5.58, N 3.69; found C 82.45, H 5.67, N 3.70.

***N*-(2,6-Diisopropylphenyl)-*N'*-cyclohexylterrylene-3,4:11,12-tetracarboxdiimide (3b)**: Compound **10b** (700 mg, 0.9 mmol), K_2CO_3 (220 mg, 1.6 mmol) and ethanolamine (10 mL) were stirred under argon for 12 h at 80 °C. After cooling to room temperature, the solution was poured into ethanol (20 mL). The precipitate was collected by filtration, washed with water, dried under vacuum, and purified by column chromatography on silica gel (CH_2Cl_2) to yield the blue product **3b** (660 mg, 95 %). M.p. >300 °C; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 8.54 (d, J = 8.5 Hz, 2H), 8.21 (m, 5H), 8.13 (d, J = 8.5 Hz, 2H), 7.43 (t, 1H), 7.29 (d, J = 7.9 Hz, 2H), 5.05 (m, 1H), 2.74 (m, 2H), 2.47 (m, 2H), 1.85 (m, 2H), 1.7 (m, 4H), 1.38 (m, 2H), 1.14 ppm (m, 12H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 100 °C): δ = 163.81, 163.65, 163.1, 144.8, 143.1, 138.5, 136.7, 136.4, 132.5, 131.3, 130.4, 130.1, 129.7, 129.0, 128.8, 128.4, 127.7, 127.4, 126.8, 126.1, 123.4, 122.7, 122.5, 120.5, 120.4, 28.4, 25.9, 24.8, 23.3 ppm; IR (KBr pellet) $\tilde{\nu}$ = 2961, 2929, 2867, 1995, 1653, 1585, 1379, 1357, 1328, 1247, 1183, 1112, 842, 810, 751 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 600 (43325), 652 nm (81850 M^{-1}cm^{-1}); MS (FD, 8 kV): m/z (%): 756 (100) [M^+]; elemental analysis calcd (%) for $C_{52}H_{40}NO_4$: C 81.3, H 5.58, N 3.69; found C 81.19, H 5.72, N 3.56.

***N,N'*-Di(2,6-diisopropylphenyl)terrylene-3,4:11,12-tetracarboxdiimides (3)**: Multistep synthesis of terrylenetetracarboxdiimides (Scheme 2): Compound **10a** (7.0 g, 8.37 mmol), K_2CO_3 (1.0 g, 7.17 mmol) and ethanolamine (1.07 g, 23.9 mmol) were stirred under argon for 12 h at 80 °C. After cooling to room temperature, the solution was poured into methanol (20 mL). The precipitate was collected by filtration, washed with water, dried under vacuum and purified by column chromatography on silica gel (CH_2Cl_2) to yield the blue product **3** (6.9 g, 95 %). The analytical data corresponded to those in the literature.[7]

One-pot synthesis of terrylenetetracarboxdiimide (Scheme 3): Perylenedicarboximide **15** (4.8 g, 10 mmol), naphthalenedicarboximide **16** (14.2 g, 40 mmol) and *t*BuONa (19.2 g, 0.2 mol) were added to a 100 mL Schlenk flask. 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN; 30 mL) and diglyme (25 mL) were then injected into the flask under argon. The mixture was stirred for 3 h at 130 °C. After cooling to room temperature, the mixture was poured into water (100 mL) to give a precipitate. The dark crude product was washed with ethanol until the colour of the filtrate became light red. A blue solid was obtained by recrystallisation from chloroform/ethanol (3.5 g, 42 %). The analytical data correspond to those in the literature.[7]

***N*-(2,6-Diisopropylphenyl)-9-(4-bromo-2,6-diisopropylphenylnaphthalene-1,8-dicarboximide)perylene-3,4-dicarboximide (13)**: Compounds **8** (3.0 g, 4.9 mmol) and **11** (3.42 g, 12.0 mmol) were dissolved in toluene (315 mL). A solution of Na_2CO_3 (13.22 g, 0.124 mol) in water (63 mL) and ethanol (20 mL) was added, and the mixture flushed with argon. $[Pd(PPh_3)_4]$ catalyst (300 mg, 0.25 mmol) was added, and the reaction mixture stirred under argon for 16 h at 90 °C. The reaction mixture was cooled to room temperature. The resulting salt was collected by filtration. The salt was poured into concentrated HCl (200 mL). The resulting **12** was collected by filtration and used without further purification in the next step (2.69 g, 80 %). Compound **12** (1.6 g, 2.36 mmol), 4-bromo-2,6-diisopropylaniline (7.0 g, 27.3 mmol) and propionic acid (40 mL) were added to a 250 mL flask. The reaction mixture was stirred for 16 h at 150 °C. Water (150 mL) was poured into the cooled solution to obtain a red precipitate, which was collected by filtration. The product was purified by column chromathography (CH_2Cl_2) to give **13** (0.84 g, 38 %). M.p. >380 °C; ^{1}H NMR (700 MHz, $C_2D_2Cl_4$, 120 °C): δ = 8.75 (d, J = 7.1 Hz, 1H), 8.66 (m, 3H), 8.59 (d, J = Hz,7.4, 1H), 8.56 (d, J = 7.7 Hz, 1H), 8.5 (d, J = 7.2 Hz, 2H), 7.92 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.2 Hz, 1H), 7.69 (d, J = 7.4 Hz, 1H), (t, J = 7.4 Hz, 1H), 7.51 (m, 2H), 7.42 (m, 3H), 7.29 (m, 2H), 2.87 (m, 2H),1.16 ppm (m, 24H),; ^{13}C NMR (75 MHz, $C_2D_2Cl_2$, 25 °C): δ = 164.4, 164.3, 148.9, 146.5, 145.3, 139.5, 137.7, 137.4, 133.8, 133.5, 132.2, 131.9, 131.8, 131.6, 130.9, 130.3, 130.0, 129.7, 129.5, 129.5, 129.3, 128.6, 127.8, 127.7, 127.3, 124.6, 124.4, 124.0, 123.7, 123.2, 122.9, 121.8, 121.7, 121.2, 121.1, 29.6, 29.4, 24.1, 23.9 ppm; IR (KBr pellet) $\tilde{\nu}$ = 2961, 1704, 1665, 1589, 1354, 1237, 846 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 513 (40106), 487 (39233), 355 (14316), 340 (16291), 264 nm (28265 M^{-1}cm^{-1}); MS (FD, 8 kV): m/z (%): 915.9 (100) [M^+]; elemental analysis calcd (%) for $C_{58}H_{47}BrN_2O_4$: C 76.06, H 5.17, N 3.06; found C 76.07, H 5.05, N 2.99.

***N*-(4-Bromo-2,6-diisopropylphenyl)-*N'*-(2,6-diisopropylphenyl)terrylene-3,4:11,12-tetracarboxdiimide (14)**: Compound **13** (350 mg, 0.38 mmol), K_2CO_3 (2.5 g, 18 mmol) and ethanolamine (3.5 mL) were stirred under argon for 3 h at 160 °C. After cooling to room temperature, the solution was poured into water (200 mL). The precipitate was collected by filtration, washed with water, dried under vacuum and purified by column chromatography on silica gel (CH_2Cl_2) to yield the blue product **14** (314 mg, 90 %). M.p. >400 °C; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 120 °C): δ = 8.69 (m, 8H), 8.60 (d, J = 7.9 Hz, 4H), 7.42 (t, J = 7.6 Hz, 1H), 7.40 (s, 1H), 7.28 (d, J = 7.7 Hz, 2H), 2.73 (m, 4H), 1.17 (d, J = 2.7 Hz, 12H), 1.15 ppm (d, J = 2.7 Hz, 12H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 120 °C): δ = 163.7, 163.6, 148.8, 136.5, 136.2, 132.0, 132.0, 131.4, 130.6, 129.4, 129.1, 127.6, 124.8, 124.7, 124.0, 122.7, 122.3, 121.9, 121.8, 29.6, 29.4, 24.0, 23.7 ppm; IR (KBr pellet) $\tilde{\nu}$ = 2963, 2930, 2870, 1704, 1663, 1585, 1378, 1359, 1332, 1250, 1180, 850, 810, 752 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 655 (129700), 602 (67247), 557 nm (21792 M^{-1}cm^{-1}); MS (FD, 8 kV): m/z (%): 914.1 (100) [M^+]; elemental analysis calcd (%) for $C_{58}H_{45}BrN_2O_4$: C 76.23, H 4.96, N 3.07; found C 76.08, H 4.89, N 3.22.

***N*-(5-Carboxpentyl)naphthalene-1,8-dicarboxiimide (17a)**: 1,8-Naphthalene anhydride (4.0 g, 20.2 mmol), 6-aminocaproic acid (5.1 g, 40 mmol) and propionic acid (250 mL) were added to a 500 mL flask. The reaction mixture was stirred for 15 h at 140 °C. The cooled solution was added to water (1.0 L) to give a white precipitate. The solid was obtained by filtration. The product **17a** was purified by recrystallisation (dichloromethane and ethanol; 5.2 g, 85 %). M.p. 136 °C; ^{1}H NMR (250 MHz, CD_2Cl_2, 25 °C): δ = 8.53 (d, J = 7.5 Hz, 2H), 8.20 (d, J = 7.5 Hz, 2H), 7.73 (t, J = 7.5 Hz, 2H), 4.13 (m, 2H), 2.37 (m, 2H), 1.72 (m, 4H), 1.47 ppm (m, 2H); ^{13}C NMR (62.5 MHz, CD_2Cl_2, 25 °C): δ = 179.7, 164.3, 134.1, 131.9, 131.2, 128.3, 127.2, 123.0, 40.3, 34.1, 27.9, 26.8, 24.7 ppm; IR (KBr pellet) $\tilde{\nu}$ = 3446, 2940, 2862, 2361, 1698, 1661, 1625, 1590, 1457, 1438, 1386, 1344, 1312, 1260, 1235, 1167, 1139, 1104, 1068, 939, 846, 781, 738, 648, 542 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 334 (14669), 349 nm (13294 M^{-1}cm^{-1}); MS

(FD, 8 kV): *m/z* (%): 311.3 (100) [M^+]; elemental analysis calcd (%) for $C_{18}H_{17}NO_4$: C 69.44, H 5.50, N 4.50; found C 69.44, H 5.51, N 4.51.

***N*-(2,6-Diisopropylphenyl)-*N'*-(5-carboxpentyl)terrylene-3,4:11,12-tetracarboxydiimide (18a)**: Compound **15** (960 mg, 2.0 mmol), naphthalenedicarboximide derivative **17a** (1.25 g, 4.0 mmol) and *t*BuONa (3.84 g, 40 mmol) were added to a 100 mL Schlenk flask. 1,5-Diazabicyclo-[4.3.0]non-5-ene (4.0 mL) and diglyme (4.0 mL) were then injected into the flask under argon. The mixture was stirred for 2 h at 130 °C. After cooling to room temperature, the mixture was poured into water (100 mL) to give a precipitate. The dark crude product was washed with chloroform until the colour of the filtrate became light red, and then with methanol (100 mL) three times to give a violet-blue solid (potassium salt). This solid was dissolved in methanol. When aqueous HCl solution was added, a blue solid was obtained. The product **18a** was purified by recrystallisation from chloroform/ethanol (560 mg, 36 %). M.p. >300 °C; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 120 °C): δ = 8.67 (d, J = 7.8. Hz, 2H), 8.55 (m, 8H), 8.45 (d, J = 7.8 Hz, 2H), 7.42 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 7.5 Hz, 2H), 4.18 (m, 2H), 2.75 (m, 2H), 2.37 (m, 2H), 1,76 (m, 2H), 1.51 (m, 2H), 1.17 ppm (d, J = 6.9 Hz, 2H); ^{13}C NMR (175 MHz, $C_2D_2Cl_4$, 140 °C): δ = 179.2, 163.8, 146.5, 132.0, 131.6, 129.4, 124.7, 124.1, 122.9, 122.7, 121.9, 121.8, 40.6, 34.4, 29.6, 28.2, 26.9, 24.7, 24.0 ppm; IR (KBr pellet) $\tilde{\nu}$ = 3432, 2958, 2362, 2336, 1694, 1653, 1583, 1431, 1356, 1303, 1248, 1202, 1023, 841, 808, 749, 673, 520 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} = 556, 600, 653 nm (the extinction coefficients could not be measured due to low solubility); MALDI-TOF MS: *m/z* (%): 788.0 (100) [M^+]; elemental analysis calcd (%) for $C_{52}H_{40}N_2O_6$: C 79.17, H 5.11, N 3.55; found C 78.91, H 5.02, N 3.79.

***N,N'*-(2,6-Diisopropylphenyl)-1,6,9,13-tetra[4-(1,1,3,3-tetramethylbutyl)-phenoxy]terrylene-3,4,11,12-tetracarboxidiimide (20a)**: Tetrabromoterrylenediimide **19** (300 mg, 0.279 mmol), *tert*-octylphenol (336 mg, 1.95 mmol) and K_2CO_3 (134 mg, 0.97 mmol) were heated in *N*-methylpyrrolidone (50 mL) at 80 °C under argon for 8 h. After cooling to room temperature the reaction mixture was poured into HCl (2N, 100 mL). The crude solid was separated under vacuum. Column chromatography on silica gel with chloroform gave **20a** (371 mg, 86 %). M.p. >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.48 (s, 4H), 8.15 (s, 4H), 7.35 (m, 10H), 7.19 (d, J = 7.63 Hz, 4H), 7.07 (d, J = 8.54 Hz, 8H), 2.57 (h, 4H), 1.52 (s, 8H), 1.02 (d, J = 6.41 Hz, 24H), 0.64 ppm (s, 36H); ^{13}C NMR (62.5 MHz, $CDCl_3$, 25 °C): δ = 162.21, 154.49, 152.12, 146.31, 144.68, 129.97, 128.16, 127.26, 124.78, 120.96, 118.40, 56.36, 37.57, 31.52, 30.57, 28.95, 28.26, 23.26 ppm; IR (KBr pellet) $\tilde{\nu}$ = 2960, 2931, 2870, 1705, 1670, 1587, 1503, 1325, 1284, 1210, 1183, 1013, 844, 811 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 679 (99716), 623 nm (50721 M^{-1} cm^{-1}); MS (FD, 8 kV): *m/z* (%): 1651.9 (100) [M^+]; elemental analysis calcd (%) for $C_{114}H_{126}N_2O_8$: C 82.87, H 7.69, N 1.70; found C 82.84, H 7.69, N 1.69.

1,6,9,14-Tetraphenoxy-*N,N'*-(2,6-diisopropylphenyl)terrylene-3,4,11,12-tetracarboxidiimide (20c): Compound **19** (230 mg, 0.2 mmol), phenol (200 mg, 2.13 mmol) and K_2CO_3 (138 mg, 1.0 mmol) were heated in *N*-methylpyrrolidone (30 mL) at 80 °C under argon for 15 h. After cooling to room temperature, the reaction mixture was poured into HCl (2 N, 100 mL). The crude solid was separated under vacuum. Column chromatography on silica gel with chloroform gave **20c** (216 mg, 90 %). M.p. >300 °C; ^{1}H NMR (250 MHz, $C_2D_2Cl_2$, 25 °C): δ = 9.50 (s, 4H), 8.25 (s, 4H), 7.44 (m, 10H), 7.31 (d, J = 7.5 Hz, 4H), 7.20 (m, 12H), 2.69 (m, 4H), 1.10 ppm (d, J = 6.75 Hz, 4H); ^{13}C NMR (62.5 MHz, $C_2D_2Cl_2$, 25 °C): δ = 163.3, 156.0, 154.6, 146.2, 131.4, 131.2, 130.6, 129.6 , 129.2, 129.1, 126.6, 124.7, 124.2, 124.1, 123.3, 122.4, 119.3, 29.2, 23.9 ppm; IR (KBr pellet) $\tilde{\nu}$ = 2961, 2925, 2868, 2362, 2337, 1706, 1668, 1587, 1448, 1412, 1349, 1326, 1275, 1198, 1053, 1014, 869, 808, 748, 687, 581, 526 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 429 (11706), 618 (70504), 671 nm (135333 M^{-1} cm^{-1}); MS (FD, 8 kV): *m/z* (%): 1203.5 (100) [M^+]; elemental analysis calcd (%) for $C_{82}H_{62}N_2O_4$: C 81.84, H 5.19, N 2.33; found C 81.76, H 5.12, N 2.11.

***N,N'*-(2,6-Diisopropylphenyl)-1,6,9,13-tetra(*N*-piperidyl)-terrylene-3,4:11,12-tetracarboxidiimide (20d)**: Compound **19** (100 mg, 0.09 mmol) and piperidine (2.0 mL) were added to a 25-mL Schlenk flask under argon. The solution was stirred for five days at 85 °C. The cooled reaction mixture was poured into water (30 mL). The resulting precipitate was washed with water (100 mL) three times. The crude product was purified by column chromatography on silica with chloroform to give a violet solid (34 mg, 34 %). M.p. >300 °C; ^{1}H NMR (250 MHz, CD_2Cl_2, 25 °C): δ = 9.88 (s, 4H), 8.42 (s, 4H), 7.51 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 3.49 (m, 8H), 2.84 (m, 8H), 2,74 (m, 4H), 1.83 (m, 20H), 1.37 (m, 4H), 1.15 ppm (d, J = 7.0 Hz, 24H); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C): δ = 164.6, 151.5, 146.5, 132.2, 132.0, 131.3, 131.0, 129.5, 126.4, 125.2, 124.3, 122.8, 122.6, 120.9, 29.4, 26.2, 24.3, 24.0 ppm; IR (KBr pellet) $\tilde{\nu}$ = 2925, 2853, 2361, 2335, 1696, 1658, 1583, 1452, 1413, 1328, 1259, 1203, 1094, 1025, 859, 806, 672, 552 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 538 (4099), 804 nm (21582 M^{-1} cm^{-1}); MS (FD, 8 kV): *m/z* (%): 1167.5 (100) [M^+]; elemental analysis calcd (%) for $C_{78}H_{82}N_6O_4$: C 80.24, H 7.08, N 7.20; found C 80.11, H 7.18, N 7.01.

1,6,9,14-Tetra(4-sulfonylphenoxy)-*N,N'*-(2,6-diisopropylphenyl)terrylene-3,4:11,12-tetracarboxidiimide (21): Compound **20c** (120 mg, 1.0 mmol) was added to concentrated sulfuric acid (1.0 mL). The flask was sealed, and the mixture stirred for 15 h at room temperature. Water (3.0 mL) was slowly added to the flask to form a precipitate, which was collected by filtration. The solid was washed with dichloromethane (50 mL) three times and then dried at 75 °C under vacuum to give blue-green **20c** (140 mg, 94 %). M.p. >300 °C; ^{1}H NMR (250 MHz, CD_3OD, 25 °C): δ = 8.76 (s, 4H), 7.75 (s, 4H), 7.54 (d, J = 8.0 Hz, 8H), 7.04 (t, J = 7.5 Hz, 2H), 6.93 (d, J = 7.5 Hz, 4H), 6.79 (d, J = 8.0 Hz, 8H), 2.34 (m, 4H), 0.7 ppm (d, J = 7.5 Hz, 24H); ^{13}C NMR (62.5 MHz, CD_3OD, 25 °C): δ = 164.2, 158.5, 155.1, 147.1, 132.1, 131.6, 130.5, 129.9, 129.8, 129.6, 129.5, 127.9, 125.4, 125.0, 124.8, 123.5, 119.5, 30.3, 24.4 ppm; IR (KBr pellet) $\tilde{\nu}$ = 3424, 2361, 1700, 1647, 1589, 1490, 1328, 1280, 1178, 1126, 1067, 1031, 1006, 878, 849, 651, 578 cm^{-1}; UV/Vis (water): λ_{max} (ε) = 437 (4020), 640 (23898) 685 nm (17875 M^{-1} cm^{-1}); MALDI-TOF MS: *m/z* (%): 1524.0 (100) [M^+]; elemental analysis calcd (%) for $C_{82}H_{62}N_2O_8S_4$: C 64.64, H 4.10, N 1.84; found C 64.21, H 4.01, N 1.75.

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