A highly crystalline perylene imide polymer (Urea-PDI) photocatalyst is successfully constructed. The Urea-PDI presents a wide spectrum response owing to its large conjugated system. The Urea-PDI performs so far highest oxygen evolution rate (3223.9 μmol g⁻¹ h⁻¹) without cocatalysts under visible light. The performance is over 107.5 times higher than that of the conventional PDI supramolecular photocatalysts. The strong oxidizing ability comes from the deep valence band (+1.52 eV) which is contributed by the covalent-bonded conjugated molecules. Besides, the high crystallinity and the large molecular dipoles of the Urea-PDI contribute to a robust built-in electric field promoting the separation and transportation of photogenerated carriers. Moreover, the Urea-PDI is very stable and has no performance attenuation after 100 h continuous irradiation. The Urea-PDI polymer photocatalyst provides with a new platform for the use of photocatalytic water oxidation, which is expected to contribute to clean energy production.

Over the years, novel photocatalytic materials have been developed to efficiently split water into hydrogen and oxygen for sustainable conversion and utilization of solar energy.[1] While most of the photocatalysts were concentrated on the reducing half reaction of hydrogen production[2] contributed by the photogenerated electrons in the conduction band (CB). For the overall water splitting into hydrogen and oxygen, the water oxidation to oxygen has been regarded as the rate-limiting step as its 4-electron process.[3] However, oxygen evolution is still a huge challenge owing to its slow reaction rate and scarce of efficient photocatalysts.[4] Hence, there is still a long way to go before the large-scale application of photocatalytic overall water splitting. And the study of oxidative half reaction contributed by the photogenerated holes in the valence band (VB) is of great significance, which provides a powerful complement to overall water splitting and photochemical conversion. Moreover, the understanding of the oxidative half reaction is important as well for the general scientific laws of the entire photocatalytic reaction.

At present, most of photocatalytic materials for H₂/O₂ evolution require the participation of noble metal cocatalysts to activate water molecules and reduce the overpotential.[5] Unfortunately, these metals are less abundant and expensive. Thus, in the long run, cocatalyst-assisted photocatalytic materials may not be the best choice for energy conservation. Therefore, it is important to develop novel photocatalysts that could overcome the limitation of cocatalysts. The novel photocatalysts should have the proper energy band positions exceeding the water decomposition potential (+1.23 vs NHE)[6] to ensure the reaction can be thermodynamically viable. And the novel photocatalysts should separate and transport the photogenerated carriers efficiently to ensure the reaction can be kinetically feasible.

Not long ago, we developed a series of novel self-assembled supramolecular photocatalysts.[7] It has been proved that the energy band and built-in electric field of the photocatalyst can be regulated by the frontier orbital energy level and dipole of the molecule. However, since the weak interaction of non-covalent interaction and hydrogen bond, the supramolecular materials were slightly deconstructed in the repeated reactions, resulting in a decrease in the performance. To solve the problem, we try to covalently link the supramolecular perylene diimide (PDI) to construct photocatalytic polymers with a better stability and performances. The specific experimental methods are described in the Supporting Information.

The urea was used as the linker to construct the Urea-PDI polymer photocatalyst.[8] The Urea-PDI presents a nanobelt morphology, which can be accumulated into secondary bulk morphology, as shown in Figure 1a and Figure S1 (Supporting Information). It is observed highly crystallized and the H-type π-π stacking interaction between the molecules can be confirmed by the clear d-spacing of 0.32 nm,[9] which corresponds to the diffraction peak of 27.2° in Figure 1b. It indicates that electron transfer channels could be formed by the face-to-face overlap of delocalized electron clouds. The chemical structure of the Urea-PDI was further confirmed. As shown in Figure 1c, the carbon atoms of the conjugated PDI central core are mainly represented by peaks of 131.88 and 141.11 ppm in the solid
The two most critical carbonyl carbons appear in the lower field. The carbonyl C of urea appeared at 175.95 ppm in the lowest field, since it is bonded with two electron-negative N atoms. Another peak at 170.88 ppm is the carbonyl C of the PDI ring. And the carbonyl linker of the Urea-PDI can also be proved with 1755 cm$^{-1}$ in the infrared spectrum (Figure S2, Supporting Information). Besides, the Urea-PDI was analyzed by ICP-AES and XPS technologies. There is no residual zinc metal in the Urea-PDI (Table S1, Supporting Information), which indicated that the Urea-PDI is a completely metal-free polymer. As shown in Figure 1d, the key C1S of carbonyl carbon in urea was detected at 288.1 eV, while which in PDI was at 285.4 eV. Further, as a result of elemental analysis, the ratio of N1S to O1s in the Urea-PDI was 1:2.5 (Table S2, Supporting Information), which was comparable to the molecular structure. The above valence bond information confirmed the accuracy of the chemical structure.

In the previous works, we pointed out that the enhancement of the molecular dipole is beneficial to enlarge the built-in electric field and promote the separation of photogenerated carriers.[7b] Similarly, we also studied the molecular dipoles of the polymer (Figure S3, Supporting Information). Since the Perylene-3,4,9,10-tetracarboxylic dianhydride (PDA) monomer is a highly symmetrical molecule, the original PDA has a very small dipole moment of only 0.0002 Debye. While in the polymer, the dipole moment increased significantly up to 0.93 Debye due to the addition of the electronegative carbonyl group. The structural advantages of such high crystallization and large dipole, which would contribute to a strong built-in electric field, make the Urea-PDI possible to have a good ability for charge separation and transportation activity. Therefore, its excellent photocatalytic performance is also expected.

The Urea-PDI performed a highly efficient oxygen evolution, which reached up the 3223.9 μmol g$^{-1}$ h$^{-1}$ on average in the absence of noble metal cocatalysts under visible light, as shown in Figure 2a and Figures S4 and S5 (Supporting Information). To further illustrate the origin of oxygen, we take the 18O isotope labeled H$_2$O as the substrate. As shown in Figure 2b and Figure S6 (Supporting Information), the labeled 18O$_2$ with m/z of 36 can be detected, which indicates that evolved oxygen gas was generated from the labeled H$_2$18O. And the labeled 18O$_2$ also is the main form that can be detected. It should be pointed out that the small amount of ordinary 16O$_2$ comes from the environmental background. Besides, as shown in Figure 2c, the performance of Urea-PDI polymer is hundreds of times higher than that of other supramolecular PDI photocatalysts reported previously.[7,10] Meanwhile, the performance is much higher as well than that of the other similar organic materials (Table S3, Supporting Information).[3a,11] The Urea-PDI has become the best organic visible light photocatalyst for oxygen evolution so far, which is a huge breakthrough in completely organic photocatalytic oxygen production materials. Thanks to the covalent
link inside the polymer, the shortcomings of supramolecular stability have been completely overcome. The Urea-PDI can be stably reused under continuous illumination for more than 100 h without any decrease in performance, as shown in Figure 2d. We deeply discussed the stability and influence of sacrificial agents on oxygen evolution performance in the Note S1 and Figures S7–S10 (Supporting Information).

Behind such superior performance, it is more important to explore the key scientific factors that affect the performance of polymer catalytic materials.

On the one hand, the energy band position of the Urea-PDI polymer is the thermodynamic factor that determines whether the photocatalytic oxidation reaction is feasible. According to the computing results (Figure S11, Supporting Information), the HOMO and LUMO of the PDI molecule are mainly distributed in the delocalized region, which means that HOMO and LUMO would be linearly recombined after \(\pi-\pi\) interaction to form a semiconductor energy band.[12] When the molecules aggregate to form a solid semiconductor, the molecular isolated energy levels are combined into the energy band, which is represented by the single absorption edge of the spectrum. Contributed by the expanded conjugated electron clouds by \(\pi-\pi\) stacking, the intrinsic absorption band edge of the Urea-PDI covered the entire visible range reaching 690 nm as shown in Figure 3a. According to Wang and Domen,[13] the photon absorption is the first step for photocatalysis. Extending absorption can drastically raise the ideal solar energy transformation efficiency (Solar to Hydrogen or Oxygen). Thus, in order to obtain a high solar energy transformation efficiency, it is crucial to fabricate the photocatalysts that can powerfully harvest light.

The specific band position can be measured by the cyclic voltammetry method. In order to ensure that the electrochemical method can accurately test the intrinsic properties of Urea-PDI in the composite electrode, the composited electrode was observed with SEM (Figure S12, Supporting Information). The Urea-PDI constructed a uniform film on the surface of ITO. As shown in Figure 3b, the CB bottom of the Urea-PDI was \(-0.27\) V. Combining the absorption edge of Urea-PDI at 690 nm, the bandgap is about 1.79 eV. From this, it can be confirmed that the VB top position of the material is around +1.52 eV, which is much higher than the potential of water decomposition, and thus the polymer can oxidize water into...
oxygen. Moreover, the reactive species on the Urea-PDI surface can be detected by the steady-state surface photovoltage (SPV) spectrum. As shown in Figure 3c the Urea-PDI produced a very obviously positive signal in the 700–300 nm, with a maximum of 27 µV. And the wavelength-dependent photocatalytic activities matched with SPV change trends very well. The positive signal indicates that photogenerated holes are transferred to the irradiated surface to oxidize the H$_2$O molecules as the main reactive species.\(^{[14]}\)

We also tested the apparent quantum yield (AQY) of Urea-PDI at different wavelengths,\(^{[15]}\) as shown in Figure 3d and Table S4 (Supporting Information). The AQY is equivalent to the absorption spectrum, whose maximum reached up to 3.86% at 450 nm. While, it must be pointed out that in the currently reported organic photocatalytic oxygen production materials, no one has clearly reported the AQY of these materials, due to the low oxygen production activity. Thus, it is difficult to compare the AQY with other materials.

On the other hand, the built-in electric field of the Urea-PDI is the kinetic factor affecting photocatalytic performance. It is one of the driving forces for separation and transportation of photogenerated carriers.\(^{[16]}\) To further verify the influence of the built-in electric field, we designed and synthesized the other two polymers with different linker molecules, Hydrazine-PDI and Ethylenediamine-PDI. The chemical structures were also characterized carefully (Figures S13–S15, Supporting Information). The crystallinity of these polymers shows a huge difference (Figure S16, Supporting Information), among which the Urea-PDI has the best crystallinity and is close to inorganic matter. The better crystallinity, the fewer recombination centers of holes and electrons.\(^{[13]}\) Besides, the molecular dipoles of different polymers were computed as well (Figure S17, Supporting Information). The dipole of Urea-PDI was much larger than that of the other two polymers due to its planer triangle linker. Both of crystallinity and molecular dipole are the important factors influencing the built-in electric field.\(^{[16]}\) The high crystallinity ensures the stable existence of the dipole-induced built-in electric field inside the polymer, as which reduces the dipole cancellation caused by the disorder assembly.\(^{[17]}\)

According to Zhang’s group\(^{[18]}\) and the Note S2 (Supporting Information), the built-in electric field is a monotonic function of its surface charge density and zeta potential for a given material. Thus, the built-in electric field can be indexed with surface charge density and Zeta potential. The surface charge density can be measured by Atomic Force Microscope with a Kelvin Probe, as shown in Figure 4a and Figure S18 (Supporting Information). The surface potential of Urea-PDI (ΔE = 30.88 mV) is much higher than that of Hydrazine-PDI (ΔE = 15.31 mV) and

Figure 3. The thermodynamic factors for highly efficient photocatalytic oxygen evolution performance of Urea-PDI. a) UV–vis–NIR diffuse reflection spectrum of Urea-PDI and solar spectrum. b) Detection of CB position with cyclic voltage measurement. c) Overlayer of wavelength-dependent oxygen evolution and SPV spectrum. d) Overlayer of UV–vis–NIR absorption spectrum and apparent quantum yield.
Ethylenediamine-PDI ($\Delta E = 8.75$ mV). As shown in Figure 4b and Table S5 (Supporting Information), the Zeta potential was also enlarged obviously. The Zeta potential of Urea-PDI was $-44.05$ mV, while that of the Hydrazine-PDI and Ethylenediamine-PDI were only $-26.23$ and $-0.15$ mV. As a result, the Urea-PDI has the strongest built-in electric field, which significantly enhanced the charge separation and transportation (Figures S19 and S20 and Table S6, Supporting Information).

Thus, the lifetime of photogenerated carriers in the polymers can be significantly prolonged as the built-in electric field increase. The intensity of the photogenerated holes is significantly different, as observed in the Figure S21 (Supporting Information) by steady SPV, due to the huge difference in crystallinity. The enhanced intensity of photogenerated holes in Urea-PDI indicated the higher separation efficiency [19] and much more photogenerated holes accumulated on the surface. More importantly, the lifetime of photogenerated holes on the surface can also be detected by the transient SPV, as shown in Figure 4c. The lifetime of photogenerated holes in the Urea-PDI can reach 46.76 µs, which is much longer than that of Hydrazine-PDI (42.28 µs) and Ethylenediamine-PDI (40.34 µs). Longer lifetime means fewer recombination and more reaction probability. [20] For the recombination behavior, we also invested the kinetic factors, as shown in Figure 4d and Figure S22 and Table S7 (Supporting Information). The fitted fluorescence lifetime $\tau_1$ of Urea-PDI reached 5.21 ns indicating the enhanced long-range transportation and reduced recombination of the photogenerated carriers, so can AQY of the Urea-PDI reach such high level as above. [21]

Generally, the metal cocatalyst was used to improve the separation of carriers and prolong the lifetime of carriers by creating an interface junction between metal and photocatalyst. [23] This is an enhancement to the kinetic performance of the photocatalyst, not a thermodynamic behavior, which does not affect the redox capacity of the photocatalyst. Due to the huge built-in electric field in the Urea-PDI, the photogenerated carriers can be separated and transported efficiently through the energy band. It is also because of such excellent kinetic property of built-in electric field that metal-free Urea-PDI can achieve efficient water oxidation in the absence of metal cocatalyst.

Based on the above, we boldly predict that from Ethylenediamine-PDI to Urea-PDI, the photocatalytic oxygen production performance will increase significantly with the enhancement of the built-in electric field. Of course, the experimental results also confirm this, as shown in Figure 4e and Figure S23 (Supporting Information). Both of Urea-PDI and Hydrazine-PDI polymer can be excited by the visible light to produce oxygen efficiently in the absence of cocatalysts. The oxygen production rate of Urea-PDI was up to 3223.9 µmol g$^{-1}$ h$^{-1}$ as 5.44 times high as that of Hydrazine-PDI (592.4 µmol g$^{-1}$ h$^{-1}$).

All the above organic semiconductor photocatalyst mechanism discussions are presented in Figure 5. To summarize briefly, the charge transfer mechanism in Urea-PDI is the same as other non-metallic semiconducting photocatalysts. [22] The energy bands (CB and VB) will be constructed by the overlap of LUMO and HOMO under $\pi-\pi$ stacking, which provided the charge transfer channels. The CB can transport electrons, and the VB can transport holes. After the Urea-PDI is excited by light, the robust built-in electric field promotes the separation of electrons and holes. The photogenerated holes are further transferred to the

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**Figure 4.** The kinetic factors for highly efficient photocatalytic oxygen evolution performance of Urea-PDI. a) Surface potential of different polymers detected with KPFM. b) Zeta potential of different polymers. c) The lifetime of photogenerated holes detected by transient SPV. d) Transient fluorescence spectrum of the polymers. e) The increased photocatalytic oxygen evolution with enhanced built-in electric field.
surface through the energy band to oxidize the H₂O into O₂. So that a complete photocatalytic reaction occurs.

In conclusion, the highly efficient Urea-PDI polymer photocatalyst was successfully constructed. The Urea-PDI achieved the highest oxygen evolution of 3223.9 μmol g⁻¹ h⁻¹ under visible light without cocatalyst, whose AQY (450 nm) was up to 3.86%. The proper energy band structure of the Urea-PDI contributes the strong ability to decompose water into oxygen. The excellent crystallization and large molecular dipole contributed to a strong built-in electric field, which promotes the separation and transportation of photogenerated carriers inside the material. The Urea-PDI can be stably reused with continuous irradiation over 100 h without decrease in performance. This work provides new ideas for solving sustainable energy production in the future with the novel polymer photocatalysts.

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.

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built-in electric field, highly crystalline materials, perylene imide polymers, photocatalytic water oxidation

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