JOC The Journal of Organic Chemistry

ARTICLE

pubs.acs.org/joc

Synthesis and Study of Redox-Active Acyclic Triazenes: Toward Electrochromic Applications

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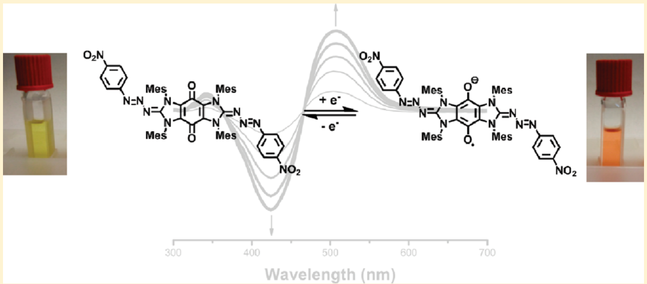
S Supporting Information

ABSTRACT: Coupling of various 4-substituted phenyl azides with two distinct quinone-containing N-heterocyclic carbenes (NHCs) afforded the respective mono- and ditopic 1,3-disubstituted acyclic triazenes in moderate to excellent yields (38−92%). Depending on their pendant substituents (derived from the azides), the acyclic triazenes exhibited intense absorptions in the visible spectrum (359−428 nm), which were bathochromically shifted by up to $\Delta\lambda$ = 68 nm upon reduction of the quinone moiety on the component derived from the NHC. Cyclic voltammetry confirmed that the aforementioned redox processes were reversible, and a related set of UV−vis spectroelectrochemical experiments revealed that bulk electrolysis may also be used to switch reversibly the colors exhibited by these triazenes.



INTRODUCTION

Electrochromic materials—materials which reversibly change their colors in response to electrochemical switching[1]—are currently of great interest for their potential utility in applications ranging from color-changing displays and windows to protective eyewear and data storage devices. While a majority of the systems in use are based on inorganic materials,[2] which inherently present challenges in processing and modification, it has been proposed that organic analogues may overcome many of these issues and enable the realization of viable alternatives.[1,3] Numerous electrochromic organic molecules have been reported to date; well-known examples include members of the viologen family,[1,4] polyanilines,[5,6] poly(3,4-ethylenedioxythiophene),[7−9] and appropriately functionalized bipyrrolic species.[10,11] However, many of these systems suffer from various drawbacks, including complicated and tedious syntheses and, in some cases, limited electrochemical stability. Hence, there remains a demand for new classes of electrochromic organic motifs that are readily accessible, feature tunable electronic and/or structural components, and exhibit reversible electrochemical behavior.

With the above needs in mind, we have focused recently on the development of new electrochromic systems derived from N-heterocyclic carbenes (NHCs).[12,13] This interest was motivated in part by our general interest in using NHCs to address outstanding challenges in the field of materials chemistry.[14,15] For example, we discovered that new classes of highly fluorescent polymers may be prepared by combining bis(NHC)s with complementary ditopic organic azides.[16] The aforementioned polymerization process utilizes the NHC/azide coupling reaction to afford acyclic triazenes (see Figure 1). Attractive features of this reaction include good yields of product, perfect atom economy, and high functional group tolerance.[17] Moreover, the acyclic triazene products have been found to exhibit high thermal stabilities and intense absorption bands in the visible spectrum (λ_{max} 364−450 nm; $\varepsilon \approx 10^4$ L mol^{-1} cm^{-1}).[18a] It was also demonstrated by experiment[19] and later confirmed by theory[20] that the electronic delocalization across the triazene linkage in these substrates was efficient and that their absorption characteristics could be tuned by installing functional groups onto the NHC and/or azide components.

In parallel with the study of the NHC/azide coupling reaction, we have also recently reported a series of quinone-annulated NHCs, NqMes (**1**)[21] and QBI (**2**),[22] featuring naphthoquinone and quinone functional groups, respectively (Figure 2). These electroactive NHCs were found to form stable complexes with a number of transition metals and enabled redox-switchable electronic communication between the two components.[23,24] We have since demonstrated that these characteristics may be harnessed to tune the catalytic properties of the coordinated metals[25] and to support ion-mediated electron transfer reactions within supramolecular host−guest ensembles.[26]

Received: January 20, 2011
Published: March 22, 2011

Building on the features intrinsic to the aforementioned systems (i.e., variable optical properties and reversible electrochemistry), we reasoned that redox-active triazenes prepared through NHC/azide coupling chemistry involving NqMes or QBI could find use in the preparation of electrochromic materials. Moreover, we expected that the high nitrogen content of the triazenes produced from these reactions would enhance their molar absorptivities[18] and that materials incorporating subunits such as **1** and **2** would prove electroactive. Herein, we describe the synthesis of a series of acyclic triazenes derived from two different redox-active NHC scaffolds and provide details of their thermal, optical, and electrochemical properties. On the basis of the results presented in this report, we conclude that these materials hold potential for application in a wide range of electrochromic devices.

RESULTS AND DISCUSSION

To explore the influence of aryl substitution on the absorption properties of the corresponding triazenes, a variety of electron-deficient and electron-rich para-substituted phenyl azides were selected as coupling partners for the quinone-containing NHCs mentioned above.[18] Treatment of **1** or **2** with an excess of various para-substituted aryl azides **3a**−**f** in THF afforded triazenes **4a**−**f** and **5a**−**c** in moderate to excellent yields (38−92%, Scheme 1). The NMR spectroscopic data recorded for **4** and **5** were consistent with those reported for other ylidene-triazenes.[18,20,22] Key spectral features include diagnostic upfield shifts in the ^{13}C NMR signals assigned to the carbene carbon atoms at the 2- (or 2,2′-) position(s) (e.g., **4**, δ 174.3−174.4; **5**, δ 165.2−165.7; CD_2Cl_2) relative to those recorded for **1** or **2**, respectively (i.e., **1**, δ 231.7, C_6D_6; **2**, δ 232.6, THF-d_8). Collectively, these findings are consistent with the loss of carbenoid character upon NHC/azide coupling.

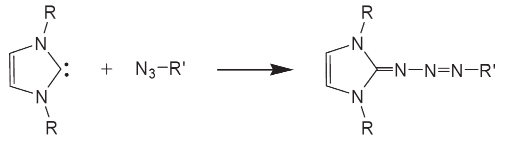
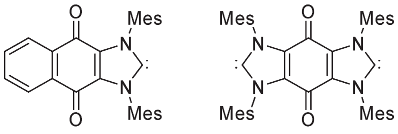


Figure 1. Triazene formation via coupling of an NHC with an azide.



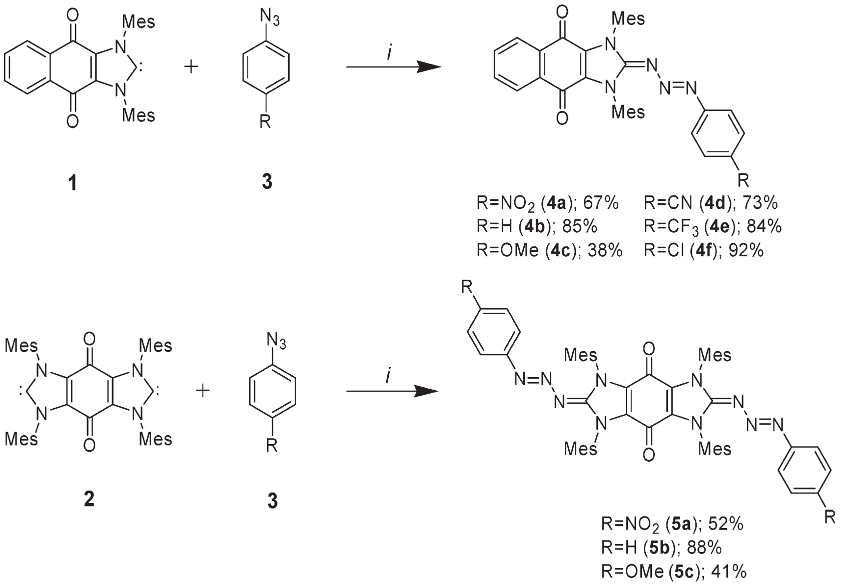
NqMes (**1**) QBI (**2**)

Figure 2. Redox-active N-heterocyclic carbenes. Mes = 2,4,6-trimethylphenyl.

With the aforementioned triazenes in hand, their thermal stabilities were evaluated by thermogravimetric analysis (TGA). Despite their relatively high nitrogen content, triazenes **4** and **5** exhibited high thermal stabilities, with decomposition temperatures (defined as the temperature at which a 5% loss in mass was observed) ranging from 257 up to 302 °C. It has previously been shown that other NHC-containing triazenes with bulky N substituents (e.g., mesityl) also show high thermal stabilities and that their decomposition proceeds through loss of dinitrogen to afford the respective guanidines.[16,18] However, the initial mass loss observed in **4** and **5** upon heating did not correspond to loss of N_2, leading us to suggest that competing decomposition processes may be operative at elevated temperatures in the case of these compounds.

The optical properties of **4** and **5** were next evaluated using UV−vis spectroscopy. In general, the triazenes exhibited intense absorptions ($\varepsilon = 3.2 \times 10^4$−$6.9 \times 10^4$ L mol^{-1} cm^{-1}) in the 300−500 nm spectral range with minor features observed between 500 and 600 nm (Table 1). Weaker, lower-energy absorptions were also observed around 550 nm and were attributed to the formation of charge transfer complexes. Dissolution of the triazenes in CH_2Cl_2 generally afforded solutions that were dark red, although solutions derived from relatively electron-rich

Scheme 1. Synthesis of Triazenes 4a−f and 5a−c[a]



[a] Legend: (i) THF, 23 °C, 12 h.

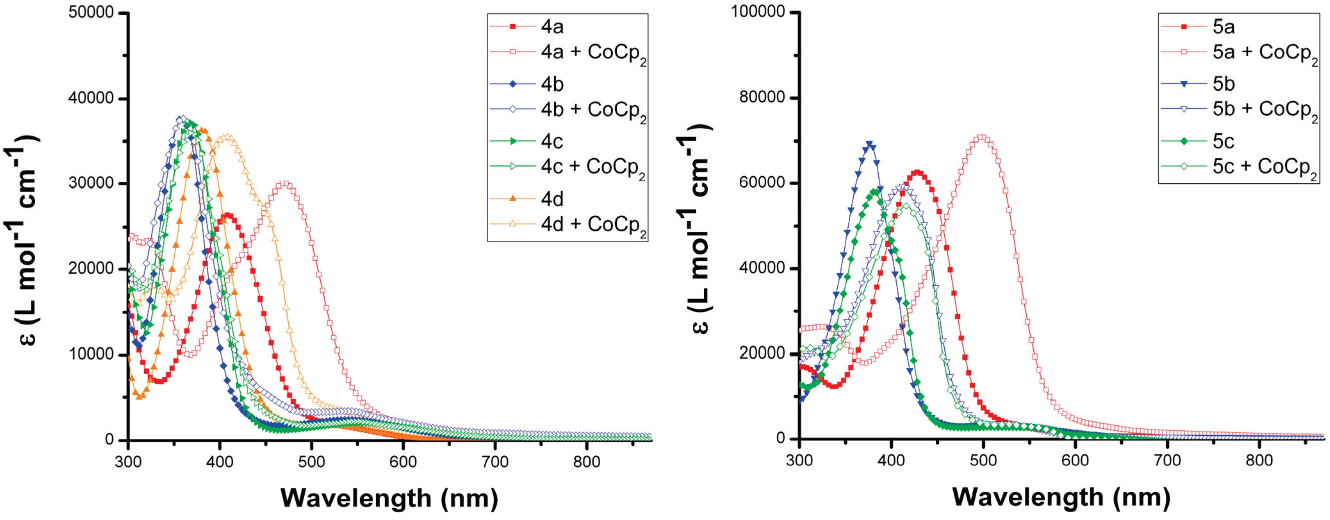


Figure 3. Selected UV−vis absorption spectra of **4** and **5** in CH_2Cl_2 (10 μM) before (solid shapes) and after (open shapes) reduction with $CoCp_2$ (2 equiv).

Table 1. Summary of UV−Vis Absorption Data for Triazenes 4 and 5

	R	λ_{max} (nm)[a]	λ_{max}(reduced) (nm)[b]	Q(Δλ) (nm)[c]	log ε[d]
4a	NO_2	408	472	64	4.51
4b	H	359	360	1	4.61
4c	OMe	368	368	0	4.54
4d	CN	381	408	27	4.56
4e	CF_3	366	380	14	4.56
4f	Cl	367	376	9	4.55
5a	NO_2	428	496	68	4.80
5b	H	377	412	35	4.84
5c	OMe	381	416	35	4.77

[a] Recorded using 10 μM solutions of analyte in CH_2Cl_2 at 23 °C. [b] Spectra were obtained after the addition of 2 equiv of $CoCp_2$ to the analyte solution. [c] $\Delta\lambda = \lambda_{max}(\text{reduced}) - \lambda_{max}$. [d] Molar absorptivity (ε) expressed in units of L mol^{-1} cm^{-1}.

azides (i.e., **4b**,**c**,**f**) were characterized by a deep violet color due, presumably, to the higher transmittance in the blue region of the visible spectrum (∼460 nm).

As shown in Figure 3, the absorption maxima of the triazenes were influenced by the substituents derived from the phenyl azide component. In general, triazenes possessing strongly electron-withdrawing groups absorbed radiation at relatively low energies compared to analogues possessing electron-rich arenes. For example, nitro-substituted **4a** and **5a** exhibited the lowest energy absorptions in their respective classes (λ_{max} = 408 and 428 nm, respectively). However, this trend did not hold for the relatively electron rich species **4c** and **5c**. Due to their electron-donating methoxy subsituents, compounds **4c** and **5c** were expected to absorb at the shortest wavelengths among the triazenes studied; conversely, their absorption maxima were red-shifted beyond what was seen even for the unsubstituted systems **4b** and **5b** (R = H), respectively. Presumably, **4c** and **5c** enable extended electronic delocalization with the pendant methoxy groups, an interaction that lowers their absorption energies in comparison to those of their unsubstituted analogues. A similar discrepancy was also observed for **4a** (R = NO_2) and **4e** (R = CF_3), which both feature strongly electron withdrawing substituents. The resonance contribution enabled in **4a** (but not in **4e**) is believed to lower its absorption energy, leading to a red-shifted absorption maxima in comparison to **4e**.

The UV−vis absorption profiles of **4** and **5** also enabled qualitative comparisons between the two series of mono- and ditopic triazenes studied. In general, QBI (**2**) appeared to be more electron rich than its monotopic congener, NqMes (**1**). This conclusion, ascribed to the presence of four electron-donating nitrogen groups in the former system (versus two in NqMes), was reflected in the analogous observation that triazenes **5** generally exhibited lower energy absorption energies than their respective monotopic analogues (**4**) possessing the same substituents. Furthermore, the extinction coefficients measured for **5** were roughly twice as large as those measured for **4** (see Figure 3), a result that suggested to us that the triazene linkage—two of which are present for **5**, while **4** possesses only one—is the primary chromophore responsible for the intense coloration exhibited by these systems. On the basis of the above spectroscopic findings, we recommend that triazenes **4** and **5** be viewed as donor−acceptor systems, wherein the NHC fragment is a donor and the component derived from phenyl azide acts as the acceptor.[18]

Recently, we reported that methylation of a triazene derived from *N*,*N*′-dimesitylimidazolylidene and *p*-nitrophenyl azide afforded a cationic species that exhibits a hypsochromically shifted λ_{max} value compared to that of its unmethylated precursor (Δλ = 65 nm).[20] Considering that triazenes **4** and **5** contain quinone moieties, subunits that may undergo one-electron reductions to form ionic species, we envisioned that reduction, being a charge-building process, would increase the electron density of the system and effectively render the NHC component a stronger donor (Scheme 2). Hence, we expected to see a measurable spectroscopic response upon reduction of **4** and **5**.

To explore their redox-induced colorimetric response, solutions of **4** and **5** in CH_2Cl_2 were independently treated with $CoCp_2$ (2 equiv)—a sufficiently strong reagent for reducing quinones[25]—and the UV−vis spectra of the resulting reaction mixtures were recorded. The λ_{max} values measured for the reduced triazenes were bathochromically shifted up to Δλ = 68 nm, a finding that is consistent with an increase in electron density arising from a reduction process. As summarized in Table 2, the magnitude of

Scheme 2. Example of the Reversible Reduction of 4

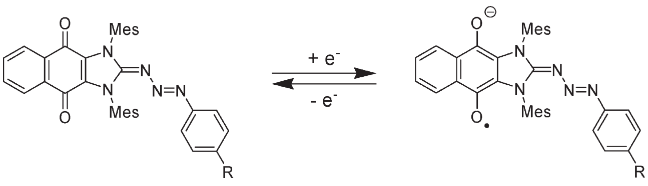


Table 2. Summary of Various Redox Potentials and Carbonyl Stretching Frequencies

	$E_{1/2}$ (V)[a]	$\nu_{C=O}$ (cm^{-1})[b]		$E_{1/2}$ (V)[a]	$\nu_{C=O}$ (cm^{-1})[b]
4a	−0.60	1668	**5a**	−0.20	1671
4b	−0.65	1663	**5b**	−0.34	1665
4c	−0.64	1664	**5c**	−0.38	1664
4d	−0.64	1668			
4e	−0.61	1668			
4f	−0.65	1664			

[a] Measurements performed using 1 mM analyte and 0.1 M $n\mathrm{Bu_4NPF_6}$ in CH_2Cl_2. [b] The quinone stretching energies $\nu_{C=O}$ were measured in KBr matrices.

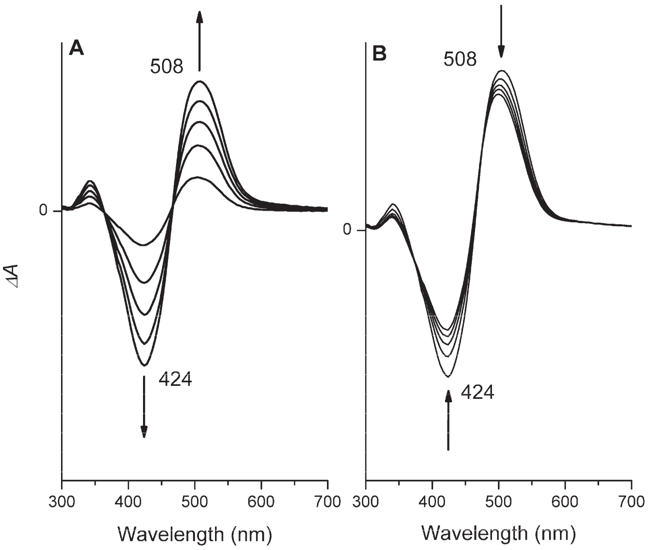


Figure 4. Normalized difference UV−vis absorption spectra recorded at 60 s intervals showing the shift in λ_{max} upon (A) reduction of **5a** (E_{app} = −0.5 V) and (B) subsequent reoxidation of **5a** (E_{app} = 0.4 V). Downward arrows indicate the consumption (A) of the neutral compound and (B) of the reduced compound; upward arrows indicate the formation (A) of the reduced compound and (B) of the neutral compound over time.

the shift correlated with the λ_{max} of the neutral species, where triazenes exhibiting low-energy absorptions exhibited the largest spectral shifts. Hence, triazenes featuring strong donor groups (e.g., QBI moiety **2**) and/or strong acceptor groups (e.g., NO_2 or CN) produced the largest spectral shifts ($\Delta\lambda$ = 14−68 nm), whereas weaker donor/acceptor combinations (e.g., **4b**,**c**) gave rise to no discernible change in λ_{max} upon reduction. By comparison, **5b**,**c**, which featured the same para substituents as **4b**,**c**, respectively, both exhibited a $\Delta\lambda$ value of 35 nm. The discrepancy is consistent with QBI (**2**) being more electron-rich than NqMes (**1**), rendering the former a relatively strong donor. Collectively, these results suggested to us that the optical properties of the triazenes may be tuned by adjusting the donor strength of the NHC or through the incorporation of pendant functional groups *via* changing the azide component employed during their synthesis.

A series of electrochemical measurements were subsequently performed to assess the reversibility of the aforementioned reduction processes. Cyclic voltammetry (CV) (using $n\mathrm{Bu_4NPF_6}$ as the electrolyte) revealed reversible one-electron-reduction features for **4** and **5** in CH_2Cl_2 (see the Supporting Information) that were consistent with the conversion of a *p*-quinone moiety to its respective semiquinone radical anion (see Scheme 2).[22] As summarized in Table 2, the half-wave potentials ($E_{1/2}$) of **4a**−**f** were dependent on the substituent derived from their respective aryl azides. Substrates containing relatively electron rich triazene fragments, such as **4b**,**c**, exhibited the highest quinone reduction potentials (−0.65 and −0.64 V vs SCE, respectively); conversely, electron-deficient species, such as **4a**, exhibited the lowest measured $E_{1/2}$ (−0.60 V) within the series of analogues included in this study. Similar trends were observed for **5a**−**c**, where the electron-donating or -withdrawing ability of the substituent derived from the aryl azide influenced the potential of the respective triazene redox couple.

IR spectroscopic analysis was also performed to evaluate the effects of the pendant functional groups on the overall electronic character of the triazenes. The strength of the quinone C=O bonds, and consequently the carbonyl stretching frequency ($\nu_{C=O}$), should increase with the electron-deficient character of the triazene. As seen in Table 2, the highest $\nu_{C=O}$ values were observed for the most electron-deficient complexes in each respective series of triazenes studied (i.e., **4a** and **5a**, respectively). As expected, the $\nu_{C=O}$ values steadily decreased with increasing electron-donating ability of the pendant substituents, although the differences were less pronounced in the case of **4** than in the case of **5**. Moreover, a correlation was observed between the $E_{1/2}$ values of **4** and **5** and their respective $\nu_{C=O}$ values, wherein an increasing $\nu_{C=O}$ value corresponded with a decreasing $E_{1/2}$ value (Table 2). Qualitatively, these results suggested to us that electron-deficient species (i.e., **4a**) undergo reduction at lower potentials than do relatively electron rich analogues (i.e., **4c**). Such a conclusion was consistent with the absorption characteristics of the triazenes discussed above.

Finally, having confirmed both the chemochromic behavior and electrochemical reversibility, we explored whether **4** or **5** displayed electrochromic characteristics. A series of UV−vis spectroelectrochemical experiments were devised: here, a solution of the analyte in CH_2Cl_2 was taken as the background, and the absorption spectra were recorded at 60 s intervals while applying a suitably cathodic potential (E_{app} = −0.5 V) to a high-surface-area Pt mesh immersed in the solution. Consistent with the UV−vis data discussed above, we observed that the signals attributable to the (neutral) triazene diminished upon bulk electrolysis, while signals associated with the reduced compound intensified (cf. Table 2). For example, the time-resolved UV−vis spectra of **5a** shown in Figure 4A revealed a diminishing signal at 424 nm upon electrochemical reduction, as the signal at 508 nm concomitantly increased. These data compared well with the absorption profiles of both neutral and chemically reduced **5a**, for which λ_{max} values of 428 and 496 nm were observed, respectively

(Table 2). To determine if the aforementioned reduction could be reversed, bulk electrolysis was performed at a sufficiently anodic potential (E_{app} = 0.4 V) following reduction, while a series of optical difference spectra were recorded. As shown in Figure 4B, signals attributable to the reduced compound diminished at this potential, while those associated with the neutral compound intensified. Similar results were observed for the other triazenes investigated (see the Supporting Information). Taken in concert, these studies served to confirm that the colors exhibited by **4** and **5** in solution could be switched using electrochemical techniques.

■ CONCLUSION

In summary, a series of mono- and ditopic redox-active 1,3-disubstituted triazenes were synthesized by coupling two distinct quinone-containing NHCs with various aryl azides. The coupling reactions were performed using the respective free NHCs, and the resulting products were obtained in modest to excellent yields (38−92%). The triazenes were thermally stable up to 302 °C, and their absorption spectra were consistent with efficient electronic delocalization through the triazene linkages. In general, the λ_{max} values of the triazenes underwent bathochromic shifts as the aryl azide moiety became more electron deficient or when the NHC moiety became more electron rich (i.e., upon reduction of the quinone). Cyclic voltammetric analyses of the triazenes revealed that these compounds were capable of undergoing reversible reduction and provided support for the proposal that there is electronic communication between the NHC and the aryl azide moieties, as evidenced by a correlation between reduction potential and the electron-withdrawing ability of the para substituent on the phenyl group. Finally, the electrochromic properties of the triazenes were verified by UV−vis spectroelectrochemical analyses, which confirmed that reversible color changes could be induced using electrochemical methods. Collectively, these results highlight the versatility of NHC−triazene coupling chemistry for the preparation of tunable and configurable optical materials. The robust nature of the products, considered in conjunction with their generally well-behaved electrochemistry, leads us to propose that triazene-based systems, such as those described herein, are poised for use in a variety of applications requiring organic electrochromic materials.

■ EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, all compounds were prepared under an atmosphere of nitrogen using drybox or Schlenk techniques. CH_2Cl_2 and THF were distilled from CaH_2 or sodium benzophenone ketyl under a nitrogen atmosphere prior to use. Solvents were degassed by three consecutive freeze−pump−thaw cycles. All other chemicals were used as received without further purification. NqMes (**1**),[21] QBI (**2**),[22] and aryl azides **3**[27,28] were prepared as previously described. ^{1}H and ^{13}C NMR spectra were recorded using a 300, 400, or 500 MHz spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual nondeuterated solvent as an internal standard. For ^{1}H NMR: $CDCl_3$, δ 7.24 ppm; CD_2Cl_2, δ 5.32 ppm. For ^{13}C NMR: CD_2Cl_2, δ 53.8 ppm. UV−vis spectroscopic measurements were made with matched quartz cuvettes with 1 cm path lengths and 3.0 mL sample solution volumes. Beer's law measurements were performed using 1, 2.5, 5, and 10 μM sample concentrations. All UV−vis spectroscopic measurements were performed in dry CH_2Cl_2 under an atmosphere of nitrogen. Thermogravimetric analyses were performed under an atmosphere of nitrogen at a scan rate of 20 °C min^{-1}. Cyclic voltammetry was conducted using a gastight, three-electrode cell under an atmosphere of dry nitrogen. The cell was equipped with gold working, tungsten counter, and silver quasi-reference electrodes. Measurements were performed in dry CH_2Cl_2 with 0.1 M [tetra-*n*-butylammonium]-[PF_6] (TBAP) as the electrolyte and decamethylferrocene (Fc*) as the internal standard. Unless otherwise noted, all potentials were determined at 100 mV s^{-1} scan rates and referenced to the saturated calomel electrode (SCE) by shifting $(Fc^*)^{0/+}$ to −0.057 V.[29] UV−vis spectroelectrochemical measurements were performed using a custom-made quartz cuvette with 0.2 cm path length equipped with custom-made platinum working, tungsten counter, and silver quasi-reference electrodes. All measurements were made in dry CH_2Cl_2 using 50 μM analyte with 0.1 M TBAP as the electrolyte.

Synthesis of 4a. A solution of free carbene **1** (87.1 mg, 0.20 mmol) and 4-nitrophenyl azide (32.8 mg, 0.40 mmol) in dry THF (2 mL) was stirred at 23 °C for 12 h. The residual solvent was then removed under reduced pressure, and the crude product was purified by column chromatography (SiO_2; 1/3 v/v hexanes/CH_2Cl_2) to afford the desired product as a dark red solid (80.0 mg, 67% yield). Mp: 195−198 °C. T_d = 276 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (dd, *J* = 2.4, 8.8 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.71 (dd, *J* = 2.4, 8.8 Hz, 2H), 7.06 (s, 4H), 6.72 (d, *J* = 8.8 Hz, 2H), 2.41 (s, 6H), 2.16 (s, 12H). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.01 (dd, *J* = 2.4, 8.8 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.75 (dd, *J* = 2.4, 8.8 Hz, 2H), 7.12 (s, 4H), 6.71 (d, *J* = 8.8 Hz, 2H), 2.46 (s, 6H), 2.17 (s, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 174.3, 155.7, 153.1, 146.4, 140.1, 135.0, 134.6, 132.3, 131.9, 129.7, 129.1, 126.8, 124.3, 122.5, 21.3, 18.0. HRMS: *m*/*z* calcd for $C_{35}H_{31}N_6O_4$ $[M + H]^+$ 599.2392, found 599.2401. FT-IR (KBr): ν_{CO} 1668 cm^{-1}. Anal. Calcd for $C_{35}H_{30}N_6O_4$: C, 70.22; H, 5.05; N, 14.04. Found: C, 70.48; H, 4.92; N, 13.83.

Synthesis of 4b. To a Schlenk flask charged with a solution of free carbene **1** (87.1 mg, 0.20 mmol) in dry THF (2 mL) was added in one portion a solution of phenyl azide (0.4 mmol) in dry THF (2 mL). The resulting solution was then stirred at 23 °C for 12 h. After the residual solvent was removed under reduced pressure, the crude product was purified by column chromatography (SiO_2; 1/2 v/v hexanes/CH_2Cl_2) to afford the desired product as a dark violet solid (94.5 mg, 85% yield). Mp: 242−244 °C. T_d = 302 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (dd, *J* = 2.4, 8.8 Hz, 2H), 7.68 (dd, *J* = 2.4, 9.2 Hz, 2H), 7.01 (m, 3H), 7.05 (s, 4H), 6.70 (dd, 2H), 2.40 (s, 6H), 2.19 (s, 12H). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.00 (dd, *J* = 2.4, 8.8 Hz, 2H), 7.73 (dd, *J* = 2.4, 9.2 Hz, 2H), 7.14−7.11 (m, 7H), 6.65 (dd, 4H), 2.46 (s, 6H), 2.19 (s, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 174.4, 162.6, 150.8, 139.7, 135.2, 134.3, 132.7, 132.0, 129.6, 129.0, 128.6, 127.8, 126.6, 122.3, 21.3, 18.1. HRMS: *m*/*z* calcd for $C_{35}H_{32}N_5O_2$ $[M + H]^+$ 554.2560, found 554.2550. FT-IR (KBr): ν_{CO} 1663 cm^{-1}. Anal. Calcd for $C_{35}H_{31}N_5O_2$: C, 75.93; H, 5.64; N, 12.65. Found: C, 75.32; H, 5.66; N, 12.20.

Synthesis of 4c. To a Schlenk flask charged with a solution of free carbene **1** (87.1 mg, 0.20 mmol) in dry THF was added in one portion a solution of 4-methoxyphenyl azide (0.4 mmol) in dry THF (2 mL). The resulting solution was then stirred at 23 °C for 12 h. After the residual solvent was removed under reduced pressure, the crude product was purified by column chromatography (SiO_2; 1/3 v/v hexanes/CH_2Cl_2) to afford the desired product as a black solid (44.4 mg, 38% yield). Mp: 208−212 °C. T_d = 294 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 2.4, 8.8 Hz, 2H), 7.66 (dd, *J* = 2.8, 8.8, 2H), 7.03 (s, 3H), 6.65 (d, *J* = 6.4 Hz, 2H), 6.60 (d, 2H), 3.75 (s, 3H), 2.36 (s, 6H), 2.17 (s, 12H). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.00 (dd, *J* = 2.4, 8.8 Hz, 2H), 7.72 (dd, *J* = 2.8, 8.8, 2H), 7.11 (s, 4H), 6.64 (dd, *J* = 6.4 Hz, 4H), 3.76 (s, 3H), 2.45 (s, 6H), 2.19 (s, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 174.3, 159.7, 152.2, 144.6, 139.6, 135.3, 132.8, 132.0, 130.0, 129.0, 126.5, 123.7, 113.7, 55.6, 21.3, 18.1. HRMS: *m*/*z* calcd for $C_{36}H_{34}N_5O_3$ $[M + H]^+$ 584.2664, found 584.2656. FT-IR (KBr): ν_{CO} 1664 cm^{-1}. Anal. Calcd for $C_{36}H_{33}N_5O_3$: C, 74.08; H, 5.70; N, 11.92. Found: C, 73.65; H, 5.72; N, 11.92.

Synthesis of 4d. A solution of free carbene **1** (87.1 mg, 0.20 mmol) and 4-cyanophenyl azide (34.6 mg, 0.24 mmol) in dry THF (2 mL) was stirred at 23 °C for 12 h. The residual solvent was then removed under reduced pressure, and the crude product was purified by column chromatography (SiO_2; CH_2Cl_2) to afford the desired product as a dark red solid (84.8 mg, 73% yield). Mp: 248−250 °C. T_d = 277 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (dd, J = 2.4, 8.8 Hz, 2H), 7.70 (dd, J = 2.4, 9.2 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.05 (s, 4H), 6.68 (d, J = 8.8 Hz, 2H), 2.40 (s, 6H), 2.15 (s, 12H). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.02 (dd, J = 2.4, 8.8 Hz, 2H), 7.76 (dd, J = 2.4, 9.2 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.13 (s, 4H), 6.69 (d, J = 8.8 Hz, 2H), 2.47 (s, 6H), 2.18 (s, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 174.3, 154.0, 153.0, 140.0, 135.0, 134.5, 132.7, 132.4, 131.9, 129.7, 129.0, 126.7, 122.7, 119.4, 110.2, 21.3, 18.0. HRMS: m/z calcd for $C_{36}H_{31}N_6O_2$ $[M + H]^+$ 579.2514, found 579.2503. FT-IR (KBr): ν_{CO} 1668 cm^{-1}. Anal. Calcd for $C_{36}H_{30}N_6O_2$: C, 74.72; H, 5.23; N, 14.52. Found: C, 74.48; H, 5.24; N, 14.24.

Synthesis of 4e. To a Schlenk flask charged with a solution of free carbene **1** (87.1 mg, 0.20 mmol) in dry THF (2 mL) was added in one portion a solution of 4-(trifluoromethyl)phenyl azide (0.4 mmol) in dry THF (2 mL). The resulting solution was then stirred at 23 °C for 4 h. After the residual solvent was removed under reduced pressure, the crude product was purified by column chromatography (SiO_2; 1/2 v/v hexanes/CH_2Cl_2) to afford the desired product as a dark red solid (104.4 mg, 84% yield). Mp: 245−246 °C. T_d = 257 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (dd, J = 2.4, 9.2 Hz, 2H), 7.69 (dd, J = 2.4, 9.2 Hz, 2H), 7.31 (d, J = 9.2 Hz, 2H), 7.05 (s, 4H), 6.73 (d, J = 8.8 Hz, 2H), 2.40 (s, 6H), 2.17 (s, 12H). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.03 (dd, J = 2.4, 9.2 Hz, 2H), 7.75 (dd, J = 2.4, 9.2 Hz, 2H), 7.95 (d, J = 9.2 Hz, 2H), 7.14 (s, 4H), 6.75 (d, J = 8.8 Hz, 2H), 2.47 (s, 6H), 2.20 (s, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 174.3, 153.6, 153.0, 139.9, 135.1, 134.5, 132.5, 131.9, 129.7, 129.0, 128.9, 128.6, 126.7, 126.1, 125.7, 125.7, 123.4, 122.4, 21.3, 18.1. HRMS: m/z calcd for $C_{36}H_{31}F_3N_5O_2$ $[M + H]^+$ 622.2420, found 622.2424. FT-IR (KBr): ν_{CO} 1668 cm^{-1}. Anal. Calcd for $C_{36}H_{30}F_3N_5O_2$: C, 69.55; H, 4.86; N, 11.27. Found: C, 69.28; H, 4.87; N, 11.16.

Synthesis of 4f. To a Schlenk flask charged with a solution of free carbene **1** (87.1 mg, 0.20 mmol) in dry THF (2 mL) was added in one portion a solution of 4-chlorophenyl azide (0.4 mmol) in dry THF (2 mL). The resulting solution was then stirred at 23 °C for 12 h. After the residual solvent was removed under reduced pressure, the crude product was purified by column chromatography (SiO_2; CH_2Cl_2) to afford the desired product as a dark violet solid (108.4 mg, 92% yield). Mp: 239−242 °C. T_d = 267 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (dd, J = 2.4, 9.2 Hz, 2H), 7.73 (dd, J = 2.4, 8.8 Hz, 2H), 7.08 (s, 4H), 7.07 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 8.8 Hz, 2H), 2.44 (s, 6H), 2.21 (s, 12H). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.00 (dd, J = 2.4, 9.2 Hz, 2H), 7.73 (dd, J = 2.4, 8.8 Hz, 2H), 7.11 (s, 4H), 7.09 (d, J = 8.8 Hz, 2H), 6.58 (d, J = 8.8 Hz, 2H), 2.46 (s, 6H), 2.18 (s, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 174.3, 152.7, 149.5, 139.8, 135.2, 134.4, 133.0, 132.6, 131.9, 129.6, 129.0, 128.7, 126.6, 123.6, 21.3, 18.1. HRMS: m/z calcd for $C_{35}H_{31}N_5O_2Cl$ $[M + H]^+$ 588.2170, found 588.2161. FT-IR (KBr): ν_{CO} 1664 cm^{-1}. Anal. Calcd for $C_{35}H_{30}N_5O_2Cl$: C, 71.48; H, 5.14; N, 11.91. Found: C, 71.46; H, 5.06; N, 11.67.

Synthesis of 5a. Free carbene **2** (50.0 mg, 0.076 mmol), 4-nitrophenyl azide (29.0 mg, 0.17 mmol), and dry THF (2 mL) were added to an oven-dried Schlenk flask. The resulting solution was then stirred at 23 °C for 12 h. The residual solvent was then removed under reduced pressure, and the crude product was triturated with hexanes (3 × 25 mL) and Et_2O (3 × 25 mL) to afford the desired product as a dark red orange solid (39 mg, 52% yield). Mp: 252−253 °C. T_d = 294 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 8.8 Hz, 4H), 6.95 (s, 8H), 6.68 (d, J = 8.8 Hz, 4H), 2.32 (s, 12H), 2.11 (s, 24H). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.93(d, J = 8.8 Hz, 4H), 7.07 (s, 8H), 6.66 (d, J = 8.8 Hz, 4H), 2.41 (s, 12H), 2.15 (s, 24H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 165.2, 155.5, 152.9, 146.5, 140.4, 134.8, 131.6, 129.9, 125.7, 124.3, 122.5, 21.3, 18.2. HRMS: m/z calcd for $C_{56}H_{53}N_{12}O_6$ $[M + H]^+$ 989.4199, found 989.4206. FT-IR (KBr): ν_{CO} 1671 cm^{-1}. Anal. Calcd for $C_{56}H_{52}N_{12}O_6$: C, 68.00; H, 5.30; N, 16.99. Found: C, 68.16; H, 5.43; N, 16.48.

Synthesis of 5b. To a Schlenk flask charged with a solution of free carbene **2** (50.0 mg, 0.076 mmol) in dry THF (2 mL) was added in one portion a solution of phenyl azide (0.22 mmol) in dry THF (2 mL). The resulting solution was then stirred at 23 °C for 12 h. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography (SiO_2; 3/1 v/v hexanes/EtOAc) to afford the desired product as a red-brown solid (60 mg, 88% yield). Mp: 244−246 °C. T_d = 268 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.06 (m, 6H), 6.91 (s, 8H), 6.64 (m, 4H), 2.29 (s, 12H), 2.12 (s, 24H). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.11−7.09 (m, 6H), 7.05 (s, 8H), 6.59 (dd, 4H), 2.40 (s, 12H), 2.16 (s, 24H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 165.6, 152.4, 150.7, 139.9, 135.0, 132.1, 129.7, 128.6, 127.9, 125.4, 122.3, 21.2, 18.2. HRMS: m/z calcd for $C_{56}H_{55}N_{10}O_2$ $[M + H]^+$ 899.4502, found 899.4504. FT-IR (KBr): ν_{CO} 1665 cm^{-1}. Anal. Calcd for $C_{56}H_{54}N_{10}O_2$: C, 74.81; H, 6.05; N, 15.58. Found: C, 75.03; H, 6.06; N, 15.51.

Synthesis of 5c. To a Schlenk flask charged with a solution of free carbene **2** (35.0 mg, 0.053 mmol) in dry THF (2 mL) was added in one portion a solution of 4-methoxyphenyl azide (0.28 mmol) in dry THF (2 mL). The resulting solution was then stirred at 23 °C for 12 h. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography (SiO_2; first 3/1 v/v hexanes/EtOAc to remove impurities then 3/2/1 v/v/v hexanes/EtOAc/CH_2Cl_2) to afford the desired product as a brown solid (21 mg, 41% yield). Mp: 260−262 °C. T_d = 237 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.90 (s, 8H), 6.60−6.58 (m, 8H), 3.73 (s, 6H), 2.29 (s, 12H), 2.11 (s, 24H). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.04 (s, 8H), 6.61 (m, 4H), 6.56 (m, 4H), 3.74 (s, 3H), 2.39 (s, 12H), 2.15 (s, 24H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 165.7, 159.7, 151.9, 144.5, 139.8, 135.1, 132.0, 129.6, 125.3, 123.6, 113.7, 55.6, 21.2, 18.2. HRMS: m/z calcd for $C_{58}H_{59}N_{10}O_4$ $[M + H]^+$ 959.4711, found 959.4715. FT-IR (KBr): ν_{CO} 1664 cm^{-1}. Anal. Calcd for $C_{58}H_{58}N_{10}O_4$: C, 72.63; H, 6.10; N, 14.60. Found: C, 72.34; H, 6.21; N, 14.08.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Figures giving cyclic voltammograms, UV−vis spectroelectrochemical data, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was made possible by the generous financial support of the National Science Foundation (Grant Nos. CHE-0645563 and CHE-0749571 to C.W.B. and J.L.S., respectively) and the Robert A. Welch Foundation (Grant Nos. F-1621 and F-1018 to C.W.B. and J.L.S., respectively). Support from the Korean WCU program (grant R32-2008-000-10217-0) is also acknowledged. We thank Prof. A. G. Tennyson for assistance with the spectroelectrochemical experiments and for insightful discussions.

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