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Novel Bisthienylethenes Containing Naphthalimide as the Center Ethene Bridge: Photochromism and Solvatochromism for Combined NOR and INHIBIT Logic Gates

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Two novel photochromic bisthienylethene derivatives BTE-NA1 and BTE-NA2 with a six-membered aryl ring of naphthalimide fluorescent moiety as the center ethene bridging unit were synthesized and fully characterized by ^{1}H NMR, ^{13}C NMR, and HRMS. They exhibit considerably high cyclization quantum yield and good fatigue resistance. Interestingly, the fluorescence of BTE-NA1 arising from the naphthalimide unit could be well modulated by photochromism and solvatochromism. Quantum chemical calculations were carried out to study their geometrical, electronic, and optical properties, which were in good accordance with the experimental data. Furthermore, a combined NOR and INHIBIT logic operation based on BTE-NA1 has been successfully mimicked with fluorescence changes as outputs.

Introduction

The bistable states of photochromic compounds with fluorescent modulation (*on* and *off*) show great prospects in potential application, such as molecular switches, logic gates, and information storage.[1] Interestingly, a series of logic gates based on photochromic moieties have been constructed with light irradiation as inputs and fluorescence as outputs, indicative of an unprecedented advantage combining all-optical performance with reset capability by means of photoinduced or thermal back isomerization.[2] In order to increase the signal/noise ratio of the binary states, a straightforward methodology to enhance the luminescence and further realize fluorescence modulation is to link a fluorescent moiety with photochromic unit via covalent bond,[3,4] in which the fluorescence changes (on and off) could be well tuned in the photocoloration reaction by an efficient energy transfer from the excited fluorescent unit to the colored form of photochromic unit. Alternatively, we have incorporated a ferrocene unit as a triplet quencher to increase the thermal stability of open-form spirooxazine, thus successfully realizing high density storage.[5]

Diarylethenes, especially bisthienylethenes (BTEs), are one of the most promising families for the applications due to their excellent thermal stability and outstanding fatigue resistance among various photochromic compounds.[1a] To date, the rational design and successful syntheses of symmetric or asymmetric diarylethenes have been established with heteroaryl units, such as thiophene or benzothiophene,[6] furan and benzofuran,[7] thiazole,[8] indole,[9] pyrazole,[10] and pyrrole[11] rings. Even a type of 6π conjugated photochromic system with a bis(2,3′-benzothienyl) unit can also exhibit efficient photochromism and thermal stability for the colored isomers.[12] Additionally, a class of photochromic compounds based on a modified hexatriene skeleton were also reported.[13] However, the center ethene bridges for most BTEs reported so far have been confined to the cyclopentene unit[1,14] or its strong electron-withdrawing analogs, such as perfluoro-cyclopentene,[15] maleic anhydride, or maleic imide.[16] Moreover, BTE systems with such vinyl bridges usually show rather small fluorescence changes upon photochromism. Therefore, in an effort to develop novel photoactive molecules with fluorescence modulation, other ethene bridges instead of cyclopentene units should be taken into account. Yam et al. have reported a photoactive diarylethene containing 1,10-phenanthroline ligand and its metal complexes to perform photochromism.[17] Herein we describe two novel bisthienylethene derivatives BTE-NA1 and BTE-NA2 (shown in Scheme 1) with the unprecedented six-membered aryl ring of naphthalimide fluorescent moiety as the center ethene bridging unit. The designs are on the basis of the following considerations: (1) With similarly strong electron-withdrawing properties of perfluoro-cyclopentene, maleic anhydride, or maleic imide, the remarkably electron-withdrawing imide group of naphthalimide unit might be expected to ensure considerable bistability and good fatigue resistance with such incorporated six-membered aryl bridge. Previously we have found that, due to the strong electron-withdrawing effect, the incorporated naphthalimide unit can increase remarkably the lifetimes of open merocyanine (MC) forms, almost three magnitudes longer than that of unsubstituted spironaphthoxazine.[18] (2) Naphthalimides are essentially fluorescent chromophores with high efficiency and chemical stability.[19] As expected, BTE-NA1 and BTE-NA2 exhibit photochromism with considerable stability and good fatigue resistance. More interestingly, the fluorescence of the bridged naphthalimide moiety can be successfully switched on and off by photoinduced conversion between the open and closed forms. Surprisingly, the fluorescence of open form BTE-NA1 is shifted from 420 nm in nonpolar cyclohexane to 550 nm in polar acetonitrile which is much larger than that of the known environment-sensitive fluorophores based on 1,8-naphthalimide derivatives.[20] To the best of our knowledge, BTE-NA1 and BTE-NA2 are the first photochromic bisthienylethene cases bearing fluorescent moiety as six-membered aryl bridge for the center ethene unit. Finally, the NOR and INHIBIT logic gates with light irradiation and polar solvent as input signals and fluores-

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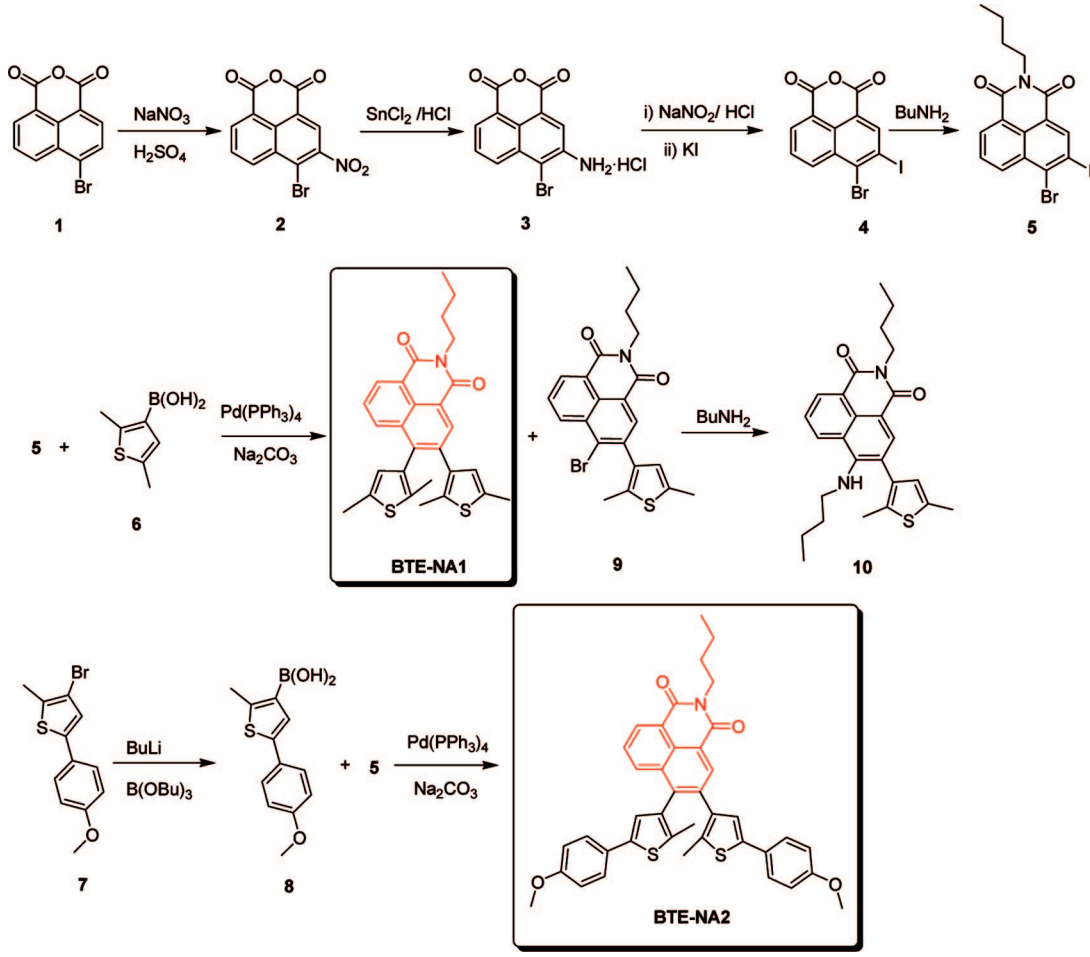
SCHEME 1: Synthetic Routes of BTE-NA1 and BTE-NA2



cence as outputs were constructed with BTE-NA1. It is worth mentioning that solvent polarity is a noticeable input signal in the molecular logic systems.[21]

Results and Discussion

Synthesis. Generally, photochromic BTE systems with center cyclopentene bridges always show weak or no fluorescence change upon photochromism under irradiation at particular wavelengths. To develop photochromic compounds with fluorescent modulation, we directly incorporated a fluorescent moiety of naphthalimide as a six-membered aryl unit for the unprecedented center ethene bridge. As illustrated in Scheme 1, the target molecules of BTE-NA1 and BTE-NA2 were prepared by conventional Suzuki cross-coupling reactions of 4-bromo-*N*-butyl-3-iodo-1,8-naphthalimide (5) with the corresponding boronic acids. The critical intermediate 5 was prepared via four steps by a modified procedure.[22] Unexpectedly, Suzuki coupling of 5 and 6 resulted in a mixture of BTE-NA1 and monocoupled byproduct 9 which were difficult to be separated by general chromatography method due to the exact similar polarity. Fortunately, after further treating the mixture with primary amine (butan-1-amine, $BuNH_2$) in ethylene glycol monomethyl ether, the monocoupling byproduct 9 can be successfully removed by converting it into 10 which has higher polarity than both 9 and BTE-NA1. In contrast, the synthesis of BTE-NA2 was straightforward by conventional Suzuki reaction. Their chemical structures were well confirmed by ^1H NMR, ^{13}C NMR and HRMS (see the Experimental Section and the Supporting Information for details).

Photochromism and Thermal Stability. BTE-NA1 and BTE-NA2 had no absorption band in the visible range, and their solution appeared to be colorless. Upon UV light irradiation, the solution of BTE-NA1 and BTE-NA2 quickly turned to green along with the increase of new peaks in the visible region (Figure 1 and Figure S1 in the Supporting Information). This is ascribed to the enlarged π system upon photochromic reaction as shown in Scheme 2. The optical properties of BTE-NA1 and BTE-NA2 before and after irradiation were summarized in Table 1. Compared with the conventional BTEs with cyclopentene as bridging unit, an absorption shoulder at the wavelength of 380 nm is noticeable (Figure 1A), which is resulted from the center bridge of the incorporated naphthalimide moiety. Generally, for photochromic BTEs, the two thienyl groups are not in the same plane due to their steric hindrance, but always in parallel and antiparallel form. Accordingly, it is the weak conjugation between thienyl groups and naphthalimide moiety in the open form that still keeps the observed characteristic absorption of naphthalimide unit.[23] Upon irradiation at 365 nm in cyclohexane, two new absorption bands at 410 and 627 nm and a shoulder at 390 nm are increased for BTE-NA1, and for BTE-NA2, the peaks are shifted to 448 and 719 nm and the shoulder at 425 nm (Figure 1). This indicates that the energy gap between HOMO and LUMO orbitals of the closed form BTE-NA2 (*c*-BTE-NA2) is smaller than that of the closed form BTE-NA1 (*c*-BTE-NA1), which probably results from the extended π system and larger push−pull effect of the contribution of 4-methoxyphenyl group.

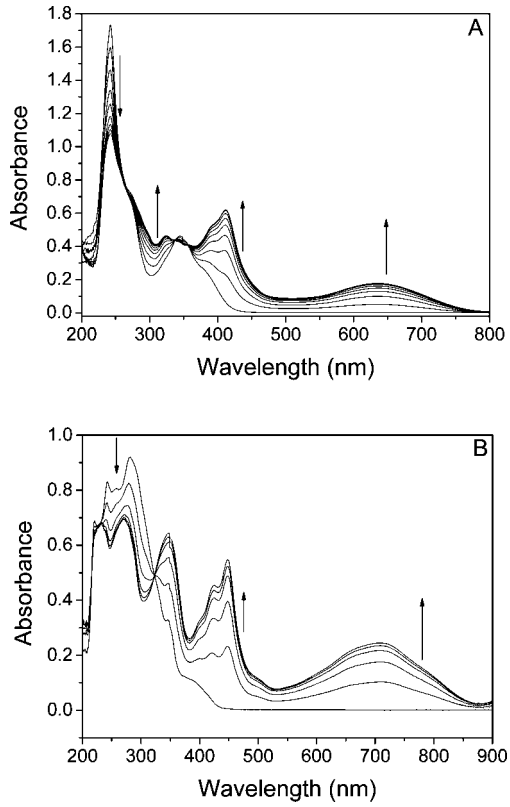
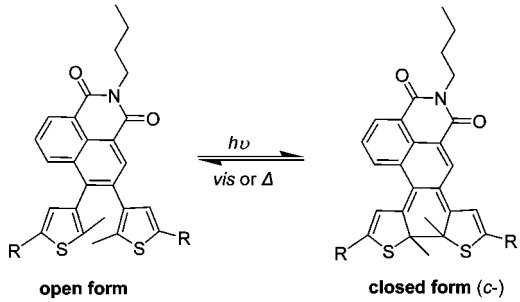


Figure 1. Absorption changes upon UV irradiation at 365 nm in cyclohexane: (A) BTE-NA1 (2.8×10^{-5} mol·L^{-1}); (B) BTE-NA2 (2.1×10^{-5} mol·L^{-1}).

SCHEME 2: Photochromism of BTE-NA1 and BTE-NA2



BTE-NA1: R = -CH_3

BTE-NA2: R = 4-methoxyphenyl

The increase of absorption intensity in the visible range corresponds to the closed form of BTE-NA1 and BTE-NA2 (Scheme 2), which can be directly evidenced from ^{1}H NMR spectral analysis before and after irradiation at room temperature. Taken BTE-NA1 as an example, it showed distinct differences in proton NMR signals between the open form and closed form both in the high-field and low-field area in that the π-delocalization system was far extended through photochromic reaction. Since *c*-BTE-NA1 was difficult to be separated from BTE-NA1 due to the thermal cycloreversion, ^{1}H NMR signal changes after UV irradiation for 5 min were shown in Figure 2. All proton signals on *N*-butyl group after photocyclization shifted upfield to some extent with respect to the open form. The methyl protons (H_a) on the butyl group which were most far from the π-delocalization had a slight shift from 1.00 to 0.96 ppm while the methylene hydrogen signals (H_d) attached with imide nitrogen changed by 0.15 ppm from 4.22 to 4.07 ppm. The four groups of methyl protons on thiophene group of BTE-NA1 were located at 1.90, 2.21, 2.34, and 2.44 ppm, respectively. In this case, the parallel and antiparallel forms did not show any obvious distinction in NMR spectrum. After photocyclization, the signals of these methyl protons were shifted to 2.08, 2.22, and 2.24 ppm or overlapped with BTE-NA1 at 2.21 ppm. As expected, the protons (H_e, H_f, H_g, and H_n) on the naphthalimide moiety shifted remarkably to the high field upon photocyclization, which might be attributed to the great changes (extended π-delocalization) in the chemical environment upon photochromic reaction. A typical triplet peak corresponding to H_f moved from 7.69 to 7.36 ppm. The singlet peak of H_n shifted greatly from 8.58 to 7.82 ppm. Additionally, the two protons (H_h, H_m) located on thiophene were 6.22 and 6.44 ppm for BTE-NA1, while they shifted to 6.29 and 6.31 ppm after photocyclization. Additionally, HPLC can also monitor the closed form in photocyclization. For instance, the ratio of the closed form in the photostationary state of BTE-NA1 in THF was 67%, obtained from the corresponding integrated areas of HPLC peaks detected at the isobestic wavelength 345 nm (Figure S2 in the Supporting Information).

Most diarylethenes may have two conformations—photochemically inactive parallel and active antiparallel—and the photocyclization reaction is allowed only from the antiparallel form.[1a] In general, the population ratio of two conformations is 1:1, therefore, the photocylization quantum yield can not exceed 0.5. Here the photocyclization yields of BTE-NA1 and BTE-NA2 in cyclohexane were 0.46 and 0.26 (Table 1), respectively. Similar results were obtained in other solvents, indicative of the satisfying quantum yield for photocyclization with respect to the reported BTE systems.[6]

The thermal stability of the closed form of both photochromic compounds was also studied. As illustrated in Figure S1 in the Supporting Information, the yellowish green appearance of *c*-BTE-NA2 in THF was gradually bleached in about one hour while *c*-BTE-NA1 still maintained its green color with slight bleaching, which indicated that the closed form *c*-BTE-NA1 in solution was much more stable than *c*-BTE-NA2 under dark condition at room temperature. Figure S3 in the Supporting Information shows the typical absorption spectra changes of the colored *c*-BTE-NA2 in dark and its photobleaching decay at 719 nm, which were acquired at certain time intervals (4 min) in the dark after UV light irradiation. The decrease of absorption band at 719 nm indicates thermal cycloreversion, and the absorbance decay followed a single-exponential kinetic. The first-order cycloreversion reaction rate constant k_T was evaluated to be 7.4×10^{-4} s^{-1} of *c*-BTE-NA2 in cyclohexane at 293 K. Also the decrease of absorption band at 636 nm revealed that the thermal bleaching from *c*-BTE-NA1 to BTE-NA1 in cyclohexane followed a similar single-exponential kinetic decay with a constant (k_T) of 7.9×10^{-6} s^{-1}. Notably, *c*-BTE-NA1 exhibited significantly long lifetime, two magnitudes longer than that of *c*-BTE-NA2 under the dark thermal relaxation. Table 2 summarizes the half-life data of *c*-BTE-NA1 and *c*-BTE-NA2 in various solvents.

Both BTE-NA1 and BTE-NA2 could reversibly perform the photochromism and thermally revert back in the dark with considerable fatigue resistance. As a case illustrated in Figure S4 in the Supporting Information, BTE-NA2 did not show any obvious degradation over 5 cycles. Clearly, BTE-NA1 and BTE-NA2 still keep the photochromic properties of parent cyclopentene bridged BTEs with considerable bistability and good fatigue resistance when replacing the five-membered cyclopentene ring by a fluorescent moiety of naphthalimide with a six-membered aryl unit as the center ethene bridge. Moreover, their

TABLE 1: Absorption Data and Photocyclization Quantum Yields (Φ_{O-C}) of BTE-NA1 and BTE-NA2 Before and After UV Irradiation in Cyclohexane and THF, Respectively

compounds	open form (λ_{max}, nm)	closed form (*c*-) λ_{max}, nm	Φ_{O-C}[a]
BTE-NA1 (in cyclohexane)	241, 340, 380 (sh)	390 (sh), 410, 627	0.46
BTE-NA1 (in THF)	242, 345, 385 (sh)	390 (sh), 410, 635	0.38
BTE-NA2 (in cyclohexane)	242, 350, 395 (sh)	425 (sh), 448, 719	0.26
BTE-NA2 (in THF)	242, 350, 395 (sh)	428 (sh), 450, 724	0.28

[a] Note: Quantum yields were calculated at 250 nm for BTE-NA1 and 275 nm for BTE-NA2, respectively, according to the literature method.[6a]

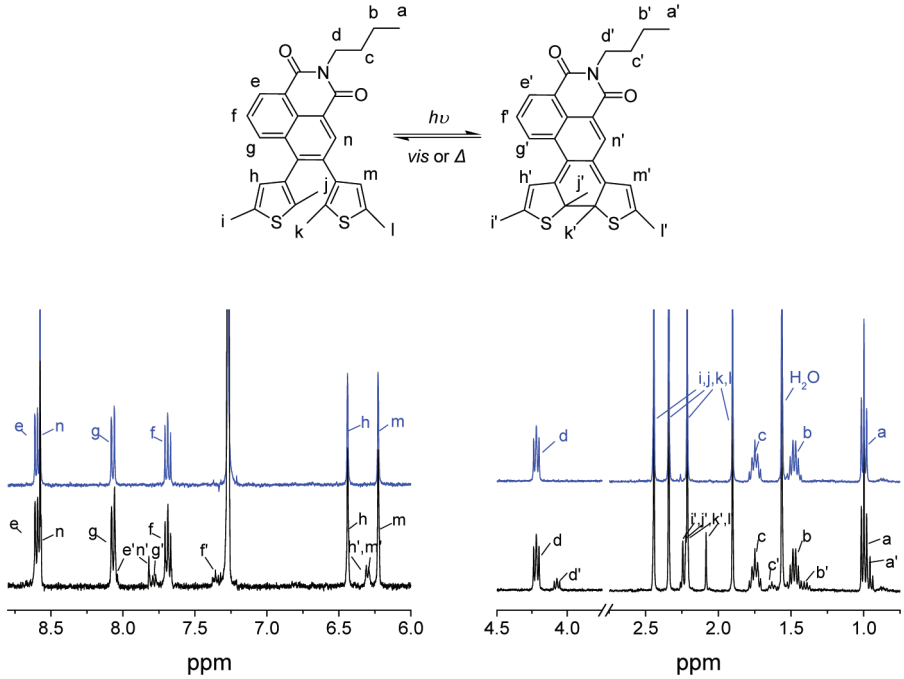


Figure 2. ^{1}H NMR signal changes of BTE-NA1 before and after photochromic reaction in $CDCl_3$.

TABLE 2: Half-life of *c*-BTE-NA1 and *c*-BTE-NA2 in Different Solvents

compounds	cyclohexane (min)	tetrahydrofuran (min)	acetone (min)	acetonitrile (min)
c-BTE-NA1	1468	167	98	96
c-BTE-NA2	15.4	7	36	1.0

photostationary states were achieved very fast within 2 min at low concentration. The good photochromism performance of fast responding and fatigue resistance might be attributed to the remarkable electron-withdrawing imide group of naphthalimide unit.

Fluorescence Modulation and Solvatochromism. Photochromic compounds could be potentially applied in recording media, wherein the two states could be read out by the properties modulated by the photochromic reaction such as the absorbance, fluorescence, electrochemical properties, IR, and refractive index.[1] Among these outputs, fluorescence emission is considered to be one of the most attractive owing to its ease of detection and the cheap fabrication of devices.[4,24] As discussed above, the naphthalimide unit as a fluorophore was directly incorporated into the center ethene bridge for the purpose of fluorescence modulation. Upon irradiation at 365 nm, both polar and nonpolar solution of BTE-NA1 exhibited a distinct fluorescence quenching (Figure 3), in which the fluorescence efficiency was distinctly dropped by 80% when reaching the photostationary state. Obviously, this is resulted from the closed form as a fluorescence quencher[3,4] in the possible channel of Förster resonance energy transfer (FRET). Upon irradiation, the generated closed form *c*-BTE-NA1 has a broad absorption which almost covers the whole visible area (Figure 1), thus resulting in an efficient overlap between the absorption and emission band. It is the FRET from the excited fluorescent chromophore unit to the ring-closed diarylethene unit that successfully switched on and off the fluorescence of the incorporated naphthalimide unit.[6f] However, considering the donor of thiophene unit and acceptor of naphthaimide moiety, also we could not strictly ruled out the possibility of photoinduced electron transfer (PIET) process. Anyway, the bistable states of BTE-NA1 and BTE-NA2 with fluorescent modulation show great prospects in potential application, such as molecular switches and information storage.

More interestingly in Figure 3, solvent polarity plays a significant role in the luminescent wavelength of BTE-NA1, which is red-shifted by 130 nm from about 420 nm in nonpolar cyclohexane to around 550 nm in polar acetonitrile. The fluorescent lifetime is 2.11 ns (51.95%) and 6.99 ns (48.05%), fitted with double exponential decaying with $\chi^2 = 1.479$ in cyclohexane, while in acetone, the value is prolonged to 5.25 ns (86.6%) and 5.80 ns (13.4%) with $\chi^2 = 1.442$. Taking together, the fluorescence color of BTE-NA1 could be well modulated by adjusting solvent polarity with a 10% increment in acetone volume proportion from 0 to 100%, which could be directly observed by naked eyes (Figure 4).

For BTE-NA1, the distinct solvatochromism upon fluorescence can be attributed to the intramolecular charge transfer (ICT) effect and solvent relaxation of the incorporated naphthalimide unit. For naphthalimide derivatives, there exists a

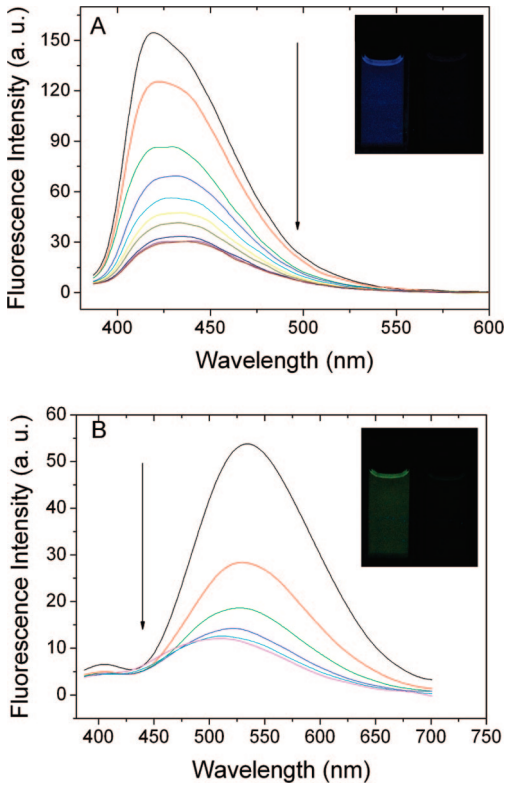


Figure 3. Fluorescence bleaching of BTE-NA1upon irradiation with UV light in cyclohexane (A) and acetone (B). (inset) Corresponding photographic images of fluorescence before (left) and after (right) UV irradiation. The fluorescence was obtained under excitation of 380 nm, and the concentration was 2.8×10^{-5} mol·L^{-1}.

"push−pull" π electron system resulting in a strong ICT in the lowest excited singlet state and considerable dipole character. The absorption and emission bands of 1,8-naphthalimide derivatives are largely dependent upon the electron donating potential of 4-substituents.[23,25] In fact, several naphthalimide derivatives have been reported as solvatochromic fluorophores.[20,23]In most cases, the dipole moment of solvatochromic fluorophore molecules in the excited state (μ_e) is usually larger than that in the ground state (μ_g) due to the ICT effect upon excitation. Following excitation, the solvent cage undergoes a relaxation or reorganization, leading to a relaxed state of minimum free energy. The higher the solvent polarity, the lower the energy of the relaxed state and the larger the red-shift of the emission spectrum.[26]

As mentioned above, the thiophene groups and naphthalimide moiety are not coplanar due to the steric hindrance, thus still keeping the solvatochromic fluorophore characteristics of naphthalimide moiety. Since the thienyl substituent in BTE-NA1 is a moderate electron-donating group, the fluorescence wavelength of BTE-NA1 at 420 nm in cyclohexane, resulting from naphthalimide unit, blue-shifted to some extent with respect to that of 4-alkylamino-1,8-naphthalimide derivatives. However, BTE-NA1 possesses a larger solvatochromic effect, which might be resulted from the difference in dipole moments between the excited and the ground states. This can also be further estimated from a Lippert−Mataga plot,[20,26] which is essentially a plot of the Stokes shift of the fluorescence emission vs the solvent polarity. The difference in the maximum absorption and emission wavelengths, expressed in wavenumbers ($\Delta\bar{\nu}$), is fitted to the following equation:

$$\bar{\nu}_A - \bar{\nu}_F = \Delta\bar{\nu} = \frac{2}{hca^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right)(\mu_e - \mu_g)^2 + \text{const} = \frac{2\Delta f}{hca^3}\Delta\mu^2 + \text{const} \quad (1)$$

Where, $\mu_e - \mu_g$ is the difference ($\Delta\mu$) between the dipole moments of the excited and the ground states, respectively, c is the velocity of light, h is Plank's constant, and α is the radius of the Onsager cavity around the fluorophore. The parameters ε and n are the solvent dielectric constant and refraction index, respectively, which are grouped in the term Δf, known as orientation polarizability. The Onsager radius was calculated to be 5.95 Å from the optimized structure obtained with a DFT minimization using the Gaussian 03 program (B3LYP functional using 6-31G(d) basis set).[27] As illustrated in Figure 5, the Stokes shift of a series of mixtures of cyclohexane/acetone or different solvents changes linearly in response to the solvent polarity which is evaluated by the parameter Δf. The difference of the two line slopes is less than 2.5% which indicated the well relationship of the Stokes shift vs the solvent polarity. The increase in the dipole moment ($\Delta\mu$) can be estimated to be 13 D according to the solvatochromic plots.

Theoretical Calculations for Electronic Structure. To gain insight into the geometrical, electronic, and optical properties of BTE-NA1 and BTE-NA2, we performed DFT calculations on the two chromophores and time-dependent DFT (TDDFT) calculations of their excited states, using the Gaussian 03 program package.[27] For comparison, the cyclopentene bridged chromophore BTE was also studied by the same theoretical model. Hybrid B3LYP exchange-correlation functional[28] and a 6-31G(d) basis set[29] were employed in consideration of both accuracy and efficiency. The ground-state geometries of BTE-NA1 and BTE-NA2 in open and closed forms have been optimized in vacuum by a standard force-minimization procedure and the vibrational spectra have been determined in order to check the absence of imaginary-frequency modes.

The ground-state geometries are shown in Figure 6 and structural parameters of open-ring and closed-ring isomers are tabulated in Table S1. The $C_2-C_{2'}$ distance always amounts to 1.54 Å in the closed forms, while in open forms, this distance increases to about 3.82 Å. In comparison with Maurel and coworkers' result for typical diarylethenes,[30] the distance for closed forms is exactly the same with their result (1.54 Å), and the value for open forms is larger than the reported distances of 3.62 ± 0.05 Å. The latter can be attributed to the larger steric hindrance in BTE-NA1 and BTE-NA2. This can also be reflected by the dihedral angles of τ_1 ($\tau_{1'}$) in the open forms, which are as large as 69.21° (66.63°) and 68.79° (66.87°) for BTE-NA1 and BTE-NA2, respectively. These dihedral angles are much larger than the reported values (40.0−52.0°).[30,31]

The excitation energies of both open-ring and closed-ring isomers are given in Table 3. For both open-ring and closed-ring isomers, the TD-DFT absorption spectra show that the λ_{max} transition corresponds to a HOMO → LUMO single excitation. Relative to *c*-BTE, *c*-BTE-NA1 and *c*-BTE-NA2 show considerable bathochromic effect by 87 and 183 nm, respectively. The calculated λ_{max} for closed-ring isomers is in good accordance with the experimental data. Nevertheless, the calculated transitions of the open forms for BTE-NA1 and BTE-NA2 are considerably red-shifted. This is related to the extended charge-transfer character of this transition, which is not properly captured by TDDFT calculations employing current exchange-correlation functionals.[32]

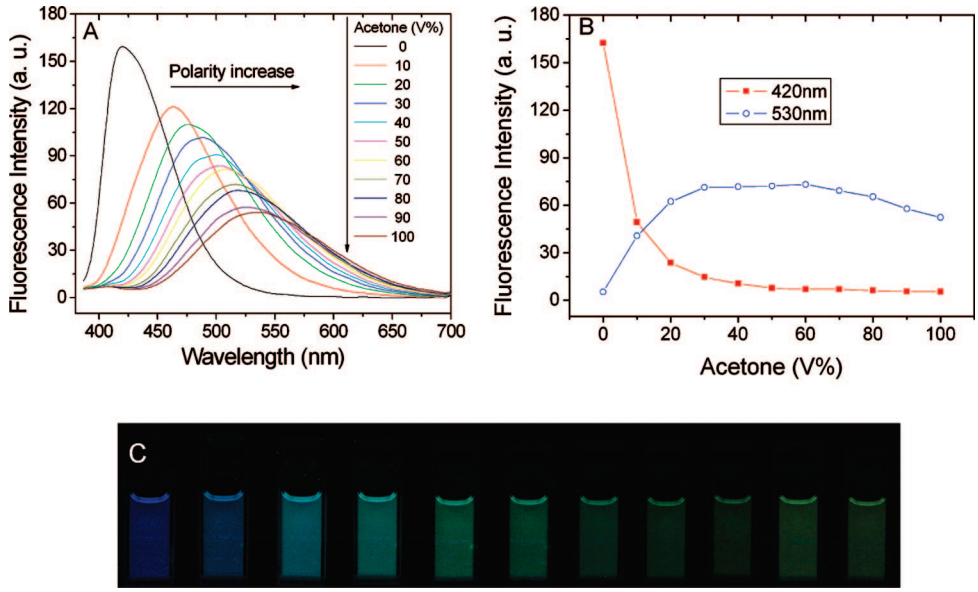


Figure 4. Solvent effect on the fluorescence of BTE-NA1 with an increase of acetone proportion in cyclohexane (excited at 380 nm): (A) the changes of fluorescence spectra; (B) the intensity changes at 420 and 530 nm; (C) from left to right, the photographic images of the fluorescence of BTE-NA1 modulated by adjusting solvent polarity with a 10% increment in acetone volume proportion from 0 to 100% (2.8×10^{-5} mol·L^{-1}).

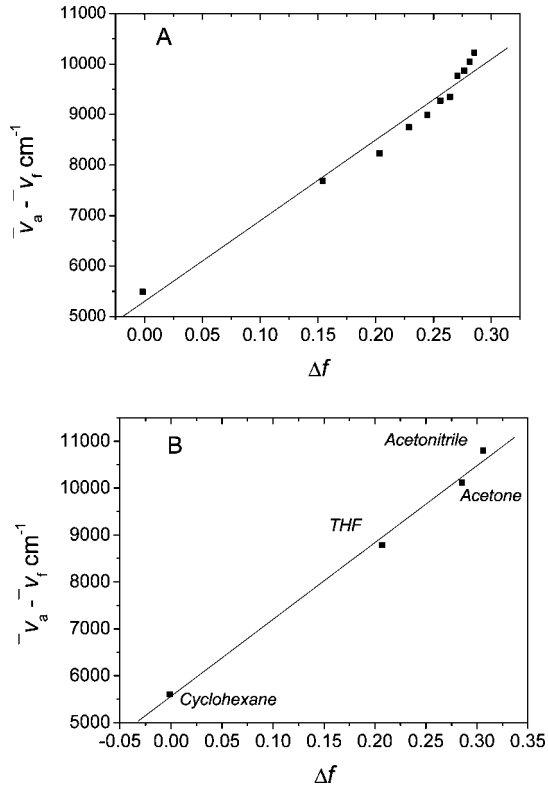


Figure 5. (A) Plot of the Stokes shift vs the solvent polarity measured as the orientation polarizability Δf derived from fluorescence spectra of BTE-NA1 in a series of cyclohexane/acetone mixtures. Δf is obtained for each mixture using ε and n values calculated using the molar fractions χ as follows: $\varepsilon = \chi_{Cyclohexane} \times 2.02 + \chi_{Acetone} \times 20.70$; $n = \chi_{Cyclohexane} \times 1.43 + \chi_{Acetone} \times 1.36$; $\chi_{Cyclohexane} + \chi_{Acetone} = 1$. (B) Lippert plot of BTE-NA1 in different solvents.

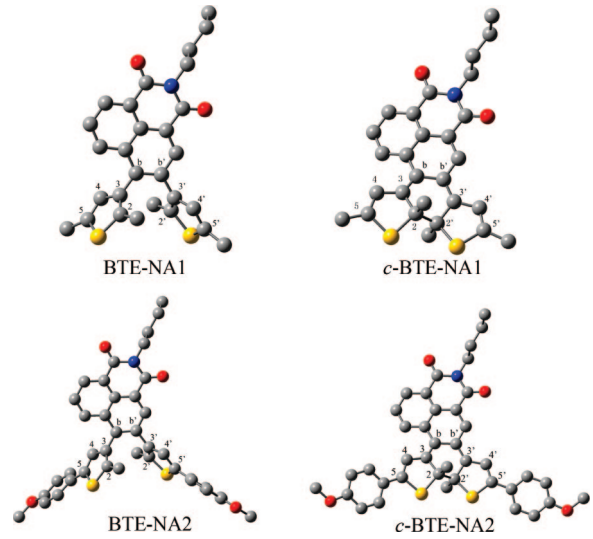


Figure 6. Optimized ground-state structures of open-ring and closed-ring isomers of BTE-NA1 and BTE-NA2 with B3LYP/6-31G(d) in gas phase. τ_1 ($\tau_{1'}$) represents the dihedral angle formed by $C_{b'}-C_b-C_3-C_2$ ($C_b-C_{b'}-C_{3'}-C_{2'}$). $r_{bb'}$ denotes the distance between C_b and $C_{b'}$. $r_{22'}$ is the distance between C_2 and $C_{2'}$. Hydrogen atoms are omitted for clarity.

The topologies of the calculated frontier orbitals are sketched in Figure 7. For BTE, HOMO mainly locates on the double bonds across the photochromic unit, and LUMO shows a significant density on the reactive carbon atoms. In *c*-BTE, LUMO shows a typical π^* character. The HOMOs of BTE-NA1 and BTE-NA2 are similar to that of BTE, but with the decreased density on the double bond of $C_b = C_{b'}$. However, the LUMOs of BTE-NA1 and BTE-NA2 are mostly centered on the top naphthalimide unit, with only a small contribution on the reactive C_2 ($C_{2'}$). It has been reported that the presence of electron-withdrawing substituent leads to a decrease in the electron density at the C_2 of the thiophene rings and a small component on one of the C_2 is sufficient to allow photocyclization.[31,33] This is in agreement with the photoreactivity of BTE-NA1 and BTE-NA2. And in *c*-BTE-NA1 and *c*-BTE-NA2, LUMOs are more delocalized over the whole chromophores than that in *c*-BTE. As compared to the common cyclopentene bridged bisthienylethene *c*-BTE, naphthalimide moiety bridged *c*-BTE-NA1 and *c*-BTE-NA2 exhibit a strong bathochromic effect. It is shown clearly in Figure 7 that in *c*-BTE-NA1 and *c*-BTE-NA2 an electron-withdrawing substituent can decrease

TABLE 3: Calculated Maximum Absorption Wavelength, Oscillator Strength, HOMO and LUMO Levels, and HLG's (HOMO and LUMO Gaps)

compounds	λ_{max} (nm)	description	oscillator strength	HOMO (eV)	LUMO (eV)	HLG (eV)
c-BTE	458.81	HOMO → LUMO	0.1786	−4.4137	−1.3908	3.0229
c-BTE-NA1	645.98	HOMO → LUMO	0.1250	−4.7838	−2.5590	2.2248
c-BTE-NA2	741.81	HOMO → LUMO	0.3491	−4.5008	−2.5987	1.9021
BTE	281.93	HOMO → LUMO	0.1063	−5.2594	−0.4552	4.8042
BTE-NA1	427.73	HOMO → LUMO	0.0187	−5.7574	−2.3258	3.4316
BTE-NA2	496.88	HOMO → LUMO	0.0087	−2.3072	−5.2741	2.9669

the antibonding character of the $C_b-C_{b'}$ bond in the HOMO orbital and the antibonding character of the C_b-C_3 and $C_{b'}-C_{3'}$ bonds in the LUMO simultaneously. This leads to simultaneous stabilization of both the HOMO and LUMO orbitals as shown in Table 3. Due to the fact that the LUMO stabilization overwhelms over the HOMO stabibization, the excitation energy decreases and λ_{max} increases, which is in good agreement with experiments.

Combined NOR and INHIBIT Logic Gates. In the light of the increasing demands of information technology (IT) in terms of miniaturization, chemistry plays a key role in the so-called bottom-up approach. Molecular and supramolecular logic gates are candidates for computation at the nanoscale level.[34] Photochromic molecules with high destiny fluorescence are ideal materials as molecular systems for their all-photon operation.[2] Since the fluorescence wavelength and the intensity can be well tuned with the photochromism and solvents to such a great extent which could be even distinguished by naked eyes, here we further illustrated two logic gates, NOR and INHIBIT gates constructed with BTE-NA1, utilizing light irradiation and polar solvent as input signals, and fluorescence as outputs. In such multifunctional logic gates, an excitation wavelength at 380 nm corresponding to the absorption peak of naphthalimide moiety was used as the power source, irradiation by 365 nm for the ring closing reaction was used as $input_1$, and the polar solvent was utilized as $input_2$ in the way by adding 10% acetone in volume to the solution of BTE-NA1 in cyclohexane. The output signals were detected at 420 and 530 nm corresponding to the fluorescence maximum of BTE-NA1 in cyclohexane and acetone, respectively. The emission intensity at 420 or 530 nm are defined as $output_1$ (F_{420}) and $output_2$ (F_{530}), respectively. Then the output signal threshold is set to be 0.7. When the irradiation at 365 nm is applied, the $input_1$ signal is on, that is to say the boolean value is "1". The $input_2$ signal is 1 when high-polar solvent of acetone is used. When $input_1$ and $input_2$ are both in the "0" state, that is to say the BTE-NA1 solution in cyclohexane is kept without irradiation, $output_1$ (F_{420}) is at its 1 state, for the luminescence excited at 380 nm is strong (higher than the defined threshold). While the BTE-NA1 solution of cyclohexane is irradiated by UV light or polarized by adding acetone, the fluorescence at 420 nm is quenched (lower than the defined threshold). In binary language, when either of $input_1$ or $input_2$ is at its 1 state, $output_1$ is 0. So the fluorescence behavior at 420 nm is coincided with the boolean logic NOR. The nonirradiated polar solution of BTE-NA1 shows a peak of fluorescence at 530 nm, so in this case the $input_1$ is 0 and $input_2$ signal is 1, the $output_2$ is at the 1 state. All of the other input states are shown to be weak or non fluorescence at 530 nm. So the performance of $output_2$ acts as INHIBIT logic operation. Here UV irradiation of BTE-NA1 could revert to its original state in the dark or by visible light. In contrast, the solvent polarity was difficult to revert to its original state. However, both cyclohexane and acetone have low boiling point at 80.7 and 56.1 °C at 101.3 kPa, respectively. So they could be removed easily under reduced pressure at room temperature. Furthermore, cyclohexane and acetone could form azotrope at 53.0 °C in which the content in weight of acetone is 67.5%, and it is easy to remove the 10% acetone under azotropic

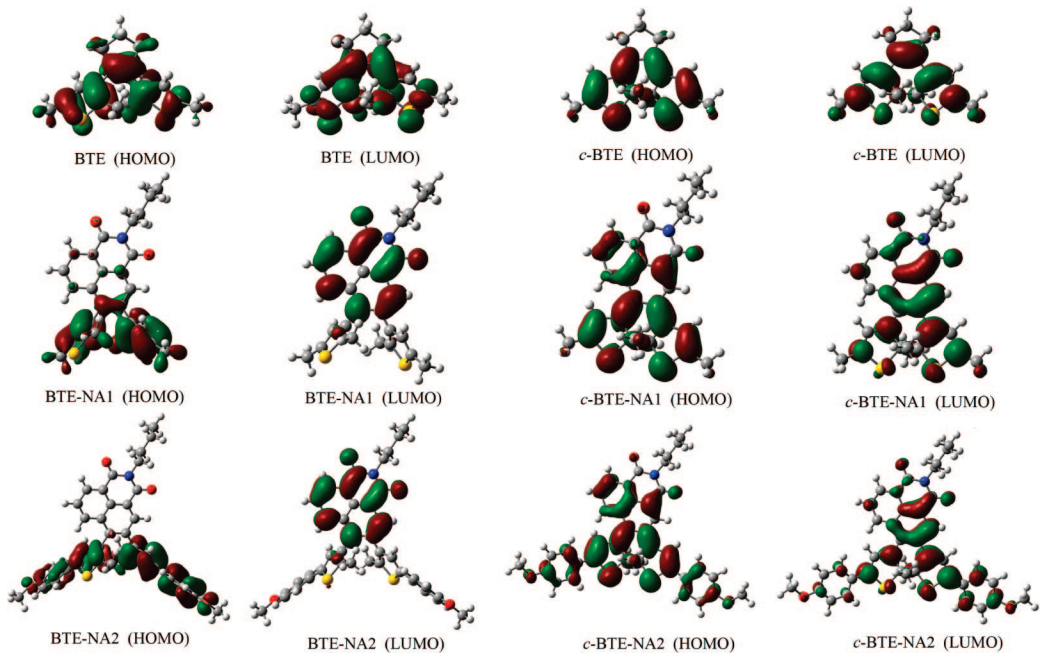
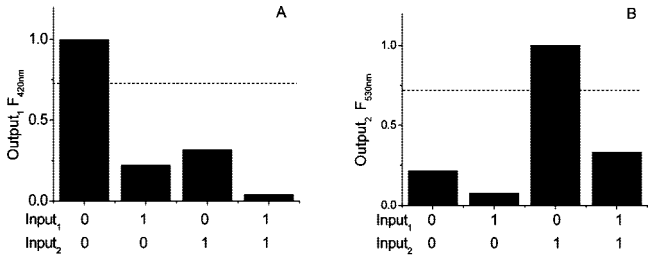


Figure 7. HOMO and LUMO orbitals of molecules BTE and *c*-BTE, BTE-NA1 and *c*-BTE-NA1, and BTE-NA2 and *c*-BTE-NA2 (isodensity = 0.025 au).



C

NOR Gate

$Input_1$	$Input_2$	$Output_1$
irradiation at 365 nm	Polar solvent	F_{420} nm
0	0	1
1	0	0
0	1	0
1	1	0

INHIBIT Gate

$Input_1$	$Input_2$	$Output_2$
irradiation at 365 nm	Polar solvent	F_{530} nm
0	0	0
1	0	0
0	1	1
1	1	0

Figure 8. (A) NOR gate function; (B) INHIBIT gate function; (C) truth table of NOR (left) and INHIBIT (right). Note that the bar graph shows the experimental emission intensity following the listed inputs (Figure S5 in the Supporting Information). The conditions for the inputs are described in the text. The doted line is a threshold level for detection of an on response.

distillation. Accordingly, the modulation of the fluorescence of BTE-NA1 in solution can be operated reversibly. Alternatively, one possible way around the difficulty of reversibly changing the solvent polarity is to immobilize the photochromic molecule on a solid substrate and to carry out the experiment in a flow cell; in this way, the solvent composition can be continuously varied without having to worry about having to evaporate one component, which would greatly reduce the feasibility of the process.[35] The logic performance is shown in Figure 8A and B and the truth table is given in Figure 8C.

Conclusion

Novel photochromic BTE-NA1 and BTE-NA2 containing naphthalimide bridging unit possess considerable high cyclization quantum yield and good fatigue resistance. The photobleaching kinetics study indicated that the closed form of BTE-NA1 was much more stable than BTE-NA2 in solution. Their fluorescence arising from naphthalimide unit could be well modulated by photochromism and solvatochromism. For BTE-NA1 and *c*-BTE-NA1, when the solvent polarity increases, LUMO is stabilized and HOMO is destabilized, thus leading to decreased HLG and bathochromic solvent effect. Solvent polarity has strong influences on the luminescence wavelength of BTE-NA1 which red-shifted by about 130 nm from nonpolar cyclohexane to polar acetonitrile. Moreover, the NOR and INHIBIT logic gates with light irradiation and polar solvent as input signals, and fluorescence as outputs were constructed with BTE-NA1. This novel molecular scaffold offers a chance to decorate photoresponsive systems with a wide range of functional groups without sacrificing photochromic behavior.

Experimental Section

General Information. ^{1}H NMR and ^{13}C NMR spectra were recorded on Brucker AM-400 or 500 spectrometers. MS were recorded on an ESI mass spectroscopy. Absorption and fluorescence spectra were recorded on Varian Cary 500 and Varian Cary Eclipse, respectively. Fluorescence lifetimes were measured on an Edinburgh Lifespec-Ps spectrofluorometer (FL920). HPLC analyses were determined by Agilen 1100 eluted by CH_3OH at a flow rate of 0.6 mL·min^{-1} detected at the isobestic wavelength 345 nm.

4-Bromo-1,8-naphthalic anhydride, and other starting materials were commercially available and purified before use. All other reagents were of analytical purity and used without further treatment. 4-Bromo-3-nitro-l,8-naphthalic anhydride (2),[36] 2,5-dimethylthiophen-3-yl boronic acid (6), and 5-(4-methoxyphenyl)-2-methylthiophen-3-yl boronic acid (8) were prepared according to the established method.[37]

3-Amino-4-bromo-l,8-naphthalic Anhydride Hydrochloric Acid Salt (3). To a previously prepared solution of $SnCl_2$ (15.5 g, 81.5 mmol) in glacial acetic acid (37 mL) saturated from hydrogen chloride was added 2 (5.0 g, 15.5 mmol) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and the precipitated solid was collected by filtration and washed with water. A reddish solid of 3 (3.7 g, 80%) was collected and dried. The product was directly used without further puration for the next step.

4-Bromo-3-iodo-l,8-naphthalic anhydride (4). To a solution of 3 (4.5 g, 15 mmol) in 22% HCl (160 mL) at 0 °C was added a solution of $NaNO_2$ (1.6 g, 23 mmol) in water (33 mL). The reaction mixture was stirred for 2 h at 0 °C. The resulting precipitate was added to a solution of KI (12.4 g, 75 mmol) in water (64 mL), and stirring was continued for 1 h. A solution of $NaHSO_3$ in water was added, and the formed solid was collected by filtration. Reflux in acetonitrile for 4 h gave 4 as a white solid (3.6 g, 60%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.04 (t, J = 7.6 Hz, 1H, naphthalene-H), 8.61 (d, J = 7.6 Hz, 1H, naphthalene-H), 8.71 (d, J = 7.6 Hz, 1H, naphthalene-H), 8.76 (s, 1H, naphthalene-H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 100.13, 119.43, 120.39, 129.45, 130.00, 130.30, 132.40, 133.44, 141.20, 142.83, 159.33, 160.24. Mass spectrometry (EI M^+): calcd, 401.8388; found, 401.8391.

4-Bromo-N-butyl-3-iodo-1,8-naphthalimide (5). A mixture of 4 (2.0 g, 5 mmol) and butan-1-amine (1.5 mL) in dioxane (30 mL) was reflux under argon for 3 h. The resulted solution was evaporated under reduced pressure. The product was purified by column chromatography using CCl_4:CH_2Cl_2 = 3:1 as eluting solvent to give 5 as a white solid (1.2 g, 52.7%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.98 (t, J = 7.2 Hz, 3H, $-CH_2CH_3$), 1.41−1.47 (m, 2H, $-CH_2CH_3$), 1.69−1.73 (m, 2H, $-NCH_2CH_2-$), 4.17 (t, J = 7.4 Hz, 2H, $-NCH_2-$), 7.85 (t, J = 7.7 Hz, 1H, naphthalene-H), 8.54−8.65 (m, 2H, naphthalene-H), 8.94 (s, 1H, naphthalene-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 13.81, 20.32, 30.13, 40.46, 97.67, 121.96, 123.27, 128.08, 128.71, 129.79, 131.41, 131.77, 140.74, 142.60, 162.31, 163.26. Mass spectrometry (EI M^+): calcd, 456.9174; found, 456.9176.

5-(4-Methoxyphenyl)-2-methylthiophen-3-yl Boronic Acid (8). A solution of 3-bromo-5-(4-methoxyphenyl)-2-methylthiophene[37a] (1.0 g, 3.54 mmol) in diethyl ether (30 mL) was cooled to −78 °C, and 2.4 mL of a 1.6 M solution of butyllithium in hexane was added under argon. The mixture was stirred for 15 min at that temperature, tributyl borate (1.2 g, 5.2 mmol) of was added in one portion, the mixture was stirred for 1 h at −78 °C. The cooling bath was removed, and the mixture was left overnight. A mixture of concentrated hydrochloric acid (1 mL) and water (15 mL) was added. The mixture was stirred for 1 h, the organic phase was separated, and the aqueous phase was extracted with diethyl ether (3 × 15 mL). The extracts were combined with the organic phase and washed with water and a 5% solution of sodium hydroxide (4 × 15 mL). The alkaline solution was washed with diethyl

ether (2 × 10 mL), cooled to −5 °C, and acidified with concentrated hydrochloric acid (10 mL) under stirring. The precipitate was filtered off, washed with a small amount of water, and dried in a desiccator to give 8 as a white solid (0.6 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.57 (s, 3H, $-CH_3$), 3.76 (s, 3H, $-OCH_3$), 6.94 (d, J = 8.4 Hz, 2H, phenyl-H), 7.43 (m, 3H, thiophene-H, phenyl-H), 7.87 (s, 2H, −OH).

BTE-NA1. The compound 5 (0.2 g, 0.44 mmol) was dissolved in dioxane (10 mL), $Pd(PPh_3)_4$ (0.1 g) was added, and the resulting mixture was stirred for 15 min at room temperature. Then aqueous Na_2CO_3 (10 mL, 2.0 mol·L^{-1}) was added. The reactive mixture was heated and refluxed at a temperature of 60 °C and the solution of 6 (0.156 g 0.1 mmol) was added dropwise via a syringe. Subsequently the mixture was refluxed for 24 h and cooled to room temperature, the reactive mixture was poured into H_2O and extracted with ether. The organic layer was separated and dried with Na_2SO_4. After concentration, the compound was purified by column chromatography on silica (petroluem: ethyl acetate = 20:1 v/v) to yield a yellowish-green solid. Then the solid was dissolved in ethylene glycol monomethyl ether, and butan-1-amine (1.2 g) was added. The mixture was refluxed for 5 h, and then the solvent was removed by reduced pressure. The resulted solid was purified by column chromatography on silica (petroluem: ethyl acetate = 20:1 v/v) to yield a yellowish-green solid (30 mg, 15%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.00 (t, J = 7.2 Hz, 3H, $-CH_2CH_3$), 1.45−1.51 (m, 2H, $-CH_2CH_3$), 1.71−1.79 (m, 2H, $-NCH_2CH_2-$), 1.90 (s, 3H, $-CH_3$), 2.21 (s, 3H, $-CH_3$), 2.34 (s, 3H, $-CH_3$), 2.44 (s, 3H, $-CH_3$), 4.22 (t, J = 7.4 Hz, 2H, $-NCH_2-$), 6.23 (s, 1H, thiophene-H), 6.44 (s, 1H, thiophene-H), 7.69 (t, J = 8.4, 7.2 Hz, 1H, naphthalene-H), 8.07 (d, J = 7.6 Hz, 1H, naphthalene-H), 8.58 (s, 1H, naphthalene-H), 8.60 (d, J = 7.2 Hz, 1H, naphthalene-H).^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 13.79, 13.84, 15.02, 15.15, 20.40, 29.68, 30.26, 40.24, 121.49, 122.76, 126.86, 126.91, 127.15, 127.43, 127.97, 130.65, 131.74, 133.08, 133.41, 133.50, 133.73, 135.03, 135.89, 136.05, 136.49, 140.29, 164.10, 164.39. Mass spectrometry (ESI positive ion mode for $[M + Na]^+$) calcd, 496.1381; found, 496.1386.

By-product 9. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.00 (t, J = 7.4 Hz, 3H, $-CH_2CH_3$), 1.43−1.51 (m, 2H, $-CH_2CH_3$), 1.71−1.79 (m, 2H, $-NCH_2CH_2-$), 2.29 (s, 3H, $-CH_3$), 2.50 (s, 3H, $-CH_3$), 4.17 (t, J = 7.6 Hz, 2H, $-NCH_2-$), 6.68 (s, 1H, thiophene-H), 7.88 (t, J = 8.0 Hz, 1H, naphthalene-H), 8.49 (s, 1H, naphthalene-H), 8.66 (d, J = 7.6 Hz, 1H, naphthalene-H), 8.69 (d, J = 7.6 Hz, 1H, naphthalene-H).

BTE-NA2. BTE-NA2 was prepared by a similar procedure as BTE-NA1 from naphthalimide 5 and 5-(4-methoxyphenyl)-2-methylthiophen-3-ylboronic acid (8) omitted of the butylamine dealing process. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.01 (t, J = 7.4 Hz, 3H, $-CH_2CH_3$), 1.46−1.52 (m, 2H, $-CH_2CH_3$), 1.73−1.81 (m, 2H, $-NCH_2CH_2-$), 2.01 (s, 3H, $-CH_3$), 2.35 (s, 3H, $-CH_3$), 3.81 (s, 3H, $-OCH_3$), 3.85 (s, 3H, $-OCH_3$), 4.24 (t, J = 7.6 Hz, 2H, $-NCH_2-$), 6.73 (s, 1H, thiophene-H), 6.82 (d, J = 8.4 Hz, 1H, phenyl-H), 6.91 (d, J = 8.8 Hz, 1H, phenyl-H), 6.98 (s, 1H, thiophene-H), 7.32 (d, J = 8.4 Hz, 2H, phenyl-H), 7.45 (d, J = 8.8 Hz, 2H, phenyl-H), 7.73 (t, J = 7.6, 8.0 Hz, 1H, naphthalene-H), 8.19 (d, J = 8.4 Hz, 1H, naphthalene-H), 8.64 (d, J = 7.2 Hz, 1H, naphthalene-H), 8.68 (s, 1H, naphthalene-H).^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 13.87, 14.03, 14.13, 20.42, 30.27, 40.30, 55.34, 55.38, 114.20, 114.34, 121.82, 122.83, 124.29, 125.08, 126.83, 126.92, 127.19, 127.55, 130.89, 131.71, 133.04, 133.44, 134.56, 134.92, 135.72, 136.43, 137.37, 139.74, 139.93, 140.72, 158.98, 159.23, 164.06, 164.32. Mass spectrometry (ESI positive ion mode for $[M + H]^+$): calcd, 658.2086; found, 658.2053.

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Supporting Information Available: Optical properties, thermal decay, photographic images of BTE-NA1and BTE-NA2 before and after UV irradiation and their thermal bleaching in the dark, HPLC traces of BTE-NA1, structural parameters of open-ring and closed-ring isomers, and ^{1}H NMR, ^{13}C NMR, and HRMS spectra of 4-bromo-*N*-butyl-3-iodo-1,8-naphthalimide, BTE-NA1, and BTE-NA2. This material is available free of charge via the Internet at http://pubs.acs.org.

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