

Photoinduced double charge accumulation in a molecular compound

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Photochemistry involves elementary steps in which single electrons are transferred, but artificial photosynthesis requires multi-electron reactions. This discrepancy necessitates light-driven charge accumulation, which has so far proved very difficult to achieve without sacrificial redox reagents. Here we report a molecular donor–photosensitizer–acceptor compound in which light absorption leads to the reversible accumulation of two positive and two negative charges. The resulting photoproduct forms with an overall quantum yield of 37%, has a lifetime of more than 100 ns and stores 3.0 eV of energy. The use of a structurally well-defined molecular compound provides fundamental insights into how light-driven multi-electron transfer can generally be performed efficiently and sustainably, at irradiance levels orders of magnitude below those required in comparable systems. This represents a step towards more application-oriented research on solar fuels from fundamental studies of photoinduced (single) electron transfer.

The first elementary redox reaction step of natural photosynthesis is the light-induced transfer of an electron from a chlorophyll pigment to a pheophytin molecule and onwards to a quinone. This results in a so-called charge-separated state (CSS), which is composed of the oxidized chlorophyll and the reduced quinone¹. Hundreds of previous studies have mimicked this photoinduced charge separation in artificial donor–photosensitizer–acceptor (D–PS–A) compounds and considered it an important step towards artificial photosynthesis^{2–4}. However, separating a single oxidation equivalent from a single reduction equivalent is obviously still a long way from turning water and carbon dioxide into biomass or any useful solar fuel.

Fuel-forming reactions require multiple electrons, whereas photoinduced elementary reaction steps are usually single electron transfer events⁵. Research on artificial photosynthesis that aims to convert solar energy into energy-rich chemical fuels therefore requires overcoming several fundamental challenges. These include the efficient harvesting of light at low irradiances, the transfer and accumulation of multiple redox equivalents^{2,6–9} and selective catalytic systems for substrate reduction and, ideally, water oxidation¹⁰. For the reduction of CO₂ in particular, multi-electron transfer appears to be essential^{5,6}.

Against this background, fundamental research on photoinduced electron accumulation often studied molecular systems that use large amounts of sacrificial redox reagents. These undergo irreversible

reactions after donating an electron to drive the reaction in only one direction^{11–20}. To avoid the use of these high-energy sacrificial reagents, recent studies have relied on bimolecular reactions with reversible electron donors such as ascorbate^{21,22}. This is a useful strategy, even though some of the natural photosynthetic elementary reaction steps are also irreversible. Nonetheless, fully integrated covalent systems that do not require any additives remain of central interest, for example for the separation of redox equivalents across a membrane²³.

Charge-separated states in D–PS–A compounds (Fig. 1a) represent the simplest form of photochemically stored energy²⁴, but these states are inherently unstable due to spontaneous electron transfer reactions occurring in the reverse direction^{25,26}. Charge recombination typically occurs within a few nanoseconds but can be decelerated to the microsecond regime by elongating the distance between the electron donor and the acceptor^{27–31}. This timescale is then in principle suitable for the slower onward reactions involved in artificial photosynthesis. However, the accumulation and storage of multiple electrons or holes in such fully integrated D–PS–A systems is substantially more difficult than the formation of single electron–hole pairs.

Without the use of external redox reagents, only a handful of previous studies have achieved either the accumulation of two reduction or two oxidation equivalents in purely molecular systems, but never both^{32–35}. Furthermore, all of these D–PS–A–PS–D-type systems

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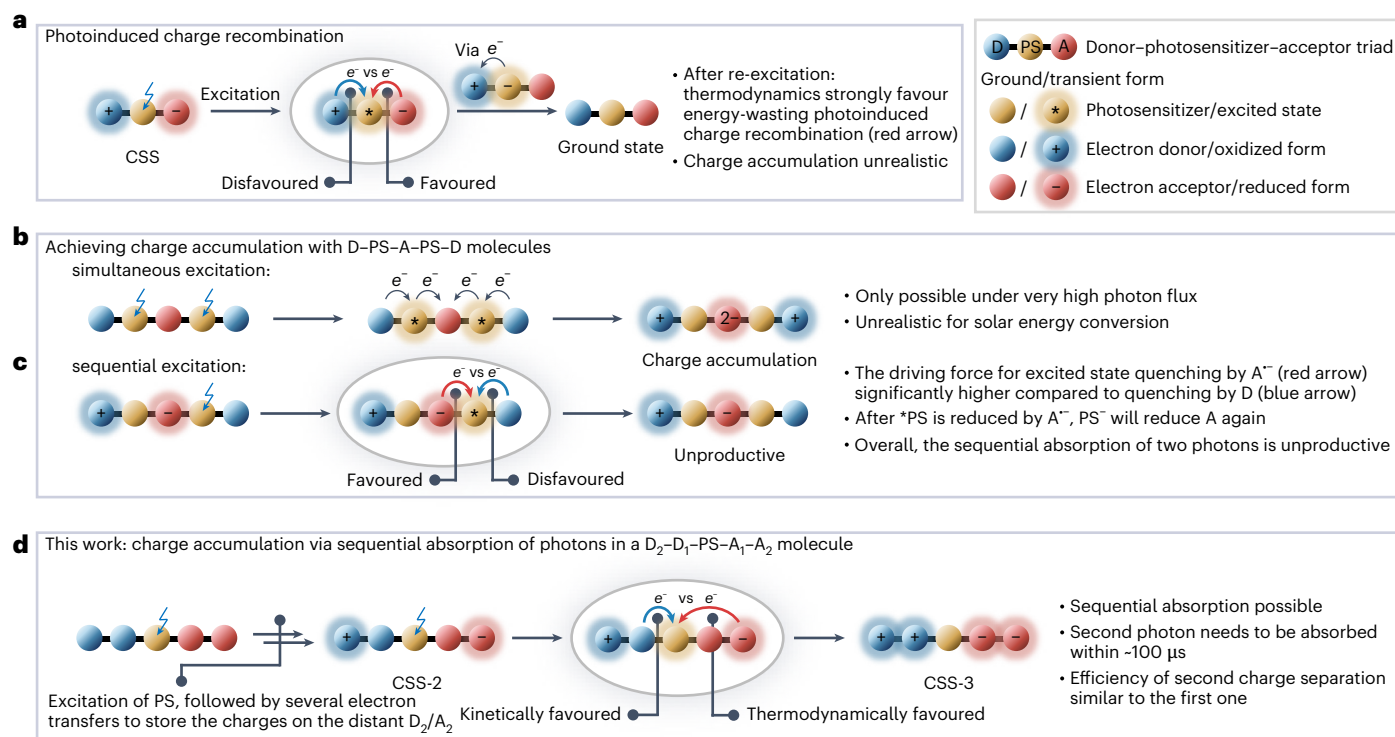


Fig. 1 | Competing processes in excited state quenching of D-PS-A-type molecules in charge-separated states. **a**, Energy-wasting photoinduced charge recombination is favoured over energy-storing charge accumulation. **b**, Simultaneous excitation of both photosensitizer units in D-PS-A-PS-D molecules circumvents the destructive processes from **a**. **c**, The sequential excitation pattern (achievable at low irradiances) in such D-PS-A-PS-D molecules cannot lead to substantial charge accumulation. **d**, A general strategy for charge accumulation via sequential photon absorption at much lower irradiances. Blue arrows denote excitation with light; black horizontal arrows

are simple reaction arrows. The initial electron-hole pair is stored peripherally, away from the photosensitizer. Secondary excitation of PS allows faster reaction with nearby electron donors and acceptors, despite greater driving force for unwanted light-induced charge recombination compared to light-induced charge accumulation. Legend: in general, for simplicity and comparability, reductive quenching of the excited state is shown. Depending on the actual donor and acceptor, oxidative quenching may also occur. The general principles apply to both cases.

reported to date lack the ability for efficient electron accumulation through sequential excitation (see above), which is considered a key requirement for a functional system under low solar irradiance^{7,8}. One study separated two electrons from two holes (electron vacancies), but used TiO₂ nanoparticles for electron accumulation³⁶. The separation of two electrons and two holes has not been achieved in fully molecular systems or been performed in a sequential manner.

A major challenge for the accumulation of electrons is overcoming the second absorbed photon to induce charge recombination (Fig. 1a)^{7,32,37–40}. When the chromophore of a CSS is excited, the electron acceptor is in its reduced form (A⁻), which is much more reducing than the originally intended electron donor. As a result, the excited state (*PS) in a CSS is quenched mainly by the reduced electron acceptor (A⁻) and not by the intended electron donor. As a consequence, the electron-hole pair, previously stabilized by the spatial separation of D⁺ and A⁻, is brought back into mutual proximity and the electron on PS⁻ recombines very quickly with the hole on D⁺. The absorption of a second photon is therefore usually not productive, but rather triggers a fast, energy-wasting charge recombination, finally resulting in A and D in their redox neutral forms and PS in its ground state (Fig. 1a).

All known fully molecular systems capable of accumulating redox equivalents without external redox reagents are of the D-PS-A-PS-D type, in which two electrons are eventually stored on a central acceptor flanked by two photosensitizers (Fig. 1b)^{32–35,41}. These previous studies addressed the challenge of photoinduced charge recombination by the simultaneous excitation of both photosensitizers. Since the formation of a typical CSS in such systems usually occurs on the order of 10 ps (ref. 42), the second PS must absorb a photon within these 10 ps,

which requires a very high irradiance. The solar irradiance is orders of magnitude too low for this purpose, and sunlight therefore allows only sequential excitation strategies^{7,8}. However, under sequential excitation of such D-PS-A-PS-D-type molecules, the same energy-wasting charge recombination as discussed above is prevalent and other unproductive processes may occur (Fig. 1c).

To overcome these severe conceptual obstacles to achieving efficient light-driven charge accumulation at more moderate irradiances, a different molecular design is needed. Our aim was to allow for the sequential absorption of two photons, where the second excitation leads to charge separation despite the greater driving force for the unwanted photoinduced charge recombination. Since electron transfer becomes slower with increasing distance, we identified a faster electron transfer from a closer donor (kinetics) as a possible mechanism to outweigh the larger driving force (thermodynamics) of the reduced acceptor (Fig. 1d). Thus, if the redox equivalents are stored further away from the photosensitizer, the immediate environment of the photosensitizer can be restored to its original state, including an electron donor in close proximity. In addition, this far separation of charges in the CSS-2 will also increase the lifetime of this CSS-2 and thus provide more time for the absorption of the second photon. This concept would, in principle, also allow for the integration of catalysts at the periphery, as outlined earlier in a forward-looking paper by Odobel and co-workers⁷.

Against this background, we designed a molecular pentad comprised of two electron donors, one photosensitizer and two electron acceptors (Fig. 2b). We hypothesized that primary excitation would establish a long-lived CSS (CSS-2 in Fig. 2d), with a long distance

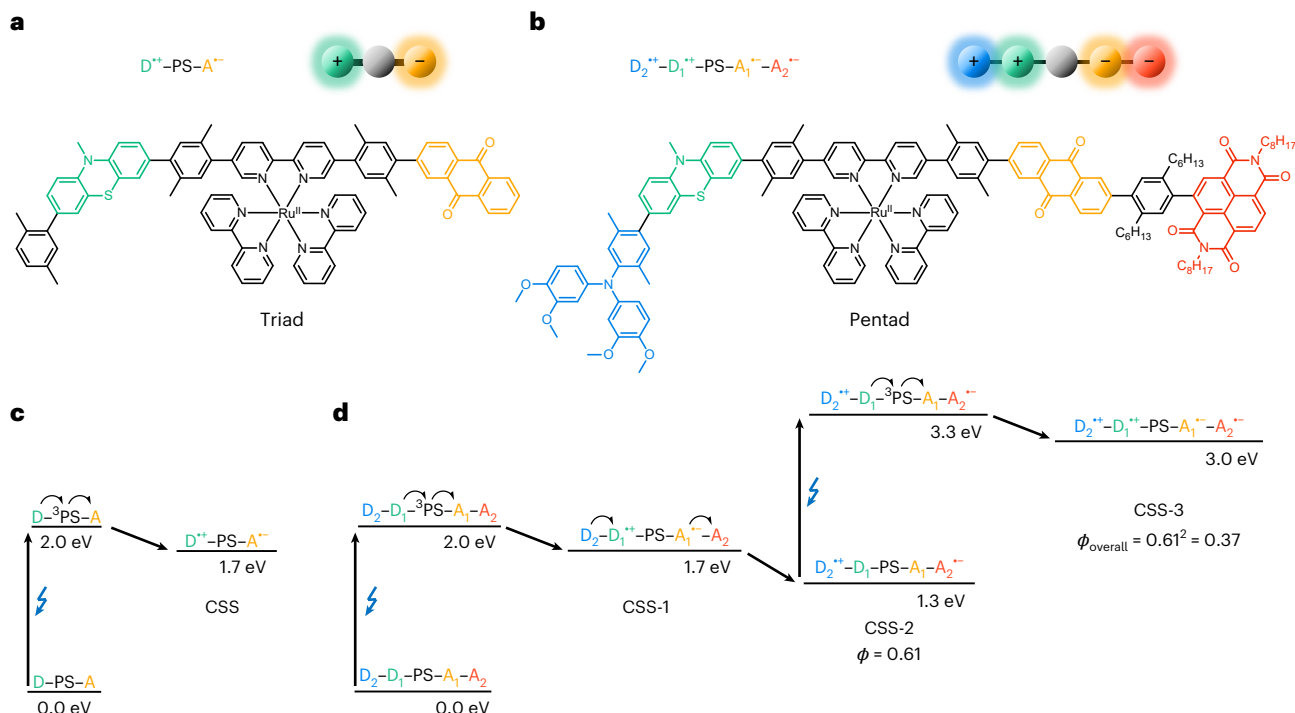


Fig. 2 | Intramolecular photoinduced electron transfer in a molecular triad and a molecular pentad. **a,b**, Molecular structures highlighting the individual electron donor (D_1 , D_2) and acceptor (A_1 , A_2) units in different colours. **c,d**, Energy-level diagrams of the key photoproducts and their corresponding energies in the triad (**c**) and the pentad (**d**). The final charge-separated state (CSS) in the

triad corresponds to the first charge-separated state in the pentad (CSS-1), which spontaneously evolves onwards to CSS-2. The central hypothesis of this study was that a secondary excitation event then leads to CSS-3 in the pentad. The two ϕ values indicate quantum yields. The quantum yields and their determination via relative actinometry are discussed in the main text. PS, photosensitizer.

(44 Å) between the oxidation (D_2^{+}) and the reduction equivalent (A_2^{-}). When exciting the photosensitizer in this constellation again, its nearest-neighbour redox partners D_1 and A_1 are as yet uncharged. This is expected to allow the accumulation of two oxidation equivalents on the donor branch in the form of D_1^{+} and D_2^{+} , as well as the accumulation of two reduction equivalents on the acceptor branch in the form of A_1^{-} and A_2^{-} (CSS-3 in Fig. 2d). Oxidative and reductive equivalents are therefore ultimately accumulated on adjacent redox units. This is conceptually different from the mutually independent charges targeted in dendrimer-based or polymer-based approaches^{43,44}. Furthermore, charge accumulation in our pentad involves sequential excitation of the same photosensitizer, and the two consecutive charge separation steps involve the same primary donor and acceptor units in an overall system that provides a clear redox gradient.

Results

Establishing the redox chain in the molecular pentad

Our covalently linked D_2 - D_1 -PS- A_1 - A_2 pentad (Fig. 2b) consists of a triarylamine (TAA) as D_2 , a phenothiazine (PTZ) as D_1 , a $[\text{Ru}(\text{bpy})_3]^{2+}$ complex as PS (bpy = 2,2'-bipyridine), an anthraquinone (AQ) as A_1 and a naphthalene diimide (NDI) as A_2 . The synthesis procedures and complete characterizations of the pentad and the triad from Fig. 2a,b as well as the reference compounds from Fig. 3a are in the Supplementary Information.

Cyclic voltammetry of the individual donor and acceptor units (Fig. 3a) verifies that D_2 is a stronger donor than D_1 and A_2 is a stronger acceptor than A_1 (Fig. 3b). When integrated into the backbone of the pentad, the redox properties remain essentially unaltered (lower half of Fig. 3b and Supplementary Table 1). The ref-PTZ $^{+}$ (D_1^{+}) and ref-TAA $^{+}$ (D_2^{+}) radical cations are easily distinguishable from one another by ultraviolet-visible (UV-vis) absorption spectroscopy (green trace in Fig. 3c versus blue trace in Fig. 3d). Analogously, the ref-AQ $^{-}$ (A_1^{-}) and ref-NDI $^{-}$ (A_2^{-}) radical anions are spectrally very different from one

another (orange trace in Fig. 3c versus red trace in Fig. 3d), as well as from the radical cation spectra.

Based on the redox potentials from Fig. 3b and the known properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ (ref. 45), the energy-level diagram in Fig. 2d can be established (see Supplementary Fig. 11 for details). Following excitation of $[\text{Ru}(\text{bpy})_3]^{2+}$, we expect the formation of a primary CSS (CSS-1) comprised of PTZ $^{+}$ (D_1^{+}) and AQ $^{-}$ (A_1^{-}). In the reference triad, this corresponds to the final observable photoproduct (CSS in Fig. 2c), but the pentad is designed such that there are spontaneous onward electron transfer reactions. TAA (D_2) is able to reduce PTZ $^{+}$ (D_1^{+}) ($\Delta G_{\text{ET}}^0 = -0.2$ eV) and AQ $^{-}$ (A_1^{-}) is able to reduce NDI (A_2) ($\Delta G_{\text{ET}}^0 = -0.3$ eV) to form CSS-2 in Fig. 2d.

Achieving long-lived single electron-hole separation

Using laser pulses of -10 ns duration, a 20 μM solution of the pentad in Ar-saturated CH_3CN was excited at 460 nm into the $[\text{Ru}(\text{bpy})_3]^{2+}$ unit. The transient UV-vis absorption spectrum recorded without time delay provides direct evidence for the formation of the anticipated CSS-2 photoproduct (Fig. 3e) and thus validates the electron transfer steps anticipated in Fig. 2d. The formation of NDI $^{-}$ is observable by transient absorption bands that match the spectroelectrochemical signature of NDI $^{-}$ from Fig. 3d (red trace). The peak at 390 nm in the spectra from Fig. 3e (marked by an asterisk) signals the formation of TAA $^{+}$ where this radical cation's absorption is not masked by an overlapping negative signal caused by the disappearance of charge-neutral NDI. The main absorption band of TAA $^{+}$ at 960 nm (Fig. 3d) is outside the detectable spectral window of the nanosecond transient absorption instrument used here, but is observable when using a femtosecond transient absorption spectrometer (see below).

All transient absorption features of TAA $^{+}$ and NDI $^{-}$ decay uniformly within approximately 1 ms (Fig. 3e). Intermolecular electron transfer processes become non-negligible at such long timescales, and therefore the transient absorption decays become multi-exponential

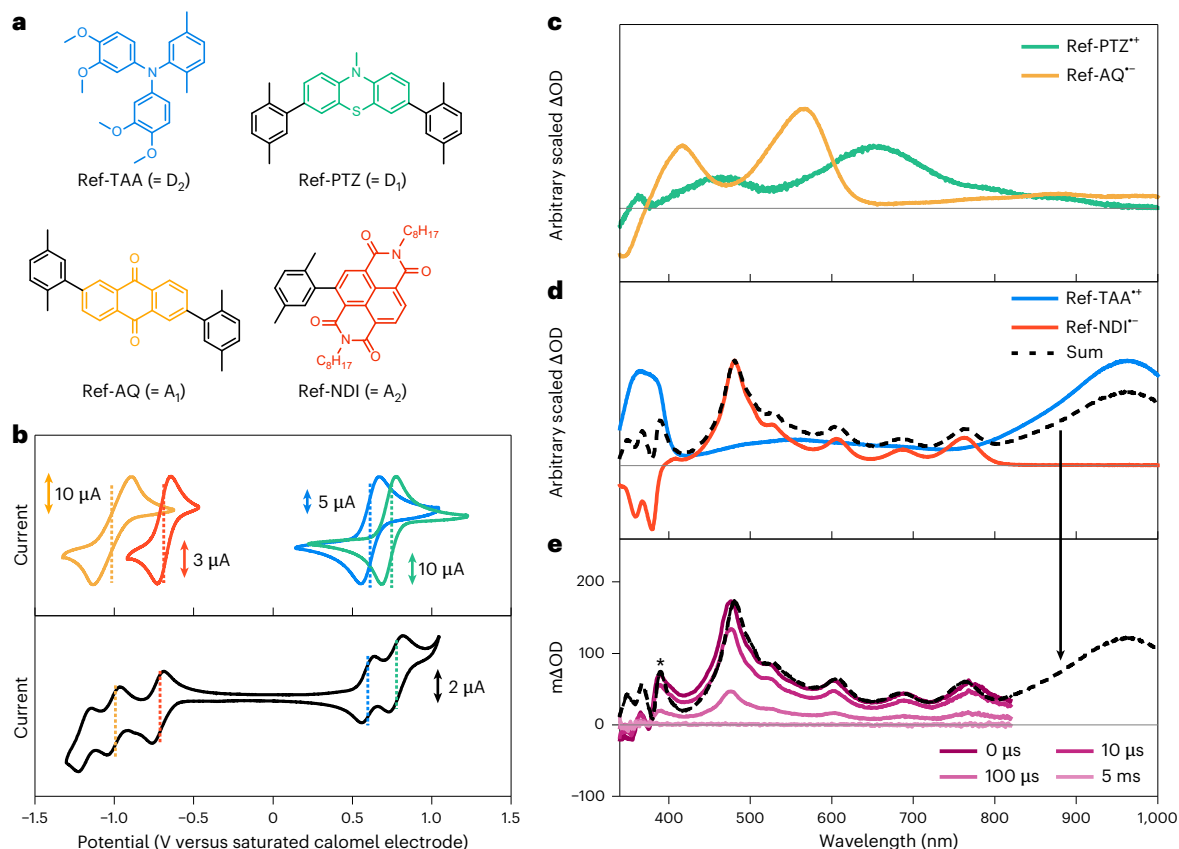


Fig. 3 | Reference compounds, (spectro-)electrochemistry and transient absorption spectroscopy. **a**, Reference molecules of the individual redox-active units of the triad and the pentad. **b**, Cyclic voltammograms of the first reduction of the reference electron acceptors ref-AQ (orange) and ref-NDI (red) along with the first oxidation of the reference electron donors ref-TAA (blue) and ref-PTZ (green) (top) and cyclic voltammogram of the main ligand of the pentad (with all organic redox-active units present but no Ru(II) coordinated) showing the same redox events and additionally the reduction of NDI²⁺ to NDI²⁺ (bottom). The dotted vertical lines indicate the midpoint between the peak potentials in the oxidative and reductive sweeps, respectively. **c**, Difference UV-vis absorption spectra obtained after electrochemical oxidation of ref-PTZ to ref-PTZ^{•+} (green) and after reducing ref-AQ to ref-AQ^{•-} (orange). **d**, Difference spectra obtained

after electrochemical oxidation of ref-TAA to ref-TAA^{•+} (blue) and after reducing ref-NDI to ref-NDI^{•-} (red). The dashed black trace is the linear combination of the two spectra using a scaling factor to take the different extinction coefficients of the ref-TAA^{•+} and ref-NDI^{•-} radicals into account. The resulting sum spectrum is the expected UV-vis absorption signature of the CSS-2 in Fig. 2d (D₂^{•+}–D₁–PS–A₁–A₂^{•-}). **e**, UV-vis transient absorption spectra of the pentad in dry Ar-saturated CH₃CN at 20 °C after excitation with 460 nm laser pulses (approximately 17 mJ) of approximately 10 ns duration, time-integrated for 200 ns after the indicated delay times (purple traces). The expected sum spectrum from **d** (black dashed trace) is included for direct comparison. The asterisk marks the signature of TAA^{•+} (see text for details).

(Supplementary Fig. 24). From concentration-dependent experiments (Supplementary Table 2), we extract a lifetime of 120 μs for CSS-2 in the pentad. Thus, CSS-2 forms within 10 ns and stores 1.3 eV (Fig. 2d) in the form of an electron–hole pair separated over 44 Å for 120 μs. There are only a few molecular systems with charge-separated states with such long lifetimes^{27–30}.

Double excitation experiment for charge accumulation

The very long-lived CSS-2 forms a good basis for exploring accumulative electron transfer upon secondary excitation of the pentad. For this purpose, we designed a cw-pump–pump–probe experiment, in which a continuous-wave (cw) pump laser is used to generate a steady population of CSS-2, followed by a secondary excitation with a pulsed pump laser and a probe pulse of adjustable delay⁴⁶. This was achieved by directing the beam of the cw laser into a commercial pump–probe spectrometer (Fig. 4a,b). The use of a cw laser instead of a pulsed laser for primary excitation is advantageous, because it allows a greater concentration of CSS-2 to form. This increases the sensitivity for the detection of the CSS-3 (Fig. 2d).

In conventional pump–probe experiments, the spectrum recorded prior to the pump pulse serves as a background (Fig. 4d(i)) and is subtracted from the spectrum recorded with a given time delay after the

pump pulse (Fig. 4d(ii)). The resulting transient difference spectrum (Fig. 4d(iii)) shows the signatures of the photoproducts formed by the pump pulse. In the cw-pump–pump–probe experiment from Fig. 4a,b, the final observable (Fig. 4e(iii)) corresponds to the photoproducts formed by the pulsed pump laser, while the photoproducts formed by the cw-pump laser become part of the background (Fig. 4e(i)). In other words, the spectral signature of the CSS-2 is removed with the background and, consequently, when aiming at the detection of CSS-3, one can merely expect to see the signatures of D₁^{•+} and A₁^{•-} whilst the signatures of the simultaneously present D₂^{•+} and A₂^{•-} will be in the background.

The cw laser pumps a sample volume of approximately 4 mm³ with an average photon flux of approximately 10¹⁸ s⁻¹ (Supplementary Section 13). The pulsed pump laser beam is roughly seven times smaller than the cw pump laser (overlap volume is approximately 0.6 mm³) and is aligned to the centre of the cw laser (Fig. 4c). For a pentad concentration of 300 μM, we estimate that the cw-pump laser provides one photon per pentad molecule roughly every 300 μs (Supplementary Section 13). Given a lifetime of CSS-2 in the same time regime (120 μs, see above), this means that one can anticipate nearly quantitative formation of CSS-2 in the pentad molecules present in the 0.6 mm³ overlap volume irradiated by the cw-pump beam. In other words, the

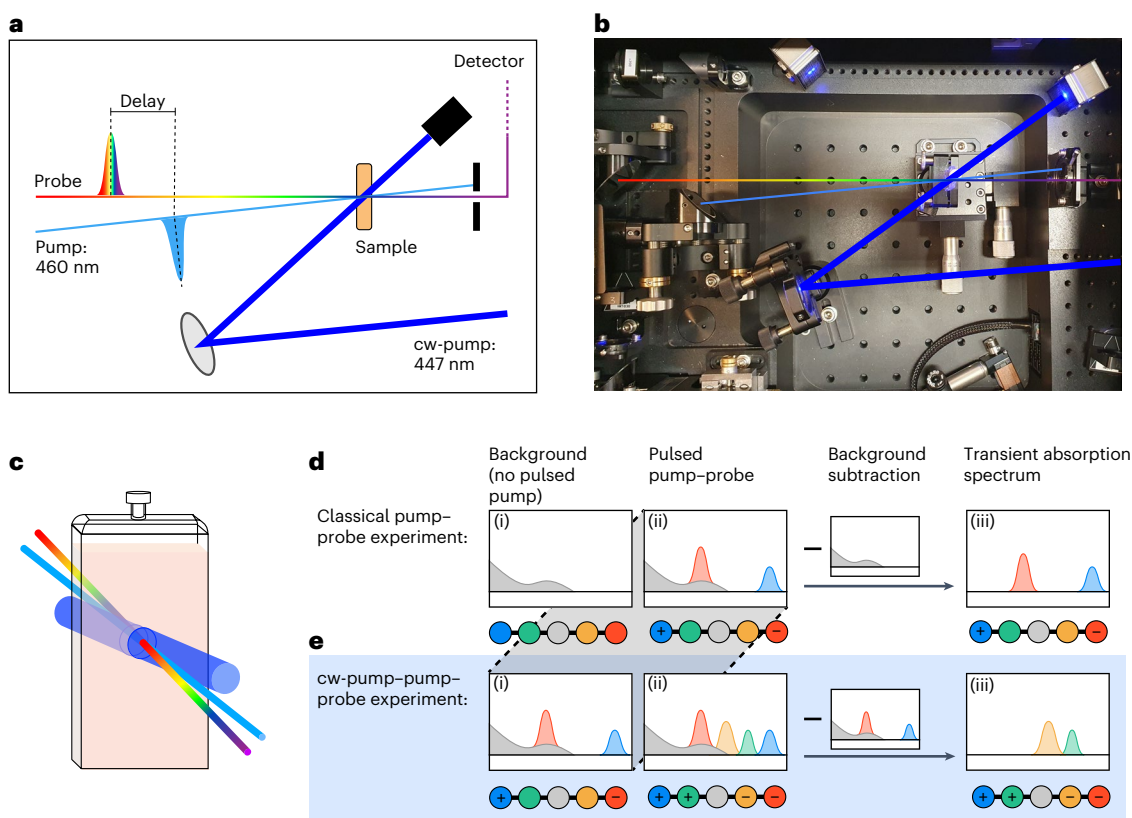


Fig. 4 | Setup for double excitation and working principle for data analysis. **a**, Schematic representation of the commercial transient absorption spectroscopy setup, into which an external continuous-wave (cw) laser has been integrated as an additional pump. The result is a cw-pump-pump-probe setup, where one pump (447 nm) is continuously irradiating the solution and the other pump (460 nm) is pulsed. **b**, Photograph of the actual setup from **a** with the directions of the individual beams shown by coloured lines. **c**, Arrangement of the three different beams at the cuvette, to highlight the fact that the cw pump beam is approximately seven times larger than the pulsed pump beam. **d**, Measurement and processing of transient absorption spectra in classical

pump-probe experiments. The unpumped spectrum (i) is subtracted from the spectrum recorded after a pump pulse (ii) providing the transient absorption (difference) spectrum (iii). The grey background in **d** and **e** highlights that the two respective spectra ((ii) in **d**; (i) in **e**) are identical. The blue background in **e** highlights the cw-pump-pump-probe experiment as a whole. **e**, In the cw-pump-pump-probe experiment, the cw pump laser continuously forms some photoproducts (red and blue in i), which become part of the background signal. Therefore, the actual observable of the cw-pump-pump-probe experiment is not the sum of all photoproducts, but only of those photoproducts formed by the pulsed pump laser (orange and green in iii).

cw-pump-pump-probe experiment in Fig. 4a,b offers the advantage that essentially all pentad molecules present in the beam of the cw laser can be promoted to CSS-2.

Achieving double charge separation

Before turning to the cw-pump-pump-probe experiments described in Fig. 4, we investigated the processes after single excitation in more detail with conventional pump-probe experiments. First, a transient absorption spectrum of the CSS in the reference triad from Fig. 2a was recorded (Fig. 5a, light blue). This CSS (Fig. 2c) is comprised of PTZ^{•+} (650 nm) and AQ^{•-} (565 nm) as is evident when comparing to the spectroelectrochemical data obtained for ref-PTZ^{•+} and ref-AQ^{•-} (Fig. 3c). These same spectroscopic features are expected for the initial intermediate photoproduct in the pentad (CSS-1 in Fig. 2d). Furthermore, these spectral signatures are expected to appear in CSS-3 of the pentad. The spectrum from the reference triad in Fig. 5a therefore serves as a reference for CSS-1 and CSS-3 in the pentad.

Since the CSS-1 in the pentad is only a short-lived intermediate on the way to the 120 μ s-lived CSS-2, we used pump-probe experiments with picosecond time resolution for its detection. Following excitation of the pentad at 460 nm, the transient absorption spectrum measured with a delay of 5 ps (Fig. 5b) contains the spectroscopic signatures of PTZ^{•+} ($D_1^{•+}$) and AQ^{•-} ($A_1^{•-}$), as is evident from the comparison to the spectrum of the reference triad in Fig. 5a (light blue trace). After a delay

of 100 ps, a new spectral signature begins to evolve and after a delay of 5 ns, the resulting spectrum in Fig. 5b is identical to that obtained from the nanosecond transient absorption experiment (Fig. 5a, dark blue), in which TAA^{•+} ($D_2^{•+}$) and NDI^{•-} ($A_2^{•-}$) are observable as confirmed by the data in Fig. 3d,e. Overall, the data in Fig. 5b document the sequential formation of CSS-1 and CSS-2 in the pentad. More importantly, the data reveal the spectral signature for the PTZ^{•+} ($D_1^{•+}$) and AQ^{•-} ($A_1^{•-}$) radical ion pair that is expected as part of CSS-3.

With this important piece of information, we then turned to the cw-pump-pump-probe experiments introduced above (Fig. 4). In addition to the conventional pump-probe method, there is now a blue cw laser (447 nm, 460 mW) that excites the pentad to generate a constant population of CSS-2. At the employed output power, the cw laser provides approximately 10^3 times more photons than the Sun and essentially all pentad molecules present within the probed sample volume are excited to CSS-2. When the sample is then further excited with 460 nm pulses of 250 fs duration, the transient absorption spectrum observed after 5 ps (Fig. 5c) is essentially identical to that obtained with the conventional pump-probe experiment in which PTZ^{•+} and AQ^{•-} are observed. When the delay time is increased to 5 ns in the cw-pump-pump-probe experiment, the transient absorption spectrum remains largely unchanged (Fig. 5c). This is in contrast to the results in Fig. 5b obtained with conventional pump-probe spectroscopy (without cw laser), in which PTZ^{•+} and AQ^{•-} spontaneously evolve

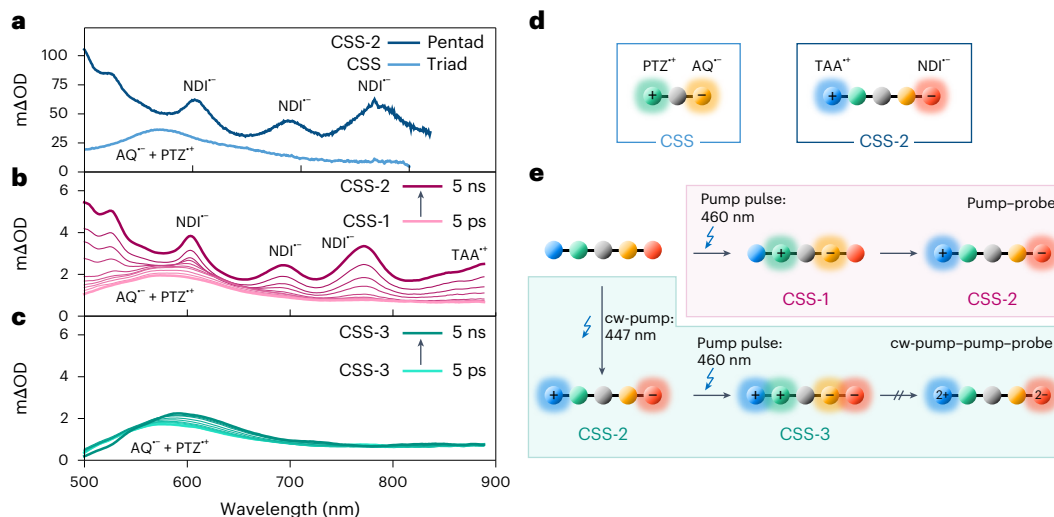


Fig. 5 | Observation of the different charge-separated states. a, Transient absorption spectra of the CSS-2 in the pentad and the CSS in the triad. The CSS of the triad is composed of $PTZ^{\cdot+}$ and $AQ^{\cdot-}$ and serves as a spectroscopic reference for the CSS-1 and CSS-3 in the pentad. The spectra were time-integrated over the first 200 ns after the excitation of a 20 μ M solution of the pentad or a 16 μ M solution of the triad in dry, Ar-saturated CH_3CN . Laser pulses of approximately 10 ns duration at 460 nm were used. **b**, Transient absorption spectra of a 300 μ M solution of the pentad in dry dimethylformamide after excitation with 460 nm pulses of approximately 250 fs duration. The CSS-1 can be observed from 5 to 100 ps, after which the spectroscopic signatures spontaneously evolve into

those of CSS-2. **c**, Transient absorption spectra recorded as described in **b** while the solution is continuously irradiated with an external cw laser of 447 nm. The spectroscopic signature of this CSS-3 is similar to the one of CSS-1 but cannot evolve any further, because $TAA^{\cdot+}$ cannot be further oxidized by $PTZ^{\cdot+}$ and $NDI^{\cdot-}$ cannot be further reduced by $AQ^{\cdot-}$. **d**, Schematic representation of the photoproducts on the μ s timescale after single excitation of the triad (CSS) and the pentad (CSS-2) as observed in **a**. **e**, Schematic representation of the photoproducts observed on the sub-nanosecond timescale in the pump-probe (**b**, purple) and the cw-pump-pump-probe (**c**, green) experiments.

to $TAA^{\cdot+}$ and $NDI^{\cdot-}$ with time. This sole observation of $PTZ^{\cdot+}$ and $AQ^{\cdot-}$ in the cw-pump-pump-probe experiment is exactly what is expected when the target state CSS-3 (Fig. 2d) is reached under these conditions, as discussed above (Fig. 4e). Since the cw-pump laser forms a steady and essentially quantitative population of CSS-2 comprised of the $TAA^{\cdot+}/NDI^{\cdot-}$ couple in the probed pentad molecules (that becomes part of the baseline signal of the cw-pump-pump-probe experiment, Fig. 4e), the pulsed pump laser can only produce the additional $PTZ^{\cdot+}/AQ^{\cdot-}$ signals, regardless of time delay. When temporarily blocking the cw-pump laser beam, the spectral features of $TAA^{\cdot+}$ and $NDI^{\cdot-}$ immediately appear (Supplementary Fig. 27), confirming that the pentad stays intact and no substantial photodecomposition has occurred.

The spectra in Fig. 5b,c were recorded from the same sample using identical excitation pulse powers, and they show essentially identical signal intensities for CSS-1 and CSS-3 (approximately 2 mΔOD at 600 nm). This strongly suggests that the initial formation of CSS-1 and the formation of CSS-3 from CSS-2 are both similarly efficient steps. The quantum yield for the formation of CSS-2 (Φ_{CSS-2}) is 61% (Supplementary Section 9), and therefore the quantum yield for the formation of CSS-1 (Φ_{CSS-1}) must be at least 61% as well. When now using the experimental information that the formation of CSS-3 from CSS-2 is as efficient as the formation of CSS-1, one obtains an overall quantum yield of 37% for the formation CSS-3 (Φ_{CSS-3}). Since the efficiency for both charge separation events is similar, we conclude that the actual charge accumulation event is not hindered by the charges already stored on D_2 and A_2 . This result is corroborated by cyclic voltammetry measurements (Supplementary Table 1) in which charges on D_2/A_2 influenced the redox properties of D_1/A_1 only by less than 0.05 V.

The femtosecond spectrometer used for the cw-pump-pump-probe experiment permits monitoring of transient signals up to 7 ns. On this short timescale, the CSS-3 does not begin to decay, and consequently it seems reasonable to infer that CSS-3 has a lifetime of at least 100 ns. Intramolecular charge recombination by spontaneous electron transfer from $AQ^{\cdot-}$ to $PTZ^{\cdot+}$ occurs with a time constant of 1,100 ns in the reference triad (Supplementary Fig. 14). On this basis, a CSS-3 lifetime

between 100 and 1,100 ns seems plausible for the pentad. CSS-3 stores roughly 3.0 eV (Fig. 2d), which is about twice as much as that normally achieved in D-PS-A triads.

Conclusions

Donor-photosensitizer-acceptor compounds have been explored for over four decades⁴⁷ to understand the initial events occurring in natural photosynthesis for their use in artificial photosynthesis^{3,7,8}. Our pentad in Fig. 2b is a completely molecular example in which two positive charges can be separated from two negative charges. Many previous studies aimed to accomplish this goal^{7,8}, but in most cases either only positive or only negative charges could be accumulated^{32–36}, and often this furthermore necessitated the use of sacrificial redox reagents^{11–20} or at least the addition of excess reversible redox reagents^{21,22}. In other cases, charge accumulation failed completely despite considerable synthesis efforts⁴⁴.

The design of our pentad allows rapid (<10 ns) initial separation of a first electron-hole pair over a distance of 44 Å, leading to a long-lived (120 μ s) CSS (CSS-2). The two redox units in immediate spatial proximity to the light-absorbing unit have returned to their initial charge-neutral redox states at that point. When exciting the photosensitizer in this constellation, productive onward electron transfer to form CSS-3 is kinetically favoured over energy-wasting photoinduced charge recombination. Thus, light-induced charge accumulation is facilitated, because energy-storing (overall thermodynamically upward) reaction steps are kinetically favoured over energy-wasting (thermodynamically downward) photoinduced reaction steps. The design principle of our pentad leads to an unprecedented scenario in which the charge accumulating reaction step proceeds with the same high quantum yield as the initial charge-separating step. We anticipate that this design principle will be broadly applicable to artificial photosynthetic systems based on light-induced charge accumulation. Future efforts in this direction will need to focus on the use of a pigment with high-energy excited states in combination with suitable catalysts (as D_2 and A_2) to ultimately provide sufficient redox power for multi-electron catalysis such as water splitting or CO_2 reduction⁴⁸.

The sequential excitation of the light-absorbing unit and the step-wise charging of the redox units in our pentad differs conceptually from previously researched artificial systems for charge accumulation, which are based on the simultaneous excitation of multiple light-absorbing units^{32–35,41}. This is a big step forward towards applications under the low flux of photons provided by the Sun. When comparing the scenario of simultaneous excitation where the time that can pass between the absorption of two photons is between 10 ps and 10 ns as in previous systems^{32–35,42}, we have elongated this time to 120 μ s. Although this is still far away from an ideal lifetime on the seconds timescale (Supplementary Section 13)⁴⁹, it represents a substantial improvement by a factor of 10^4 to 10^7 . Thus, our strategy allows the use of irradiances that are five orders of magnitude lower than those used in comparable systems. Introducing additional fundamental concepts⁵⁰, for example light-harvesting antennas^{2,7–9,51,52}, seems to be necessary for efficient charge accumulation under solar irradiation. Nevertheless, this implementation of a sequential light-absorption strategy represents an important step towards harnessing relatively diffuse solar light for vectorial charge accumulation and subsequent sustainable formation of solar fuels.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41557-025-01912-x>.

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Data availability

The data from the main paper are available from Figshare (<https://doi.org/10.6084/m9.figshare.28839578>) (ref. 53); all other data are in the Supplementary Information. Source data are provided with this paper.

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Author contributions

M.B. designed, synthesized and characterized all molecules and conducted all spectroscopic and electrochemical experiments. B.P. designed the cw-pump–pump–probe experiment and assisted with the execution of this key experiment. O.S.W. conceived the project, helped design the pentad and provided guidance. M.B. and O.S.W. wrote the manuscript with input from B.P.

Competing interests

The authors declare no competing interests.

Additional information

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