Efficient Photoinduced Electron Transfer from Pyrene-o-Carborane Heterojunction to Selenoviologen for Enhanced Photocatalytic Hydrogen Evolution and Reduction of Alkynes

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A series of pyrene or pyrene-o-carborane-appendant selenoviologens (Py-SeV$_2^{2+}$, Py-Cb-SeV$_2^{2+}$) for enhanced photocatalytic hydrogen evolution reaction (HER) and reduction of alkynes is reported. The efficient photoinduced electron transfer (PET) from electron-rich pyrene-o-carborane heterojunction (Py-Cb) with intramolecular charge transfer (ICT) characteristic to electron-deficient selenoviologen (SeV$_2^{2+}$) ($k_{ET} = 1.2 \times 10^{10}$ s$^{-1}$) endows the accelerating the generation of selenoviologen radical cation (SeV$_2^{2+}$) compared with Py-SeV$_2^{2+}$ and other derivatives. The electrochromic/electrofluorochromic devices’ (ECD and EFCD) measurements and supramolecular assembly/disassembly processes of SeV$_2^{2+}$ and cucurbit[8]uril (CB[8]) results show that the PET process can be finely tuned by electrochemical and host–guest chemistry methods. By combination with Pt-NPs catalyst, the Py-Cb-SeV$_2^{2+}$-based system shows high-efficiency visible-light-driven HER and highly selective phenylacetylene reduction due to the efficient PET process.

1. Introduction

Solar energy is considered a renewable energy source to replace fossil fuels to achieve carbon-neutral destinations, which could satisfy the growing global energy demand.$^{[1-2]}$ The artificial photosynthesis system aims to transfer solar energy to chemical energy and store it in chemical fuels, such as hydrogen, methane or methanol, etc.$^{[3-6]}$ The main steps of artificial photosynthesis involve absorbing photons, converting them into charge-separated states (electron-hole pairs) and transferring the electron to a catalyst, where the photocatalytic reaction occurred.$^{[7-9]}$ It is not difficult to find that an ideal photocatalytic system not only needs an efficient photosensitizer, proper electron mediator and catalyst, but also needs a highly efficient electron transfer process. For the photocatalytic hydrogen evolution reaction (HER), the Pt-containing compounds or nanoparticles have been proven to be the most efficient catalyst.$^{[10-11]}$ Thus, developing novel photosensitizer and electron mediator, as well as accelerating the electron transfer process became the alternative strategy to construction more efficient photocatalytic system.

During the past several decades, the photosensitizers have been gained significant progress, lots of photosensitizers, such as nanoparticles,$^{[12-14]}$ organic dyes$^{[15-17]}$ and [Ru(bpy)$_3$]$^{2+}$ derivatives,$^{[18-19]}$ etc. have been reported,$^{[20]}$ which showed good light absorption properties in the photocatalytic system. Compared with the photosensitizers, the development of electron mediators received less attention.$^{[21-23]}$ Among the rarely reported
electron mediator, viologen (MV\(^{2+}\)) was considered as ideal electron transfer agent for photocatalytic reaction due to its multiple redox states and electron accepting properties.\(^{[19,24]}\) For instance, MV\(^{2+}\) can accept electrons from [Ru(bpy)\(_3\)]\(^{2+}\) or g-C\(_3\)N\(_4\) accompanying the formation of radical cations (MV\(^{2+}\)) via photoinduced electron transfer (PET) process, followed with HER on Pt-based catalyst (Figure 1a).\(^{[25–26]}\) However, the multi-step electron transfer from photosensitizer to electron mediator to catalyst greatly reduces the utilization of electrons, thereby reducing the efficiency of photocatalytic reactions.

Developing multi-functional agents which can be used both as photosensitizer and electron mediator provided a new strategy...
to enhance the photocatalytic performance. However, viologen has a large energy gap (>3.5 eV) due to its noncoplanar spin structure,[27–30] making it unable to be used as a photosensitizer. To solve this problem, our group developed a series of chalcogenoviologens with narrow-bandgap, fast electron transfer properties, especially selenoviologen (SeV2•+), which were used as both photosensitizer and electron transfer agent for HER with excellent performance.[31–32] Although the design improves and simplifies the photocatalytic system, the production of hydrogen is still far away from the real application due to the slow rate of selenoviologen radical cation (SeV2•+) formation. Undoubtedly, introducing light trapping group or photosensitizer into SeV2•+ could accelerate the generation of SeV2•+ via PET process, and significantly enhance the photocatalytic efficiency.

Different from the conjugated donor small molecule and polymers,[33–37] the conjugated D-A structured heterojunction has been proven to promote electron charge separation within molecules and increase the electron transfer rate.[38–39] Recently, using D-A heterojunction (perylenediimide derivative and poly[fluorene-co-phenylene]) as electron donor group has successfully realized the biotransformation from carbon dioxide to acetic acid due to the effective separation of electrons and holes and greatly accelerated the electron transfer with bacteria.[40] Pyrene (Py) usually acts as a donor due to its good aromaticity and large conjugation system, which has been widely used in the field of organic optoelectronic materials.[41–43] The efficient electron transfer between pyrene derivatives and viologen has also been widely used in biochemical and medicinal applications.[44–45] The pyrene-o-carborane (Py-Cb) heterojunction composed with Py and typical electron-deficient o-carborane has shown excellent electron transfer characteristics, charge separation, and optical properties as a result of the intramolecular charge transfer (ICT) process.[46–49] It can be envisioned that introducing the Py or Py-Cb units as donors to transfer the electrons to electron-deficient SeV2•+ should efficiently accelerate the generation of SeV2•+ via PET process, which could significantly improve the photocatalytic performances of HER and organic reactions.

Based on the considerations, pyrene or pyrene-o-carborane-appendant selenoviologens (Py-SeV2•+, Py-Cb-SeV2•+) and viologens (Py-MV2•+, Py-Cb-MV2•+) were synthesized by using Py or Py-Cb dyad as donor groups and SeV2•+ or MV2•+ as acceptors. The efficient ICT of Py-Cb heterojunction enhanced the PET from Py-Cb to SeV2•+ in Py-Cb-SeV2•+, of which electron transfer rate is the highest than other analogues, accelerating the generation of selenoviologen radical cation (SeV2•+). The controllable PET process can be finely tuned by the spectroelectrochemistry and host–guest chemistry methods. By using Pt nanoparticles as the catalyst, the Py-Cb-SeV2•+ system showed higher photocatalytic efficiency in HER and realized the reduction of phenylacetylene reaction (Figure 1).

2. Results and Discussion

The synthetic route for pyrene or pyrene-o-carborane-appendant selenoviologens (Py-SeV2•+, Py-Cb-SeV2•+), and viologens (Py-MV2•+, Py-Cb-MV2•+) for comparison) were synthesized by using Py or Py-Cb dyad as donor groups and SeV2•+ or MV2•+ as acceptors. The efficient ICT of Py-Cb heterojunction enhanced the PET from Py-Cb to SeV2•+ in Py-Cb-SeV2•+, of which electron transfer rate is the highest than other analogues, accelerating the generation of selenoviologen radical cation (SeV2•+). The controllable PET process can be finely tuned by the spectroelectrochemistry and host–guest chemistry methods. By using Pt nanoparticles as the catalyst, the Py-Cb-SeV2•+ system showed higher photocatalytic efficiency in HER and realized the reduction of phenylacetylene reaction (Figure 1).
7 and 8 have an extra reduction potential at around −1.4 V than 11 and 12 due to molecular hybridization, which are consistent with previous work about carborane-based viologen materials.[56] The molecular HOMO and LUMO values versus NHE were calculated based on UV–vis and CV data (Figure S14, Supporting Information), which indicated that compounds 7, 8, 11, and 12 may provide enough thermodynamic driving force for HER.

To understand the relationships between the molecular structures and optical properties, the emission properties of the molecules in both solution and solid states were tested. As shown in Figure 3a, 5, 7, and 8 show the similar dual emissions accompanying with weak fluorescence in DMF. The emissions around 430 nm was originated from the LE states of the pyrene units, and the broad emissions around 680 nm are attributed to the CT emissions from the Cb-Py heterojunction to MV2+ or SeV2+. [57] Compared with 5, the maximum emission bands of 7 and 8 are red-shifted from 600 to 650 and 700 nm in the solid state (Figure 3b), and the fluorescence quantum yields (Φ) of 7 and 8 obviously decreased from 55.8% to around 0.7% and 0.4%, respectively. The redshifted emission and fluorescence quenching phenomenon confirmed the PET process and the ICT between Cb and Py moiety can enhance the PET process. In contrast with 7 and 8, 11 and 12 still show strong fluorescence at around 510 nm with Φ = 18.1%, 13.2%, respectively, which suggested that PET process in 7 and 8 is more efficient than 11 and 12 (Figure 3c).

Based on the fluorescent data, the CIE chromaticity coordinates were prepared, which were almost the same as the actual luminescence of molecules (Figure 3d).

**Scheme 1.** Synthetic approach toward Py-MV2+ (7), Py-Cb-SeV2+ (8), Py-MV2+ (11), and Py-Cb-SeV2+ (12).
To further explore the electron transfer within the molecule, the electron-transfer constants \( (K_{ET}) \) were calculated according to the molecular photoluminescence lifetimes \( (\tau) \) and quantum yield. The results were summarized in Table S2 (Supporting Information). The \( K_{ET} \) of 7/8 (7.22 \times 10^9 for 7; 1.20 \times 10^{10} \) for 8) were an order of magnitude more than 11/12 (2.29 \times 10^9 for 11; 3.34 \times 10^{10} for 12), which were attributed to the carborane moiety enhancing the electron transfer rate. Although the \( K_{ET} \) of carborane-based viologen has not been reported, the \( K_{ET,11} \) and \( K_{ET,12} \) are basically consistent with the literatures.\(^{[56]} \) In order to further verify this result, the electrical conductivities of 7, 8, 11, and 12 were tested. The results show that the electrical conductivities of 7, 8, 11, and 12 are 1.10 \times 10^{-8}, 9.93 \times 10^{-9}, 1.16 \times 10^{-9}, and 8.7 \times 10^{-10} \text{ S m}^{-1}, respectively, which indicate that the introduction of carborane into molecules (7 and 8) can effectively improve electron transfer.\(^{[56]} \) Thus, 7 and 8 might exhibit better photocatalytic performance due to the faster electron transfer rate. Besides, the emission spectra were studied in different solvents with different polarities such as DMSO (7.2), MeOH (6.6), DMF (6.4), and AcOH (6.2), which were shown in Figures 3e and S5.
which may be attributed to the formation of neutral state (absorption peak gradually decreased with red color presentation, with the voltage being further increased to -0.8 V, the maximum increasing due to the formation of the radical cation (yellow to green with the absorption bands at 517, 651, and 728 nm) tape (Figure S6, Supporting Information). When indium-tin oxide (ITO)-coated glasses and double side adhesive nent was injected into the cavity, which was made up of two state consistent with the reported results in the literatures. [59–60].

Take trofluorochromic devices (ECD and EFCD) were studied in situ. As significant linear relationship was obtained from the plots with the peak positions observed around 650 and 520 nm, which can show that the acceptor in the four compounds shown in Figure 3f. In addition, the transition dipole moment was estimated as 5.10 D (Figure S9, Supporting Information). To further prove the existence of two states (Zn and Na (Figure S9, Supporting Information). To further prove the existence of two states (8’ and 8’’), the EPR spectroscopy was tested. The results show that the g-factor is 2.0023 for Zn reduct and no signal for Na reduction, which are consistent with the previous work (Figure S11, Supporting Information). In addition, the emission at 681 nm was decreasing along with the −0.6 V voltage applied, and the emission band at 437 nm was increasing until the voltage up to −0.8 V. Then the emission peak was slightly blue shifted to 671 nm (Figure 4c). This data confirmed that the PET in the molecules was turned off after the SeV2+ unit getting two electrons to neutral state. Meanwhile, 7, 11, and 12 showed similar phenomena (Figures S7–S10, Supporting Information).

To further insight into electron transfer dynamics between donor (Py-Cb heterojunction) and acceptor (SeV2+), we established a supramolecular model combination of a host (cucurbit[8]uril, CB[8]) and guest (SeV2+) [61–64]. When added CB[8] (2 × 10−3 M) to 8 (5 × 10−6 M, 2.5 mL in water), the results presented a significant decrease of the emission band at around 648 nm, which was accompanied by a wide peak around 436 nm. When CB[8] was dropped to ten equivalents of 8, the maximum emission peak was obviously blueshifted to 624 nm, and the emission peak at 460 nm had a significant increase (Figure 4c). The results suggested that CB[8] also could prevent the electron transfer process, which were consistent with the previous result. [50] Clearly, both electrochemistry and supramolecular chemistry can efficiently regulate the intramolecular PET process (Figure 4b).

Considering the strong visible-light absorption, narrow bandgaps, efficient charge separation and fast electron transfer rate of Py-Cb-SeV2+, a visible-light photocatalyst hydrogen evolution system was designed. Taking 7, 8, 11, and 12 as active compounds, colloidal platinum particles (Pt-PVP) as catalysts, and EDTA as electron sacrifice agent, the reaction was taken place in a pyrex bottle (20 mL) with buffer solution (pH = 5.0, 5 mL) under Xenon light (λ > 400 nm) at 100 mW. As the results are shown in Figure 5b,c, hydrogen evolution of 7 (3.3 μmol) significantly increased after irradiation 24 h compared with 11 (total hydrogen evolution 0.1 μmol), which could be attributed to the PET process can enhance the PET efficiency of the molecule (Figure S19, Supporting Information). [64] Interestingly, the total hydrogen evolution of 12 (34.4 μmol total 12 h) is about 3 times more than Se-BnV2+ (13.04 μmol total 12 h), [32] which indicated that the PET process greatly improved the molecular absorption and significantly accelerate the generation of SeV•*, resulting in the improved efficiency of HER (Figure S20, Supporting Information). Compared with 7 and 11, the hydrogen evolution of 8 and 12 significantly increased. Benefit from the special molecular structure, 8 generated 114.4 μmol hydrogen (TON: 44.5, hydrogen generation rate: 1.91 mmol h−1 g−1, apparent quantum yield AQY: 0.79%), which is much higher than 12 (82.8 μmol hydrogen, TON: 28.3, hydrogen generation rate: 1.34 mmol h−1 g−1, AQY: 0.54%), due to the more efficient generation of SeV•*. Considering the dispersibility of the catalyst in water has a great influence on the photocatalytic effect, the dispersibility of the PCs was studied by TEM spectra. As shown in Figure S12 (Supporting Information), 7 and 8 are better dispersed in water than 11 and 12 due to the hydrophobic nature of carbazole unit. Furthermore, almost no hydrogen was detected without PCs or irradiation in 8-based system, which means the catalytic system is a complete photocatalytic system. When the molecules 4, 5, and 9 were physically mixed with selenoviologen or viologen as a catalyst to participate in photocatalytic hydrogen evolution, the experimental results show that simple physical mixing does not significantly improve the hydrogen production effect of the viologen system, which further shows that the PET strategy is effective (Table S3, Supporting Information).

### Table 1. Calculated driving force (ΔG°) for 7, 8, 11, 12 in MeOH and DMSO at 25 °C.

| Compound | EOX [V] | ENa [V] | E00 [eV] | ΔG° [eV] |
|----------|---------|---------|----------|----------|
|          | MeOH    | DMSO    | MeOH     | DMSO     |
| 7        | 0.45    | -0.46   | 1.89     | -1.06    | -0.90   |
| 8        | 0.46    | -0.58   | 1.89     | -0.93    | -0.77   |
| 11       | 0.15    | -0.64   | 2.74     | -2.01    | -1.89   |
| 12       | 0.21    | -0.62   | 2.74     | -1.97    | -1.85   |

a,b) The donor and acceptor redox potentials in DMF; c) determined from absorption and fluorescence measurements; d) calculated from ΔG° = e(EOX - ENa) - E00 + \(\frac{\mu}{\pi \epsilon_0 \epsilon}\left(\frac{1}{r_1} - \frac{1}{r_2}\right)\).
Figure 4. a) Spectroelectrochemistry of 8 and images of ECD color changes for three are shown as the inset. b) Electrochemical and supramolecular chemistry methods to control the intramolecular PET process. c) Fluorescence spectra of 8 in DMF solution and images of EFCD color changes for three states are shown as the inset. d) Fluorescence spectra of 8 without and with CB[8] in H₂O and images of color changes are shown as the inset.

Figure 5. a) The plausible mechanism of Py-Cb-SeV⁺ for photoinduced hydrogen evolution and reduction of phenylacetylene (RPA). b) Time-dependent hydrogen generation from aqueous solution under xenon lamp. c) Total hydrogen generation of active components. d) Hydrogen evolution and styrene formation versus reaction times. e) The yields of styrene versus active components.
To further clarify the stability of the molecules in the process of photocatalytic hydrogen evolution, molecule 8 with the best catalytic performance was selected to test cycle stability, and every 12 h is a cycle. The experimental results showed that the hydrogen production effect could still be maintained at about 82% after five cycles (Figure S27, Supporting Information). After 60 h light irradiation, it is not difficult to find from the 1H NMR data of molecule 8 that more than 80% of molecule 8 remains unchanged, which indicate that the molecules have good light stability (Figure S28, Supporting Information). To the best of our knowledge, the hydrogen production efficiency of 8 is the highest value compared with other organic viologen-containing photocatalytic hydrogen evolution systems (Table 2).

Similar to photocatalytic HER, photocatalytic organic reactions are also considered to be an effective way to solve the energy crisis. Alkene is an important building block in various natural products, pharmaceuticals and agrochemicals. It was usually obtained via selective hydrogenation of alkynes.\[^{[65–66]}\] However, it is still a challenge to obtain both high conversion and selectivity. Therefore, we choose Py-Cb-SeV\(^2\) to study the photocatalytic reduction of phenylacetylene to styrene. Based on the optimal photocatalytic hydrogen production conditions, an additional organic solvent (DMF, CH\(_3\)CN, DCM, MeOH, cyclohexane) was added to promote the dissolution of phenylacetylene in the system. After 48 h of irradiation, styrene was only detected in the system containing cyclohexane (5% yields). When the ratio of cyclohexane/buffer solution was reduced from 4/1 to 1/1, the yield of styrene was significantly increased to 24%. When the amount of additive was increased 2.5 times, the desired product styrene was obtained in higher yields (37%, Table S4, entry 10, Supporting Information). After screening the acid strength of the buffer solution, the results showed that weak acidity (pH = 5.0) was beneficial to product formation. Under the optimal conditions, hydrogen evolution and styrene formation versus reaction times were studied. As shown in Figure 5d, it is beneficial to generation hydrogen at the beginning of the reaction. When the concentration of hydrogen in the system reaches a certain value (3.2 \(\mu\)mol mL\(^{-1}\)), the production rate of styrene begins to be faster than hydrogen. For comparison, the system generated 172 \(\mu\)mol hydrogen within 48 h without phenylacetylene. These results showed that the production of styrene and hydrogen was always in a competitive relationship. Other active compounds (7, 11, and 12) were also tested in this reaction. Among them, 8 showed the best performance with yields of 37% and TON of 15.1. Importantly, almost no reduction products of phenylethane were detected (Figure 5e). In order to further expand the scope of application of photocatalytic reduction of alkynes, the low toxicity of alkyl alkyne (1-hexyne) has also been investigated. After photocatalytic reduction, the target product 1-hexene can be obtained with a yield of 21% and a selection of more than 99%. The high selectivity may be attributed to the competitive hydrogen production and alkyne reduction, preventing the formation of a completely reduced byproduct, alkane.

To further understand the photocatalytic reaction mechanism, the supramolecular method was employed by using CB[8] and amantadine (AD) through supramolecular assembly and disassembly processes.\[^{[67–69]}\] Take 8 as an example, the total hydrogen evolution is 16.3 \(\mu\)mol after irradiation 6 h, and the total hydrogen evolution markedly decreased to 2.7 \(\mu\)mol with the CB[8] being added for irradiation 6 h. Once AD was added and irradiated another 6 h, the hydrogen evolution increased to 11.6 \(\mu\)mol. The results indicated that the CB[8] may combine with SeV\(^2\) to inhibit

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**Table 2.** Hydrogen generation activities of some organic photocatalytic system.

| Classify | Catalysts | Hydrogen generation rate [mmol h\(^{-1}\) g\(^{-1}\)] | TON/AQY | Conditions | Reference |
|----------|-----------|---------------------------------------------------|---------|------------|-----------|
| Metal-bearing organic small molecule | MV(NO\(_3\))\(_2\), [Ru(bpy)\(_3\)](NO\(_3\))\(_2\) \(\cdot\) 3H\(_2\)O, Co(dmgH\(_3\))(pyridine)Cl | 0.016 | – | BS, \[^{[4]}\] | [70] |
| | PBDT-BPY (10–20% CoCl\(_2\)) | 0.14 | 0.025% (AQY) | 30 vol% diethylamine/water | [71] |
| | [PtCl\(_2\)(dpbb V\(_2\))]Cl\(_6\) \(\cdot\) 16H\(_2\)O | 0.33 | – | BS. | [72] |
| | Zn(II)PPIX/C\(_6\)N\(_6\) hybrid system; MV\(^2\) (PT) | 5.67 | 2.2 (TON) | Tris-buffer | [73] |
| Organic small molecule with photosensitizer | MV\(^2\) (PT) | 0.074 | 0.064% (AQY) | Pure aqueous \(\lambda > 420\) nm | [33] |
| | SWCNT/ dendrimer nanohybrids; MV\(^2\) (PT) | 0.074 | – | Tris-HCl buffer | [74] |
| | Thiocarbonyl dye/SWCNT/C\(_6\)0; MV\(^2\) (PT) | 0.098 | 7.6 (TON) | Tris-HCl buffer | [75] |
| Organic small molecule without metal | Se-BnV\(^2\) | 0.31 | 0.17% (AQY) | Pure aqueous \(\lambda > 400\) nm | [32] |
| | Se-PhV | 0.71 | 11.4 (TON) | BS, \(\lambda > 400\) nm | [31] |
| | 8 | 1.91 | 44.5 (TON) | BS, \(\lambda > 400\) nm | This work. |
| | 12 | 1.34 | 28.3 (TON); 0.54% (AQY) | BS, \(\lambda > 400\) nm | This work. |

\[^{[4]}\] Aqueous acetate buffer solution (BS., 0.03 m CH\(_3\)COOH and 0.07 m CH\(_3\)COONa).
3. Conclusion

A series of pyrene or pyrene-o-carborene-appendant selenoviologens (Py-SeV\textsuperscript{2+}, Py-Cb-SeV\textsuperscript{2+}) was successfully synthesized. The intramolecular electron transfer (IET) of Py-Cb heterojunction strongly enhance the PET from the donor to electron-deficient SeV\textsuperscript{2+} compared with the Py-SeV\textsuperscript{2+}, Py-MV\textsuperscript{2+}, and Py-Cb-MV\textsuperscript{2+}, which accelerate the formation of selenoviologen radical cations (SeV\textsuperscript{3+}) efficiently. The Py-MV\textsuperscript{2+} and Py-Cb-MV\textsuperscript{2+} showed ACQ effect, and the Py-SeV\textsuperscript{2+}, Py-Cb-SeV\textsuperscript{2+} showed AIE property due to the CT process. It was found that the PET process can be controlled by the electrochemical or host–guest chemistry methods via electrochromic and electrofluorochromic devices’ (ECD and EFCD) measurements and supramolecular assembly/disassembly processes of SeV\textsuperscript{2+} and cucurbit[8]uril (CB[8]). Py-Cb-SeV\textsuperscript{2+} were used as electron mediator and photosensitizers for controllable HER and selectively reduction of phenylacetylene to styrene due to the excellent optoelectronic properties. Notably, the Py-Cb-SeV\textsuperscript{2+} showed the highest reported value to date for viologen-based visible-light-driven HER. This contribution provided a new strategy to develop highly efficient viologen analogues-based organic photocatalyst, which laid a solid foundation for the solar energy conversion.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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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 in the supplementary material of this article and are available from the corresponding author upon reasonable request.

Keywords

α-Carborane, hydrogen evolution reaction, photoinduced electron transfer, pyrene, viologen

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