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Article

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Donor-acceptor Stenhouse Adducts with Three Orthogonally Controlled Intrinsic Stationary States

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Abstract

Photoresponsive molecules with more than two intrinsic stationary states are very interesting. Here, we demonstrate a series of crown ether (CE) substituted donor-acceptor Stenhouse adducts (DASAs) that can be switched between three stationary states under orthogonal control of light and metal ions. DASA-CE molecules are self-assembled into 1:1 head-to-tail supramolecular structures to form *di-linear* states due to strong van der Waals interactions between electron-donating and -withdrawing moieties. Furthermore, treatment with metal ions (Na⁺ or K⁺) switches the *di-linear* back to the *linear* state, which is reversible after adding free crown ether. On the other hand, green light irradiation induces *linear-to-cyclic* isomerization of DASA-CE, while the photoisomerization from *di-linear* to *cyclic* state is inhibited. The reverse *cyclic-to-linear* isomerization can occur under heating in the dark. All in all, the orthogonal switching of DASA-CE between *di-linear*, *linear* and *cyclic* states enables the development of smart materials in environments with complex stimuli.

Keywords: donor-acceptor Stenhouse adducts, photoresponsive, orthogonal, isomerization, supramolecular chemistry.

Donor-acceptor Stenhouse adducts (DASAs) are a new class of photoresponsive molecules, and have drawn plenty of attention in the past 5 years¹⁻⁶. DASAs show *linear-to-cyclic* isomerization under visible-light irradiation, while the opposite *cyclic-to-linear* isomerization occurs under heating⁷⁻¹⁰. The molecular isomerization significantly changes the properties of DASAs in terms of molecular structure, color and polarity^{6, 11-14}, which further makes DASAs favorable in the applications of photolithography¹⁵, light-controlled molecular or macromolecular self-assembly¹⁶⁻¹⁷ and light-switched wettability on surfaces^{6, 18-19}.

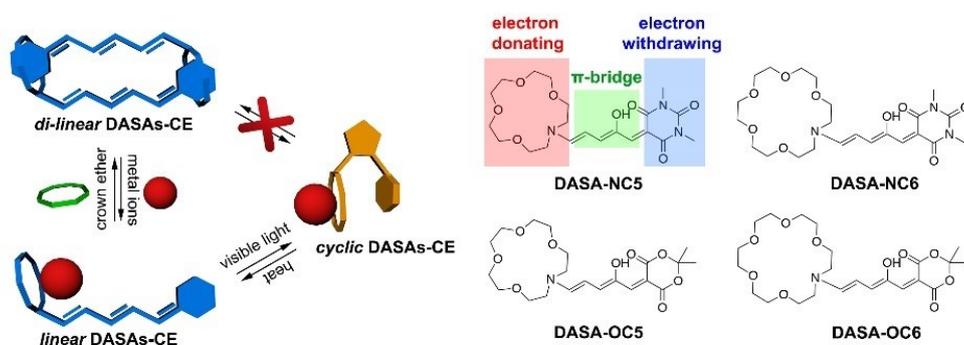
However, similar to the well-studied traditional photoresponsive molecules (*e.g.* azobenzene (Azo)²⁰⁻²², spiropyran²³⁻²⁵, and diarylethene²⁶⁻²⁸), DASAs show only two photostationary states (*i.e.* *linear* and *cyclic*). In other words, the photoresponsive materials based on DASAs can only switch between two corresponding functional states, such as assembled/disassembled (in controlling molecular self-assemblies), hydrophilic/hydrophobic (in controlling surface wettability) and invisible/visible (in invisible inks). This limits the applications of DASA-based materials in environments with complex stimuli, and compounds that are switchable between multiple ($n > 2$) functional states are urgently needed.

To achieve this, the introduction of two or more stimuli-responsive functional groups into one molecular or macromolecular system, which can be controlled in an orthogonal manner, has been reported. For example, Feringa *et al* demonstrated an intramolecular combination of photoswitching based on DASAs and Azo, while the isomerization of DASAs and Azo could be controlled separately¹⁴. Therefore, the resulting molecule could be switched between four independent states by controlling light and heat. This orthogonal control realized at the molecular level may open up applications for these materials in multi-stimuli environments. However, introducing more stimuli-responsive functional groups increases the complexity of the systems, which is not ideal for future developments. Instead, is it possible to realize intrinsically orthogonal switching between multiple ($n > 2$) stationary states in a single molecule without introducing other stimuli-responsive groups? This is the question that needs to be answered.

Typical DASAs consist of electron-donating and -withdrawing moieties with a triene π -bridge in between²⁻³, which makes DASAs a “push-pull” system (**Scheme 1**). Therefore, van der Waals interactions may exist between the electron-donating and -withdrawing moieties, which leads to the self-assembly of DASAs and induces the formation of a third state. However, this phenomenon has not been previously reported. This might be the reason of mismatched molecular geometries between the two moieties.

In the current work, we synthesized a series of new DASA derivatives (DASA-CE) using crown ethers (CEs) with different sizes (15-crown-5 and 18-crown-6) as the electron-donating moiety, while Meldrum’s acid and barbituric acid were selected for the electron-withdrawing moiety (**Scheme 1**). For the first time, *linear* DASA-CE self-assembles into a 1:1 head-to-tail supramolecular structure (*di-linear* state in **Scheme 1**) due to the strong van der Waals interaction between the crown ether (electron-rich) and the electron-withdrawing moiety.

Adding metal ions (Na^+ or K^+) switches the *di-linear* state back to *linear* state, which is reversible by introducing free crown ethers into the system. Visible light irradiation with a wavelength of 530 nm induces the *linear-to-cyclic* isomerization of DASA-CE. However, for the *di-linear* DASA-CE, the photoisomerization is inhibited. Therefore, DASA-CE switching between three states (*di-linear*, *linear* and *cyclic* state) under orthogonal control of light and metal ions have been realized.



Scheme 1. Schematic illustration of orthogonal isomerization of DASA-CE under controlling of light and metal ions.

A series of DASA-CE were synthesized using 15-crown-5 and 18-crown-6 as the electron-donating moieties, and Meldrum's acid or barbituric acid as the electron-withdrawing moieties (**Scheme S1**, see detail in Supporting Information (SI)). The synthesized DASA-CE were termed **DASA-NC5**, **DASA-NC6**, **DASA-OC5** and **DASA-OC6**, respectively (**Scheme 1**). All four compounds have similar physical properties. Therefore, **DASA-NC5** will be used to represent all DASA-CE in forthcoming discussions.

The three stationary states of **DASA-NC5** could be clearly observed in one single ^1H nuclear magnetic resonance (NMR) spectrum (**Figure S1**). The switching between the three independent states will be discussed in detail.

DASA-NC5 shows abnormally low absorbance in visible light region compared with the well-studied diethylamine-substituted DASAs (**DASA-N**) when dissolved in tetrahydrofuran (THF) (**Figure 1a**). However, the addition of NaBF_4 sharply increases the absorbance in the visible light region, which makes the **DASA-NC5** solution strongly colored (**Figure 1a**). The absorbance of **DASA-NC5** in the visible light region is closely and directly related to the concentration of added Na^+ ions, which reaches equilibrium when the Na^+ concentration approaches 1:1 with the **DASA-NC5** (**Figure S2**). In addition, the absorbance in UV light region, which correlates to the electron-withdrawing moiety, shows a ~ 20 nm red shift after the introduction of Na^+ ion. On the other hand, **DASA-N** does not show obvious absorbance change after adding NaBF_4 (**Figure S3**). This indicates that the *linear* **DASA-NC5** forms a centrosymmetric molecular system. The coplanarity of the centrosymmetric molecular structure is obviously reduced, leading to the "hypochromic effect"²⁹, which limits the absorbance of the entirely conjugated molecule in visible light region of *linear* **DASA-NC5**. The centrosymmetric self-assembly of **DASA-NC5** is supposed to be a 1:1 head-to-tail supramolecular structure (*di-linear* state), which will be discussed in detail later in this article (**Scheme 1**).

After introducing NaBF_4 into the system, the metal ions could coordinate with the 15-crown-5 group in the electron-donating moiety, and further induce the disassembly of the centrosymmetric structure (*di-linear-to-linear* transition). The *di-linear-to-linear*

transition of **DASA-NC5** does not occur in all solvents. In protic solvents (*i.e.* ethanol), the addition of Na^+ does not increase the absorbance of **DASA-NC5** in visible light region, which is different to that in tetrahydrofuran (THF) and dichloromethane (**Figure S4** and **S5**). These might be attributed to the interaction between Na^+ ion and 15-crown-5 in protonic solvents³⁰⁻³¹. **DASA-OC5**, **DASA-NC6** and **DASA-OC6** also show metal-ion induced *di-linear-to-linear* transition in THF (**Figure S6-S9**). **DASA-CE** with 15-crown-5 substituted electron-donating moieties are responsive to Na^+ ions, while 18-crown-6 substituted DASAs are sensitive to K^+ ions (see detail in SI).

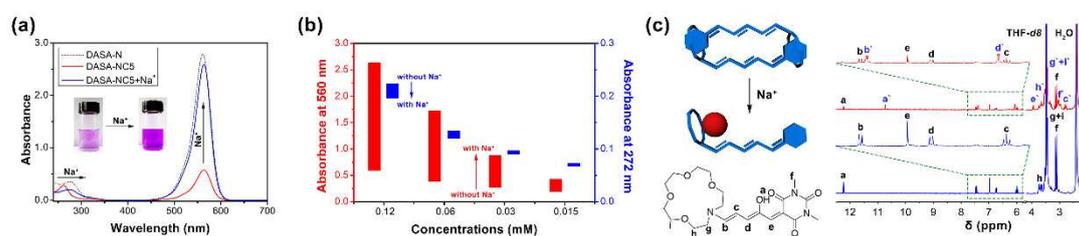


Figure 1. (a) UV/vis spectra of *linear* **DASA-N** (black, dot) and **DASA-NC5** before (red, solid) and after (blue, solid) adding NaBF_4 ($[\text{DASA-NC5}] = [\text{NaBF}_4] = 0.12$ mM in THF). The inset shows the color change after adding NaBF_4 ; (b) Absorbance variation at 560 (red) and 272 nm (blue) for **DASA-NC5** with different concentrations after adding NaBF_4 solution; (c) ^1H NMR spectra (400 MHz at 298 K) of **DASA-NC5** before (red) and after (blue) adding NaBF_4 ($[\text{DASA-NC5}] = 3$ mM in $\text{THF-}d_8$). (a, b, c... (black) represent the protons in *linear* **DASA-NC5**, a', b', c'... (blue) represent the protons in *di-linear* **DASA-NC5**).

The absorbance variation in the visible light region caused by the addition of Na^+ ion was investigated on concentrations of **DASA-NC5** between 0.12 and 0.015 mM (**Figure 1b**, red). The absorbance in the visible light region increases more upon adding Na^+ ions to higher concentrations of **DASA-NC5** in THF, indicating more *di-linear* states are formed under higher concentrations. Similar changes could be noticed for the absorbance in the UV light region (**Figure 1b**, blue).

The *di-linear-to-linear* transition of **DASA-NC5** was further monitored by ^1H

NMR spectroscopy (**Figure 1c**). Two states of **DASA-NC5** could be clearly identified before the addition of Na^+ ions (**Figure 1c**, red). The signals of the *di-linear* state is broader than those of the *linear* state (e.g. Hb' is broader than Hb), which is attributed to molecular aggregation. Approximately 75% of **DASA-NC5** are in the *di-linear* state. After the introduction of Na^+ ions, all of the *di-linear* **DASA-NC5** switches to the *linear* state (**Figure 1c**, blue). These are in good accordance with the results of the UV/vis spectroscopy investigation.

The *di-linear* state was further investigated by density functional theory (DFT) calculations. The electrostatic potential calculation shows a heterogenous distribution of the electrostatic potential of the *linear* state, where the electron-donating moiety of the *linear* state is more electron rich (red) than the electron-withdrawing moiety (blue) (**Figure 2a**). This indicates that the van der Waals interaction between the electron-donating and -withdrawing moieties is favorable. Moreover, the other DASAs (**DASA-N** and other **DASA-CE**) show similar electrostatic potential distributions to **DASA-NC5** (**Figure S10-S13**), which is in good accordance with the “push-pull” nature of DASAs. *Linear* **DASA-NC5** shows a partially planar molecular structure, and the 15-crown-5 shows a slightly larger cavity than the electron-withdrawing moiety, which is ideal for the 1:1 head-to-tail self-assembly (**Figure 2b**). Therefore, it is possible for barbituric acid to enter the cavity of 15-crown-5 and further trigger the formation of *di-linear* **DASA-NC5**. The molecular sizes of the electron-donating and electron-withdrawing moieties are similar to the other **DASA-CE** (**Figure S14-S16**, see detail in SI).

The formation of the *di-linear* state was further demonstrated by 2D ^1H , ^1H nuclear Overhauser effect spectroscopy (2D-NOESY), and the protons on the triene π -bridge were investigated in detail. For the *linear* state, strong correlations of a-b, a-c, b-c and c-d are observed (**Figure 2c**, black). No correlations of d-a and d-b exist, due to the long distance between the protons (**Figure 2c**, blue). In contrast, a clear correlation of $\text{d}'\text{-a}'$ is observed for the *di-linear* state, indicating the formation of the head-to-tail supramolecular structure (**Figure 2c**, red).

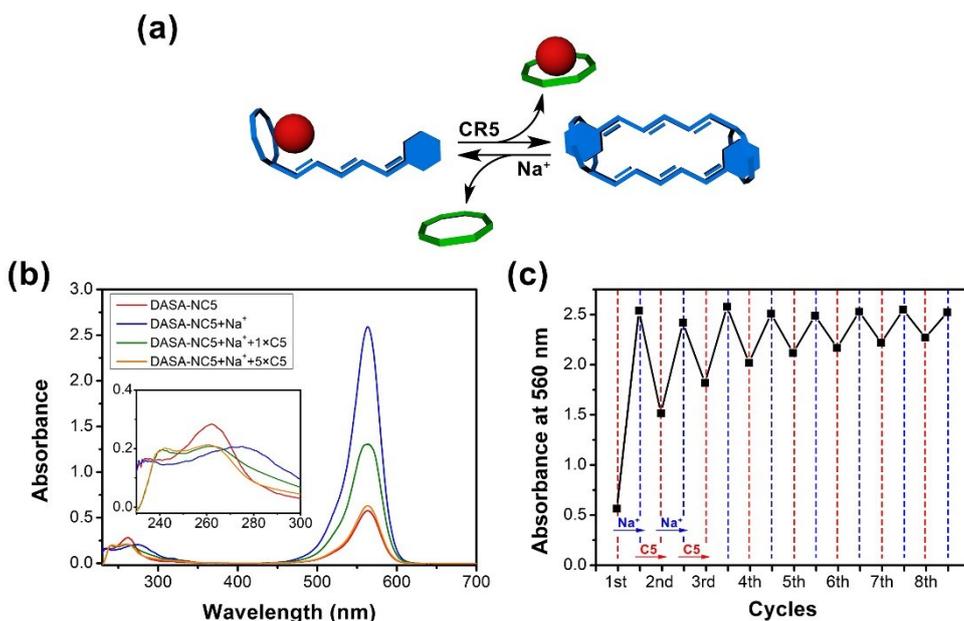


Figure 3. (a) Schematic illustration of the reversible transition of **DASA-NC5** between the *linear* and *di-linear* states; (b) UV/vis spectra of **DASA-NC5** before and after sequential treatment with NaBF₄ and 15-crown-5 ([**DASA-NC5**] = [NaBF₄] = 0.12 mM in THF). The inset shows the UV light region in detail; (c) Variation of absorbance at 560 nm of **DASA-NC5** after repeated treatment with NaBF₄ and 15-crown-5 ([**DASA-NC5**] = 0.12 mM in THF; the amount of NaBF₄ and 15-crown-5 added are kept the same for each cycle (in molar ratio)).

The light-induced *linear-to-cyclic* isomerization of DASAs has been well-studied over the past 5 years. According to the previous published theory⁴⁻⁵, DASA-CE belong to the first-generated DASAs, which are mainly in the zwitterionic *cyclic* state after visible light irradiation (**Figure 4a**). **DASA-NC5** does not show obvious *linear-to-cyclic* isomerization under 530 nm green light irradiation (40 mW/cm², 10 min) before introducing Na⁺ ions (**Figure 4b**, black). The slightly decreased absorbance in the visible light region is due to the residual *linear* state in the system. After the NaBF₄ addition, the absorbance in visible light region decreases sharply under green light irradiation, which is reversible after heating in the dark (**Figure 4b**, red and **Figure S18**). Therefore, the photoisomerization of the *di-linear* state is restricted. The light-induced isomerization of *linear* and *di-linear* states are further demonstrated by ¹H

NMR spectra (**Figure 4c**). The signals of the *linear* and *di-linear* state could be clearly identified in the same spectrum (**Figure 4c**, black). After green light irradiation, the signals of the *linear* state disappear, while the new generated signals for the *cyclic* state are formed, indicating the light induced *linear-to-cyclic* isomerization. In contrast, the signals of the *di-linear* state do not change after light irradiation, indicating the photoisomerization of *di-linear* state is restricted. These are attributed to the formed stable head-to-tail supramolecular structure.

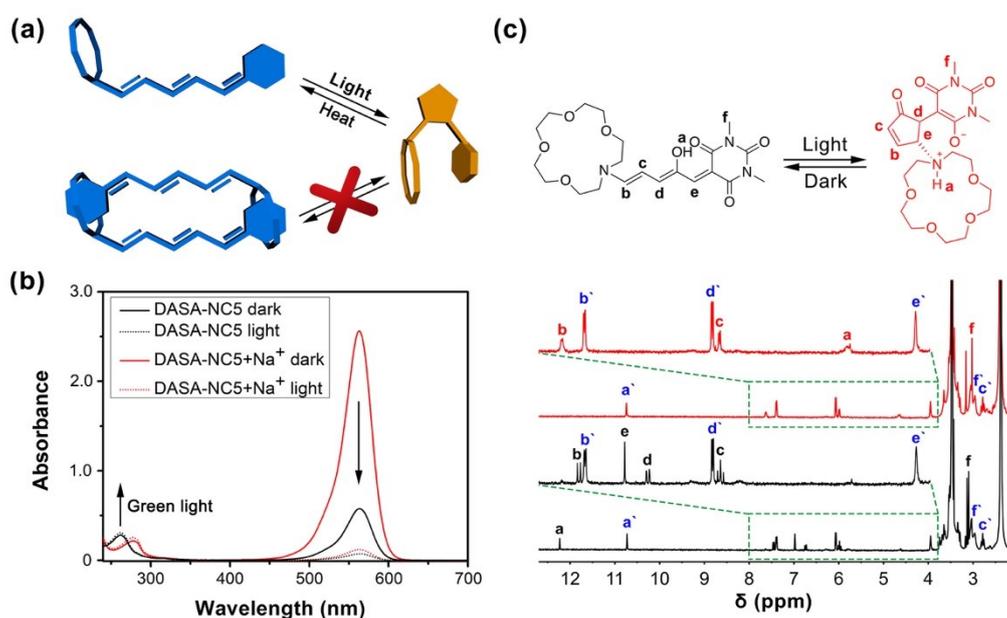


Figure 4. (a) Schematic illustration of light-induced isomerization between *linear*, *di-linear* and *cyclic* **DASA-NC5**; (b) UV/vis spectra of **DASA-NC5** under dark (solid) and visible light irradiation (dot) before (black) and after (red) NaBF₄ addition ([**DASA-NC5**] = 0.12 mM in THF); (c) ¹H NMR spectra (400 MHz at 298 K) of **DASA-NC5** under dark and visible light irradiation before NaBF₄ addition ([**DASA-NC5**] = 3 mM in THF-*d*₈). (a, b, c...(red) represent the protons in *cyclic* **DASA-NC5**)

In summary, we synthesized a series of crown ether-substituted DASA derivatives. The switching of the DASA-CE between *di-linear*, *linear* and *cyclic* states under orthogonal control of light and metal ions was realized. Taking **DASA-NC5** as an example, in aprotic solvents (*e.g.* THF, dichloromethane), DASA-CE exist mainly in the *di-linear* state, which is a 1:1 head-to-tail supramolecular structure self-assembled

through the van der Waals interaction between the electron-donating and -withdrawing moieties. The addition of Na^+ induces *di-linear-to-linear* transition, while the reverse *linear-to-di-linear* transition occurs after adding free 15-crown-5. Similar to the reported DASAs, *linear* **DASA-NC5** isomerizes to *cyclic* **DASA-NC5** after 530 nm green light irradiation, and switches back to the *linear* state under heating. However, the photoisomerization of the *di-linear* state is inhibited. We have successfully achieved switching of multiple ($n>2$) stationary states in a single molecule, which is beneficial for the future development of smart materials used in environments with complex stimuli. This also leads to more intelligent photoresponsive materials, including multi-drug release systems and interpenetrating polymer hydrogels.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Y. Duan and H. Zhao contributed equally to this work.

Declaration of Interests

The authors declare no competing interests

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Figures

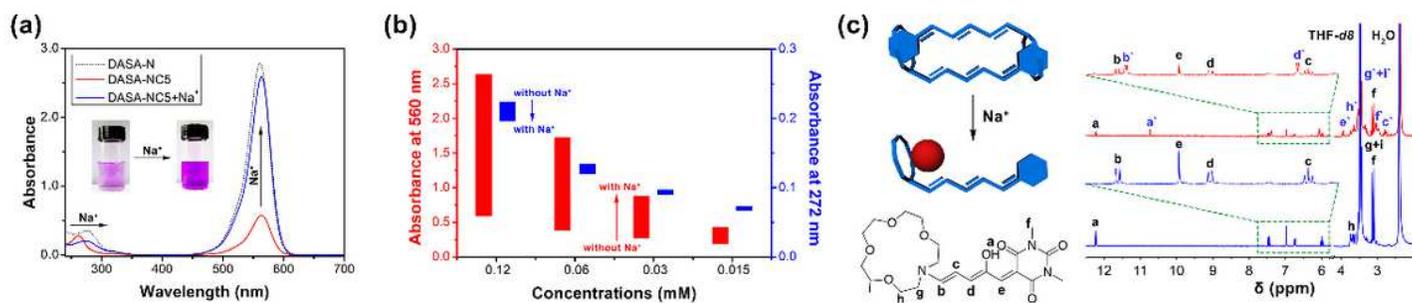


Figure 1

(a) UV/vis spectra of linear DASA-N (black, dot) and DASA-NC5 before (red, solid) and after (blue, solid) adding NaBF₄ ([DASA-NC5] = [NaBF₄] = 0.12 mM in THF). The inset shows the color change after adding NaBF₄; (b) Absorbance variation at 560 nm (red) and 272 nm (blue) for DASA-NC5 with different concentrations after adding NaBF₄ solution; (c) ¹H NMR spectra (400 MHz at 298 K) of DASA-NC5 before (red) and after (blue) adding NaBF₄ ([DASA-NC5] = 3 mM in THF-d₈). (a, b, c... (black) represent the protons in linear DASA-NC5, a, b, c'... (blue) represent the protons in di-linear DASA-NC5).

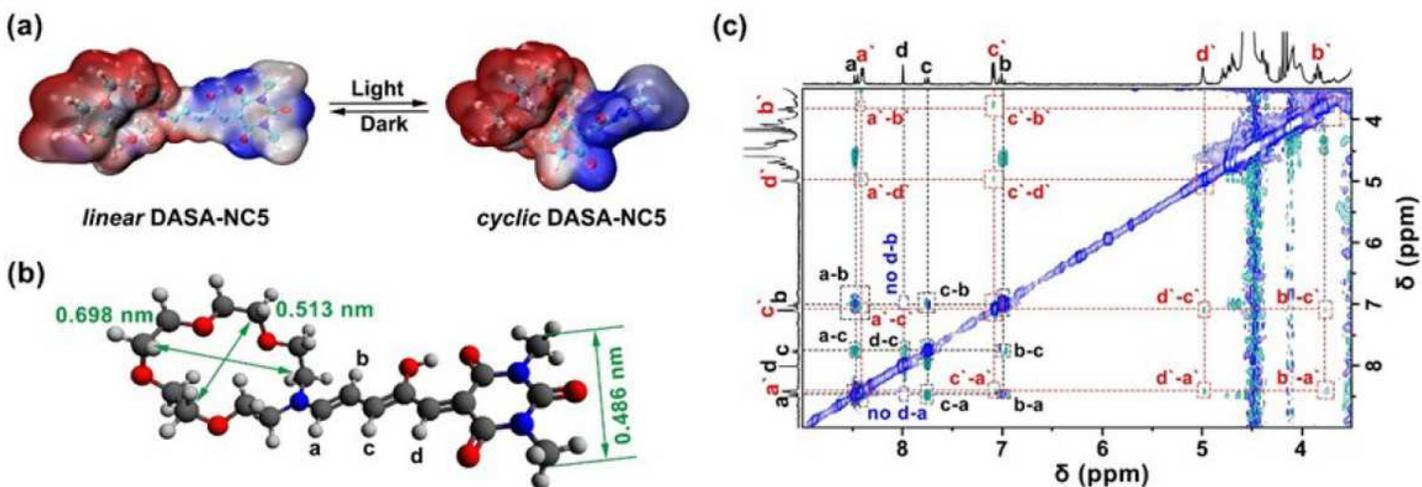


Figure 2

(a) Calculated electrostatic potential distributions of linear and cyclic DASA-NC5; (b) Calculated molecular structure of linear DASA-NC5; (c) ¹H,¹H NOESY spectrum (400 MHz at 298 K) of DASA-NC5 before adding NaBF₄ ([DASA-NC5] = 6 mM in THF-d₈).

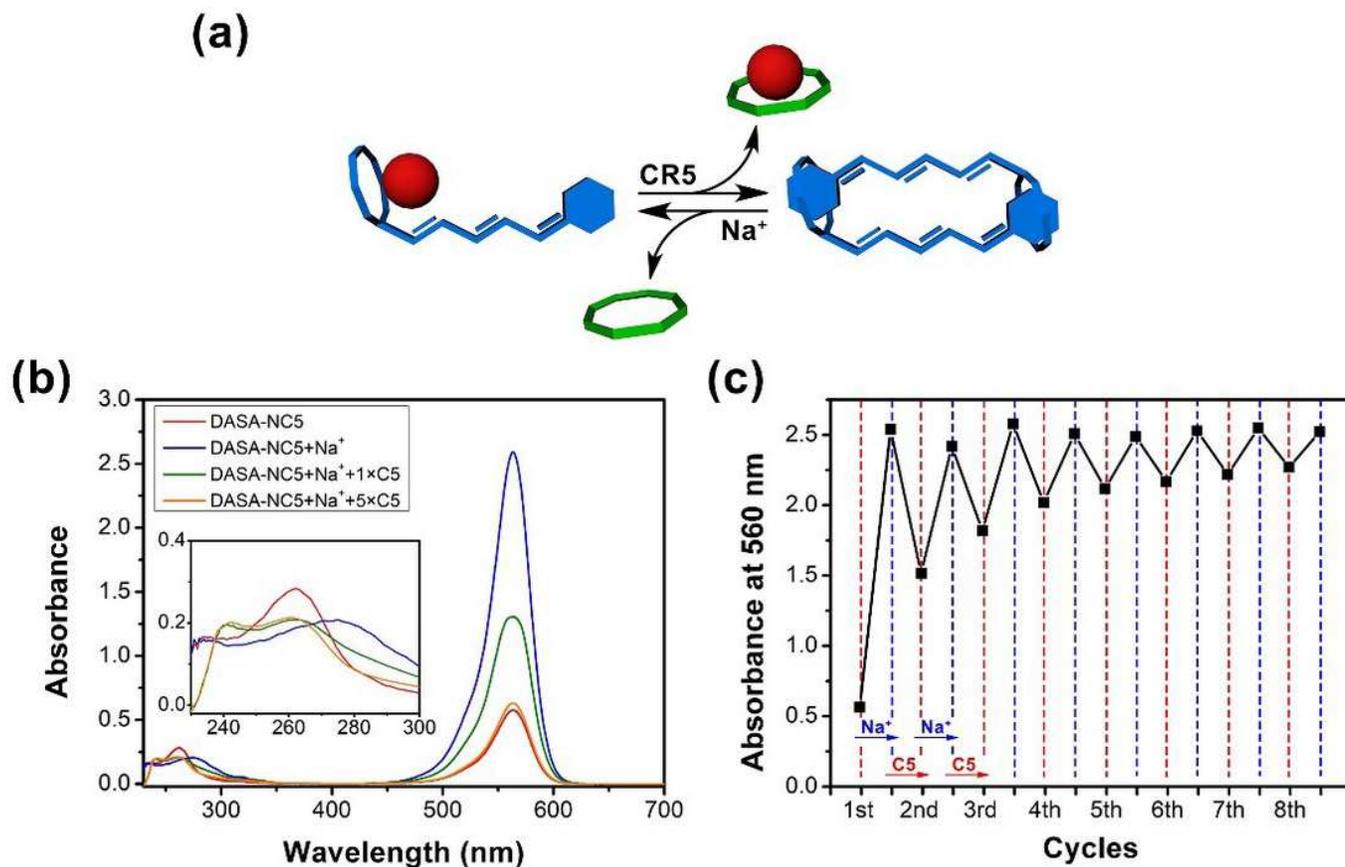


Figure 3

(a) Schematic illustration of the reversible transition of DASA-NC5 between the linear and di-linear states; (b) UV/vis spectra of DASA-NC5 before and after sequential treatment with NaBF₄ and 15-crown-5 ([DASA-NC5] = [NaBF₄] = 0.12 mM in THF). The inset shows the UV light region in detail; (c) Variation of absorbance at 560 nm of DASA-NC5 after repeated treatment with NaBF₄ and 15-crown-5 ([DASA-NC5] = 0.12 mM in THF; the amount of NaBF₄ and 15-crown-5 added are kept the same for each cycle (in molar ratio)).

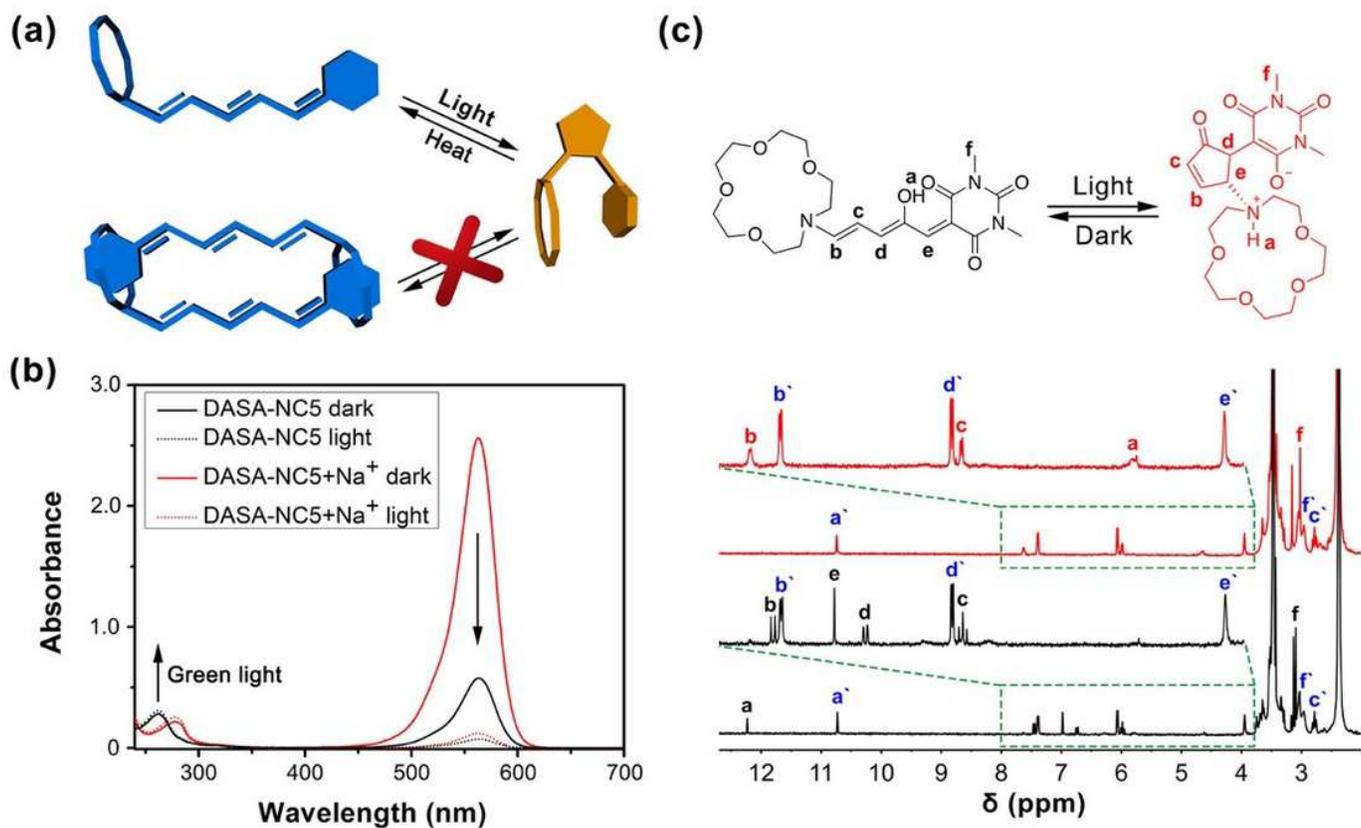


Figure 4

(a) Schematic illustration of light-induced isomerization between linear, di-linear and cyclic DASAs-NC5; (b) UV/vis spectra of DASAs-NC5 under dark (solid) and visible light irradiation (dot) before (black) and after (red) NaBF₄ addition ([DASAs-NC5] = 0.12 mM in THF); (c) 1H NMR spectra (400 MHz at 298 K) of DASAs-NC5 under dark and visible light irradiation before NaBF₄ addition ([DASAs-NC5] = 3 mM in THF-d₈). (a, b, c... (red) represent the protons in cyclic DASAs-NC5)

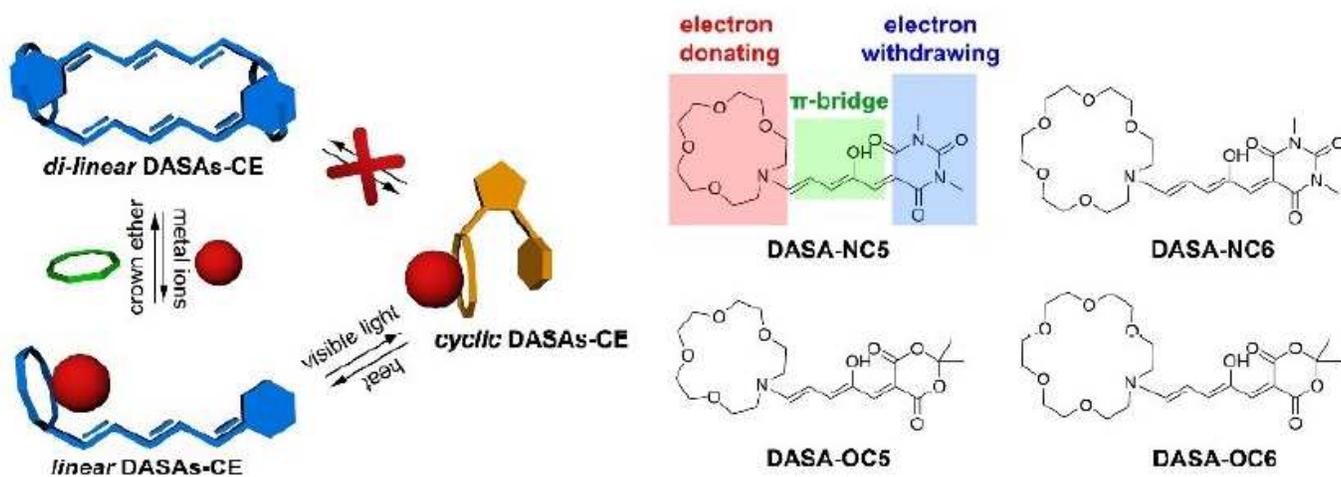


Figure 5

Scheme 1. Schematic illustration of orthogonal isomerization of DASA-CE under controlling of light and metal ions.

Supplementary Files

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- [SupportingInformation1.pdf](#)