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Visible Light–Driven Hydrogen Production by Carbon based Polymeric Materials

Palas Baran Pati, SU-IL In and Haining Tian

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Abstract

Converting solar energy into storable solar fuels such as H_2 from earth abundant source—water—is a nice approach to find the solution of energy crisis and environmental protection. There are two half reactions; first, water oxidation into oxygen and proton and followed by proton reduction led to H_2 evolution from water. After two decades of continuous attempts, there have been several efficient water oxidation photocatalysts introduced, whereas the proton reduction photocatalyst were relatively less explored. Major portion of reported photocatalysts for proton reduction are mainly derived from either noble metals or precious metals. Carbon-based organic photocatalysts have become attractive recently. These organic materials have several advantages like light weight, cheap, well-defined structure-property relationship and the most attractive one is better batch to batch reproducibility. Here, the reported organic photocatalysts and their performance are summarized which in fact help others to get an idea about ongoing progress in this area of research and to understand the basic designing principle for efficient photocatalysts for fuel production.

Keywords: solar fuels, photochemical hydrogen generation, proton reduction, photocatalysts, carbon nitride, conjugated polymers, polymer dots, porous materials

1. Introduction

Due to the limited storage of fossil fuels and the environmental hazards from burning of fossil fuels, there is urgent need for renewable energy sources. Harvesting solar energy is an ideal alternative solution. Silicon solar cell is already proven as an efficient technology for converting solar energy into electrical energy. In past two decades, enormous attempts have been done to replace silicon solar cells by organic carbon-based compound such as dyes and

polymers for developing efficient solar energy harvesting cells [1, 2]. But all these solar cells can convert solar energy into electrical energy. From the total consumption of energy in our society, we can see that only around 20% of the energy consumed is electrical energy and the rest is used as fuel form. So, storing solar energy into fuels is another important solution to energy crisis.

The light-induced water splitting into chemical fuels, oxygen and hydrogen, by sunlight represents an unlimited source of energy from naturally abundant resources. To carry out the process, it requires a photocatalyst and the key half reactions of water splitting are the oxidation of water to form oxygen and protons and the reduction of the protons to form hydrogen. The standard reduction potentials of these processes (pH = 0) are 1.23 V and 0 V vs. Normal Hydrogen Electrode (NHE), respectively, and the catalyst has to utilise photons of sufficient energy to generate at least this potential in order to split water, in practise a significant over potential usually results in a potential of at least 2V being required [3]. Groundbreaking work by Fujishima and Honda in 1972 showed that hydrogen generation *via* water splitting is possible using photocatalysts based on oxide semiconductors capable of adsorbing ultraviolet light energy [4]. For efficient hydrogen generation, development of efficient proton reduction catalyst is very essential. Enormous attempts have been done during the last few years to develop efficient proton reduction catalyst. Molecular catalyst-photosensitizer assemblies and inorganic material photocatalysts have been intensively developed [5]. On the other hand, organic photocatalysts have also attracted intense interests from scientists due to their facile structure modification, less environmental footprints, tunable light absorption and promising photocatalytic reactivity.

Conjugated materials can absorb visible light because of their delocalized π-system. These properties have led to applications in organic electronics and organic photonics [2]. In early 1985, Yanagida et al. have used linear poly(p-phenylene) for hydrogen generation which is known as the first report on carbon-based material for photochemical hydrogen generation [6]. This material only showed very low activity (apparent quantum yield (AQY) = 0.006%) and worked under ultraviolet (UV)-light (λ >366 nm). Another disadvantage was the insolubility, which delimits the further advancement on these materials. After two decades, carbon nitride has established itself as an efficient proton reduction catalyst [7]. Carbon nitride (g-C_3N_4) shows good efficiency on proton reduction in the presence of some co-catalysts such as Ni and Ni-P [8]. In the presence of co-catalyst, carbon nitride even can oxidize water [9]. But in the absence of co-catalysts, carbon nitride showed unsatisfactory performance for proton reduction. Due to the fixed structure of carbon nitride, there are few chances to tune the properties mainly light harvesting ability, which delimits the efficiency of the materials. Due to the high activity of carbon nitride and the restriction towards further improvement, scientists started to look and use conjugated materials for solar light-driven hydrogen production. The major advantage of the carbon-based organic semiconductor is that easily synthetic and purifying process and better batch to batch reproducibility. Well-established structure-property relationship helps to design and modify the structure to improve the performance of the materials. Very recently, various pure organic semiconducting materials such as poly(azomethine)s [10], covalent organic framework [11], phenyl-triazine oligomers [12], microporous organic nanorods [13], heptazine networks [14] and polybenzothiadiazoles [15]

have been successfully applied in the photocatalytic hydrogen production. These organic materials work as heterogeneous catalyst which associated with poor dispersibility in aqueous medium. The difficult dispersibility results in the low efficiency and stability of these materials. So, there is chance and need for improvement and betterment in this field to get highly efficient organic photocatalysts for photochemical hydrogenation.

Herein, in this chapter, we summarized and discussed the facile synthesis and latest developments of carbon-based photo-active organic materials usable for photochemical hydrogen generation. We will discuss the working principle and the thermodynamics behind the process for showing proton reduction ability to generate hydrogen. The discussion of available organic materials will be subdivided into following types: (a) covalent organic frameworks (COFs), (b) covalent triazine frameworks (CTFs), (c) carbon nitride-based polymers, (d) conjugated microporous polymers (CMP), (e) conjugated linear polymers and very recently introduced (f) polymer dots (Pdots). Our discussion particularly focuses on the modification of synthesis, structure and properties, aiming at better understanding of the intimate structure-performance relationship and further enhancement of photocatalytic activities. We believe that this chapter will be helpful for the readers to understand the working principle and structure-property relationship to devise a high-efficient photocatalyst. It is very timely on the aspect of renewable energy source finding.

2. Thermodynamics and driving force for proton reduction hydrogen generation process

Figure 1 shows the thermodynamics of water splitting (**Figure 1(a)**, at pH = 0) and photochemical hydrogen generation steps from water. Both the half reaction water oxidation and proton reduction are pH dependent. For the efficient water oxidation, the band gap of the conjugated material should be higher than 1.23 eV with well-stabilized oxidized state of the material
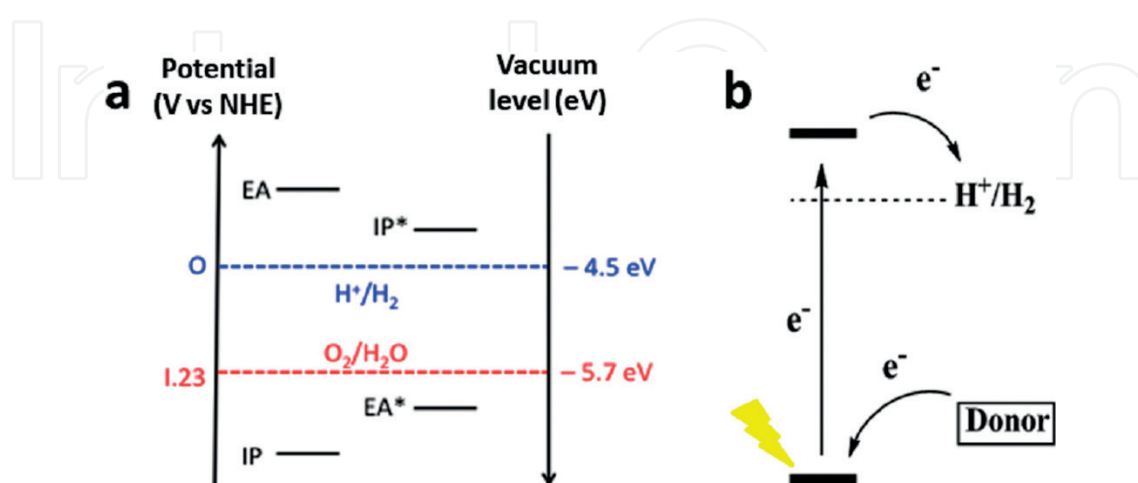

Figure 1. (a) Energy diagram of water splitting reaction. (b) Photochemical hydrogen generation energy diagram in the presence of a sacrificial electron donor.

to donate photogenerated hole for water oxidation to oxygen and proton. The excited state should be higher in energy to donate photoexcited electron to produce hydrogen upon reduction of proton. In case of photochemical hydrogen production (**Figure 1(b)**), the photoexcited material gets reduced by oxidizing sacrificial electron donor and the reduced material carries out the reduction of proton to produce hydrogen. There are many sacrificial donors used for the reaction; the most popular ones are triethanolamine (TEOA) and sodium ascorbate.

3. Materials

3.1. Covalent organic framework

Covalent organic frameworks (COFs) are highly ordered two- or three-dimensional crystalline polymers [16, 17]. These materials specially attract the interest in the area of photochemical hydrogen generation due to high surface area and tuneable pore size, which are essential criteria for heterogeneous catalysis [18]. By varying the molecular synthons, the optical and electrical properties of the resulted COFs can be nicely tuned. Stegbauer et al. enriched the library on this area by synthesizing and characterizing a series of COFs and further they successfully applied these materials for photochemical hydrogen generation in the presence of co-catalyst and a sacrificial electron donor [11]. Acid-catalysed Schiff base reaction resulted a two-dimensional (2D) mesoporous hydrazine-based COFs (TFTP-COF) with honeycomb-type network (**Figure 2**). It showed a high surface area of 1603 m^2 g^{-1} with a pore size of 3.8 nm. These polymers with a band gap of 2.8 eV show light absorption ability in the visible range. It shows high hydrogen evolution performance (230 μmol h^{-1} g^{-1}) when Pt nanoparticle and sodium ascorbate were used as co-catalyst and sacrificial electron donor, respectively, under visible light (>420 nm) irradiation. Indeed, it showed higher hydrogen evolution rate (1970 μmol h^{-1} g^{-1}) with a AQY of 2.2% when triethanolamine (TEOA) was used instead of sodium ascorbate as sacrificial electron donor.

Again Vyas et al. further synthesize a series of 2D azine-linked COFs with varying amount of nitrogen by solvothermal method from hydrazine and triphenylarylaldehydes [19]. The high BET-surface area (1537 m^2 g^{-1}) suggests that the COFs are highly porous. All COFs absorb in the UV region and the blue part of the visible region with an absorption edge around 465–475 nm which led to an optical band gap of 2.6–2.7 eV (**Figure 3**). The **N₃-COF** showed hydrogen evolution rate of 1703 μmol h^{-1} g^{-1} when TEOA used as sacrificial electron donor and hexachloroplatinic acid for in situ generation of Pt-nanoparticle.

The above study suggests that with the increase of N containing in the central core of COFs the photocatalytic activity is increased so further they tried to introduced N atom in the peripheral unit of COF also [20]. They introduced pyridine containing azine-linked COFs by solvothermal process between **PTP-CHO** and hydrazine hydrate (**Figure 4**). Photocatalytic hydrogen evolution rate was tested in the presence of TEOA as electron donor and hexachloroplatinic acid as in situ formation for Pt-nanoparticle used as co-catalyst. The hydrogen evolution rate is lower for **PTP-COF** (83.83 μmol h^{-1} g^{-1}) than **N₃-COF** (1703 μmol h^{-1} g^{-1}).
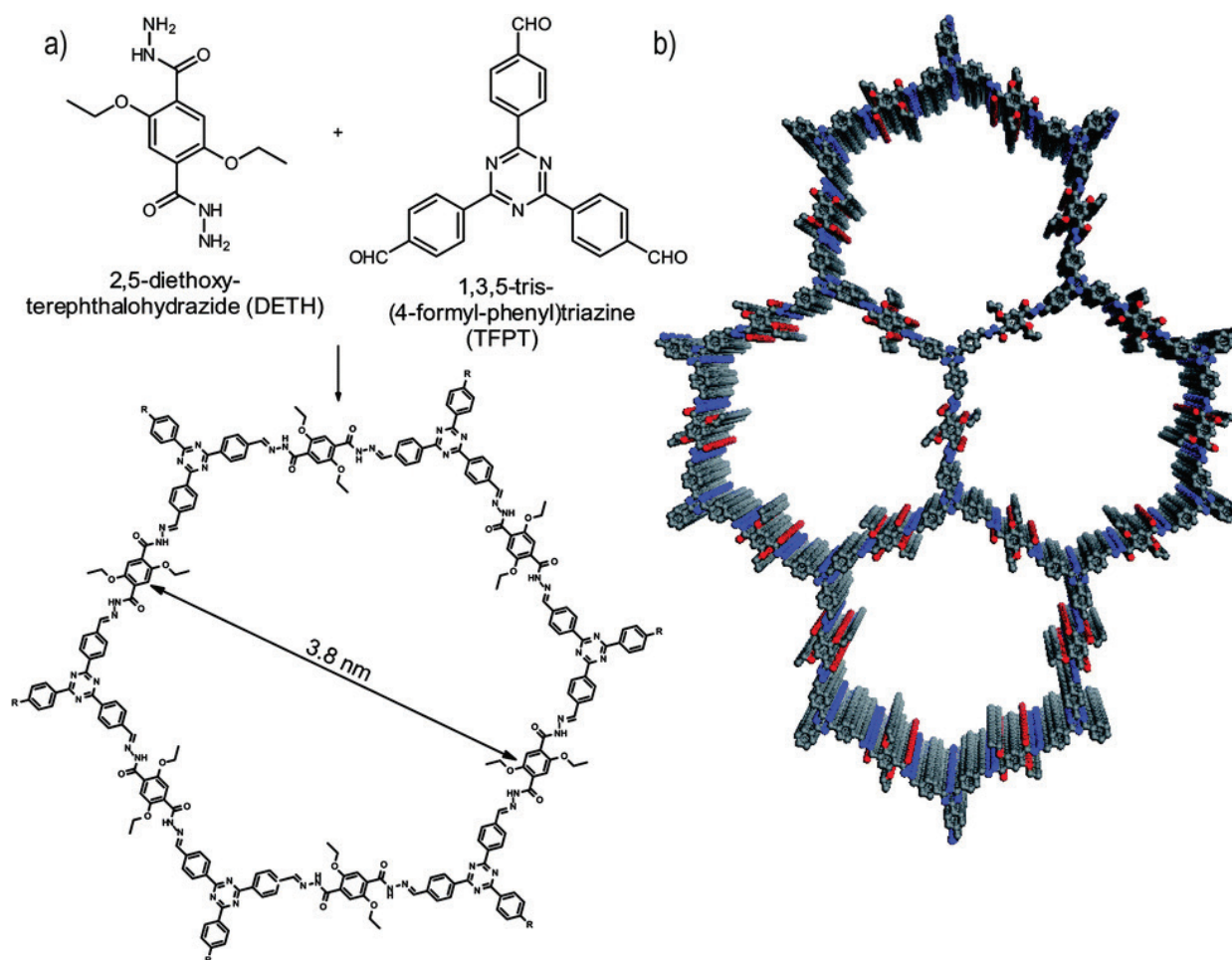
Figure 2. Acetic acid-catalysed hydrazone formation furnishes a mesoporous 2D network with a honeycomb type in plane structure. (a) Scheme showing the condensation of the two monomers to form the TFPT-COF. (b) TFPT-COF with a cofacial orientation of the aromatic building blocks, constituting a close-to eclipsed primitive hexagonal lattice (grey: carbon, blue: nitrogen, red: oxygen). Reproduced with permission from RSC; see Ref. [11].

3.2. Covalent triazine-based frameworks (CTFs)

It is believed that due to incorporation of electronegative nitrogen centre the H_2 evolution can be strongly enhanced. On this aspect, triazine or heptazine framework in the organic polymeric system can be beneficial for photochemical hydrogen production. CTFs are typically prepared by ionothermal trimerization of aromatic nitriles such as 1,4-dicyanobenzene (DCB), 1,3,5-tris(4-cyanophenyl)benzene (TCPB) and 2,6-dicyanopyridine (DCP) process in the presence of $ZnCl_2$ which acts both as catalyst and solvent [21]. These systems are typically microporous structure with high surface area. Typically, CTFs are black in colour with very low band gap (~1 eV) which in fact is insufficient for both photochemical water splitting and generated proton reduction. Schwinghammer et al. synthesized yellow phenyl-triazine oligomers by reducing carbonization effect through lowering temperature (300 °C) and prolonging reaction time (150 h) [12]. These synthesized CTFs showed the band gap in the range of 3.2–3.3 eV. In the presence of Pt as co-catalyst and TEOA as sacrificial donor, the most active CTF sample showed a hydrogen evolution rate of 1076 (±278) $\mu mol\ h^{-1}\ g^{-1}$. Although the hydrogen
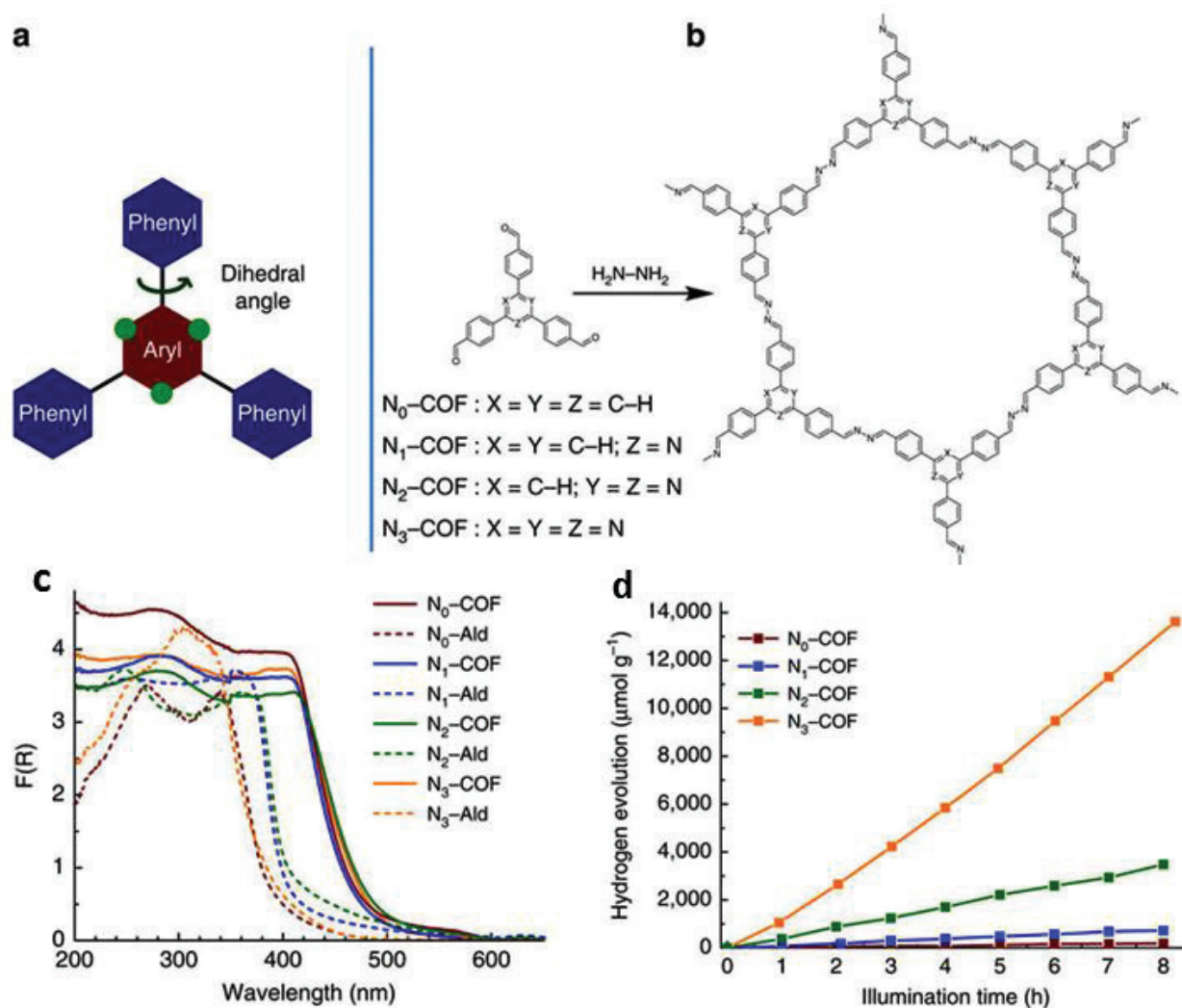
Figure 3. Design (a) and synthesis (b) of the **N_x-COFs**. Absorption spectra of precursor aldehydes **N_x-Alds** in dichloromethane at 22°C (c). Hydrogen production monitored over 8 h using **N_x-COFs** as photocatalyst in the presence of triethanolamine as sacrificial electron donor (d). Reproduced with permission from Nature Publication Group; see Ref. [19].

evolution rate (121 μmol h^{-1} g^{-1}) is low but most active CTF is active in photochemical hydrogen production in the absence of co-catalyst. The apparent quantum yield (AQY) of the highest active CTF is determined to be 5.5% at 400 (±20) nm. On an intension of efficient CTFs by manipulating structural and optical properties, Wu et al. introduced the DCB-based **CTF-T1** by incorporating methyl group in monomer through trifluoromethanesulfonic acid-catalysed reaction. The optical band gap of devised CTF was determined to be 2.9 eV. The CTF showed water splitting to produce H$_2$ in the presence of sacrificial electron donor. The AQY of hydrogen evolving reaction was calculated to 2.4% in 400–440 nm **(Figure 5)**.

3.3. Carbon nitride-based polymers

Since 2009, after successful demonstration in water splitting reaction, carbon nitride analogues become matter of interest. Commonly, it is believed that two different analogues, namely *s*-triazine
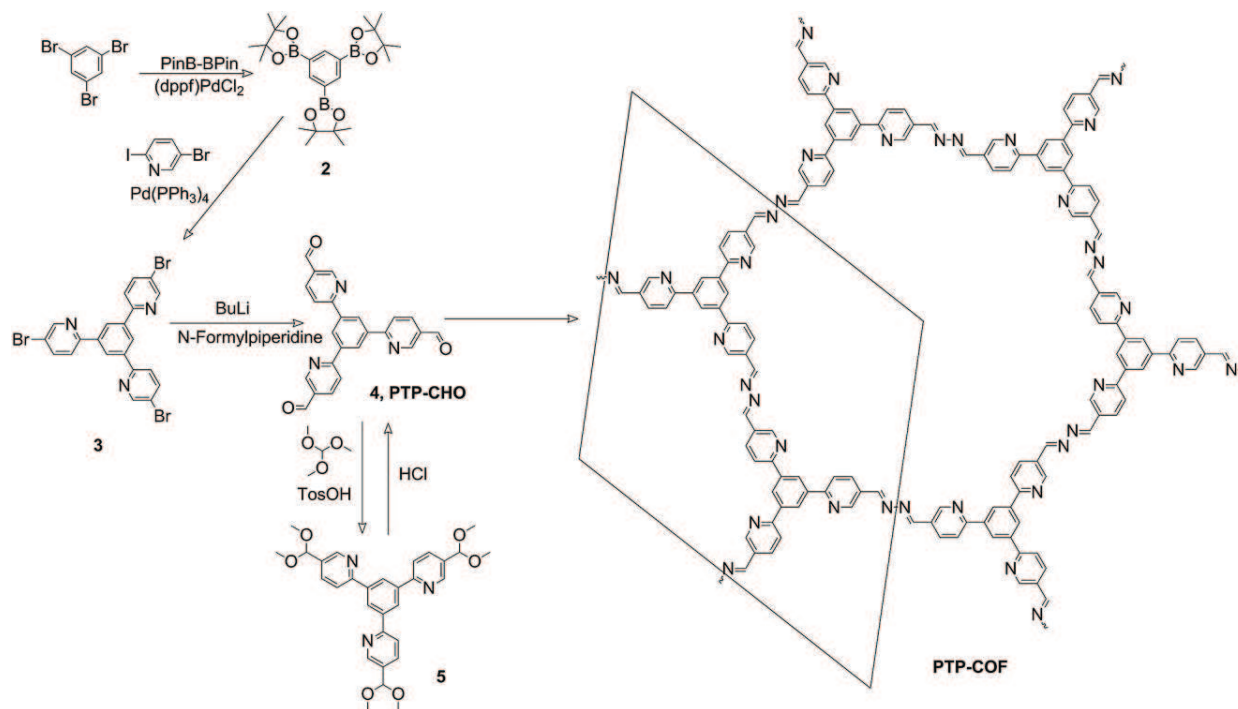
Figure 4. Synthesis of precursor **PTP-CHO** and **PTP-COF**. The in-plane unit cell is indicated on the right. Reproduced with permission from RSC; see Ref. [20].

and tri-*s*-triazine (heptazine), are co-existed to separately construct the ideal polymeric carbon nitride units [22–25]. Being energetically higher s-triazine is thermodynamically unfavourable to synthesize carbon nitride with pure s-triazine unit. In fact, poly(triazine imide) (PTI) and melon, which belong to typical s-triazine and tri-*s*-triazine structure, respectively, are always experimentally synthesized to obtain the binary carbon nitride polymers with 2D electronic structures [22–29]. PTI always features high level of crystallinity, whereas most of the melons are amorphous or semi-crystalline in structure. Besides, quite different optical properties were also generated due to the different degrees of conjugation. In this case, these two counterparts showed different photocatalytic performances for photocatalytic H_2 evolution. Ham et al. first reported that PTI/Li$^+$Cl$^-$ exhibited a steady H_2 evolution rate under visible light irradiation in the presence
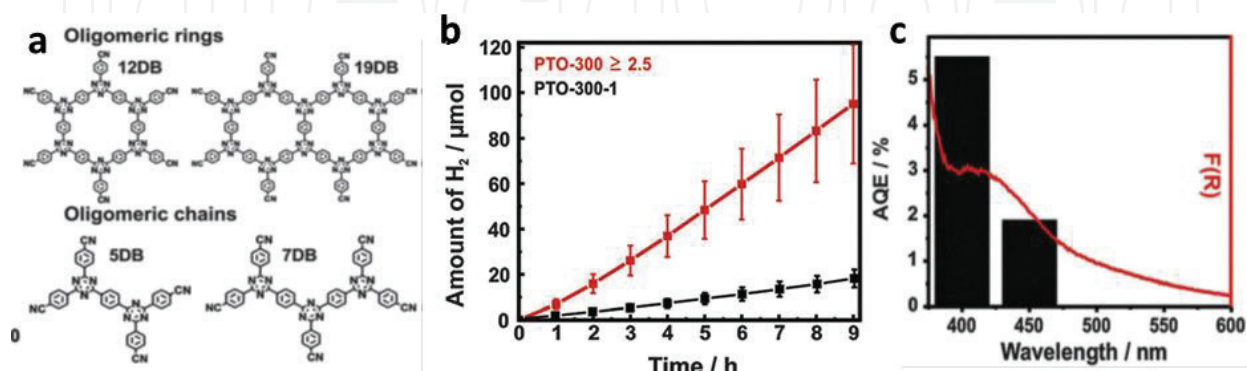

Figure 5. (a) Possible ring- and chain-like oligomers, (b) average hydrogen evolution curve and (c) quantum yield with a function of wavelength. Reproduced with permission from RSC; see Ref. [12].

of sacrificial agents and co-catalyst (Pt, 5 wt.%), whereas it showed low activity in comparison to that of Pt/g-C$_3$N$_4$ which may be assigned to the weak optical absorption in the visible light region [30]. Schwinghammer et al. modify the PTI/Li$^+$Cl$^-$ by using 4-amino-2, 6-dihydroxypyrimidine (**4AP**) as the dopant [31]. This modified PTI showed red-shifted absorption spectrum compared to the crystalline PTI and more similar to the melon structure, which improves the visible light absorption. By using this doped PTI, AQY of hydrogen evolution can be improved five times (3.4%), which is more than that of raw melon (0.6%). By supramolecular aggregation allowed by ionic melt polycondensation (IMP) of melamine and 2,4,6-triaminopyrimidine as dopants, Bhunia et al. introduced a new crystalline carbon nitride which exhibited an AQY of 15% for photocatalytic H$_2$ production at 400 nm [32]. Thus, molecular doping proved itself as very efficient technique for efficient H$_2$ production. Tri-s-triazine-based g-C$_3$N$_4$ is commonly prepared from the thermal polymerization of carbon and nitrogen containing organic and inorganic materials such as melamine, cyanamide, urea, thiourea, ammonium thiocyanate and guanidine sulphate [33–41]. These materials are known as efficient photocatalysts for splitting of water. The g-C$_3$N$_4$ polymers prepared from different starting materials usually show different properties such as surface morphology, optical absorption, charge carrier ability and electronic band structure. So, particularly by this way, the performance for photochemical reaction can be varied. To create porosity in the structure, strategies, such as hard template method, self-assembly (SA) and exfoliation, are conducted to improve the photocatalytic performances. Maeda et al. successfully introduced the spine nanosphere carbon nitride *in situ* deposited with 3 wt% Pt as co-catalysts as efficient photocatalyst for hydrogen generation with a hydrogen evolution rate (HER) of 574 μmol h^{-1} [42]. The AQY for H$_2$ evolution at 420 nm can reach a value of 9.6%.

3.4. Conjugated microporous polymers (CMPs)

Conjugated polymers with extended π-conjugation have been intensively explored in organic electronics and semiconductor device due to electronic and physical properties. Copolymerization of various monomeric units (building block) led to conjugated polymers, which allow to design various kind polymers with different electronic properties by varying the structural modification in monomeric units. Very recently, this kind of conjugated microporous polymers (CMPs) were successfully applied for photochemical hydrogen generation. Sprick et al. reported a series of CMP by varying the ratio of monomeric unit (**Figure 6**) [43]. The surface area is also tuneable
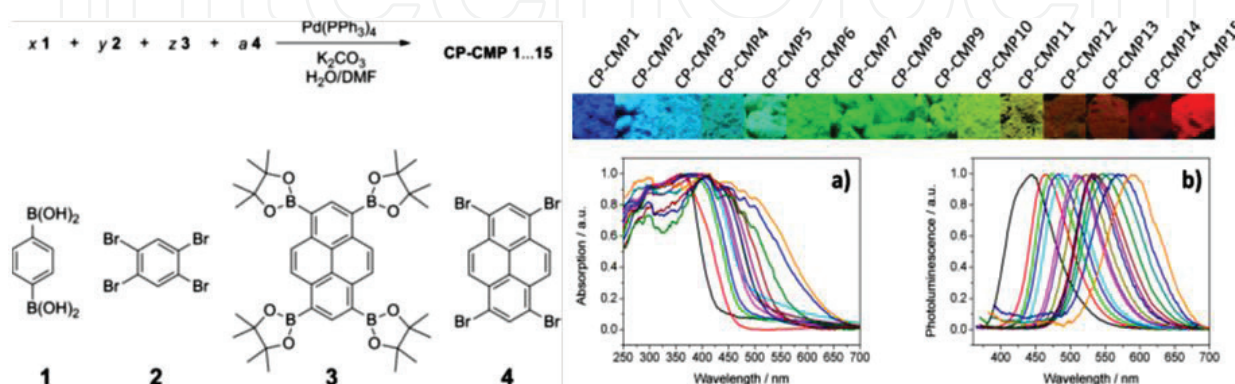

Figure 6. Schematic representation of reactions for the synthesis of CP-CMPs. Optical properties of the conjugated copolymer photocatalysts. Reproduced with permission from ACS; see Ref. [43].

by changing the monomers. Optical properties are also tuned by different amount of monomers which reflect in the range of optical band gap between 1.94 and 2.95 eV with an absorption band edge 445–588 nm. When in a water/methanol mix solvent in the presence of TEOA, photocatalytic reaction to generate hydrogen of these materials was tested. **CP-CMP10** shows the highest activity with a hydrogen evolution rate of 17.4 μmol h^{-1}. These polymers even showed hydrogen evolution performance without any co-catalyst such as Pt. It showed the optimal AQY for visible light H$_2$ production is 2.62% in the presence of 80 vol.% diethylamine as the sacrificial agent.

Subsequently, Li et al. introduced donor-acceptor type microporous polymer by co-polymerization method [44]. Two types of monomeric units, electron-rich units (**M2**-**M4**) and electron-deficient (**M1**) units, were copolymerized with different ration of weak donor biphenyl and weak acceptor bipyridine to produce a series of four polymers (**Figure 7**). The calculated band gaps of all polymers were in the range of 2.0–2.8 eV. The light absorbing ability of these polymers is significantly improved. Charge separation is facilitated due to the intra-molecular charge transfer, which is in fact very essential to generate excited holes and electrons for water oxidation and proton reduction, respectively. **PCP4e** showed the best performance for photocatalytic hydrogen production with a HER of 33.0 μmol h^{-1}. Bipyridyl-substituted polymers showed better performance than the biphenyl-containing polymer which can be attributed due to the presence of more electronegative N-atom, which may facilitate hydrogen adsorption through hydrogen bonding to enhance the proton reduction process.

On the other hand, Yang et al. reported benzothiadiazole-based donor-acceptor type conjugated microporous polymers as photocatalysts for hydrogen generation [15]. Benzothiadiazole unit is highly explored in organic conjugated materials for electronic devices due to its unique electron withdrawing ability. By co-polymerization technique starting with benzene and benzothiadiazole as basic monomeric unit and changing the substitution in benzene ring, they are able to synthesize a series of conjugated polymer from 1D to 3D in nature (**Figure 8**). **B-BT-1,4**
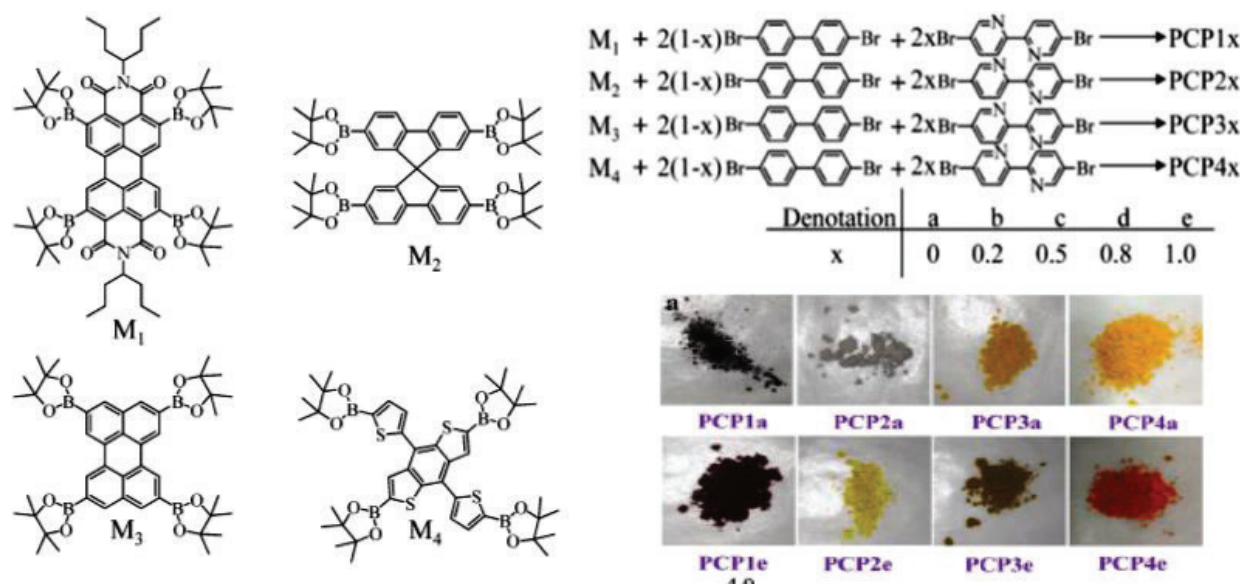

Figure 7. Structures of monomers and synthesis of PCP photocatalysts by Suzuki polycondensation and photographs of the prepared **PCPa** and **PCPe** photocatalysts. Reproduced with permission from ACS; see Ref. [44].
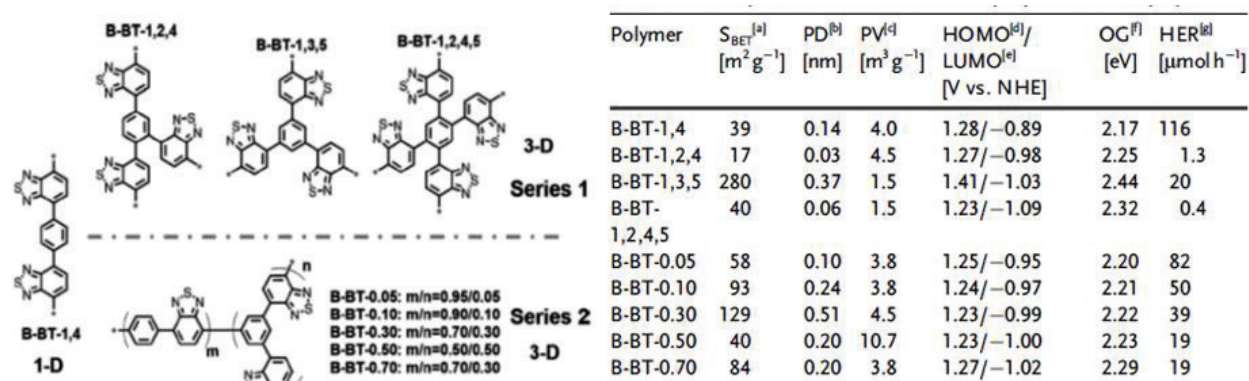
Polymer	S_{BET}[a] [$m^2 g^{-1}$]	PD[b] [nm]	PV[c] [$m^3 g^{-1}$]	HOMO[d]/ LUMO[e] [V vs. NHE]	OG[f] [eV]	HER[g] [$\mu mol\, h^{-1}$]
B-BT-1,4	39	0.14	4.0	1.28/−0.89	2.17	116
B-BT-1,2,4	17	0.03	4.5	1.27/−0.98	2.25	1.3
B-BT-1,3,5	280	0.37	1.5	1.41/−1.03	2.44	20
B-BT-1,2,4,5	40	0.06	1.5	1.23/−1.09	2.32	0.4
B-BT-0.05	58	0.10	3.8	1.25/−0.95	2.20	82
B-BT-0.10	93	0.24	3.8	1.24/−0.97	2.21	50
B-BT-0.30	129	0.51	4.5	1.23/−0.99	2.22	39
B-BT-0.50	40	0.20	10.7	1.23/−1.00	2.23	19
B-BT-0.70	84	0.20	3.8	1.27/−1.02	2.29	19

Figure 8. Structures of two series of polybenzothiadiazoles with different molecular designs and porosity data and electrochemical properties of the polymers. Reproduced with permission from Wiley-VCH; see Ref. [15].

itself showed photocatalytic activity with a HER of 12.0 $\mu mol\, h^{-1}$. Upon addition of 3 wt% Pt as cocatalyst, the HER was enhanced to 116.0 $\mu mol\, h^{-1}$. The AQY of **B-BT-1,4** for hydrogen evolution was found to be as high as 4.01%.

Chu et al. reported crystalline polyimide (PI) via high temperature dehydration reaction between melamine (MA) and pyromellitic dianhydride (PMDA) (**Figure 9**) [45]. A series of PIs with different optical band gaps (2.56–3.39 eV) were synthesized and the degree of polymerization is controlled by tuning the heating temperature. These polymers showed photocatalytic activity to produce hydrogen from water in the presence of Pt and TEOA as cocatalyst and sacrificial donor, respectively. Out of all PIs, **PI-325** showed the best activity with a HER of 150 $\mu mol\, h^{-1}$ and 15.2 $\mu mol\, h^{-1}$ under UV and visible light irradiation, respectively. **PI-325** showed AQY of 0.2% at 420 nm light irradiation.

In early 2010, Schwab et al. successfully introduced a series of imine-based conjugate poly (azomethine) materials [10]. The Schiff-base condensation reaction were adopted between the 1,3,5-tris(4- aminophenyl)benzene (**1**) as amine residue with different aldehydes such as 1,4-phthalaldehyde (**2**), naphthalene-2,6-dicarbaldehyde (**3**), anthracene-2,6-dicarbaldehyde (**4**) and anthracene-9,10-dicarbaldehyde (**5**) to synthesize the polymers. The optical band gaps of the synthesized polymers were located in the range of 1.96–2.38 eV with an optical band edge of 532–632 nm. These polymers showed photocatalytic activity under UV-light irradiation with a HER of 7 $\mu mol\, h^{-1}$ (**ANW-2**), whereas under visible light these polymers did not show any photocatalytic activity (**Figure 10**).

3.5. Conjugated linear and planarized polymers

As we mentioned before, Yanagida et al. in early 1985 reported poly(p-phenylene) as active photochemical hydrogen production catalyst under UV-light illumination [6]. Due to the solubility and low activity, there is no further advancement in this area. Recently, Sprick et al. synthesized and characterized a series of planar polymers by comprising phenylene and fluorine, carbazole, or dibenzo [b,d] thiophene [46]. From the study, they concluded that planar polymers showed higher photocatalytic activity to produce hydrogen. The pure copolymers
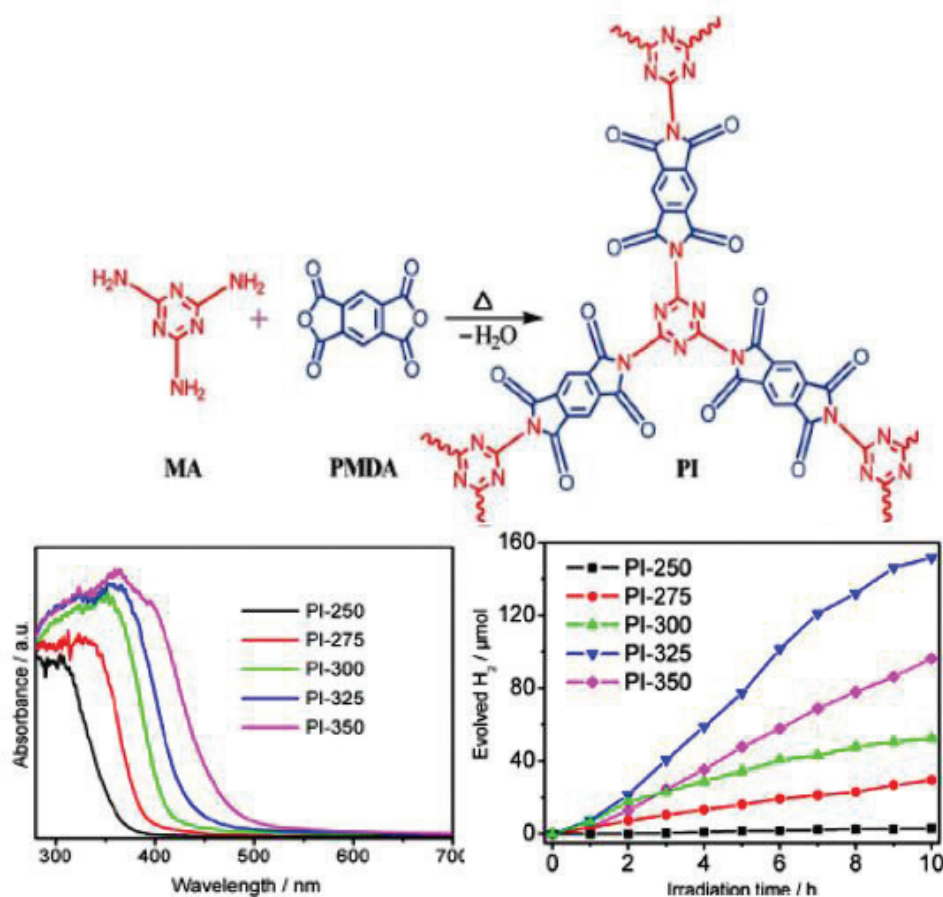
Figure 9. Reaction scheme for the synthesis of PI, UV-vis absorption spectra of PI samples processed at different temperatures and time course of H_2 evolution from a 10 vol% aqueous methanol solution by Pt-deposited PI samples under visible light irradiation (λ>420 nm). Reproduced with permission from Elsevier; see Ref. [45].
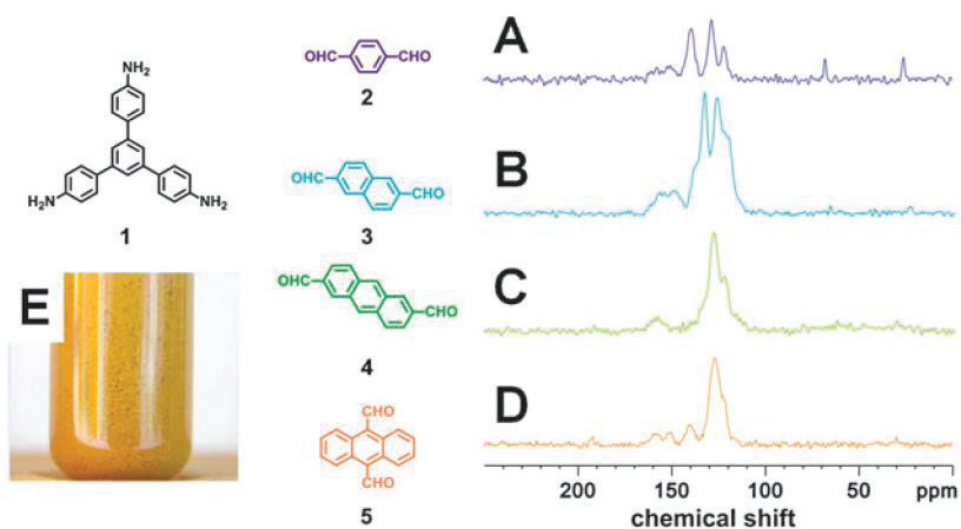

Figure 10. Molecular structures of the building units for the **ANW** materials and time course of H_2 production through **ANW** networks from water containing 10vol. % triethanolamine as electron donor (λ>300 nm). Reproduced with permission from RSC; see Ref. [10].

(**P1-P7**) are also exhibited excellent visible light-induced H$_2$ evolution activities even without depositing any co-catalysts, whereas methanol and triethylamine mixture were used as the sacrificial electron donors. Out of all planar co-polymers, **P7** showed the highest photocatalytic activity with HER of 92 μmol h^{-1}, while the rate was further found to be increased up to 116 μmol h^{-1} in the presence of Pt-nanoparticles as a co-catalyst. The AQY of hydrogen generation for **P7** was measured as 2.3% at 420 nm (**Figure 11**).

3.6. Polymer dots (Pdots)

Till discussed all materials behaved as heterogeneous catalyst because these all have poor dispersibility in water, to run the photocatalytic experiment in absolutely aqueous condition and the organic/water mixed solvent were commonly used to make good dispersibility. Another drawback is that majority materials were worked under UV light and also in the presence of a co-catalyst such as Pt. In the absence of co-catalyst and visible light, all show very unsatisfactory performances. Tian et al. used the conjugated polymer dots (Pdots), which is nicely dispersible in aqueous solution for photocatalytic proton reduction [47]. The Pdots of hydrophobic conjugated polymer (**PFBT**) were prepared through nanoprecipitation method by mixing with an amphiphilic co-polymers (**PS-PEG-COOH**). Typically, **PFBT** was dissolved in THF together with the co-polymer **PS-PEG-COOH** and then was poured into water. THF was removed later by continuously sonicating and Ar purging. The well-dispersed nanoparticles in water were obtained. Particle size of the nanoparticles was around 30–50 nm measured by dynamic light scattering (DLS). The optical band gap of PFBT Pdots was 2.38 eV. Without any co-catalyst in the presence of ascorbic acid as sacrificial donor, Pdots showed excellent photocatalytic activity with a HER of 8.3±0.2 mmol h^{-1} g^{-1}. Pdots configuration is very important because the pristine polymer itself did not show activity under the same test condition. The AQY of hydrogen evolution was 0.5% at 445 nm. However, after 1.5 h, the Pdots deactivated and precipitated out from the aqueous medium by forming bigger particle (**Figure 12**).

In order to further improve the system and study the reactivity sites of photocatalysis, Tian et al. subsequently investigated structures insight for highly efficient Pdots by both experimental and theoretical prospect. Pdots prepared from **1** and **2** (**Figure 13**) with benzothiadiazole (BT) units showed photocatalytic activity with a HER of 8.3±0.2 mmol h^{-1} g^{-1} and 50±0.5 mmol h^{-1} g^{-1}, whereas Pdots of **3** without such a unit did not show any photocatalytic activity. It suggests that the BT unit has crucial role in proton reduction reaction [48]. The theoretical study suggests that proton adsorption is facilitated due to the presence of N sites in the electron withdrawing BT unit which in fact enhances the photocatalytic activity. With
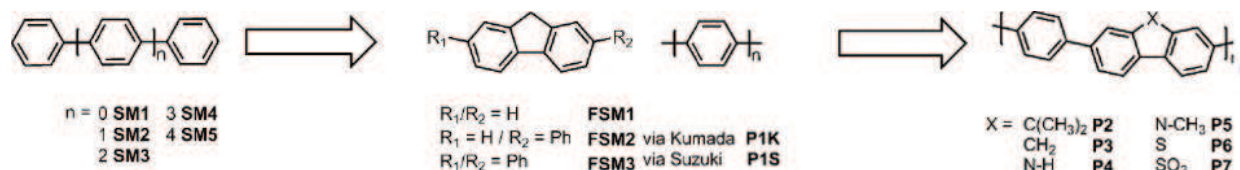

Figure 11. Schematic representation of reactions for the synthesis of planarized conjugated polymers. Reproduced with permission from Wiley-VCH; see Ref. [46].
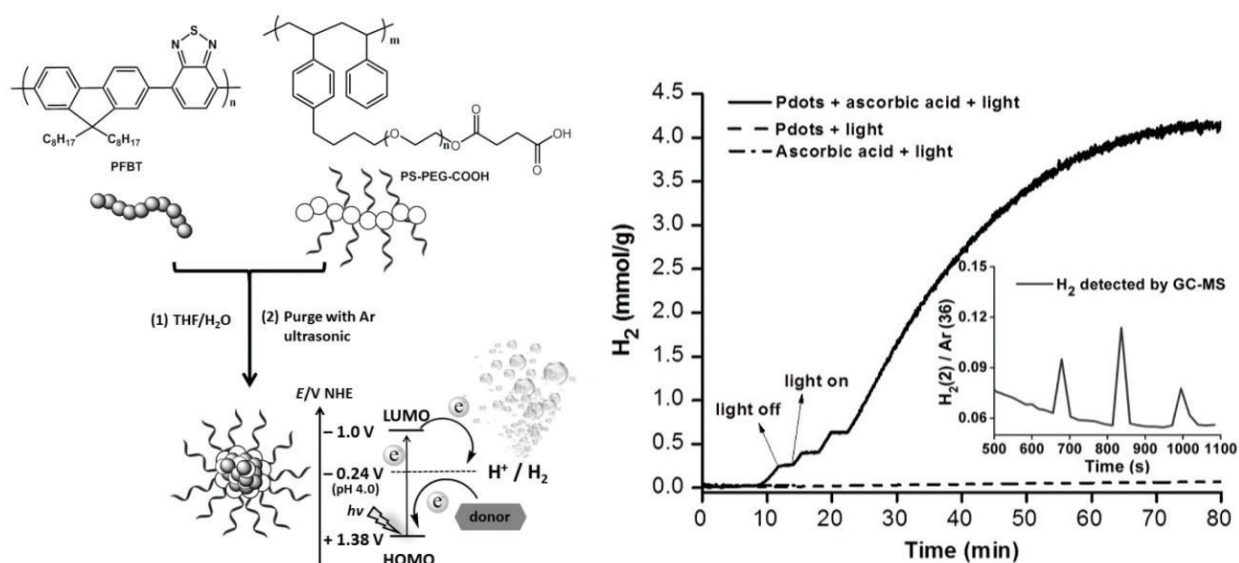
Figure 12. Preparation of PFBT Pdots and the diagram for light-driven hydrogen generation; visible light-driven hydrogen generation from water at room temperature. Conditions: **PFBT** Pdots, ca. 16.8 mg/mL; ascorbic acid: 0.2 M; pH 4.0 (adjusted with 1 M NaOH); LED lamp: white light (l>420 nm); the kinetic curve is monitored by a hydrogen sensor (see details in the Supporting Information). Inset: H_2 generation confirmed by GC-MS, the three peaks are signals from three injections of the headspace gas in the reaction flask. Reproduced with permission from Wiley-VCH; see Ref. [47].

respect to **Pdots 1**, **Pdots 2** shows even more stability and works for more than 4 hour. The AQY for H_2 generation of **Pdots 2** was measured as 0.6% at 550 nm. The isotopic labelling experiment, using D_2O and NaOD instead of H_2O and NaOH in a photocatalytic experiment of **Pdots 2**, suggests that the evolving hydrogen is mainly coming from the water. Since this kind of conjugated polymers is prepared by Pd-catalysed copolymerization method, where the residual Pd is known to be a good catalyst for proton reduction and it could behave as co-catalyst for this photocatalytic reaction. However, from the Pd poisoning experiments with carbon monoxide (CO) and ethylenediaminetetraacetic acid (EDTA), it suggests that the Pdots
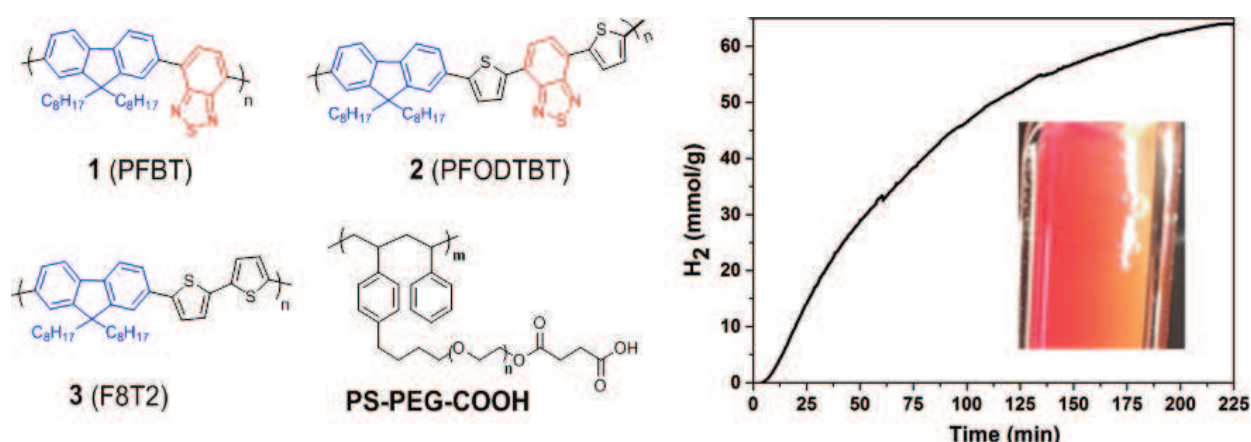

Figure 13. Molecular structures of three organic D–A polymers (**1**, **2** and **3**) and a co-polymer PS-PEG-COOH; light-driven hydrogen generation of Pdots **1** (17 μg/ml), **2** (13 μg/ml) and **3** (19 μg/ml) in water at ambient temperature. Conditions: ascorbic acid: 0.2 M; pH 4.0 (adjusted with 1 M NaOH); white LED light (420 nm, 17 W, 5000 K). Inset: H_2 bubbles observed during photocatalysis. Reproduced with permission from RSC; see Ref. [48].

are the real photocatalysts. The DFT computation also suggests the unique structure of the Pdots from aggregated polymers benefits for lowering the energy barrier of proton reduction process via N atoms in BT units.

4. Perspective

Library of carbon-based organic photocatalysts are very few in comparison to the inorganic photocatalysts. The performance of these materials are still unsatisfactory but these organic materials have several advantages such as light-weight, easily processable and better reproducibility upon batch-to-batch variation. The organic photocatalysts are of great interest because there is a wide opportunity to introduce several new materials with different optical and electrochemical properties by small structural modification. By proper structural modification, the performance of these materials can be tuned and would be comparable with the inorganic materials. The major drawback of all of these organic carbon-based material is water dispersibility because of very poor solubility in water. The polymer dot encounters the solubility issue by some extent whereas rather need optimization to solve the associated problem such as unwanted aggregation along with light illumination, which causes deactivation and so on.

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