Synthesis, computational, and photophysical characterization of diaza-embedded [4]helicenes and pseudo[4]helicenes and their pyridinium and viologen homologues.

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ABSTRACT

Synthesis of three [4]heli-viologens and their helical precursors, and two “pseudo-[4]helicenes” and their alkylated derivatives, which have potential device and catalysis applications, are reported. Their structures and racemization barriers have been explored with the B3LYP/6-311+G(2d,p), M06-2X/6-311+G(2d,p), and M11/6-311+G(2d,p) computational models. The photophysical properties of the helicenes and pseudo-helicenes and their alkylated derivatives have been measured. Unusual singlet-triplet energy gaps, ΔE_{ST} , were measured and discussed for the charged alkylation products.

Keywords: Helicenes, Viologens, Photophysics, Computational Chemistry, Racemization Barriers

1. Introduction

[n]Helicenes are a polyaromatic hydrocarbon family consisting of an array of ortho-fused aromatic rings, **1**.¹ Their best known, and most intriguing, characteristic is their chiral helical topology which is first expressed in [4]helicene, **1**(n=4). This topology leads to extraordinary physical and chiroptical properties that have been used to advantage by many workers during construction of novel molecular switches, sensing devices, and catalysts, and for the synthesis of supramolecular, opto-electronic, and non-linear materials.^{2,3}

Recently considerable effort has been expended to synthesize and study heterohelicenes formed by embedding a heteroatom into one or more of the aromatic rings of the carbocyclic [n]helicene or by replacing one or more of the aromatic rings with a heteroaromatic ring (e.g. furan, or thiophene).⁴⁻⁶ The impetus for these studies was

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the observations of interesting, useful, and enhanced properties induced by heteroatom substitution.⁷ In 2006 the complete series of seven mono-aza[5]helicenes was reported.⁸ This remarkable achievement came 98 years after the first report of the synthesis of [5]helicene.⁹ The wait, however, was worth it, since access to the entire series has provided compelling evidence that judicious placement of the nitrogen atom within the helical framework can be used to selectively modulate a wide-range of physicochemical properties of these valuable molecules.¹⁰ Building on this exceptional body of work, we recently embedded viologen functionality into [5]helicene.¹¹ (Figure 1) Addition of the viologen functional group simultaneously generates a redox addressable helicene,¹²⁻¹⁴ a fluorescent organic salt,^{15,16} and a potent photoacid,¹⁷⁻¹⁹ which are properties of current interest for device construction.

Figure 1. Helical Viologens and their Redox States

We now extend these efforts, to embed nitrogen functionality into the helical scaffolds of [4]helicene, **1** ($n=4$), and benzo[*b*]-[4]helicene and report the synthesis and photophysical behavior of three diaza[4]helicenes, **2a-c**, two planar diaza[*b*]benzo[4]helicenes (pseudo-helicenes), **3a** and **3b**, three heli-[4]viologens, **2j-l**, and two pyridinium derivatives, **3d** and **3g**. We also describe computational studies of these compounds and several derivatives of **2** and **3** to provide insight into their structural features and racemization barriers.

2. Results and discussion

Synthesis. Syntheses of the diaza[4]helicenes (Figure 2a) and diazabenzo[4]helicenes (Figure 2b) were accomplished in straightforward two-pot procedures and were then alkylated in one additional step to generate their monoalkylated (pyridinium) or dialkylated (viologen) derivatives. The first step in both procedures is the Pd-catalyzed vinylation (Hiyama-Heck reactions) of bromopyridines or bromoquinolines with triethoxyvinylsilane.^{20,21} Both the sequential one-pot two step and the one-step Hiyama-Heck couplings leading to unsymmetrical, **4**, and symmetrical **5** (E)-1,2-diarylethylenes, respectively, occurred in good to excellent yields (65-91%). The photocyclizations to form the helicenes occurred in modest yields and in the case of the (E)-diquinoylethenes, **5**, to a separable mixture of cyclization products (**3a** and **6** (R = H) or **3b** and **6** (R = CH₃)). The structure of **6** (R = H) was unambiguously assigned by comparison to an authentic sample.¹¹ Despite the low yield of **6** (R = CH₃) and our inability to isolate it pure, we argue that it is 2,13-dimethyl-5,10-diaza[5]helicene based on the analogous formation of **6** (R = H) in the reaction of **5** (R = H), mechanistic considerations, and a crude proton NMR spectrum. (See Supplementary Material) The ratio [**3b**]/[**6**; R = CH₃] was much greater than [**3a**]/[**6**; R = H] reflecting dramatic steric destabilization of 2, 13-dimethyl-5,10-diaza[5]helicene, (**6**; R = CH₃).

Figure 2. Synthesis of diazahelicenes

The alkylations were conducted with trimethyloxonium tetrafluoroborate, $(\text{CH}_3)_3\text{OBF}_4$, and led to the viologens in reactions of the [4]helicenes, **2a**, **2b**, and **2c**, and to pyridinium tetrafluoroborates in the reactions of the benzo[b]-1,8-diaza[4]helicenes, **3a** ($\text{R} = \text{H}$) and **3b** ($\text{R} = \text{CH}_3$). The reactions with diaza[b]benzo[4]helicenes, **3a** ($\text{R} = \text{H}$) and **3b** ($\text{R} = \text{CH}_3$) but not with the [4]helicenes, **2a**, **2b**, and **2c** required DBU (1,8-diazabicycloundec-7-ene). It is tempting to suggest that adventitious HBF_4 impurity in the $(\text{CH}_3)_3\text{OBF}_4$ preferentially protonates the exposed nitrogen rather than the nitrogen in the cove regions of **3a** and **3b**. (Scheme 1a) Subsequent alkylation is then directed to the unprotonated sterically inaccessible buried nitrogen in the cove regions and consequently fails. In the case of the [4]helicenes, **2a**, **2b**, and **2c** initial protonation still leaves an exposed nitrogen where alkylation can occur. Rapid loss of the acidic hydrogen from the mono-alkylated-protonated [4]helicene, **7**, followed by the second alkylation gives the viologen without the need for DBU. (Scheme 1b)

The scenario in Scheme 1 is supported by the observation that addition of triethylamine to the $(\text{CH}_3)_3\text{OBF}_4$ /**3b** reaction mixture without DBU resulted in an immediate color change from reddish-yellow to yellow consistent with a change in the protonated/deprotonated equilibrium (Scheme 1). The diminished basicity of the cove region nitrogen is also supported by B3LYP and M06-2X calculations using the 6-311+G(2d,p) basis set in CH_3CN that show that **3a** protonated at the cove nitrogen is 3.36 and 3.26 kcal/mol less stable, respectively, than **3a** protonated at the exposed nitrogen. This corresponds to the exposed nitrogen (N_8) being more basic than the less sterically accessible nitrogen (N_1) by 2.4-2.6 pKa units. (Scheme 1)

Scheme 1. Alkylations of diazahelicenes in the absence of DBU.

2.1 Structural Aspects

Key B3LYP and M06-2X/6-311+G(2d,p) structural features of diaza[4]helicenes, **2a**, **2b**, and **2c**, and their viologen counterparts **2j**, **2k**, and **2l** in the absence of their weakly coordinating BF_4^- counterions,¹¹ are compared to their carbocyclic analogue [4]helicene, **1** ($n = 4$) in Table 1. All six compounds adopt a helical structure. The non-planar geometry of **1** ($n = 4$), and the reliability of our computational methods, are convincingly demonstrated by X-ray crystallography,²² proton²³ and carbon NMR,²⁴ and by PES²⁵. The dihedral angles, $\Theta_{12,12a,12b,12c}$ and $\Theta_{12a,12b,12c,1}$, that define the cove region decrease along the series [4]helicene > viologens > diaza[4]helicenes. (Table 1) These dihedral angles are very similar to the two outer dihedral angles that define the fjord region in the analogues [5]helicene. For example the three B3LYP/6-311+G(2d,p) dihedral angles that define the fjord region in **1** ($n = 5$) [18.2° , 30.2° , and 18.1°], are larger than in the viologen dimethyl-5,10-diaza[5]helicene viologen [17.0° , 29.8° , 17.0°], which are larger than in 5,10-diaza[5]helicene [16.9° , 27.9° , 16.9°]. The smaller intra-cove dihedral angles in the diaza[4]helicenes in comparison to the corresponding angle in [4]helicene can be attributed to a slight increase in the $d_{1,12}$ distance (Table 1) in the diaza[4]helicenes that allows the ring system to adopt a more planar geometry with a reduced energetic cost. The increases in $\Theta_{12a,12b,12c,1}$ upon alkylation of **2a**, **2b**, and **2c** to give the viologens are consistent with an energetic preference to decrease the overlap between the two-pyridinium rings. However, these B3LYP and M06-2X/6-311+G(2d,p) dihedral angles of 17.6° - 17.9° and 18.4° - 18.8° , respectively, are substantially smaller than the 40° inter-pyridinium ring angle adopted in methyl viologen, which is not constrained from adopting the electronically preferred dihedral angle.²⁶

Table 1. Key B3LYP and M06-2X/6-311+G(2d,p) Structural Features for [4]Helicene and Diaza[4]Helicenes.^a

	$\Theta_{\square\square\square\square\square\square\square\square}$ $\square\square\square\square\square\square$	$\Theta_{\square\square\square\square\square\square\square\square}$ $\square\square\square\square\square\square$	$d_{12b,12c}$	$d_{1,12}$
1^c	18.7(19.5) ⁰	18.5(19.5) ⁰	1.453Å (1.451Å)	3.044Å (3.024Å)
2a	15.7(17.0) ⁰	15.4(16.6) ⁰	1.450Å (1.448Å)	3.108Å (3.086)
2b	15.7/(16.9) ⁰	15.5(16.6) ⁰	1.451Å (1.448Å)	3.110Å (3.085Å)
2c	15.9/(17.2) ⁰	15.5/(16.1) ⁰	1.451Å (1.448Å)	3.109Å (3.087Å)
2j	17.1(18.2) ⁰	17.7(18.4) ⁰	1.450Å (1.448Å)	3.084Å (3.060Å)
2k	17.1(18.0) ⁰	17.6(18.7) ⁰	1.450Å (1.449Å)	3.087Å (3.061Å)
2l	17.0(18.2) ⁰	17.9(18.8) ⁰	1.453Å (1.451Å)	3.090Å (3.067Å)

a. Calculations in the gas phase in the absence of a counterion. b. M06-2X values in parenthesis. c. ($n = 4$)

Key B3LYP and M06-2X/6-311+G(2d,p) structural features of benzo-diaza[4]helicenes, **3a** and **3b**, and two pyridinium derivatives of **3b**, (**3g** and **3h**), are

compared in Table 2. The most striking feature of these benzo-diaza[4]helicenes is that they are planar despite their ortho-fused aromatic ring topology (i.e. they are pseudo-helicenes). Their planarity can be attributed to the polarizable nitrogen lone-pair on N₁ that is sterically less demanding than the hydrogen on C₁ in the diaza[4]helicenes, which adopt a more stable helical geometry. The average B3LYP and M062-X/6-311+G(2d,p) N₁-C₁₂ distances, d_{N₁,12}, in these pseudo helicenes (B3LYP-2.876Å; M06-2X-2.864Å Table 2) are approximately 0.22 Å and 0.23Å shorter than the corresponding average C₁-C₁₂ distances, d_{1,12}, in the diaza[4]helicenes (B3LYP-3.098Å; M06-2X-3.074Å; Table 1). In addition, the N₁---H-C₁₂ distances are shorter than the range given for a modest to weak N---H-C hydrogen bond (N---HC distances 2.5-3.2Å) that exhibit bond strengths of between 1.5 and 4 kcal/mol.²⁷ On the other hand, the B3LYP and M06-2X/6-311+G(2d,p) N--H-C₁₂ angles are between 122° and 127° far from the idealized 180° for the maximum hydrogen bond strength. Nevertheless, a NBO (Natural Bond Orbital) analysis²⁸ of **3a** reveals a second order perturbative interaction energy as a result of donation from N₁ to the acceptor C₁₂-H antibonding NBO of 4.62 kcal/mol, consistent with a hydrogen bond interaction. The unique characters of the hydrogen on C₁₂ in these compounds are manifested in remarkable downfield chemical shifts at 11.45 and 11.28 for **3a** and **3b**, respectively. These unusual chemical shifts were reproduced computationally with the Gauge-Independent Atomic Orbital (GIAO) method²⁹ using the B3LYP (Figure 3) and M06-2X/6-311+G(2d,p) (slope = 0.8422; R² = 0.99019) models.

Table 2. Key B3LYP and M06-2X/6-311+G(2d,p) Structural Features of Benzodiaza[4]helicenes and Alkylated Derivatives.^{a,b}

	3a	3b	3g	3h
Θ□□□□□□□□□□□□□□	0.0(0.0) ^o	0.1(0.0) ^o	0.1(0.0) ^o	0.1(0.7) ^o
Θ□□□□□□□□□□□□□□	0.2(0.0) ^o	0.0(0.0) ^o	0.1(0.0) ^o	0.2(0.7) ^o
d _{12b,12c}	1.466Å (1.466Å)	1.465Å (1.465Å)	1.461Å (1.462Å)	1.459Å (1.460)
d _{N₁,12}	2.889Å (2.880Å)	2.893Å (2.883Å)	2.858Å (2.843Å)	2.862Å (2.850)
d _{N₁,12H}	2.150Å (2.152Å)	2.146Å (2.149Å)	2.084Å (2.083Å)	2.110Å (2.111)
ΘN ₁ H ₁₂ C ₁₂	123.73° (122.79)	124.31° (123.22°)	126.54° (125.36°)	124.74° (123.56)

a. Calculations in the gas phase in the absence of a counterion. b. M06-2X values in parenthesis.

Figure 3. Experimentally observed ¹H NMR versus calculated chemical shifts for **3a**.

Despite our inability to alkylate or protonate the cove-region nitrogen in **3a** or **3b** we were able to locate energy minima corresponding to reaction at this sterically very inaccessible site in **3a**. (Table 3) As anticipated, protonation or alkylation at N₁ converted the planar pseudo-helicene to a non-planar helicene. On the other hand, alkylation or protonation at N₈ does not significantly change the geometry of the pseudo-helicene. The degree of helicity created by reaction at N₁ can best be evaluated by examination of the two dihedral angles, $\theta_{12a,12b,12c,N}$ and $\theta_{12,12a,12b,12c}$, in the cove region of benzo[b]-1,8-diaza[4]helicene. These two dihedral angles shown as the bold fragments in the structures depicted in Table 3 are fundamentally different. $\theta_{12a,12b,12c,N}$ can be viewed as the dihedral angle of a Z,Z-1,3-diene fragment and $\theta_{12,12a,12b,12c}$ as the dihedral angle in a less congested Z-1,3-diene fragment (Table 3). Consequently, $\theta_{12a,12b,12c,N}$ increases substantially with increasing size of the substituent on N₁ in the order lone-pair < H < CH₃ from 0.0°-1.4° to 12.6°-15.9° to 29.4°-30.1°. In contrast, $\theta_{12,12a,12b,12c}$ is very insensitive to the size of R₁ and is found in the very narrow range of 14.9° to 18.2° for both hydrogen and methyl and is similar to the corresponding dihedral angle of 18.6° in [4]helicene. It is also noteworthy that cove dihedral angles in **3e** are smaller than in its carbocyclic analogue [4]helicene. We suggest this change reflects the shorter N-H in **3e** (1.013Å) than the corresponding 1.079Å C-H bond length in **1** (n = 4).

Table 3. B3LYP and M06-2X/6-311+G(2d,p) Cove Region Dihedral Angles.^{a,b,c}

	R ₁	R ₈
3a	●●	●●	0.56(0.02) ^o	0.38(0.02) ^o
3c	CH ₃	●●	29.39(29.63) ^o	15.53(15.22) ^o
3d	●●	CH ₃	1.06(0.00) ^o	1.25(0.00) ^o
3e	H	●●	12.56(13.90) ^o	16.83(17.74) ^o
3f	●●	H	1.37(0.01) ^o	1.12(0.01) ^o
3i	CH ₃	CH ₃	30.08(30.14) ^o	15.69(15.56) ^o
3j	H	CH ₃	14.41(15.88) ^o	17.48(18.18) ^o
3k	CH ₃	H	29.97(30.14) ^o	14.94(14.88) ^o
3l	H	H	14.78(15.78) ^o	16.67(17.32) ^o

a. All calculations are in acetonitrile. b. See the Supplementary Data for the calculated structures in the gas phase. c. M06-2X/6311+G(2d,p) values in parenthesis.

A comparison of the thermally corrected energies of the isomers in Table 3 reveals that addition of both hydrogen and methyl are energetically preferred on N₈ rather than on N₁. (Figure 4) The preference for the least congested N₈ at the B3LYP/6-311+G(2d,p) level is only 2.85 kcal/mol for hydrogen but 13.49 kcal/mol for the larger methyl group. In the bis-substituted dications **3j** and **3k** the isomer with the methyl at N₁ is also less stable by 10.68 kcal/mol. This difference is nearly identical to $\Delta E(\mathbf{3c}/\mathbf{3d}) - \Delta E(\mathbf{3f}/\mathbf{3e}) = 10.64$ kcal/mol. (Figure 4) This suggests that the effect of adding two substituents on the benzo[b]-1,8-diaza[4]helicene backbones are additive (i.e. $E(\mathbf{3j}) = E(\mathbf{3d}) + E(\mathbf{3f})$ and $E(\mathbf{3k}) = E(\mathbf{3c}) + E(\mathbf{3e})$). The same conclusion is reached by examining the M06-2X/6-311+G(2d,p) data with the exception that placing the methyl group on N₁ is 2.2-2.5 kcal/mol less costly. Consequently, there must be no thermodynamic synergistic

interaction between the two substituents. However, exclusive alkylation at N₈ reveals a clear kinetic preference for reaction at the least congested nitrogen.

Figure 4. B3LYP(M06-2X)/6-311+G(2d,p) Energy Differences between Benzo[b]-1,8-diaza[4]helicene Isomers.

The activation barriers for racemizations of several diaza[4]helicenes are given in Table 4. These were determined by taking the difference between the B3LYP or M06-2X/6-311+G(2d,p) optimized ground and transition state structures. The transition structures were located using the synchronous transition-guided quasi-Newton (STQN) method using optimized structures for the enantiomers and both planar³⁰ (C_s) and saddle-like³¹ (C₁ for **3i**) guesses for the transition state geometries. Optimized transition structure, **2j**, was also demonstrated to be the transition state connecting the two enantiomers using an intrinsic reaction coordinate calculation.

Table 4. Diaza[4]Helicene and Benzo[n]-1,8-diaza[4]Helicene Racemization Barriers at the B3LYP and M06-2X/6-311+G(2d,p) levels.^a

$\Delta G_{calc}^{\ddagger}$ ^a (kcal mol ⁻¹) ^b		$\Delta G_{calc}^{\ddagger}$ ^a (kcal mol ⁻¹) ^b	
1	3.4(5.3)	2j	3.3(3.9) ^d
2a	2.2(3.0)	3i	22.2(24.4)
2e	3.1(3.8) ^d		

a. B3LYP/6-311+G(2d,p) model results with M06-2X/6-311+G(2d,p) results in parenthesis. b. Gibbs free energies at 25°C calculated from potential energies and adjusted for zero point energies and thermal corrections. c. (n = 4). d. located using a simple guess at the TS geometry rather than QST3.

The racemization barrier of [4]helicene, **1** (n = 4), decreases by 1.2 kcal/mol and 2.3 kcal/mol using the B3LYP and M06-2X functionals, respectively, when two nitrogens are introduced into the helical framework to give **2a**. Similar, slightly larger, decreases

upon substitution of nitrogen for carbon in [5]helicenes have previously been noted.^{11,32} The nitrogen-induced decrease in the racemization barrier can be attributed to an increase in the H₁-H₁₂ distance in the transition state for **2a** in comparison to **1** using either computational model. (See Table S8 and S18 in the supplementary data for more transition state structural data) However, we cannot rule out a minor contribution from the reduced energetic cost of deforming a pyridine, in comparison to a benzene ring, as a result of the 8 kcal/mol smaller resonance energy in pyridine.³³ Methylation to give **2e** increases the B3LYP barrier by 0.9 kcal/mol and di-methylation to produce **2j** increases it by an additional 0.2 kcal/mol so that the racemization barriers for [4]helicene, **1** (n = 4) and the viologen, N,N'-dimethyl-3,8-diaza[4]helicene **2j** are nearly identical. The transition states for racemizations of **1** (n = 4), **2a**, **2e**, and **2j** are all planar with C_s core symmetry. The angles in the bay region of **2a** (<12,12a,12b; <12a,12b,12c; and <12b,12c,1) open up by approximately 2° to allow the helical structure to collapse into the planar transition state. The distance between hydrogens H₁ and H₁₂ on the terminal rings decrease from 1.980 Å in the P or M enantiomer to 1.594 Å in the transition state. (P and M, respectively, are stereochemical descriptors for right and left-handed helices.) The energy to twist by 20° around the long axis of naphthalene at the B3LYP/6-31G(d) level of theory is only 3.2 kcal/mol.³⁴ Consequently, it is not surprising that the recovered resonance energy obtained by flattening [4]helicenes does not pay for the increased Van der Waals repulsion between H₁ and H₁₂ in the transition states. The 1.594 Å distance between H₁ and H₁₂ in the B3LYP transition structure for racemization of **2j** is well within the sum of the Van der Waals radii of two hydrogens (2.4 Å).³⁵ Replacement of one of the cove C-H₁ or C-H₁₂ groups with an N-CH₃ group as in **3i** destabilizes the planar transition structure to the extent that racemization chooses to occur via a novel saddle-like transition state (Figure 5) with an activation barriers of 22.2 kcal/mol (B3LYP) and 24.4 kcal/mol (M06-2X). The closest approach distance of a N₁CH₃ hydrogen and the cross cove CH₁₂ hydrogen decreases using the B3LYP functional from 2.288 Å in P or M **3i** to 1.758 Å in the saddle-like transition state. (Figure 5) The area of the cove region using the B3LYP functional is substantially larger in the **3i** than in the **2j** P or M enantiomers as revealed by large increases of 2.67°, 5.54°, and 2.11° in angles >12,12a,12b, >12a,12b,12c, and >12b,12c,N₁, respectively. This suggests that helicene **3i** has significantly more strain energy than helicene **2j**.

Figure 5. A Comparison of Two Views of the Planar and Saddle-Like Transition Structures for racemization of **2j** and **2i**, respectively.

2.2 Photophysical Parameters

A photophysical study of **2a-c**, **3a,b** and their viologen and pyridinium homologues has been conducted. Attaching methyls to the carbon framework of **2a** and **3a** and to the carbons of their viologen and pyridinium derivatives had predictable and for the most part minor effects on the photophysics of their core structures. Consequently, in the following discussion we focus on the photophysics of **2a** and **3a** and of their viologen, **2j**, and pyridinium, **3d**, homologues, respectively, and relegate the photophysical parameters of the methylated isomers, **2b,c,k,l**, and **3b,g** to Tables in the Supplementary Material.

The UV-Vis spectra of 3,8-diaza[4]helicene, **2a**, and its dimethyl viologen, **2j**, and of benzo[b]-1,8-diaza[4]helicene, **3a**, and its pyridinium derivative 8-methyl-benzo[b]-1,8-diaza[4]helicene, **3d**, are shown in Figure 6. The spectra for the viologen dication and pyridinium cation are of the same color as their synthetic precursors **2a** or **3a**, respectively, but are depicted with dotted rather than solid lines. The wavelengths of the most bathochromic set of peaks in each compound are depicted in Table 5 along with other photophysical data. Time domain density functional calculations (TD-DFT) using B3LYP, M06-2X, or M11, functionals support assignment of these peaks in **2a** and **3a** (Table 5) to vibrational envelopes of the $S_0 \rightarrow S_1$ transitions. Their spacing of approximately $1300\text{-}1400\text{cm}^{-1}$ corresponds to either a C-H bend or to a C-C/C-N stretch.

Figure 6. UV-Vis spectra in acetonitrile.

TD-DFT calculations (B3LYP, M11, and M062-X/6-311+G(2d,p)) also reveal that the HOMO $\rightarrow$ LUMO determinant is the primary contributor to the excited state density or wavefunction of the $S_0 \rightarrow S_1$ transitions in **2a**, **2j**, **3a**, and **3d**. Consequently, the onsets of the $S_0 \rightarrow S_1$ envelopes in these compounds provide an estimate of the band gaps in these compounds as given in Table 5. The reasonable HOMO/LUMO energy differences provide confirmation of the reliability of this estimate. The optical and calculated band gaps decrease upon dimethylation of **2a** and methylation of **3a** corresponding to 48 and 41 nm alkylation induced red shifts, respectively, of the lowest energy peak in each compound.

Table 5. Photophysical Properties of [4]Helicenes and their Pyridinium and Viologen Derivatives.

	2a	2j	3a	3d
$\lambda_{\text{MAX}}(\text{nm})$	377(0.46 $\pm$ 0.01) ^a 358(0.40 $\pm$ 0.01)	425(0.61 $\pm$ 0.01) ^a 403(0.54 $\pm$ 0.01) 362(0.60 $\pm$ 0.01)	407(0.87 $\pm$ 0.01) ^a 386(0.79 $\pm$ 0.01) 366(0.68 $\pm$ 0.01) 349(0.57 $\pm$ 0.01)	448(0.44 $\pm$ 0.02) ^a 424(0.44 $\pm$ 0.02)
$\lambda_{\text{F}}(\text{nm})$	385(1.0), ^b 404(0.96), 427(0.40)	452	414(1.0), ^b 435(0.98), 459(0.44)	502
$\lambda_{\text{P}}(\text{nm})$	504, 533	584	610(1.0), ^b 666(0.51), 721(0.13)	560
Stokes-shift(cm^{-1} ;eV)	551;0.068	1,405;0.174	415;0.051	2,401;0.300
$\tau_{\text{F}}(\text{ns})$	2.9	6.9	1.4	3.4
$\tau_{\text{P}}(\text{s})$	1.5	0.146	0.094	0.00083
Φ_{F}	0.123 $\pm$ 0.006	0.117 $\pm$ 0.001	0.0027 $\pm$ 0.0001	0.040 $\pm$ 0.002
E(S ₁) (kcal/mol)	75.2 $\pm$ 0.1	65.4 $\pm$ 0.1	69.9 $\pm$ 0.1	61.5 $\pm$ 0.1
E(T ₁) (kcal/mol)	56.7 $\pm$ 0.5	55.0 $\pm$ 2	46.9 $\pm$ 0.1	56.0 $\pm$ 0.1
ΔE_{ST} (kcal/mol)	18.5	10.4	23	5.5
E _{gap} (eV) ^c	3.25(4.07) ^d	2.70(3.34eV) ^d	2.95(3.50) ^d	2.03(2.84) ^d

a. Extinction coefficient in 10⁴M⁻¹cm⁻¹ in CH₃CN. b. Relative Intensity in Parenthesis. c. Optical Band Gap determined by low energy onset of the UV-Vis Spectrum. d. Calculated (B3LYP/6-311+G(2d,p)) Band Gap.

A systematic relationship between the structure, electronic character, and the optical properties of *polyaromatic* hydrocarbons has previously been well-established.³⁶ Consequently, it comes as no surprise that the observed photophysical properties (Table 5) of these *heteropolyaromatic* [4]helicenes are conveniently predicted by comparison to other members of their ortho-annelated diaza[n]series. For example, the long-wavelength bands of [4]helicene **2a** (377 nm) and [4]heli-viologen **2j** (425 nm) are within experimental error the average value of the long-wavelength absorption bands in their 3-aromatic ring (3,8-diazaphenanthrene)³⁷ and 5-aromatic ring (5,10-diaza[5]helicene)¹¹ homologues. (i.e. (3,8-diazaphenanthrene [356 nm]) + (5,10-diaza[5]helicene [397 nm])/2 = 376.5 nm; (N,N-dimethyl-3,8-diazaphenanthrene [387 nm]) + (N, N'-dimethyl-5,10-diaza[5]helicene [465 nm])/2 = 426 nm). The S₀ → S₁ transition in **2j** is also 168 nm (44.0 kcal/mol) bathochromic of the S₀ → S₁ band in methyl viologen, **MV**²⁺. (Figure 1) This shift is consistent with the dramatic decrease in the HOMO-LUMO energy gap (5.41 to 3.34 eV) that occurs as the viologen backbone host is changed from biphenyl to [4]helicene, respectively.

The fluorescence and phosphorescence spectra for **2a** and **3a** and their viologen, **2j**, and pyridinium, **3d**, derivatives, respectively, are given in Figure 7 and serve as signatures for the population of both singlet and triplet excited states. The singlet energies were determined from the crossing points of intensity normalized fluorescence and absorption spectra. Triplet energies were determined from the highest energy (0-0) vibronic peak in the phosphorescence spectrum (e.g. **3a** Figure 7) or from the high-energy onset of the phosphorescence peak if the peak lacked vibronic fine structure or was too noisy.

The singlet triplet energy gaps, ΔE_{ST} , of the uncharged bipyridines **2a** and **3a** are significantly larger than for their charged counterparts **2j** and **3d**. The decrease in ΔE_{ST} of more than a factor of 4 upon alkylation of **3a** is very evident from the very large difference in the fluorescence-phosphorescence spectral wavelength separation for **3a** and **3d** (Figure 7). ΔE_{ST} for **2j** (10.4 kcal/mol) is also unusually small when compared to other molecules with $\pi\pi^*$ electronic character. For example, ΔE_{ST} for many planar polyaromatic hydrocarbons are between 20 and 30 kcal/mol.³⁸ From a theoretical perspective ΔE_{ST} is equal to twice the electron exchange energy J (Eqn. 1).³⁹ E_0^* is the Hartree-Fock one-electron orbital energy devoid of any electron correlation. K is the coulomb energy due to electron-electron correlation and J is the exchange energy. Conceptually J is also electron-electron correlation energy and can be thought of as a correction for the Pauli exclusion principle. In a $(\pi\pi^*)^1$ electronic state the electrons in the π and in the π^* orbitals can closely approach one another and J increases the energy of the singlet. (Eqn. 1) In a $(\pi\pi^*)^3$ the Pauli exclusion principle prevents close approach of the two electrons and J lowers the energy of the triplet. (Eqn. 1) Consequently, J is very small for **2j** (i.e. $\Delta E_{ST} = 10.4$ kcal/mol = $2J$; $J = 5.2$ kcal/mol). The mechanism for this charge-induced decrease of electron-electron correlation is not known with certainty and will require further theoretical analysis.⁴⁰ However, it is tempting to suggest that the attractive interaction between an electron and the charged molecular framework effectively *localizes* the electron by charge transfer and diminishes the average electron-electron repulsion energy. Charge transfer excited states are known to have smaller than expected singlet-triplet energy gaps.⁴⁰ This potentially useful effect may be a general phenomenon since unexpectedly small ΔE_{ST} are also observed for cation **3d** (5.5 kcal/mol) and for viologen dications N,N'-dimethyl-5,10-diaza[5]helicene (5.3 kcal/mol)⁴¹ and several 3,8-diazaphenanthrenes (0.3-4.0 kcal/mol).³⁷

$$\Delta E_{ST} = E_{S1} - E_{T1} = (E_0^* + K + J)_{S1} - (E_0^* + K - J)_{T1} = 2J \quad 1$$

Figure 7. Fluorescence Spectra in CH_3CN at Room Temperature and Phosphorescence Spectra at -196°C in ethanol glass.

3. Conclusion

The syntheses and photophysical properties of the first examples of [4]heli-viologens and their helical precursors have been reported. In addition, the syntheses of two new diaza-aromatics, **3a** and **3b**, with the ortho-fused aromatic ring topologies that were expected to produce helical structures have been reported. Dialkylation of these compounds did not occur even under forcing conditions (e.g. elevated pressure, high temperatures, and microwave irradiation). Computational studies demonstrated that these compounds are planar “pseudo-helicenes” with one nitrogen in a highly congested location that resists alkylation. Photophysical studies revealed that alkylation resulting in an unexpected decrease in the singlet-triplet energy gap, ΔE_{ST} , is a more general phenomenon than we had realized when we first encountered it during a study of the heli-viologen, N,N'-dimethyl-5,10-diaza[5]helicene.¹¹ This observation is potentially important because of the role that ΔE_{ST} plays in diverse phenomenon such as triplet-triplet annihilation,⁴² intersystem crossing,⁴³ delayed fluorescence,⁴⁴ and singlet fission.⁴⁵⁻

⁴⁷ These processes play critical roles in many optoelectronic applications and as a consequence considerable effort has been devoted to controlling the size of ΔE_{ST} .⁴⁸

4. Experimental Section

4.1 General Information

Computational investigations were done using the Gaussian 03/09 programs. (See supporting information). Geometry optimizations were conducted using the B3LYP/6-311+G(2d,p), M06-2X/6-311+G(2d,p), and M11/6-311+G(2d,p) computational models and the character of all stationary points were verified using frequency calculations. Calculations in acetonitrile were accomplished using the polarizable continuum model and polarizable conductor calculations. Emission spectra were collected in acetonitrile by irradiation into the $S_0 \rightarrow S_1$ absorption band using excitation and emission slit widths of 5 or 10 nm. Fluorescence quantum yields were measured with diphenylanthracene ($\Phi = 0.90$) as the standard.⁴⁹ Fluorescence lifetimes were measured using a pulsed 340 nm LED lamp in conjunction with a 400 nm cutoff filter. The instrument response function was determined using a dilute colloidal silica solution. High resolution mass spectra were produced using TOF-TOF-MALDI.

4.2 Fluorescence Quantum Yield Measurements

The fluorescence quantum yields were determined by plotting the integrated fluorescence intensity as a function of wavelength at 5 or more concentrations versus the measured absorbance (kept at < 0.015 absorbance units). This is done for both the helicene and for the standard diphenyl anthracene. This then gives two slopes that are used with the following equation, where n is the refractive index of the solvent used and ST is 9,10-diphenylanthracene, to give the quantum yield of fluorescence for the helicene. This is then repeated 2 or more times to give the reported fluorescence quantum yields in Table 5.

$$\Phi_{\text{helicene}} = \Phi_{ST} \left(\frac{\text{Slope}_{\text{helicene}}}{\text{Slope}_{ST}} \right) \left(\frac{n_{\text{helicene}}^2}{n_{ST}^2} \right)$$

This graphical method is very accurate despite the differences in the quantum yields of the helicene and standard (i.e. 0.9 vs. 0.1) and allows use of 9,10-diphenylanthracene, which has both its excitation and emission wavelength very close to the helicenes.

4.3 Synthesis

(E)-1-(3-Pyridyl)-2-(3-quinolinyl)-ethene (4; $R_2 = R_{11} = H$).^{20,21} Triethoxyvinylsilane (0.77 mL, 3.54 mmol), 3-bromopyridine (0.178 mL, 1.78 mmol), 2.14 g of PEG 2000, and palladium(II) acetate (0.4 mg, 1.8 μ mol) were added to a 50 mL pressure containing 10 mL of 0.50 M aqueous sodium hydroxide. The mixture was warmed at 150°C for 3 hours. Subsequently, the mixture was cooled to room temperature and 3-bromoquinoline (0.247 mL, 1.78 mmol) and palladium(II) acetate (0.4 mg, 1.8 μ mol) were added and then warmed and stirred at 150°C for an additional 12 hours. The mixture was then extracted with ethyl acetate (3 $\times$ 30 mL). The organic layer was combined and dried over MgSO₄. The solvent was removed under reduced pressure. The residue was triturated in ethyl acetate and then dried in a vacuum for 12 hours. Yield: 0.330 g (1.42 mmol, 80%). ¹H NMR (400 MHz, CDCl₃): δ 9.14 (d, 1H, J = 2.3Hz), 8.81 (d, 1H, J = 2.0Hz), 8.55 (dd, 1H, J = 1.5, 4.6Hz), 8.22 (d, 1H, J = 2.0Hz), 8.11 (d, 1H, J = 8.5Hz), 7.91 (d, 1H, J = 8.0Hz with additional long range unresolvable coupling), 7.85 (d, 1H, J = 8.0Hz), 7.72 (dd, 1H, J = 7.4, 7.4Hz), 7.57 (dd, 1H, J = 7.4, 7.4Hz), 7.34 (dd, 1H, J = 4.9, 8.0Hz), 7.32(s, 2H).

(E)-1-(3-Pyridyl)-2-(6-methyl-3-quinolinyl)-ethene (4; $R_2 = H$, $R_{11} = CH_3$). Triethoxyvinylsilane (0.77 mL, 3.54 mmol), 3-bromopyridine (0.178 mL, 1.78 mmol), 2.14 g of PEG 2000, and 1 mg of Pd(OAc)₂ were added to 11 mL of 0.5 M aqueous NaOH in a pressure vessel and warmed at 140°C for 8 hours. The mixture was then cooled to room temperature and 3-bromo-6-methylquinoline, (394 mg, 1.78 mmol), and 1mg of Pd(OAc)₂ were added and heated at 140°C for an additional 12 hours. The solid was then filtered, washed with water (3 $\times$ 10 mL) and dried in a vacuum for 12 hours. Yield: 332 mg (1.35 mmol, 76%). ¹H NMR (400 MHz, CDCl₃): δ 9.08 (s, 1H), 8.82 (s, 1H), 8.56 (d, 1H, J = 4.5Hz), 8.14 (s, 1H), 8.01 (d, 1H, J = 8.6Hz), 7.92 (d, 1H, J = 8.5Hz), 7.62 (s, 1H), 7.56 (d, 1H, J = 8.6Hz), 7.36 (m, 2H), 7.31 (s, 1H), 2.58 (s, 3H).

(E)-1-(4-Methyl-3-pyridyl)-2-(3-quinolinyl)-ethene (4; $R_2 = CH_3$, $R_{11} = H$). Triethoxy(vinyl)silane (1.54 mL, 7 mmol), 4.28 g of PEG 2000, 6-methyl-3-bromopyridine (0.62 g, 3.56 mmol), and palladium(II) acetate (0.8 mg, 3.6 μ mol) were added to 21.4 mL of aqueous 0.50 M sodium hydroxide. The mixture was warmed at 150°C for 5 hours. Subsequently, 3-bromoquinoline (0.5 mL, 3.56 mmol) and palladium(II) acetate (0.4 mg, 1.8 μ mol) were added and the mixture warmed at 150°C for an additional 12 hours. The mixture was then extracted with ethyl acetate (3 $\times$ 50 mL). The organic layer was combined and dried over MgSO₄ and the solvent removed under reduced pressure. The residue was triturated in ethyl acetate and then dried in a vacuum for 12 hours. Yield: 0.664 g (2.71 mmol, 76%). ¹H NMR (400 MHz, CDCl₃): δ 9.15 (s, 1H), 8.70 (s, 1H), 8.22 (s, 1H), 8.12 (d, 1H, J = 8.6Hz), 7.85 (m, 2H), 7.72 (dd, 1H, J = 8.2, 7.2Hz), 7.53 (dd, 1H, J = 8.0, 7.3Hz), 7.30 (m, 2H), 7.22 (d, 1H, J = 8.4Hz), 2.62 (s, 3H).

3,8-Diaza[4]helicene (2a). (E)-1-(3-Pyridyl)-2-(3-quinolinyl)-ethene (4; $R_2 = R_{11} = H$) (330 mg, 1.42 mmol)^{20,21} was dissolved in 300 mL of ethyl acetate and irradiated with

UV light for 48 hours. After the solvent was removed, the residue was purified by column chromatography (eluent was ethyl acetate). Yield: 136 mg (0.58 mmol, 41%). ¹H NMR (400 MHz, CDCl₃): δ 9.42 (s), 9.35 (s), 8.99 (d, 1H, J = 8.4Hz), 8.88 (d, 1H, J = 6.0Hz), 8.82 (d, 1H, J = 6.0Hz), 8.34 (d, 1H, J = 8.2Hz), 8.06 (d, 1H, J = 8.5Hz), 8.01 (d, 1H, J = 8.5Hz), 7.81-7.87 (m, 1H), 7.73-7.80 (m, 1H). ¹³C NMR (400MHz, CDCl₃): δ 152.9, 152.5, 146.6, 145.2, 132.9, 130.7, 129.4, 129.3, 128.9, 127.6, 127.3, 126.9, 126.8, 126.0, 124.3, 120.4. HRMS (TOF/TOF MALDI) m/z: [M]⁺ Calcd for C₁₆H₁₁N₂ 231.0922; Found 231.0947.

11-Methyl-3,8-diaza[4]helicene (2b). (E)-1-(3-Pyridyl)-2-(6-methyl-3-quinolinyl)-ethene (**4**; **R**₂ = **H**, **R**₁₁ = **CH**₃) (80 mg, 0.33 mmol) was dissolved in 100 mL of ethyl acetate and irradiated with UV light for 24 hours. The solvent was then removed under reduced pressure and the residue was purified by column chromatography (eluent was ethyl acetate). Yield: 39 mg (0.16 mmol, 48%). ¹H NMR (400MHz, CDCl₃): δ 9.47 (s, 1H), 9.35 (s, 1H), 9.00 (d, 1H, J = 6.1Hz), 8.88 (m, 2H), 8.26 (d, 1H, J = 8.4Hz), 8.13 (d, 1H, J = 8.5Hz), 8.08 (d, 1H, J = 8.5Hz), 7.70 (dd, 1H, J = 8.4, 1.6Hz), 2.73 (s, 3H). ¹³C NMR (400 MHz, CDCl₃): δ 152.9, 151.6, 145.2, 145.1, 137.8, 133.1, 130.7, 130.5, 129.4, 129.0, 127.1, 127.0, 126.9, 125.6, 124.4, 120.5, 22.3. HRMS (TOF/TOF MALDI) m/z: [M]⁺ Calcd for C₁₇H₁₃N₂ 245.1079; Found 245.1082.

2-Methyl-3,8-diaza[4]helicene (2c). (E)-1-(6-Methyl-3-pyridyl)-2-(3-quinolinyl)-ethene (**4**; **R**₂ = **CH**₃, **R**₁₁ = **H**) (0.664 g, 2.71 mmol) was dissolved in 700 mL of ethyl acetate and irradiated with UV light for 24 hours. The solvent was then removed under reduced pressure and the residue purified by column chromatography (eluent was ethyl acetate : hexane = 5:1). Yield: 251 mg (1.05 mmol, 39%). ¹H NMR (400MHz, CDCl₃): δ 9.40 (s, 1H), 9.39 (s, 1H), 9.11 (d, 1H, J = 8.2Hz), 8.85 (s, 1H), 8.36 (d, 1H, J = 8.2Hz), 8.10 (d, 1H, J = 8.8Hz), 8.02 (d, 1H, J = 8.8Hz), 7.85 (m, 2H), 2.91 (s, 3H). ¹³C NMR (400 MHz, CDCl₃): δ 154.7, 152.9, 152.6, 147.0, 134.0, 131.0, 129.4, 128.9, 127.8, 127.7, 127.6, 127.4, 126.4, 126.0, 124.8, 119.2, 25.2. Calculated for C₁₇H₁₂N₂ 83.58% C, 4.95% H, 11.47% N. Found 82.16% C, 5.03% H, 11.04% N.

N,N'-Dimethyl-3,8-diaza[4]helicene bis-tetrafluoroborate (2j). 3, 8-Diaza[4]helicene (**2a**) (100 mg, 0.435 mmol) was dissolved in 50 mL of dry dichloromethane. Trimethyloxonium tetrafluoroborate (193mg, 1.30 mmol) was then added. The mixture was stirred under nitrogen for 24 hours. The precipitate was filtered and washed with ethanol. It was then recrystallized from an acetonitrile and ether mixture (5:1). The yellow solid was then dried in vacuum. Yield: 105 mg (0.24 mmol, 56%). ¹H NMR (400 MHz, CD₃CN): δ 10.04(s, 1H), 9.88(s, 1H), 9.62(d, 1H, J = 7.0Hz), 9.29(d, 1H, J = 8.4Hz), 8.88(d, 1H, J = 7.2Hz), 8.70(m, 3H), 8.42(t, 1H, J = 7.3Hz), 8.36(t, 1H, J = 7.0Hz), 4.84(s, 3H), 4.66(s, 3H). ¹³C NMR (400 MHz, CD₃CN): δ 155.1, 151.7, 140.4, 137.9, 136.0, 135.4, 135.1, 133.6, 133.5, 132.4, 131.5, 129.9, 129.1, 128.8, 127.3, 121.6, 50.3, 48.3. Calculated for C₁₈H₁₆B₂F₈N₂, 49.82% C, 3.72% H, 6.46% N. Found 49.72% C, 3.72% H, 6.57% N.

11-Methyl-N,N'-dimethyl-3,8-diaza[4]helicene bis-tetrafluoroborate (2k). 11-Methyl-3,8-diaza[4]helicene (**2b**) (39 mg, 0.16 mmol) was dissolved in 10 mL of dry dichloromethane. Trimethyloxonium tetrafluoroborate (94 mg, 0.64 mmol) was then added. The mixture was stirred under nitrogen for 24 hours. The precipitate was filtered and washed with ethanol. The yellow solid was then dried in vacuum. Yield: 50 mg (0.11 mmol, 70%). ¹H NMR (400 MHz, CD₃CN): δ 9.91(s, 1H), 9.83(s, 1H),

9.64(d, 1H, J = 7.3Hz), 9.03(s, 1H), 8.85(d, 1H, J = 7.1Hz), 8.65(m, 2H), 8.56(d, 1H, J = 8.9Hz), 8.23(d, 1H, J = 8.9Hz), 4.78(s, 3H), 4.64(s, 3H), 2.85(s, 3H). ¹³C NMR (400 MHz, CD₃CN): δ 153.8, 151.6, 145.4, 140.3, 137.0, 136.3, 136.0, 134.5, 133.4, 132.4, 131.3, 129.2, 128.9, 128.8, 127.4, 121.3, 50.2, 48.2, 22.4. HRMS (TOF/TOF MALDI) m/z: [M]⁺ Calcd for C₁₉H₁₈N₂ 274.1470; Found 274.1494.

2-Methyl-N,N'-dimethyl-3,8-diaza[4]helicene bis-tetrafluoroborate (2l). 2-Methyl-3,8-diaza[4]helicene (**2c**) (244 mg, 1 mmol) was dissolved in 30 mL of dry dichloromethane. Trimethyloxonium tetrafluoroborate (441 mg, 3 mmol) was then added. The mixture was stirred under nitrogen for 7 days. The yellow precipitate was filtered and washed with ethanol (2 × 5 mL), acetonitrile (1 × 2 mL), and methanol (2 × 5 mL). It was then dried under a vacuum. The product was a mixture of 2-methyl-N,N'-dimethyl-3,8-diaza[4]helicene bis-tetrafluoroborate (**9**) and the mono-methylated adduct 2,8-dimethyl-3,8-diaza[4]helicene tetrafluoroborate (5:1). Yield: 259mg (216 mg of **9** (48%) and 43 mg of 2,8-dimethyl-3,8-diaza[4]helicene tetrafluoroborate (10%)). ¹H NMR of **9** (400 MHz, CD₃CN): δ 9.99(s, 1H), 9.85(s, 1H), 9.45(s, 1H), 9.37(d, 1H, J = 8.4Hz), 8.68 (d, 1H, J = 8.5Hz), 8.61(m, 2H), 8.39(m, 2H), 4.83(s, 3H), 4.52(s, 3H), 3.08 (s, 3H). HRMS (TOF/TOF MALDI) m/z: [M]⁺ Calcd for C₁₉H₁₈N₂ 274.1470; Found 274.1504.

(E)-1,2-Di(quinolin-3-yl)ethene (5, R = H).²¹ Triethoxy(vinyl)silane (0.4 mL) was added to a 100 mL pressure vessel containing 15 mL of 0.5 M aqueous of sodium hydroxide followed by 3-bromoquinoline (0.416 mL, 3.0 mmol) and palladium(II) acetate (2.0 mg, 9 μmol). The vessel was then sealed and warmed at 140°C for 3-5 hours. When the reaction cooled to room temperature, the green precipitate was filtered and washed with ethyl acetate/chloroform 10:1. The yellow solid was then dried in vacuum. Yield: 0.38 g (2.7 mmol, 91%). ¹H NMR (400 MHz, CDCl₃): δ 9.20(d, 2H, J = 2.1Hz), 8.26(d, 2H, J = 2.1Hz), 8.11(d, 2H, J = 8.4Hz), 7.86(d, 2H, J = 7.9Hz), 7.72(ddd, 2H, J = 8.4, 7.0, 1.5Hz), 7.58(ddd, 2H, J = 8.1Hz, 6.8Hz, 0.9Hz), 7.48(s, 2H).

(E)-1,2-bis(6-methylquinolin-3-yl)ethene (5, R = CH₃). 6-Methyl-3-bromoquinoline (2.5 g, 11.3 mmol), triethoxyvinylsilane (1.56 mL, 7.1 mmol), and 5 mg of palladium(II) acetate were added to 60 mL of 0.5 M aqueous NaOH and heated in a sealed 100 mL pressure vessel at 140°C for 6 hours. After the reaction was cooled down to room temperature, the yellow precipitate was filtered and washed with water (3 × 50 mL) and ether (3 × 30 mL) and then dried in vacuum. Yield: 1.16g (3.73 mmol, yield 65%). ¹H NMR (400 MHz, CDCl₃): δ 9.14(d, 2H, J = 2.2Hz), 8.18(d, 2H, J = 2.2Hz), 7.99(d, 2H, J = 8.5Hz), 7.64(s, 2H), 7.57(dd, 2H, J = 8.6, 1.9Hz), 7.47(s, 2H), 2.59(s, 6H).

Benzo[b]-1,8-diaza[4]helicene (3a, R = H). (E)-1,2-Di(quinolin-3-yl)ethane (**5, R = H**) (0.282 g, 1.0 mmol) was dissolved in ethyl acetate (150 mL) in a Pyrex vessel open to air. The solution was irradiated with UV light for 24 hours. The irradiation was then stopped and the solvent was removed under reduced pressure. The residue was purified by column chromatography (eluent was ethyl acetate : hexane = 5:1) to give two products 5,10-diaza[5]helicene (**6, R = H**)³⁹ in 66% yield (0.66 mmol) and (**3a, R = H**) in 10% yield (0.10 mmol). Benzo[b]-1,8-diaza[4]helicene (**3a, R = H**) was further purified by recrystallization from acetone to provide the following structural data. ¹H NMR (400 MHz, CDCl₃): δ 11.45 (d, 1H, J = 8.5Hz), 9.45 (s, 1H), 8.87 (s, 1H), 8.58 (d, 1H, J = 8.6Hz), 8.35 (d, 1H, J = 8.2Hz), 8.11 (m, 2H), 7.85-8.01 (m, 4H), 7.70 (dd, 1H, J =

7.4, 7.3Hz). ^{13}C NMR (400 MHz, CDCl_3): δ 152.5, 148.4, 148.3, 147.7, 147.6, 136.3, 130.6, 130.5, 130.4, 130.3, 129.0, 128.6, 128.3, 128.0, 127.8, 127.7, 127.4, 126.7, 126.1, 126.0. Calculated for $\text{C}_{20}\text{H}_{12}\text{N}_2$: 85.69% C, 4.31% H, 9.99% N. Found: 85.52% C, 4.47% H, 9.83% N.

4-Methylbenzo[b]-11-methyl-1,8-diaza[4]helicene (3b, R = CH₃). (E)-1,2-bis(6-methylquinolin-3-yl)ethene (**5**, R = CH₃) (1 g, 3.2 mmol) was dissolved in 1 L of ethyl acetate and irradiated with UV light for 48 hours through a Pyrex filter. The solvent was then removed under reduced pressure and the residue purified by column chromatography (eluent was ethyl acetate : hexane = 3:1). Two products were isolated i.e. 4-methylbenzo[b]-11-methyl-1,8-diaza[4]helicene (**5**, R = CH₃) and 2,13-dimethyl-5,10-diaza[5]helicene (**6**, R = CH₃). Yield of (**3b**, R = CH₃): 585mg (1.9 mmol, 59%). Yield of 2,13-dimethyl-5,10-diaza[5]helicene (**6**, R = CH₃) : 117 mg (0.38 mmol, 12%). 3-methylbenzo[b]-11-methyl-1,8-diaza[4]helicene (**3b**, R = CH₃), ^1H NMR (400 MHz, CDCl_3): δ 11.28(s, 1H), 9.37(s, 1H), 8.75(s, 1H), 8.44(d, 1H, J=8.6Hz), 8.22(d, 1H, J=8.3Hz), 8.06(d, 1H, J=8.6Hz), 7.95(d, 1H, J=8.9Hz), 7.85(s, 1H), 7.79(dd, 1H, J=8.8, 1.2Hz), 7.70(dd, 1H, J= 8.4, 1.2Hz), 2.81(s, 3H), 2.69(s, 3H). ^{13}C NMR (400 MHz, CDCl_3): δ 151.3, 147.4, 146.6, 145.8, 137.7, 136.9, 134.6, 132.9, 130.4, 129.7 (2C), 129.6, 129.3, 128.0, 127.4, 127.3, 126.3, 125.8, 125.6, 125.5, 22.6, 21.9. Calculated for $\text{C}_{22}\text{H}_{16}\text{N}_2$ 85.69% C, 5.23% H, 9.08% N. Found 85.56% C, 5.33% H, 9.03% N. 2,13-Dimethyl-5,10-diaza[5]helicene (**6**, R = CH₃), ^1H NMR (400 MHz, CDCl_3): δ 9.41(s, 2H), 8.55(s, 2H), 8.20(d, 2H, J=8.4Hz), 8.12(s, 2H), 7.62(dd, 2H, J=8.4, 1.5Hz), 2.46(s, 6H).

8-Methyl-benzo[b]-1,8-diaza[4]helicene tetrafluoroborate (3d). Trimethyloxonium tetrafluoroborate (147 mg, 1.0 mmol) was added to 30 mL of CHCl_3 under a nitrogen atmosphere. DBU (1,8-diazabicycloundec-7-ene; 151 mg, 0.78 mmol) was then added. The mixture was stirred for 10 minutes before the addition of benzo[b]-1,8-diaza[4]helicene (**3a**, R =H) (93 mg, 0.33 mmol) and then for an additional 4 hours under a nitrogen atmosphere. The yellow precipitate was filtered and washed with a 1:1 mixture of ethanol and acetonitrile (3×5 mL). It was then dried in a vacuum overnight. Yield: 114 mg (0.30 mmol, 90%). ^1H NMR (400 MHz, CD_3CN): δ 11.89 (dd, 1H, J = 8.7, 1.7Hz), 9.84 (s, 1H), 9.29 (s, 1H), 8.66 (dd, 1H, J = 8.8, 0.8Hz), 8.56 (dd, 1H, J = 8.5, 1.1Hz), 8.50 (d, 1H, J = 9.0Hz), 8.27-8.38 (m, 3H), 8.23 (d, 1H, J = 8.9Hz), 8.12 (ddd, 1H, J = 8.9, 7.1, 1.4Hz), 7.91 (ddd, 1H, J = 8.5, 7.1, 1.0Hz), 4.77 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 153.4, 147.8, 145.0, 138.2, 138.0, 136.0, 133.4, 132.4, 132.2, 131.5, 131.3, 130.9, 129.7, 129.0, 128.3, 126.9, 126.8, 126.4, 125.1, 119.6, 46.3. HRMS (TOF/TOF MALDI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{21}\text{H}_{15}\text{N}_2$ 295.1235; Found 295.1256.

4-Methylbenzo[b]-8,11-dimethyl-1,8-diaza[4]helicene tetrafluoroborate (3g). of Trimethyloxonium tetrafluoroborate (115 mg, 0.78 mmol) was added to 20 mL of CHCl_3 under a nitrogen atmosphere. DBU (1,8- diazabicycloundec-7-ene) (118 mg, 0.78 mmol) was then added and the mixture stirred for 10 min. before addition of 4-methylbenzo[b]-11-methyl-1,8-diaza[4]helicene (**3b**, R = CH₃) (80 mg, 0.26 mmol). The mixture was stirred under nitrogen for an additional 4 hours. The yellow precipitate was filtered and washed with a 1:1 mixture of ethanol and acetonitrile (3×5 mL). It was then dried in a vacuum overnight. 70 mg of compound (**3g**, R = CH₃) was collected. Yield: 70 mg (0.51 mmol, 66%). ^1H NMR (400 MHz, CD_3CN): δ 11.66(s, 1H), 9.70(s,

1H), 9.08(s, 1H), 8.49(d, 1H, J = 8.6Hz), 8.41 (m, 2H), 8.15(d, 1H, J = 9.0Hz), 8.11(d, 1H, 9.0Hz), 8.05(s, 1H), 7.96(d, 1H, J = 9.0Hz), 4.72(s, 3H), 2.90(s, 3H), 2.70(s, 3H). ¹³C NMR (600 MHz, DMSO-d₆): δ 151.2, 145.8, 143.4, 140.8, 138.8, 135.8, 134.3, 133.6, 133.5, 131.9, 130.9, 129.8, 128.7, 128.4, 126.2, 126.0, 125.8, 125.5, 124.4, 118.7, 45.9, 21.7, 21.5. HRMS (TOF/TOF MALDI) m/z: [M]⁺ Calcd for C₂₃H₁₉N₂ 323.1548; Found 323.1568.

Acknowledgement. We thank the National Science Foundation (CHE-1147542) for their generous support of this research.

Supplementary Data. Supplementary data related to this article can be found at <http://dx.doi.org/>. These data include computational details, fluorescence, absorption, and phosphorescence spectra, ¹³C and ¹H NMR spectra, photophysical properties for **2b**, **2c**, **2k**, **2l**, **3b**, and **3j**.

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Graphical Abstract

Synthesis, computational, and photophysical characterization of diaza-embedded [4]helicenes and their pyridinium and viologen homologues.

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