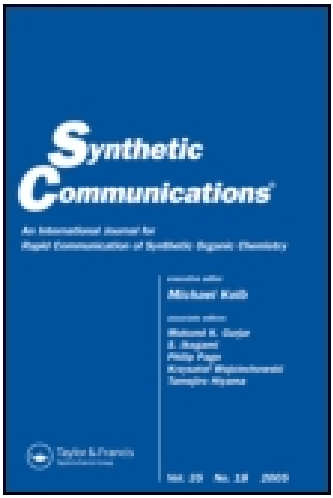

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Syntheses of a Series of Electron Donor and Electron Acceptor Derivatives

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SYNTHESES OF A SERIES OF ELECTRON DONOR AND ELECTRON ACCEPTOR DERIVATIVES

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New electron donor and electron acceptor compounds have been prepared suitable for direct covalent attachment to a photosensitizer or other synthetic subunit. In each case, a saturated three-carbon chain separates a reactive functional group (an alkyl bromide, an amine, or an alcohol) from the electron donor (a phenylenediamine) or electron acceptor (a viologen).

There has been widespread interest in multipart compounds that include an electron donor and/or an electron acceptor, primarily for purposes of investigating the features that govern photoinduced electron transfer reactions.[1] In general, such compounds are prepared by linear syntheses, in which the electron donor or acceptor

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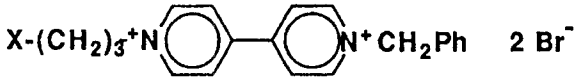
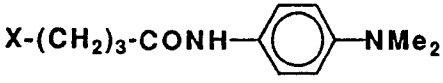
components are built into the molecules at opportune stages of the syntheses. Occasionally, there is a need for an electron donor or electron acceptor unit which is fully assembled, including a reactive functional group for attachment to a subunit of interest. For example, we considered that such compounds would be desirable for attachment to polymeric porphyrin films,[2,3] where a single simple reaction could be used to link an electron donor or acceptor unit to the finished film. Accordingly, we have prepared a series of four derivatives: two viologens, representing electron acceptors, and two derivatives of phenylenediamine, representing electron donors (Scheme I). In each case, the derivative includes a saturated three-carbon chain with a terminal functional group that was selected to be suitable for reaction with either a nucleophilic or electrophilic substrate.

Scheme I



1 X = HO

2 X = Br



3 X = NH_2

4 X = Br

The synthetic strategies used for the viologens relied on the selection of solvent to enhance the desired product formation. The initial alkylation of 4,4'-bipyridyl with benzyl bromide was performed in a nonpolar solvent, toluene, so that the initially formed pyridinium salt would precipitate out before disubstitution could take place. The second alkylation was performed in acetonitrile, a solvent sufficiently polar to dissolve the pyridinium salt but from which viologen precipitates. The amine-substituted electron donor compound (3) was prepared with initial BOC protection before carbodiimide coupling to the N,N-dimethyl-p-phenylenediamine. The bromo-substituted electron donor compound (4) was difficult to isolate in good yield, probably because of self reactions between the available amine groups and the alkyl bromide.

Experimental Section

Materials. Reagents and solvents were the best commercial grade available and used as received unless indicated otherwise. The following were obtained from Aldrich Chemical Co, Milwaukee, WI: 4-bromobutanoic acid, 4-bromobutyryl chloride, 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU), 1-(3'-dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride, phosphomolybdic acid (20% solution in ethanol), 2-(*t*-butoxycarbonyloxyimino)-2-phenylacetonitrile (BOC-ON), thionyl chloride, triethylamine, and trifluoroacetic acid. The following were obtained from TCI Chemicals, Portland, OR: benzyl bromide, 3-bromo-1-propanol, 1,3-dibromopropane, and 4,4'-dipyridyl. Acetonitrile (Aldrich AR grade) was distilled from

P_2O_5, then redistilled from K_2CO_3. Chloroform (Aldrich AR grade) was dried over $CaCl_2$, distilled, and stored over Molecular Sieve 4A. Dichloromethane (Baker HPLC grade) was stored over Molecular Sieve 4A. Pyridine was kept over KOH pellets overnight, distilled, and stored over Molecular Sieve 4A. N,N-Dimethyl-1,4-phenylenediamine (TCI) was vacuum distilled immediately before use. Silica gel for column chromatography was purchased from Aldrich, grade 60, 60Å, 230-400 mesh.

Analyses. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Infrared spectra were taken as KBr pellets using a Perkin-Elmer Model 1600 FTIR. ^1H NMR spectra were taken either at 90 MHz on a Varian EM-390 or at 400 MHz on a Bruker AMX-400 spectrometer. ^{13}C NMR spectra were taken on the Bruker spectrometer at 100 MHz. Mass spectra were obtained on a VG 7070E-HF mass spectrometer in fast atom bombardment mode, using an IonTech ion gun with Xe atoms at 8 kV and either glycerol or 3-nitrobenzyl alcohol as matrix. Thin layer chromatography was performed on Kodak silica gel plates and spots visualized with a phosphomolybdic acid spray.

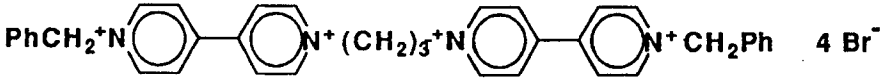
1-Phenylmethyl-4-(4'-pyridyl)pyridinium bromide (5). 4,4'-Dipyridyl (10.0 g, 64 mmol) was dissolved in 300 mL toluene in a 1 L 3-neck round-bottom flask equipped with reflux condenser and addition funnel. The solution was heated to 100° and benzyl bromide (8.7 mL, 73 mmol) was added. Within 2 minutes, precipitate was observed. After 2 hours, TLC showed unreacted dipyridyl, and an additional 6.0 mL (50 mmol) of benzyl bromide was added. The reaction mixture

was heated a total of 3.5 hours, then allowed to cool overnight. The yellow precipitate was filtered, washed with diethyl ether, and allowed to dry under vacuum. This product did not give a blue color upon treatment with aqueous sodium dithionite, indicating the absence of viologen. The yield was 6.7 g (32%): mp 228-230°C; IR (KBr pellet) 3424, 3025, 2978, 2931, 1637, 1595, 1548, 1531, 1495, 1454, 1413, 1225, 1178, 1161, 720 cm^{-1}; ^1H NMR (90 MHz, D_2O) δ 5.83 (s, 2H, CH_2), 7.50 (s, 5H, C_6H_5), 7.86 (d, 2H, J = 5 Hz, Pyr-3'-H), 8.38 (d, 2H, J = 7 Hz, R^+-Pyr-3-H), 8.73 (d, J = 5 Hz, 2H, Pyr-2'-H), 9.06 (d, J = 7 Hz, 2H, R^+-Pyr-3-H); ^{13}C NMR (D_2O, 100 MHz) δ 66.8 (CH_2), 124.9, 128.5, 131.8, 132.3, 132.6, 135.2, 144.2, 147.3, 152.6, 155.8 (Ph and Pyr).

1-(3"-Hydroxypropyl)-1'-phenylmethyl-4,4'-bipyridinium dibromide (1). 1-Phenylmethyl-4-(4'-pyridyl)pyridinium bromide (5) (2.0 g, 6.0 mmol) was dissolved in 200 mL acetonitrile by heating to 80°. 3-Bromo-1-propanol (1.1 mL, 12 mmol) was added at once and the solution refluxed for 4 days. After 9 hours, an additional 1.1 mL (12 mmol) of 3-bromo-1-propanol was added. The first evidence of yellow precipitate appeared after 24 hours of reflux. After cooling to room temperature, the reaction mixture was filtered, washed with fresh acetonitrile, and dried in vacuum. The yield was 1.3 g (47%): mp 236-238°C; IR (KBr pellet) 3330 (O-H), 3107, 3025, 2989, 2872, 1637, 1554, 1507, 1495, 1448, 1366, 1325, 1172, 1072, 873, 732, 690, 614 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz) δ 2.30 (m, 2H, 2"-CH_2), 3.68 (t, 2H, 3"-CH_2), 4.90 (t, 2H, 1"-CH_2), 6.03 (s, 2H, CH_2-Ph), 7.47 (m, 3H, Ph-H), 7.63 (m, 2H, Ph-H), 8.72 (m, 4H, Pyr-H), 9.34 (m, 4H, Pyr-H); ^{13}C NMR (CD_3OD, 100 MHz) δ 34.5 (C-2"), 59.0 (C-3"), 60.9 (C-1"),

65.8 (CH_2-Ph), 128.3, 128.6, 130.5, 130.8, 131.2, 134.3, 147.0, 147.4, 151.1, 151.7 (Ph and Pyr); FAB-MS (glycerol matrix) m/z (assignments based on parent HydroxyViologen dication as M^{+2}) (relative intensity) 397 (M^{+2} + glycerol alkoxide) (4), 338 (M^+ - HOC_3H_6 + glycerol) (11), 306 (M^+) (100), 247 (M^+ - HOC_3H_6) (14), 215 (M^+ - $PhCH_2$) (69), 157 (M^+ - HOC_3H_6 - $PhCH_2$) (17). Anal. Calcd for $C_{20}H_{22}Br_2N_2O$: C, 51.53; H, 4.76; Br, 34.28; N, 6.01. Found: C, 51.28; H, 4.84; Br, 34.36; N, 5.89.

1-(3"-Bromopropyl)-1'-phenylmethyl-4,4'-bipyridinium dibromide (2). 1-Phenylmethyl-4-(4'-pyridyl)pyridinium bromide (**5**) (2.6 g, 7.9 mmol) was dissolved in 300 mL of acetonitrile by heating to 80°. 1,3-Dibromopropane (8.1 mL, 79 mmol) was added at once and the solution allowed to reflux for 9 days. The first yellow precipitate was observed during the second day. After cooling to room temperature, the reaction mixture was filtered, washed with fresh acetonitrile, and dried in vacuum. The isolated sample was always contaminated with a small amount of a coupling product (**6**), approximately 5% in the sample whose data are reported below.



(**6**)

The yield was 2.4 g (56%): mp 300°C with decomposition; IR (KBr pellet) 3436, 3095, 3025, 2989, 2860, 1631, 1554, 1507, 1495, 1448, 1360, 1270, 1208, 1172, 826, 737 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 2.70 (m, 2H, 2"-CH_2), 3.01 (m, 0.1H, central CH_2 of **6**), 3.61 (t, 2H, 3"-CH_2), 4.98 (t, 2H, 1"-CH_2), 5.09 (t, 0.2H, central CH_2N^+ of **6**), 6.06 (s, 2H,

CH_2-Ph), 7.47 (m, 3H, Ph-H), 7.65 (m, 2H, Ph-H), 8.74 (m, 4H, Pyr-H), 9.39 (m, 4H, Pyr-H); ^{13}C NMR (CD_3OD, 100 MHz) δ 29.5 (C-2"), 34.7 (C-3"), 61.6 (C-1"), 65.7 (CH_2-Ph), 128.5, 128.6, 130.5, 130.7, 131.1, 134.3, 147.0, 147.3, 151.3, 151.4 (Ph and Pyr); FAB-MS (glycerol matrix) *m/z* (assignments based on parent BromoViologen dication as M^{+2}) (relative intensity) 616, 618 ($\mathbf{6}^{+2}$ + Br^-) (17), 536 ($\mathbf{6}^+$) (2), 369, 371 (M^+) (57), 338 (M^+ - BrC_3H_6 + glycerol) (94), 278, 280 (M^+ - $PhCH_2$) (67), 247 (M^+ - BrC_3H_6) (100), 197 (M^+ - Br - $PhCH_2$) (33), 157 (M^+ - BrC_3H_6 - $PhCH_2$) (36). Anal. Calcd for $C_{20}H_{21}Br_3N_2$: C, 45.35; H, 4.09; Br, 45.26; N, 5.29. Found: C, 43.27; H, 4.16; Br, 46.31; N, 5.20.

4-(t-Butoxycarbamoyl)butanoic acid. 4-Aminobutanoic acid (8.0 g, 77 mmol) and triethylamine (16.2 mL, 116 mmol) were dissolved in a solution of 70 mL water and 50 mL dioxane, then 21.0 g (85.3 mmol) of 2-(t-butoxycarbonyloxyimino)-2-phenylacetonitrile (BOC-ON) was added and the solution was stirred for 24 hours. Water (50 mL) and ethyl acetate (100 mL) were added and the layers separated. The aqueous phase was acidified to pH 3 and extracted three times with 100 mL of ethyl acetate. The combined organic phases were rotary evaporated to give a yellow viscous oil. Pale yellow crystals were obtained after storage in the refrigerator overnight. The crystals were dissolved in ether and extracted twice with 0.5 M $NaHCO_3$ solution. The combined aqueous layers were acidified with 5% citric acid and extracted three times with 100 mL of ether. The combined organic layers were dried over $MgSO_4$, filtered and rotary evaporated. Cooling of the resultant oil in the refrigerator led to formation of white crystals. The yield was 12.2 g (83%):

mp 54-55°C; IR (KBr pellet) 3365 (O-H), 3224, 2978, 2931, 2860, 2813, 1725 (O=COH), 1678 (OC=ONH), 1542, 1454, 1366, 1278, 1166, 1014, 861, 661 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.43 (s, 9H, tBu), 1.83 (m, 2H, 3-CH_2), 2.35 (t, 2H, 2-CH_2), 3.18 (t, 2H, 4-CH_2), 4.85 (s, 1H, NH).

4-(t-Butoxycarbamoyl)-N-(4'-dimethylaminophenyl)butanamide (7). The amide coupling was performed with a standard carbodiimide reagent.[4] 4-(t-Butoxycarbamoyl)butanoic acid (6.05 g, 32 mmol) and triethylamine (4.4 mL, 31.7 mmol) were dissolved in 50 mL dichloromethane in a 250 mL round-bottom flask. Freshly vacuum-distilled N,N-dimethyl-p-phenylenediamine (4.3 g, 31.7 mmol) and 1-(3'-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (6.1 g, 32 mmol) were added to this solution, which was stirred at room temperature for 16 hours. The solution was washed sequentially with 80 mL water, 80 mL 50% citric acid, 80 mL water, 80 mL saturated $NaHCO_3$ solution and 80 mL water. The organic phase was dried over $MgSO_4$, filtered and rotary evaporated. A white-brown solid was obtained, which was recrystallized from cyclohexane/dioxane (16/3, v/v) to give white crystals. The yield was 7.25 g (74%): mp 117°C; IR (KBr pellet) 3342 (N-H), 3307 (N-H), 3177, 2978, 2931, 2872, 2790, 1684 (OC=ONH), 1648 (C=ONH), 1607, 1595, 1531, 1443, 1272, 1166, 808 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.50 (s, 9H, tBu), 1.90 (m, 2H, 3-CH_2), 2.40 (t, 2H, 2-CH_2), 2.93 (s, 6H, NMe_2), 3.25 (t, 2H, 4-CH_2), 4.91 (s, 1H, NH), 6.81 (d, 2H, Ar-H), 7.56 (d, 2H, Ar-H), 8.28 (s, 1H, Ar-NH); FAB-MS (glycerol matrix) *m/z* (relative intensity) 643 (M_2H^+) (9), 321 (M^+) (100), 266 ($M^+ - C_4H_8$) (49), 222 ($M^+ - C_4H_8 - CO_2$) (47), 205 ($M^+ - C_4H_9CO_2NH_2$) (46), 137

($Me_2NArNH_2^+$) (87), 121 (Me_2NArH^+) (21). Anal. Calcd for $C_{17}H_{27}N_3O_3$: C, 63.53; H, 8.47; N, 13.07. Found: C, 63.47; H, 8.44; N, 12.99.

4-Amino-N-(4'-dimethylaminophenyl)butanamide (3).

Removal of the protecting group was performed according to standard procedures.[5] BOC-protected AminoDonor (**7**) (250 mg, 0.81 mmol) was stirred with 1.5 mL (19.4 mmol) of trifluoroacetic acid at room temperature for 15 minutes. Immediate gas evolution and a slight color change to purple were observed. The solution was cooled in an ice bath and adjusted to pH 13 by addition of 6 M NaOH, at which point the purple color disappeared. The aqueous solution was extracted three times with 25 mL of dichloromethane and the combined organic layers were dried over Na_2SO_4, filtered, rotary evaporated, and further dried under vacuum. Because the free amine was sensitive to air oxidation, the dihydrochloride derivative was also prepared for characterization (see below). The yield of crude **3** was 177 mg (99%): IR (film) 3424 (N-H), 3295 (N-H), 3107, 2954, 2884, 2790, 1654 (C=ONH), 1631, 1601, 1519, 1478, 1443, 1319, 1161, 814, 520 cm^{-1}. The dihydrochloride of **3** was prepared by addition of 3 M HCl (0.25 mL) to 50 mg of **3**, followed by vacuum removal of excess water and HCl. IR (KBr pellet) 3436, 3283, 3236, 3189, 3048, 2966, 2884, 2684, 2637, 2578, 2496, 2449, 1684, 1601, 1548, 1519, 1478, 1313, 1137, 849 cm^{-1}; ^1H NMR (90 MHz, D_2O) δ 2.08 (m, 2H, 3-CH_2), 2.66 (t, 2H, 2-CH_2), 3.16 (t, 2H, 4-CH_2), 3.33 (s, 6H, NMe_2), 7.78 (m, 4H, Ar-H).

4-Bromo-N-(4'-dimethylaminophenyl)butanamide (4).

4-Bromobutyryl chloride was either commercial material or prepared from 4-bromobutyric acid and freshly distilled thionyl chloride

followed by vacuum distillation. 4-Bromobutyryl chloride (5.93 g, 32 mmol) was dissolved in 25 mL DMF, and pyridine (3.3 ml, 41.6 mmol) and N,N-dimethyl-p-phenylenediamine (4.22 g, 31 mmol) were added. The solution was stirred at room temperature overnight. To this solution 40 mL of 1 M NaOH was added, and the brown solution was extracted twice with 100 mL of ether, twice with 50 mL of 1 M HCl, and once with 60 mL of water. The aqueous solution was neutralized with $NaHCO_3$ and extracted twice with 100 mL of ether. The combined organic layers were dried over Na_2SO_4 and the solvent rotary evaporated. The residue was redissolved in ether and the product precipitated out by addition of cyclohexane. The precipitate was filtered, recrystallized from cyclohexane and dried in vacuum. The yield was 0.42 g (5%): mp 114-116°C; IR (KBr pellet) 3260 (N-H), 3166, 3107, 3048, 2907, 2801, 1648 (C=ONH), 1613, 1590, 1525, 1437, 1260, 1161, 814, 520 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 2.26 (m, 2H, 3-CH_2), 2.56 (t, 2H, 2-CH_2), 3.03 (s, 6H, NMe_2), 3.73 (t, 2H, 4-CH_2), 6.81 (d, 2H, Ar-H), 7.41 (d, 2H, Ar-H).

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