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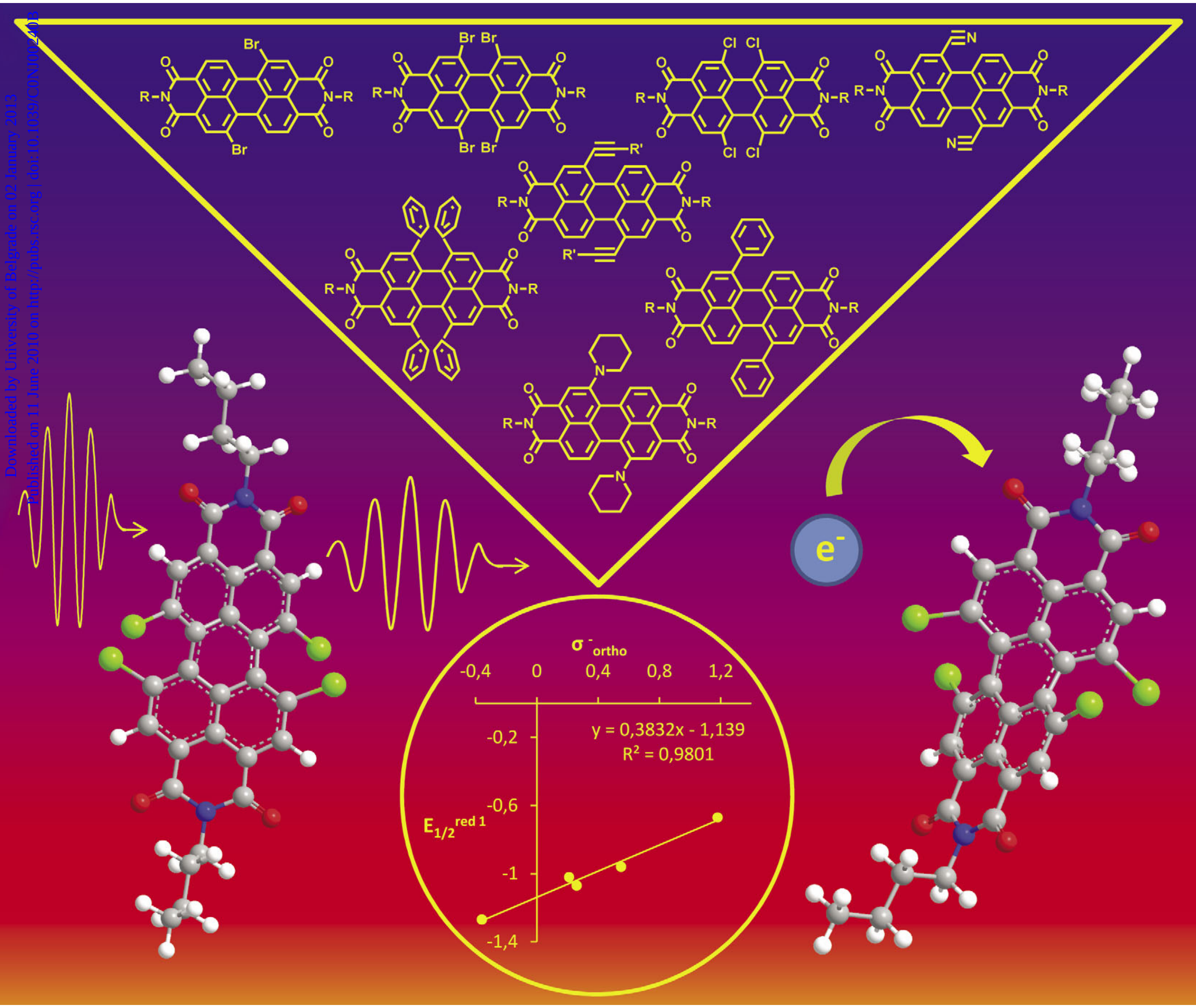

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PAPER
Norbert Hoffmann *et al.*
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3,4:9,10-diimide derivatives

Synthesis and characterization of 1,7-disubstituted and 1,6,7,12-tetrasubstituted perylenetetracarboxy-3,4:9,10-diimide derivatives

Mathieu Queste,[a] Cyril Cadiou,[b] Bernard Pagoaga,[a] Louis Giraudet[c] and Norbert Hoffmann*[a]

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A variety of perylenetetracarboxy-3,4:9,10-diimide derivatives have been synthesized. Particular attention was paid to substituents in positions 1, 6, 7 or 12. The energy differences between the frontier orbitals have been determined using optical spectroscopy (UV and fluorescence). The energy of the lowest unoccupied orbitals (LUMOs) were obtained by cyclic voltammetry. From both studies, the energies of the highest occupied orbitals (HOMOs) were also been calculated. A Hammett-type relationship was observed for the reduction potentials ($E_{1/2}^{\text{red1}}$) when correlated with the σ^-_{ortho} parameter. The energies of the frontier orbitals define the domains of application of these compounds. They significantly depend on the substitution in positions 1, 6, 7, or 12.

Introduction

Due to their interest for numerous applications in various domains, a large variety of perylenetetracarboxy-3,4:9,10-diimide derivatives have been synthesized.[1] Such compounds have been studied, for example, in the context of sensitizers in solar cells,[2] organic light-emitting diodes (OLED),[3] field-effect transistors,[4] dyes,[5] fluorescent labels[6] (for instance for bio-imaging probes[7]), single-molecule spectroscopy,[8] liquid crystals[9] and supramolecular structures,[10] for instance for transmembrane transport of ions.[11] Perylenetetracarboxy-3,4:9,10-diimide derivatives can easily be modified in order to fulfil requirements of solubility and absorption/fluorescence wavelengths. A large spectrum of structures can easily be synthesized by variation of the substituents at the imine nitrogen as well as in positions 1, 6, 7 and 12 of the perylene core. The most attractive property of these compounds is their air and water stability, in particular as electron-transporting materials. For most of the applications, a detailed characterization of there redox properties is necessary which implies the determination of the energies of the frontier orbitals (HOMO, LUMO). In the present paper, we describe the synthesis and the characterization of various 1,7-disubstituted and 1,6,7,12-tetrasubstituted perylenetetracarboxy-3,4:9,10-diimide derivatives.

Results and discussion

Synthesis of perylene derivatives

Halogenated perylene derivatives are themselves suitable compounds to be studied as organic semi-conductors, chromophores or fluorophores. They are also key intermediates for the synthesis of further perylene derivatives possessing the same kind of properties. We started our synthetic investigations with the preparation of the tetrachloroderivative **2**. This compound was easily obtained by chlorination of perylenetetracarboxy-3,4:9,10-dianhydride **1** with chlorosulfuric acid,[12] which represents an improvement of a previously published process (Scheme 1).[13,14] Subsequent condensation with various primary amines yielded perylenetetracarboxy-3,4:9,10-didiimides **3a–e**. This condensation of the tetrachloroderivative **2** is performed under significantly milder conditions than the corresponding transformation of the non-chlorinated perylene derivative **1**.[14] Bromine derivatives were also synthesized. Dibromination of perylenetetracarboxy-3,4:9,10-dianhydryde **1** was manly mainly occurred in the positions 1 and 7 (**4**) when 2.4 equivalents of bromine were added (Scheme 2).[15,16] Smaller amounts of the 1,6-diboromo isomer and the 1,6,7-tribromated perylene derivatives were also isolated (see Experimental section). Tetrabromination of **1** in the position 1, 6, 7 and 12 (**5**) selectively occurred with 4.4 equivalents of bromine.[17] Condensation with primary amines yielded the corresponding imines **3a–e**[18] (Scheme 1), **6a–d**[16,19–21] and **7a,c,d**[21,22] (Scheme 2).

Further series of perylenebisimide derivatives have been obtained from substitution reactions. The Suzuki reaction of the tetrachlorobisimide derivative **3a** or the dibromobisimide **6a** with phenylboronic acid **8** yielded the corresponding 1,6,7,12-tetraphenyl- (**9**) or 1,7-diphenylperylene (**10**) derivatives respectively (Scheme 3). In the Suzuki reaction, arylbromides are generally more reactive than their chlorine analogues.[23,24] Nevertheless, the readily available 1,6,7,12-tetrachlorinated product **3a** was successfully transformed into **9**. The transformation of 1,7-dihalogenated perylenebisimides is much easier than that of the corresponding 1,6,7,12-tetrahaologenated derivatives (compare also ref. 17) Therefore compound **10** was obtained in high yield. 1,6,7,12-Tetraphenylperylene derivatives are highly twisted, and their synthesis is particularly difficult.

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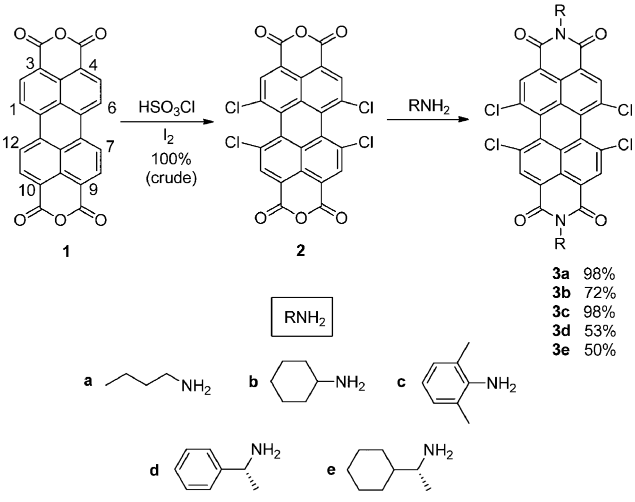
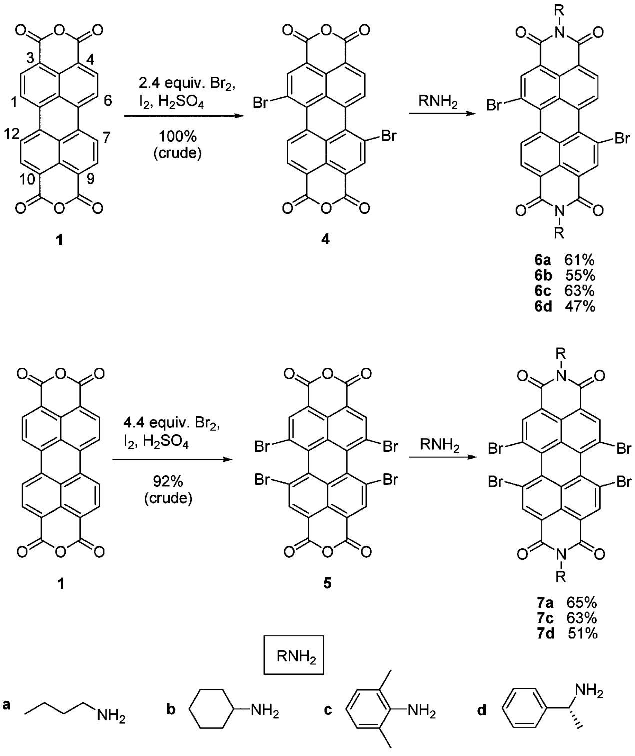
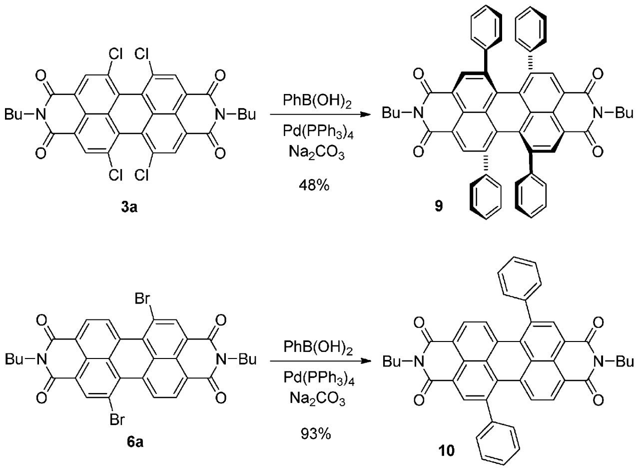
[a] *Université de Reims Champagne Ardenne, Institut de Chimie Moléculaire de Reims, UMR CNRS No. 6229, Equipe de Photochimie, UFR Sciences, B.P. 1039, 51687 Reims, France*
[b] *Université de Reims Champagne Ardenne, Institut de Chimie Moléculaire de Reims, UMR CNRS No. 6229, Equipe Chimie de Coordination, UFR Sciences, B.P. 1039, 51687 Reims, France*
[c] *Université de Reims Champagne Ardenne, Laboratoire de Microscopie et d'Etude de Nanostructures, UFR Sciences, B.P. 1039, 51687 Reims, France. E-mail: norbert.hoffmann@univ-reims.fr; Fax: +33 (0)3 26 91 31 66*



Scheme 1 Synthesis of various 1,6,7,12-tetrachloroperylenetetracarboxy-3,4:9,10-diimide derivatives.



Scheme 2 Synthesis of various 1,7-dibromo- and 1,6,7,12-tetrabromoperylenetetracarboxy-3,4:9,10-diimide derivatives.

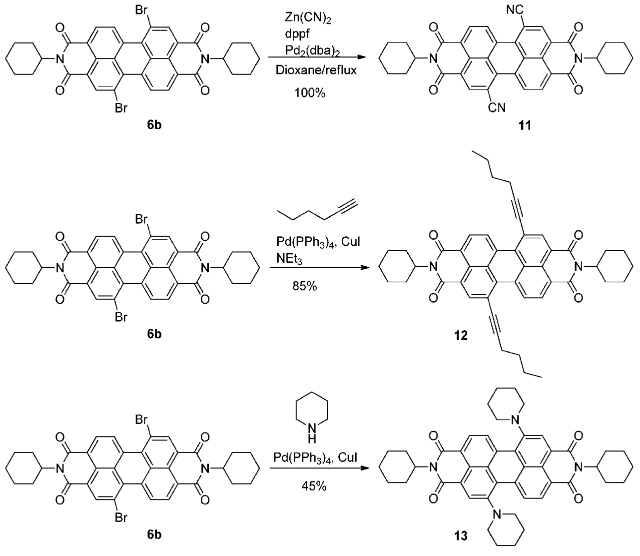


Scheme 3 Synthesis of *N*,*N*′-dibutyl-1,7-diphenyl- (**10**) and *N*,*N*′-dibutyl-1,6,7,12-tetraphenylperylenetetracarboxy-3,4:9,10-diimide **9** using the Suzuki reaction.

Further 1,7-disubstituted perylenebisimide derivatives have been obtained by cyanation of the corresponding 1,7-dibromopeyrlenebisimide **6b** (Scheme 4). Using standard reaction conditions[25] with CuCN as the cyanide source under reflux in DMF, only 50% of the corresponding product **11** was isolated. The yields were significantly improved when Pd(0) catalysis was applied.[26] Using $Zn(CN)_2$ as cyanide source under these conditions, **11** was quantitatively isolated.[27] A corresponding 1,6,7,12-tetrabromoperylenebisimide derivative could not selectively be transformed under analogous conditions. These reaction conditions resemble those of the Sonogashira reaction.[28] This transformation was applied to the synthesis of corresponding perylene derivatives.[20,29,30] Using standard conditions of this reaction, 1-hexyne was added to the perylene core of **6b** (Scheme 4). The resulting perylenebisimide derivative **12**[31] (see also ref. 29) was obtained in high yields. In the Hagihara reaction, Pd/Cu catalysis is used to establish a C–N bond. 1,7-Dibromopeyrlenebisimide **6b** was thus transformed with piperidine into compound **13**.[22,32] Corresponding transformations have been applied to the transformation of various perylene derivatives.[16,30,33]

Determination of frontier orbital energies

Many properties of perylenetetracarboxy-3,4:9,10-diimide derivatives and thus the domains of application depend on the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). These energy levels can be determined by cyclic voltammetry – the HOMO level is deduced from the oxidation



Scheme 4 Synthesis of *N*,*N*′-cyclohexyl-1,7-disubstituted perylenetetracarboxy-3,4:9,10-diimide derivatives.

potential while the LUMO is determined by the reduction potential. In the case of the perylene derivatives **3a–e**, **6a–d**, **7a,c,d** and **9–13** most frequently, only reduction potentials could be determined by this method and thus only the LUMO levels were accessible.[34] Only in the cases of compounds **9** and **13** could the corresponding oxidation potentials be determined, and thus also the energy of the HOMO. The energy gap between the frontier orbitals approximately corresponds to the excitation energy, which can be determined by UV/vis spectroscopy. Especially in cases of low Stokes shifts, a better value of the HOMO–LUMO energy difference is obtained when the 0–0 transition between the S_0 and the S_1 potential energy surface is determined from UV/vis absorption and fluorescence spectra.[35] The corresponding energy is determined from the intersection (λ_{inter}) of the absorption and the normalized emission curves of both spectra. Two typical examples are depicted in Fig. 1. The corresponding data are assembled in Table 1. The substitution on the imine nitrogen has no major influence on the this energy difference (see for example entries 1–5). The number of halogen atoms in positions 1, 6, 7 or 12 of the perylene moiety affects slightly the HOMO–LUMO energy difference. It is slightly diminished when 4 bromine atoms are present in these positions (entries 10–12) instead of only two in positions 1 and 7 (entries 6–9). The effect is enhanced when bigger substituents such as phenyl groups are attached in these positions. This tendency is observed when the 1,7-diphenyl derivative **10** is compared to the 1,6,7,12-tetraphenyl derivative **9** (entries 13 and 14). Generally, bigger substituents increase the twisting of the perylene core[21] and thus diminish the conjugation in the polycyclic aromatic system, which results in an energy approaching those of the frontier orbitals. Electronic effects also affect the energy gap between the HOMO and LUMO. In the case of the electron-withdrawing cyano substituent in positions 1 and 7 (**11**, entry 15), the gap is rather large and may be compared to corresponding compound possessing a bromine atom in the 1 and 7 positions (**6a–d**, entries 6–9). On the other hand, an electron-donating substituent such as 1-piperidyl in compound **13** (entry 17) considerably diminishes the energy gap.

Using cyclic voltammetry, we have determined the reduction potential of all the perylene derivatives reported in Table 1. The ferrocene/ferrocinium couple ($V(\text{Ag/Ag}^+) - V(\text{Fc/Fc}^+) = 0.397$ V) was taken as the reference. Solutions of the perylene derivatives (10^{-3} M) in dichloromethane containing Bu_4NPF_6 (0.1 M) were measured with a scan rate of 100 mV s^{-1}. Two typical examples are depicted in Fig. 2. In the case of compound **12**, as in almost all cases, only two reversible reduction potentials were detected. In the case of compound **9**, an additional oxidation was observed under the experimental conditions. From the first reduction potentials $E_{1/2}^{\text{red1}}$ and the ferrocene value of −4.8 eV below the vacuum level, the energy of the LUMOs were calculated.[36] Using the values for the HOMO–LUMO gap determined by UV and fluorescence spectroscopy (Scheme 4 and Table 1), the energies of the HOMOs were calculated. The corresponding values are listed in Table 2. The energies of the tetrachloro- (**3a–e**, entries 1–5), dibromo- (**6a–d**, entries 6–9) and tetrabromoperylene derivatives (**7a,c,d**, entries 10–12) are of the same order of magnitude. More sterically demanding substituents such as phenyl groups in positions 1, 6, 7 or 12 (**9**, **10**) increase the energies of the frontier orbitals (entries 13 and 14) which may be explained by an increased twisting of the perylene core.[21] Electron-withdrawing substituents in positions 1 and 7 such as the nitrile goups (**11**) decrease the energy of the frontier orbitals. In the case of compound **13** possessing two piperidinyl substituents in position 1 and 6, the electronic effect as well as the steric effect contributes to an increase of the HOMO and LUMO energies (entry 17). The contribution of the steric effect can be estimated when compared to the values measured for compound **10** (entry 14) possessing two phenyl substituents in the same position.

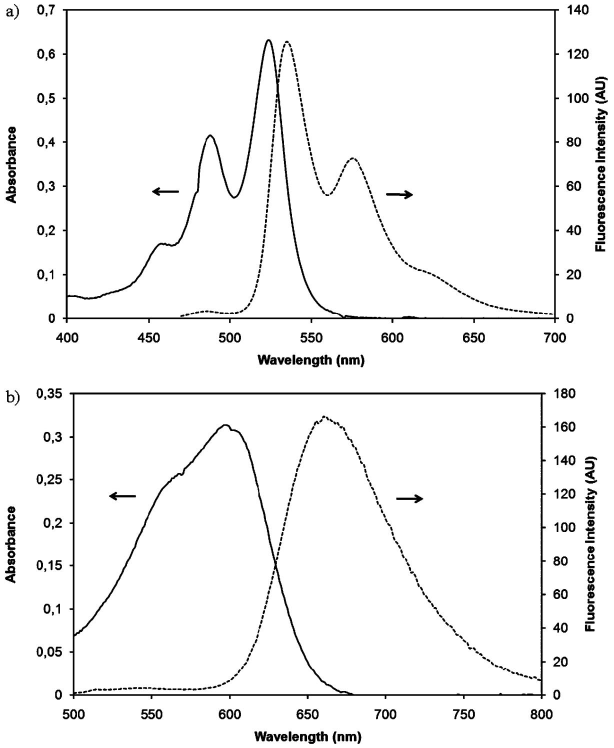


Fig. 1 UV and fluorescence spectra of compounds **11** (a) and **9** (b). The energy difference between the HOMO and LUMO approximately corresponds to the wavelength at the intersection of the normalized absorption and fluorescence bands.

The electronic effects seem to be homogeneous since they follow a Hammett-type relationship. The $E_{1/2}^{\text{red1}}$ values correlate with σ^-_{ortho} values obtained from NMR studies of *ortho*-substituted phenols (Fig. 3).[37,38] These parameters have been chosen because the positions 1, 6, 7 and 12 of the perylene system are comparable to *ortho* positions in benzene-derived aromatics. The σ^- values are appropriate for reactions in which a negative charge is involved and conjugation is possible (*e.g.* *ortho* and *para* positions of a benzene ring). In the case of the halogen compounds carrying alkyl substituents at the imine nitrogens (**3a,b,d,e**, **6a,b,d** and **7a,d**), the average values of $E_{1/2}^{\text{red1}}$ have been taken into account because the reduction potential dependence on these groups is negligible in the present compound family. Hammett-type relationships in chemical reactions seldom apply to *ortho* substitution because particular interactions of the substituents with the reaction

Table 1 Determination of the HOMO–LUMO gap using UV/vis and fluorescence spectronscopy

Entry	Compound	λ_{max} abs. (nm)	λ_{max} fluor. (nm)	λ_{inter} (nm)	$E_{HOMO-LUMO}$ (eV)
1	**3a**	516	546	531	2.33
2	**3b**	517	547	532	2.33
3	**3c**	518	549	533	2.32
4	**3d**	520	546	533	2.32
5	**3e**	518	547	532	2.33
6	**6a**	522	542	531	2.33
7	**6b**	523	545	534	2.32
8	**6c**	526	546	535	2.32
9	**6d**	526	547	536	2.31
10	**7a**	528	565	545	2.27
11	**7c**	531	569	548	2.26
12	**7d**	530	568	547	2.27
13	**9**	597	661	629	1.97
14	**10**	547	604	576	2.16
15	**11**	524	535	529	2.34
16	**12**	548	567	555	2.23
17	**13**	673	756	723	1.71

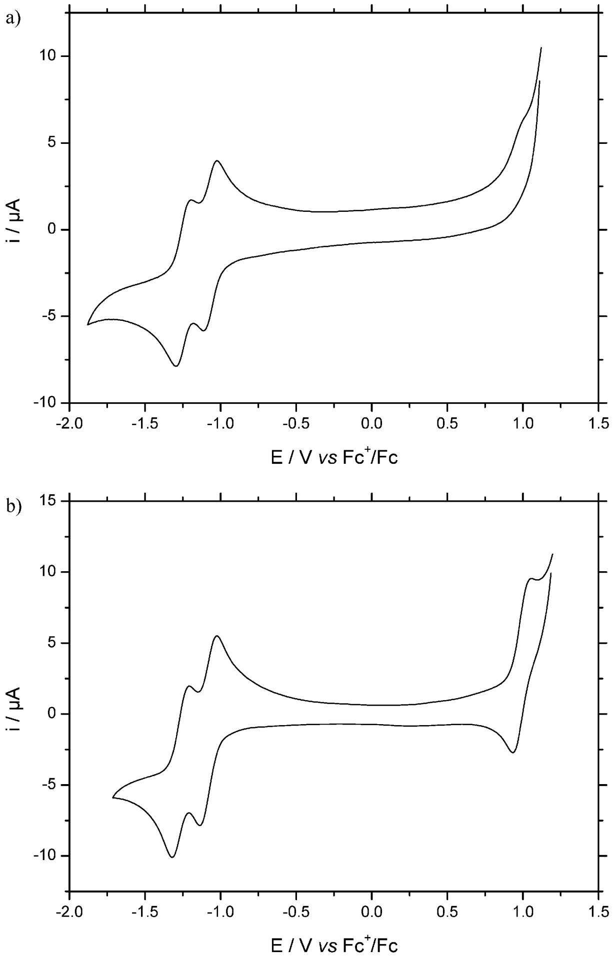


Fig. 2 Cyclic voltammograms of compounds **12** (a) and **9** (b) scaled to Fc/Fc^+.

center, such as anchimeric assistance or steric hindrance, are possible. These interactions are not described by a Hammett relationship.[39] When such neighboring-group effects are weak, as in the mentioned NMR study[37] or in our case, such relationships may nevertheless be observed. Various sets of σ-parameters for *meta*- and *para*-substitution did not show acceptable correlations. In the case of 1,6,7,12-tetrasubstituted derivatives (Fig. 3b), the slope which corresponds to the ρ-parameter in a Hammett relationship, and thus to the dependence of the reduction potential $E_{1/2}^{red1}$ on the substitution, is higher than for 1,7-diasubstituted derivatives (Fig. 3a). This tendency results from the increased number of electron-active substituents in the first case.

Conclusion

A variety of perylenetetracarboxy-3,4:9,10-diimide derivatives have been synthesized. Particular attention was paid to substituents in positions 1, 6, 7 or 12. Thus a convenient synthesis of *N*,*N*-dibutyl-1,6,7,12-tetraphenylperylenetetracarboxy-3,4:9,10-diimide starting from the corresponding 1,6,7,12-chloroperylenetetracarboxy-3,4:9,10-diimide was carried out. The energies of the frontier orbitals have been obtained from UV and fluorescence spectroscopic studies and cyclic voltammetry. These energies significantly depend on the substitution in the 1, 6, 7 and 12 positions, while the substitution on the imine nitrogen plays a minor role. Electronic as well as steric effects of the substituents have been detected. The electronic effects seem to be homogeneous, since a Hammett-type relationship is observed. Substituents at the imine nitrogen may, nevertheless, become important when the crystal, micro-crystal or other supramolecular structures affect the properties of the material.

Experimental section

General

NMR spectra were recorded with a Bruker AC 250 instrument (250 MHz for ^{1}H and 62 MHz for ^{13}C). Chemical shifts are given in ppm relative to TMS using residual solvent signals as secondary references. IR spectra were recorded on a Nicolet AVATAR 320 FT-IR. UV spectra were recorded with a UVKON 941 PLUS (Kontron Instruments). Fluorescence

Table 2 Calculation of the frontier orbital energies using reduction potentials from cyclic voltammetry and the energy gaps (see Table 1)

		Reduction potential *vs.* Fc/Fc$^+$				
Entry	Compound	$E_{1/2}^{\text{red1}}$ (V)	$E_{1/2}^{\text{red2}}$ (V)	E_{LUMO} (eV)	$E_{\text{HOMO–LUMO}}$ (eV)	E_{HOMO} (eV)
1	**3a**	−0.84	−1.01	−3.96	2.33	−6.29
2	**3b**	−0.87	−1.05	−3.93	2.33	−6.26
3	**3c**	−0.72	−0.94	−4.08	2.32	−6.40
4	**3d**	−0.81	−1.03	−3.99	2.32	−6.31
5	**3e**	−0.84	−1.05	−3.96	2.33	−6.29
6	**6a**	−0.96	−1.18	−3.84	2.33	−6.17
7	**6b**	−0.99	−1.19	−3.81	2.32	−6.13
8	**6c**	−0.90	−1.11	−3.90	2.32	−6.22
9	**6d**	−0.92	−1.14	−3.88	2.31	−6.19
10	**7a**	−0.82	−1.02	−3.98	2.27	−6.25
11	**7c**	−0.74	−0.99	−4.06	2.26	−6.32
12	**7d**	−0.76	−0.97	−4.04	2.27	−6.31
13	**9**	−1.09	−1.27	−3.71	1.97	−5.68[a]
14	**10**	−1.02	−1.24	−3.78	2.16	−5.94
15	**11**	−0.67	−0.98	−4.13	2.34	−6.47
16	**12**	−1.07	−1.24	−3.73	2.23	−5.96
17	**13**	−1.27	−1.43	−3.53	1.71	−5.24[b]

[a] The value −5.79 eV was measured by cyclic voltammetry (compare Fig. 2). [b] The value −5.10 eV was measured by cyclic voltammetry.

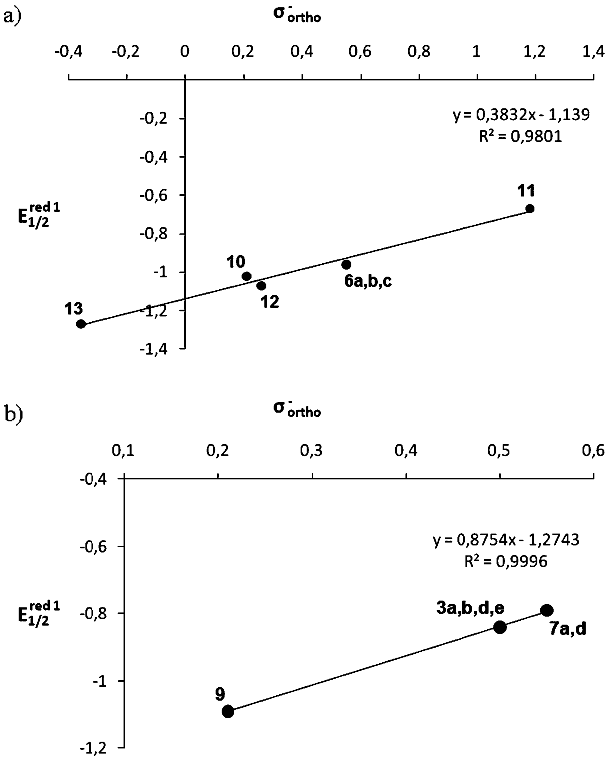


Fig. 3 Hammett-type plots: (a) 1,7-disubstituted perylenetetracarboxy-3,4:9,10-diimides **6a,b,d** (average value for $E_{1/2}^{\text{red1}}$), **10**, **11**, **12** and **13** (σ^- value for NMe_2); (b) 1,6,7,12-tetrasubstituted perylenetetracarboxy-3,4:9,10-diimides **3a,b,d,e** (average value for $E_{1/2}^{\text{red1}}$), **7a,d** (average value for $E_{1/2}^{\text{red1}}$) and **9**.

spectra were recorded on a Perkin-Elmer LS50B Spectrometer. Optical rotations were recorded on a Perkin-Elmer 341 Polarimeter. TLC was carried out with Kieselgel 60F254 plates from Merck. Preparative chromatography was carried out with silica gel 60A from Carlo Erba Reactifs-SDS.

Syntheses of the 1,7-disubstituted and 1,6,7,12-tetrasubstituted perylenetetracarboxy-3,4:9,10-diimide derivatives

Preparation of compound 2. A stirred mixture of perylenetetracarboxy-3,4:9,10-dianhydride **1** (5 g, 12.7 mmol), chlorosulfuric acid (57.2 g, 0.5 mol) and iodine (0.9 g, 3.45 mmol) was heated to 60–70 °C for 20 h. At room temperature, the mixture was treated with ice–water. The solid was filtered, washed with ice–water and dried *in vacuo*. Yield: 6.8 g.

Synthesis of 3a. Under argon atmosphere, a mixture of **2** (1.0 g, 1.9 mmol), *n*-butylamine (0.6 g, 7.5 mmol) and propionic acid (20 ml) was heated under reflux for 20 h. At room temperature, the mixture was filtered. The solid was washed several times with water, then with saturated $NaHCO_3$ solution. The solid was dried *in vacuo*. No additional purification was needed. Yield: 1.2 g (98%).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.68 (s, 4 H), 4.22 (t, 4 H, J = 3,7 Hz), 1.74 (m, 4 H), 1.47 (m, 4 H), 1.00 (t, 6 H, J = 7,3 Hz) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 162.7, 135.8, 134.1, 133.2, 131.8, 129.0, 123.7, 41.1, 30.6, 20.8, 14.2 ppm. IR (KBr): ν = 3051, 2959, 2930, 2870, 1700, 1664, 1586, 1494, 1430, 1393, 1369, 1353, 1315, 1288, 1263, 1235, 1187, 1159, 1110, 1050, 1009 cm^{-1}. UV (CH_2Cl_2): $\lambda_{\max}(\varepsilon)$ = 516 (34 000) nm. Elemental analysis: calcd (%) for $C_{32}H_{22}Cl_4N_2O_4$ (640.34): C 65.22, H 2.99, N 3.80; found: C 64.65, H 2.61, N 3.77.

Synthesis of compound 3b. Using the same conditions as for the synthesis of **3a**, compound **3b** was obtained after chromatography (eluent: dichloromethane). Yield 1.1 g (72%).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.64 (s, 4H), 5.02 (m, 2H), 2.53 (m, 2H), 2.53 (m, 4H), 1.92 (m, 4H), 1.75 (m, 6H), 1.49 (m, 6H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 163.3, 162.7, 140.3, 135.3, 133.0, 132.9, 125.4, 123.8, 118.6, 54.5, 29.1, 29.1, 26.5, 25.4 ppm. IR (KBr): ν = 2973, 2931, 2853, 1784, 1751, 1706, 1667, 1589, 1563, 1453, 1397, 1375, 1343, 1314, 1280, 1258, 1238, 1188, 1158, 1075 cm^{-1}. UV (CH$_2$Cl$_2$): $\lambda_{max}(\varepsilon)$ = 517 (19 000) nm.

Synthesis of compound 3c. Using the same conditions as for the synthesis of **3a**, compound **3c** was obtained. Yield 1.4 g (98%).

^{1}H NMR (250 MHz, CDCl$_3$): δ = 8.69 (s, 4H), 7.22 (m, 6H), 2.53 (m, 2H), 2.11 (m, 12H), ppm. ^{13}C NMR (62 MHz, CDCl$_3$): δ = 162.0, 136.1, 135.9, 133.8, 133.5, 129.8, 129.4, 129.2, 124.4, 123.8, 123.7, 18.4 ppm. IR (KBr): ν = 3067, 2973, 2924, 1776, 1714, 1677, 1590, 1556, 1473, 1409, 1382, 1341, 1315, 1295, 1243, 1197, 1168, 1149, 1021, 1005 cm^{-1}. (+)-HRESIMS: *m*/*z* 735.0411 [M + H]$^+$ (cald for C$_{40}$H$_{23}$N$_2$O$_4$Cl$_4$, 735.0412). UV (CH$_2$Cl$_2$): $\lambda_{max}(\varepsilon)$ = 518 (33 000) nm.

Synthesis of compound 3d. Using the same conditions as for the synthesis of **3a**, compound **3d** was obtained after chromatography (eluent: dichloromethane–toluene: 90:10). Yield 0.7 g (53%).

^{1}H NMR (250 MHz, CDCl$_3$): δ = 8.57 (s, 4H), 7.44 (d, 4H), 7.24 (m, 6H), 6.47 (q, J = 7.3 Hz, 2H), 1.94 (d, J = 7.2 Hz, 6H) ppm. ^{13}C NMR (62 MHz, CDCl$_3$): δ = 162.7, 151.8, 150.3, 140.4, 135.8, 133.6, 133.2, 128.7, 127.7, 127.7, 123.9, 51.3, 16.6 ppm. IR (KBr): ν = 3062, 3029, 2977, 2943, 2915, 1705, 1667, 1588, 1494, 1452, 1413, 1389, 1372, 1343, 1315, 1276, 1242, 1189, 1150, 1077, 1066, 1023 cm^{-1}. MS (*m*/*z*, ESI): 737.1 (M + H)$^+$, 760.1 (M + Na)$^+$. UV (CH$_2$Cl$_2$): $\lambda_{max}(\varepsilon)$ = 520 (53 000) nm. $[\alpha]_D^{25}$ = +2.3 (c = 0.1 mg ml^{-1} in CH$_2$Cl$_2$). Elemental analysis: calcd (%) for C$_{40}$H$_{22}$Cl$_4$N$_2$O$_4$ (736.43): C 65.24, H 3.01, N 3.80; found: C 64.65, H 2.61, N 3.77.

Synthesis of compound 3e. Using the same conditions as for the synthesis of **3a**, compound **3e** was obtained after chromatography (eluent: dichloromethane). Yield 0.7 g (50%).

^{1}H NMR (250 MHz, CDCl$_3$): δ = 8.64 (s, 4H), 5.02 (m, 2H), 2.53 (m, 4H), 1.92 (m, 4H), 1.75 (m, 6H), 1.49 (m, 6H) ppm. ^{13}C NMR (62 MHz, CDCl$_3$): δ = 162.6, 162.5, 135.5, 133.9, 133.2, 131.5, 128.6, 123.6, 55.9, 55.5, 39.4, 39.3, 31.2, 30.1, 26.3, 26.1, 25.9, 16.6, 16.5 ppm. IR (KBr): ν = 2973, 2931, 2853, 1784, 1751, 1706, 1667, 1589, 1563, 1453, 1397, 1375, 1343, 1314, 1280, 1258, 1238, 1188, 1158, 1075 cm^{-1}. UV (CH$_2$Cl$_2$): $\lambda_{max}(\varepsilon)$ = 518 (19 000) nm.

Preparation of compound 4. A mixture of perylenetetracarboxy-3,4:9,10-dianhydride **1** (30 g, 76.5 mmol) in sulfuric acid (98%, 350 ml) was stirred at room temperature for 2 h. After heating to 85 °C, iodine (738 mg, 3.0 mmol) was added. Then bromine (26.9 g, 168.2 mmol) was added drop by drop. Stirring was continued for about 16 h at 85 °C. After cooling to room temperature, the excess of bromine was eliminated by bubbling argon in the reaction mixture. The reaction product was precipitated by slow addition of ice–water (200 ml). After filtration the solid was washed with water until the mixture was pH neutral. After drying at 120 °C *in vacuo*, 42.0 g of red solid was obtained. A NMR analysis (96–98% D$_2$SO$_4$ in D$_2$O) revealed the presence of 1,7-dibromo-3,4:9,10-dianhydride **4**, 1,6-dibromo-3,4:9,10-dianhydride and 1,6,7-tribromo-3,4:9,10-dianhydride **5** in a ratio of 76:20:4.

Synthesis of compound 6a. A stirred mixture of crude 1,7-dibromo-3,4:9,10-dianhydride **4** (2 g, 3.6 mmol), butylamine (0.8 g, 10.9 mmol) in acetic acid (1 ml) was heated to 100 °C under argon atmosphere for 10 h. After cooling to room temperature, water was added and the precipitate was filtered. After abundant washing with water, the product was dried *in vacuo*. An initial purification was carried out with chromatography (eluent: dichloromethane–toluene: 70:30). The first fraction contained *N*,*N*-dibutyl-1,6,7-tribromo-3,4:9,10-tetracarboxylic acid diimide. The second fraction contained an 80:20 mixture of *N*,*N*-dibutyl-1,7-dibromo-3,4:9,10-tetracarboxylic acid diimide **6a** and *N*,*N*-dibutyl-1,6-dibromo-3,4:9,10-tetracarboxylic acid diimide, which could not be separated by chromatography. Pure **6a** was obtained by recrystallization. Yield: 1.5 g (61%).

^{1}H NMR (250 MHz, CDCl$_3$): δ = 9.44 (d, J = 8.1 Hz, 2H), 8.87 (s, 2H), 8.66 (d, J = 8.1 Hz, 2H), 4.21 (t, J = 7.3 Hz, 4H), 1.73 (m, 4H), 1.47 (m, 4H), 1.00 (t, J = 7.3 Hz, 6H) ppm. ^{13}C NMR (62 MHz, CDCl$_3$): δ = 163.0, 162.5, 138.2, 132.8, 132.8, 130.1, 129.2, 128.6, 127.0, 123.4, 122.9, 121.1, 41.0, 30.5, 20.8, 14.3 ppm. IR (KBr): ν = 2957, 2931, 2871, 1702, 1666, 1594, 1559, 1507, 1434, 1411, 1393, 1377, 1349, 1332, 1295, 1269, 1237, 1198, 1155, 1116, 1090, 1032 cm^{-1}. UV (CH$_2$Cl$_2$): $\lambda_{max}(\varepsilon)$ = 522 (68 000) nm.

Synthesis of compound 6b. Using the same conditions as for the synthesis of **6a**, compound **6b** was obtained after chromatography (eluent: dichloromethane–toluene: 70:30). Yield 1.42 g (55%).

^{1}H NMR (250 MHz, CDCl$_3$): δ = 9.48 (d, J = 8.2 Hz, 2H), 8.88 (s, 2H), 8.67 (d, J = 8.2 Hz, 2H), 5.03 (m, 2H), 2.54 (m, 4H), 1.92 (m, 4H), 1.76 (m, 6H), 1.41 (m, 6H) ppm. ^{13}C NMR (62 MHz, CDCl$_3$): δ = 161.8, 161.3, 136.5, 131.3, 131.1, 128.5, 127.7, 127.0, 125.5, 122.2, 121.8, 119.2, 52.8, 27.6, 25.0, 23.9 ppm. IR (KBr): ν = 2928, 2852, 1701, 1660, 1589, 1560, 1498, 1451, 1419, 1398, 1382, 1328, 1302, 1258, 1239, 1187, 1144, 1116 cm^{-1}. UV (CH$_2$Cl$_2$): $\lambda_{max}(\varepsilon)$ = 523 (89 000) nm. Elemental analysis: calcd (%) for C$_{36}$H$_{28}$Br$_2$N$_2$O$_4$ (712.43): C 60.69, H 3.96, N 3.93; found: C 60.85.65, H 4.11, N 4.02.

Synthesis of compound 6c. Using the same conditions as for the synthesis of **6a**, compound **6c** was obtained after chromatography (eluent: dichloromethane–toluene: 70:30). Yield 1.7 g (63%).

^{1}H NMR (250 MHz, CDCl$_3$): δ = 9.58 (d, J = 8.0 Hz, 2H), 9.02 (s, 2H), 8.81 (d, J = 8.1 Hz, 2H), 7.32 (m, 6H), 2.17 (s, 12H) ppm. ^{13}C NMR (62 MHz, CDCl$_3$): δ = 162.7, 162.1, 138.9, 137.3, 135.9, 133.9, 133.7, 133.7, 131.0, 129.6, 129.2, 128.1, 124.5, 123.7, 123.3, 121.5, 18.3 ppm. IR (KBr): ν = 3054, 2919, 1706, 1668, 1590, 1501, 1474, 1445, 1413, 1387, 1333, 1304, 1240, 1200, 1145, 1035 cm^{-1}. UV (CH$_2$Cl$_2$): $\lambda_{max}(\varepsilon)$ = 526 (91 000) nm.

Synthesis of compound 6d. Using the same conditions as for the synthesis of **6a**, compound **6d** was obtained after chromatography (eluent: dichloromethane–toluene: 70:30). Yield 0.9 g (47%).

^{1}H NMR (250 MHz, CDCl$_3$): δ = 9.43 (d, J = 8.1 Hz, 2H), 8.86 (s, 2H), 8.64 (d, J = 8.1 Hz, 2H), 7.50 (m, 10H), 7.10 (d, J = 7.1 Hz, 2H), 2.00 (d, J = 7.1 Hz, 6H) ppm. ^{13}C NMR

(62 MHz, $CDCl_3$): δ = 163.1, 162.6, 140.3, 138.4, 133.1, 133.0, 130.4, 128.6, 128.4, 127.4, 123.6, 123.2, 120.9, 50.8, 16.4 ppm. IR (KBr): ν = 3049, 2923, 2852, 1702, 1659, 1590, 1560, 1494, 1457, 1416, 1392, 1379, 1327, 1299, 1237, 1187, 1146, 1070, 1031, 1014 cm^{-1}. UV (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 526 (80 000) nm.

Synthesis of compound 5. A mixture of perylenetetracarboxy-3,4:9,10-dianhydride **1** (30 g, 76.5 mmol) in sulfuric acid (98%, 350 ml) was stirred at room temperature for 2 h. After heating to 65 °C, iodine (1.6 g, 6.1 mmol) was added. The reaction mixture was then heated to 85 °C and a portion bromine (26.9 g, 168.2 mmol) was added drop by drop over a period of 2 h. After heating to 110 °C, the second portion of bromine (26.9 g, 168.2 mmol) was added drop by drop over a period of 4 h. Heating was continued at this temperature for 16 h. After cooling to room temperature, the excess bromine was eliminated by a light stream of argon. The reaction product was precipitated by slow addition of ice–water (200 ml). After filtration the solid was washed with water until the mixture was pH neutral. After drying at 120 °C *in vacuo*, 50 g of red solid was obtained. Due to low solubility in organic solvents, the crude material was used for further transformations.

Synthesis of compound 7a. A stirred mixture of crude 1,6,7,12-tetrabromo-3,4:9,10-dianhydride **5** (2 g, 2.8 mmol), butylamine (1.2 g, 16.9 mmol) in propionic acid (1 ml) was heated to 140 °C under argon atmosphere for 10 h. After cooling to room temperature, water was added and the precipitate was filtered. After washing with saturated $NaHCO_3$ solution, the product was dried *in vacuo*. TLC revealed the presence of different products, which were separated by column chromatography (eluent: dichloromethane). The first fraction contained *N*,*N*′-dibutyl-1,6,7,12-tetrabromo-3,4:9,10-diimide **7a**. The second fraction contained *N*,*N*′-dibutyl-1,6,7-tribromo-3,4:9,10-diimide and the third contained a mixture of *N*,*N*′-dibutyl-1,7-dibromo-3,4:9,10-tetracarboxylic acid diimide **6a** and *N*,*N*′-dibutyl-1,6-dibromo-3,4:9,10-tetracarboxylic acid diimide. The ratio of these three fractions was 6:2:1. Yield of compound **7a**: 1.5 g (65%).

^1H NMR (250 MHz, $CDCl_3$): δ = 8.82 (s, 4H), 4.22 (t, *J* = 4.9 Hz, 4H), 1.74 (m, 4H), 1.46 (m, 4H), 1.00 (t, *J* = 7.3 Hz, 6H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 162.6, 136.5, 132.1, 131.8, 124.4, 124.3, 123.1, 41.1, 30.6, 20.7, 14.3 ppm. IR (KBr): ν = 2957, 2929, 2869, 1702, 1664, 1583, 1489, 1432, 1411, 1387, 1368, 1307, 1283, 1232, 1187, 1156 cm^{-1}. UV (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 528 (54 000) nm.

Synthesis of compound 7c. Using the same conditions as for the synthesis of **7a**, compound **7c** was obtained after chromatography (eluent: dichloromethane). Yield 1.4 g (63%).

^1H NMR (250 MHz, $CDCl_3$): δ = 8.82 (s, 4H), 7.21 (m, 6H), 2.12 (m, 12H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 159.8, 134.8, 133.7, 131.4, 130.4, 127.7, 127.1, 123.6, 122.9, 122.5, 121.0, 16.3 ppm. IR (KBr): ν = 2961, 2922, 1713, 1677, 1584, 1474, 1443, 1409, 1375, 1307, 1290, 1239, 1197, 1139, 1032 cm^{-1}. UV (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 531 (51 000) nm. Elemental analysis: calcd (%) for $C_{40}H_{22}Br_4N_2O_4$ (914.23): C 52.55, H 2.43, N 3.06; found: C 52.99, H 3.00, N 3.18.

Synthesis of compound 7d. Using the same conditions as for the synthesis of **7a**, compound **7d** was obtained after chromatography (eluent: dichloromethane–toluene: 70:30). Yield 1.3 g (51%).

^1H NMR (250 MHz, $CDCl_3$): δ = 8.82 (s, 4H), 7.21 (m, 6H), 6.54 (q, *J* = 7.1 Hz, 2H), 2.00 (d, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 162.6, 140.4, 136.7, 132.0, 129.5, 128.7, 127.8, 127.7, 125.7, 124.4, 123.4, 51.3, 16.7 ppm. IR (KBr): ν = 2966, 2927, 1704, 1665, 1583, 1543, 1494, 1450, 1414, 1382, 1369, 1307, 1272, 1240, 1188, 1145, 1079 cm^{-1}. UV (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 530 (44 000) nm. Elemental analysis: calcd (%) for $C_{32}H_{22}Br_4N_2O_4$ (818.83): C 46.98, H 2.71, N 3.42; found: C 47.23, H 2.80, N 3.71.

Synthesis of compound 9. Under argon atmosphere, a mixture of **3a** (0.5 g, 0.8 mmol), benzene (10 ml) and water (5 ml) was prepared. Successively, a solution of Na_2CO_3 (0.8 g, 7.8 mmol) in ethanol (2 ml), phenylboronic acid (1.9 g, 15.6 mmol) and finally tetrakis(triphenylphosphine)-palladium(0) (45 mg, 5 mol%) were then added. The resulting mixture was heated to 80 °C for 6 h. The colour changed from red to blue-violet. After cooling to room temperature, water (30 ml) was added. The mixture was extracted three times with dichloromethane (30 ml). The combined organic phases were dried with $MgSO_4$ and the solvent was evaporated after filtration. The crude material was purified by column chromatography (eluent: dichloromethane–toluene: 60:40). Yield: 302 mg (48%).

^1H NMR (250 MHz, $CDCl_3$): δ = 8.29 (s, 4H), 7.20 (m, 10H), 6.83 (m, 10H), 4.23 (t, *J* = 7.4 Hz, 4H), 1.78 (m, 4H), 1.50 (m, 4H), 1.01 (t, *J* = 7.4 Hz, 6H) ppm, ^{13}C NMR (62 MHz, $CDCl_3$): δ = 164.1, 143.0, 140.8, 134.1, 132.2, 131.6, 130.1, 128.0, 126.3, 122.6, 121.1, 40.9, 30.8, 20.9, 14.3 ppm. IR (KBr): ν = 2956, 2927, 2856, 1698, 1659, 1591, 1448, 1433, 1413, 1351, 1315, 1302, 1265, 1222, 1148, 1076 cm^{-1}. (+)-HRESIMS: *m*/*z* 829.3038 $[M + Na]^+$ (cald for $C_{56}H_{42}N_2O_4Na$, 829.3042). UV (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 597 (25 000) nm.

Synthesis of compound 10. Under argon atmosphere, a mixture of **6a** (0.2 g, 0.3 mmol), benzene (5 ml) and water (2.5 ml) was prepared. Successively, a solution of Na_2CO_3 (96.3 mg, 7.8 mmol) in ethanol (1 ml), phenylboronic acid (0.3 g, 0.9 mmol) and finally tetrakis(triphenylphosphine)-palladium(0) (10.5 mg, 3 mol%) were then added. The resulting mixture was heated to 80 °C for 6 h. The colour changed from red to fuchsia-blue. After cooling to room temperature, water (30 ml) was added. The mixture was extracted three times with dichloromethane (30 ml). The combined organic phases were dried with $MgSO_4$ and the solvent was evaporated after filtration. The crude material was purified by column chromatography (eluent: dichloromethane–toluene: 90:10). Yield: 184 mg (93%).

^1H NMR (250 MHz, $CDCl_3$): δ = 8.60 (s, 4H), 8.13 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 4.19 (t, *J* = 7.3 Hz, 4H), 1.72 (m, 4H), 1.45 (m, 4H), 1.00 (t, *J* = 7.3 Hz, 6H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 163.8, 163.7, 142.4, 141.4, 135.5, 135.0, 132.7, 132.1, 130.6, 129.6, 129.4, 129.1, 127.8, 122.5, 122.2, 118.7, 40.8, 30.7, 20.8, 14.3 ppm. IR (KBr): ν = 2958, 2929, 2868, 2363, 2343, 1697, 1657, 1595, 1562, 1545, 1510, 1493, 1446, 1407, 1332, 1267, 1244, 1223, 1190, 1133, 1080 cm^{-1}. (+)-HRESIMS: m/z 677.2431 [M + Na]$^+$ (cald for $C_{56}H_{42}N_2O_4Na$, 677.2416). UV (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 547 (68 000) nm.

Synthesis of compound 11. Under argon atmosphere, a solution of **6b** (0.2 g, 0.3 mmol) in dioxane (20 ml) was prepared. Successively, zinc cyanate (260 mg, 2.2 mmol), 1,1′-bis(diphenylphosphino)ferrocene (21.8 mg, 0.04 mmol) and tris(dibenzylideneacetone)dipalladium(0) (36.0 mg, 0.04 mmol) were then added. The resulting mixture was heated under reflux for 20 h. After cooling to room temperature, the reaction mixture was diluted with chloroform (20 ml) and filtered with Celite. After evaporation, the product was purified by column chromatography (eluent: dichloromethane). Yield: 170 mg (100%).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.69 (d, J = 8.0 Hz, 2H), 8.94 (s, 2H), 8.89 (d, J = 8.0 Hz, 2H), 5.00 (m, 2H), 2.53 (m, 4H), 1.94 (m, 4H), 1.77 (m, 6H), 1.51 (m, 4H), 1.32 (m, 14H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 162.1, 161.7, 138.0, 136.1, 133.4, 131.3, 128.9, 128.7, 119.4, 108.3, 54.7, 29.2, 29.1, 29.0, 26.5, 25.4 ppm. IR (KBr): ν = 3053, 2933, 2854, 2362, 2220, 1706, 1662, 1604, 1454, 1411, 1347, 1331, 1260, 1248, 1198, 1136 cm^{-1}. UV (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 524 (38 000) nm.

Synthesis of compound 12. Under argon atmosphere, a solution of **6b** (0.2 g, 0.3 mmol) in 1:1 THF–triethylamine (20 ml) was prepared. With vigorous stirring, tetrakis(triphenylphosphine)palladium(0) (20 mg, 8 mol%) and copper iodide (5.3 mg, 10 mol%) were then added successively. Through a septum, hex-1-yne (92 mg, 1.1 mmol) was added slowly drop by drop. With stirring, the mixture was heated to 85 °C for 16 h. After cooling to room temperature, cold 1:3 HCl–H_2O (20 ml) was added and the product was extracted with dichloromethane. After neutralization, the organic phases were dried with $MgSO_4$. The crude product was purified by column chromatography (eluent: dichloromethane–toluene: 1:1). Yield: 171 mg (85%).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 10.0 (d, J = 8.0 Hz, 2H), 8.61 (s, 2H), 8.50 (d, J = 8.0 Hz, 2H), 4.97 (m, 2H), 2.56 (m, 4H), 1.85 (m, 4H), 1.77 (m, 6H), 1.67 (m, 4H), 0.98 (m, 14H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 163.8, 163.4, 138.2, 134.0, 133.6, 133.0, 129.9, 127.1, 126.5, 123.4, 122.4, 120.6, 102.6, 82.8, 54.4, 30.7, 30.1, 29.5, 27.0, 26.0, 22.8, 20.4, 14.2 ppm. IR (KBr): ν = 3437, 2930, 2855, 2210, 1701, 1657, 1601, 1564, 1456, 1409, 1342, 1327, 1260, 1244, 1225, 1194, 1138, 1104 cm^{-1}. UV (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 548 (29 000) nm.

Synthesis of compound 13. Under argon atmosphere, a solution of **6b** (0.2 g, 0.3 mmol) in 1:1 THF/piperidine (20 ml) was prepared. While stirring, copper iodide (5.3 mg, 10 mol%) and tetrakis(triphenylphosphine)palladium(0) (20 mg, 8 mol%) were then added successively. With stirring, the mixture was heated to 75 °C for 8 h. After cooling, as much solvent as possible was solvent was evaporated and the residue was subjected to column chromatography (eluent: dichloromethane–toluene: 7:3). Yield: 91.1 mg (45%).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.61 (d, J = 8.4 Hz, 2H), 8.41 (s, 2H), 8.40 (d, J = 8.2 Hz, 2H), 4.98 (m, 2H), 3.44 (m, 4H), 2.88 (m, 4H), 2.50 (m, 4H), 1.76 (m, 18H), 1.38 (m, 10H) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 164.4, 164.2, 151.0, 135.7, 130.2, 128.5, 123.9, 123.5, 123.3, 123.2, 121.6, 121.5, 53.9, 53.0, 29.3, 26.7, 25.9, 25.7, 23.9 ppm. IR (KBr): ν = 2924, 2853, 1692, 1656, 1592, 1562, 1546, 1510, 1460, 1413, 1325, 1260, 1109 cm^{-1}. UV (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 673 (9000) nm.

Cyclic voltammetry

Cyclic voltammetry was carried out with an Autolab PGSTAT12 potentiostat from ECO Chemie coupled to an electrochemical cell with three electrodes. A platinum disk was used as working electrode and a Pt wire as counter. $Ag/AgNO_3$ was used as the reference electrode. Solutions of the perylene derivatives (10^{-3} M) in dichloromethane containing Bu_4NPF_6 (0.1 M) were measured with a scan rate of 100 mV s^{-1}. Fc^+/Fc was used as the reference.

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