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Regioselective Functionalization of Core-Persubstituted Perylene Diimides

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Abstract: Regioselective functionalization of core per-substituted perylene diimides has been achieved efficiently based on a new versatile building block, named tetrabromotetrachloro-perylene-3,4:9,10-tetracarboxylic acid dianhydride (Br_4Cl_4-PTCDA), which affords a series of novel chromophores with impressive optoelectronic properties. Direct palladium-catalyzed fourfold intramolecular ring fusion affords successfully unique propeller-shaped biscarbazole[2,3-*b*]carbazole diimides with six annulated rings.

The design and synthesis of high-performance electron-deficient conjugated molecules is highly desirable due to the urgent demand for effective electron-transporting materials and functional components in organic electronics.[1] Perylene diimides (PDIs, Figure 1) are a fascinating group of candidates, which received considerable interest as a result of their most promising application in n-type organic field effect transistors, light-emitting diodes, and solar cells.[2] To date, the classical modifications of PDIs are focused on the bay-region (1, 6, 7, 12-positions) via halogen atoms and subsequent transformation to gain enormously valuable derivatives to comply with various applications.[3] Only recently, has functionalization on non-bay regions (2, 5, 8, 11-positions) been available by direct alkylation, arylation, and borylation through metal-catalyzed C–H bond cleavage.[4] The first perchloro-substituted PDIs (Cl_8-PTCDI) are also reported as high-performance n-channel materials.[5] However, the number of the examples of non-bay region functionlization PDIs is still very limited due to a lack of a simple and efficient building blocks, not to mention the regioselective functionalization of octa-substituted PDIs so far.

We are highly enthusiastic about the design and synthesis of novel electron-deficient conjugated systems based on rylene diimides. Recently, we reported the facile homocoupling and cross-coupling of PDIs and naphthalene diimides (NDIs) toward fully conjugated rylene arrays by an Ullmann reaction, Stille reaction, and C–H transformation.[6] Very lately, a series of non-bay-region cyano-substituted tetrachloro-perylene diimides from Br_xCl_4-PDIs (x = 1,2,3,4) with linearly correlated LUMO levels have been developed by our group.[7] Herein, these developments have inspired us to design and synthesize a series of core-persubstituted PDIs by a facile regioselective functionalization from a simple and versatile building block, named tetrabromotetrachloro-perylene-3,4:9,10-tetracarboxylic acid dianhydride (**5**, Br_4Cl_4-PTCDA). In general, the accessibility of these non-bay positions firstly allows us to functionalize the aromatic cores regioselectively (**2**, Figure 1) to tune the optoelectronic properties, in particular, higher electron affinities, facilitating electron injection. Furthermore, the retaining of the chlorine atoms in the bay region renders the possibility for further extension of the conjugated systems. Accordingly, direct palladium-catalyzed intramolecular ring fusion affords propeller-shaped biscarbazolo[2,3-*b*]carbazole diimides with six annulated rings (**3**, Figure 1).

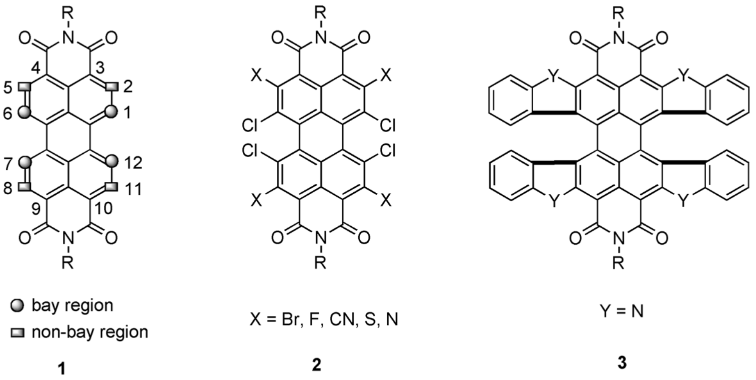

Figure 1. Perylene diimides (PDIs, **1**), 1,6,7,12-tetrachloro-2,5,8,11-tetrasubstituted perylene diimides (X_4Cl_4-PDIs, **2**), and biscarbazolo[2,3-*b*]carbazole diimides (**3**), R = alkyl and aryl groups.

The key building block, Br_4Cl_4-PTCDA (**5**, Scheme 1) was prepared by bromination of easily available tetrachloroperylene dianhydride **4** with 2.5 equivalents dibromoisocyanuric acid in an excellent yield. Suitable block-shaped single crystals for

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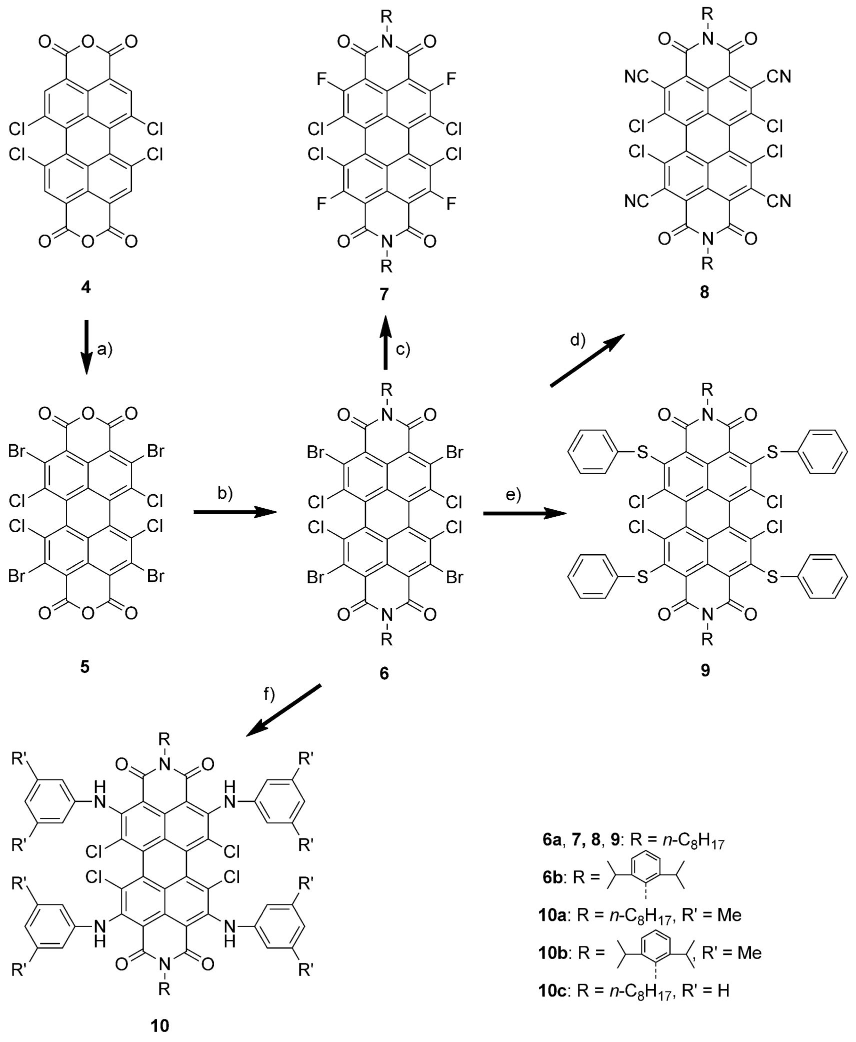


Scheme 1. a) DBI, 50% oleum, 50 °C, 95%; b) *n*-octylamine or 2,6-diisopropylaniline, acetic acid, reflux, **6a** (47%) and **6b** (30%); c) potassium fluoride, 18-crown-6, sulfolane, 160 °C, 30%; d) zinc cyanide and copper bromide DMF, reflux, 64%; e) thiophenol, K_2CO_3, $CHCl_3$, reflux, 90%; f) 3,5-dimethylaniline or aniline, 120 °C, **10a** (93%), **10b** (85%) and **10c** (92%). DBI=dibromoisocyanuric acid.

X-ray structure analysis were obtained by slow evaporation of the mixture of dichloromethane and methanol solution at room temperature, which further determines the molecular structure of the Br_4Cl_4-PTCDA. The crystal structure of compound **5** shows a twisted perylene backbone with a dihedral angle of 56.75° between the C(7), C(8), and C(9) rings and C(17), C(18), and C(19) rings (Figure 2), and the torsion angles associated with the bay C atoms C(4)-C(5)-C(6)-C(7) and C(14)-C(15)-C(16)-C(17) are nearly the same, with a value of 39.45 and 40.43°, respectively,[8] which is close to the reported value of Cl_8-PTCDI (37 and 38°).[5] The desired tetrabromotetrachloroperylene diimides **6** (Br_4Cl_4-PDI) were obtained by the imidization with *n*-octylamine or 2,6-diisopropylaniline in glacial acetic acid in moderate yields, subsequently they were used as precursors for straightforward transformation with electron-withdrawing fluoride, cyanide, as well as electron-donating amine and thiophenol (Scheme 1).

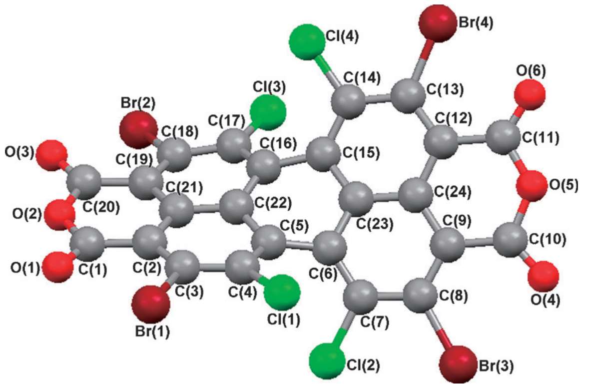
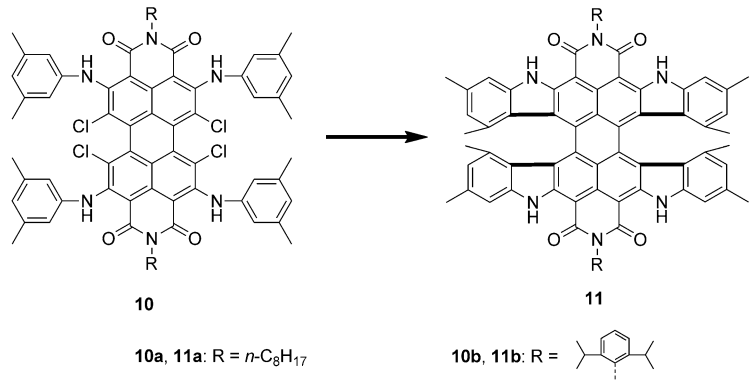


Figure 2. Single crystal of compound **5**, showing a twisted perylene backbone.

Fluorine atoms could be introduced into the non-bay regions by nucleophilic halogen exchange of bromine atoms selectively with potassium fluoride in the presence of [18]crown-6 in sulfolane to produce tetrachlorotetrafluoro-PDI (Cl_4F_4-PDI, **7**).[9] Reaction of compound **6** with zinc cyanide and copper bromide (or only CuCN) in refluxed DMF can afford tetrachlorotetracyano-PDI (Cl_4CN_4-PDI, **8**) in a good yield without metal catalyst. The introduction of electron-deficient groups like fluoro (**7**) and cyano (**8**) would have a strong influence on their charge-transport properties,[10,3h] particularly by decreasing the LUMO levels to achieve air stability of the semiconductors. Tetrachlorotetrathio-substituted PDI **9** can be smoothly obtained by nucleophilic substitution with thiophenol in the presence of potassium carbonate as the base in chloroform. Similarly, all four bromine atoms of molecule **6** could be replaced by using amine as a nucleophile, which results in the corresponding tetrachlorotetraamino-functionalized PDIs **10a** and **10c** in an almost quantitative yield;[11] this same nucleophilic substitution method could also be successfully extended to aryl-substituted PDIs **10b**. This incorporation of the electron-donating thiophene



Scheme 2. $[Pd_2(dba)_3]$, $P(tBu)_3$, K_3PO_4, 1,4-dioxane, reflux, argon, **11 a** (45%), **11 b** (32%). dba = dibenzylideneacetone.

(**9**) and amino (**10**) groups would bring chromophores with excellent absorption properties, which could be used for efficient light-harvesting in supramolecular antennae systems.[12] This highly regioselective non-bay functionalization protocol is efficient, probably due to the combination of steric effect and reactivity difference between bromo and chloro substituents.

Further extension of the conjugated systems is expected to be carried out by intramolecular ring fusion because of the retaining chlorines at the bay regions. Direct C–H functionalization has proved to be a special and efficient tool for carbon–carbon bond formation in organic synthesis.[13] In particular, intramolecular direct arylation reactions employ tethers to limit the degree of freedom in a system, thereby controlling the regioselectivity of the reaction. Thus, an expedient synthesis of biscarbazolo[2,3-*b*]carbazole diimides (BCCD) **11 a** and **11 b** can be achieved with tris(dibenzylideneacetone)dipalladium(0) as a catalyst, tri-*tert*-butylphosphine as a ligand, and K_3PO_4 as a base in 1,4-dioxane from tetrachlorotetraamino-PDIs **10 a** and **10 b** in moderate yields (Scheme 2).[14] This fourfold intramolecular cyclization to afford these unique propeller-shaped molecules with π-extended system is really efficient if calculated with average yield per C–C coupling.[15] The extension of conjugated π-systems would lead to molecules with desirable electronic properties and reduced HOMO–LUMO gaps for applications in organic electronics and organic photovoltaic devices.[16] All these core per-substituted PDIs and BCCD have good solubility in common organic solvent, such as dichloromethane, chloroform, and THF etc. and all these new compounds are characterized by mass spectrometry and ^1H and ^{13}C NMR spectroscopy (for details see the Supporting Information).

Room temperature absorption spectra of the compounds **6**–**11** are shown in Figure 3 and Figure S2 (Supporting Information), in which a comparison with TDDFT/PBE1PBE/6-31G*/PCM spectra, computed at the optimized geometries (Figure S5), is also reported. As we expected, the functionalization of PDIs by non-bay region substitution has triggered an eminent progress in controlling the optical and redox properties. The presence of the bromo and cyano substituents on the 2,5,8,11-positions of PDI does not shift significantly the absorption maximum, the maximum absorption of Cl_4F_4-PDI **7** is hypsochromically shifted to 496 nm. Introduction of four arylthio substituents at the perylene core causes an obvious bathochromic shift with a maximum at 558 nm for compound **9**. The more strongly electron-donating arylamino substituents at the perylene core evoke a further redshift of the absorption band, for example, the absorption band of **10 a** shows an absorption maximum wavelength at 632 nm. As we expected, the absorption of the BCCD **11** is much red-shifted to the near-infrared region with a maximum wavelength at about 716 nm for **11 a** and 720 nm for **11 b**, in contrast with their precursors **10 a** and **10 b**, which could be attributed to the extension of the conjugated system along the laterally annulated carbazole rings as well as the intramolecular donor–acceptor interactions. The broad and NIR absorption of BCCD implies that these kinds of derivatives could be potential objects in solar cells.[16] The fluorescence spectra of these compounds are also characterized and summarized in Table 1, Table S1 (Supporting Information), and Figure S3 (Supporting Information). Both of the Br_4Cl_4-PDIs **6 a** and **6 b** are weakly fluorescent with a quantum yield of about 4.0%. The Cl_4F_4-PDI **7** exhibits an increased quantum yield of 67.4% with an emission maximum at 532 nm, whereas Cl_4CN_4-PDI **8** has a relatively low quantum yield of 10.4%. Furthermore, BCCDs **11 a** and **11 b** are very weakly fluorescent ($\Phi_{fl} = 1.0\%$) with an emission band maxmium at about 740 nm, while tetrachlorotetrathio PDIs and tetrachlorotetraarylamino PDIs are not fluorescent.

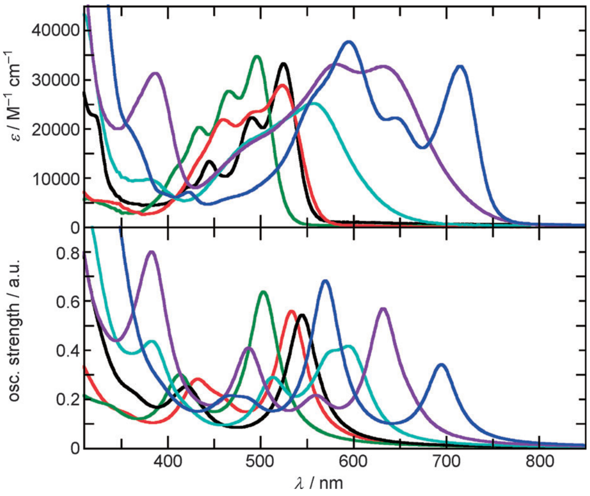


Figure 3. UV/vis absorption spectra of tetrachlorotetrasubstituted PDIs: **6 a** (red), **7** (olive), **8** (black), **9** (cyan), **10 a** (purple), and biscarbazolo[2,3-*b*]carbazole diimides **11 a** (blue) in chloroform (top), and comparison with TDDFT/PBE1PBE/6-31G*/PCM computed spectra not including vibronic structures (bottom).

The theoretical absorption spectra from **6** to **11** largely agree well with the experimental spectra (Figure 3 and Figures S2 and S6–S13 in the Supporting Information). The spectral redshift can be traced back to a reduction in the HOMO–

Table 1. Optical and electronic properties of compounds **6**–**11**.

Comp.	λ_{abs} [nm][a]	λ_{em} [nm]	E_{1r} [V][c]	E_{LUMO} [eV][d]	E_g [eV][e]
PDI[f]	520 (528)	546	−0.84	−4.13 (−4.10)	2.27 (2.26)
6a	525 (534)	574	−0.63	−4.24 (−4.36)	2.22 (2.24)
6b	528 (534)	582	−0.56	−4. 31 (−4.36)	2.18 (2.24)
7	496 (503)	532	−0.66	−4.21 (−4.28)	2.31 (2.37)
8	525 (545)	554	−0.21	−4.65 (−4.89)	2.19 (2.19)
9	558 (598)	–[b]	−0.75	−4.11 (−4.10)	1.89 (1.96)
10a	632 (632)	–[b]	−0.98	−3.88 (−3.74)	1.65 (1.82)
10b	636 (632)	–[b]	−0.93	−3.93 (−3.74)	1.64 (1.82)
10c	612 (623)	–[b]	−0.95	−3.91 (−3.79)	1.72 (1.82)
11a	716 (695)	742	−1.27	−3.64 (−3.43)	1.64 (1.73)
11b	720 (695)	746	−1.22	−3.67 (−3.43)	1.63 (1.73)

[a] Peak in the visible region. [b] No fluorescence. [c] Half-wave reduction potential (V vs. Fc/Fc$^+$) measured in CH_2Cl_2 with a scan rate of 0.1 V s^{-1}. [d] Estimated from the onset potential of the first reduction wave, applying the equation $E_{LUMO} = -(4.80 + E_{1r})$. [e] Obtained from the edge of the absorption spectra, $E_g = 1240/\lambda_{onset}$. [f] *N*,*N'*-bis(octyl)perylene-1,6,7,12-tetrachloro-3,4:9,10-tetracarboxylic acid diimides. Theoretical PBE1PBE/6-31G*/PCM predictions in parentheses (see the Supporting Information for details).

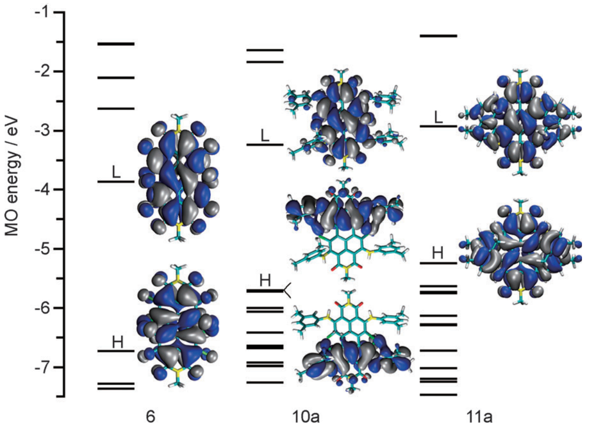


Figure 4. Energies and shapes of PBE1PBE/6-31G*/PCM frontier orbitals (HOMO and LUMO) of model Br_4Cl_4-PDI **6**, tetrachlorotetraamino-PDI **10a**, and biscarbazolo[2,3-*b*]carbazole diimides **11a**.

LUMO gap from **6** to **11** (Figure 4), due to a more pronounced rise of the HOMO compared to the LUMO. For the HOMO of **10a**, the aromatic system favors to extend from the core across to outer phenyl rings in the upper half of the molecule mediated by a 3p orbital of Cl. Together with the quasi-degenerate HOMO-1, which is delocalized over the lower half of the molecule **10a**, this gives rise to the double peak around 600 nm.

To gain further insight into the electronic properties of core-tetrachlorotetrasubstituted PDIs, cyclic voltammetries (CVs) were performed in dichloromethane (Table 1 and Figure S4, Supporting Information). Compounds **6**–**11** exhibit two reversible reduction waves, whereas **11a** and **11b** exhibit additionally two reversible oxidation waves. In contrast to reference Cl_4-PDI, which shows a half-wave potential $E_{1/2}$ at −0.84 and −1.03 V (vs. Fc/Fc$^+$), the half-wave reduction potential of Br_4Cl_4-PDI **6a** is less negative at −0.63 and −0.81 V. Furthermore, a progressive enhancement of the electron affinity is observed from Cl_4F_4-PDI **7** to Cl_4CN_4-PDI **8**, showing a half-wave reduction potential wave at −0.66 and −0.88 V for **7** and −0.21 and −0.56 V for **8**, which indicates that **8** are considerably stronger electron acceptors with progressively increased electron affinity. For the tetrachlorotetrathio-PDI **9**, there are two reversible reduction potentials (−0.75 and −0.94 V), whereas for the tetrachlorotetraamino-PDIs **10**, significantly lower reduction potentials were observed (−0.98 and −1.09 V for **10a**, −0.93 and −1.05 V for **10b**, −0.95 and −1.07 V for **10c**). Furthermore, In contrast to the corresponding **10a** and **10b**, two more negative reversible reduction potentials (−1.27 and −1.45 V for **11a**, −1.22 and −1.44 V for **11b**) and another additional two reversible positive oxidative potentials (0.98 and 1.31 V for **11a**, 1.02 and 1.35 V for **11b**) can be observed within the available potential range, which implies that the fusion of the electron-rich carbazole rings has greatly changed their redox properties.[16b]

The LUMO levels of these PDIs and BCCD derivatives could be obtained from the reduction potentials discussed above, according to the calculations (Table 1), all of the LUMO levels of **6a**, **6b**, **7**, and **8** with four electron-withdrawing groups at non-bay regions are below −4.20 eV, particularly, the LUMO value of the Cl_4CN_4-PDI (−4.65 eV) is the lowest reported value for PDI derivatives, which indicates that they could serve as air stable n-type organic semiconductors. Region-selective donor-group-functionalized PDIs had the effect of not significantly changing the LUMO levels compared with those of Cl_4-PDI (−4.11 for **9**, −3.88 for **10a**, −3.93 for **10b**, and −3.91 eV for **10c**), which are consistent with the calculated electron distribution of the LUMO of **10a**, mainly focused on the PDI skeletons (Figure 4). Moreover, the BCCD derivatives have significantly higher LUMO levels with energies of −3.64 and −3.67 eV for **11a** and **11b**, respectively. The HOMO levels calculated from the onset of the first oxidation wave are −5.21 eV for **11a** and −5.25 eV for **11b**, the relatively higher LUMO levels of these new π extension system could also be explained from the theoretical calculation (Figure 4), both of the LUMO and HOMO levels are delocalized over the whole π system. The HOMO–LUMO band gaps of **11a** and **11b** calculated from CV experiments agree well with the band gaps obtained from the edge of UV/Vis absorption spectra.

In conclusion, a new building block of Br_4Cl_4-PTCDA for core-persubstituted perylene diimides has been synthesized efficiently. We have prepared a new series of 1,6,7,12-tetrachloro-2,5,8,11-tetrasubstituted perylene diimides (Cl_4X_4-PDIs) by regioselective functionalization of bromine atoms at the non-bay regions. Notably, we can also extend the system along the lateral axis by fusion of additional few carbazole rings by retaining chlorine atoms to achieve biscarbazolo[2,3-*b*]carbazole diimides by intramolecular direct arylation of palladium-catalyzed C−H functionalization. In light of their unique structure and attractive photophysical and optoelectronic properties, this new molecular skeleton would be a novel promising candidate for various applications.

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Keywords: perylene diimides · intramolecular arylation · non-bay regions · palladium · regioselectivity

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Materials Chemistry

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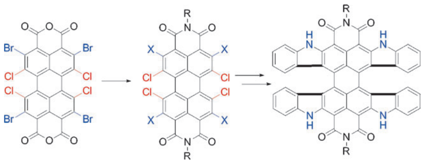
Regioselective Functionalization of Core-Persubstituted Perylene Diimides



Organic electronics: A series of novel chromophores were afforded by regioselective functionalization of core persubstituted perylene diimides (PDIs) (see scheme). Furthermore, new BCCD derivatives with an extended π-conjugated system were synthesized by direct palladium-catalyzed intramolecular ring fusion.