JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

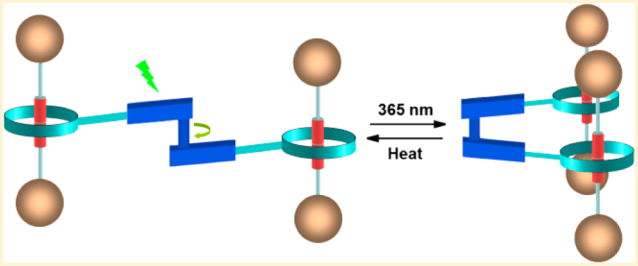
Photodriven Clamlike Motion in a [3]Rotaxane with Two [2]Rotaxane Arms Bridged by an Overcrowded Alkene Switch

Wei Zhou, Ya-Jing Guo, and Da-Hui Qu*

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, P. R. China

Supporting Information

ABSTRACT: A [3]rotaxane with two [2]rotaxane arms bridged by an overcrowded alkene switch has been constructed to perform the clamlike motion in response to light stimulus. We demonstrated that this [3]rotaxane can undergo reversible conformational changes caused by the *trans*−*cis* isomerizations of the central double bond with a favorable photostationary state (up to 90% conversion). It has been shown that the clamlike motion causes remarkable UV−vis and fluorescence spectral changes, allowing it to behave as a reversible optical molecular switch.



INTRODUCTION

The precise control over the motions in supramolecular and molecular systems is one of the great challenges that might lead to considerable advances in the field of molecular machinery[1] and nanoscience.[2] Inspired by fascinating biological and macroscopic analogues, a variety of artificial molecular machines have been constructed,[3] including molecular switches,[4] muscles,[5] motors,[6] gears,[7] and shuttles[8] that exhibit structural changes as well as changes in their photophysical properties in response to external stimuli. The use of light stimulation[9] has many advantages in terms of a fast response with light excitation and the possibility of a fine resolution. The overcrowded alkene,[10] which can be driven by light, has been extensively studied as light-driven molecular motors[11] and switches.[12] Several functional moieties have been introduced into the overcrowded alkene systems to realize special functions, such as the alterations of aggregation,[12a] magnetic interaction,[12b] and even in situ switching of the chiral preference of a catalytic system.[12c] The overcrowded alkene system has potential to construct versatile molecular machines that can perform specific mechanical motions due to its favorable photostationary state and remarkable structural changes caused by *trans*−*cis* isomerizations of the central double bond.[10] In this paper, we report a [3]rotaxane, with two [2]rotaxane arms separated by an overcrowded alkene switch, to perform the clamlike motion and mimic the action of dumbbell exercise. The photoinduced *trans-to-cis* isomerization of the central double bond has a favorable photostationary state (PSS) up to 90% conversion, and the generated *cis* isomer can be thermally converted to the original *trans* isomer. Importantly, the clamlike motion caused by the *tran*−*cis* isomerization can generate remarkable UV−vis and fluorescence spectral changes, making it behave as a reversible molecular switch with optical signals.

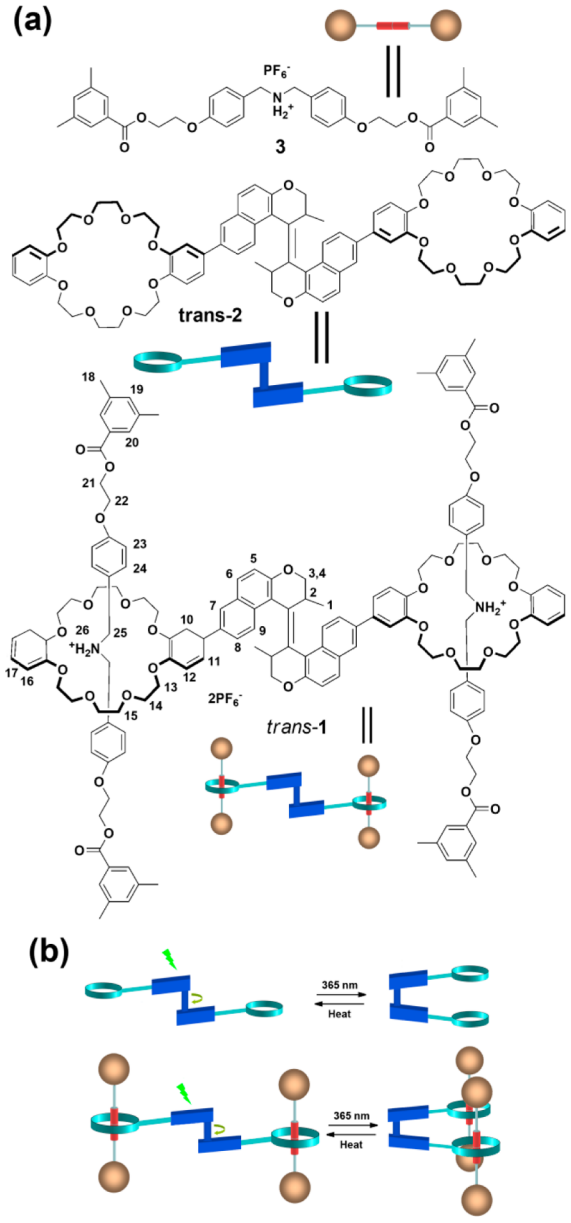
RESULTS AND DISCUSSION

Molecular Design and Syntheses. The chemical structures of the [3]rotaxane *trans*-**1** and its two precursors, the overcrowded alkene switch *trans*-**2** with two dibenzo-24-crown-8 (DB24C8) macrocycle rings, and the dumbbell-shaped compound **3** are illustrated in Scheme 1. As shown in Scheme 1, *trans*-**2** was designed with two DB24C8 macrocycles as arms, which are covalently linked with and separated by an overcrowded alkene switch. The [3]rotaxane *trans*-**1** also contains the same overcrowded alkene as a bridge to separate two DB24C8 rings, each of which is interlocked onto a dumbbell-shaped thread component bearing two 3,5-dimethylbenzene stoppers and a dibenzylammonium (DBA) station.[13] The key feature of [3]rotaxane *trans*-**1** and macrocycle *trans*-**2** is the introduction of an overcrowded alkene switch, which has good photochemical properties, including high *trans*−*cis* conversion in the photostationary state, fast response, etc. The photoinduced *trans-to-cis* isomerizations and the thermally driven *cis-to-trans* isomerizations of both *trans*-**1** and *trans*-**2** can generate remarkable change in the structures, which are shown in Scheme 1b.

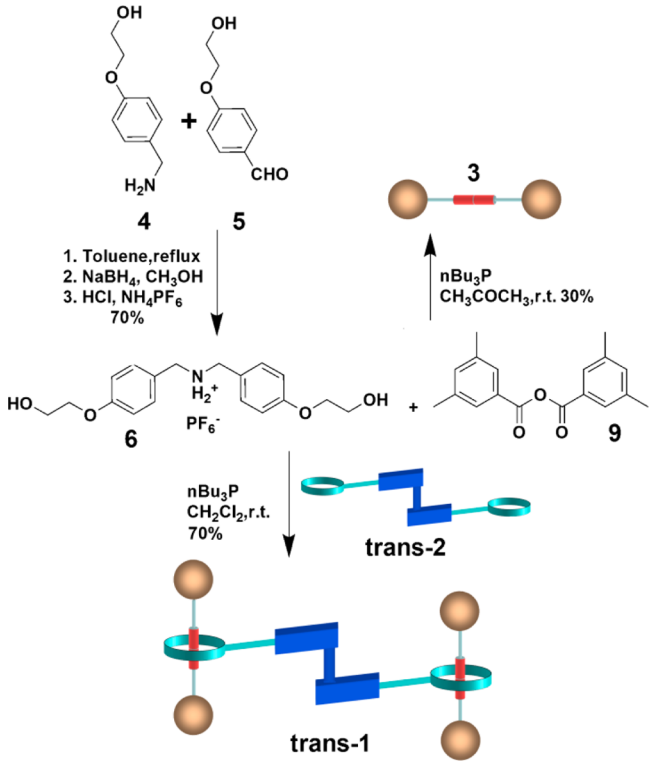
The syntheses of an overcrowded alkene switch *trans*-**2**, [3]rotaxane *trans*-**1**, and a dumbbell-shaped thread component **3** are shown in Schemes 2 and 3, respectively. As shown in Scheme 2, the bromo-substituted DB24C8 **10** was treated with bis(pinacolato)diboron in the presence of $Pd(dppf)Cl_2$ as catalyst to obtain macrocycle **11** in 90% yield. Starting from bromo-substituted ketone **7**, the well-known McMurry[14] coupling reaction can yield dibromo-substituted overcrowded alkene **8** in a moderate yield (45%), and the subsequent Suzuki coupling reaction between alkene **8** and macrocycle **11** results

Received: November 5, 2012
Published: December 18, 2012

Scheme 1. (a) Chemical Structures and Schematic Representations of [3]Rotaxane *trans*-1, an Overcrowded Alkene Switch *trans*-2, and a Dumbbell-Shaped Component 3. (b) Photochemically and Thermally Induced Reversible *Trans*−*Cis* Interconversions of [3]Rotaxane 1 and Alkene *trans*-2



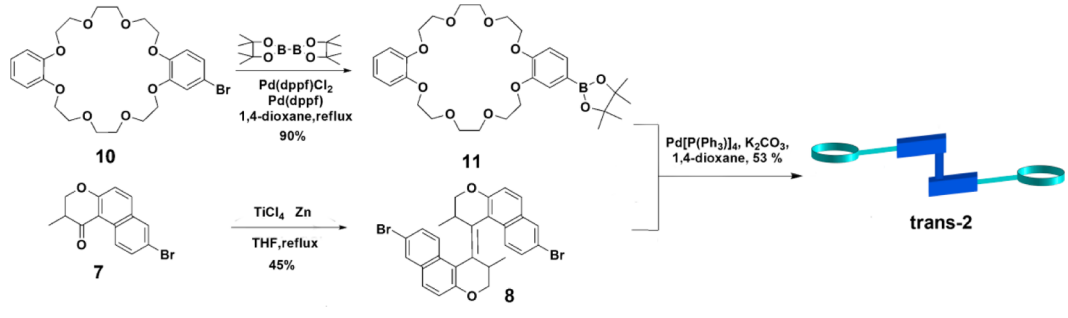
Scheme 3. Synthesis of [3]Rotaxane *trans*-1 and Dumbbell 3



in the formation of di-DB24C8-functionalized alkene *trans*-**2** in a 53% yield.

As shown in Scheme 3, the condensation of aldehyde **4** and benzylamine **5** was conducted in refluxing toluene, after which the obtained white Schiff base was then reduced with $NaBH_4$ in methanol, followed by acidification and ion exchange to give **6** in a 70% yield. Using a threading-followed-by-stoppering strategy,[15] [3]rotaxane *trans*-**1** was prepared in a relatively high yield (70%) via the tri-*n*-butylphosphine-catalyzed esterification[16] of dihydroxyl-functionalized thread **6** and anhydride **9** in the presence of macrocycle *trans*-**2**. The dumbbell-shaped compound **3** was also synthesized in a 30% yield as a reference compound in a similar strategy in the absence of macrocycle *trans*-**2**. Compared to a low yield (30%) in the preparation of dumbbell **3**, the relatively high yield (70%) in the preparation of [3]rotaxane *trans*-**1** is due to the inclusion function between the DB24C8 and dibenzylammonium, which can protect the ammonium center from being destroyed by the anhydride **9** in the presence of *n*-Bu_3P.

Scheme 2. Synthesis of *trans*-2



dx.doi.org/10.1021/jo302426c | J. Org. Chem. 2013, 78, 590−596

[3]Rotaxane *trans*-**1**, alkene *trans*-**2**, and dumbbell **3** were characterized by ^{1}H NMR and ^{13}C NMR spectroscopies and HR-ESI mass spectrometry (Supporting Information). The HR-ESI spectrum provides obvious evidence for the formation of the [3]rotaxane *trans*-**1**, which has the most intense peak at 1225.0732 m/z as a doubly charged peak for $[M - 2PF_6^-]^{2+}$, consistent with the calculated value (1225.0701).

^{1}H NMR Measurements. Comparison of the ^{1}H NMR spectra of the [3]rotaxane *trans*-**1**, alkene *trans*-**2**, and dumbbell **3** can provide sufficient evidence to confirm that the macrocycle is predominantly over the DBA binding site. As shown in Figure 1, the peaks for the methylene protons H_{25} on

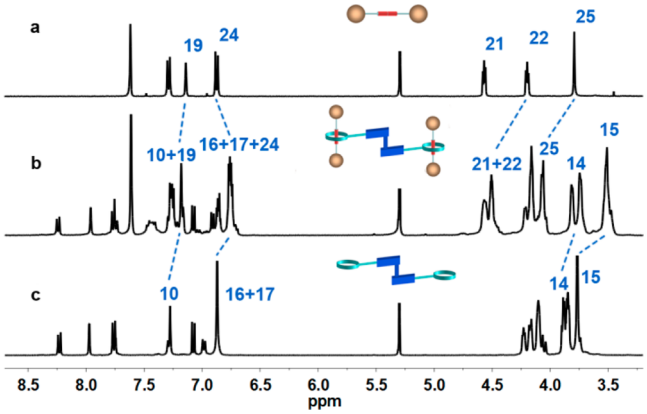


Figure 1. Partial ^{1}H NMR spectra (400 MHz, 298 K, CD_2Cl_2) of (a) dumbbell **3**, (b) [3]rotaxane *trans*-**1**, and (c) alkene *trans*-**2**. The assignments correspond to the structures shown in Scheme 1.

the DBA station shifted downfield ($\Delta\delta$ = 0.59 ppm) and the peak of proton H_{22} shifted downfield ($\Delta\delta$ = 0.31 ppm) after the formation of [3]rotaxane *trans*-**1**. The peaks of protons H_{14} and H_{15} on the DB24C8 experienced upfield shift ($\Delta\delta$ = −0.05, −0.23 ppm, respectively) relative to the ones of alkene *trans*-**2**, which was due to a combination of [N−H···O] and [C−H···O] hydrogen bonds.

The photoinduced *trans*−*cis* isomerizations of the central double bond of [3]rotaxane *trans*-**1** and macrocycle *trans*-**2**, which can generate a clamlike motion, were monitored with low-temperature ^{1}H NMR spectroscopy. Upon irradiation of *trans*-**1** (365 nm, 3 h, −40 °C) in CD_2Cl_2, a new signal corresponding to the *cis*-**1** isomer appeared (Figure 2) that was manifested by a decrease in the peak at 1.08 ppm (*trans*-H_1 on the switching unit) and the emergence of a peak at 1.69 ppm (*cis*-H_1). The peaks for the aromatic protons (H_{6-9}) of the naphthalene units were shifted upfield from 8.00 to 7.25 ppm. In the photostationary state, around 90% *cis*-**1** was generated. Upon allowing the solution to stand for 30 min at 30 °C in the dark, the *cis*-**1** was thermally converted back to *trans*-**1**, as evidenced by the regeneration of the original ^{1}H NMR spectrum.

The operating processes of *trans*-**2** are similar to those for *trans*-**1**. Irradiation at λ = 365 nm can convert *trans*-**2** into *cis*-**2**. In the PSS, the ratio between *cis*-**2** and *trans*-**2** is 91:9. The subsequent thermal conversion of the *cis*-**2** to *trans*-**2** was fully determined by the ^{1}H NMR changes (Figure 3). It should be mentioned that, in the light-driven molecular motor systems based on overcrowded alkenes,[6b] two photoinduced *trans*−*cis* isomerizations were followed by two irreversible thermal helix inversion steps, which completed a 360° rotary motion of the

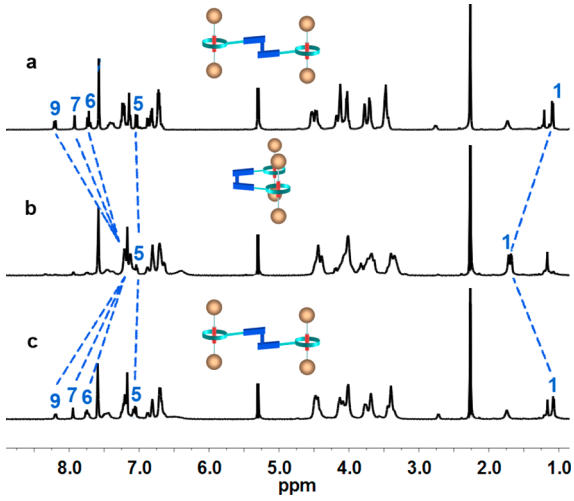


Figure 2. Partial ^{1}H NMR spectra (400 MHz, 233 K, CD_2Cl_2) of (a) rotaxane *trans*-**1**, (b) *PSS*-**1**, and (c) the solution obtained after standing for 30 min at 30 °C in the dark.

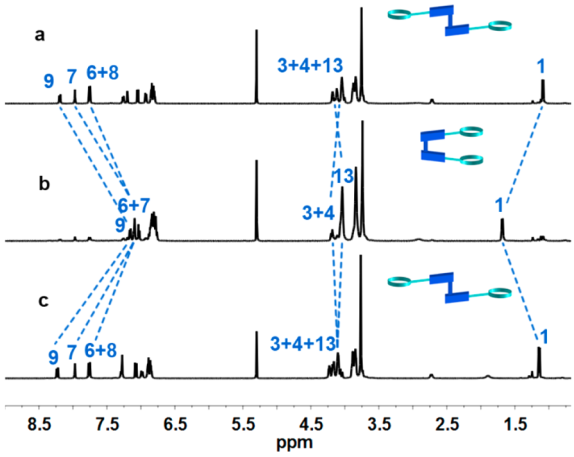


Figure 3. Partial ^{1}H NMR spectra (400 MHz, 233 K, CD_2Cl_2) of (a) alkene *trans*-**2**, (b) *PSS*-**2**, and (c) the solution obtained after standing for 30 min at 30 °C in the dark.

upper half rotor relative to the lower half stator. However, in the system presented here, large steric hindrance of the *cis* isomers of both **1** and **2** prevents the helix inversions and subsequent thermal relaxation recovers the system to the original *trans* isomers completely.

Photophysical Properties of [3]Rotaxane *trans*-1 and Alkene *trans*-2. Most importantly, the switching processes from *trans* to *cis* of alkene *trans*-**2** and rotaxane *trans*-**1** could be easily detected by the changes in color and fluorescence[17] with high sensitivity. The CH_2Cl_2 solution of *trans*-**1** was irradiated (365 nm, 10 min, −40 °C) to reach the PSS, and a new absorption band (λ_{max} = 423 nm) was observed due to the enhanced twist of the central olefinic bond in the *cis*-**1** state. An isosbestic point was displayed at 387 nm, which indicated a unimolecular process. Subsequent warming of the sample to room temperature resulted in the recovery of the original absorption band, thus suggesting the regeneration of *trans*-**1**. The fluorescence spectrum of *trans*-**1** exhibited a strong emission at 428 nm, and upon irradiation of *trans*-**1** with 365 nm, the emission intensity decreased by 90% (Figure 4c). The absolute quantum yield of fluorescence reduced from 4.8% (*trans*-**1**) to 0.31% (*PSS*-**1**). Subsequent warming of the sample

dx.doi.org/10.1021/jo302426c | J. Org. Chem. 2013, 78, 590−596

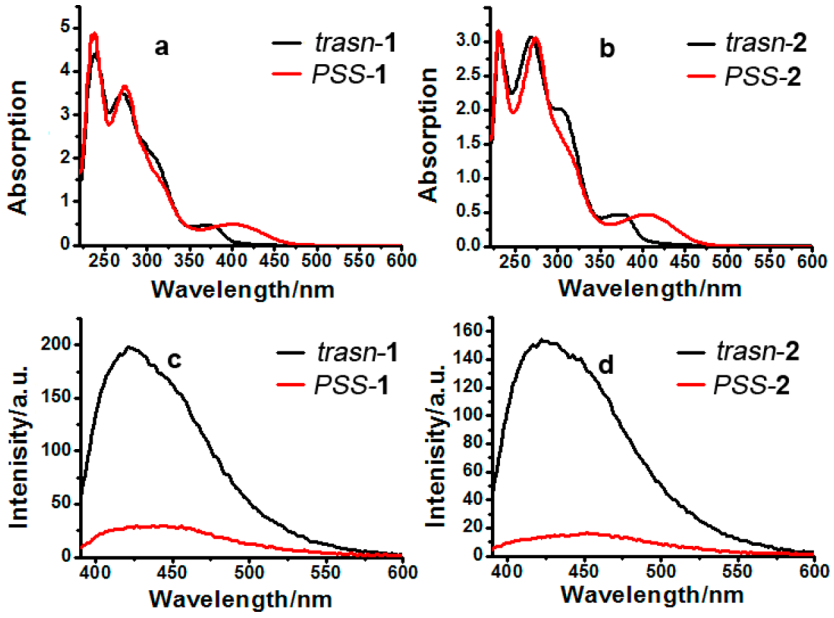


Figure 4. UV−vis spectral changes in CH_2Cl_2 (a) from [3]rotaxane *trans*-**1** (1×10^{-5} M) to the *PSS*-**1** obtained after irradiation with 365 nm for 10 min and (b) from alkene *trans*-**2** (1×10^{-5} M) to the *PSS*-**2** after irradiation with 365 nm for 10 min. Fluorescence spectral changes in CH_2Cl_2 (c) from [3]rotaxane *trans*-**1** to the *PSS*-**1** obtained after irradiation with 365 nm for 10 min and (d) from alkene *trans*-**2** to the *PSS*-**2** after irradiation with 365 nm for 10 min. Excitation wavelength for both fluorescence spectra was 380 nm.

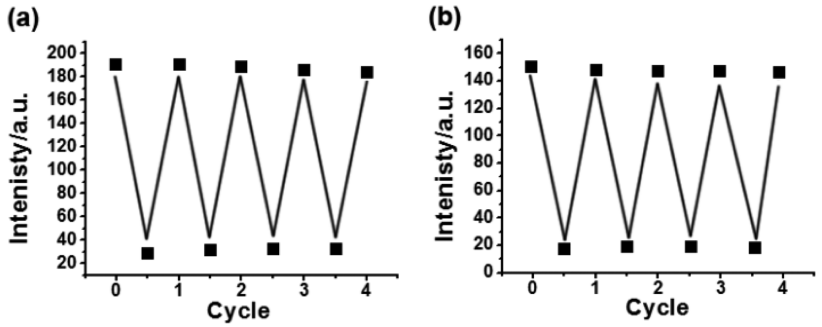


Figure 5. (a) Fluorescence intensity of *trans*-**1** (1×10^{-5} M, CH_2Cl_2) at 428 nm under irradiation (365 nm) and heat (30 °C) for four cycles. (b) Fluorescence intensity of *trans*-**2** (1×10^{-5} M, CH_2Cl_2) under irradiation (365 nm) and heat (30 °C) for four cycles. Excitation wavelength for both fluorescence spectra was 380 nm.

to room temperature led to the recovery of the fluorescent intensity. Similar experiments starting with *trans*-**2** demonstrated a corresponding *trans*−*cis* isomerization with remarkable UV−vis and fluorescent changes, as shown in parts b and d, respectively, of Figure 4. The absolute quantum yield of fluorescence for *trans*-**2** was 2.5%, which decreased to 0.42% of the *PSS*-**2**. It should be noted that thermal relaxation could also convert *cis*-**2** to its original *trans*-**2** state, evidenced by the recovery of the fluorescence intensity.

The fluorescence quenching of both *trans*-**1** and *trans*-**2** in response to 365 nm irradiation could be ascribed to the formation of the nonfluorescent *cis* isomers. When the PSS solution of **1** or **2** was excited with 423 nm, which was the maximum absorption wavelength of the *cis* isomers, almost no fluorescence was observed. It can be deduced that the fluorescence quenching upon UV light irradiation is due to different fluorescence quantum yields between *trans* isomer (high) and *cis* isomer (low). The *cis* isomer has more twisted structure and higher energy in the excited states, and its isomerization is driven by thermodynamics and relief from steric crowding when excited, so the fluorescence quantum yield of *cis* isomer is lower compared with that of *trans* isomer.

Meanwhile, time-resolved fluorescence measurements were also conducted for both *trans*-**1** (Figures S1 and S2, Supporting Information) and *trans*-**2** (Figures S3 and S4, Supporting Information) in response to UV light irradiation. The time-resolved fluorescence of *trans*-**1** revealed a bi-exponential decay with lifetimes of 2.11 ns (40.65%) and 7.31 ns (59.35%) ns, which was typical of substituted stilbene derivatives.[18] In the PSS of [3]rotaxane **1**, no obvious change was observed in the time-resolved fluorescence, which also showed a bi-exponential decay with lifetimes of 2.09 ns (43.77%) and 7.15 ns (56.23%). It can be explained that the *cis*-**1** has no fluorescence, which implies the fluorescence of *PSS*-**1** came from remaining *trans*-**1** (just dilution), so the time-resolved fluorescence of *PSS*-**1** hardly changed compared with that of the staring *trans*-**1**. The change of time-resolved fluorescence of *trans*-**2** upon 365 nm irradiation (Figures S3 and S4, Supporting Information) was nearly the same as [3]rotaxane **1**, from 2.07 ns (58.17%) and 7.01 ns (41.83%) of *trans* isomer to 2.02 ns (53.19%) and 6.46 ns (46.81%) of *cis* isomer, respectively.

dx.doi.org/10.1021/jo302426c | J. Org. Chem. 2013, 78, 590−596

The quantum yields of photochemical conversion for the *trans*-**2** and the rotaxane *trans*-**1** were 0.133 and 0.128, respectively, which revealed that the photochemistry of the overcrowded alkene *trans*-**2** was unaffected by the introduction of two dumbbells and the formation of [3]rotaxane. It should be noted that the photoinduced *trans*−*cis* isomerization and thermal-induced *cis*−*trans* isomerization of *trans*-**2** and *trans*-**1** could be repeated many times without obvious degradation, as evidenced by the reversible fluorescent change cycles (Figure 5). Although comparison of the spectroscopic behaviors of **1** and **2** shows that the rotaxane architecture is not necessary to switch fluorescence, the architecture of this interlocked system is rather unique and appealing. Most importantly, the main novelty of this new system is that the macrocycle and the dumbbells in macrocycle **2** and [3]rotaxane **1** prevent thermal relaxation from *cis* isomers to *trans* isomers which converts the system from a unidirectional motor to a very good switch with very favorable photochemical properties, which has potential application in the designing new molecular switches and stimuli-responsive materials.

■ CONCLUSION

In summary, we have designed and constructed a novel [3]rotaxane with an overcrowed alkene switch as a bridge carrying two rotaxane arms, which can perform reversible clamlike motion in response to external light and thermal stimuli. It should be noted that the reversible motion is accompanied by remakable color and fluorescent changes. The performance of the alkene switching unit is essentially unaffected by the two bulky rotaxane arms. The large conformation change generated from the external-responsive isomerization of the overcrowded alkene provides an alternative possibility in the design of molecular muscles that can perform programmed contraction and stretching movements.

■ EXPERIMENTAL SECTION

General Methods. ^{1}H NMR and ^{13}C NMR spectra were measured on a 400 MHz spectrometer (^{1}H: 400 MHz; ^{13}C: 100 MHz). The electronic spray ionization (ESI) mass spectra were tested on a TOF mass spectrometer. The UV−vis absorption spectra and fluorescence spectra were also recorded on a Varian Cary 100 spectrometer and a Varian Cary Eclipse (1-cm quartz cell used), respectively. Irradiation experiments were performed using a Spectroline model ENB-280C/FE lamp at λ = 365 nm, ± 30 nm. All reagents and solvents were used as supplied, unless stated otherwise. The fluorescence lifetime measurements were performed by using the time correlated single photon counting (TCSPC) technique following excitation by nanosecond flash lamp. The quantum yields of fluorescence were measured by using a Fluoromax-4 fluorescence spectrophotometer equipped with the quantum yield measuring accessory and report generator program.

Material. Chemicals were used as received from commercial sources. All solvents were reagent grade, which were dried and distilled prior to use according to standard procedures. The molecular structures were confirmed using ^{1}H NMR, ^{13}C NMR, and high-resolution ESI mass spectroscopy. Compounds 7,[13d] **9**,[16] and **10**[15d] were synthesized and purified acoording to the previous literature.

Synthesis of Compound 6. A mixture of compound **4** (0.5 g, 3 mmol) and **5** (0.46 g, 3 mmol) was refluxed overnight in 50 mL of toluene using a Dean−Stark technique. The mixture was placed in a round-bottom flask, and the solvent was removed under reduced pressure. The residue was dissolved in methanol, and $NaBH_4$ (0.4 g, 10.5 mmol) was added in small portions under an ice bath. The mixture was stirred at room temperature for a further 6 h. Water was added to quench the excess $NaBH_4$. The solvent was evaporated off, and the residue was extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4. After being concentrated in vacuo, the white solid was dissolved in MeOH (20 mL), and HCl (6 M, 2 mL) was added. After being stirred for a few minutes, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (20 mL), followed by the addition of saturated NH_4PF_6 aqueous solution, which resulted in a suspension. The precipitate was collected by suction filtration. Recrystallization from MeOH gave **6** (1.12 g, 70%) as a white solid. Mp = 150−151 °C. ^{1}H NMR (400 MHz, CD_3SOCD_3, 298 K): δ = 7.22 (d, J = 8.6 Hz, 4H), 6.87 (d, J = 8.6 Hz, 4H), 4.92 (t, J = 4.7 Hz, 2H), 3.95 (t, J = 5.0 Hz, 4H), 3.70 (m, 4H), 3.57 (s, 4H). ^{13}C NMR (100 MHz, CD_3SOCD_3): δ 159.1, 131.5, 123.4, 114.5, 69.5, 59.4, 49.3, 40.1, 39.9, 39.6, 39.4, 39.2, 39.0, 38.8 HRMS (ESI) m/z: $[M - PF_6]^+$ calcd for $C_{18}H_{24}NO_4$ 318.1705, found 318.1707.

Synthesis of Compound 8. To a suspension of zinc powder (2.0 g, 31.3 mmol) in 20 mL of dry THF was added 1.63 mL of $TiCl_4$ at 0 °C. The mixture was heated at reflux under Ar for 2 h. After the mixture was cooled to room temperature, compound **7** (2.0 g, 8.0 mmol) dissolved in 10 mL of THF was added. The mixture was again heated at reflux under Ar for 36 h. After being cooled to room temperature, the mixture was directly charged onto a silica gel column using CH_2Cl_2 as eluent to remove the metal salts. The product was further purified by chromatography on silica gel using PE/CH_2Cl_2 (10:1) as eluent to yield **8** (0.94 g, 45%) as a slightly green solid. Mp = 91−92 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.99 (d, J = 9.0 Hz, 2H), 7.96 (d, J = 2.0 Hz, 2H), 7.63 (d, J = 8.9 Hz, 2H), 7.56 (dd, J = 9.0, 2.1 Hz, 2H), 7.09 (d, J = 8.9 Hz, 2H), 4.14 (dd, J = 10.7, 2.9 Hz, 2H), 4.06 (dd, J = 10.7, 1.5 Hz, 2H), 2.72 (m, 2H), 1.09 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 152.5, 131.3, 130.7, 130.4, 130.3, 129.6, 128.3, 126.2, 119.3, 116.9, 114.4, 77.5, 77.3, 76.7, 74.1, 32.7, 29.7, 13.8. HRMS(ESI) m/z: $[M]^+$ calcd for $C_{28}H_{22}O_2Br_2$ 549.9962, found 549.9966.

Synthesis of Compound 11. In a flask, compound **10** (0.53 g, 1 mmol), bis(pinacolato)dibron (0.38 g, 1.5 mmol), potassium acetate (0.3 g, 3 mmol), and dry 1,4-dioxane (10 mL) were added. To the milk white suspension were then added Pd(dppf)Cl_2 (10 mg, 0.015 mmol) and DPPF (7 mg, 0.015 mmol). The dark red mixture was heated to reflux under an Ar atmosphere for 24 h. The crude mixture was purified by column chromatography using CH_2Cl_2/MeOH (100:1) as eluent to give **11** (0.5 g, 90%) as a white solid. Mp = 78−79 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.39 (dd, J = 7.9, 1.3 Hz, 1H), 7.27 (d, J = 1.3 Hz, 1H), 6.90−6.84 (m, 5H), 4.23−4.11 (m, 8H), 3.92 (d, J = 6.8, 8H), 3.84 (d, J = 1.4 Hz, 8H), 1.33 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 151.6, 148.9, 148.1, 128.9, 121.4, 119.4, 114.1, 112.7, 83.6, 71.3, 69.9, 69.8, 69.4, 69.1, 24.8. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{30}H_{43}BNaO_{10}$ 597.2841, found 597.2847.

Synthesis of Compound 3. To a solution of **6** (0.5 g, 1 mmol) and **9** (0.81 g, 3 mmol) in acetone (2 mL) was added *n*-Bu_3P (4 uL, 0.05 mmol) under an Ar atmosphere. After the solution was stirred for 5 h, the solvent was evaporated. The residue was purified by chromatography on silica gel using CH_2Cl_2/MeOH (20:1) as eluent to yield **3** (0.22 g, 30%) as a white solid. Mp = 131−132 °C. ^{1}H (400 MHz, $CDCl_3$, 298 K): δ = 7.66 (s, 4H), 7.33 (d, J = 8.6 Hz, 4H), 7.18 (s, 4H), 6.91 (d, J = 8.6 Hz, 4H), 4.61 (t, J = 6.4 Hz, 4H), 4.24 (t, J = 6.4 Hz, 4H), 3.83 (s, 4H), 2.34 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.7, 166.8, 159.4, 138.1, 134.9, 131.7, 129.6, 127.4, 122.5, 115.2, 65.9, 62.9, 21.2. HRMS (ESI) m/z: [M − PF6]$^+$ calcd for $C_{36}H_{40}NO_6$ 528.2850, found 528.2854.

Synthesis of Compound *trans*-2. Compound **8** (0.55 g, 1 mmol), **11** (1.7 g, 3 mmol), and ground K_2CO_3 (0.28 g, 2 mmol) were dissolved in dry 1,4-dioxane (10 mL). The mixture was degassed for 15 min, and $Pd(PPh_3)_4$ (0.058 g, 0.05 mmol) was then added. The dark brown mixture was heated to reflux under an atomosphere of Ar for 24 h. The reaction mixture was concentrated in vacuo, and water (50 mL) was added. The brown solid was filtered, washed with water, dried overnight, and purified by chromatography on silica gel using CH_2Cl_2/MeOH (20:1) as eluent to yield **2** (0.58 g, 53%) as a faint yellow solid. Mp = 106−107 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 298

dx.doi.org/10.1021/jo302426c | J. Org. Chem. 2013, 78, 590−596

K): δ = 8.16 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 1.6 Hz, 2H), 7.69 (dd, J = 8.9, 2.7 Hz, 4H), 7.22 (d, J = 7.5 Hz, 4H), 7.01 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 6.80 (s, 8H), 4.11 (m, 18H), 3.99 (d, J = 9.5 Hz, 2H), 3.84−3.75 (m, 8H), 3.69 (d, J = 11.2 Hz, 8H), 2.74 (d, J = 6.8 Hz, 2H), 1.08 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 152.2, 149.2, 148.9, 148.5, 135.7, 134.4, 131.3, 131.2, 129.3, 125.7, 125.7, 125.1, 121.4, 120.1, 118.6, 114.4, 114.2, 114.1, 113.3, 74.1, 71.3, 69.9, 69.7, 69.5, 69.4, 69.4, 32.9, 29.7, 13.9 HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{76}H_{84}NaO_{18}$ 1307.5550, found 1307.5563.

Synthesis of Compound *trans*-1. A mixture of *trans*-**2** (0.15 g, 0.12 mmol) and **6** (0.23 g, 0.35 mmol) was dissolved in CH_2Cl_2 (2 mL). Then, **9** (0.25 g, 0.9 mmol) and n-Bu_3P (4 uL, 0.05 mmol) were added to the mixture under Ar atmosphere. After the mixture was stirred for 5 h, the solvent was evaporated. Subsequent purification by chromatography on silica using CH_2Cl_2/MeOH (100:1) as eluent yielded rotaxane *trans*-**1** (0.18 g, 70%) as a green foam. Mp = 140−141 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 8.30 (d, J = 8.7 Hz, 2H), 8.02 (d, J = 1.6 Hz, 2H), 7.81 (dd, J = 8.7 Hz, 4H), 7.67 (s, 8H), 7.50 (s, 4H), 7.37−7.27 (m, 10H), 7.23 (d, J = 6.9 Hz, 6H), 7.13 (d, J = 8.9 Hz, 2H), 6.97 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 7.3, 4H), 6.85−6.74 (m, 12H), 4.60 (m, 16H), 4.34−4.06 (m, 28H), 3.82 (m, 16H), 3.55 (m, 16H), 2.85 (m, 2H), 2.36 (s, 24H), 1.18 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 166.8, 159.0, 152.3, 147.8, 147.4, 146.9, 138.1, 135.0, 134.7, 134.6, 131.3, 131.2, 130.7, 130.7, 129.7, 129.4, 129.3, 127.3, 125.7, 125.5, 125.1, 124.1, 124.1, 121.6, 120.0, 118.6, 114.6, 114.6, 114.4, 113.0, 112.6, 111.5, 74.1, 70.7, 70.7, 70.6, 70.2, 70.1, 68.3, 68.2, 68.1, 65.9, 62.9, 51.9, 32.9, 29.6, 21.1, 13.8. HRMS (ESI) m/z: $[M - 2PF_6]^{2+}$ calcd for $C_{148}H_{164}N_2O_{30}$ 1225.0701, found 1225.0732.

■ ASSOCIATED CONTENT

Supporting Information

Full experimental details pertaining to the preparation and characterization of all compounds including NMR and MS spectra and fluorescence assay results. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: +86-21 64252288. E-mail: dahui_qu@ecust.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the NSFC/China (20902024, 21272073 and 21190033), the National Basic Research 973 Program (2011CB808400), the Foundation for the Author of National Excellent Doctoral Dissertation of China (200957), the Fok Ying Tong Education Foundation (121069), the Fundamental Research Funds for the Central Universities and the Innovation Program of Shanghai Municipal Education Commission, and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, for financial support.

■ REFERENCES

(1) (a) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348. (b) Browne, W. R.; Feringa, B. L. *Nat. Nanotechnol.* **2006**, *1*, 25. (c) Saha, S.; Stoddart, J. F. *Chem. Soc. Rev.* **2007**, *36*, 77. (d) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72. (e) Qu, D.-H.; Tian, H. *Chem. Sci.* **2011**, *2*, 1011. (f) Delius, M. V.; Leigh, D. A. *Chem. Soc. Rev.* **2011**, *40*, 3656. (g) Belowich, M. E.; Stoddart, J. F. *Chem. Soc. Rev.* **2012**, *41*, 2003.

(2) (a) Kelly, T. R.; Silva, H. D.; Silva, R. A. *Nature* **1999**, *401*, 150. (b) Leigh, D. A.; Wong, J. K. Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, *424*, 174. (c) Hernández, J. V.; Kay, E. R.; Leigh, D. A. *Science* **2004**, *306*, 1532.

(3) (a) Blanco, M. J.; Jiménez, M. C.; Chambron, J. C.; Heitz, V.; Linke, M.; Sauvage, J.-P. *Chem. Soc. Rev.* **1999**, *28*, 293. (b) Kinbara, K.; Aida, T. *Chem. Rev.* **2005**, *105*, 1377. (c) Balzani, V.; Credi, A.; Venturi, M. *Molecular Devices and Machines-Concepts and Perspectives for the Nanoworld*; Wiley-VCH: Weinheim, 2008. (d) Baroncini, M.; Silvi, S.; Venturi, M.; Credi, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 4223. (e) Campaña, A. G.; Carlone, A.; Chen, K.; Dryden, D. T. F.; Leigh, D. A.; Lewandowska, U.; Mullen, K. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 5480.

(4) (a) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789. (b) Tuncel, D.; Özsar, Ö.; Tiftik, H. B.; Salih, B. *Chem. Commun.* **2007**, 1369. (c) Spruell, J. M.; Paxton, W. F.; Olsen, J.-C.; Benítez, D.; Tkatchouk, E.; Stern, C. L.; Trabolsi, A.; Friedman, D. C.; Goddard, W. A.; Stoddart, J. F. *J. Am. Chem. Soc.* **2009**, *131*, 11571.

(5) (a) Jiménez, M. C.; Buchecker, C. D.; Sauvage, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3284. (b) Coutrot, F.; Romuald, C.; Busseron, E. *Org. Lett.* **2008**, *10*, 3741. (c) Wu, J.-S.; Leung, K. C.-F.; Benitez, D.; Han, J.-Y.; Cantrill, S. J.; Fang, L.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 7470. (d) Chuang, C.-J.; Li, W.-S.; Lai, C.-C.; Liu, Y.-H.; Peng, S.-M.; Chao, I.; Chiu, S.-H. *Org. Lett.* **2009**, *11*, 385.

(6) (a) Mandl, C. P.; König, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 1622. (b) Pollard, M. M.; Klok, M.; Pijper, D.; Feringa, B. L. *Adv. Funct. Mater.* **2007**, *17*, 718. (c) Leigh, D. A.; Lusby, P. J.; Slawin, A. M.; Walker, D. B. *Chem. Commun.* **2012**, *48*, 5826.

(7) (a) Ng, J. M. K.; Fuerstman, M. J.; Grzybowski, B. A.; Stone, H. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **2003**, *125*, 7948. (b) Kao, C.-Y.; Hsu, Y.-T.; Lu, H.-F.; Chao, I.; Huang, S.-L.; Lin, Y.-C.; Sun, W.-T.; Yang, J.-S. *J. Org. Chem.* **2011**, *76*, 5782. (c) Frantz, D. K.; Linden, A.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **2012**, *134*, 1528.

(8) (a) Aprahamian, I.; Dichtel, W. R.; Ikeda, T.; Heath, J. R.; Stoddart, J. F. *Org. Lett.* **2007**, *9*, 1287. (b) Coutrot, F.; Busseron, E. *Chem.—Eur. J.* **2008**, *14*, 4784. (c) Alonso, A. M. *Chem. Commun.* **2010**, 9089. (d) Ahmed, R.; Altieri, A.; D'Souza, D. M.; Leigh, D. A.; Mullen, K. M.; Papmeyer, M.; Slawin, A. M. Z.; Wong, J. K. Y.; Woollins, J. D. *J. Am. Chem. Soc.* **2011**, *133*, 12304. (e) Yang, W.-L.; Li, Y.-J.; Zhang, J.-H.; Yu, Y.-W.; Liu, T.-F.; Liu, H.-B.; Li, Y.-L. *Org. Biomol. Chem.* **2011**, *9*, 6022. (f) Zhang, H.; Hu, J.; Qu, D.-H. *Org. Lett.* **2012**, *14*, 2334. (g) Avellini, T.; Li, H.; Coskun, A.; Barin, G.; Trabolsi, A.; Basuray, A. N.; Dey, S. K; Credi, A.; Silvi, S.; Stoddart, J. F.; Venturi, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 1611. (h) Zhang, H.; Zhou, B.; Li, H.; Qu, D.-H.; Tian, H. *J. Org. Chem.* **2012**, DOI: 10.1021/jo302107a. (i) Li, H.; Zhang, H.; Zhang, Q.; Zhang, Q.-W.; Qu, D.-H. *Org. Lett.* **2012**, *14*, 5900.

(9) (a) Balzani, V.; Credi, A.; Venturi, M. *Chem. Soc. Rev.* **2009**, *38*, 1542. (b) Silvi, S.; Venturi, M.; Credi, A. *Chem. Commun.* **2011**, *47*, 2483. (c) Zhang, H.; Strutt, N. L.; Stoll, R. S.; Li, H.; Zhu, Z.; Stoddart, J. F. *Chem. Commun.* **2011**, *47*, 11420.

(10) (a) Koumura, N.; Zijlstra, R. W. J.; van Delden, R. A.; Feringa, B. L. *Nature* **1999**, *401*, 152. (b) Bell, T. W.; Catalano, V. J.; Drew, M. G. B.; Phillips, D. J. *Chem.—Eur. J.* **2002**, *8*, 5001. (c) Landaluce, T. F.; London, G.; Pollard, M. M.; Rudolf, P.; Feringa, B. L. *J. Org. Chem.* **2010**, *75*, 5323.

(11) (a) Matthijs, K. J.; Wiel, T.; van Delden, R. A.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2005**, *127*, 14208. (b) Browne, W. R.; Pollard, M. M.; Lange, B. D.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2006**, *128*, 12412. (c) Pollard, M. M.; Meetsma, A.; Feringa, B. L. *Org. Biomol. Chem.* **2008**, *6*, 507.

(12) (a) Wang, J.-B.; Kulago, A.; Browne, W. R.; Feringa, B. L. *J. Am. Chem. Soc.* **2010**, *132*, 4191. (b) Wang, J.-B.; Hou, L.-L.; Browne, W. R.; Feringa, B. L. *J. Am. Chem. Soc.* **2011**, *133*, 8162. (c) Wang, J.-B.; Feringa, B. L. *Science* **2011**, *331*, 1429.

(13) (a) Ashton, P. R.; Baxter, I. W.; Raymo, F. M.; Stoddart, J. F.; White, A. J. P.; Williams, D. J.; Wolf, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1913. (b) Wang, F.; Han, C.-Y.; He, C.-L.; Zhou, Q.-Z.; Zhang, J.-Q.; Wang, C.; Li, N.; Huang, F.-H. *J. Am. Chem. Soc.* **2008**, *130*, 11254. (c) Jiang, Q.; Zhang, H.-Y.; Han, M.; Ding, Z.-J.; Liu, Y. *Org. Lett.*

2010, *12*, 1728. (d) Qu, D.-H.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2010**, *49*, 1107. (e) Dong, S.-Y.; Luo, Y.; Yan, X.-Z.; Zheng, B.; Ding, X.; Yu, Y.-H.; Ma, Z.; Zhao, Q.-L.; Huang, F.-H. *Angew. Chem., Int. Ed.* **2011**, *50*, 1905. (f) Yang, W.-L.; Li, Y.-J.; Zhang, J.-H.; Chen, N.; Chen, S.-H.; Liu, H.-B.; Li, Y.-L. *J. Org. Chem.* **2011**, *76*, 7750. (g) Dasgupta, S.; Wu, J.-S. *Chem. Sci.* **2012**, *3*, 425.

(14) (a) Villiers, C.; Ephritikhine, M. *Chem.—Eur. J.* **2001**, *7*, 3043. (b) Benz, L.; Haubrich, J.; Quiller, R. G.; Jensen, S. C.; Friend, C. M. *J. Am. Chem. Soc.* **2009**, *131*, 15026. (c) Lubbe, A. S.; Ruangsupapichat, N.; Caroli, G.; Feringa, B. L. *J. Org. Chem.* **2011**, *76*, 8599.

(15) (a) Hirose, K.; Shiba, Y.; Ishibashi, K.; Doi, Y.; Yang, Y.-T. *Chem.—Eur. J.* **2008**, *14*, 981. (b) Hirose, K.; Shiba, Y.; Ishibashi, K.; Doi, Y.; Tobe, Y. *Chem.—Eur. J.* **2008**, *14*, 3427. (c) Zhang, Z.-J.; Zhang, H.-Y.; Wang, H.; Liu, Y. *Angew. Chem., Int. Ed.* **2011**, *50*, 10834. (d) Zhang, H.; Kou, X.-X.; Zhang, Q.; Qu, D.-H.; Tian, H. *Org. Biomol. Chem.* **2011**, *9*, 4051.

(16) Tachibana, Y.; Kawasaki, H.; Kihara, N.; Takata, T. *J. Org. Chem.* **2006**, *71*, 5093.

(17) (a) Qu, D.-H.; Wang, Q.-C.; Ren, J.; Tian, H. *Org. Lett.* **2004**, *6*, 2085. (b) Wang, Q.-C.; Qu, D.-H.; Ren, J.; Chen, K.-C.; Tian, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 2661. (c) Marois, J.-S.; Cantin, K.; Desmarais, A.; Morin, J.-F. *Org. Lett.* **2008**, *10*, 33.

(18) (a) DiCesare, N.; Lakowicz, J. R. *J. Phys. Chem. A.* **2001**, *105*, 6834. (b) Schuster, D. I.; Nuber, B.; Vail, S. A.; MacMahon, S.; Lin, C.; Wilson, S. R.; Khong, A. *Photochem. Photobiol. Sci.* **2003**, *2*, 315. (c) Pucci, A.; Cuia, F. D.; Signoriab, F.; Ruggeri, G. *J. Mater. Chem.* **2007**, *17*, 783.