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Bandrowski's Base Revisited: Toward a Unprecedented Class of Quinonediimines or New Two-Way Chromophoric Molecular Switches

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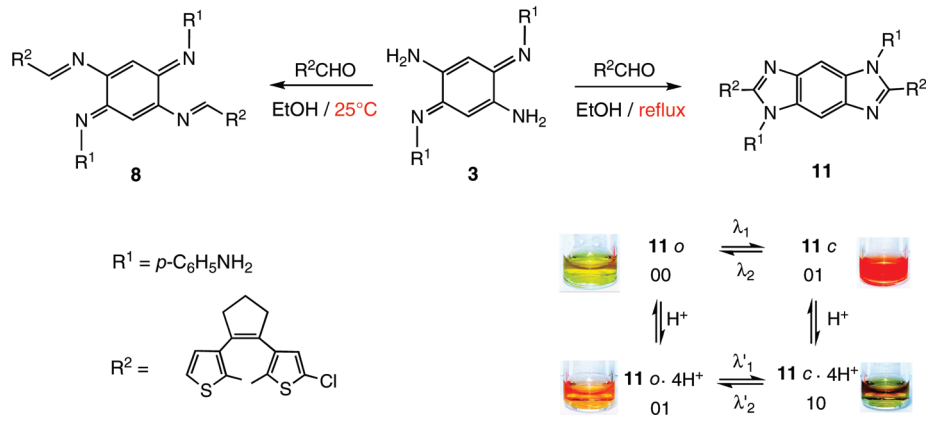

Temperature-controlled reactivity places Bandrowski's base **3** at the crossroads of a new versatile strategy for the preparation of two different categories of chromophores. We describe the access to a new class of quinonediimines (**8**) with an extended π-conjugation owing to the presence of imine functions. Under slightly different conditions, Bandrowski's base appears to be the precursor of choice in the preparation of a novel pH- and light-dependent binary molecular switch. This molecule (**11**) is constituted of a benzobis(imidazole) core that can be reversibly protonated and a diarylethene unit which can be reversibly converted into its closed form upon irradiation. Triggered by two independent variables, **11** provides four distinct optical states for molecular number processing.

Introduction

The field of molecular switches has been very attractive for years owing to the possibility of performing simple logic operations.[1] Photochromic compounds such as bisthienylethenes (BTE) **1**, widely investigated,[2] are of particular interest[3] since the use of light as an external stimulus for the interconversion of two states allows rapid and clean processes.[4] Molecules exhibiting a quinoid structure have attracted the interest of a large scientific community owing to their remarkable chemical and physical properties.[5a]

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(4) (a) Irie, M. *Jpn. J. Appl. Phys.* **1989**, *28* (Suppl. 28−3), 215. (b) Uchida, K.; Nakayama, Y.; Irie, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1311. (c) Nakayama, Y.; Hayashi, M.; Irie, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 789. (d) Iwata, S.; Ishihara, Y.; Qian, C.-P.; Tanaka, K. *J. Org. Chem.* **1992**, *57*, 3726. (e) Saika, T.; Irie, M.; Shimidzu, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2123.

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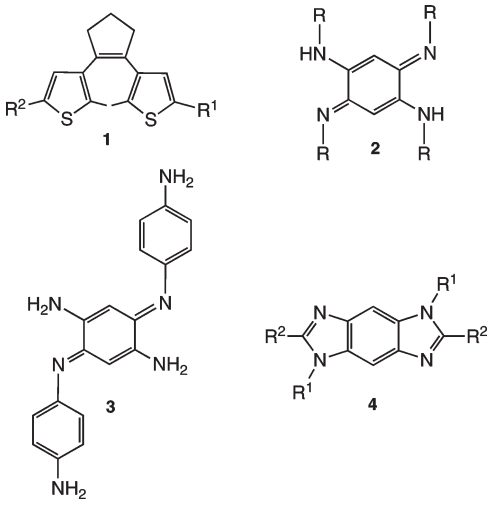
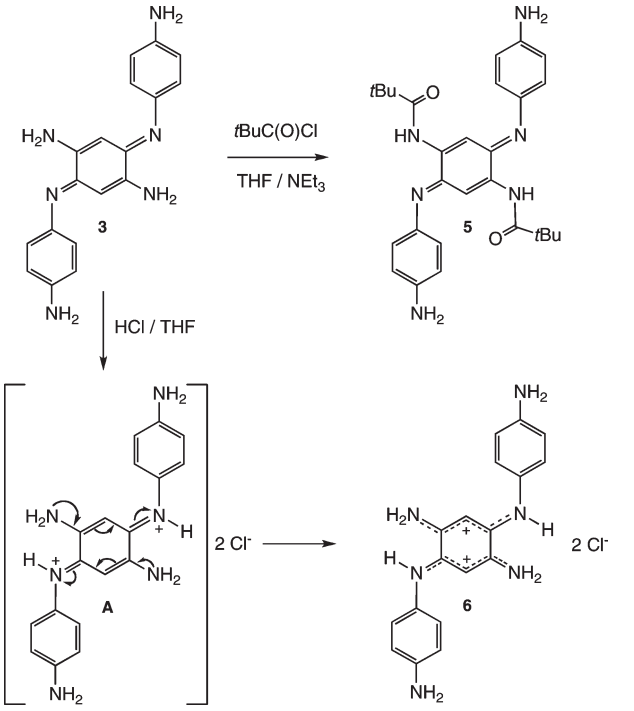
In particular, quinoid compounds of type **2** appeared more recently as very attractive acidichromic systems because of the presence of two localized π-subunits that can be tuned by reversible protonation to become delocalized.[5b,c] Thus, integration of diarylethenes **1** in **2** would give access to a new class of multistate molecular switches combined in a single molecule.



The long-known quinonediimine **3**, called Bandrowski's base,[6,7] appeared to be a reagent of choice that might be easily functionalized owing to the presence of two types of NH_2 groups which can be viewed as aniline-type or cyanine-type amino functions. As a result, a selectivity of the NH_2 reactivity, which prevents protection/deprotection steps, might be envisaged. Curiously and to the best of our knowledge, although prepared more than one century ago,[6] the chemistry of **3** has remained unexplored, and this compound has been used only in hair colorants and cosmetics for decades[8] or more recently as bioactive species in biology.[9] In the course of this study, we observed the unexpected formation of benzobis(imidazoles) of type **4** which are of growing interest as precursors of modular fluorescent probes,[10] polymers,[11] or Janus bis(carbene)s and transition-metal complexes.[12]

Herein, we report a new class of molecules (**11**) with two addressable subunits that can undergo individual and/or cumulative effects in switching cycles. Compound **11** consists of (a) a benzobis(imidazole) core that can be reversibly protonated and (b) a diarylethene unit which can be reversibly converted into its closed form upon UV−vis irradiation. This molecule (**11**) was obtained from the versatile Bandrowski's base (**3**) that is also able to lead under different temperature conditions to a new class of quinonediimines (**8**).

SCHEME 1. Reactivity of the Bandrowski's Base 3



Results and Discussion

The reactivity of **3** was first investigated by theoretical calculations for which the geometry optimization was done using B3LYP/6-31G(d,p).[13] The overall charges on the NH_2 groups show clearly that the amino functions $H_2N(1)$ and $H_2N(2)$ are more electron-rich than those located on $H_2N(3)$ and $H_2N(4)$ (Figure 1).

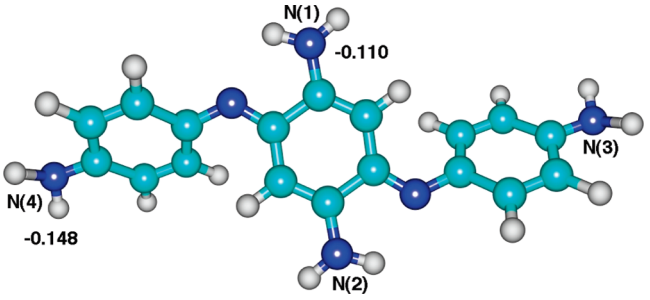


FIGURE 1. Electronic density of the NH_2 functions in the Bandrowski's base (**3**).

Consequently, the two resonance peaks observed by ^1H NMR at 4.15 and 5.32 ppm for **3** can be assigned to the "nonaromatic" (i.e., cyanine-type) and "aromatic" (i.e., aniline-type) NH_2 groups, respectively (Figure 2). Interestingly,

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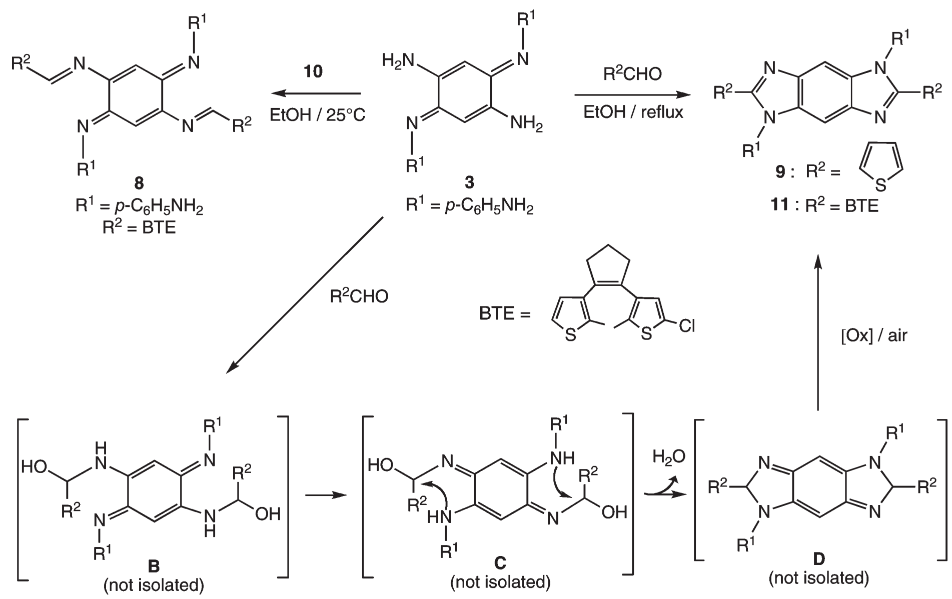
SCHEME 2. Synthesis of 9 and 11



molecule **3** does not exist in solution as a degenerated structure resulting from the presence of two tautomers in equilibrium in solution, in contrast to N-substituted analogues.[5,14]

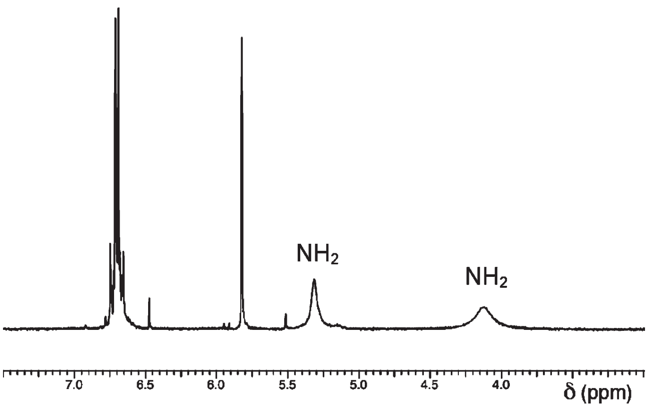


FIGURE 2. ^{1}H NMR spectrum of the Bandrowski's base **3**.

This theoretical study reveals a stronger nucleophilic character (i.e., higher electron density) of the cyanine-type NH_2 groups [i.e., N(1) and N(2)] by comparison with the aniline-type NH_2 functions [i.e., N(3) and N(4)] (Figure 1). This observation would suggest a selectivity of the NH_2 groups which was confirmed experimentally by acylation of **3**. Molecule **3**[7] was smoothly reacted with *t*-BuC(O)Cl (2 equiv) in the presence of base to afford **5** (Scheme 1). The almost-quantitative yield obtained (99%) accounts for a selectivity of the cyanine-type amines which prevents protection and deprotection steps. The ^{1}H NMR spectrum of **5** showed a singlet at 5.50 ppm and a broad peak at 9.21 ppm corresponding to the olefinic and amido NH protons, respectively. The resonance at 6.30 ppm is the diagnostic signal of the aniline-type NH_2 protons which accounts for an acylation of the cyanine-type amino groups, as expected.

The reactivity of **3** as base was also investigated, and we observed upon protonation a drastic color change from yellow to blue. This observation is consistent with the protonation of the imine functions and the formation of a dicationic species **A** which is stabilized by intramolecular delocalization to afford **6** (Scheme 1).[5b,c] The charge distribution in **3** shows a higher electronic density on the imine nitrogens than on the cyanine-type amino N (−0.643 vs −0.659, respectively, see Figure S16 in the Supporting Informations). Thus, the protonation occurs at the imine sites to form cyanine subunits $\mathbf{[H_2N{\cdots}C{\cdots}CH{\cdots}C{\cdots}NH]^+}$ which are more stable than the $[H_3N{-}C{=}CH{-}C{=}N]^+$ moieties (in case of protonation of the $-NH_2$ groups).[5b,c] The ^{1}H NMR spectrum of **6** shows the presence of a singlet at 5.95 ppm (I = 2H) which is in agreement with a symmetrical geometry in solution resulting from a double protonation reaction.

The strategy of union of bisthienylethene (BTE) **1** and the benzoquinonediimine core was first tested by condensation of thiophene-2-carboxaldehyde **7** with Bandrowski's base **3** in refluxing EtOH (Scheme 2). The use of the commercially available molecule **7** was envisaged as a model compound (i.e., analogue of BTE) in order to validate this approach for connecting the two species through conjugation (formation of the imine function). The expected quinone of type **8** (R^2 = thiophene) was not obtained, and we isolated instead the unexpected benzobis(imidazoles) **9** as a yellow-brown solid in

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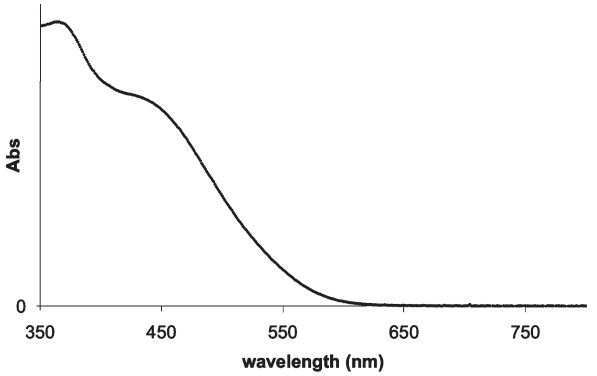
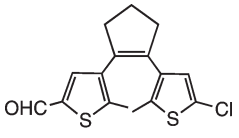


FIGURE 3. UV−vis absorption of **8** in acetone at 20 °C.

57% yield. Its ^{1}H NMR spectrum shows aromatic signals in the range 6.80−7.64 ppm in agreement with the presence of benzenic protons as expected for **9** in contrast to a quinoid-type structure of type **8**.[15] The broad resonance at 5.64 ppm corresponds to the NH_2 protons linked to the phenyl groups.

In contrast to the preparation of benzobis(imidazolium) salts from related benzoquinonediimines which requires para→ortho isomerization of the quinonediimine skeleton,[15] the formation of **9** can be explained as follows: (1) nucleophilic attack of **3** (i.e., *p*-quinonediimine) leading to **B**, (2) prototropic rearrangement to give **C**, (3) cyclization reaction and water elimination yielding **D**, and (4) air oxidation to afford **9** (Scheme 2).

Similarly, compound **11** was then synthesized in 54% yield from reaction between **10**[16] and **3** in refluxing dry EtOH (Scheme 2). The ^{1}H NMR spectrum of **11** shows the diagnostic signals of the bisthienylethene moieties (BTE) such as, for instance, the presence of the methyl resonances at 1.81 and 1.92 ppm.



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By studying this reaction in more details, we have now found that the same reaction carried out at room temperature furnishes **8** which precipitated as an orange solid in 80% yield. The formation of **8** was monitored by GC/MS until the disappearance of Bandrowski's base **3** (3 days). Its ^{1}H NMR spectrum reveals a resonance at 5.66 ppm and an additional peak at 8.46 ppm, compared to **11**, in agreement with the presence of quinoid C−H and iminic protons, respectively. The UV−vis spectrum of **8** shows an absorption band with a shoulder at λ_{max} = 363 nm consistent with $\pi-\pi^*$ transitions as already observed in related quinonediimines (Figure 3).[5]

Unfortunatly, molecule **8** decomposes rapidly in solution preventing further optical studies of the new chromophore with two addressable subunits. This high instability would be probably due to the sensitivity of the conjugated imine functions toward side reactions such as hydrolysis.[17]

In contrast, the reversible states and the stability could be studied for **11** upon the combined UV−vis irradiation and/or pH switching processes in acetone solution at $c = 1.64 \times 10^{-5}$ mol/L (Figure 4).

The irradiation of **11** (i.e., when BTE is on the open form **11***o*) at λ_1 = 381 nm under air induced a rapid conversion from yellow to the red form **11***c* with a bathochromic shift (λ = 511 nm) which results from a ring-closure of BTE and an extension of the π-conjugation.

The photostationary equilibrium is attainable in about 1 min, and the compound decomposes slowly but totally when irradiated continuously at λ_1 = 381 nm for 95 min (see Figure S12 in the Supporting Information). Thus, the pure closed form **11***c* could not be isolated but appeared to be thermally stable for 5 days at 20 °C as expected for bisthienylethenes.[1] The ^{1}H NMR spectrum of **11***o* in acetone-d_6 irradiated during 10 min at 381 nm shows in the range 5.50−7.50 ppm the signals of **11***o* and the presence of two new peaks at 6.40 and 5.82 ppm in agreement with the proton shielding of the thiophene rings in the closed form **11***c* (see Figure S13 in the Supporting Information), as already observed in related dithienylcyclopentenes.[18] According to this experiment, only 10% of **11***c* is obtained, which accounts for a slow conversion at the NMR scale (concentration ~1000 times higher than that for UV−vis studies). Increasing the irradiation time led to decomposition reactions as shown previously by UV−vis spectroscopy. Irradiation at the wavelength corresponding to the red absorption band of **11***c* (λ_2 = 511 nm) gave cycloreversion to the open isomer **11***o*, and the solution turns back to light yellow (Figure 4). A time of 20 min for irradiation is necessary to induce a complete cycloinversion. Several cycles of photocoloration/photodiscoloration at λ_1 = 381 and λ_2 = 511 nm, respectively, have been achieved, demonstrating a good reversibility of the system. However, the fatigue resistance of **11** upon twelve switching cycles, which was determined by the decrease of the absorption at 511 nm, revealed a loss of efficiency of about 50% (Figure 5).

Protonation of **11***o* by addition of HCl in excess in acetone ($c = 6.10^{-6}$ M) affords **11***o*.4H$^+$ as indicated by a bathochromic effect of $\Delta\lambda$ = 13 nm (λ_{max} = 394 nm) (Figure 4). This red shift is due to the delocalization of the π system, induced by protonation, in order to stabilize the positive charges (color change from yellow to orange). UV irradiation of **11***o*.4H$^+$ at λ'_1 = 394 nm for 3 min led to the formation of the corresponding closed form **11***c*.4H$^+$ which is characterized by an absorption band at 573 nm (green color). This photochromic response for **11***c*.4H$^+$ was also confirmed by protonation of **11***c* with diluted HCl. The observed bathochromic shifts can be explained by a cumulative effect (irradiation plus protonation) which allows an extension of the delocalization of the positive charges throughout the whole π-system. Deprotonation of **11***o*.4H$^+$ and **11***c*.4H$^+$ with Et_3N leads to the formation of **11***o* and **11***c*, respectively, as expected (Figure 4). Irradiation of **11***c*.4H$^+$ at λ'_2 = 573 nm for

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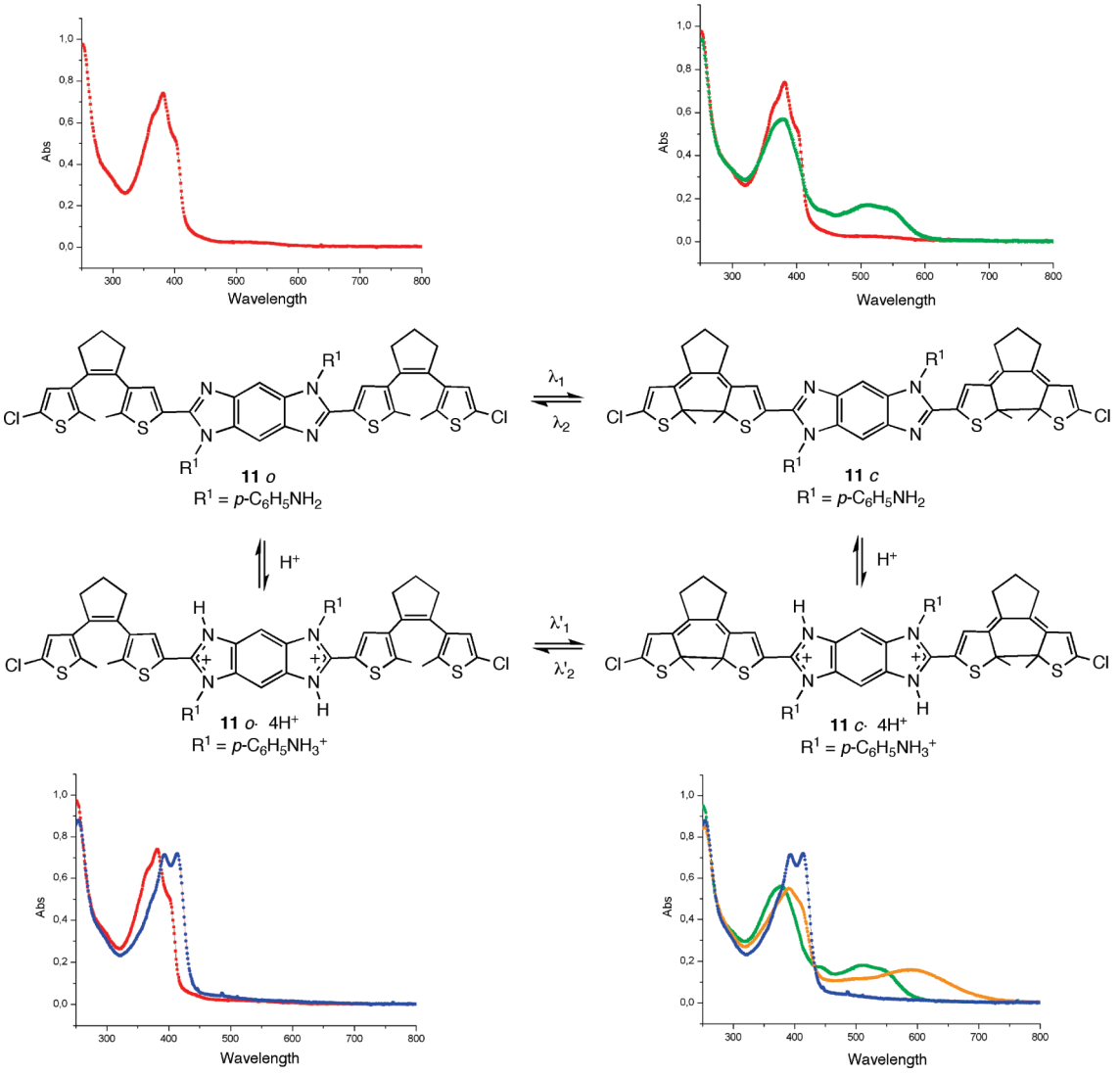

FIGURE 4. Absorption spectra of **11** ($c = 1.64 \times 10^{-5}$ mol/L) in acetone at 20 °C upon protonation with HCl ($c = 6.10^{-6}$ mol/L) and/or irradiation with UV−vis light.

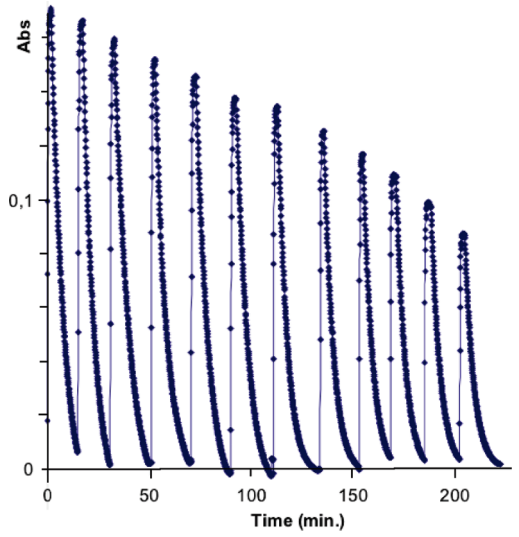

FIGURE 5. Fatigue resistance of the molecular switch **11** in acetone at 20 °C.

32 min furnished the corresponding open form **11***o*·4H$^+$. The ^{1}H NMR spectrum of **11***o*·4H$^+$ in acetone-d_6 (protonation of **11***o* in the NMR tube) shows three singlets and two doublets in the aromatic range (i.e., at 6.70, 7.75, 7.86, 8.09, and 8.21 ppm, respectively) in agreement with a symmetrical molecule (see Figures S14 and S15 in the Supporting Information). These signals are downfield shielded compared to **11***o* as expected upon protonation. The disappearance of the NH_2 resonance is consistent with the protonation of the aromatic amines and the formation of **11***o*·4H$^+$. The protonated forms **11***o*·4H$^+$ and **11***c*·4H$^+$ are stable for days at room temperature. However, their fatigue resistance upon protonation, determined by the decrease of the absorption at 573 nm, shows a loss of efficiency of 18% after five cycles.

Thus, the above interconversion can be described with binary logic.[19] The input signals are UV light (381 nm, *I1*) and proton ions (H$^+$, *I2*). Each signal can be either *on* or *off*

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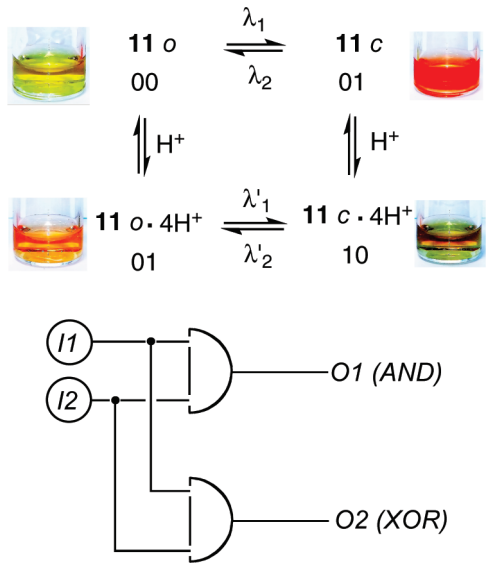

FIGURE 6. Schematic representation of the 2-input logic half-adder circuit.

TABLE 1. Truth Table of the 2-Input Logic Half-Adder Circuit

I1 (light)	*I2* (pH)	*O1* (AND) (carry digit)	*O2* (XOR) (sum digit)	half-adder (added number)
0	0	0	0	00
1	0	0	1	01
0	1	0	1	01
1	1	1	0	10

representing the *1* and *0* of the binary digit system **11**.[20] The presence of **11***c*, **11***o*·4H$^+$, and **11***c*·4H$^+$ can be characterized by their corresponding typical absorption bands. The absorption band at 511 nm (due to the open form **11***c* after UV light irradiation, *I1*) can be considered as one of the output signals (*O2*) (Figure 6).

Similarly, the absorption band of **11***o*·4H$^+$ at 394 nm is a second output signal (*O2*) observed in acidic medium (H$^+$, *I2*). Namely, if either *I1* = 1 and *I2* = 0 or *I1* = 0 and *I2* = 1, *O2* = 1 in the binary logic convention. Therefore, the variation of the absorbances upon UV light and protonation can be interpreted as an XOR gate (Figure 6 and Table 1). Molecule **11***c*·4H$^+$ was formed in solution only under the simultaneous actions of UV light (*I1*) and H$^+$ (*I2*), namely, only when *I1* = 1 and *I2* = 1, the output signal *O1* is 1. Otherwise, *O1* is equal to 0. Therefore, the presence of the absorption band at 573 nm upon the two inputs (*I1* and *I2*) can be viewed as an "AND" logic gate (Table 1).[19]

Concluding Remarks

In summary, we determined the reactive sites of Bandrowski's base **3** as a reagent in organic synthesis. The temperature-controlled reactivity places **3** at the crossroads of a new versatile strategy for the preparation of two different categories of chromophores: (1) a new class of quinonediimines of type **8** with conjugated imine functions and (2) a unexpected novel binary molecular switch (**11**) that is controlled by light and pH. Molecule **11** is constituted of a benzobis(imidazole)s core that can be reversibly protonated and a diarylethene unit which can be reversibly converted into its closed form upon irradiation. Triggered by two independent variables, **11** provides four distinct optical states that might be usable for molecular number processing. The addition of binary numbers which requires the implementation of a molecular half-adder could be achieved by **11** for which one or two high inputs lead to a significant displacement of the absorption band. Such a potential application would need an improvement of the stability of this binary molecular switch (**11**) as well as an effective photochemical quantum yield, currently under investigation.

Experimental Section

Synthesis of *N*,*N*′-[(3*Z*,6*Z*)-3,6-Bis[(4-aminophenyl)imino]cyclohexa-1,4-diene-1,4-diyl]bis(2,2-dimethylpropanamide) (5). To a solution of the Bandrowski's base **3** (*m* = 200 mg, 0.63 mmol) in THF, in the presence of an excess of NEt_3, was added trimethylacetyl chloride (*m* = 150 mg, 1.25 mmol). After the mixture was stirred for 12 h at room temperature, the solvent was evaporated under reduced pressure and the residue was taken up in water. The obtained precipitate is then isolated by filtration and washed with water affording **5** as a beige solid (*m* = 305 mg, 99% yield): ^{1}H NMR (DMSO-d_6) δ = 1.28 (s, 18H, CH_3), 5.50 (s, 2H, olefinic H), 6.30 (br s, 4H, NH_2), 6.77 (d, 4H, aromatic H), 7.66 (d, 4H, aromatic H), 9.21 (br s, 2H, NH); MS (ESI) *m*/*z* = 487 [M+H]$^+$. Anal. Calcd for $C_{28}H_{34}N_6O_2 \cdot H_2O \cdot {}^1/_2$THF: C, 66.64; H, 7.46; N, 15.54. Found: C, 66.32; H, 7.02; N, 15.24.

Synthesis of *N*,*N*′-(2,5-Diaminocyclohexa-2,5-diene-1,4-diylidene)bis(4-aminobenzenaminium) Dichloride (6). To a solution of **3** (*m* = 180 mg, 0.56 mmol) in THF was added dropwise HCl. The obtained precipitate is then isolated by filtration and washed with Et_2O affording **6** as a deep blue solid (*m* = 130 mg, 60% yield): ^{1}H NMR (MeOD-d_3) δ = 5.95 (s, 2H, olefinic H), 6.65 (d, 4H, aromatic H), 6.82 (d, 4H, aromatic H). Anal. Calcd for $C_{18}H_{20}N_6Cl_2$: C, 55.25; H, 5.15; N, 21.48. Found: C, 55.69; H, 5.52; N, 21.38. The dication **6** could not be detected by MS (ESI).

Synthesis *N*1,*N*1′-[(1*Z*,4*Z*)-2-[((1*E*)-[4-[2-(5-Chloro-2-methyl-3-thienyl)cyclopent-1-en-1-yl]-5-methyl-2-thienyl]methylene)-amino]-5-[((1*Z*)-[4-[2-(5-chloro-2-methyl-3-thienyl)cyclopent-1-en-1-yl]-5-methyl-2-thienyl]methylene)amino]cyclohexa-2,5-diene-1,4-diylidene]dibenzene-1,4-diamine (8). 4-[2-(5-Chloro-2-methyl-3-thienyl)cyclopent-1-en-1-yl]-5-methylthiophene-2-carbaldehyde (**10**) (155 mg, 0.488 mmol) and Bandrowski's base **3** (73 mg, 0.286 mmol) were dissolved in EtOH (*v* = 3 mL) in the presence of one drop of piperidine. The mixture was stirred at room temperature for 3 days. The obtained precipitate was isolated by filtration affording **8** as an orange solid (*m* = 195 mg, 80% yield): ^{1}H NMR ($CDCl_3$) δ = 1.87 (s, 6H, CH_3), 2.06 (br s, 10H, CH_3, CH_2), 2.53−2.57 (m, 8H, CH_2), 4.94 (br s, 4H, NH_2), 5.66 (s, 2H, olefinic H), 6.60 (s, 2H, aromatic H), 6.89 (d, 4H, CH), 7.11 (s, 2H, aromatic H), 7.23 (d, 4H, aromatic H), 8.46 (s, 2H, −HC=N−); MS (ESI) 927.2 [M + H]$^+$. No ^{13}C NMR data or satisfactory CHN analyses could be obtained owing to the unstability of **8**.

Synthesis of 1,5-Diphenylamine 2,6-Bis(2-thienyl)benzo[1,2-*d*:4,5-*d*′]diimidazole (9). Compound **7** (m = 21.0 mg, 0.17 mmol) and Bandrowski's base **3** (m = 24.9 mg, 0.08 mmol) were dissolved in EtOH, and the mixture was heated to reflux under argon. After being stirred for 20 h, the mixture was then cooled to room temperature and the obtained precipitate was isolated by filtration and washed with ethanol to give **9** as a brown solid (*m* = 21.6 mg, 57% yield): ^{1}H NMR (DMSO-d_6) δ = 5.64 (s, 4H, NH_2), 6.80 (d, $^3J_{HH}$ = 8.5 Hz, 4H, aromatic H), 6.91 (m, 2H, aromatic H), 7.01−7.04 (m, 2H, aromatic H), 7.12−7.17 (m,

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6H, aromatic H), 7.62−7.64 (m, 2H, aromatic H); ^{13}C NMR (DMSO-d_6) δ = 97.7, 114.6, 123.3, 127.6, 127.7, 128.8 (aromatic C), 129.0 (C−S), 132.7, 136.4, 139.9 (C−N), 148.0, 150.0 (C=N); HRMS (ESI) calcd for $C_{28}H_{20}N_6S_2$ $[M + H]^+$ 505.1264, found 505.1259.

Synthesis of 1,5-Diphenylamine 2,6-Bis(2-[4-[2-(5-chloro-2-methyl-3-thienyl)cyclopent-1-en-1-yl]-5-methylthienyl)benzo[1,2-*d*:4,5-*d*′]diimidazole (11). 4-[2-(5-Chloro-2-methyl-3-thienyl)-cyclopent-1-en-1-yl]-5-methylthiophene-2-carbaldehyde (**10**) (140.0 mg, 0.43 mmol) and Bandrowski's base **3** (62.75 mg, 0.197 mmol) were dissolved in EtOH in the presence of one drop of piperidine. The mixture was stirred under reflux during 20 h under argon. The solvent was then removed under reduced pressure, and the residue was purified by column chromatography (eluent cyclohexane/EtOAc (6/4)) affording **11** as an orange solid (m = 102 mg, 54% yield): ^{1}H NMR (DMSO-d_6) δ = 1.81 (s, 6H, CH_3), 1.92 (br s, 10H, CH_3, CH_2), 2.58−2.75 (m, 8H, CH_2), 5.65 (br s, 4H, NH_2), 6.66 (s, 2H, CH), 6.76−6.84 (m, 6H, CH), 7.05−7.11 (m, 6H, aromatic H); ^{13}C APT NMR (DMSO-d_6) δ = 13.75, 13.83 (CH_3), 22.08, 37.63 (CH_2), 97.47 114.46, 123.24, 123.57, 127.19, 128.51, 128.58, 128.73, 133.08, 133.81, 134.28, 134.80, 135.73, 136.26, 137.39, 139.91 (aromatic C), 147.67, 149.84 (C=N), only two peaks could be observed for the CH_2 groups owing to a signal overlap; ^{13}C DEPT 135 NMR (DMSO-d_6) δ = 13.76, 13.84 (CH_3), 22.07, 37.63 (CH_2), 97.47, 114.46, 127.19, 128.58, 128.72 (aromatic CH); HRMS (ESI) calcd for $C_{50}H_{42}N_6S_4Cl_2$ $[M + H]^+$ 925.1804, found 925.1810.

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Supporting Information Available: NMR data of the new compounds and atomic coordinates of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.