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Diarylethene Isomerization by Using Triplet–Triplet Annihilation Photon Upconversion

Wera Larsson,^[a] Masakazu Morimoto,^[b] Masahiro Irie,^[b] Joakim Andréasson,^{*[a]} and Bo Albinsson^{*[a]}

Abstract: Green-to-blue triplet–triplet annihilation photon upconversion with the well-studied upconversion pair 9,10-diphenylanthracene (DPA)/platinum octaethylporphyrin (PtOEP) was used to reversibly drive the photoisomerization of diarylethene (DAE) photoswitches by using visible light. By carefully selecting the kinetic and spectral properties of the molecular system as well as the experimental geometry, a single green light source can be used to selectively trigger both the ring-opening and the ring-closing reactions, whilst

also inducing fluorescence from the colored closed isomer that can be used as a readout to monitor the isomerization process in situ. The upconversion solution and the DAE solution are kept physically separated, allowing them to be characterized both concomitantly and individually without further separation processes. The ring-closing reaction using upconverted photons was quantified and compared to the efficiency of direct isomerization with ultraviolet light.

Introduction

Manipulating light by triplet–triplet annihilation photon upconversion (TTA-UC)^[1] is a versatile tool that is used to overcome spectral mismatches between available light and the needs and requirements of the application at hand. This type of light manipulation has been used in various applications, including photovoltaics,^[2] solar energy storage,^[3] and photopharmacology.^[4] The motivation to use TTA-UC depends on the intended use, and includes increased efficiencies,^[2b] decreased photodegradation,^[5] and the possibility of using low-intensity noncoherent^[6] sunlight rather than conventional light sources powered by electricity.

Focusing on photochemical reactions driven by upconverted photons, the common aim is to facilitate photochemical transformations by upconverting light of lower energy into light with enough energy to drive the reactions. This could for example be used in the production of solar fuels, using the abundant visible sunlight to produce fuels that conventionally

would require ultraviolet (UV) light.^[7] Other examples of TTA-facilitated photochemistry include dimerization,^[8] photodissociation,^[9] photoelectrochemistry,^[10] photocatalysis,^[11] and photoisomerization.^[12] There have also been successful studies on upconversion in water,^[13] which pave the way for further photochemical applications. Reversible photoswitching of photochromic molecules between two isomers require light of two different wavelengths; typically one to drive the colorization reaction and another to drive the reverse (decolorization) reaction.^[14] By combining photoisomerization with photon upconversion, diarylethene (DAE) photoswitches has previously been used to control TTA-UC emission.^[15] Another possibility that arises when combining photoisomerization with photon upconversion is that a single light source can be used to facilitate both the colorization and the decolorization reactions. This has been described in the previous literature using upconverting rare-earth nanoparticles.^[16] Other examples are the use of TTA-UC in a covalently fused annihilator photoswitch complex,^[17] and acid/base color-tunable TTA-UC to achieve reversible photoisomerization.^[18]

Below, we show that a single green light source can be used to not only drive the ring-opening reaction and inducing fluorescence from the closed colored isomer of a series of fluorescent DAE derivatives,^[19] but also to drive the ring-closing reaction. The latter process requires higher energy light (shorter wavelengths, typically in the UV region) and we use green-to-blue TTA-UC for this purpose by passing the green light through a solution of platinum octaethylporphyrin (PtOEP) as the sensitizer and 9,10-diphenylanthracene (DPA) as the annihilator. Blue light, with sufficiently short wavelength to trigger the ring-closing reaction, results. By separating the DAE photoswitches from the upconversion solution in two separate chambers, we can conveniently choose to trigger selectively either the DAE ring-opening or ring-closing reaction, simply by green light irradiation of only the DAE chamber or also through

[a] W. Larsson, Prof. J. Andréasson, Prof. B. Albinsson
Department of Chemistry and Chemical Engineering
Chalmers University of Technology
41296 Göteborg (Sweden)
E-mail: a-son@chalmers.se
balb@chalmers.se

[b] Prof. M. Morimoto, Prof. M. Irie
Department of Chemistry and
Research Center for Smart Molecules,
Rikkyo University
171-8501 Tokyo (Japan)

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the upconversion (UC) chamber, respectively. Additional advantages with the two-chamber approach are related to its versatility; the two solutions can easily be transferred and characterized both individually and in synchrony, and there is a large freedom in the choice of solvents, molecular systems, and concentrations. TTA-UC allows for this type of physical separation as the excitation energy is carried by photons, as opposed to triplet sensitization driven isomerization^[20] where the sensitizer and the photoreactant must be in close, molecular contact. Physical separation is also a requirement if we are to in future applications do solid state TTA-UC to drive photochemical reactions, in which case the physical separation would be enforced by the upconversion and the photochemical systems being in different phases.

Results and Discussion

Both the UC and the DAE parts of our devised system are shown in Figure 1. The photographs in the top panel show how the two parts are kept separated in a two-chambered quartz cuvette, where the chamber to the left shows one of the DAE derivatives (DAE2) in toluene and the chamber to the right contains the UC solution, also in toluene. As seen in the rightmost photograph, green light is irradiated from the left and hence it first reaches the DAE chamber of the cuvette (yellow) before reaching the UC chamber (purple). In both the top and the bottom panels, the green arrows indicate the 532 nm laser light used in the setup and the blue arrows indicate the blue upconverted fluorescence from DPA.

The top panel of Figure 1 also shows a Jablonski diagram to conceptualize the TTA-UC process, and structures of the sensitizer PtOEP and the annihilator DPA. Absorption and emission spectra of PtOEP and DPA are shown in Figure S3 in the Supporting Information. Green light excites the sensitizer molecules from the singlet ground-state S to the singlet excited state $^1S^*$, followed by rapid relaxation to the triplet excited state $^3S^*$ by intersystem crossing (ISC). The energy is subsequently transferred to an annihilator molecule by triplet energy transfer (TET) resulting in a triplet excited annihilator $^3A^*$. Two triplet excited annihilator molecules can then undergo TTA yielding one molecule in its ground state A and one in the singlet excited state $^1A^*$ from where a blue photon can be emitted through fluorescence.

Structures and isomerization scheme of the three DAEs used in this study (referred to as DAE1, DAE2, and DAE3) are shown in the bottom panel of Figure 1. Synthesis of DAE2 is described in the Supporting Information (see Synthesis of 1,2-Bis(2-isobutyl-6-(3-methylthiophen-2-yl)-1-benzothiophen-1,1-dioxide-3-yl)perfluoro-cyclopentene (DAE2a)), whereas DAE1^[21] and DAE3^[22] were synthesized according to previously described procedures. DAEs exist in two isomeric forms (open and closed) with excellent thermal stability, referred to as DAEo (left structure in the isomerization scheme) and DAEc (right structure in the isomerization scheme). DAEo absorb mainly in the UV region, whereas DAEc display strong absorption also in the visible region (see Figure 2). The ring-closing reactions proceed

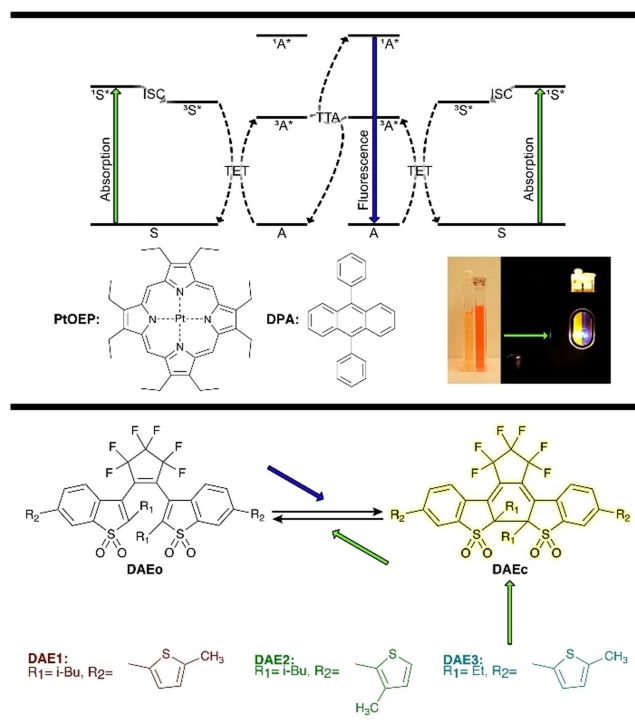


Figure 1. Green arrows are used to indicate 532 nm laser light, and blue arrows are used to visualize the upconverted fluorescence from DPA in both panels. Top: Jablonski diagram of the upconversion process together with structures of the sensitizer PtOEP (“S”) and the annihilator DPA (“A”), and photographs of the two solutions in the two-chambered cuvette used in the upconversion-facilitated isomerization experiments. The photograph to the left shows the solutions in a lit room, with DAE2 in the left cuvette chamber and the upconversion solution in the right cuvette chamber; both in toluene. The photograph to the right shows the same cuvette with the same solutions in the dark during an upconversion-facilitated isomerization experiment. The incoming green 532 nm laser light (indicated by a green arrow) travels through the DAE2 solution, inducing fluorescence of its closed-form isomers, before reaching the chamber to the right where the light is upconverted to blue light. Bottom: Structures and isomerization scheme of the three DAEs “DAE1”, “DAE2” and “DAE3” used in this study. DAEo (left) is isomerized to DAEc (right) by using the upconverted fluorescence. DAEc is isomerized back to DAEo by 532 nm laser light, and this light is also used to induce fluorescence of DAEc.

with isomerization quantum yields of 0.30,^[21] 0.39, and 0.23^[22] for DAE1, DAE2, and DAE3, respectively, whereas the reverse ring-opening reactions are less efficient with quantum yields of $3.4 \cdot 10^{-5}$,^[21] $2.4 \cdot 10^{-4}$, and $< 1.0 \cdot 10^{-5}$.^[22] DAEc emit intense fluorescence with quantum yields of 0.77,^[21] 0.83, and 0.78,^[22] for DAE1, DAE2, and DAE3, respectively, whereas DAEo do not emit any significant fluorescence. The isomerization and fluorescence quantum yields presented above are all determined in 1,4-dioxane.

As seen in Figure 2, the upconverted blue fluorescence from the UC solution (10 mM DPA and 0.5 mM PtOEP in toluene, $\lambda_{\text{ex}} = 532 \text{ nm}$) reaching the DAE chamber overlaps the absorption of DAEo and can thus be used to drive the ring-closing reaction (see Absorption and emission of UC components, and Figure S4 in the Supporting Information for measurement details). Indeed, the blue fluorescence also overlaps the absorption of DAEc, implying that the blue light could also

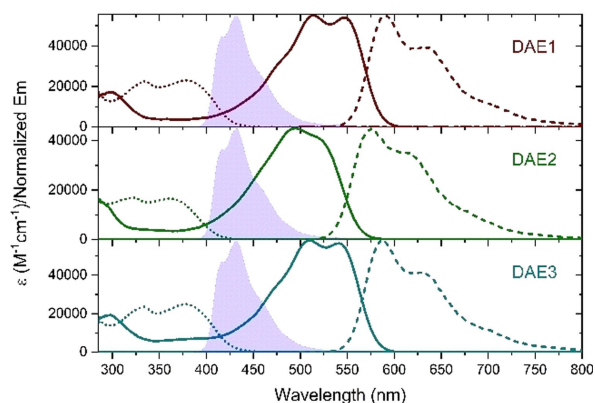


Figure 2. Absorption and normalized emission spectra of DAE1 (top), DAE2 (middle) and DAE3 (bottom) in toluene (10–20 μM ; $\lambda_{\text{ex}} = 490 \text{ nm}$) together with normalized upconverted emission ($\lambda_{\text{ex}} = 532 \text{ nm}$) from a DPA (10 mM) and PtOEP (0.5 mM) solution also in toluene (all). Dotted lines: absorption of DAEo. Solid lines: absorption of DAEC. Dashed lines: emission from DAEC. Filled spectra: upconverted emission measured semi-front face in a two-chamber cuvette (see Absorption and emission of UC components and Figure S4 in the Supporting Information for further details).

induce the reverse ring-opening reaction. At the same time, the green laser light also triggers the ring-opening reaction as well as induces fluorescence emission by direct absorption of DAEC. Thus, the green light directly or indirectly triggers three different photophysical processes of the DAEs (ring-opening, ring-closing and excitation for emission readout). The resulting distribution between DAEo and DAEC at the photostationary state (PSS) depends on the relative rates of the above-mentioned isomerization processes and will be discussed in detail below.

The two-chambered cuvettes were prepared as shown in the photographs in the top panel of Figure 1. The DAEs were prepared one by one in their as-synthesized DAEo non-fluorescent form in toluene with an approximate concentration of 10–20 μM for the different samples (see Concentration estimations of DAE solutions in the Supporting Information for details). The UC chamber was filled and sealed in a glovebox under N_2 to avoid oxygen quenching of the UC process (see Figure S5 for oxygen effect on DAE1 fluorescence intensity). The UC solution was prepared with concentrations (10 mM DPA and 0.5 mM PtOEP in toluene) resulting in around 99% attenuation of the 532 nm light intensity within the first 1 mm of the UC chamber. When irradiating the sample from the left as illustrated in the photograph in the top panel of Figure 1 (through the DAE chamber) most of the upconversion will occur close to the quartz wall separating the two chambers. This results in a short distance for the upconverted light to travel back before reaching the DAE chamber, thereby minimizing secondary inner-filter effects of the blue fluorescence from the UC solution before reaching the DAE chamber.

Figure 3 shows the fluorescence intensity time-profile of DAEC for the three DAE derivatives at their respective emission maxima (592 nm for DAE1 and DAE3, and 578 nm for DAE2) using the described setup. Initially, the DAEs were in the DAEo non-fluorescent form. Thus, no absorption of the 532 nm light

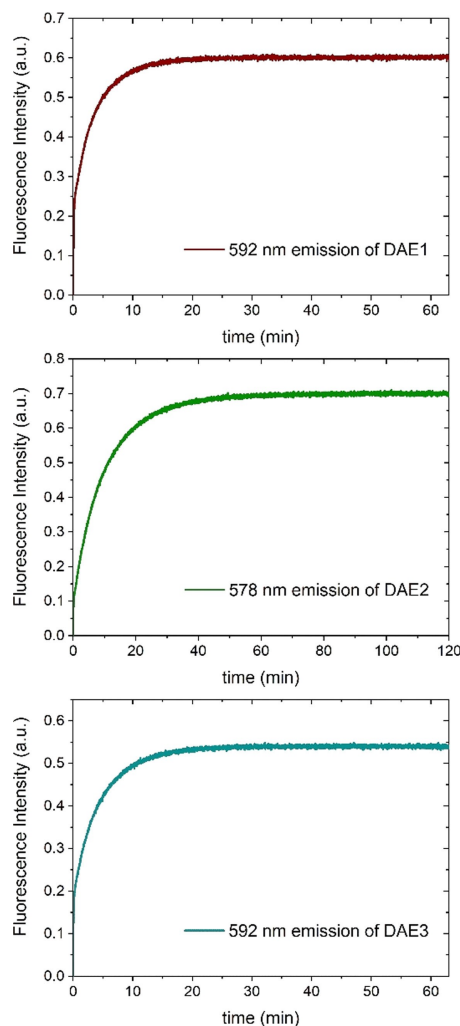


Figure 3. DAEC fluorescence ([DAE] = 10–20 μM in toluene) measured at the emission peak over time in the two-chamber cuvette setup with upconversion solution ([DPA] = 10 mM and [PtOEP] = 0.5 mM in toluene) in the other chamber. At the start of the measurement, the DAEs were in their DAEo nonfluorescent form. A continuous 532 nm laser (22 mW) was turned on at time zero, inducing upconversion. This in turn induces the isomerization of the DAEs to the fluorescent DAEC, and the fluorescence seen in the figure is also induced by the laser light. For all three DAEs, the fluorescence intensity reaches a stable level over time. Note the difference in scale of the three time-axes. The initial fast rise of varying magnitude in all three traces is due to unavoidable scattering of the laser light not fully removed by the 532 nm notch filter.

occurs in the DAE chamber at time zero. As irradiation proceeds, colored DAEC is formed, and fluorescence is induced by the 532 nm light. In a separate control experiment with only toluene in the UC chamber (Figure S6), no significant rise in the emission from the DAEC was detected, clearly showing that the upconversion of the 532 nm green light to blue light is triggering the ring-closing reaction. This is also supported by noting that the absorption spectra before and after the control experiments were identical. The initial rise in the fluorescence intensity is hence a measure on how efficiently the upconverted photons can facilitate the ring-closing reaction for each of the three DAE derivatives. The fluorescence intensity levels out with

time to reach a stable level corresponding to the fluorescence intensity at the PSS. The time required to reach the PSS is reflected in the time constants of the mono-exponential rise (k_{obs}). k_{obs} equals the sum of the rates for ring-opening (k_{open}) and ring-closing (k_{close}), that is, $k_{\text{obs}} = k_{\text{open}} + k_{\text{close}}$. Under the assumption that k_{close} is much larger than k_{open} (see below), the latter rate constant can be neglected so that $k_{\text{obs}} = k_{\text{close}}$. Given that the intensity of the upconverted blue light is identical for the three separate experiments with DAE1, DAE2, and DAE3, variations in k_{close} throughout the series of these compounds are ascribed only to the differences in the product between the quantum yield of ring-closing (ϕ_{closing}) and the effective overlap (O_{eff}) between the upconverted blue light and the absorption spectrum of the respective DAEo (taking into account differences in the molar absorption coefficients). k_{obs} was determined to $4.2 \cdot 10^{-3}$, $1.6 \cdot 10^{-3}$, and $3.4 \cdot 10^{-3} \text{ s}^{-1}$ for DAE1, DAE2, and DAE3, respectively, giving a ratio of 2.6:1:2.1.

It is very encouraging to note that the corresponding ratio for $\phi_{\text{closing}} \cdot O_{\text{eff}}$ was determined to 2.5:1:2.3 that is, in excellent agreement with the ratio of k_{obs} . Thus, it is clear that the isomerization kinetics reflects almost exclusively the rate of the ring-closing reaction induced by the upconverted blue light, validating the above approximation that $k_{\text{obs}} = k_{\text{close}}$. This is also consistent with the resulting distribution of DAEc and DAEo at the PSS. DAE1 and DAE3 were found to be quantitatively converted to DAEc, whereas DAE2 displays an 81% conversion (Figure S7). The lower number observed for DAE2 is explained by the tenfold higher quantum yield for the ring-opening reaction compared to DAE1 and DAE3, implying that k_{open} makes a small but non-negligible contribution to k_{obs} for this compound.

A two-chamber cuvette sample with DAE2c in one chamber and UC solution in the other chamber was prepared and irradiated with the 532 nm laser used in the previous experiments. This time, only the DAE2 chamber was subjected to the green light and hence no TTA-UC occurred. To ensure this, the light was now irradiated parallel to the quartz wall separating the two chambers. In Figure 4 the absorption spectra of DAE2o and DAE2c are shown together with the absorption spectra of the sample after 1, 3 and 5 h of 532 nm irradiation on the DAE2 chamber initially only containing DAE2c. As can be seen, almost all DAE2c have been isomerized to DAE2o after 5 h. This together with the results shown in Figure 3 and Figure S7 shows that by simply irradiating our two-chamber cuvette from different directions, we can selectively trigger either the ring-closing or the ring-opening reaction using the same 532 nm light source.

Having proved that the upconversion-driven isomerization worked in the proposed experimental setup, we aimed at a quantification of the performance. This was done for DAE2 (Figure 5) by comparing the upconversion-driven isomerization with a 365 nm LED-driven isomerization. The experimental setup used for this comparison is shown in Figure S8. To assure the same irradiation volume, allowing for a more straightforward comparison, a pinhole with a diameter smaller than the laser beam was used. Highly concentrated solutions (ca.

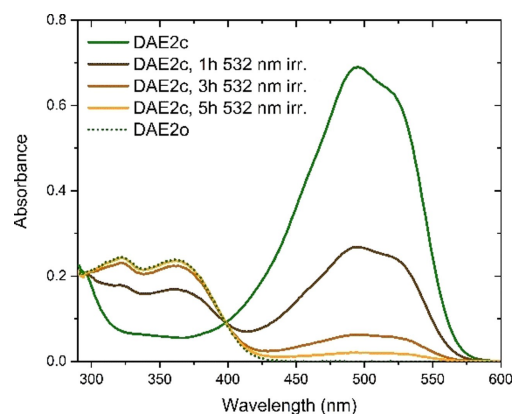


Figure 4. Absorption spectra of DAE2o and DAE2c, together with the absorption of DAE2c after 1, 3 and 5 h of 532 nm laser irradiation (22 mW; [DAE2] = 10 μM in toluene). The sample subjected to 532 nm irradiation was prepared in the two-chamber cuvette with one UC and one DAE chamber, starting with only DAE2c in the DAE chamber at time zero. To selectively trigger ring-opening, only the DAE chamber was subjected to the laser light, resulting in no TTA-UC and hence only the ring-opening reaction was triggered. After 5 h, almost all DAE2c had isomerized to DAE2o.

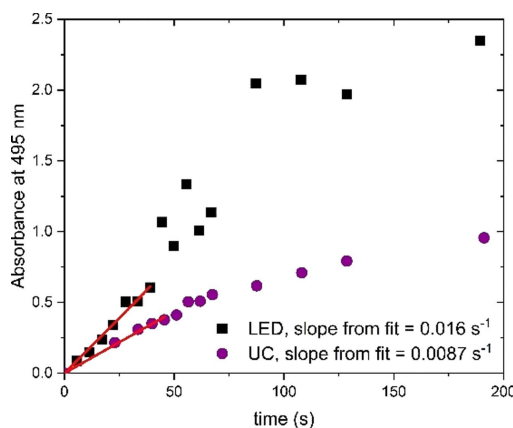


Figure 5. Comparison between 532 nm laser-induced UC (16 mW; [DPA] = 10 mM and [PtOEP] = 0.5 mM in toluene) and 365 nm LED (0.21 mW) isomerization of highly concentrated (ca. 800 μM) DAE2 in toluene; see Upconversion-driven vs. direct UV isomerization of highly concentrated DAE2 in the Supporting Information for measurement details. The high concentration of DAE2 results in total absorption of the upconverted/UV light when all DAEs are in the open form at time zero, resulting in zeroth-order kinetic behavior at the start of the measurement. The figure shows absorbance of the DAE2c peak at 495 nm over time, and because of the zeroth-order kinetics, a linear fit (red lines) of the absorbance change over time gives a slope proportional to the rate constants of the isomerization.

800 μM) of DAE2 were used to allow for the approximation of total absorption of the upconverted and the 365 nm photons.

Under this approximation, initial zeroth-order kinetics is expected for both samples. When measuring the absorbance of DAE2 at 495 nm over time, the absorbance change is indeed initially linear. Subsequent deviations from linearity occur due to the inner-filter effect from DAE2c when the absorbance at 532 nm reaches a sufficiently high value. A linear fit of the absorbance changes during the zeroth-order kinetic period gives a value proportional to the effective rate constants of the

isomerization. The power of the 532 nm and UV light sources measured through the pinholes were 16 and 0.21 mW, respectively. Considering the difference in power together with the results from the linear fittings in Figure 5, this indicates that the direct LED isomerization at 365 nm was approximately 140 times more efficient than the upconversion-driven isomerization. Some factors that can help to explain this comparatively low estimated efficiency of upconversion-driven isomerization are the poor spectral overlap of the DAE2o absorption and the upconverted emission, the angular spread of upconverted photons, and the upconversion efficiency. Using the following estimations: 23% effective overlap (O_{eff} , estimated at the 800 μM DAE2 concentration and using the UC emission spectra in Figure 2, see Upconversion-driven vs. direct UV isomerization of highly concentrated DAE2 in the Supporting Information for details), 50% utilization of upconverted photons (rough estimations of the experimental geometry) and an observed upconversion quantum yield approximation of 9% (see Upconversion-driven vs. direct UV isomerization of highly concentrated DAE2 in the Supporting Information for details), this efficiency difference can be accounted for. Note that these numbers are mere approximations and that most of the loss factors can be improved substantially by further optimization of the geometry of the experimental setup and the selection of molecular systems used.

Conclusions

In this study, we have shown that a single visible light source at 532 nm can be used to trigger both ring-opening and ring-closing as well as excitation for emission readout of a group of diarylethene molecular photoswitches. This is made possible by combining the DAEs with green-to-blue TTA-UC, in a simple and versatile experimental setup in which the DAEs and the upconversion solution are kept in separate chambers in a two-chambered cuvette. The separation of the two solutions allows for in situ characterization of the DAE and upconversion solutions both individually and in synchrony, and there is no need for further separation procedures if the DAEs are to be used in further applications. The upconversion-driven isomerization of one of the DAEs (DAE2) was quantified, showing that the isomerization was approximately 140 times less efficient than the corresponding process induced by direct exposure to UV light at 365 nm. We ascribe this low number to a poor spectral overlap of the DAE2o absorption and the upconverted emission, the angular spread of upconverted photons and the fairly low upconversion efficiency. By further optimizing the experimental setup (e.g., by the use of mirrors or changing the sample geometry to one where the UC solution chamber is immersed in an outer photoreactant chamber^[12,18] to utilize a larger fraction of the upconverted photons), the performance of the system would improve.

Experimental Section

Materials: 9,10-Diphenylanthracene (DPA) and platinum octaethylporphyrin (PtOEP) were purchased from Sigma-Aldrich and used without further purification. Diarylethene derivatives DAE1^[21] and DAE3^[22] were synthesized according to previously described procedures, and the DAE2 synthesis is further described in the Supporting Information.

Sample preparation: All measurements (apart from synthesis related measurements presented for DAE2) were performed using toluene (spectroscopic grade) as a solvent. Samples were prepared in quartz cuvettes with different dimensions depending on the measurement at hand. Absorption and emission spectra of DAEs shown in Figure 2 together with DPA and PtOEP absorption and emission spectra shown in Figure S3 were measured in 4 mm · 10 mm cuvettes. The PtOEP spectra were measured in a screw cap cuvette and prepared under N₂ in a glovebox (Innovative Technologies) to ensure an oxygen-free environment. All other absorption and emission spectra were measured in a two-chambered quartz cuvette with chamber dimensions of 4 mm · 10 mm. Upconversion (UC) solutions were also prepared in the N₂ atmosphere glovebox and sealed with a B-434 MetaLabel (Brady AB) sticker using Teflon tape to cover the cuvette opening. DAE solutions were prepared in their as-synthesized open form, and the DAE chamber was sealed with an ordinary cuvette cap.

Instrumentation: 400 MHz ¹H and 100 MHz ¹³C NMR spectra of DAE2 were recorded with JEOL ECX-400P NMR spectrometer. For CDCl₃ solution, tetramethylsilane (TMS) was used as an internal standard. For CD₂Cl₂ solution, the solvent signal (CH₂Cl₂: 5.32 ppm) was used as a standard. Mass spectrometry (MS) on DAE2 was carried out with Shimadzu GCMS-QP2010Plus mass spectrometer based on electron-impact (EI) ionization. Elemental analysis on DAE2 was carried out with an elemental analysis system (Elementar, Vario MICRO Cube). Absorption spectra were recorded using a Cary50 UV-vis spectrometer. Steady-state fluorescence spectra of the individual compounds were recorded using a SPEX Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon). Steady-state upconversion fluorescence spectra together with DAE fluorescence measurements over time were recorded using a home-built system. Samples were excited by a 532 nm OBIS laser (Coherent) with a beam diameter of 0.7 mm and detected using a photomultiplier tube (PMT). In the quantification measurement of the upconversion-driven isomerization of DAE2, a 365 nm LED (Engin LZ1 10UV00, FWHM = 11 nm, 0.21 mW at the sample) was used as the excitation source for the reference sample.

Isomerization quantum yields: The cyclization quantum yield of DAE2 in 1,4-dioxane was determined using 1,2-bis(2-ethyl-6-phenyl-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene in 1,4-dioxane ($\Phi_{\text{oc}} = 0.62$)^[23] as a reference under irradiation with 313 nm light. The cycloreversion quantum yield of DAE2 in 1,4-dioxane was determined using 1,2-bis(2-ethyl-6-phenyl-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene in 1,4-dioxane ($\Phi_{\text{co}} = 5.9 \cdot 10^{-4}$)^[23] as a reference under irradiation with 480 nm light.

TTA-UC quantum yield: For upconverted fluorescence quantum yield (Φ_{UC}) determination, relative measurements were performed using Rhodamine 6G ($\Phi_{\text{F}} = 0.95$)^[24] as the reference compound. Both upconversion fluorescence spectra and reference fluorescence spectra were recorded using the home-built system described above, both under irradiation with 532 nm light.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: diarylethenes · photoisomerization · photon upconversion · photoswitches · triplet-triplet annihilation

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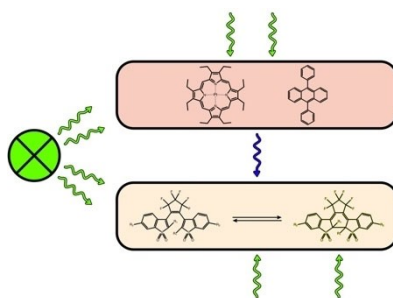
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RESEARCH ARTICLE

A single green light source is used to selectively control both the ring-opening and ring-closing reactions of diarylethene (DAE) photoswitches, by using green-to-blue triplet-triplet annihilation photon upconversion (TTA-UC). Whilst using TTA-UC to trigger the ring-closing reaction, the green light also induces fluorescence from the colored closed isomer of the DAE, which was used as an in-situ readout to monitor the isomerization process.



W. Larsson, Prof. M. Morimoto, Prof. M. Irie, Prof. J. Andréasson*, Prof. B. Albinsson*

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Diarylethene Isomerization by Using Triplet–Triplet Annihilation Photon Upconversion

