



Easy and mild fluoride-mediated direct mono- and dialkoxylation of perylenediimides



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ABSTRACT

The reaction of perylenediimides with alcohols in the presence of fluoride anions yields 1-alkoxy- or 1,6(7)-dialkoxyperylene-diimides under very mild metal-free conditions. The reaction can also be applied to bay- and ortho-brominated perylenediimides.

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1. Introduction

Perylene-diimides (PDIs) are planar molecules characterized by extremely high thermal and chemical stabilities, intense absorption in the UV–vis, fluorescence quantum yields close to unity, strong electron-accepting character and high electron mobilities [1]. As a consequence, they have been extensively investigated as building blocks for artificial photosynthetic systems [2] and biolabels [3], or as molecular materials for field effect transistors [4], solar cells [5], light-emitting displays [6] and lasers [7]. The electronic and optic properties of PDIs can be modulated over a wide range by introducing substituents at the so-called bay positions (positions 1,6,7,12 of the aromatic core, see Scheme 1 for position numbering). Thus, the presence of two or four electron-donating aryloxy/alkoxy or two amino groups moves bathochromically the absorption, so green or blue pigments are obtained which can even act as electron-donors (e.g. amino substitution), although the molecules are not planar anymore and their photophysical properties are compromised relative to PDIs without bay substituents. The incorporation of such interesting substituents is achieved by a two steps procedure involving halogenation (either dibromination or

tetrachlorination) of the bay positions followed by halogen displacement with the help of an alcohol or amine under basic conditions [8]. However, the halogenation step affords mixtures of monobromo-, dibromoPDI (as a mixture of 1,6 and 1,7 regioisomers, the latter being the major compound) and unreacted material, thus precluding high yields [9]. On the other hand, there is much current interest in monosubstituted derivatives of PDI, as they are expected to be flatter, thus preserving their superior photophysical properties. Here again, a bromination step is required which typically affords ca. 55% of bromoPDI [9]. Thus, bromination has become a real bottleneck in the way to mono- or disubstitution with alcohols. However, in the course of our investigations in the area of the PDIs, we have discovered that it is possible to perform the alkoxylation process directly in one step, avoiding the bromine participation, this being the subject of the present contribution.

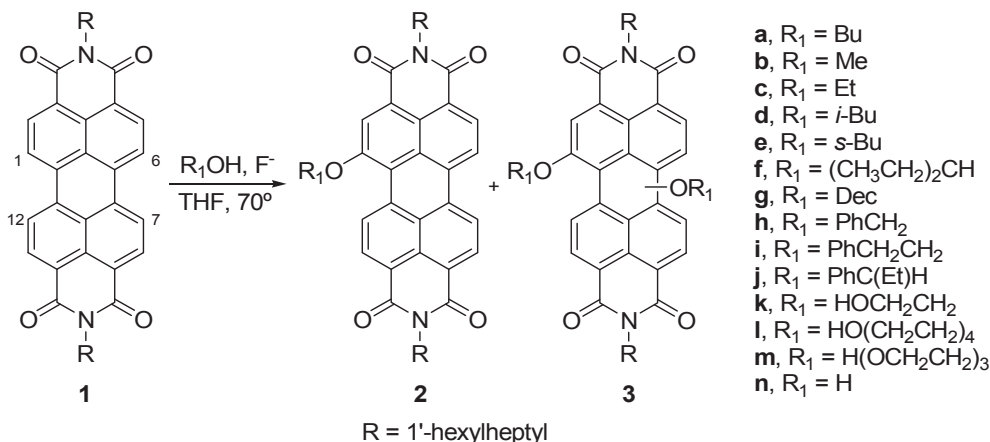
2. Experimental

2.1. General

Solvents and reagents were obtained from commercial sources and used as received. Column chromatography: SiO₂ (40–63 μm) TLC plates coated with SiO₂ 60F254 were visualized by UV light. NMR spectra were recorded at 25 °C using a Bruker AC300

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Scheme 1. Fluoride-mediated alkoxylation of PDIs.

spectrometer. The solvents for spectroscopic studies were of spectroscopic grade and used as received. UV-vis spectra were measured with a Helios Gamma spectrophotometer. IR spectra were recorded with a Nicolet Impact 400D spectrophotometer. High resolution Mass spectra were obtained from a Bruker Reflex II matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) using dithranol as matrix.

2.2. Method A: 1-alkoxy-3,4,9,10-perylenetetracarboxydiimide

The alcohol (0.4 mmol) and TBAF (1 M solution in THF, 0.24 mmol) were added to a solution of **1** (0.1 mmol) in dry THF (0.3 mL). The reaction was refluxed 24 h under argon atmosphere and, after cooling, it was extracted with dichloromethane and washed with water. The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated. Purification was carried out by silica gel column chromatography using toluene as eluent, unless otherwise specified.

2.2.1. *N,N'*-Di(hexylheptyl)-1-butoxy-3,4,9,10-perylenetetracarboxydiimide (**2a**)

Yield: 75%. Purple solid. Mp >200 °C. $^1\text{H NMR}$ (CDCl_3) δ 0.82 (t, 12H), 1.10 (t, 3H), 1.25 (br, 32H), 1.68 (m, 2H), 1.87 (m, 4H), 2.07 (m, 2H), 2.26 (m, 4H), 4.53 (t, 2H), 5.20 (m, 2H), 8.60 (m, 6H), 9.60 (d, 1H). $^{13}\text{C NMR}$ (CDCl_3) δ 13.86, 14.02, 19.56, 22.57, 26.94, 29.20, 29.23, 29.67, 31.37, 31.75, 31.76, 32.36, 54.57, 70.36, 120.47, 121.7, 123.31, 124.25, 126.90, 128.25, 128.30, 129.16, 133.76, 134.42, 157.82, 163.67, 164.53. HRMS MALDI-TOF m/z . [M^+] calc. for $\text{C}_{54}\text{H}_{70}\text{N}_2\text{O}_5$ 826.5279, found 826.5289. IR (KBr): 2955, 2926, 2838, 1701, 1654, 1590, 1456, 1333, 1251, 814, 755 cm^{-1} . UV vis (CH_2Cl_2), $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 518 (4.8), 554 (4.9).

2.2.2. *N,N'*-Di(hexylheptyl)-1-methoxy-3,4,9,10-perylenetetracarboxydiimide (**2b**)

Yield: 33%. Purification was carried out by silica gel column chromatography using chloroform:hexane 4:1 as eluent. Purple solid. Mp >200 °C. $^1\text{H NMR}$ (CDCl_3) δ 0.83 (t, 12H), 1.24 (br, 32H), 1.87 (m, 4H), 2.25 (m, 4H), 4.34 (s, 3H), 5.20 (m, 2H), 8.57 (m, 6H), 9.49 (d, 1H). $^{13}\text{C NMR}$ (CDCl_3) δ 14.02, 22.57, 26.94, 29.21, 29.22, 31.76, 32.38, 54.61, 56.84, 120.74, 121.87, 123.41, 124.46, 126.96, 128.39, 128.53, 129.20, 133.92, 134.30, 134.48, 158.29, 163.54, 164.68. HRMS MALDI-TOF m/z . [M^+] calc. for $\text{C}_{51}\text{H}_{64}\text{N}_2\text{O}_5$ 784.4888, found 784.4839. IR (KBr): 2855, 1695, 1658, 1597, 1462, 1409, 1327, 1262, 1094, 804, 747 cm^{-1} . UV vis (CH_2Cl_2), $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 514 (5.7), 552 (5.9).

2.2.3. *N,N'*-Di(hexylheptyl)-1-ethoxy-3,4,9,10-perylenetetracarboxydiimide (**2c**)

Yield: 39%. Purple solid. Mp >200 °C. $^1\text{H NMR}$ (CDCl_3) δ 0.83 (t, 12H), 1.24 (br, 32H), 1.73 (t, 3H), 1.89 (m, 4H), 2.27 (m, 4H), 4.54 (m, 2H), 5.20 (m, 2H), 8.48 (m, 6H), 9.50 (d, 1H). $^{13}\text{C NMR}$ (CDCl_3) δ 14.01, 15.01, 22.56, 26.94, 26.95, 29.19, 29.22, 29.65, 31.74, 31.75, 32.35, 54.56, 54.80, 66.11, 70.55, 120.31, 121.63, 123.18, 124.20, 126.79, 128.20, 129.06, 133.64, 134.29, 157.56, 163.54, 164.52. HRMS MALDI-TOF m/z . [$\text{M} + \text{H}$] $^+$ calc. for $\text{C}_{52}\text{H}_{67}\text{N}_2\text{O}_5$ 799.5044, found 799.5060. IR (KBr): 2855, 1770, 1662, 1585, 1458, 1323, 1258, 804, 747 cm^{-1} . UV vis (CH_2Cl_2), $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 518 (4.7), 553 (4.8).

2.2.4. *N,N'*-Di(hexylheptyl)-1-*i*-butoxy-3,4,9,10-perylenetetracarboxydiimide (**2d**)

Yield: 46%. Purple solid. Mp >200 °C. $^1\text{H NMR}$ (CDCl_3) δ 0.82 (t, 12H), 1.25 (br, 38H), 1.89 (m, 4H), 2.27 (m, 4H), 2.44 (m, 2H), 4.30 (d, 2H), 5.20 (m, 2H), 8.59 (m, 6H), 9.63 (d, 1H). $^{13}\text{C NMR}$ (CDCl_3) δ 14.01, 19.54, 22.57, 22.58, 26.93, 28.56, 29.20, 29.23, 29.66, 31.75, 32.36, 54.58, 120.56, 121.75, 123.34, 124.26, 126.90, 128.29, 128.32, 129.17, 133.78, 134.43, 157.90, 163.80, 164.66. HRMS MALDI-TOF m/z . [M^+] calc. or $\text{C}_{54}\text{H}_{70}\text{N}_2\text{O}_5$ 826.5279, found 826.5209. IR (KBr): 2949, 2926, 2850, 1695, 1654, 1584, 1456, 1333, 1263, 808, 744 cm^{-1} . UV vis (CH_2Cl_2), $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 517 (4.4), 554 (4.6).

2.2.5. *N,N'*-Di(hexylheptyl)-1-*s*-butoxy-3,4,9,10-perylenetetracarboxydiimide (**2e**)

Yield: 35%. Purple solid. Mp >200 °C. $^1\text{H NMR}$ (CDCl_3) δ 0.83 (t, 12H), 1.12 (t, 3H), 1.25 (br, 35H), 1.87 (m, 4H), 2.10 (m, 2H), 2.26 (m, 4H), 4.98 (m, 1H), 5.20 (m, 2H), 8.49–8.66 (m, 6H), 9.72 (d, 1H). $^{13}\text{C NMR}$ (CDCl_3) δ 9.83, 14.02, 19.83, 22.57, 26.57, 26.92, 29.20, 29.23, 29.63, 29.68, 31.74, 31.75, 54.57, 78.78, 121.86, 123.44, 124.37, 127.12, 128.36, 128.68, 129.27, 133.91, 134.65, 157.75, 163.12, 164.85. HRMS MALDI-TOF m/z . [M^+] calc. for $\text{C}_{54}\text{H}_{70}\text{N}_2\text{O}_5$ 826.5279, found 826.5263. IR (KBr): 2920, 2850, 1695, 1660, 1584, 1403, 1327, 1251 cm^{-1} . UV vis (CH_2Cl_2), $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 520(4.8), 554 (4.9).

2.2.6. *N,N'*-Di(hexylheptyl)-1-(ethylpropoxy)-3,4,9,10-perylenetetracarboxydiimide (**2f**)

Yield: 40%. Purple solid. Mp >200 °C. $^1\text{H NMR}$ (CDCl_3) δ 0.82 (t, 12H), 1.08 (t, 6H), 1.25 (br, 32H), 1.87 (m, 4H), 1.99 (m, 4H), 2.27 (m, 4H), 4.86 (m, 1H), 5.20 (m, 2H), 8.49 (s, 1H), 8.67 (m, 5H), 9.70 (d, 1H). $^{13}\text{C NMR}$ (CDCl_3) δ 9.59, 14.02, 22.57, 26.35, 26.92, 29.20, 29.23, 29.69, 31.74, 31.75, 32.38, 54.58, 83.69, 121.43, 121.89, 123.49, 124.37, 127.17, 128.35, 128.75, 129.32, 133.94, 134.73, 135.23, 157.67,

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