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Efficient Tuning of LUMO Levels of 2,5,8,11-Substituted Perylenediimides via Copper Catalyzed Reactions

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ABSTRACT

Via one-step copper catalyzed procedures it was possible to synthesize 2,5,8,11-tetrabromo, tetrachloro, and tetracyano derivatives of perylenediimides. Characterization of optical and electrochemical properties of these materials proves substantial enhancement of the electron affinity, with a LUMO level as low as -4.4 eV in the case of the tetracyano perylenediimide.

Perylenediimides (PDIs) represent one of the most extensively studied classes of functional materials in the field of organic electronics.[1] Their thermal, chemical, and photochemical stability as well as their high electron affinities and charge carrier mobilities render these dye molecules rather attractive for the development of n-type semiconducting materials.[2]

A key issue thereby is the tuning of the energy of molecular orbitals and more precisely the possibility to lower the energy of the lowest unoccupied molecular orbitals (LUMOs) to improve charge injection at the electrode and enhance stability in the presence of impurities such as water and oxygen.[3] Chemical functionalization of PDIs has already demonstrated the possibility to decrease the energy of molecular orbitals via core substitution.[4,5] In particular, enhanced electron affinities and improved air stability in operating devices have been achieved via introduction of electron-withdrawing halo or cyano substituents.[5] LUMO values as low as -4.5 eV could be achieved.[6] 1,6,7,12-Substitution, due to steric reasons, induces a deviation of the perylene core from planarity.[7] The degree of bending depends upon the nature

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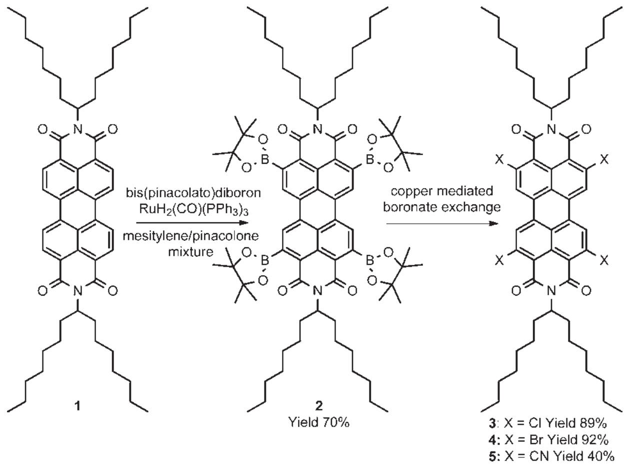
Scheme 1. Synthesis of 2,5,8,11-Tetrasubstituted Perylenediimides[a]



[a] Reaction conditions: Synthesis of **2**: **1** (0.12 mmol), bis(pinacolato)-diboron (0.99 mmol) $RuH_2(CO)(PPh_3)_3$ (0.06 mmol), mesitylene 2 mL, pinacolone 0.15 mL, 140 °C, 24 h. Synthesis of **3** and **4**: **2** (0.76 mmol) and CuX_2 (9.13 mmol) in 160 mL of 5/2/1 mixture of dioxane/MeOH/H_2O, 120 °C, 12 h. Synthesis of **5**: **2** (0.05 mmol), $Zn(CN)_2$ (0.58 mmol), CsF (0.19 mmol) and $Cu(NO_3)_2$ (0.38 mmol), 6 mL of 1/5 mixture methanol/dioxane 80 °C, 5 min.

and number of substituents, but nonplanarity is sometimes undesirable for the solid state packing.

Recently selective functionalization of the 2,5,8,11-positions (which we define as *ortho*-positions) of the core of perylenediimides has been reported.[8] Subsequent experiments have demonstrated the possibility of tuning the optical and electrochemical properties via the introduction of alkyl and aryl substituents, but without affecting the planarity of the perylene core.[8,9] Nevertheless the number of examples of *ortho*-substituted PDIs still remains limited and substantial enhancements of the electron affinities have not been shown.

The possibility to selectively tetraborylate the *ortho*-positions of perylenediimides was reported by the group of Shinokubo via an iridium catalyzed reaction.[10] At the same time a different protocol for the synthesis of compound **2** was developed in our group, based on $RuH_2(CO)(PPh_3)_3$.[11] In this work we report the conversion of building block **2** into 2,5,8,11-tetrahalogenated and tetracyanated perylenediimides, a novel class of electron-deficient PDIs.

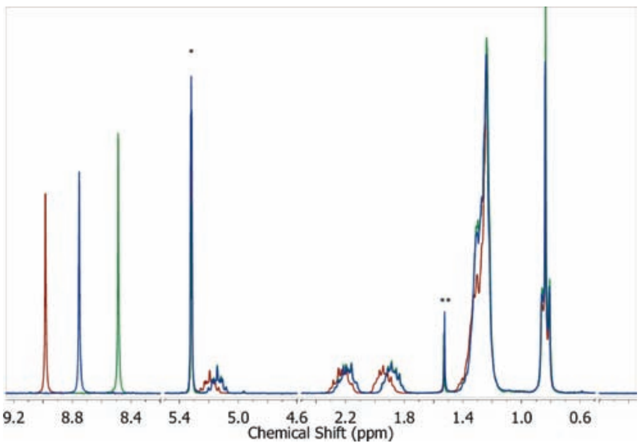


Figure 1. ^1H NMR (250 MHz) in CD_2Cl_2 of compounds **3** (green), **4** (blue), and **5** (red).

Table 1. Optical Properties of Reported PDIs

PDI[a]	ε [M^{-1} cm^{-1}][b]	λ_{max} [nm]	λ_{em} [nm][c]	φ_f[d]
1	81 000	526	538	0.97
3	57 000	505	515	0.47
4	79 000	509	519	0.21
5	70 000	518	528	0.55

[a] Optical properties measured in dichloromethane. [b] Measured at λ_{max}. [c] Excited at λ_{max}. [d] Determined using Rhodamine 6G as standard.

The synthetic procedures follow the work done by Hartwig and co-workers for the copper(II) catalyzed conversion of aryl boronates into chlorinated,[12] brominated,[12] or cyanated[13] derivatives and are described in Scheme 1; a major modification is the use of a dioxane–methanol–water mixture for the reaction to improve the solubility of the perylenediimide derivative **2**, otherwise too insoluble in a methanol–water mixture.

While the conversion of compound **2** into **3** and **4** proceeds smoothly, the yield of **5** does not exceed 40%. Nevertheless such values are in agreement with the ones previously reported in literature. ^1H NMR spectra of compounds **3**, **4**, and **5** are shown in Figure 1.

Compounds **2**, **3**, and **4** were characterized by cyclic voltammetry, UV–visible optical absorption spectroscopy and photoluminescence spectroscopy. Compared to compound **1** a hypsochromic shift in the absorption and emission is observed for the derivatives **3**, **4**, and **5** (Figure 2), the tetrachloro derivative showing the greater shift, followed by the tetrabromo and tetracyano. A substantial decrease in the fluorescence quantum yields is also observed (Table 1).

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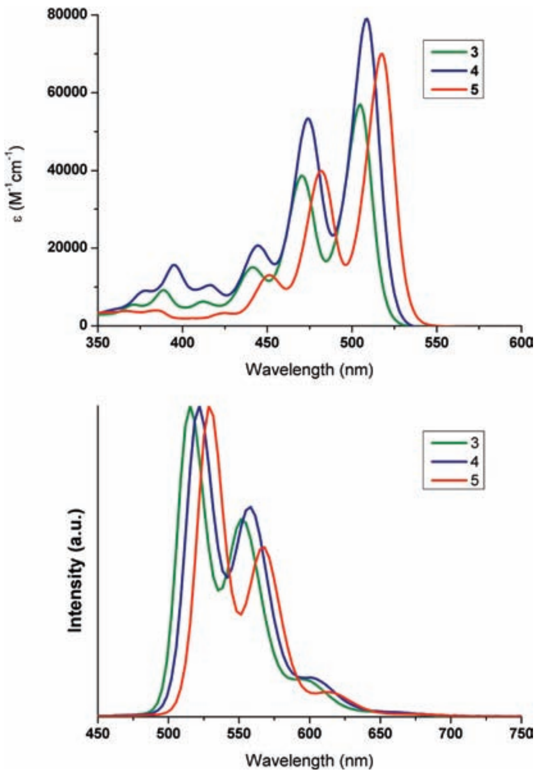

Figure 2. UV–visible absorption spectra (top) and fluorescence spectra (bottom) of compounds **3** (λ_{exc} = 505 nm), **4** (λ_{exc} = 509 nm), and **5** (λ_{exc} = 518 nm) in dichloromethane.

Cyclic voltammetric analysis showed two reversible reduction waves corresponding to the formation of the radical anions and dianions for compounds **3**, **4**, and **5**, but no oxidation could be observed in the potential window investigated (Figure 3). The halfwave potentials, together with calculated HOMO and LUMO values, are reported in Table 2. A progressive enhancement of the electron affinity is observed proceeding in the series from **4** to **3** and **5**. It is worth noting that the LUMO value of the tetracyanated derivative **5** is the lowest reported for *N*,*N'*-alkyl-substituted perylenediimides.

In conclusion, a series of 2,5,8,11-tetrasubstituted perylenediimides could be synthesized via a one-step copper catalyzed conversion of tetraboronic ester PDIs. Tetrachlorinated, tetrabrominated, and tetracyanated derivatives show enhanced electron affinity, compared to the unsubstituted parent compound. Studies toward the use of these materials in electronic devices are currently ongoing in our group.

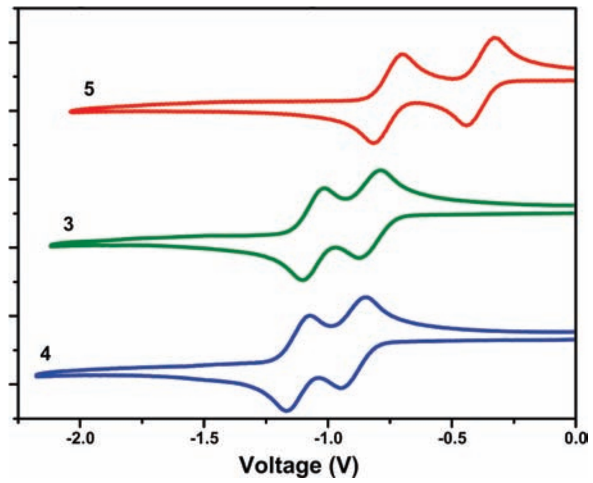

Figure 3. Cyclic voltammetric measurement for compounds **3**, **4**, and **5**. Experimental details are reported in Table 2.

Table 2. Electrochemical Properties of Reported PDIs

PDI	E_{red1} [V][a]	E_{red2} [V][a]	LUMO [eV][b]	HOMO [eV][c]
1	−0.98	−1.21	−3.82	−6.13
3	−0.83	−1.06	−3.97	−6.33
4	−0.90	−1.12	−3.90	−6.26
5	−0.38	−0.75	−4.42	−6.73

[a] Determined by cyclic voltammetric measurement in 0.1 M solution of Bu_4NPF_6 in CH_2Cl_2: vs Fc/Fc$^+$. [b] Estimated vs vacuum level from E_{LUMO} = 4.80 eV − E_{red1}. [c] Estimated from HOMO = LUMO − E_g, where E_g = optical gap, calculated from the optical absorption data.

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Supporting Information Available. Full experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.