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Modulating the Ground- and Excited-State Oxidation Potentials of Diaminonaphthalene by Sequential N-Methylation

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A series of 1,5-diaminonaphthalene derivatives were synthesized and characterized to provide ground- and excited-state electron donors of similar structure but varying potential. Electrochemical and spectroscopic properties of the series are reported and together illustrate two opposing consequences of alkyl substitution on the aryl amines. Inductive effects of methylation are evident from the decrease in ground-state oxidation potential for derivatives containing monomethylamino substituents. In contrast, steric effects seem to dominate the increase in the ground-state oxidation potential of derivatives containing dimethylamino substituents since the conformational constraints created by dimethylation suppress delocalization of the nonbonding electrons. Absorption and emission properties also respond to increasing levels of N-methylation, and the excited-state oxidation potentials of the parent 1,5-diaminonaphthalene and its monomethylamine derivatives (ca. −3.2 V) are approximately 200 mV lower than the corresponding dimethylamino derivatives (−3.0 V).

1. Introduction

Photoinduced electron transfer continues to receive significant attention due to its application in a broad range of topics including photolithography,[1] organic synthesis,[2] photocaging,[3] photosynthesis[4] and photovoltaics.[5] Recent advances in nanomaterials provide even greater opportunity for both fundamental investigation and application of electron transfer. For example, DNA has proven to be a valuable material for constructing nanomaterials due to its ready availability and predictable assembly into helical structures.[6,7] The aromatic stacking within these structures in particular has provided impetus to investigate the ability of DNA to facilitate electron transfer for use in electronic devices.[8,9]

Electron transfer in DNA is additionally quite relevant to human health since it mediates many of the therapeutic and damaging effects of radiation.[10,11] Furthermore, electron transfer plays a role in the repair of DNA in some organisms[12] and perhaps even in the detection of DNA lesions as well.[13] Our laboratory has focused on transfer of excess electrons through duplex DNA, in part, because this process is less susceptible to quenching by molecular oxygen than the complementary hole transfer.[14–17] The intrinsic ability of DNA to sustain electron transfer may also account for its apparent ability to promote self-repair of its major photochemical lesion, a thymine–thymine cyclobutane dimer.[18,19] Mechanistic investigation of these electron transfer processes and especially their dependence on driving force potential would greatly benefit from a series of compounds offering a range of oxidation potentials with minimal change of structure. Already, 1,5-diaminonaphthalene (**1**) demonstrated a much greater ability to initiate excess electron transfer in DNA than its *N*1,*N*1,*N*5,*N*5-tetramethyl derivative (**6**), which is a weaker donor.[16] We have now prepared and characterized the complete series of N-methylated derivatives of **1** to create a collection of closely related structures of differing ground- and excited-state potentials. This series should find application in a number of photoinduced and ground-state studies requiring an incremental progression of photochemical and redox properties.

2. Results and Discussion

2.1. Synthesis

The parent compound, 1,5-diaminonaphthalene (**1**), is available commercially and was used to prepare *N*1,*N*1,*N*5,*N*5-tetramethyl-1,5-diaminonapthalene (**6**) by treatment with dimethyl sulfate under basic conditions as described previously.[16,20] Synthesis of the remaining derivatives containing an intermediate number of N-methyl groups relied on Buchwald–Hartwig couplings (Scheme 1). The naphthyl bromide **7** required for this strategy was prepared in 43% yield from 1-nitronaphthalene and $Br_2/FeCl_3$.[21] Subsequent coupling with methylamine and dimethylamine alternatively yielded **8** (65% yield) and **9** (75% yield). Standard use of the strong base sodium tert-butoxide in these couplings was not compatible with the nitro group pres-

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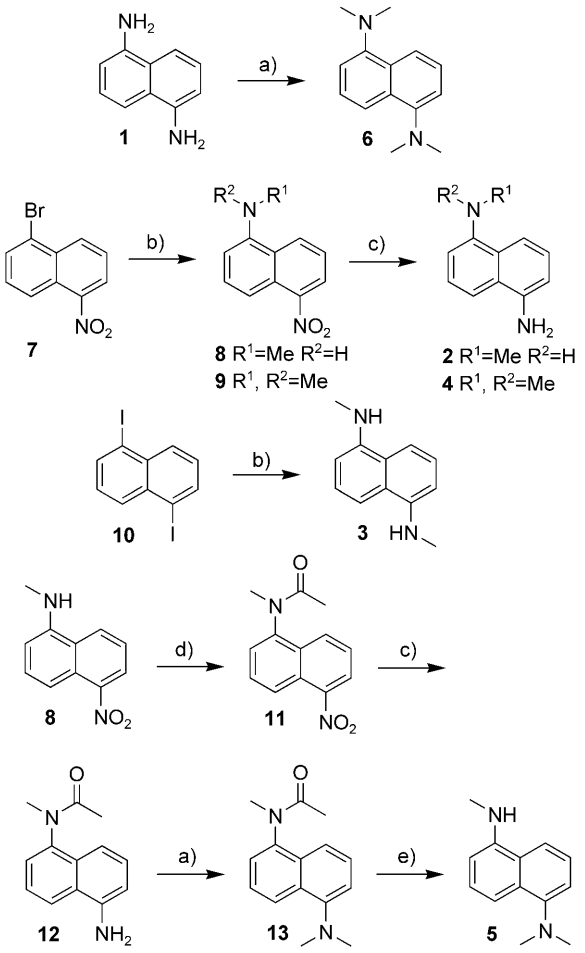

Scheme 1. Synthesis of compounds **2**–**6**: a) Me_2SO_4, Na_2CO_3, MeOH/H_2O/THF (2:1:1); b) ±-BINAP, $Pd(OAc)_2$, Cs_2CO_3, R^1R^2NH, toluene, 80 °C; c) 10% Pd/C, HCOOH, MeOH; d) Ac_2O, reflux; e) 2 N HCl, reflux.

ent in **7**,[22] and consequently the milder base Cs_2CO_3 was used instead.[23,24] Attempts to reduce the nitro groups in **8** and **9** with either Zn/HCl or H_2/Pd-C provided only incomplete conversion even after extended reaction time (>14 h). In contrast, reduction with formic acid/Pd–C yielded the desired products **2** and **4** in good yield (65% and 80%, respectively) within 0.5 h.

Generation of the symmetric bis-methylamine **3** was accomplished in two steps. A Sandmeyer-type reaction was used to convert the diamine **1** to its diiodo derivative **10** in a 65% yield (Scheme 1).[25] This derivative was then coupled with methylamine in excellent yield (89%) under Buchwald–Hartwig conditions as described above. Finally, synthesis of the unsymmetric trimethyl derivative **5** required use of a protecting group to prevent over methylation. The methylamino group of **8** was acetylated in 73% yield prior to reduction of its nitro group (81% yield) under the same formic acid/Pd–C conditions used above to reduce **7** (Scheme 1). Dimethylation to form **13** was accomplished in 80% yield under the same conditions used to convert **1** to **6** above. Reductive alkylation has also been used for methylating a protected 1,5-diaminonaphthalene,[16] but this approach was not as robust herein as methylation by dimethyl sulfate. Finally, the acetyl protecting group of **13** was removed in high yield (90%) by treatment with 2 N HCl.

2.2. Absorption and Emission Properties of the Diaminonaphthalene Derivatives

All of the diaminonaphthalene derivatives exhibit low wavelength absorption with a relatively invariant λ_{max} of 231–232 nm under the solvent conditions most relevant to future studies with nucleic acids (Figure 1a). In contrast, the extinction coefficients at these wavelengths consistently decrease as the extent of methylation increases beyond one (Table 1). Addition of four methyl groups collectively reduces the extinction coefficient by approximately 50% as evident from comparison of the values for **1** and **6**. *N*1,*N*1-Dimethylation also suppresses absorption in this region significantly more than *N*1,*N*5-dimethylation. This trend is just one consequence of the likely twisting of the *N*1,*N*1-dimethylamino group out of conjugation

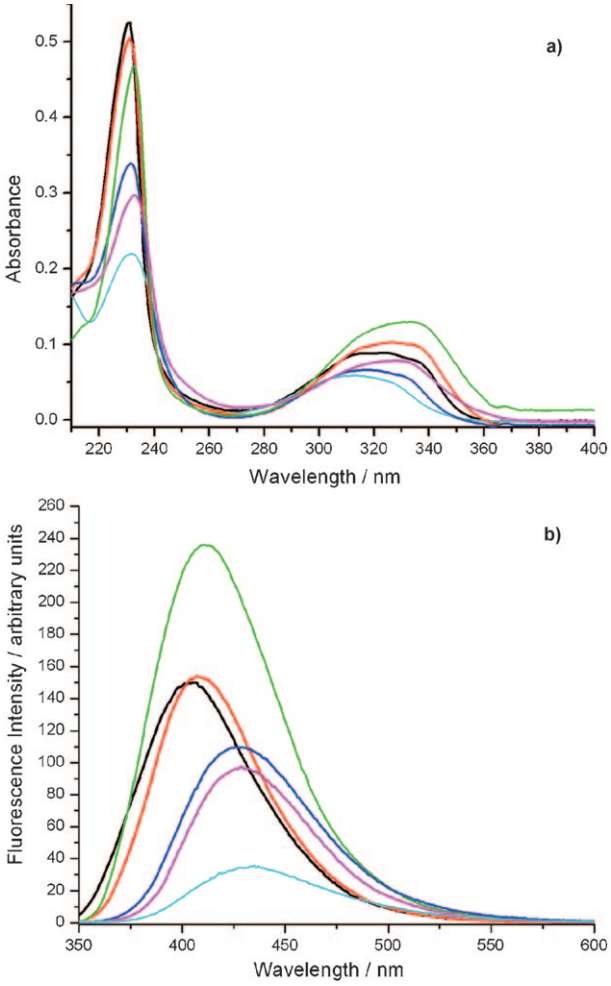

Figure 1. a) Absorption spectra of compounds **1**–**6** (normalized to 10 μM) and b) their relative fluorescence emission spectra in 100 mM NaCl and 10 mM sodium phosphate pH 7. Each emission spectrum is normalized to its relative extinction coefficient at λ_{ex} (See Table 1 for details). Compound **1** is indicated in black, **2** in red, **3** in green, **4** in blue, **5** in purple and **6** in cyan. The emission quantum yield of **6** (0.11) was determined previously.[16]

Table 1. Spectral data and redox properties of the diaminonaphthalene series **1**–**6**.

	λ_{max} [nm]	ε [$mM^{-1}cm^{-1}$][a]	λ_{ex} [nm]	λ_{em} [nm]	λ_{00}[b] [nm]	E_{ox} [V][a]	E_{00} [kcal mol^{-1}]	E_{ox}* [V]
1	231 324	50.0 ± 1.30 8.86 ± 0.13	323	404	355	0.250 ± 0.020	80.5	−3.24 ± 0.02
2	231 326	50.5 ± 4.40 10.7 ± 0.20	327	409	362	0.220 ± 0.006	79.0	−3.24 ± 0.01
3	232 332	42.4 ± 0.80 10.8 ± 0.40	334	414	364	0.208 ± 0.001	78.6	−3.18 ± 0.01
4	231 318	33.9 ± 0.60 7.28 ± 0.06	317	427	366	0.380 ± 0.006	78.1	−3.01 ± 0.01
5	232 327	28.9 ± 0.70 7.88 ± 0.51	327	429	372	0.350 ± 0.002	76.9	−2.98 ± 0.01
6	231 312	22.0 ± 1.10 5.93 ± 0.31	312	433	366	0.400 ± 0.007	78.1	−2.99 ± 0.01

[a] Average values of no less than three independent measurements. Uncertainty represents the standard deviation. [b] See Figure S1 (Supporting Information).

from the aromatic system to relieve steric strain produced by a *peri* interaction with H8. Such twisting is also predicted from conformational analysis based on molecular mechanics calculations (Supporting Information, Figure S2).

Each diaminonaphthalene derivative also exhibits a weak absorption in the range of 300–360 nm, and again, the extinction coefficients vary by approximately 50% from a maximum for **2** and **3** to a minimum for **6** (Figure 1a, Table 1). For this absorption band, however, addition of a single methyl group to each amine enhances the extinction coefficient whereas its further conversion to a geminal N,N-dimethyl group suppresses this coefficient relative to that of the unmethylated parent chromophore. Competing effects of methylation are also evident in the λ_{max} values of this band. Whereas monomethylation induces a bathochromic shift, geminal dimethylation induces a hypsochromic shift resulting in a range of λ_{max} values centered around that of the unmethylated parent **1** and delimited by those of its tetramethylated **6** and the dimethylated **3** derivatives.

The emission properties of this series also exhibit a dependence on the level of N-methylation. The trend of fluorescence efficiency is comparable to the trend of absorptivity at long wavelength, and this correlation persists even after the emission spectra are normalized for differences in excitation efficiency (Figure 1b). Moreover, fluorescence efficiency ranges ten-fold from a maximum for *N*1,*N*5-dimethyldiamine **3** to a minimum for the *N*1,*N*1,*N*5,*N*5-tetramethyldiamine **6**. The comparable range in absorptivity is only two-fold. Emission λ_{max} also responds to N-methylation of the parent **1** but not in the same manner as fluorescence efficiency. Each successive methylation shifts the emission maximum to lower energies, and the greatest difference is observed between **3** containing one methyl group on each amine and **4** containing two methyl groups on a single amine (Table 1). The λ_{00} values were also determined in order to measure the E_{00} values that were used below to estimate the excited-state potentials. The E_{00} values conform to the same general trend exhibited by the λ_{em} except that the biggest decrease is apparent after the first methylation (**1** vs **2**). Also, the last methylation (**5** vs **6**) reverses this trend toward lower energies.

2.3. Redox Properties of the Diaminonaphthalene Derivatives

Electrochemistry

Our goal in preparing the various diaminonaphthalene derivatives was to create a closely related series of compounds with complementary photochemical and redox properties. The inductive effect of the added methyl groups was expected to lower the oxidation potential in this series and yet these modifications could also raise this potential by suppressing delocalization of the nonbonding electrons of the nitrogen due to *peri* interactions of the fused aromatic rings (Figure S2). These competing effects were evident from the spectroscopic characterization above and were also evident in the redox chemistry. Cyclic voltammetry was initially considered for measuring the E_{ox} values for **1**–**6**, but all attempts at this were thwarted by irreversible oxidation and polymerization of the compounds that, for others, were used successfully to generate electroactive films.[26] Replacing the neutral aqueous solvent system used in these attempts might have minimized the competing reactions, but would also have diminished the significance of the results for electron transport in DNA. Instead, the solvent conditions were retained and the strategy for measuring oxidation potentials was changed. Alternative use of AC voltammetry was successful as this approach detected only redox processes that were intrinsically reversible in our system.[27] Sample voltammograms are illustrated for diaminonaphthalene derivatives (Figure 2 and Supporting Information, Figure S3), and the resulting E_{ox} values are summarized in Table 1. Collectively, these compounds offer E_{ox} values ranging from almost 0.2 V to 0.4 V by only varying the level of N-methylation. The inductive effect of single methyl substitutions is evident from the decrease in E_{ox} from **1** to **3**, but the steric effects of geminal N,N-dimethyl substitution then dominate the remaining series from **4** to **6**.

Excited-State Oxidation Potential

The diaminonaphthalenes should find utility in two different aspects of photoinduced electron transfer. They provide electron donors to photoexcited oxidants for which their E_{ox} is crucial, and additionally they may serve in their excited state as strong reducing agents, an application our laboratory is currently investigating.[16,28,29] The E_{ox}* can be estimated by the Weller equation[30] based on the ground-state potential E_{ox}, the singlet excited-state energy represented as E_{00} (Table 1) and a solvent correction term that is negligible for polar solvents.[31]

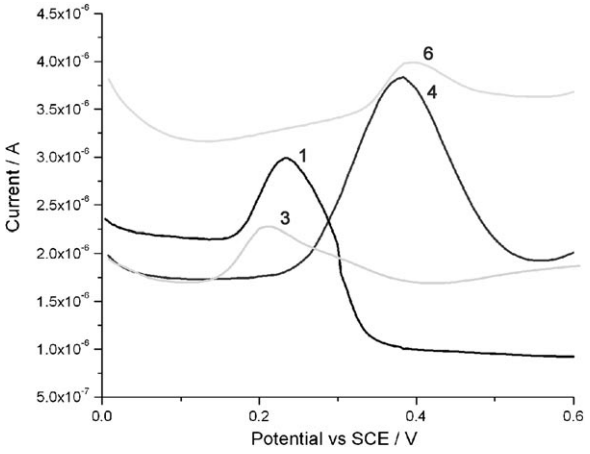

Figure 2. AC voltammograms of selected diaminonaphthalenes. The data represents the average of three independent measurements for each compound.

The E_{00} values in turn can be estimated from λ_{00} as detected by the overlay of the normalized fluorescence excitation and emission spectra (Table 1 and Supporting Information, Figure S1).[32] These values are compensatory to the structural effects influencing the ground state E_{ox}, and consequently a broad variation in E_{ox}* is suppressed. The excited-state donor strength of the diaminonaphthalenes is most readily characterized by the degree of substitution on the amine groups. The derivatives **1**–**3** containing no more than a single methyl group on each amine are relatively strong electron donors, and the remaining derivatives **4**–**6** containing one or more dimethylamine groups are weaker excited-state electron donors by ca. 200 mV. However, both groups are among the strongest donors that have been used for study of excess electron transfer in DNA and should have the power to reduce all of the nucleobases including guanine with a potential of lower than −2.76 V.[33,34]

3. Conclusions

A new series of electron donors has been constructed and characterized to support mechanistic investigation of photoinduced electron transfer. In particular, these diaminonaphthalene derivatives will help in the future to identify the parameters controlling electron injection and transfer in DNA. This series also has the potential for application in numerous other systems for which an incremental variation in potential is needed. The derivatives **1**–**6** illustrate the opposing effects of the inductive and steric properties of N-methylation in naphthyl amines. Influence of this methylation is evident in the photochemical excitation and emission as well as ground- and excited-state oxidation of diaminonaphthalenes. Both λ_{ex} and E_{ox} respond similarly to 1) the stabilization provided by the electron donating ability of a methyl substituent and 2) the destabilization caused by a diminished conjugation of the nitrogen lone pair into the aromatic system that results from a steric clash between the N-methyl and its proximal aryl hydrogen. In contrast, the λ_{em} and λ_{00} are primarily influenced by the extent, but not position of the N-methylation, because the electron-donating characteristic of the methyl groups appear to dominate the excited state properties.

Experimental Section

General Methods and Materials: Solvents, starting materials, and reagents of the highest commercial grade were used without further purification unless noted. All aqueous solutions were prepared with water purified to a resistivity of 17.8–18.0 MΩ. Commercially available 1,5-diaminonaphthalene was recrystallized in ethanol. *N*1,*N*1,*N*5,*N*5-Tetramethyl-1,5-diaminonapthalene (**6**) [16,20], 1-bromo-5-nitronapthalene (**7**) [21] and 1,5-diiodonaphthalene (**10**) [25] were prepared as described previously. All UV/Vis measurements were obtained with a Hewlett Packard 8453 UV/Vis spectrophotometer, and all fluorescence spectra were obtained with a Hitachi F-4500 spectrophotometer. NMR spectra were recorded with a Bruker AM400 spectrometer and referenced to residual protons in the solvents. Chemical shifts (δ) are reported in parts per million (ppm), and coupling constants (J) are reported in hertz (Hz).

Preparation of *N*1-Methylnaphthalene-1,5-diamine (**2**): A solution of **8** (300 mg, 1.48 mmol) and methanol (20 mL) was added to an oven-dried round-bottom flask with a magnetic stir bar. This mixture was stirred at room temperature until **8** was dissolved, at which time 10% palladium on carbon (200 mg, 0.13 mmol) and formic acid (2 mL) were added. The reaction was stirred under nitrogen atmosphere for 2 h at room temperature, and the resulting mixture was filtered through a plug of Celite 545®. The filtrate was diluted with CH_2Cl_2, and then washed with saturated $NaHCO_3$, water and brine. The organic layer was dried with anhydrous magnesium sulfate, filtered and concentrated to dryness. The crude material was purified by silica gel flash column chromatography with 10% ethyl acetate:hexanes yielding the desired product as a dark red solid (168 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (t, J = 8.00, 1H), 7.23 (t, J = 2.71 Hz, 1H), 7.18 (d, J = 8.03 Hz, 1H), 6.77 (d, J = 2.57 Hz, 1H), 6.75 (d, J = 2.54 Hz, 1H), 6.62–6.56 (m, 1H), 4.41 (s, 1H), 4.11 (s, 2H), 2.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.2, 143.1, 126.1, 125.5, 124.7, 124.5, 111.0, 110.3, 110.2, 104.3, 31.5.

Preparation of *N*1,*N*5-Dimethylnaphthalene-1,5-diamine (**3**): Anhydrous toluene (2 mL) and ±-BINAP (66 mg, 0.11 mmol) were combined and sealed in an oven-dried round-bottom flask with a magnetic stir bar. The mixture was heated to 80 °C until the ±-BINAP dissolved. The resulting solution was then cooled to approximately 30 °C before addition of palladium acetate (47.5% palladium, 12 mg). The resulting dark orange solution was further cooled to room temperature while stirring for 5 min. Next, **10** (125 mg, 0.329 mmol) was added, and after another 10 min, Cs_2CO_3 (203 mg, 1.05 mmol) was added. The mixture was stirred for an additional 20 min and then methylamine (2 M solution in THF, 0.5 mL) was added. The reaction vessel was quickly sealed and heated to 80 °C for 48 h. The resulting reaction mixture was filtered through a plug of Celite 545®, and the plug was rinsed with several portions of CH_2Cl_2. The filtrate was concentrated to dryness. The resulting solid was purified by silica gel flash chromatography using a gradient of 5–30% ethyl acetate in hexanes yielding the desired product as a dark red, viscous oil (55 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (t, J = 7.96 Hz, 2H), 7.15 (d, J = 8.50 Hz, 2H), 6.60 (d, J = 7.56 Hz, 2H), 4.42 (s, 2H), 2.99 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.1, 125.5, 123.8, 108.7, 103.9, 31.1.

Preparation of *N*1,*N*1-Dimethylnaphthalene-1,5-diamine (**4**): Reduction of **9** (761 mg, 3.45 mmol) in methanol (100 mL) was performed equivalently to that described in preparation of **2** above using 10% palladium on carbon (370 mg, 0.350 mmol) and formic acid (2 mL) to yield the desired product (523 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.69$ (d, $J = 8.52$ Hz, 1H), 7.49 (d, $J = 8.44$ Hz, 1H), 7.36 (t, $J = 7.94$ Hz, 1H), 7.27 (t, $J = 7.94$ Hz, 1H), 7.06 (d, $J = 7.37$ Hz, 1H), 6.76 (d, $J = 7.35$ Hz, 1H), 4.09 (s, 2H), 2.87 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 151.2$, 142.4, 140.3, 130.1, 125.5, 124.7, 115.5, 115.1, 114.0, 100.8, 45.2.

Preparation of *N*1,*N*1,*N*5-Trimethylnaphthalene-1,5-diamine (**5**): A mixture of **13** (100 mg, 0.413 mmol), 25 mL THF and 5 mL 2 N HCl was heated to reflux overnight, cooled to room temperature, and diluted with ethyl acetate. The resulting organic layer was then neutralized with saturated $NaHCO_3$, washed with brine, dried over $MgSO_4$, filtered and concentrated to dryness to yield **5** (74 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.68$ (d, $J = 8.54$ Hz, 1H), 7.51 (d, $J = 8.48$ Hz, 1H), 7.45 (m, 2H), 7.11 (d, $J = 7.41$ Hz, 1H), 6.64 (d, $J = 7.51$ Hz, 1H), 4.45 (s, 1H), 3.04 (s, 3H), 2.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 151$, 145, 129, 126, 125, 124, 115, 114, 113, 104, 45, 31

Preparation of *N*-Methyl-5-nitronaphthalen-1-amine (**8**): The desired compound was produced using analogous conditions to those described for **3** with ±-BINAP (247 mg, 0.397 mmol), palladium acetate (47.5% palladium, 71 mg, 0.32 mmol), **7** (1.0 g, 0.40 mmol), Cs_2CO_3 (160 mg, 0.48 mmol) and methylamine (2 M in THF, 2.40 mL). The crude material was purified by silica gel flash column chromatography using a 5–10% gradient of ethyl acetate in hexane to yield the desired solid (523 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.05$ (t, $J = 8.50$ Hz, 1H), 7.76 (d, $J = 8.69$ Hz, 1H), 7.53 (t, $J = 8.22$ Hz, 1H), 7.39 (t, $J = 8.05$ Hz, 1H), 6.67 (d, $J = 7.72$ Hz, 1H), 4.62 (s, 1H), 3.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 147.5$, 144.8, 130.4, 126.0, 125.9, 124.6, 123.3, 122.5, 111.3, 105.5, 31.0. m.p.: 135–137 °C.

Preparation of *N*1,*N*1-Dimethyl-5-nitronaphthalen-1-amine (**9**): The desired compound was produced using analogous conditions to those described for **3** with ±-BINAP (25 mg, 0.040 mmol), palladium acetate (47.5% palladium, 9.4 mg, 0.020 mmol), **7** (100 mg, 0.40 mmol) Cs_2CO_3 (160 mg, 0.48 mmol) and dimethylamine (2 M in THF, 0.30 mL). The crude material was purified by silica gel flash column chromatography with 5% ethyl acetate:95% hexanes to provide **9** in 75% yield (64 mg) as a dark red oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.53$ (d, $J = 8.49$ Hz, 1H), 8.13–8.07 (m, 2H), 7.54 (t, $J = 8.14$ Hz, 1H), 7.46 (t, $J = 8.04$ Hz, 1H), 7.14 (d, $J = 7.48$ Hz, 1H), 2.85 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 151.6$, 147.3, 130.7, 130.1, 129.4, 126.5, 123.6, 123.1, 117.2, 115.5, 45.3.

Preparation of *N*-Methyl-*N*-(5-nitronaphthalen-1-yl)-acetamide (**11**): Acetic anhydride (3 mL) and **8** (52 mg, 0.26 mmol) were refluxed overnight, cooled to room temperature and diluted with 25 mL water. The resulting solution was adjusted to pH 7 using saturated aqueous $NaHCO_3$. The solution was extracted 3×50 mL with CH_2Cl_2. The organic layers were combined, washed (100 mL water and 100 mL brine), dried over magnesium sulfate, and concentrated to dryness. The resulting yellow-orange solid was purified by silica gel flash chromatography using 5–20% ethyl acetate in hexane to yield the desired product (46 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.30$ (d, $J = 8.53$ Hz, 1H), 7.50 (m, 3H), 7.36 (d, $J = 7.16$ Hz, 1H), 7.16 (dd, $J = 6.36$ Hz, 1H), 3.37 (s, 3H), 2.94 (s, 6H), 1.80 (s, 3H).

Preparation of *N*-(5-Aminonaphthalen-1-yl)-*N*-methyl-acetamide (**12**): Reduction of **11** (200 mg, 0.989 mmol) in methanol (20 mL) was performed equivalently to that described for preparation of **2** above using 10% palladium on carbon (105 mg, 0.0989 mmol) and formic acid (2 mL) to yield the desired product (175 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.88$ (d, $J = 8.53$ Hz, 1H), 7.49–7.43 (m, 1H), 7.40–7.32 (m, 2H), 7.23 (d, $J = 8.42$ Hz, 1H), 6.85 (d, $J = 7.38$ Hz, 1H), 4.33 (s, 2H), 3.34 (s, 3H), 1.77 (s, 3H).

Preparation of *N*-[5-(Dimethylamino)naphthalen-1-yl]-*N*-methylacetamide (**13**): Methanol (6 mL), water (3 mL) and THF (3 mL) were combined and used to suspend **12** (100 mg, 0.467 mmol) and Na_2CO_3 (198 mg, 1.87 mmol). Dimethyl sulfate (0.176 mL, 1.87 mmol) was added to the mixture, and together stirred at room temperature overnight under N_2. The reaction was quenched with 1 M NaOH to a pH > 11 and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$, filtered and concentrated to dryness to yield the desired material (94 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.30$ (d, $J = 8.53$ Hz, 1H), 7.50 (m, 3H), 7.36 (d, $J = 7.16$ Hz, 1H), 7.16 (dd, $J = 6.36$ Hz, 1H), 3.37 (s, 3H), 2.94 (s, 6H), 1.80 (s, 3H). ^{13}C NMR (101 mHz, $CDCl_3$): $\delta = 171.2$, 152.3, 141.0, 132.3, 130.7, 127.1, 126.9, 125.3, 124.2, 117.1, 115.1, 45.9, 37.2, 22.2.

AC Voltammetry and Excited-State Oxidation Potential: Measurements were carried out using a CH Instruments 660 A electrochemical workstation (Austin, TX) courtesy of the Army Research Labs, Adelphi, MD. Experiments were run in a three component electrode cell with a platinum working electrode, platinum wire counter and saturated calomel reference electrode. Phosphate buffered saline (PBS, 10 mM potassium phosphate, 137 mM NaCl and 2.7 mM KCl, pH 7.4) was used as the electrolyte. Stock solutions of diaminonaphthalenes (500 mM) were prepared with HPLC-grade acetonitrile and added (10 μL) to a final concentration of 500 μM in 10 mL PBS and less than 5% acetonitrile. AC voltammetry [incr E(V) = 0.004, amplitude (V) = 0.025, frequency (Hz) = 10] was performed a minimum of three times for each compound. E_{ox} values were identified by the apex of the average of these scans, and E_{ox}* values were then calculated from the relationship: E_{ox}*(V) = E_{ox}(V) − E_{00} (kcal mol^{-1})/23.06.[30]

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Keywords: diaminonaphthalenes · electron transfer · excited-state electron donor · fluorescence · voltammetry

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