

A Donor–Acceptor [2]Catenane for Visible Light Photocatalysis

Yang Jiao,[†] Luka Đorđević,[†] Haochuan Mao, Ryan M. Young, Tyler Jaynes, Hongliang Chen, Yunyan Qiu, Kang Cai, Long Zhang, Xiao-Yang Chen, Yuanning Feng, Michael R. Wasielewski, Samuel I. Stupp,* and J. Fraser Stoddart*

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ABSTRACT: Colored charge-transfer complexes can be formed by the association between electron-rich donor and electron-deficient acceptor molecules, bringing about the narrowing of HOMO-LUMO energy gaps so that they become capable of harnessing visible light. In an effort to facilitate the use of these widespread, but nonetheless weak, interactions for visible light photocatalysis, it is important to render the interactions strong and robust. Herein, we employ a well-known donor-acceptor [2]catenane-formed by the mechanical interlocking of cyclobis(paraquat-p-phenylene) and 1,5-dinaphtho[38]crown-10-in which the charge-transfer interactions between two 4,4'-bipyridinium and two 1,5dioxynaphthalene units are enhanced by mechanical bonding, leading to increased absorption of visible light, even at low concentrations in solution. As a result, since this [2] catenane can generate persistent bipyridinium radical cations under continuous visiblelight irradiation without the need for additional photosensitizers, it can display good catalytic activity in both photo-reductions and -oxidations, as demonstrated by hydrogen



production-in the presence of platinum nanoparticles-and aerobic oxidation of organic sulfides, such as L-methionine, respectively. This research, which highlights the usefulness of nanoconfinement present in mechanically interlocked molecules for the reinforcement of weak interactions, can not only expand the potential of charge-transfer interactions in solar energy conversion and synthetic photocatalysis but also open up new possibilities for the development of active artificial molecular shuttles, switches, and machines.

INTRODUCTION

The past few decades have witnessed tremendous progress in the area of photocatalysis,¹⁻⁶ which not only represents a promising approach to acquire sustainable $energy^{7-14}$ from solar power but also provides a powerful toolkit for the realization of various synthetic transformations¹⁵⁻¹⁷ that are challenging¹⁸⁻²⁰ when relying solely on conventional thermal pathways. In a photocatalytic process, light excitation is the critical step in order to unlock²¹ the chemical reactivity of molecules in their excited states. Compared with high-energy UV irradiation, visible light²²⁻²⁴ is a cleaner and milder power source with fewer safety concerns. Meanwhile, most organic substrates are colorless and cannot be excited directly by visible light. It follows that photocatalysts-including transition metal complexes,²⁵ inorganic nanoparticles,²⁶ organic dyes,²⁷ and so on—are usually required in order to harvest the energy of visible light and trigger desirable photochemical reactions.

In addition to these well-recognized photocatalysts, a fundamentally different way to uncover more highly designed photocatalytic systems that harness visible light has been the source of some increased attention²⁸⁻³¹ during the past few years. These new strategies, which take advantage of chargetransfer (CT) interactions 32-34 between an electron-rich donor (D) and an electron-deficient acceptor (A), can bring about (Figure 1a) the hybridization and modulation of the relevant energy levels and lead to the narrowing³⁵⁻³⁷ of HOMO-LUMO energy gaps. As a result, a colored CT complex is formed with an absorption band red-shifted into the visible region of the spectrum, even although both D and A components of this complex are individually colorless. Moreover, photoexcitation $^{38-40}$ with visible light is more likely to induce single-electron transfer (Figure 1b) within CT complexes and generate radical-ion pairs composed of D^{•+} and $A^{\bullet-}$ radicals. This photo-induced electron-transfer (PET) process offers new opportunities for promoting catalysis on account of its ability to produce radical species under very mild conditions and without the need for photosensitizers. A fly in the ointment, as far as this strategy is concerned, is the weak association between D and A components. In general, the binding constants⁴¹ associated with a single set of CT interactions are no larger than 10^3 M⁻¹, making the

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b) Photo-Induced Generation of Radicals for Catalysis



Figure 1. (a) The charge-transfer (CT) interaction between an electron-rich donor molecule and an electron-deficient acceptor molecule can induce the hybridization of energy levels, leading to the narrowing of the HOMO–LUMO energy gap. (b) A new strategy for visible-light photocatalysis using the radical species generated by the direct excitation of a colored CT complex. (c) The structural formulas of a donor–acceptor [2]catenane, DA[2]C⁴⁺, and a donor–acceptor supramolecular complex, DACom⁴⁺, used for visible-light photocatalysis in this research.

complexation far from being strong, especially in solution at low concentrations. In order to create sufficient visible-light-harvesting ability, we need to consider how to render these weak interactions stronger and more robust⁴² through molecular design.

Mechanically interlocked molecules⁴³⁻⁴⁵ (MIMs) can enhance weak interactions by obliging their components to occupy nanoconfined spaces, a property which is helpful in investigating $^{46-48}$ weak functional group interactions and constructing $^{49-53}$ kinetically trapped systems. Theoretically, stoichiometric CT complexation can be achieved in donoracceptor MIMs regardless of concentration. Moreover, in contrast with covalently linked donor-acceptor dyads,^{54,55} the mechanical bonding between the D and A components in MIMs fosters³² the dynamic nature of CT interactions to a considerable extent, rendering it possible to use them in adaptive catalytic processes. These features have prompted us to exploit the use of donor-acceptor MIMs in visible-light photocatalysis. As a proof of principle, we have employed (Figure 1c) a donor-acceptor [2]catenane,^{56,57} namely $DA[2]C^{4+}$ in which an electron-deficient cyclophane, cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺), and an elec-tron-rich ring, 1,5-dinaphtho[38]crown-10 (DN38C10), are mechanically interlocked-to perform photocatalytic reactions

by irradiation with visible light. The molecular nature of $DA[2]C^{4+}$ comes with multiple advantages, which include (i) the single-step synthesis of this compound, (ii) the good solubility of its Cl⁻ salt in water-even if one of the component rings, DN38C10, is only sparingly soluble in water—facilitating the involvement of aqueous chemistry, (iii) enhanced CT interactions between 4,4'-bipyridinium (BIPY²⁺) and 1,5-dioxynaphthalene (DNP) units so as to facilitate the harnessing of visible light, (iv) the fact that the BIPY²⁺ units can serve as precursors of persistent radicals⁵⁸ to act as catalysts, and (v) better photostability than its analogous supramolecular complex. Herein, after describing the synthesis and characterization of $DA[2]C^{4+}$ following a literature procedure,^{56,57,59} we undertake an investigation of its ability to generate radical species on irradiation with visible light and without the need for photosensitizers. Furthermore, we have tested the catalytic activity of $DA[2]C^{4+}$ in the contexts of both photo-reduction and -oxidation by demonstrating hydrogen production-in conjunction with platinum nanoparticles-and the aerobic oxidation of organic sulfides using Lmethionine as a model substrate. In order to highlight the effect of the mechanical bonding within $DA[2]C^{4+}$, a noninterlocked donor-acceptor complex, DACom⁴⁺-formed between CBPQT⁴⁺ and 1,5-bis[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]naphthalene (BHEEEN)—is used (Figure 1c) as a control and compared with $DA[2]C^{4+}$ in terms of photocatalytic performance.

EXPERIMENTAL SECTION

Synthesis of DA[2]C·4Cl. The donor-acceptor [2]catenane, DA[2]C·4Cl, was synthesized (Figure 2a and Figure S1) using our previously reported⁵⁹ single-step procedure. CBPQT 4PF₆ (200 mg, 0.18 mmol) and DN38C10 (230 mg, 0.36 mmol) were dissolved in anhydrous MeCN (50 mL), forming a light pink solution. Thereafter, tetrabutylammonium iodide (TBAI, 15 mg, 0.041 mmol) was added, and the reaction mixture was stirred at 80 °C for 2 weeks. During this time, the color of the solution turned gradually from light pink to deep purple, indicating the enhancement of CT interactions. After cooling to room temperature, the MeCN solution was concentrated to 3 mL, followed by the addition of CH₂Cl₂ (100 mL) to produce a purple precipitate. After filtration, this crude product was purified using reverse-phase flash chromatography (C18: 0.1% TFA in $H_2O/$ 0.1% TFA in MeCN). Counterion exchange of the productcontaining fractions from TFA⁻ to PF_6^- (NH₄PF₆/H₂O), and subsequently from PF₆⁻ to Cl⁻ (TBACl/MeCN), generated a precipitate, which was collected by filtration, washed with Me₂CO several times, and dried under vacuum to afford DA[2]C·4Cl as a purple solid (146 mg, 62%). See the Supporting Information for further details.

Photo-induced Electron Transfer of DA[2]C·4Cl. Photoinduced electron transfer of DA[2]C·4Cl was performed in order to generate persistent BIPY*+ radical cations, using triethanolamine (TEOA) as the sacrificial electron donor. A septum-capped cuvette was charged with a stock solution of $DA[2]C \cdot 4Cl$ (500 µL, 1.0 mM in H_2O) and diluted with a stock solution of TEOA (500 μ L, 500 mM in buffer, adjusted to pH = 7.0) in a N₂-filled glovebox. The resulting solution was irradiated with visible light, using a home-built photoreactor made of royal blue (450 nm) LEDs with a light intensity of 370 mW cm⁻². The formation of BIPY⁺⁺ radical cations during the irradiation process was detected by UV/vis and EPR spectroscopy. This home-built photoreactor was also used for the photocatalytic production of H₂ and aerobic oxidation of Lmethionine, in which vials containing the reaction mixtures were suspended on the top of a single LED, equipped with a lens, and using a home-built sample holder.



Figure 2. (a) Single-step synthesis of $DA[2]C\cdot4Cl$ from its component rings, cyclobis(paraquat-*p*-phenylene) (CBPQT·4PF₆) and 1,5dinaphtho[38]crown-10 (DN38C10), by tetrabutylammonium iodide (TBAI)-catalyzed reversible ring opening and closure of the tetracationic cyclophane. (b) Annotated ¹H NMR spectrum (500 MHz, D₂O, 298 K) of DA[2]C·4Cl.

Photocatalytic Hydrogen Production. Photocatalytic production of H₂ (pages S21-S28 and Figures S19-S26 in the Supporting Information) was performed under Ar, using DA[2]C·4Cl as the photocatalyst, N,N,N',N'-ethylenediamine tetrakis(methylenephosphonic acid) (EDTP, TCI) as the sacrificial electron donor, along with platinum nanoparticles (Pt NPs, 3 nm size and 1000 ppm dispersion in H₂O, Sigma-Aldrich) as the catalyst for proton reduction and the 450-nm LED as light source. A screw-cap vial (9 mL) was charged with 500 μ L of DA[2]C·4Cl (or DACom·4Cl) stock solution $(1.0 \text{ mM in H}_2\text{O})$ and diluted with a stock solution of EDTP (500 μ L, 200 mM in buffer, adjusted to pH 3.5). Subsequently, a 100- μ L dispersion of Pt NPs was added. The vial containing the reaction mixture was sealed and purged for 15 min with Ar, and the pressure of gas in the headspace was equilibrated to 1 atm. Afterward, the vial was subjected to irradiation with 450-nm light. The gas evolved in the headspace was analyzed by gas chromatography (GC) to determine the volume of H₂ generated during the reaction. All the experiments were performed in duplicate to make sure the errors associated with each data point were no more than 5%.

Photocatalytic Aerobic Oxidation of L-Methionine. Photocatalytic aerobic oxidation (pages S28–S39 and Figures S27–S38 in the Supporting Information) was performed under an atmosphere of pure O2, using L-methionine (Sigma-Aldrich) as the substate, DA[2]C·4Cl as the photocatalyst, and 450-nm LED as the light source. A screw-cap vial (9 mL) was charged with 500 μ L of DA[2]C. 4Cl (or DACom·4Cl) stock solution (1.0 mM in H₂O) and diluted with a stock solution of L-methionine (500 μ L, 10 mM in H₂O). The vial containing the solution was sealed and purged for 15 min with O_{22} and the pressure of the gas in the headspace was equilibrated to 1 atm. Thereafter, the vial was subjected to irradiation with 450-nm light. An aliquot (10 μ L) was taken from the reaction mixture and analyzed by high-performance liquid chromatography (HPLC) to determine the conversion of L-methionine and obtain the yield of its sulfoxide during the reaction. In order to record the standard HPLC trace (Figure \$29), L-methionine sulfoxide was prepared according to a previously reported⁶⁰ procedure.

3,3',5,5'-Tetramethylbenzidine⁶¹ (TMB) was used to probe (Scheme S1) the formation of reactive oxygen species (ROS) during the irradiation. A stock solution of DA[2]C·4Cl (100 μ L, 1.9 mM in $\rm H_2O)$ was added to a septum-capped cuvette containing an acetate buffer (2.0 mL, 0.2 M acetic acid, 0.2 M sodium acetate, 1:1 v/v), followed by the addition of a stock solution of TMB (40 μ L, 4.2 mM in Me_2SO). The cell was either purged with Ar or O_2, or kept in air, before being irradiated with 450-nm light. The photo-oxidation of TMB was performed with stirring and monitored by UV/vis spectroscopy, focusing on the changes in the intensity of the absorption peaks for the oxidized TMB at around 650 and 900 nm. Different ROS scavengers, 62 including superoxide dismutase (SOD), D-mannitol, L-tryptophan, and catalase, were added into the system, and their influence on the photo-oxidation processes of TMB was compared in order to identify which kind of ROS serves as the oxidant.

RESULTS AND DISCUSSION

Synthesis and Characterization of the [2]Catenane. $DA[2]C^{4+}$ was synthesized from its component rings, CBPQT⁴⁺ and DN38C10, using our previously reported⁵ single-step procedure conducted under thermodynamic control. Tetrabutylammonium iodide (TBAI) was employed as a nucleophilic catalyst to open and close reversibly the CBPQT⁴⁺ ring in the presence of DN38C10. The pairwise CT interactions between the BIPY²⁺ units in $CBPQT^{4+}$ and the DNP units in DN38C10 drive the reaction equilibrium (Figure S1) toward the formation of the thermodynamically more stable product, namely $DA[2]C^{4+}$. This piece of dynamic covalent chemistry⁵⁹ was performed (Figure 2a) by stirring the reaction mixture, containing CBPQT·4PF₆ and DN38C10, along with catalytic amounts of TBAI at 80 °C for 2 weeks, followed by the purification of the [2]catenane using reversephase column chromatography and two counterion exchanges to afford $DA[2]C \cdot 4Cl$ in 62% overall yield.

The structure and purity of $DA[2]C^{4+}$ were confirmed by a variety of NMR spectroscopic techniques (Figure 2b and Figures S2–S8) as well as by HR-MS spectrometry (Figure S9). In the ¹H NMR spectrum (Figure 2b) recorded at 298 K,



Figure 3. (a) UV/vis spectra of CBPQT⁴⁺, DA[2]C⁴⁺, and DACom⁴⁺ in aqueous solutions. Inset: Magnification of the visible region ($\lambda > 400$ nm) showing clearly the CT absorption band. (b) Concentration-dependent UV/vis spectra of DA[2]C⁴⁺ in aqueous solution. Inset: Linear relationship between the absorbance at 525 nm and the concentration of DA[2]C⁴⁺, indicating the intramolecular CT interactions present in this system. (c) Differential pulse voltammetry (DPV) of CBPQT⁴⁺ and DA[2]C⁴⁺ in aqueous solutions, with 0.1 M NaCl as the supporting electrolyte and Ag/ AgCl as the reference electrode. (d) Calculated HOMO and LUMO energy levels showing a smaller energy gap for DA[2]C⁴⁺ than for CBPQT⁴⁺.

all the protons belonging to both BIPY²⁺ and DNP units are separated into two sets of signals because both the circumrotation and pirouetting motions^{43,63} within **DA**[2]C⁴⁺ are slow on the ¹H NMR time scale in D₂O at room temperature. Compared with free **CBPQT⁴⁺**, the signals for the BIPY²⁺ protons in **DA**[2]C⁴⁺ display, in some cases, dramatic upfield shifts (Figure S5) as a consequence of shielding effects induced by intramolecular [$\pi \cdots \pi$] stacking and CT interactions. The DOSY NMR spectrum (Figure S8) showed only one diffusion constant in D₂O for **DA**[2]C⁴⁺, verifying the mechanically interlocked nature of the molecule.

When dissolved in H₂O, $DA[2]C \cdot 4Cl$ exhibits a magenta color, different from the colorless solution of CBPQT·4Cl. This difference in color is consistent with the UV/vis spectrum (Figure 3a), in which a characteristic⁶⁴ CT absorption band $(\lambda_{\text{max}} = 525 \text{ nm})$ is observed for the DA[2]C·4Cl in aqueous solution. Moreover, the CT absorption of $DA[2]C \cdot 4Cl$ is higher than that of DACom·4Cl recorded at the same concentration, indicating the presence of mechanically bondenhanced CT association. When a series of UV/vis spectra were recorded, they revealed a linear relationship (Figure 3b) between the absorbance at 525 nm and the concentration of $DA[2]C \cdot 4Cl$, confirming the intramolecular CT interactions present within this [2]catenane. The molar absorption coefficient of DA[2]C·4Cl was calculated to be 1.13×10^3 M^{-1} cm⁻¹, which is an acceptable value⁶⁴ with no dependence on the concentration. This property of $DA[2]C^{4+}$ enables the adequate absorption of visible light, even at low concentrations in solution, rendering it practical as a photocatalyst.

In order to elucidate the influence of CT interactions on the HOMO and LUMO energy levels, the reduction potentials of $DA[2]C\cdot4Cl$ and $CBPQT\cdot4Cl$ were measured (Figure 3c and Figure S10) by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The single reduction peak of CBPQT·4Cl at -460 mV versus Ag/AgCl can be ascribed

to the two-electron reduction from CBPQT⁴⁺ to CBPQT^{2(\bullet +)}. In contrast, the transformation from $DA[2]C^{4+}$ to DA[2]- $C^{2(\bullet+)}$ is accomplished in a stepwise fashion with two singleelectron reduction peaks at -530 and -630 mV versus Ag/ AgCl. This splitting of the reduction peak arises because the inside $BIPY^{2+}$ unit of $DA[2]C^{4+}$ is influenced by CT interactions more significantly⁵⁶ than the alongside one, leading to a larger negative shift of the reduction potential of the former. Based on the data from spectroscopic and electrochemical measurements, the HOMO and LUMO energy levels of CBPQT⁴⁺ were calculated (Figure 3d and Table S1) to be -7.91 and -3.92 eV, respectively, with an energy gap of 3.99 eV. In contrast, the HOMO and LUMO energy levels of $DA[2]C^{4+}$ were calculated to be -5.78 and -3.85 eV, respectively, with the energy gap being narrowed down to 1.93 eV. The decrease in the energy gap makes it possible to excite $DA[2]C^{4+}$ with visible light.

Photo-induced Radical Formation with the [2]-**Catenane.** Since CT interactions involve the hybridization of energy levels, in which the contribution to the HOMO is mainly from the donor unit while the contribution to the LUMO is mainly from the acceptor unit, we asked ourselves if the excitation of $DA[2]C^{4+}$ with visible light might induce single-electron transfer from a DNP unit to a BIPY²⁺ unit. In an attempt to answer this question, the photophysical properties of DA[2]C·4Cl were investigated (Figure 4a) by femtosecond transient absorption (fsTA) spectroscopy. Upon excitation at 520 nm with a 100 fs pulsed laser, $DA[2]C^{4+}$ showed increases in absorbance at 399 and 645 nm, indicating the formation⁴⁰ of the bipyridinium radical cation (BIPY^{$\bullet+$}). Moreover, the increases in absorbance at 876 and 990 nm can possibly be assigned⁶⁵ to the dioxynaphthalene radical cation (DNP^{•+}), since these features are not observed in the UV/vis spectrum (Figure S13) of electrochemically reduced $CBPQT^{2(\bullet+)}$. Global analysis (Figure 4b) reveals that all the



Figure 4. (a) UV/vis/NIR femtosecond transient absorption (fsTA) spectra of $DA[2]C^{4+}$ in aqueous solution at room temperature, following pulsed excitation at 520 nm. (b) Multiple-wavelength fits of the kinetics of the $DA[2]C^{4+}$ excited state, showing that all the positive features at different wavelengths have a common lifetime of 2.8 ps. (c) Evolution of the UV/vis spectra during the continuous irradiation of $DA[2]C^{4+}$ with 450-nm light in the presence of an excess of a sacrificial donor. Inset: Photographs of the $DA[2]C^{4+}$ aqueous solution before and after irradiation. (d) EPR spectra before and after irradiation of $DA[2]C^{4+}$, confirming the generation of persistent radical species. (e) Graphical representation of the photo-induced electron-transfer process. The direct excitation of $DA[2]C^{4+}$ with visible light leads to the formation of the charge-separated state, which, in the presence of an excess of a sacrificial donor, can be transformed into $DA[2]C^{2+(\bullet+)}$, bearing one long-lived bipyridinium radical cation (BIPY^{•+}) that resides in the alongside position in the [2]catenane.

positive features at different wavelengths in the fsTA spectrum have similar kinetics, with a common lifetime of 2.8 ps—that is to say, a charge-separated state of $DA[2]C^{4+}$, composed of an equal number of BIPY^{•+} and DNP^{•+} units, is generated by intramolecular electron transfer upon excitation at 520 nm.

The charge-separated state of $DA[2]C^{4+}$ can, in principle, produce persistent BIPY⁺⁺ radical cations in the presence of sacrificial electron donors. The efficiency of this diffusioncontrolled electron-transfer process, however, is rather limited because of the short lifetime of the CT excited state. In order to overcome this problem, the sacrificial donor needs to be selected very carefully. Previous literature⁶⁶ tells us that the introduction of special counterions, such as (tetrakis[3,5bis(trifluoromethyl)phenyl]borate), can promote significantly the formation of BIPY*+ upon irradiation with visible light, thanks to the interactions between BIPY²⁺ and the counterions. Although this hydrophobic tetraphenylborate anion cannot be employed directly in our system, we took inspiration from this example and selected TEOA as the sacrificial donor, on account of its excellent water solubility and ability⁶⁷ to interact with BIPY²⁺—although somewhat weakly.

Continuous light irradiation of $DA[2]C^{4+}$ (0.8 mM) was performed under a N₂ atmosphere using a large excess of TEOA (0.4 M), and the PET process was monitored by UV/ vis spectroscopy. Whereas the characteristic absorption of BIPY^{•+} at around 600 nm is close to the CT absorption band at 525 nm, during the 15 min irradiation, we observed clearly (Figure 4c) the appearance and rise of a new absorption peak at 620 nm. This change in the UV/vis spectrum, in combination with the color change of the solution from pink to blue, indicates the formation of the BIPY^{•+} radical cation. The EPR signal (Figure 4d) observed for $DA[2]C^{4+}$ in aqueous solution after irradiation confirms the existence of persistent radicals.

By comparing the UV/vis spectrum of $DA[2]C^{4+}$ solution after PET with the spectra of $DA[2]C^{2(\bullet+)}$ (double-reduced [2]catenane) and $DA[2]C^{2+(\bullet+)}$ (mono-reduced [2]catenane) obtained by spectroelectrochemistry (Figures S14 and S15), the PET product was assigned to be $DA[2]C^{2+(\bullet+)}$, in which only one BIPY²⁺ unit is reduced, and the resulting BIPY⁰⁺ is located alongside the DN38C10 ring so as to maximize the CT interactions between the remaining BIPY²⁺ unit and the encircled pair of DNP units. According to the molar absorption



Figure 5. (a) Graphical representation of the proposed mechanism for photocatalytic H₂ production using $DA[2]C^{4+}$. First, as a result of visiblelight irradiation, $DA[2]C^{4+}$ is reduced by a sacrificial donor to form $DA[2]C^{2+(\bullet+)}$. Second, this long-lived radical species can reduce protons to produce H₂ on the surface of platinum nanoparticles (Pt NPs), while recovering $DA[2]C^{4+}$ to sustain the catalytic cycle. (b) Stacked gas chromatography (GC) traces to compare the amount of H₂ evolution after 31.5 h irradiation of the photocatalytic systems containing $DA[2]C^{4+}$ or $DACom^{4+}$. (c) Comparison of kinetic traces for H₂ production using either $DA[2]C^{4+}$ or $DACom^{4+}$. The amount of H₂ evolution was determined from the GC traces. The experiments were performed in duplicate to make sure the error was no more than 5% for each point. (d) Comparison of the amount of H₂ evolution after 3.5 h irradiation of the photocatalytic systems containing $DA[2]C^{4+}$.

coefficient⁶⁸ of BIPY^{•+} at 606 nm, the yield of $DA[2]C^{2+(\bullet+)}$ by PET was estimated to be around 80%, showing a high efficiency for the electron transfer from TEOA to $DA[2]C^{4+}$. Thus, we have demonstrated (Figure 4e) that the direct irradiation of $DA[2]C^{4+}$ with visible light induces the formation of a charge-separated state, which, in the presence of an appropriate sacrificial electron donor, can be transformed into $DA[2]C^{2+(\bullet+)}$, a persistent radical species. See the detailed analysis on the PET pathways in the Supporting Information. The process is free of the need for additional photosensitizers, suggesting its potential in the construction of a simple photocatalytic system.

Photocatalytic Hydrogen Production Using the [2]-Catenane. Considering that the BIPY⁺⁺ radical cation has often been used⁶⁹⁻⁷¹ to reduce protons on the surface of platinum nanoparticles (Pt NPs), we attempted to use $DA[2]C \cdot 4Cl$ for photocatalytic production of H₂. In the mechanism proposed in Figure 5a, $DA[2]C^{2+(\bullet+)}$ serves as an electron mediator, which is formed by the PET of $DA[2]C^{4+}$ and then reduces the protons in conjunction with Pt NPs. In the interest of proton reduction, a low pH value of the solution is favorable for the production of H₂ because of the increased concentration of protons. Under this condition, however, TEOA tends to be protonated, resulting in the loss of its ability to act as a sacrificial electron donor. In order to address this issue, N, N, N', N'-ethylenediamine tetrakis(methylenephosphonic acid) (EDTP) was selected for the photocatalytic H₂ production, on account of its effectiveness as a sacrificial electron donor in acidic solutions.

In order to test the photocatalytic activity of $DA[2]C^{4+}$ for H_2 production, a degassed buffer solution (1.1 mL, pH = 3.5) containing $DA[2]C^{4+}$ (0.5 mM), EDTP (100 mM), and Pt NPs (100 ppm) was subjected to 450-nm light irradiation. The

combined use of a strong sacrificial electron donor, EDTP, and highly active proton-reduction catalysts, Pt NPs, is expected to facilitate the evolution of H₂. See the detailed discussion in the Supporting Information. During the photocatalysis by DA[2]- C^{4+} , analysis of the sample headspace by gas chromatography (GC) showed a continuous evolution of H_2 (Figure 5b,c), with a total of 18.0 μ mol measured over 31.5 h. In comparison, although employing the complex DACom⁴⁺ as the photocatalyst led to H₂ evolution, it was at a lower rate and yielded a smaller amount (8.5 μ mol after 31.5 h). The higher photocatalytic activity of $DA[2]C^{4+}$ compared with that of its non-interlocked analogue, DACom⁴⁺, highlights the advantage of the mechanical bonding present in the [2]catenane in reinforcing the CT interactions and promoting the harnessing of visible light. Notably, the loading of $DA[2]C^{4+}$ in this photocatalytic system can be lowered from 0.5 to 0.25 mM (Figure 5d) without loss of H_2 -evolution activity. Furthermore, an appreciable amount of H₂ was still detected even at a very low concentration (0.05 mM) of $DA[2]C^{4+}$. Although some metal complexes, e.g., [Ru(bpy)₃]²⁺, exhibit stronger photosensitizing power (Figure S24) than $DA[2]C^{4+}$, they must be used together⁷² with an electron relay—such as CBPQT⁴⁺ for efficient photocatalysis. We lay claim to the fact that, by using $DA[2]C^{4+}$ instead of a combination of colorless viologen derivatives and colored photosensitizers, we have constructed a simple photocatalytic system to produce hydrogen under visible-light irradiation.

Photocatalytic Aerobic Oxidation of L-Methionine Using the [2]Catenane. In an attempt to display the versatility of $DA[2]C^{4+}$, we explored its use in photocatalytic aerobic oxidation (Figure 6a) since it has been reported^{73,74} that BIPY^{•+} can produce reactive oxygen species (ROS) in the presence of O₂. At the outset, we investigated the power of



Figure 6. (a) Reaction equation and standard experimental conditions for the photocatalytic aerobic oxidation of L-methionine to its sulfoxide using $DA[2]C^{4+}$. (b) The evolution of UV/vis spectra during the oxidation of 3,5,3',5'-tetramethyl-benzidine (TMB), a probe molecule, confirms the generation of $O_2^{\bullet-}$ by visible-light irradiation of $DA[2]C^{4+}$ in air. (c) Stacked high-performance liquid chromatography (HPLC) traces to compare the yields of the L-methionine oxidation catalyzed by either $DA[2]C^{4+}$ or $DACom^{4+}$. (d) Control experiments of the L-methionine oxidation under different conditions, showing the necessity of $DA[2]C^{4+}$, visible light, and O_2 , and suggesting the superoxide radical anion ($O_2^{\bullet-}$)-mediated oxidation mechanism. (e) Graphical representation of the proposed mechanism for this photocatalytic aerobic oxidation. First, visible-light-induced electron transfer between L-methionine and $DA[2]C^{4+}$ generates S-centered radical cations and $DA[2]C^{2+(\bullet+)}$. Second, $DA[2]C^{2+(\bullet+)}$ reacts with O_2 to form $O_2^{\bullet-}$ and regenerate $DA[2]C^{4+}$ to sustain the catalytic cycle. Finally, $O_2^{\bullet-}$ oxidizes the S-centered radical cations to produce L-methionine sulfoxide.

DA[2]C⁴⁺ to generate ROS using 3,3',5,5'-tetramethylbenzidine⁶¹ (TMB) as a probe molecule. On visible-light irradiation of a mixture of $DA[2]C^{4+}$ and TMB in air, we observed characteristic absorption peaks (Figure 6b) of the oxidized TMB at around 650 and 900 nm, suggesting the formation of ROS. The absorption became higher or lower for similar experiments (Figure S27) performed with pure O_2 or Ar, respectively, indicating that the process is indeed oxygendependent. Furthermore, in order to identify which kind(s) of ROS was/were generated during the irradiation, different ROS scavengers,⁶² including D-mannitol (for [•]OH), L-tryptophan (for ${}^{1}O_{2}$), catalase (for $H_{2}O_{2}$), and superoxide dismutase (SOD, for superoxide), were added (Figure S28) to the system. In the event, SOD quenched the absorption of oxidized TMB almost completely, while other scavengers exhibited negligible effects. These results manifested themselves in the formation of the superoxide radical anion $(O_2^{\bullet-})$ upon visible-light irradiation of $DA[2]C^{4+}$ in the presence of O_{2} , in agreement with previous reports in the literature.⁷⁴

Subsequently, we tested the feasibility of $DA[2]C^{4+}$ for photocatalytic aerobic oxidation of organic sulfides using Lmethionine as a model substrate. This reaction (Figure 6a) was performed with 10 mol% $DA[2]C^{4+}$, 1 atm O₂, and 450-nm light. Analysis of the reaction mixture by HPLC showed that the oxidation proceeds continuously (Figure S30) for 11 h until it reaches a plateau. Finally, L-methionine sulfoxide is generated (Figure 6c) selectively from L-methionine in 83% HPLC conversion. In attempts (Figures S36 and S37) to lower the loading of the photocatalyst, 5 mol% $DA[2]C^{4+}$ was found to be efficient in achieving a similar yield of L-methionine sulfoxide after 20 h irradiation. Further decreasing the amount of $DA[2]C^{4+}$ to 1 mol% can still promote this transformation at a lower rate. The control experiments (Figure 6d) under different conditions indicate that all the factors, including $DA[2]C^{4+}$, visible light, and O_2 , play critical roles in this oxidation. Moreover, different ROS scavengers (Figure 6d and Figure S33) were introduced into the reaction mixture, and their influence on the oxidation process was compared. The results showed that only SOD inhibited the oxidation, while the other scavengers did not, confirming that $O_2^{\bullet-}$ serves as a key intermediate for the oxidation of L-methionine.

Based on all this data, we propose a mechanism (Figure 6e) for the photocatalytic aerobic oxidation. First, photo-induced electron transfer occurs between $DA[2]C^{4+}$ and L-methionine, leading to the formation of $DA[2]C^{2+(\bullet+)}$ and S-centered radical cations. Second, $DA[2]C^{2+(\bullet+)}$ can react with O₂ to give $O_2^{\bullet-}$ while recovering $DA[2]C^{4+}$ to sustain the catalytic cycle. Finally, the S-centered radical cations are likely to be oxidized⁷⁵ by the highly reactive $O_2^{\bullet-}$, affording L-methionine sulfoxide as the final product.

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When employing DACom⁴⁺ as the photocatalyst for this reaction, we observed the over-oxidation (Figure 6c) of Lmethionine, resulting in the formation of its sulfone in addition to the sulfoxide. In order to explore the reasons for the diminished selectivity, ROS scavenger experiments (Figure \$34) were performed on the DACom⁴⁺ photocatalytic system, showing that the transformation is inhibited only by Ltryptophan. This finding means that ${}^{1}O_{2}$, rather than $O_{2}^{\bullet-}$, serves as the intermediate during the oxidation catalyzed by **DACom**⁴⁺, which is different from the $O_2^{\bullet-}$ -mediated pathway in the case of $DA[2]C^{4+}$. In addition, a severe bleaching (Figure S35) of DACom⁴⁺ was observed after the photocatalysis, whereas $DA[2]C^{4+}$ remained stable, with little change in color. These results indicate that, compared with the supramolecular complex, the donor-acceptor [2] catenane has improved catalytic activity, selectivity, and stability during the oxidation. Therefore, besides the application in photoreduction to produce hydrogen, we have demonstrated that $DA[2]C^{4+}$ can also be used for selective photo-oxidation of organic sulfides on account of its ability to harness visible light.

CONCLUSION

Although charge-transfer interactions are widely used^{76–79} in the templated synthesis of mechanically interlocked molecules, the potential value of these colored compounds as photocatalysts has been overlooked for a long time. In this research, we have employed-we believe for the first time-a donoracceptor [2] catenane in order to implement visible-light photocatalysis without the need for additional photosensitizers. By virtue of the intramolecular charge-transfer interactions between bipyridinium dications and dioxynaphthalene units, this donor-acceptor [2] catenane exhibits sufficient power to harness visible light, especially in aqueous solutions of low concentrations, facilitating the photo-induced electron transfer to form a persistent bipyridinium radical cation. This photogenerated radical is capable of (i) hydrogen production in water as a result of proton reduction and (ii) aerobic oxidation of L-methionine by generating the highly reactive superoxide radical anion. Although this proof of concept is noteworthy as far as the design of new photocatalysts is concerned and highlights the benefits of mechanical bonding, it carries some of the drawbacks intrinsic to donor-acceptor systems-e.g., the short lifetime of their charge-transfer excited states and low molar absorption coefficients-that limit the efficiency of the system. Future investigations, therefore, should aim to incorporate different donor-acceptor pairs^{80,81} with tailored photophysical and photoredox properties into mechanically interlocked molecules.

In its broadest sense, this research has demonstrated that the nanoconfinement^{82,83} present in mechanically interlocked molecules is powerful in reinforcing weak interactions so that the potentials of these forces—including but not limited to charge-transfer interactions—can be exploited in order to modulate the properties of systems and achieve desirable outcomes. We envision that this research will not only provide a new strategy for solar energy conversion and synthetic photocatalysis but also open up fresh possibilities for the design and synthesis of artificial molecular shuttles, switches, and machines.^{44,84–86}

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c01493.

Detailed synthetic procedures and supplemental characterization data (NMR, EPR, and UV/vis absorption spectra, and electrochemical measurements as well as GC and HPLC traces) (PDF)

AUTHOR INFORMATION

Corresponding Authors

- J. Fraser Stoddart Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia; Department of Chemistry, Zhejiang University, Hangzhou 310027, China; Orcid.org/0000-0003-3161-3697; Email: stoddart@northwestern.edu
- Samuel I. Stupp Department of Chemistry, Center for Bioinspired Energy Science, and Department of Biomedical Engineering, Northwestern University, Evanston, Illinois 60208, United States; Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States; Department of Medicine, Northwestern University, Chicago, Illinois 60611, United States; Simpson Querrey Institute, Northwestern University, Chicago, Illinois 60611, United States; o orcid.org/0000-0002-5491-7442; Email: s-stupp@northwestern.edu

Authors

- Yang Jiao Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-8437-0038
- Luka Đorđević Department of Chemistry and Center for Bio-inspired Energy Science, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-8346-7110
- Haochuan Mao Department of Chemistry and Institute for Sustainability and Energy at Northwestern, Northwestern University, Evanston, Illinois 60208, United States;
 orcid.org/0000-0001-8742-089X
- Ryan M. Young Department of Chemistry and Institute for Sustainability and Energy at Northwestern, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-5108-0261
- **Tyler Jaynes** Department of Chemistry and Center for Bioinspired Energy Science, Northwestern University, Evanston, Illinois 60208, United States
- Hongliang Chen Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-4442-7984
- Yunyan Qiu Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0001-9279-4714
- Kang Cai Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-8883-0142
- Long Zhang Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-4631-158X
- Xiao-Yang Chen Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States;
 orcid.org/0000-0003-3449-4136

Yuanning Feng – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-8832-0767

Michael R. Wasielewski – Department of Chemistry and Institute for Sustainability and Energy at Northwestern, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0003-2920-5440

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.1c01493

Author Contributions

[†]Y.J. and L.Đ. contributed equally to this work.

Notes

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