Solar-Driven Hydrogen Generation Catalyzed by g-C₃N₄ with Poly(platinaynes) as Efficient Electron Donor at Low Platinum Content

Xuan Zhou, Yurong Liu, Zhengyuan Jin, Meina Huang, Feifan Zhou, Jun Song,* Junle Qu, Yu-Jia Zeng,* Peng-Cheng Qian,* and Wai-Yeung Wong*

A metal-complex-modified graphitic carbon nitride (g-C₃N₄) bulk heterostructure is presented here as a promising alternative to high-cost noble metals as artificial photocatalysts. Theoretical and experimental studies of the spectral and physicochemical properties of three structurally similar molecules Fo–D, Pt–D, and Pt–P confirm that the Pt(II) acetylide group effectively expands the electron delocalization and adjusts the molecular orbital levels to form a relatively narrow bandgap. Using these molecules, the donor–acceptor assemblies Fo–D@CN, Pt–D@CN, and Pt–P@CN are formed with g-C₃N₄. Among these assemblies, the Pt(II) acetylide-based composite materials Pt–D@CN and Pt–P@CN with bulk heterojunction morphologies and extremely low Pt weight ratios of 0.19% and 0.24%, respectively, exhibit the fastest charge transfer and best light-harvesting efficiencies. Among the tested assemblies, 10 mg Pt–P@CN without any Pt metal additives exhibits a significantly improved photocatalytic H₂ generation rate of 1.38 µmol h⁻¹ under simulated sunlight irradiation (AM1.5G, filter), which is sixfold higher than that of the pristine g-C₃N₄.

1. Introduction

Artificial photosynthetic fuels have attracted enormous interest due to their potential in addressing the global energy and climate crisis.¹ Hydrogen (H₂) generation from water splitting emerged as a renewable process for conversion, storage, and utilization of solar energy in an environmentally clean, economical, and efficient manner.² A photocatalytic H₂ generation system should be photoactive, catalytically active, and stable. Many semiconductor materials such as zinc oxide,³ titanium dioxide,⁴ organic dyes,⁵ and graphitic carbon nitride (g-C₃N₄)⁶ have suitable energy band edges and are thus photoactive to perform light-harvesting function, but the high overpotentials make them kinetically inert for H₂ evolution. On the contrary, many metals and metal complexes such as platinum (Pt),⁷ palladium,⁸ cobalt,⁹ manganese dioxide,¹⁰ ruthenium,¹¹ and Pt(II) complexes¹² are less photoactive but catalytically active and have low overpotentials for molecular activation. A smart engineering strategy is the coassembly of a photocatalytic material and a catalytically active material to form a donor–acceptor system that drives the photocatalytic H₂ evolution reaction. In the past decades, noble metals especially Pt metal have been widely adopted as the most efficient cocatalysts because they generally own the advantage of lower overpotential for water-splitting than non-noble metals despite the cost and rarity problems.¹³

2D semiconductors could act as accessible π-donors in composites with noble metals to form bulk heterojunction (BHJ) systems through cation–π interactions.¹⁴ For instance,
graphene-supported Pt and ruthenium have shown improved performance in the degradation of contaminants.\textsuperscript{[15]} Moreover, 2D g-C\textsubscript{3}N\textsubscript{4}, with periodical pyridinic nitrogen atoms, is a good candidate for assembly with a metal complex.\textsuperscript{[16]} Abundant unsaturated nitrogen with higher electronegativity than carbon makes g-C\textsubscript{3}N\textsubscript{4} a Lewis base acting as a nucleophile to metal ions, which facilitates the formation of a stable BHJ system with rich photocatalytic activity. On the other hand, poly(platinaynes), generated by elaborately inserting Pt(II) bis-acetylide into a polymeric molecular skeleton, is a highly promising electron donor for solar cell and molecular optoelectronic applications.\textsuperscript{[17]} Differing from Pt metal, poly(platinaynes) is characterized by a strong absorption in the visible spectral region, high carrier transport mobility, tunable energy band edge, and self-assembly ability but has not been studied yet regarding their photocatalytic function. Novel composites between poly(platinaynes) and g-C\textsubscript{3}N\textsubscript{4} may form a new photocatalytic system with unprecedented properties for H\textsubscript{2} generation. Furthermore, poly(platinaynes) only contains a relatively small amount of Pt element and can be prepared in a large area via low-cost solution-processed technology, resulting in cocatalysts at lower costs for practical application with respect to Pt metal on the one hand. On the other hand, the spectral property, molecular orbital energy levels, bandgap as well as relative photocatalytic function can be easily tuned by skeleton modification of poly(platinaynes), and thus it is feasible to enhance the photocatalytic activity via optimization of the molecular structure. In our work, three structurally similar and solution-processible molecules, including the organic acetylide Fo–D, the Pt(II) acetylide Pt–D, and the poly(platinaynes) Pt–P (see Figure 1), were synthesized and well characterized. All these molecules are \(\pi\)-conjugated with g-C\textsubscript{3}N\textsubscript{4} but display different film morphologies. Among these molecules, the composite of poly(platinaynes) and g-C\textsubscript{3}N\textsubscript{4} with BHJ morphology and very low Pt weight ratio of 0.24\% exhibits the most efficient separation of photogenerated charge carriers and an enhanced light-harvesting capability, leading to six times improvement of the optimal photocatalytic H\textsubscript{2} generation rate with respect to pristine g-C\textsubscript{3}N\textsubscript{4} under simulated sunlight irradiation (AM1.5G filter) without the Pt metal additive. This performance is outstanding with respect to g-C\textsubscript{3}N\textsubscript{4} cocatalyzed by the loading of a pure Pt metal.\textsuperscript{[7,18]}

2. Results and Discussion

2.1. Molecular and Experimental Design

With the aim to obtain a cocatalyst with good transport capability for charge carriers and broadband light-harvesting, the “push-pull” poly(platinaynes) molecule Pt–P has been designed by the introduction of an electron-accepting fluorenone to the electron-donating Pt(II) bis-acetylide moiety. To reveal the effects of the Pt(II) bis-acetylide moiety and the polymeric chain on the material’s structure and properties, respectively, two other small molecules, Fo–D and Pt–D, which are structurally similar to the Pt–P monomer, were developed for comparison. Poly(platinaynes) is a well-known electron donor, while g-C\textsubscript{3}N\textsubscript{4} is a versatile \(\pi\)-conjugated electron acceptor.\textsuperscript{[19]} Molecular simulation by density functional theory (DFT) at the PBE1PBE/6-31G(d) level by using Gaussian 09 Revision D.01\textsuperscript{[20]} initially revealed that the organic acetylide Fo–D, Pt(II) acetylide Pt–D, and poly(platinaynes) Pt–P (Figure 1, top) possess suitable molecular conformation, molecular orbital (MO) symmetry, and charge density distribution for composite formation with g-C\textsubscript{3}N\textsubscript{4}. The total electron density distribution is shown in Figure 1 (bottom).

Molecular modeling of g-C\textsubscript{3}N\textsubscript{4} revealed a planar conformation for heptazine with a partially positively charged center and a negatively charged periphery for electron distribution. On the contrary, molecular modeling of Fo–D, Pt–D, and Pt–P showed a planar conformation with a negatively charged center and a positively charged periphery for the fluorenone group. Furthermore, the metal–molecule–metal structure of Pt(II)-acetylide \(\pi\)-bridged fluorenone increases the electron delocalization over the whole molecule, resulting in an electron-rich structure with a narrow bandgap \((E_{g})\) to provide strong electrostatic interactions with 2D electron acceptors in addition to the \(\pi–\pi\) interactions. We assumed that these molecules form composites with g-C\textsubscript{3}N\textsubscript{4} based on donor–acceptor interactions via the aromatic \(\pi\) systems, which

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Chemical structures of Fo–D, Pt–D, Pt–P, and g-C\textsubscript{3}N\textsubscript{4} (top) and their total electron density distributions calculated using TD-DFT (PBE1PBE/GENECP) level (bottom; blue: electron-deficient area; red: electron-rich area).}
\end{figure}
has been confirmed by calculations with Gaussian 09 Revision D.01 using DFT-D3 at the PBE1PBE/6-31+G(d, p) level\[21\] (Figure S7, Supporting Information). Composite formation between Fo–D, Pt–D, or Pt–P and g-C₃N₄ is an exothermic process with an enthalpy change (ΔH) of about −107.97, −96.24, and −113.42 kJ mol⁻¹, respectively. Composite formation between Pt–P and g-C₃N₄ exhibits the highest enthalpy change, implying that Pt–P is the strongest electron donor among the studied molecules, which enables the strongest donor–acceptor interactions with g-C₃N₄. Afterwards, Fo–D, Pt–D, and Pt–P (1 mg each) were experimentally added to g-C₃N₄ (100 mg) in chloroform solution to form BHJ photocatalysts Fo–D@CN, Pt–D@CN, and Pt–P@CN, respectively. For comparison on the photocatalytic activity, pristine g-C₃N₄ was used as a benchmark and subjected to the same procedure. The synthetic details and characterization results are provided in the Supporting Information.

2.2. Morphological Characterization

The microstructures of the BHJ photocatalysts were observed by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). Interestingly, Pt–P@CN showed a petaloid-like morphology (Figure 2a), which could be ascribed to a relatively loose packing of g-C₃N₄.\[22\] In contrast, the morphologies of Pt–D@CN (Figure 2b) and Fo–D@CN (Figure 2c) are similar to that of the bulk g-C₃N₄ (Figure S8a, Supporting Information), where the multilayers are relatively tightly stacked.\[23\] This difference in morphology may originate from the self-assembly of poly(platinaynes).\[24\] These observations were further confirmed by HRTEM. Pt–P exhibited aggregates of continuous nanowires with diameters of about 2–4 nm (Figure 2d), which implies a unique bicontinuous phase structure for Pt–P@CN. From Figure 2e,f, the lattice fringe with spacing of 0.22 and 0.20 nm can be identified from the images of Fo–D@CN and Pt–D@CN, respectively. The lattice fringes should be assigned to Fo–D and Pt–D, as the reported lattice fringe spacing of g-C₃N₄ is 0.33 nm, much larger than the observed spacings. The observations illustrate the successful generation of BHJ composites and both Fo–D and Pt–D were distributed in a scattered manner on g-C₃N₄ without obvious aggregation. Similarly, Pt–P, Pt–D, and Fo–D also exhibited distinct self-assembled structures in pristine solid state (Figure S8b–d, Supporting Information, and inset of Figure 2d), where Pt–P exhibited nanowires with diameters in 2–6 nm.\[23\] Afterwards, the miscibility of these heterostructured photocatalysts was explored by energy-dispersive X-ray spectroscopy (EDS) elemental mapping. The obtained mapping images demonstrated uniform distributions of Fo–D (characterized by O), Pt–D (characterized by P and Pt), and Pt–P (characterized by P and Pt) on g-C₃N₄ (Figures S10–S12, Supporting Information).

Furthermore, the composite surfaces were analyzed by X-ray photoelectron spectroscopy (XPS). XPS wide-scan spectra (Figure S14, Supporting Information) confirm that the composites...
contain the elements C, N, O, P, and Pt. The Pt 4f and N 1s XPS high-resolution spectra of Pt–D, Pt–D@CN, Pt–P, and Pt–P@CN are presented in Figure 3a,b. Interactions between the donor molecules and g-C3N4 are indicated by changes in the binding energy of the Pt 4f and N 1s core levels. Pt–D exhibited two peaks at 72.74 and 76.04 eV, which were attributed to Pt 4f7/2 and Pt 4f5/2, respectively. After the formation of the D–A heterojunction Pt–D@CN, the Pt 4f7/2 and Pt 4f5/2 peaks were positively shifted to 72.91 and 76.28 eV, respectively. Similarly, the Pt 4f7/2 and Pt 4f5/2 peaks of Pt–P at 72.50 and 75.80 eV were shifted to the higher values of 72.79 and 76.10 eV, respectively, upon the formation of Pt–P@CN. The positive shift of Pt 4f XPS peaks in the composite systems unveiled the decrease in electron density, indicating the transfer of electron from Pt–D or Pt–P to g-C3N4.

On the other hand, g-C3N4 exhibited N 1s peak at 398.60 eV. In contrast, N 1s peak of the Fo–D@CN, Pt–D@CN, and Pt–P@CN are negatively shifted to 398.40, 398.20, and 398.50 eV, respectively, showing a slight increase in electron density of N in g-C3N4 after forming the composites. It should be attributed to the addition of the electron donors Fo–D, Pt–D, and Pt–P. These findings render the successful modification of the g-C3N4 surface with Pt–D and Pt–P based on the donor–acceptor interactions via the aromatic π system.[26]

2.3. Absorption Spectroscopy

The BHJ photocatalysts display different colors (pale yellow for g-C3N4, yellow for Fo–D@CN, orange for Pt–D@CN, and red for Pt–P@CN) (inset of Figure 4a). Their spectral properties were further studied by UV–vis diffuse reflectance spectroscopy (Figure 4a), showing good light-harvesting capabilities with an intense absorption in the range of 300–460 nm, characteristic for g-C3N4 and a moderate absorption in the range of 460–600 nm. The latter absorption range is characteristic for Fo–D, Pt–D, and Pt–P, which has been confirmed by their individual UV–vis spectra (Figure 4b, Table 1). Solutions of Fo–D, Pt–D, and Pt–P showed two absorption peaks at 348, 350, and 382 nm as well as 426, 464, and 508 nm, respectively, with molar extinction coefficients of 7.23 × 10^4, 6.20 × 10^4, and 5.80 × 10^4 m⁻¹ cm⁻¹ as well as 0.93 × 10^4, 0.66 × 10^4, and 0.47 × 10^4 m⁻¹ cm⁻¹, respectively. Similarly, solids of Fo–D, Pt–D, and Pt–P (Figure S15a, Supporting Information) also exhibited two absorption peaks at 348, 350, and 382 nm as well as 451, 466, and 519 nm, respectively. The UV–vis absorptions of Fo–D, Pt–D, and Pt–P supported the visible light-harvesting capabilities of the correspond-

Table 1. Spectral and electrochemical data of Fo–D, Pt–D, and Pt–P.

| Sample | λ_{αυ} [c × 10^{4} m⁻¹ cm⁻¹] | CV | LUMO [eV] | HOMO [eV] | E_g [eV] |
|--------|-------------------------------|----|-----------|-----------|--------|
|        | Solution [nm] | Solid [nm] | DFT |          |          |
| Fo–D   | 348 (7.23), 426 (0.93) | 348, 451 | 330, 435 | −5.73 | −3.32 | 2.41 |
| Pt–D   | 350 (6.20), 464 (0.66) | 350, 466 | 356, 474 | −5.62 | −3.39 | 2.23 |
| Pt–P   | 382 (5.80), 508 (0.47) | 382, 519 | 343, 499 | −5.51 | −3.50 | 2.01 |

CV = −(4.61 + E_{red}); HOMO = −(4.61 + E_{ox}). Ferrocene was used as an internal standard.

Adv. Sci. 2021, 8, 2002465 © 2021 The Authors. Advanced Science published by Wiley-VCH GmbH
Figure 4. a) UV–vis diffuse reflectance spectra of solids (inset: images of g-C$_3$N$_4$, Fo–D@CN, Pt–D@CN, and Pt–P@CN); b) UV–vis absorption spectra of solutions of Fo–D, Pt–D, and Pt–P (10 × 10$^{-6}$M); c) absorbance spectra of Fo–D, Pt–D, and Pt–P calculated by DFT at the B3LYP/GENECP level; d) main molecular orbitals involved in the electron transitions of the visible absorption peaks of Fo–D, Pt–D, and Pt–P; e) fluorescence spectra of BHJ photocatalysts, g-C$_3$N$_4$, Fo–D, Pt–D, and Pt–P solids (excitation wavelength: 370 nm); f) excitation spectra of Fo–D, Pt–D, and Pt–P solids with scanning wavelength of 562, 544, and 602 nm, respectively. g) Lifetime decay curves of g-C$_3$N$_4$, Fo–D@CN, Pt–D@CN, and Pt–P@CN solids (excitation wavelength: 370 nm).

The solid-state fluorescence spectra of the pristine g-C$_3$N$_4$, Fo–D, Pt–D, and Pt–P, and the BHJ photocatalysts were obtained, as shown in Figure 4e. All the BHJ photocatalysts Fo–D@CN, Pt–D@CN, and Pt–P@CN exhibited emissions at around 450 nm, which should arise from g-C$_3$N$_4$. It is noteworthy that the emissions, especially for Pt–P@CN, are noticeably weakened relative to pristine g-C$_3$N$_4$. Meanwhile, the emissions from the corresponding donor molecules Fo–D (562 nm), Pt–D (544 nm), and Pt–P (602 nm) are negligible. These observations give an obvious evidence of fluorescence quenching due to the formation of the heterojunctions, resulting from the electron-transfer characteristics of the donor molecules.

The life-times of the sample solids were tested by time-resolved photoluminescence (TRPL) (Figure 4g, Table 2). The afforded curves of the g-C$_3$N$_4$, Fo–D@CN, Pt–D@CN, and Pt–P@CN were fitted ascribed to the HOMO→LUMO+1 transition with a contribution of 93%. All orbitals involved in these transitions for Pt–D and Pt–P include contributions of the Pt(II) acetylidy moiety. At the same time, Fo–D, Pt–D, and Pt–P have increased dipole moments of 6.12, 6.25, and 6.51 a.u., respectively. These results indicate that the enhanced visible-light absorptions of the BHJs result from the electron-transfer characteristics of the donor molecules.
Figure 5. a) Cyclic voltammograms of the donor molecules (oxidative/reductive potentials of Fo–D, Pt–D, and Pt–P are 1.12/−1.29, 1.00/−1.22, and 0.90/−1.11 eV, respectively); b) optimal ground-state geometries of the donor molecules, as calculated by DFT at the PBE1PBE/GENECP level using Gaussian Revision D.01 (the molecular model of polymer Pt–P was defined as Pt–P*); c) frontier orbital distributions and energy levels of donor molecules calculated at the same level; d) typical alignment of the frontier energy levels of donor molecules and g-C3N4.

Table 2. Lifetime parameters of excitons of g-C3N4, Fo–D, Pt–D, and Pt–P.

| Sample  | \( A_1 \) \(^a) \) | \( t_1 \) \[^n\] | \( A_2 \) \(^a) \) | \( t_2 \) \[^n\] | \( \tau \) \[^n\] |
|---------|------------------|----------------|------------------|----------------|----------------|
| CN      | 1.37             | 121.15         | 365.59           | 9.97           | 10.47          |
| Fe-D@CN | 1.83             | 111.09         | 3365.15          | 6.89           | 7.80           |
| Pt-D@CN | 1.41             | 105.43         | 3365.53          | 6.87           | 7.50           |
| Pt-P@CN | 1.08             | 51.02          | 3358.49          | 6.13           | 6.25           |

\(^a) \) The fitted parameters of dual-exponential model \( I(t) = A_1 e^{t / \tau_1} + A_2 e^{t / \tau_2} \);
\(^b) \) Average lifetime.

with dual-exponential model \( I(t) = A_1 e^{t / \tau_1} + A_2 e^{t / \tau_2} \) and yielded an average lifetime \( \tau \) of 10.47, 7.80, 7.50, and 6.25 nm, respectively. The shortened average lifetime suggests that Fo–D@CN, Pt–D@CN, and Pt–P@CN have more convenient charge separation and transfer with respect to pristine g-C3N4. Further analysis of the excitations spectra of Fo–D, Pt–D, and Pt–P solids (Figure 4f) revealed that Fo–D can be excited in both UV (≤400 nm) and visible (400–520 nm) spectral regions, while Pt–D and Pt–P are excited in broader visible spectral regions of 400–550 and 400–600 nm, respectively. The effective excitations of these three electron donors in the broad visible spectral region endow the BHJ photocatalysts with good visible light-harvesting capability.

2.4. Electrochemical Characterization

The electrochemical properties of Fo–D, Pt–D, and Pt–P were examined by cyclic voltammetry (Figure 5a), revealing HOMOs/LUMOs of −5.73/−3.32, −5.62/−3.39, and −5.51/−3.50 eV, respectively, with \( E_g \) of 2.41, 2.23, and 2.01 eV. The electrochemical properties were further confirmed by DFT calculations using Gaussian 09 Revision D01 at the PBE1PBE/GENECP level. The DFT calculations at the PBE1PBE/GENECP level have been widely adopted to study the spectral and electronic properties of conjugating molecules.\(^{30} \) As depicted in Figure 5b, Fo–D has a highly planar and rigid backbone. In contrast, Pt–D and Pt–P have relatively twisted conformations around the Pt(II) acetylide unit with dihedral angles of 16° and 76°, respectively. Further analysis of the molecular orbital distributions (Figure 5c) showed that the frontier orbitals of Pt–D and Pt–P are delocalized over the Pt(II) acetylide units. Therefore, the \( E_g \) of Fo–D, Pt–D, and Pt–P decreased to 3.52, 3.22, and 3.04 eV, respectively. In addition, cyclic voltammetry (Figure S17, Supporting Information) reveals that the LUMO and HOMO of g-C3N4 are located at −3.58 and −6.28 eV, respectively,\(^{31} \) which supports the notion that the frontier orbital energy levels of the electron donor Fo–D, Pt–D, or Pt–P and the electron acceptor g-C3N4 are well aligned in the BHJs (Figure 5d).

2.5. Photocurrent and Impedance Tests

Transient photocurrent responses were recorded for several on–off cycles under intermittent irradiation using Fo–D@CN, Pt–D@CN, Pt–P@CN, or g-C3N4 as electrode (Figure 6a). The results suggest that the photogenerated electrons are effectively transferred to the back contact through the samples, resulting in a photocurrent under light irradiation.\(^{32} \) Compared with g-C3N4, Fo–D@CN, Pt–D@CN, and Pt–P@CN produced higher photocurrents, supporting that the BHJ structures have better
light-harvesting capability and faster electron–hole separation rate.\[33\] Electrochemical impedance spectroscopy (EIS) Nyquist plots obtained at a bias potential of 0.5 V (Figure 6b) showed semicircles with smaller radii for Fo–D@CN, Pt–D@CN, and Pt–P@CN, indicating lower charge transfer resistances for the BHJ structures than for g-C_3N_4. At the same time, the higher photocurrent response and lower charge transfer resistance suggest a diminished electron–hole recombination, which implies that Fo–D@CN, Pt–D@CN, and Pt–P@CN would have enhanced photocatalytic activities than g-C_3N_4. Furthermore, the highest photocurrent response and the lowest charge transfer resistance reveal that Pt–P@CN has the highest activity among these BHJ photocatalysts for H_2 generation.

2.6. Photocatalytic Performance and Mechanism

Solar-driven H_2 generation tests of the BHJs Fo–D@CN, Pt–D@CN, and Pt–P@CN were performed in aqueous solution using triethanolamine as a sacrificial agent under irradiation with simulated solar light (AM1.5, 100 mW cm\(^{-2}\)) and without addition of Pt metal or any other cocatalyst. The apparent quantum efficiency (AQE) was detected using 3 W LEDs at the central wavelength of 420 nm and calculated based on the following equation

\[
AQE(\%) = \frac{2N_{H_2}}{N_p}
\]

where \(N_{H_2}\) is the number of generated H_2 molecules and \(N_p\) is the number of emitted photons. The H_2 generation was monitored each hour by gas chromatography with thermal conductivity cell detector. Before irradiation, all the samples have been treated according to standard photocatalytic procedures in darkness, and no H_2 generation was observed due to the photocatalytic reaction of any donor molecule Fo–D, Pt–D, or Pt–P without g-C_3N_4 or due to any other non-photocatalytic reaction. Figure 6c displays the photocatalytic H_2 generation rates (HPRs) of
the pristine g-C$_3$N$_4$ and the BHJ photocatalysts for each 10 mg g-C$_3$N$_4$ showed a relatively low HPR of 0.22 µmol h$^{-1}$, probably due to the significant recombination of hole–electron pairs.\[60\] In contrast, Fo–D@CN, Pt–D@CN, and Pt–P@CN exhibited improved HPRs of 0.30, 0.99, and 1.38 µmol h$^{-1}$, respectively. Especially, the HPR of Pt–P@CN is 6.27-fold higher than that of the pristine g-C$_3$N$_4$, which is comparable to the best performance of g-C$_3$N$_4$ cocatalyzed by the generally loaded Pt metal.\[34\] In addition, Pt–P@CN exhibited a considerable AQE of 1.43% while the pristine g-C$_3$N$_4$ showed a negligible AQE at 420 nm (Figure S16, Supporting Information). Obviously, Pt–P@CN with a much less loading of Pt (0.24 wt%) holds a promise for a more economical application than pure Pt and noble metals. To test the stability, the photocatalytic experiment was continued for 18 h, showing no obvious decrease in the photocatalytic activity (Figure 6d) and thereby ascertaining the good stability of the photocatalytic system.

Based on the above discussion, a possible mechanism is proposed in Figure 6e. With tunable molecular energy band edges and visible light absorption spectra, Fo–D, Pt–D, and Pt–P have played a dual role as efficient electron donor in the BHJs and as light absorber complementary to g-C$_3$N$_4$, which supplies more excitons and facilitates the electron transfer to g-C$_3$N$_4$ when irradiated by simulated solar light. On the other hand, g-C$_3$N$_4$ can also transfer its photogenerated holes to the electron donor molecule and hence suppress the significant recombination of holes and electrons. The oxidation and H$_2$ evolution rates are both accelerated, and hence the photocatalytic performances of these BHJ photocatalysts are improved. Among the tested BHJ photocatalysts, Pt–P@CN with finely self-organized behavior and the largest spectral absorption provides more valid charge carrier channels and hence shows an outstanding photocatalytic performance.\[25\]

3. Conclusion

In conclusion, we designed three new structurally similar molecules Fo–D, Pt–D, and Pt–P with organic, organometallic, and polymeric organometallic skeletons, respectively. Their spectral and physicochemical properties were comparatively studied by theoretical and experimental methods, qualitatively and quantitatively confirming that the planarines moiety can effectively increase the electron density, extend the electron delocalization along the molecular backbone and thus act as a strong electron donor. Furthermore, the introduction of the planarines unit adjusts the molecular orbital levels to form a relatively narrow $E_g$ which thereby widens the visible light-harvesting region. The electron donors Fo–D, Pt–D, and Pt–P were allowed to form composites with 2D g-C$_3$N$_4$ as the electron acceptor to afford heterojunction photocatalysts. These donor–acceptor BHJ systems exhibit not only better light-harvesting capabilities but also higher efficiencies of electron–hole separation than the pristine g-C$_3$N$_4$. Especially, when used for the generation of H$_2$, Pt–P@CN exhibited the highest HPR of 1.38 µmol h$^{-1}$ for each 10 mg among all the studied BHJs, which is six times higher than that of the pristine g-C$_3$N$_4$ and also surpasses those of the Pt and noble metal co-catalysts for g-C$_3$N$_4$.\[14\] This study paves the way for a new generation of highly efficient, relatively low-cost noble metal-based photocatalysts for solar-driven H$_2$ generation.
