

Organic Semiconducting Polymers for Augmenting Biosynthesis and Bioconversion

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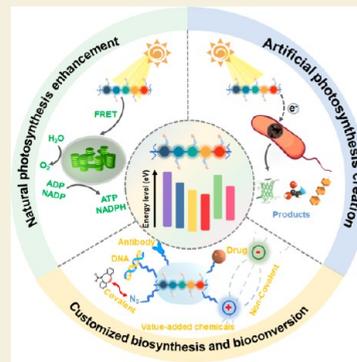
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ABSTRACT: Solar-driven biosynthesis and bioconversion are essential for achieving sustainable resources and renewable energy. These processes harness solar energy to produce biomass, chemicals, and fuels. While they offer promising avenues, some challenges and limitations should be investigated and addressed for their improvement and widespread adoption. These include the low utilization of light energy, the inadequate selectivity of products, and the limited utilization of inorganic carbon/nitrogen sources. Organic semiconducting polymers offer a promising solution to these challenges by collaborating with natural microorganisms and developing artificial photosynthetic biohybrid systems. In this Perspective, we highlight the latest advancements in the use of appropriate organic semiconducting polymers to construct artificial photosynthetic biohybrid systems. We focus on how these systems can enhance the natural photosynthetic efficiency of photosynthetic organisms, create artificial photosynthesis capability of nonphotosynthetic organisms, and customize the value-added chemicals of photosynthetic synthesis. By examining the structure–activity relationships and emphasizing the mechanism of electron transfer based on organic semiconducting polymers in artificial photosynthetic biohybrid systems, we aim to shed light on the potential of this novel strategy for artificial photosynthetic biohybrid systems. Notably, these coupling strategies between organic semiconducting polymers and organisms during artificial photosynthetic biohybrid systems will pave the way for a more sustainable future with solar fuels and chemicals.



KEYWORDS: organic semiconducting polymers, biological organisms, artificial photosynthetic biohybrid systems, biosynthesis and bioconversion, structure–activity relationship, high-value chemical production

1. INTRODUCTION

In recent years, the shortage of nonrenewable fossil energy sources and the exacerbation of environmental problems have become increasingly serious, necessitating the development of alternative energy sources.^{1–4} Solar energy is clean, environmentally friendly, and an abundant source of renewable energy compared to fossil fuels, and it has attracted a lot of attention from chemists.^{5–8} Photosynthesis, the paramount chemical reaction on Earth, encompasses the biosynthesis process in which green plants, algae, and cyanobacteria convert carbon dioxide (CO₂) into carbohydrates and liberate oxygen from water under the irradiation of sunlight.^{4,9–15} By investigating these natural photosynthetic systems, scientists have constructed a series of solar-driven artificial photosynthetic biohybrids by perfectly combining light-harvesting chemical materials with biologically active components for converting and storing solar energy effectively.^{16–20} Compared to common organic materials and organic insulating materials, organic semiconducting materials are usually chosen for their excellent light-harvesting performance and better electron transport capacity, which are favored to augment the biosynthesis process, produce high value-added chemicals, and eventually overcome the limitations of natural photosyn-

thesis.²¹ More importantly, these advanced artificial systems can achieve more efficient carbon fixation and nitrogen fixation using only sunlight, air, and water as starting materials which could outpace natural photosynthesis.^{22,23} Moreover, some more microorganisms, such as nonphotosynthetic bacteria, are also satisfying candidates for converting CO₂ into renewable carbon matter through a diverse array of metabolic pathways when the extracellular electron has been uptake.^{24–28} By being integrated with semiconducting materials into a biohybrid system, these microorganisms were endowed with the ability to harvest and utilize solar light, and utilize photogenerated electrons for high-value chemical production.^{6,29–38}

Organic semiconducting polymers are a class of excellent semiconducting materials with large π -conjugated backbones and a delocalized electronic structure which endow them with promising optical properties, electrical properties, and photo-

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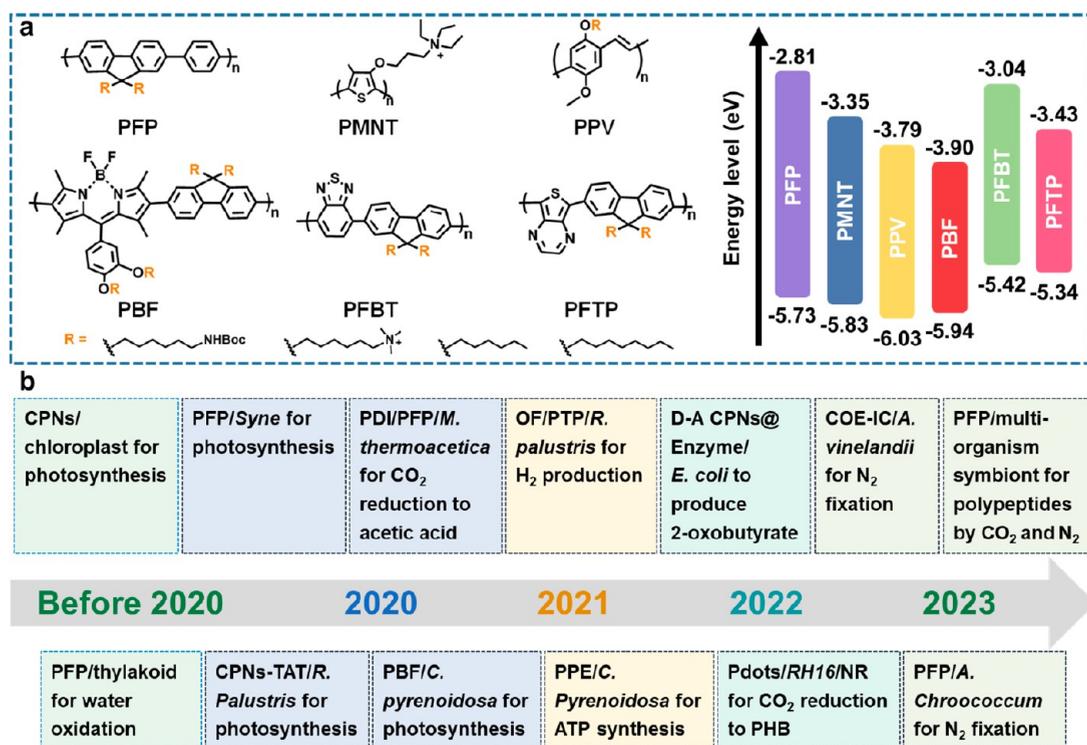


Figure 1. (a) The common organic semiconducting polymers for artificial photosynthetic biohybrid systems and the corresponding energy levels. (b) Historical development of organic semiconducting polymer-based artificial photosynthetic biohybrid systems, and the corresponding applications of biosynthesis and bioconversion.^{38,55–66}

electric conversion properties.^{39–45} As early as 2000, the Nobel Prize in Chemistry was awarded to Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa for their discovery and development of conducting polymers.⁴⁴ So semiconducting materials have attracted much attention in the field of organic light emitting devices, organic field effect transistors, and so on, which is attributed to their unique advantages including the controllable structure and tunable energy levels.^{46–52} Despite their relatively fixed main-chain structure, the organic semiconducting polymers can be modified, and a range of novel materials can be prepared by tuning the main-chain backbone structures or modifying the functional side-chain groups.⁵³ Changes in structural properties could in turn effectively alter band gap energies and the positions of the lowest unoccupied molecular orbital (LUMO) energy levels (E_{LUMO}) and the highest occupied molecular orbital (HOMO) energy levels (E_{HOMO}), further affecting optical absorption and the emission and electron transfer process.^{21,54} Some of the well investigated and applied organic semiconducting polymers have been listed in Figure 1a, namely, poly(flourene-*co*-phenylene) (PFP), poly(3-alkoxy-4-methylthiophene) (PMNT), poly(*p*-phenylenevinylene) (PPV), poly(boron-dipyrromethene-*co*-flourene) (PBF), poly(flourene benzothiadiazole) (PFBT), poly(flourene-*alt*-thienopyrazine) (PFTP), separately.^{38,55–63} These organic semiconducting polymers have been widely used in the fields of chemical, biological, and material sciences in very recent years. However, most of the semiconducting polymers are at the initial stage of constructing artificial photosynthetic biohybrid to enhance the biosynthesis and bioconversion effects (Figure 1b).^{38,55–66} These recent studies have highlighted the critical role of semiconducting polymers in regulating electron transfer and energy conversion in constructed artificial biohybrid systems, leading to the

enhancement, creation, and regulation of biological functions. Organic semiconducting polymers possess good photostability to maintain their structural integrity and optical/electronic properties under prolonged exposure to light.^{46,52,54} In addition, several strategies have been developed to enhance the photostability of organic semiconducting polymers, including the use of stabilizers or copolymers that protect against degradation, modification of the polymer with improved backbone rigidity or π -conjugated side chains that quench excited states and reduce degradation pathways, and encapsulation of the active materials. And the toxicity of organic semiconducting polymers is an important consideration when combined with biological systems.^{52,54} Results from studies suggest that many common organic semiconducting polymers are inherently nontoxic and have good biocompatibility, which was assessed mainly by the growth of bacteria in the presence of polymer materials. Moreover, charge transfer mechanisms between organic semiconducting polymers and organisms play a critical role in biohybrid systems, and different pathways for energy transfer exist depending on the specific system being studied, such as redox-active mediators or mediator-free, Förster resonance energy transfer (FRET), photon emission (bioluminescence or electroluminescence), inner/outer sphere electron transfer, etc. And the efficiency of energy or charge transfer often depends on the distance between the interacting partners. Proximity generally promotes more efficient transfer.^{55–60} Thus, the conjugated molecules are also expected to construct artificial photosynthetic biohybrid systems with biological organisms by efficient energy conversion and precise regulation of bioelectronic processes for more desirable high-value chemical products.

Here, we mainly introduce some latest achievements in organic semiconducting polymer-based artificial photosynthetic biohybrid systems for augmenting biosynthesis and bioconversion (Figure 2). The structure–activity relationship

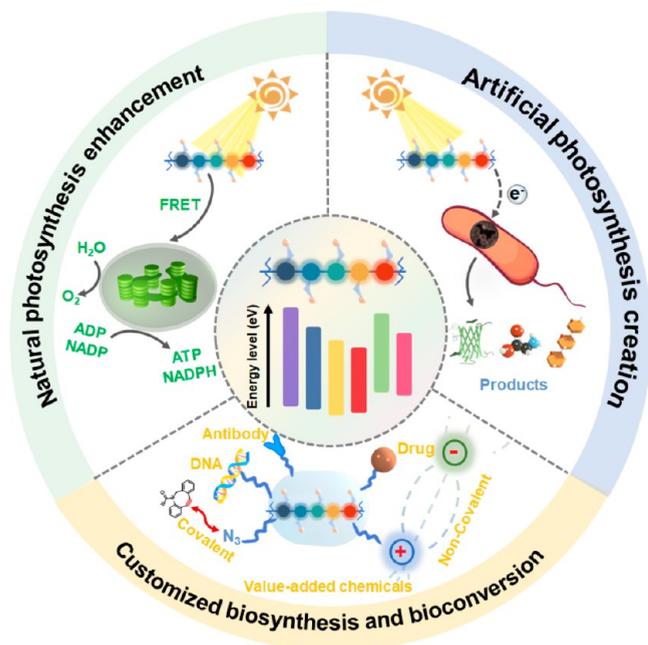


Figure 2. Schematic overview of organic semiconducting polymer-based artificial photosynthetic biohybrid systems for augmenting biosynthesis and bioconversion.

between the energy levels of the organic semiconducting polymers themselves and the biocatalysis and biosynthesis of organisms are highlighted. First, in the biohybrid containing photosynthetic organisms, the selected organic semiconducting polymers with suitable band gap energy and photophysical properties are advantageous for broadening solar light absorption, improving energy conversion, and enhancing the biosynthesis properties of photosynthetic organisms, such as cyanobacteria, algae, plants, and photoheterotrophic bacterium. Subsequently, in the biohybrid contains nonphotosynthetic organisms, the structure-dependent energy level positions of organic semiconducting polymers could determine the possible electron transfer pathways between the chemical materials and the nonphotosynthetic organisms, which mean the organic semiconducting polymers as electron donors could transfer the photogenerated electron to organisms as electron acceptors. The biohybrids consisting of *Moorella thermoacetica* (*M. thermoacetica*),⁶³ *Sporomusa ovata* (*S. ovata*), and others can use the direct or indirect electron transfer process to realize CO₂ fixation, nitrogen (N₂) fixation, and hydrogen (H₂) production to convert into value-added chemicals and fuels under sunlight irradiation.⁶⁰ Finally, organic semiconducting polymer-based nanoparticles could be further surface modified to customize the biological functional applications of artificial photosynthetic biohybrid systems. The advantages in tunability and structural variability of polymer materials systems are also further illustrated and expanded by learning from the corresponding inorganic materials systems in recent years. Looking ahead, we propose the potential of artificial photosynthetic biohybrid systems enabled by organic semiconducting polymers for enhanced

energy conversion efficiency and product selectivity and also suggest some considering methods and techniques for further practical applications in the future.

2. ENHANCEMENT OF NATURAL PHOTOSYNTHETIC EFFICIENCY

As the most abundant and sustainable source, enhancing the conversion and utilization of solar energy will play a role in the photosynthesis of photosynthetic organisms.^{21,67–70} Photosynthesis is the process that occurs over a wide range of solar light wavelengths, by which plants, algae, and some bacteria convert solar energy into chemical energy. However, the absorption spectra of natural light-absorbing species are limited to certain regions of the absorption spectrum because most photosynthetic pigments absorb light most efficiently at specific wavelengths (Figure 3a).²¹ The two main types of pigments used in photosynthesis are chlorophylls and carotenoids. Chlorophyll a is the primary pigment responsible for capturing light energy in photosynthesis with an absorption peak at around 680 nm. Chlorophyll b, another chlorophyll pigment, has a similar structure and absorbs light most efficiently at around 435 nm. Carotenoids are another pigment found in photosynthetic organisms that help protect against damage from excess light with a blue-green absorption range of 450–500 nm. Other natural light-absorbing species include phycobilins, which are pigments found in certain types of algae and cyanobacteria. Phycobilins absorb light most efficiently in the blue- and red-violet regions of the spectrum, between 450 and 650 nm. Optimizing the wavelength of the light source and expanding the photosynthetically active radiation (PAR) spectrum will artificially improve the efficiency of natural photosynthesis. Under sunlight, carbon dioxide and water can be converted into carbohydrates and oxygen by photosynthetic organisms, such as cyanobacteria, algae, and green plants.^{71,72} However, the photosynthetic efficiency in natural conditions is limited by around 1% energy conversion efficiency, due to over half of the sunlight not utilization for the photosynthesis process.²¹

As the critical organelles in photosynthesis, natural chloroplasts were used to design hybrid systems by coupling with light-harvesting materials for much available light.^{73,74} Here we can find that the regulation of the molecular structure then affects the energy levels which is crucial for the optical performance and finally for a practical hybrid photosynthesis system. Wang et al. constructed a bio-optical hybrid photosynthesis system by reforming natural chloroplast with conjugated polymer nanoparticles (CPNs).⁵⁶ Two types of conjugated polymers, PFP and PFBT, were chosen to obtain PFP-NPs and PFBT-NPs by rapidly coprecipitating with poly(styrene-co-maleic anhydride) (PSMA) (Figure 3b). The backbone structure of polymers containing fluorene units with different aromatic groups determines the location of the energy level, and the unique energy level makes sure the optical band gap is suitable for the outstanding performance of the light absorption and light emission of CPNs (Figure 3c,f). Specifically, ultraviolet (UV) light as photosynthetically inefficient radiation (PIR) usually could not be used in a chloroplast, and the PFP-NPs with a broad bandgap (~2.92 eV) could convert this part of UV-light to blue emission, which overlays well with the absorption of chloroplast. The PFBT-NPs with a narrow bandgap (~2.38 eV) could transform the light at 300–550 nm to green emission. Then much more light could be used for plant photosynthesis with the help of surface-

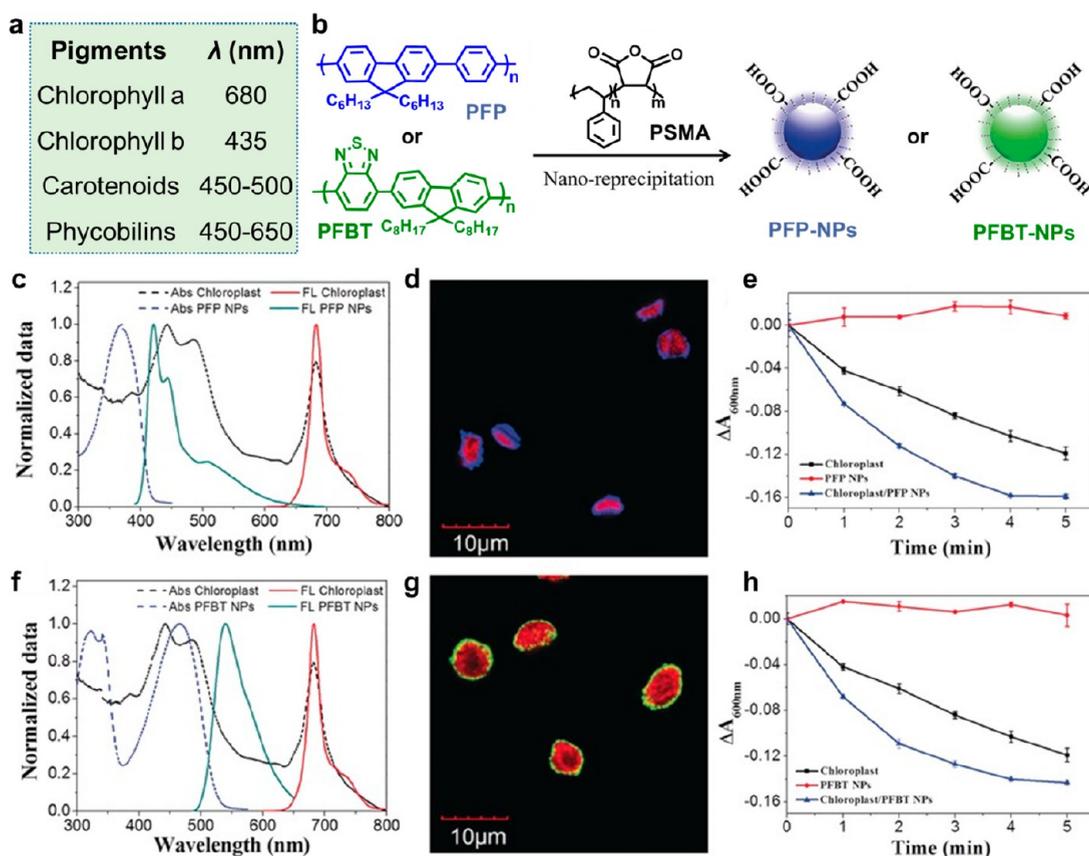


Figure 3. (a) Natural light-absorbing species pigments in photosynthetic units and the related specific wavelengths. (b) The preparation of CPNs by the nanoprecipitation method with PSMA. The optical spectra of (c) PFP-NPs, (f) PFBT-NPs, and chloroplasts. The confocal images of (d) chloroplast/PFP-NPs complexes and (g) chloroplast/PFBT-NPs complexes. The DCPIP reduction assay of (e) chloroplast/PFP-NPs complexes and (h) chloroplast/PFBT-NPs complexes upon irradiation for 5 min. Reprinted with permission from ref 56. Copyright 2017 Wiley-VCH.

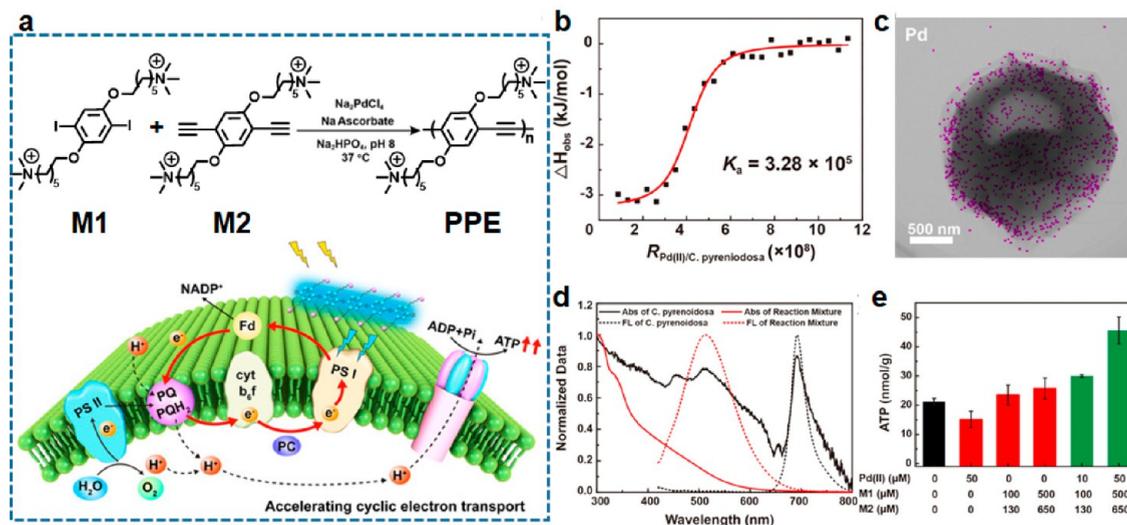


Figure 4. (a) In situ Sonagashira polymerization system for photoactive PPE by the bio-Pd catalysts on *C. pyrenoidosa* surface. (b) The isothermal titration microcalorimetry (ITC) curve by titrating palladium ion into *C. pyrenoidosa*. (c) The EDS map of Pd nanoparticles on the *C. pyrenoidosa* surface. (d) The normalized UV/vis and fluorescence spectra of *C. pyrenoidosa* and photoactive PPE on cell surfaces. (e) Enhanced ATP synthesis under light irradiation induced by polymerization. Reprinted with permission from ref 57. Copyright 2021 Wiley-VCH.

attached CPNs (Figure 3d,3g), and this is equivalent to indirectly broadening the range of light absorption capacity of chloroplasts. The Hill reaction is often used to investigate the photosynthetic activity by determining the reduction rate of 2,6-dichlorophenolindophenol (DCPIP), which could capture

the electrons transported from photosystem (PS) II to PS I during the photoreaction of chloroplasts. It turns out that the DCPIP reduction rate of the chloroplast/CPN groups is obviously quicker than that of the free chloroplast bio-optical hybrid photosynthesis system, which suggested that CPNs

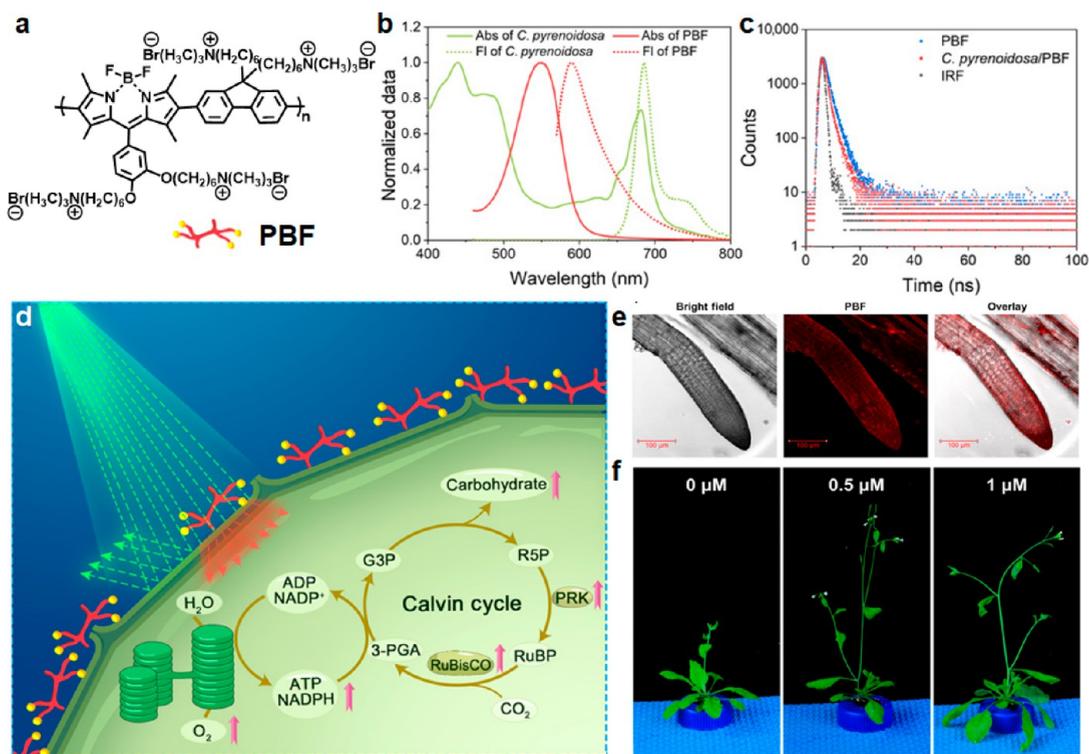


Figure 5. (a) Polymer structure of PBF. (b) Normalized optical absorption and emission spectra of PBF and *C. pyrenoidosa* ($\lambda_{\text{ex}} = 550$ and 470 nm, respectively). (c) Fluorescence decay kinetic curves of PBF and *C. pyrenoidosa*/PBF. (d) Schematic diagram of the PBF polymer assembly with *C. pyrenoidosa*. (e) CLSM images of the roots from the PBF-treated *A. thaliana*. The red color represents PBF ($\lambda_{\text{ex}} = 559$ nm; $\lambda_{\text{em}} = 580$ to 620 nm). (f) Photographs of PBF-treated *A. thaliana* with different contents of PBF in the fifth week. Reprinted with permission from ref 59. Copyright 2020 American Association for the Advancement of Science.

endow the chloroplast with better solar energy conversion for enhancing the sunlight utilization (Figure 3e,3h). Furthermore, to promote the photosynthesis efficiency of cyanobacterium by PFP, Zeng et al. have also constructed photoactive conjugated polymer-based hybrid biosystems by combining light-harvesting PFP with blue fluorescence and *Synechococcus* sp. PCC7942 (*Syne*).⁶² The suitable bandgap helps the PFP harvest more light energy from UV light and convert it into visible light for *Syne* to augment photosynthesis.

The *in situ* polymerization strategy of conjugated polymers on living cell surfaces is proposed based on cell surface engineering, in order to modulate cell activity more effectively.⁵⁷ Considering the multiple palladium (Pd) binding sites on the cell surface, such as amino, carboxyl, and phosphate groups, Pd nanoparticles with higher catalytic activity than colloid Pd could form on the bacterial surface (bio-Pd). By this cell-generated bio-Pd catalyst, Qi et al. synthesized photoactive polyphenyleneethynylene (PPE) on *Chlorella pyrenoidosa* (*C. pyrenoidosa*) surface by Pd-catalyzed Sonogashira polymerization successfully, which would favor the enhancement of biological functions (Figure 4a).⁵⁷ First, they demonstrated that the Pd^{II} ions in aqueous solution could strongly bind to *C. pyrenoidosa* electrostatically with the large binding constant ($K_a = 3.28 \times 10^5 \text{ M}^{-1}$) measured by isothermal titration microcalorimetry (ITC, Figure 4b), and then Pd⁰ species occurred by the reduction of sodium ascorbate on *C. pyrenoidosa* surface (Figure 4c). Based on the unique structural properties of PPE with monomers of 1,4-bis(oxy-hexamethylene-trimethylammonium bromide)-2,5-diiodobenzene (M1) and 1,4-bis(oxy-hexamethylene-trimethylammonium bromide)-2,5-diethynylbenzene (M2), PPE pos-

sesses superior light harvesting and blue emissions (Figure 4d). More importantly, the fluorescence emission spectra of the PPE *in situ* synthesized could match well with the absorption spectra of *C. pyrenoidosa*, which indicated that the blue light from conjugated polymers could be utilized by *C. pyrenoidosa* and improve the light harvesting efficiency of photosynthesis (Figure 4e). The 115% increase of adenosine triphosphate (ATP) production under white light irradiation for *C. pyrenoidosa* could be achieved benefited from the *in situ* synthesized PPE by enhanced light absorption and accelerated electron-transport pathways.

The proposed *in situ* polymerization strategy inside organisms inspires us that the obtained polymer molecules with suitable structures are also helpful in enhancing and regulating the biological function of the organism itself. Whether the intracellular energy transfer is intracellular or not, well-designed materials are crucial for solar-to-chemical energy conversion in photosynthetic biohybrid systems. To further artificially improve a natural photosynthetic system like higher plants by expanding the PAR spectrum, Zhou et al. prepared the PBF with a narrow bandgap of ~ 2.04 eV, a HOMO energy level of -5.94 eV, and a LUMO energy level of -3.90 eV (Figure 5a).⁵⁹ Due to the shorter optical bandgap, long wavelength light (470–650 nm) could be primarily absorbed by PBF, and it is hard to capture by *C. pyrenoidosa* (Figure 5b). The far-red fluorescence (570–800 nm) originating from PBF could completely overlap the absorption of *C. pyrenoidosa* for better light utilization. Due to the cationic quaternary ammonium groups and conjugated structure of PBF, when assembled with *C. pyrenoidosa* to be *C. pyrenoidosa*/PBF complex, the polymer could be surrounded close onto the

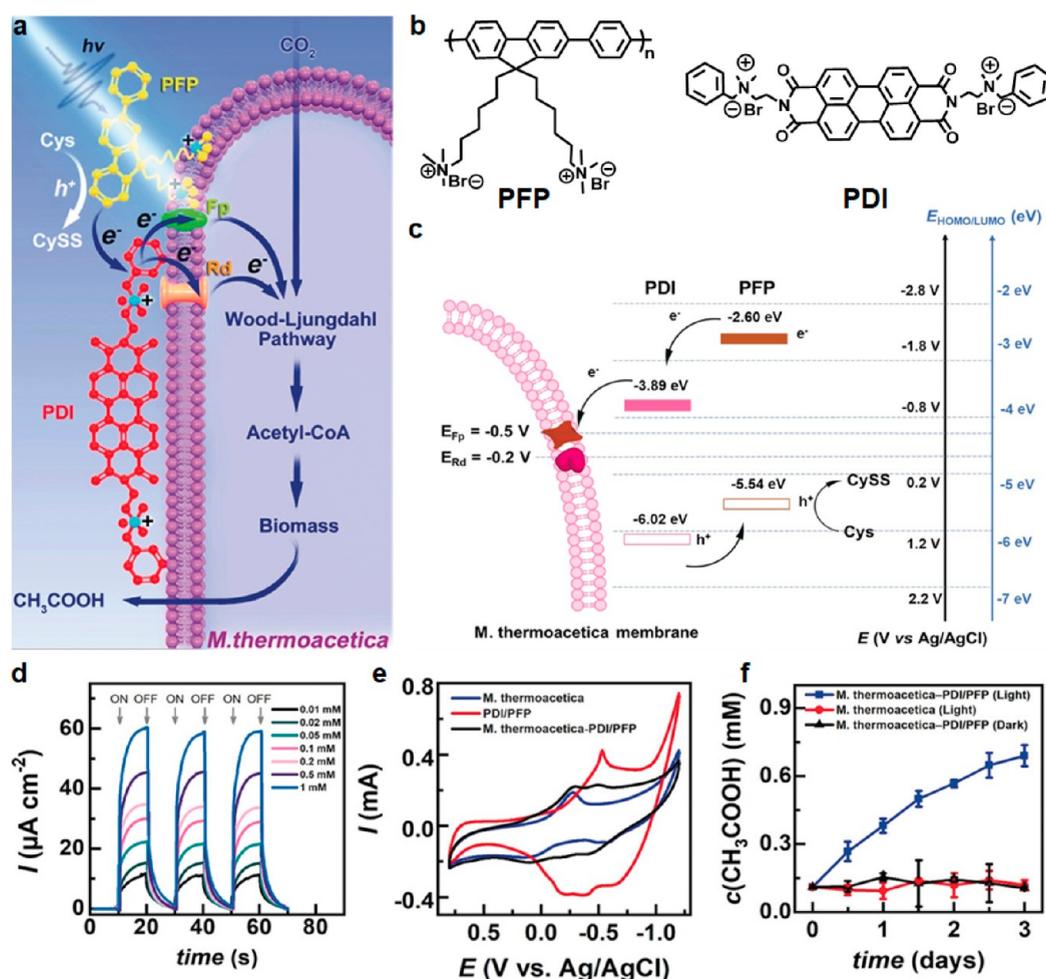


Figure 6. (a) Schematic illustration of the PDI/PFP/*M. thermoacetica* photosynthetic biohybrid system for the reduction of CO_2 to acetic acid (CH_3COOH). (b) The chemical structures of PFP and PDI. (c) Proposed electron transfer process in biohybrid systems and energy-level diagram of PDI/PFP heterojunction. (d) The photocurrent responses of PDI/PFP heterojunction electrode. The (e) cyclic voltammetry (CV) curve and (f) produced acetic acid concentrations of the PDI/PFP/*M. thermoacetica* photosynthetic biohybrid system. Reprinted with permission from ref 63. Copyright 2020 Wiley-VCH.

C. pyrenoidosa surface through electrostatic and hydrophobic interactions, which would be beneficial for the photosynthesis of *C. pyrenoidosa*. As a result, the decreased fluorescence lifetime was obtained, which suggests that the energy transfer from PBF to *C. pyrenoidosa* happened under illumination (Figure 5c). Upon the addition of PBF, the growth vigor of *C. pyrenoidosa* has been promoted noticeably under the same illumination conditions (Figure 5d). As light-dependent reaction products, oxygen (O_2), ATP, and NADPH [reduced form of nicotinamide adenine dinucleotide phosphate (NADP^+)] of the *C. pyrenoidosa*/PBF hybrid systems were increased by 120% (179.72 nmol), 76% (21.68 nmol/g), and 97% (44.00 nmol/g), respectively. Finally, the dry cell weight (DCW) of *C. pyrenoidosa* containing the optimal PBF concentration could be increased from 0.976 to 1.118 g liter $^{-1}$ compared to the bare *C. pyrenoidosa*. More importantly, the unique polymer structure makes the PBF have a far-red emission that is matched for the absorption of PS I (P700) better than that of PS II (P680). The state transition phenomenon happened, and the more excited PSI by PBF could further improve the activity of PS II (Figure 5d). In light-dependent reactions, the light absorption, utilization, and electron transfer as the behaviors of photosynthetic activity of

PS II were all notably improved by measuring the chlorophyll fluorescence parameters of ABS/RC, TRo/RC, ET_o/RC, REo/RC, ABS/CSm, TRo/CSm, ET_o/CSm, and REo/CSm from *C. pyrenoidosa*/PBF. In light-independent reactions, the activity and expression level of the RuBisCO were also prominently enhanced, and finally, the overall biomass content was increased by 16% during the cultivation with PBF. Subsequently, as a higher plant model, *Arabidopsis thaliana* (*A. thaliana*) was chosen and grown to evaluate the augmenting photosynthesis in the presence of PBF. The PBF could be readily absorbed by the roots of *A. thaliana* (Figure 5e), and speed up the progression of the mitotic cell cycle, resulting in the PBF-treated *A. thaliana* being stronger and taller. Finally, the flowering time was advanced by a week compared to the control group without PBF treatment (Figure 5f).

3. CONSTRUCTION OF ARTIFICIAL PHOTOSYNTHESIS FUNCTIONALITY

In addition to light utilization by photosynthetic organisms, nonphotosynthetic microorganisms can efficiently combine with semiconducting photosensitizers to create artificially photosynthetic biohybrid systems capable of capturing and converting solar light.^{75,76} In these biohybrid systems, the

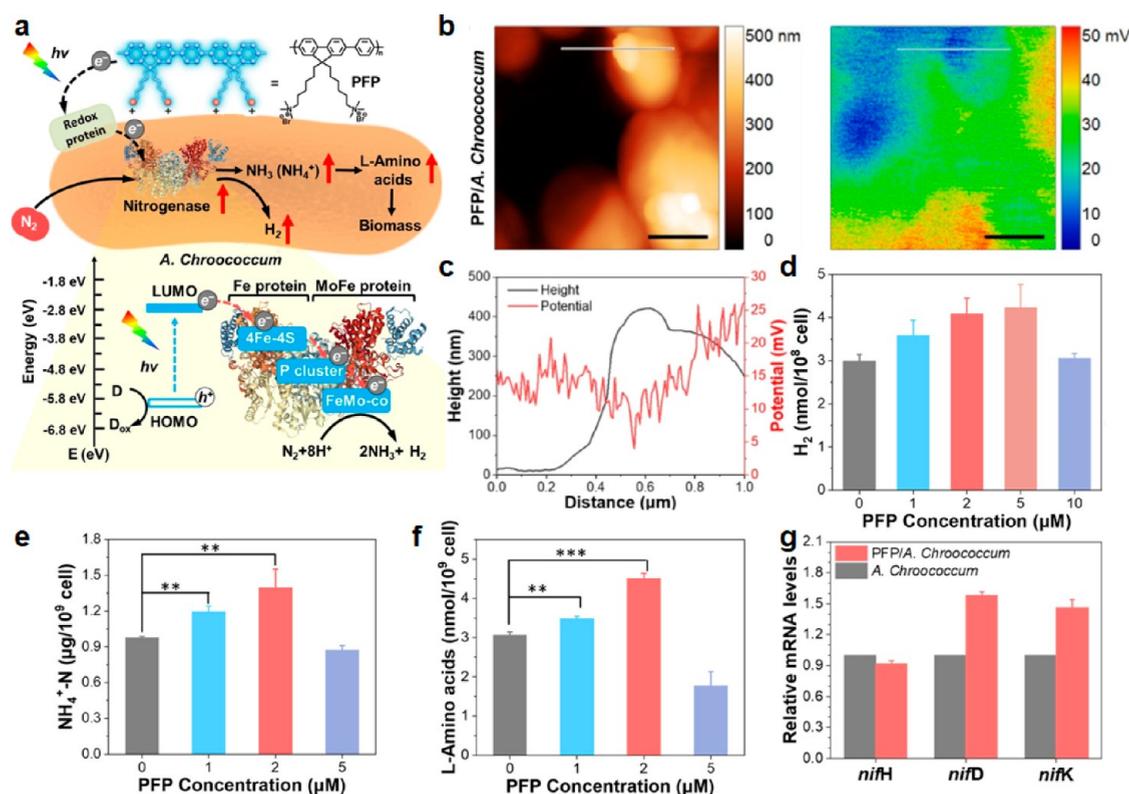


Figure 7. (a) Schematic illustration of photosynthetic hybrid biosystems consisting of PFP and *A. chroococcum*. And the transfer process of photoexcited electrons from PFP to *A. chroococcum* membrane under irradiation, and the relevant energy level diagram. (b) The height and surface potential images (Scale bar = 500 nm), and (c) representative profile along the marked lines by KPFM measurement of the PFP/*A. chroococcum* biohybrid. At different PFP concentrations, (d) the hydrogen evolution, (e) intracellular $\text{NH}_4^+\text{-N}$ content, and (f) intracellular L-amino acids content of PFP/*A. chroococcum* biohybrid systems for 48 h. Compared to the free *A. chroococcum*, (g) the relative mRNA expression level of *nifH*, *nifD*, and *nifK* associated with nitrogen fixation of the PFP/*A. chroococcum* biohybrid systems. Reprinted with permission from ref 55. Copyright 2023 Wiley-VCH.

generated photoelectrons could be converted into the metabolic pathways of microorganisms and activate biosynthesis and bioconversion. For example, Yang et al. developed pioneeringly solar-to-chemical synthesis platforms by the combination of the light-harvesting power of inorganic semiconductors with the catalytic capabilities of biology to create a biological-inorganic *M. thermoacetica*–cadmium sulfide (CdS) hybrid, which inspires more photosynthetic semi-conducting biohybrids to be exploited and applied.¹⁹ Inspired by the advantages of polymers as light-harvesters, the Wang group demonstrated a PDI/PFP/*M. thermoacetica* photosynthetic biohybrid system as solar-to-chemical synthesis platforms for CO_2 reduction into acetic acid (Figure 6a,b).⁶³ According to the calculated E_{HOMO} and E_{LUMO} of p-type PFP (−5.54 and −2.60 eV) and n-type Perylene diimide derivative (PDI) (−6.02 and −3.89 eV) (Figure 6c), the intermolecular electron transfer and charge separate process could happen effectively in the p–n heterojunction of PDI/PFP under simulated solar irradiation (Figure 6d). Moreover, the close electrostatic and hydrophobic interactions of PDI/PFP heterojunction and *M. thermoacetica* could be favorable for the photogenerated electrons transfer upon intimate bio-organic interfaces. More importantly, the redox mediators rubredoxins (Rd) and flavoproteins (Fp) on the bacterial membrane have been measured by a couple of redox peaks at −0.2 V and a reduction peak at −0.5 V (Figure 6e), which are lower than the reduction potentials of the PDI/PFP

heterojunction and ensure the sufficient driving force for the direct photoexcited-electron transfer across the bacterial membrane. Therefore, the photogenerated electrons could be induced under sunlight from illuminated PDI/PFP heterojunction with an appropriate band structure across the membrane proteins and were ultimately transformed to the Wood–Ljungdahl pathway of the nonphotosynthetic CO_2 -reducing bacterium *M. thermoacetica* for photosynthetic products toward acetic acid by biocatalytic CO_2 fixation. The rate of acetic acid production could be regulated and the overall quantum yield of 1.6% in 3 days from the PDI/PFP/*M. thermoacetica* photosynthetic biohybrid system (Figure 6f), which is comparable to the previous inorganic biohybrid system. As a landmark study, this tunable platform can easily be scaled up in synthetic biology by the replacement of chemical materials or organisms. The light-to-chemical quantum yields of light-driven chemical generation could also be regulated by matching the light absorbed with bioconversion rates and thereby improving energy conversion in these biohybrids.

The ambient N_2 fixation is the defining process of the biogeochemical nitrogen cycle and agriculture industries.⁷⁷ Constructing semiconductor-based photosynthetic biohybrid systems by integrating both natural (biotic) and artificial (abiotic) catalytic routes will enhance biological nitrogen fixation by solar-to-chemical conversion. Early in 2016, the cadmium sulfide (CdS):nitrogenase molybdenum–iron

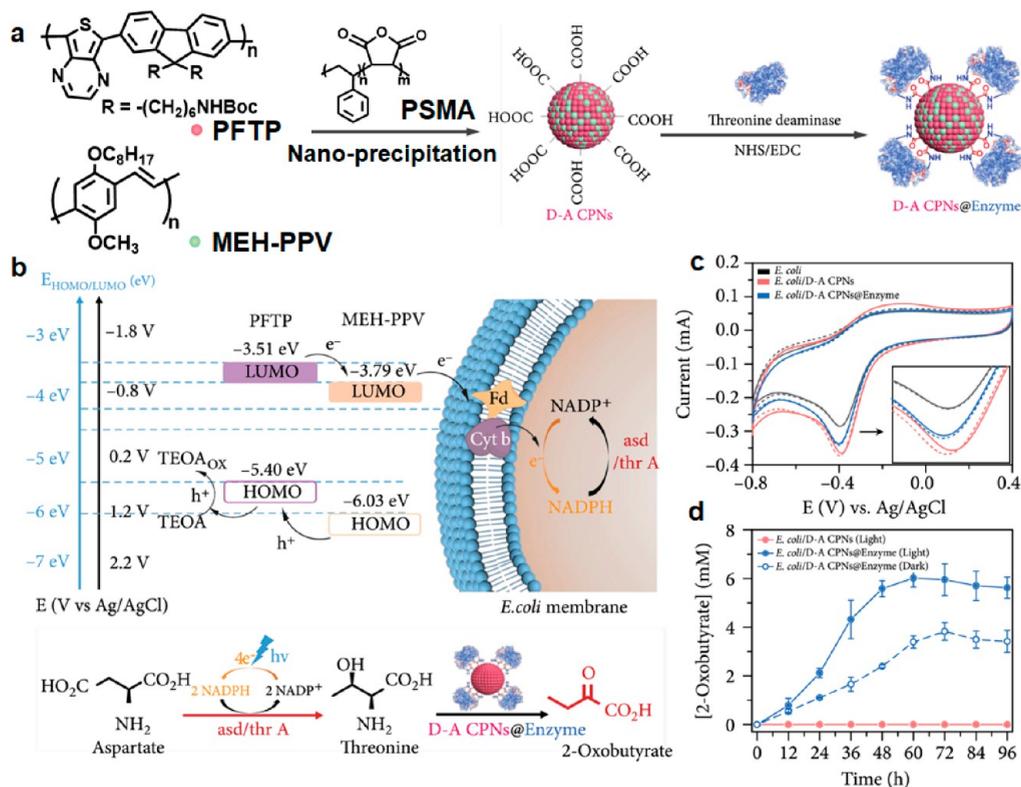


Figure 8. (a) The preparation of D-A CPNs@Enzyme by MEH-PPV, PFTP, and PSMA through nanoprecipitation and covalent interactions. (b) The electron transfer between the D-A CPNs and the bacteria. (c) CV curves of the *E. coli*, *E. coli*/D-A CPNs, and *E. coli*/D-A CPNs@Enzyme. (d) 2-Oxobutyrate concentration of the *E. coli*/D-A CPNs@Enzyme biohybrid system under illumination. Reprinted with permission from ref 60. Copyright 2022 China Association for Science and Technology.

(MoFe) protein biohybrid was designed to achieve the light-driven N_2 reduction to ammonia (NH_3). Among them, the photoexcited cadmium sulfide (CdS) nanocrystals (-0.8 V versus NHE) as light-harvesting nanomaterials could effectively drive the photogenerated electrons transfer to the nitrogenase MoFe protein (-0.31 V versus NHE).⁷⁸ Different from the isolated nitrogenase, Zeng et al. designed successfully a PFP/*A. chroococcum* photosynthetic biohybrid system by combining cationic conjugated PFP with the whole cell of nonphotosynthetic nitrogen-fixing *Azotobacter chroococcum* (*A. chroococcum*) for promoting the nitrogen fixation pathway under illumination (Figure 7a).⁵⁵ It has been demonstrated that the PFP has excellent light harvesting capability and efficient photoinduced charge separation with an optical band gap of 2.92 eV. Considering the electron mediator of Fp on the surface of bacterial cells, its reduction potential (-3.99 eV) is lower than the LUMO energy level of PFP (-2.81 eV), which would ensure the sufficient driving force for the electronic communication from PFP into *A. chroococcum* (Figure 7a). Moreover, the close interactions and good electrical conductivity in PFP/*A. chroococcum* photosynthetic biohybrid was investigated by Kelvin probe force microscopy (KPFM) (Figure 7b). The PFP aggregates have occurred on the relatively smooth surface of *A. chroococcum*, and shortened the potential difference between the PFP/*A. chroococcum* and the substrate (Figure 7c), which means the satisfying conductivity of PFP and ensures a better electron transfer process. Under light irradiation, the Fp protein on the surface of *A. chroococcum* reasonably facilitates the photoelectrons generated by PFP through the surface efficiently into bacterial cells for the biological nitrogen fixation process. Of practical relevance

is that finally the nitrogenase activity and nitrogen fixation ability of PFP/*A. chroococcum* photosynthetic biohybrid has been promoted by 37%, meanwhile, the production of hydrogen, NH_4^+-N , and L-amino acids was also increased by 260%, 44%, and 47% (Figure 7d–f). From a deep point of view, the expression levels of *nifD*, *nifK* and the proteins associated with electron transport and nitrogen fixation were upregulated significantly to achieve higher nitrogen fixation efficiency (Figure 7g). Charge transfer between semiconducting polymers and living organisms usually requires the addition of external sacrificial electron donors, such as TEOA, cysteine (Cys), and so on. It is worth noting that this system has been used without the addition of external electron sacrificial agents, as the amino acids secreted by bacteria could be used as sacrificial agents to regenerate the neutral polymer chains. The results indicate that it is significant to build the correlation between the optical energy level of PFP and the potential of redox proteins inside organisms based on the material–microbial interface of integrated materials/microorganisms. In order to develop more extensive and efficient biological nitrogen fixation systems for the future, we need to explore new avenues such as developing diversified structures of organic conjugated molecules that have broad light-harvesting performance and excellent biocompatibility. We suggest fundamental advances across the broad scientific enterprise to provide innovative options for consideration and application.

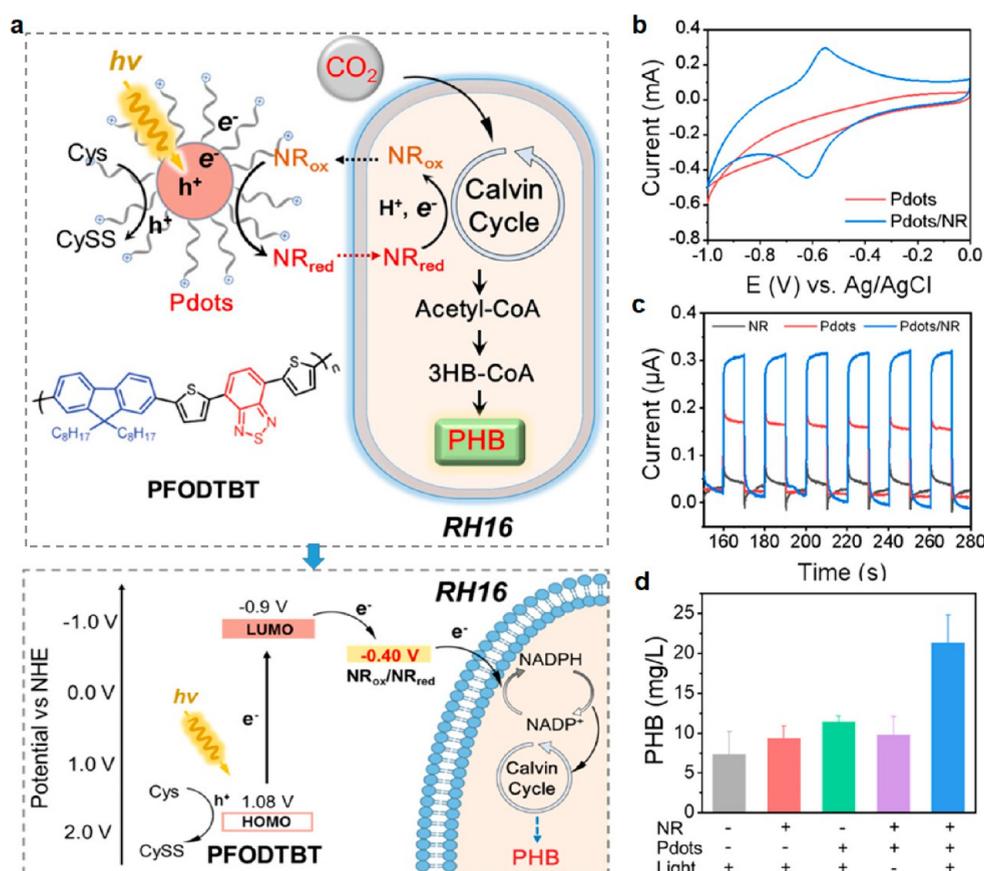


Figure 9. (a) The process of CO₂ reduction into PHB in Pdots-based transmembrane electron transport photosynthetic biohybrid system (RH16/NR/Pdots), and the schematic diagram of transmembrane electron transport from the photosynthetic biohybrid system. The (b) CV curves and (c) corresponding photocurrent signals of NR/Pdots under light illumination. (d) PHB production of the photosynthetic biohybrid systems by CO₂ reduction under light illumination. Reprinted with permission from ref 58. Copyright 2023 American Chemical Society.

4. CUSTOMIZED PHOTOSYNTHETIC SYNTHESIS OF VALUE-ADDED CHEMICALS

Compared with the organic semiconducting polymers, many research advances have also demonstrated excellent optoelectronic capabilities and good biocompatibility of the CPNs with the advantages of both convenient synthesis procedures and simple separation steps. More importantly, attributed to the large surface of nanoparticles and versatile surface modification strategies, many functional chemical groups or specific biological agents (such as antibodies, siRNA, and enzymes) could be modified actively on the CPNs for customization of biological functions with value-added chemicals.⁴² Integrating the optoelectronic, biological, and chemical catalysis, Yu et al. proposed a photosynthetic biohybrid system based on semiconductor-microorganism by combining *Escherichia coli* (*E. coli*) with threonine deaminase-modified donor-acceptor conjugated polymer nanoparticles (D-A CPNs@Enzyme) for transforming renewable carbon sources into more valuable chemicals (Figure 8a).⁶⁰ In this work, the light-harvesting D-A CPNs were constructed by electron donor poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and electron acceptor PFTP through nanoprecipitation, and then the threonine deaminase was modified with the surface of D-A CPNs through covalent interactions to construct D-A CPNs@Enzyme. The HOMO-LUMO energy levels of the two conjugated polymers could be calculated by ultraviolet photoelectron spectra (UPS) and UV-vis spectra. And we find

that the LUMO energy level of MEH-PPV (−3.79 eV) was lower than that of PFTP (−3.51 eV) which gave enough driving force to transfer the photogenerated electrons of PFTP to MEH-PPV (Figure 8b). Meanwhile, triethanolamine (TEOA) could be oxidized by holes at the HOMO energy levels to ensure efficient separation of electrons and holes. Then the shorter fluorescence lifetime of the MEH-PPV/PFTP complex (1.23 ns) could be observed at 655 nm than that of PFTP (1.83 ns). A similar phenomenon happens on the D-A CPNs prepared by nanoprecipitation due to the beneficial donor-acceptor structure. Subsequently, the reasonable design of the D-A type of MEH-PPV/PFTP also helps D-A CPNs obtain a higher photocurrent than only MEH-PPV NPs or PFTP NPs. Thus, due to the more positive reduction potential (Figure 8b), the redox mediator Fp and *Cytochrome b* (*Cyt b*) on the bacterial membrane could effectively obtain the photogenerated electrons from D-A CPNs to further regenerate NADPH in the cytoplasmic media for the production of threonine. The CV results showed that *E. coli* have a reduction peak in the range of −0.2 ~ −0.6 V of conjectural Fp and *Cyt b* (Figure 8c). The improved electron transfer between D-A CPNs with bacteria resulted in the enhanced reduction current of *E. coli*/D-A CPNs than that of free *E. coli*. Finally, under light irradiation, the cumulative threonine production of *E. coli*/D-A CPNs has significantly increased by 37% than the free *E. coli* (11.3 mM vs 7.8 mM) after 4 days (Figure 8d). The yield of 2-oxobutyrates of about

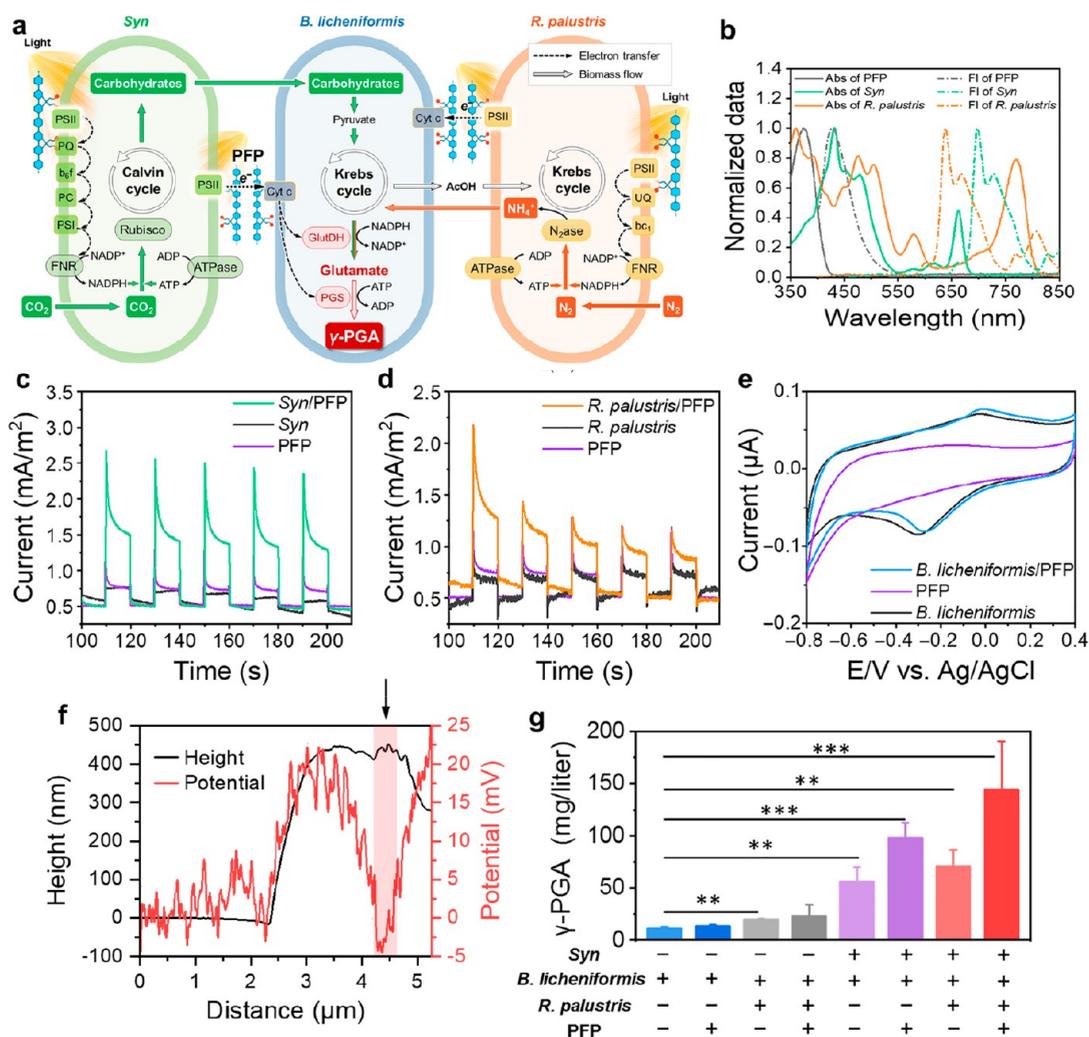


Figure 10. (a) Proposed electron and substance transfer pathways in the symbiont of *Syn*/*R. palustris*/*B. licheniformis*/PFP. The blue molecule cartoons represent the polymer structure of PFP. (b) Normalized UV-vis absorption spectra and fluorescence spectra of PFP, *Syn*, and *R. palustris*. The photocurrent responses of (c) *Syn*/PFP and (d) *R. palustris*/PFP. (e) Cyclic voltammetry of *B. licheniformis*/PFP. (f) The height and surface potential profile at the marked lines by KPFM of the *Syn*/*R. palustris*/*B. licheniformis*/PFP biohybrid. (g) Synthesis production of γ -PGA in different logic synthesis circuits over 10 days. Reprinted with permission from ref 38. Copyright 2023 American Association for the Advancement of Science.

10 mM was also increased by 58% in comparison to that in the dark after 3 consecutive days.

Apart from the direct membrane-mediated electron transport, some electron mediators with compatible redox potential, such as ferredoxin (Fd), Fp, Rd, riboflavin, and neutral red (NR), were used to help the transmembrane electron transfer between chemical materials with microorganisms in photosynthetic biohybrid systems for the following biosynthesis and bioconversion.⁷⁹ Recently, Yu et al. also showed an organic semiconductor-microbial photosynthetic biohybrid system based on transmembrane electron transport to deliver the electrons from conjugated polymer dots (Pdots) to the microbe of *Ralstonia eutropha* H16 (*RH16*) with the NR as the electron shuttle (Figure 9a).⁵⁸ The appropriate energy level relationship in the *RH16*/NR/Pdots biohybrid system favors the final biosynthesis to start the Calvin cycle to fix CO_2 and produce poly-3-hydroxybutyrate (PHB), which is an intracellular high polyester to be used as a degradable plastic. First, to synthesize the PFODTBT Pdots, the hydrophobic conjugated polymers PFODTBT, triblock copolymer poly-

(*N,N*-dimethylamino ethyl methacrylate)-*B*-poly(9,9-*N*-dihexyl-2,7-fluorene)-*B*-poly(*N,N*-dimethylamino ethyl methacrylate), and polystyrene grafting with carboxyl-group-functionalized ethylene oxide was mixed through the typical nanoprecipitation methods. They calculated the optical band gap of 1.98 eV for the uniform PFODTBT Pdots by using UV-vis spectra and CV curve, with a HOMO energy level of 1.08 V vs normal hydrogen electrode (NHE), and a LUMO energy level of -0.90 V vs NHE (Figure 9a). Considering the more negative reduction potential of Pdots than that of NR (-0.4 V vs NHE) from the CV curves (Figure 9b), electron transfer from Pdots to NR could be easily achieved, and the corresponding anode photocurrent was increased subsequently of the Pdots/NR (Figure 9c). More importantly, the photogenerated electrons could be transferred to the inside of bacteria carried by the reduced NR to further improve the intracellular NADPH for converting CO_2 into PHB. Thus, the intracellular NADPH/NADP⁺ ratio of *RH16* was significantly increased to 1.25. And the reduced PHB concentration from the biohybrid system of *RH16*/NR/Pdots was 21.3 ± 3.8 mg/

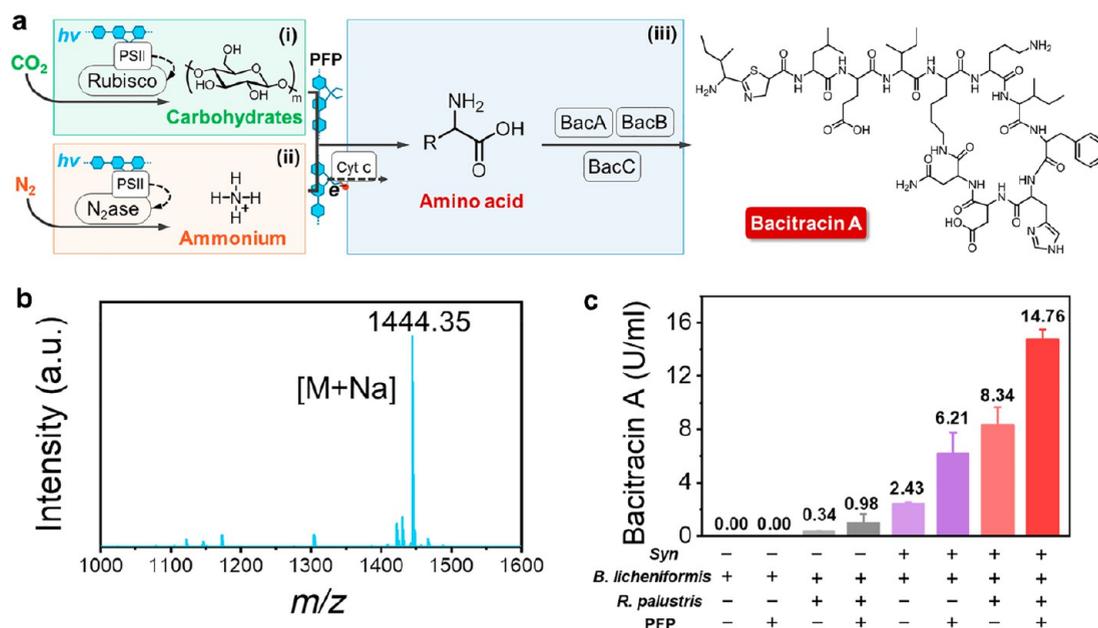


Figure 11. (a) Proposed bacitracin A biosynthesis pathway. The blue molecule cartoons represent the polymer structure of PFP. (b) Mass spectrometry of bacitracin A and (c) its synthetic production in different logic synthesis circuits over 10 days by the *Syn/R. palustris/B. licheniformis*/PFP biohybrid. Reprinted with permission from ref 38. Copyright 2023 American Association for the Advancement of Science.

L after the light–dark cycle for 48 h, 192% larger than that of the free *RH16* (Figure 9d). The study revealed that the well-designed conjugated organic semiconducting Pdots are also firmly beneficial to help transmembrane electron transport through rational energy level and the suitable electron shuttle to achieve efficient synthesis of high-value natural products.

Usually, compared to the single photosynthetic or non-photosynthetic species, the multiorganism symbiont will have crucial implications for the customization of biological functions with value-added chemicals by the intimate electronic and substance communications between microorganism species. However, the low efficiency of substance and energy transfer limits the prospecting of broad applications of biological symbiosis systems. Here Yu et al. and his workers designed and engineered an artificial photosynthetic symbiont of *Syn/R. palustris/B. licheniformis*/PFP by connecting multi-organisms with conducting polymers to fix CO₂ and N₂ for solar-powered biosynthesis into high-value products by optimizing the photosynthetic process and photoelectron production (Figure 10a).³⁸ Benefiting from the suitable bandgap and good conductivity of conducting polymers, the PFP showed excellent photoelectric performance and electron transfer capability in biohybrid systems compared to bare organisms. The light emission of the PFP from 400 to 550 nm could be overlapped with the light absorption of *Synechocystis sp. PCC6803* (*Syn*) and *Rhodospseudomonas palustris* (*R. palustris*) as photosynthetic units (Figure 10b), which could be demonstrated by the notably enhanced fluorescence of *Syn*/PFP and *R. palustris*/PFP compare to the free *Syn* or *R. palustris*. Subsequently, under light illumination, the enhanced photocurrent suggested that the photoelectrons of *Syn*/PFP and *R. palustris*/PFP could be generated more and transfer faster between PFP and the microbial system (Figure 10c,d), which resulted in the improvement of photosynthesis and the promotion of biomass conversion. The *Cyt c* on the surface of *Bacillus licheniformis* (*B. licheniformis*) as electron transport redox proteins with stable redox peaks at -0.25 and 0.05 V (vs

Ag/AgCl) could accept the electron from *Syn* and *R. palustris* under white light illumination. Another evidence is that the charge transfer resistance (R_{ct}) of the *Syn*/PFP electrode, *B. licheniformis*/PFP, and *R. palustris*/PFP electrode were all decreased (Figure 10e). Moreover, the KPFM measurements of the *Syn/R. palustris/B. licheniformis*/PFP biohybrids were also carried out to obtain the smaller potential difference between the samples and the mica substrate than that of free *Syn/R. palustris/B. licheniformis* (5 mV vs 22 mV) (Figure 10f), which confirms the effective bioconductivity from PFP and favors the direct interspecific electron transfer. The excellent conductivity enables the PFP to promote direct interspecific electron transfer among the three organisms. And a conducting network could be formed to shorten the distance and increase the substance communication in the microbial system. Then the increased carbohydrate production from *Syn* and the promoted NH₄⁺ content from *R. palustris* as the carbon and nitrogen source with the presence of PFP will favor efficiently synthesis of the γ -polyglutamic acid (γ -PGA) in multiorganism symbiont mimic system (144.2 mg/Liter) than the *B. licheniformis* alone (10.7 mg/Liter) (Figure 10g).

Based on the programmable biosynthesis strategy above, more high-value products, such as functional peptides and proteins, could be customized and produced by adjusting the microbial synthesis module in the artificial symbiont. Interestingly, the *B. licheniformis* CICC 23642 could replace the origin *B. licheniformis* as the synthesis module to construct the new multiorganism symbiont mimic system of *Syn/R. palustris/B. licheniformis*/PFP for the production of bacitracin A with a mass of 1444.35 (Figure 11a,b). As expected, the synthesis production of *Syn/R. palustris/B. licheniformis*/PFP was increased to 14.76 U/ml under sunlight (Figure 11c), which was 77% higher than the control group without the addition of PFP, which further successfully validated the generalizability of the symbiotic strategy. In a multiorganism symbiont mimic system, the photoelectron transfer upon the material-microbial interface and the substance communications

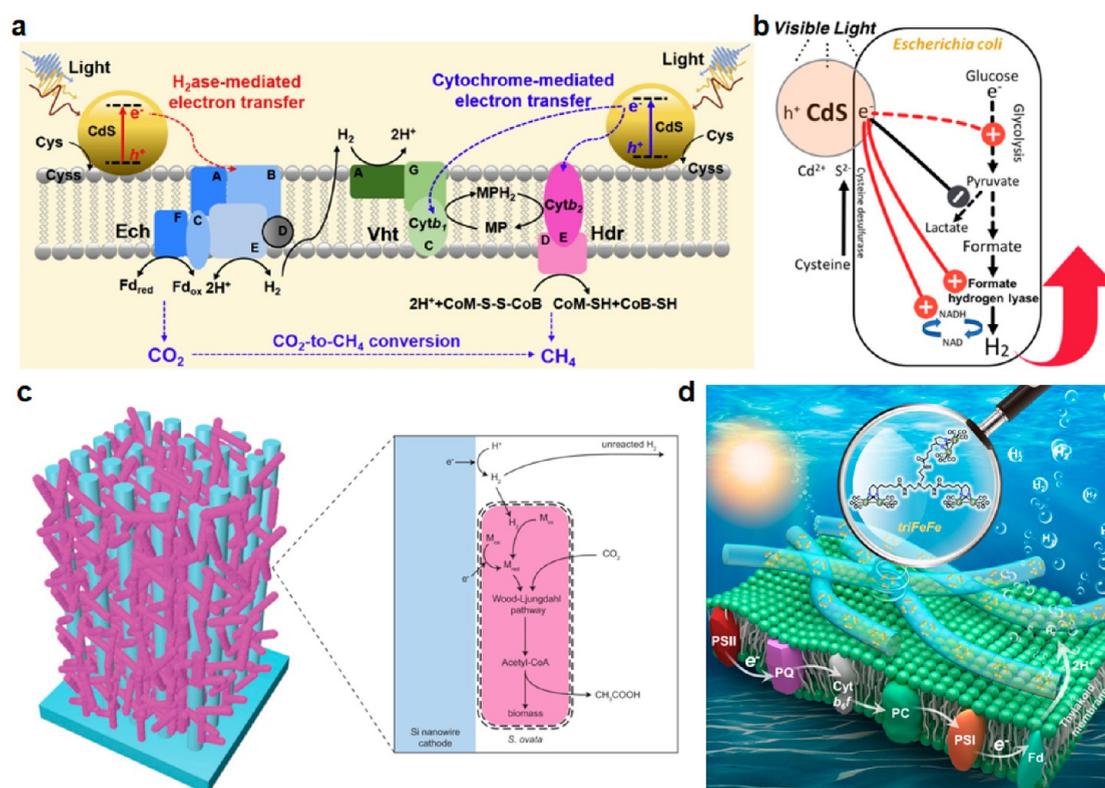


Figure 12. (a) Diagrammatic illustrations of the *M. barkeri*-CdS biohybrid. Reproduced with permission from ref 85. Copyright 2019 Elsevier. (b) Illustration of whole-cell *E. coli*-CdS hybrid system. Reproduced with permission from ref 87. Copyright 2017 Wiley-VCH. (c) Schematic of the nanowire-bacteria hybrid. Reproduced with permission from ref 33. Copyright 2020 Elsevier. (d) Illustration of the self-assembled protein hybrid nanofibrils based on [FeFe]-hydrogenase mimics. Reproduced with permission from ref 20. Copyright 2023 Chinese Chemical Society.

between species could be improved by conducting polymer of PFP on demand for programmable biosynthesis and bioproduction applications. This study could also provide a general platform by regulating the organisms precisely and finely to customize more variety of products and achieve higher production efficiency for solar-powered value-added chemicals.

5. CONCLUSIONS AND PERSPECTIVES

Here the major advances of organic semiconducting polymers for the coupling with the organisms into artificial photosynthetic biohybrid systems began this Perspective and provide an account of the combining advantages between the efficient optoelectrical properties of chemical materials and the excellent biocatalytic capacity of biological organisms. The biohybrid could enhance the natural photosynthetic efficiency of photosynthetic organisms by organic semiconducting polymers. Nonphotosynthetic organisms can also be functionalized to have artificial photosynthesis capability in the biohybrid of organic semiconducting polymers. More importantly, customized photosynthetic synthesis of artificial photosynthetic biohybrid systems could be realized for value-added chemicals by organic semiconducting polymer-based nanoparticles. Although the significant approaches and advances for solar energy conversion have been demonstrated to be versatile, sustainable, and distinct in this field of research, the state-of-the-art systems of biosynthesis and bioconversion are required to further develop and meet the needs of practical applications for foods, pharmaceuticals, and fuels in future.

Although inorganic semiconducting materials have heavy-metal cytotoxicity and phototoxicity are unavoidable (e.g., Cr, Cd, and so on), high-performance optical and electrical properties make them also be used in the design of biohybrid systems for solar-driven H_2 evolution, CO_2 reduction, and N_2 fixation.^{6,32,80–83} Compared with organic semiconducting materials, inorganic semiconducting materials also have tunable energy levels and regulated electron transfer in many aspects. And the applications of biohybrid systems based on inorganic semiconducting materials could, in turn, inspire and support the development of biohybrid systems based on organic semiconducting materials. As one of the value-added chemicals and an energy carrier, methane (CH_4) could also be converted from the catalyzing CO_2 reduction via the whole-cell microorganisms such as methanogens, which could address the issue of selectivity and oxygen intolerance of chemical catalysts and biocatalysts.⁸⁴ He et al. constructed the *Methanosarcina barkeri* (*M. barkeri*)-CdS biohybrid by combining the semiconducting nanoparticles with nonphototrophic methanogens to achieve CO_2 -to- CH_4 conversion (Figure 12a).⁸⁵ Owing to the direct band gap (E_g) of 2.69 eV for *M. barkeri*-CdS biohybrid and the LUMO (-0.63 V vs NHE) of CdS nanoparticles, the CO_2 reduction to CH_4 was feasible thermodynamically. Under light irradiation, the photoelectrons of solar-driven self-replicating biocatalytic system could be transferred via H_2 ases-mediated or cytochromes-mediated pathways possibly from the photoactive CdS nanoparticles to the out-membrane proteins of *M. barkeri* to achieve CO_2 -to- CH_4 conversion with a quantum efficiency of 0.34%. Besides the CO_2 fixation to multicarbon products and the N_2

reduction, microbial H₂ production is still significant to pay specific biological catalytic power in photosynthetic biohybrid systems. Compared to the photo(electro)catalytic water splitting in recent years,⁸⁶ biological hydrogen production has also attracted great attention due to the mild reaction conditions, the use of no electron transfer agents, and the highly specific biological catalytic power. As the most well-studied microorganism, *E. coli* could produce bio-H₂ by endogenous [Ni–Fe]-hydrogenase under dark fermentation without any genetic engineering. Wong and his co-workers have reported a whole-cell *E. coli*–CdS hybrid system for enhanced biological hydrogen production by natural sunlight.^{32,87} More importantly, the *E. coli*–CdS hybrid system with excellent light-harvesting ability exhibited increased hydrogen production, which is better than other photoheterotrophic bacteria. Apart from the semiconducting nanoparticles, the light-absorbing Si nanowire arrays could also capture light for efficient reducing equivalents (H₂) to *Sporomusa ovata* (*S. ovata*) as nanowire-bacteria hybrid for solar CO₂ reduction into acetic acid under mild conditions (Figure 12c).³³ In addition to the previously biological whole-cell biohybrids, the artificial photosynthetic biohybrid system-based enzymes or enzyme mimics have also attracted much attention in the field of synthetic biology. Chen and co-workers reported the self-assembled protein hybrid nanofibrils by incorporating the [FeFe]–hydrogenase mimics and uniform hybrid protein nanofibrils for efficient H₂ generation performance (Figure 12d).²⁰ The lower reduction peak signal at –0.8 V (versus Ag/AgCl) of the hybrid protein nanofibrils favors the interface electron transfer from the photosensitizer of Ru(bpy)₃Cl₂ to the [FeFe]–hydrogenase mimics inside the nanofibrils for proton reduction to hydrogen. In view of the above examples from inorganic semiconducting materials, it is worth learning that more organic semiconducting polymer-based artificial photosynthetic biohybrid systems need to be developed for the CO₂-to-CH₄ conversion and the H₂ evolution. Also, the organic semiconducting polymers could be designed to be the ordered electrode material systems and advanced enzymes/enzyme mimics hybrid, and these works provide the possibility for the future of based on organic semiconducting polymers.¹⁵

Some of the typical organic semiconducting polymers have been used as excellent candidates as desirable light-harvesters for biohybrids by effective light harvesting, promoted photoelectron separation, and accelerated electron transfer. More semiconducting polymers, such as poly(3-hexylthiophene) (P3HT), polypyrrole (Ppy), and so on, need to be further developed and used for artificial photosynthetic biohybrid systems in the future, and more challenges need to be met. For most of the phototrophs, for example, cyanobacteria, algae, plants, and photoheterotrophic bacterium, when augmenting photosynthetic conversion efficiency using synthetic light-harvesting polymer materials as light absorbers, expanding the solar spectrum utilization, accelerating the electron transfer, and improving photosynthetic efficiency are closely related to the optical absorption and emission wavelengths of organic semiconducting materials. For nonphotosynthetic organisms, such as CO₂-fixing bacteria, N₂-fixing bacteria, and so on, the appropriate E_{LUMO} and E_{HOMO} favor the energy harvesting, photogenerated charge separation, photoelectrons transport from the LUMO of the polymer into metabolic pathways by mediated or unmediated electron transfer modes between material and microorganism. According to the structure–

property–function relationships, the molecular backbone structures of polymers are the intrinsic property of the material, and the main optical and electronic performance is the extrinsic property of the material and is determined with the HOMO–LUMO energy levels as the key properties of the material. It is therefore proposed that novel organic semiconducting polymers can be reasonably designed and synthesized with effectively customized and subtly tuned absorption and energy levels by modifying the molecular structures of the main and side chains. For example, increasing the effective conjugation length and introducing heteroatoms such as N, O, and Se will significantly benefit the extent of the absorption region and the red-shifted or blue-shifted absorption peak. The excellent harvesting ability of green light and the optically matched far-red light fluorescence performance of polymer materials with excellent optoelectronic and physicochemical properties would enhance the light harvesting of plant photosynthesis to further increase agricultural productivity. The selection of the donor and acceptor units with matching energy levels is an effective strategy for the molecular design and synthesis of donor–acceptor (D–A) heterojunction type conjugated conducting polymers for the narrow bandgap, the strong absorption in the long wavelength region, and enhanced charge transport. The introduction of alkyl, aryl, or other substituents could result in fine-tuning of the optical and electronic properties. Moreover, the desired polymers by in situ catalytic polymerization, which have a suitable energy level structure and corresponding photoelectrochemical properties, are more relevant for biocatalytic processes. Simultaneously the multifunctional and novel CPNs as promising candidates deserve to be further designed and developed with the modification of the specific functional groups or specific functional elements (peptide, protein, enzyme, etc.) for the high fluorescence brightness, efficient electron transfer, and the appended catalytic property. As a crucial part of artificial photosynthetic biohybrid systems, all of the above factors make it useful to design reasonably new organic semiconducting polymers for constructing novel biohybrids and achieving great feats of solar-to-chemical biosynthesis and bioconversion.

On the other hand, given the synergistic relationship between light, organisms, and semiconducting materials, suitable organisms should be selected to accept the photo-generated electron to suppress the recombination of photo-induced charge carriers in the photoirradiated conjugated polymers. And in the fields of synthetic biology, genetic engineering technologies, and the De novo protein design will help the construction of efficient metabolic pathways, the optimization of custom electron transport chains, and the upregulating of the protein expression levels for the higher biosynthesis efficiency of biohybrid complexes.²⁴⁸⁸ More tools on the biological aspect should be applied to the in-depth mechanism study, such as functional gene analysis, transcriptional analysis, cryo-electron microscopy, and proteomic and metabolomic methodologies, to elucidate the underlying mechanisms of molecular pathways of electron uptake.^{25,89} The solar-driven biological symbiosis system of symbiotic algae and microorganisms will go beyond natural synthesis limitations for the revolutionary development of agricultural and food industries.

More importantly, based on the relationship of structure, interface, and energy level, there are many points deserving notice for the assembly process of the photosynthetic

semiconducting biohybrids, such as the reasonable design of organic semiconducting polymers, the match mediator of biotic/abiotic interface, the thorough understanding of extracellular electron transfer, and so on. Side chain optimization by the addition of cationic quaternary ammonium groups and anionic carboxyl groups endows the conjugated conducting polymers with sufficient water solubility and assembled interactions with the cell membrane of microorganisms for further substance communication and electron transfer. More advanced and new characterization techniques (e.g., KPFM to characterize the electronic properties of organic semiconducting polymers and to determine the local electronic structure at the nanoscale, X-ray synchrotron techniques to study the chemical and electronic structure of organic semiconducting polymers, scanning probe microscopy to image the surface topography and to study the electronic behavior of polymer materials, infrared and Raman spectroscopy to identify functional groups and to study the vibrational modes of organic semiconducting polymers) have also been developed with particular success to follow the photoelectron transfer and the catalytic reaction process.^{38,55,90,91} Moreover, machine learning (ML) and artificial intelligence (AI) have a potential role in predicting polymer properties and designing polymers for desired properties by combining high-throughput synthesis experimentation.^{92–96} Meanwhile, the rapidly growing field of artificial intelligence will explore interactions between novel nanophotocatalysts and microorganisms and further benefit the improved performance of the organic semiconducting polymers based artificial photosynthetic biohybrid systems to inverse design the workable polymers for matching with the appropriate microorganisms. The insights would help to fully and conceivably provide feedback to guide more appropriate polymer synthesis for better electron flow pathways between polymers and organisms.

Nowadays, the performance, affordability, and sustainability of sunlight-powered photosynthetic biohybrid systems would support them to be further industrialized efficiently and effectively. It will be extremely interesting to ensure a more sustainable bright future for biosynthesis and bioconversion based on biohybrids. The intersection of materials science, semiconductor technology, and synthetic biology is likely to be a research focus in the coming years. Such disruptive improvements in biological-material hybrid make us confident that artificial photosynthetic biohybrid systems will lead the way to attain real-world applications toward a diverse range of solar fuels and chemicals in the near future.

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CRedit: **Weijian Chen** conceptualization, data curation, formal analysis, methodology, software, writing-original draft; **Hongrui Lin** formal analysis, methodology, software, writing-original draft; **Wen Yu** data curation, formal analysis, methodology, software, writing-original draft; **Yiming Huang** data curation, formal analysis, methodology, software; **Fengting Lv** formal analysis, methodology, software; **Haotian Bai** conceptualization, project administration, supervision, writing-original draft; **Shu Wang** conceptualization, funding acquisition, supervision, writing-review & editing.

Notes

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