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3,4:9,10-Perylenebis(dicarboximide) chromophores that function as both electron donors and acceptors

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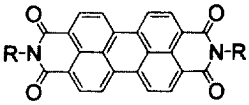
Abstract

Five green 3,4:9,10-perylenebis(dicarboximide) dyes that both donate and accept electrons have been synthesized under mild conditions in high yields. These chromophores undergo reversible one-electron oxidation and reduction in butyronitrile at modest potentials. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: polycyclic aromatic compounds; amination; electron transfer; optical properties.

Red chromophores based on 3,4:9,10-perylenebis(dicarboximide)s (**1**) have shown great promise in a variety of applications owing to their outstanding chemical, thermal and photochemical stability.[1-3] They have been used widely in reprographic processes,[4] solar cells,[5] photovoltaic devices,[6] and dye lasers.[7] Our own work with these chromophores has focused on their photoinduced electron transfer reactions with special emphasis on their potential as components in organic molecular switches.[8] The optical absorption characteristics of 3,4:9,10-perylenebis(dicarboximide)s can be tuned to some degree by varying the substituents on the imide functions.[9,10] However, direct substitution of the perylene nucleus should provide a more versatile means of varying both the optical and redox characteristics of these chromophores.[11] We now report that the introduction of a dialkylamino group -NR_2 at 1- and/or 7-positions of the 3,4:9,10-perylenebis(dicarboximide)s affords green products that exhibit intense optical absorption bands near 700 nm. Moreover, these new chromophores undergo reversible one-electron oxidation and reduction reactions at modest potentials.



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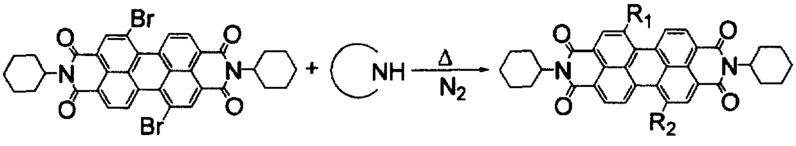

2

3a: $R_1 = R_2$ = N-pyrrolidinyl, 98%
3b: $R_1 = R_2$ = N-piperidinyl, 92%
3c: $R_1 = R_2$ = N-morpholinyl, 76%
4: R_1 = Br; R_2 = N-pyrrolidinyl, 82%
5: R_1 = H; R_2 = N-pyrrolidinyl, 67%

The reactions of secondary cyclic amines such as pyrrolidine, piperidine, and morpholine with **2** are very sensitive to changes in temperature. At room temperature the reactions are very slow, and monosubstituted 3,4:9,10-perylenebis(dicarboximide)s (**4**) are the major products; at high temperatures (above 130°C) the 1-bromine is replaced by a hydrogen atom and compounds **5** are formed as the major products. Selective formation of the desired products, **3** were made possible by careful adjustment of solvents and temperatures (see Experimental for details). On the other hand, reaction of **2** with both primary and secondary acyclic amines leads primarily to debromination of **2** at both the 1- and 7-positions. These observations are consistent with an S_NAr amination mechanism.

The UV–visible spectra of **2** and **3a–c** are shown in Fig. 1. Introduction of pyrrolidinyl, piperidyl, and morpholinyl groups at the 1- and 7- positions of **2** induce dramatic bathochromic shifts relative to the lowest energy optical transition of **2** (λ_{max}=526 nm in chloroform). The maxima of the longest wavelength absorption bands of **3a–c** are 699.5 nm, 676.5 nm, and 647.5nm, respectively.

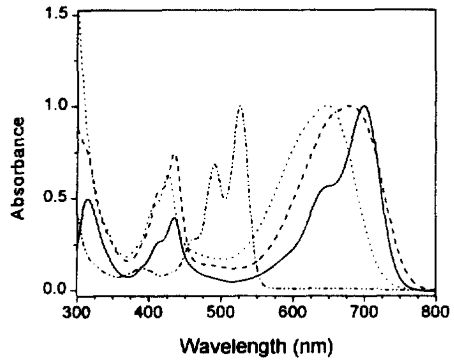

Figure 1. Normalized UV–visible spectra of **2** (– · · –), **3a** (—), **3b** (- - - -), **3c** (· · · ·) in chloroform

Electrochemical one-electron oxidation and reduction of **3–5**, as well as reduction of **2** are all reversible (59 mV peak-to-peak cyclic voltammograms) at a platinum electrode. Table 1 gives the half-wave potentials for these reactions. A comparison between these potentials and the corresponding potentials for **2** shows that substitution of the -NR_2 groups on the perylene nucleus shifts its reduction potential negative by only 0.3 V, whereas its oxidation potential is shifted negative by up to 1.2 V. Thus, these chromophores oxidize at convenient potentials that make them serious candidates for incorporation into donor–acceptor arrays that may be useful for the design and preparation of molecular opto-electronic devices.

Table 1
Redox potentials, V vs SCE[13]

Compound	2	3a	3b	3c	4	5
$E_{1/2}$(red)	-0.45	-0.76	-0.64	-0.59	-0.56	-0.63
$E_{1/2}$(ox)	>2.0	0.72	0.80	0.87	1.01	0.96

1. Experimental

General information: Proton nuclear magnetic resonance spectra were recorded on a Gemini-300 NMR spectrometer using TMS as an internal standard. Laser desorption mass spectra were obtained with a Kratos MALDI III spectrometer using 2-hydroxy-1-naphthoic acid as a matrix. The starting material, 1,7-dibromo-*N,N'*-dicyclohexyl-3,4:9,10-perylenebis(dicarboximide), was synthesized according to a literature procedure.[12] All other solvents and regents were used as received. Column chromatography was performed using Merck silica gel 60.

1,7-Bis(*N*-pyrrolidinyl)-*N,N'*-dicyclohexyl-3,4:9,10-perylenebis(dicarboximide) (**3a**): Compound **2** (116 mg, 0.163 mmol) was dissolved in 5.0 mL pyrrolidine. The solution was heated at 60°C under dry nitrogen for 24 h with stirring. Excess pyrrolidine was removed on the rotary evaporator and the residue was column chromatographed on silica with 50:5:45 chloroform:acetone:hexane (V/V/V, R_f=0.43) to afford 110 mg green product (theory 112 mg, 98%). ^{1}H NMR δ ($CDCl_3$): $H_{5,11}$ 8.36, 2H, d, $J_{5,6}$ 8.10 Hz; $H_{6,12}$ 7.64, 2H, d, $J_{6,5}$ 8.10 Hz; $H_{2,8}$ 8.44, 2H, s; N-C*H* in *c*-C_6H_{11} 5.08, 2H, m; CH_2N in pyrrolidinyl, 3.73 and 2.82, 8H (4H each, broad singlet); *c*-C_6H_{11} 2.61, 4H, m; *c*-C_6H_{11} and pyrrolidinyl 1.85–2.20, 12H, m; *c*-C_6H_{11} 1.75, 6H, m; *c*-C_6H_{11} 1.30–1.60, 6H, m. MS: 692.53 (calcd 692.85). UV–vis (chloroform): λ_{max}=699.5, 434.5, 315.0 nm.

1,7-Bis(*N*-piperidyl)-*N,N'*-dicyclohexyl-3,4:9,10-perylenebis(dicarboximide) (**3b**): Compound **2** (60 mg, 0.084 mmol) was dissolved in 2.5 mL piperidine. The solution was heated at 60°C under dry nitrogen for 3 days with stirring. Excess piperidine was removed on the rotary evaporator and the residue was column chromatographed on silica with 50:5:45 chloroform:acetone:hexane (V/V/V, R_f=0.47) to afford 56 mg green product (theory 60.7 mg, 92%). ^{1}H NMR δ ($CDCl_3$): $H_{5,11}$ 9.60, 2H, d, $J_{5,6}$ 8.24 Hz; $H_{6,12}$ 8.38, 2H, d, $J_{6,5}$ 8.24 Hz; $H_{2,8}$ 8.44, 2H, s; N-C*H* in *c*-C_6H_{11} 5.05, 2H, m; CH_2N in piperidyl, 3.48 and 2.90, 8H (4H each, m); *c*-C_6H_{11} 2.58, 4H, m; *c*-C_6H_{11} and piperidyl 1.90, 8H, m; *c*-C_6H_{11} and piperidyl 1.77, 12H, m; *c*-C_6H_{11} and piperidyl 1.28–1.51, 8H, m. MS: 720.82 (calcd 720.92). UV–vis (chloroform): λ_{max}=675.5, 434.5 nm.

1,7-Bis(*N*-morpholinyl)-*N,N'*-dicyclohexyl-3,4:9,10-perylenebis(dicarboximide) (**3c**): Compound **2** (50 mg, 0.070 mmol) was dissolved in 3.5 mL morpholine. The solution was heated at 70°C under dry nitrogen for 6 days with stirring. Excess morpholine was removed on the rotary evaporator and the residue was column chromatographed on silica with 95:5 chloroform:acetonitrile (V/V, R_f=0.20) to afford 39 mg blue-green product (theory 51 mg, 76%). ^{1}H NMR δ ($CDCl_3$): $H_{5,11}$ 9.68, 2H, d, $J_{5,6}$ 8.24 Hz; $H_{6,12}$ 8.38, 2H, d, $J_{6,5}$ 8.24 Hz; $H_{2,8}$ 8.36, 2H, s; N-C*H* in *c*-C_6H_{11} 5.04, 2H, m; CH_2O in morpholinyl, 3.93, 8H, m; CH_2N in morpholinyl, 3.36 and 3.08, 8H (4H each, m); *c*-C_6H_{11} 2.57, 4H, m; *c*-C_6H_{11} 1.93, 4H, m; *c*-C_6H_{11} 1.79, 6H, m; *c*-C_6H_{11} 1.28–1.51, 6H, m. MS: 724.24 (calcd 724.85). UV–vis (chloroform): λ_{max}=647.5, 426.0 nm.

1-(*N*-Pyrrolidinyl)-7-bromo-*N,N'*-dicyclohexyl-3,4:9,10-perylenebis(dicarboximide) (**4**): Compound **2** (116 mg, 0.163 mmol) was dissolved in 5.0 mL pyrrolidine. The solution was heated at 80°C under dry nitrogen for 35 min with stirring. Excess pyrrolidine was removed on the rotary evaporator and the residue was purified by prep. TLC (R_f on silica gel TLC in chloroform is 0.95) to afford 93 mg green product (theory 112 mg, 82%). ^{1}H NMR δ ($CDCl_3$): H_6 9.48, 1H, d, $J_{6,5}$ 8.0 Hz; H_8 8.85, 1H, s; H_5 8.61, 1H, d, $J_{5,6}$ 8.0 Hz; H_2 8.50, 1H, s; H_{11} 8.44, 1H, d, $J_{11,12}$ 8.0 Hz; H_{12} 7.39, 1H, d, $J_{12,11}$ 8.0 Hz; N-C*H* in *c*-C_6H_{11} 5.05, 2H, m; CH_2N in pyrrolidinyl, 3.73 and 2.80, 4H (2H each, broad singlet); *c*-C_6H_{11} 2.58, 4H, m; pyrrolidinyl, 2.10, 2H, broad singlet; pyrrolidinyl, 2.00, 2H, broad singlet; *c*-C_6H_{11} 1.86–1.96, 4H, m; *c*-C_6H_{11} 1.76, 6H, m; *c*-C_6H_{11} 1.42–1.54, 4H, m; *c*-C_6H_{11} 1.30–1.42, 2H, m. MS: 700.92 (calcd 702.65). UV–vis (chloroform): λ_{max}=654.5, 437.0 nm.

1-(*N*-Pyrrolidinyl)-*N,N'*-dicyclohexyl-3,4:9,10-perylenebis(dicarboximide) (**5**): Compound **2** (50 mg, 0.07 mmol) and 25 mg pyrolidine (0.35 mmol) were added to 5.0 mL NMP (1-methyl-2-pyrrolidinone). The solution was heated to reflux under dry nitrogen for 1.5 h with stirring. The reaction was cooled, diluted with chloroform, and washed twice with water, and dried over anhydrous potassium carbonate. The solvent was removed on the rotary evaporator and the residue was column chromatographed on silica with chloroform (R_f=0.80) to afford 46 mg green product (theory 69 mg, 67%). ^{1}H NMR δ ($CDCl_3$); H_8 8.61, 1H, d, $J_{8,7}$ 6.5 Hz; H_7 8.59, 1H, d, $J_{7,8}$ 6.5 Hz; H_2 8.49, 1H, s; $H_{5,6,11}$ 8.41–8.48, 3H, m; H_{12} 7.51, 1H, d, $J_{12,11}$ 8.0 Hz; N-C*H* in *c*-C_6H_{11} 5.07, 2H, m; C*H*$_2$N in pyrrolidinyl, 3.76 and 2.77, 8H (4H each, broad singlet); *c*-C_6H_{11} 2.60, 4H, m; pyrrolidinyl, 2.11, 4H each, broad singlet; *c*-C_6H_{11} and pyrrolidinyl 1.88–2.50, 8H, m; *c*-C_6H_{11} 1.77, 6H, m; *c*-C_6H_{11} 1.43–1.55, 4H, m; *c*-C_6H_{11} 1.30–1.43, 2H, m. MS: 623.29 (calcd 623.75). UV–vis (chloroform): λ_{max}=645.5, 430.5 nm.

Acknowledgements

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