Indanone-based conjugated polymers enabling ultrafast electron transfer for visible light-driven hydrogen evolution from water†

Tse-Fu Huang, a,b Ying-Rang Zhuang, a Chih-Li Chang, a Ching-Li Huang, b Wei-Cheng Lin, a,b Zi-Cheng Jiang, c Li-Yu Ting, a Islam M. A. Mekhemer, a Yu-En Sun, a Pinit Kidkhunthod, d Jeng-Lung Chen, e Yi-Chan Huang, a Hung-Kai Hsu, c Yuan-Ting Tseng, a Yi-Hsiang Wu, a Bing-Heng Li, a Shang-Da Yang, a,c Yen-Ju Cheng a,b and Ho-Hsiu Chou a,b,c

Photocatalytic hydrogen production (PHP) from water is a promising solution for environmental pollution due to its high energy density and the abundant availability of water and solar energy on Earth. 1,1-dicyanomethylene-3-indanone (IC) has been widely used as an end group in organic photovoltaics owing to its strong electron-withdrawing ability and planarity. However, research on the application of IC structures in PHP is limited due to synthesis challenges. In this study, we designed a series of novel IC-based monomers incorporating a dibenzothiophene-5,S-dioxide unit through Suzuki coupling. These monomers were used to synthesize polymers with varying degrees of malononitrile substitution, referred to as ICFTDB, ICTDB, and IDMTDB. We investigated the correlation between the optical, electrochemical, and hydrogen evolution performances of these polymers. Through transient absorption spectroscopy, we demonstrated that ICTDB exhibited enhanced capabilities for ultrafast electron transfer and reduced recombination effects. As a result, ICTDB, photocatalysts with IC-containing structures achieved a hydrogen evolution rate of 30.0 mmol g⁻¹ h⁻¹, which was 11.5 times higher than that of ICFTDB, the polymer with no malononitrile substitution. This study provides valuable insights into the potential of IC-based conjugated polymers for photocatalytic hydrogen evolution.

Introduction

Photocatalytic hydrogen production (PHP) from water is a highly promising avenue for addressing environmental pollution and achieving zero-emission goals. Hydrogen energy offers several advantages, including a high energy density, the abundance of water and solar energy, and the production of only water and heat upon combustion, without harmful environmental waste. In recent years, organic semiconductors have emerged as attractive photocatalysts for hydrogen evolution. Compared to traditional inorganic materials, they offer benefits such as low-temperature processing, cost-effective production, and the ability to tailor their structure and band positions for optimized light-harvesting properties, representing a significant advancement. Since the discovery of the application of graphitic carbon nitride in hydrogen evolution in 2009,¹ there has been a surge in research focusing on polymeric semiconductors as potential catalysts. Various types of polymeric materials have been made; for instance, linear conjugated polymers,²–¹¹ conjugated microporous polymers,¹²–¹³ covalent triazine frameworks,¹⁴–²² and covalent organic frameworks,²⁷–³⁵ have been explored for their photocatalytic properties in hydrogen evolution. These diverse organic semiconductors offer a wide range of properties and functionalities, presenting exciting opportunities for further advancements in PHP technology. Meanwhile, a significant body of literature highlights the remarkable potential of donor–acceptor (D–A) type copolymers in achieving outstanding efficiency in photocatalytic hydrogen evolution. One of the primary factors contributing to their enhanced performance is the facilitation of intramolecular charge transfer within the copolymer structure. This is achieved by incorporating electron-withdrawing...
acceptor units, which promote efficient charge transfer between neighboring molecules. Additionally, it enables the effective separation of photoinduced excitons, resulting in an overall improvement in photocatalytic activity.\textsuperscript{35,36} On the other hand, organic photovoltaics (OPVs) have experienced rapid development ever since the introduction of fused-ring electron acceptors (FREAs). FREAs are characterized by their bulky fused-ring structure, complemented by electron-withdrawing end groups, imparting them with several key attributes such as broad absorption spectra and tunable orbital levels. The end groups (EGs) of FREAs play a pivotal role in shaping their optoelectronic properties. With their strong electron-withdrawing ability and planarity, EGs have a significant impact on the overall performance of FREAs. By lowering the bandgap, EGs render the entire structure electron-deficient, a critical aspect of facilitating charge separation and promoting efficient charge transport. Moreover, the conjugated plane of EGs leads to intermolecular π-π stacking, which not only enhances charge mobility but also contributes to well-ordered morphologies, ultimately benefiting overall performance. In 2020, Wang et al. demonstrated that Y6, a FREA with an end-capped structure of 1,1-dicyanomethylene-3-indanone (IC), achieved an impressive efficiency of over 15.7%.\textsuperscript{35,36} The incorporation of the IC structure played a critical role in elevating its performance. This unique structure, synthesized by introducing malononitrile into the first position of 1,3-indanedione, strengthens its electron-withdrawing capabilities,\textsuperscript{37} while maintaining planarity due to the linear C≡N group with sp hybridization.\textsuperscript{38} These defining characteristics of the IC structure, including excellent charge transfer ability, planarity, and light absorption, position it as a promising candidate for use in conjugated polymers for photocatalytic applications. While the potential of the IC structure in photocatalytic hydrogen production (PHP) is recognized, its application in this field remains constrained. To date, there are no IC-based monomers readily available for direct use in Suzuki coupling polymerization, primarily due to the synthetic challenges associated with the IC structure. This limitation hampers its broader adoption in PHP research. Nevertheless, considering its advantageous properties, further efforts in developing efficient synthetic pathways for IC-based monomers hold the promise of unlocking new avenues for enhancing the performance of conjugated polymers in photocatalytic applications.

In this study, we introduce a series of novel conjugated polymers containing indanone-based monomers as photocatalysts, with the goal of enhancing intermolecular charge transfer and investigating the potential of the IC structure in the context of PHP. First, we utilized 5-bromo-1H-indene-1,3(2H)-dione (ICBrF) as a precursor and synthesized two monomers with one and two malononitrile substitutions via Knoevenagel condensation, respectively. Subsequently, aldol condensation with 5-bromo-2-thiophenecarboxaldehyde was carried out to produce three monomers with varying numbers of malononitrile substitutions, namely ICFTBr, ICTBr, and IDMFTBr. Notably, these indanone-based monomers for polymerization have never been reported or synthesized in any field, making them pioneering additions to the study of conjugated polymers. Furthermore, we employed these monomers to fabricate three indanone-based polymers through Suzuki–Miyaura coupling, denoted as ICTDB, IDCNTB, and IDMCTDB. This study presents an effective strategy for enhancing visible-light-driven hydrogen evolution by incorporating the IC structure into polymer photocatalysts, shedding light on the potential of the IC structure for future PHP applications. Additionally, it offers valuable insights into the prospective utilization of indanone derivatives.

**Experimental**

**Synthesis of ICFTBr**

ICBrF (2.24 g, 10 mmol), 5-bromo-2-thiophenecarboxaldehyde (1.82 g, 9.5 mmol), and acetic acid (120 ml) were added to a reaction flask and refluxed at 140 °C under a nitrogen atmosphere overnight. The solution was allowed to cool to room temperature to make the precipitate occur. The mixture was filtered through a funnel to obtain the crude product and further washed with water and n-hexane to afford ICFTBr (2.81 g, 7.11 mmol, yield 74.8%).\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 8.08 (s, 1H), 7.89 (d, \(J = 9\) Hz, 1H), 8.86 (s, 1H), 7.82 (d, \(J = 9\) Hz, 1H), 7.64 (d, \(J = 4\) Hz, 1H) and 7.21 (d, \(J = 4\) Hz, 1H).\textsuperscript{13}C NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 188.87, 188.54, 188.06, 143.08, 142.46, 144.40, 141.80, 140.28, 138.96, 138.38, 138.78, 138.23, 138.78, 138.41, 137.80, 137.76, 137.82, 137.37, 137.35, 135.12, 135.92, 131.67, 131.64, 130.61, 130.47, 128.27, 128.19, 126.40, 126.33, 124.58, 124.51, 124.13, and 29.70. HRMS (FD): calc for C\textsubscript{13}H\textsubscript{8}Br\textsubscript{2}O\textsubscript{3}S: 395.8545 [M\textsuperscript{+}], found: m/z 395.8461.

**Synthesis of ICTBr**

ICBr (1.37 g, 5 mmol), 5-bromo-2-thiophenecarboxaldehyde (0.48 g, 2.5 mmol), and acetic acid (50 ml) were added to a reaction flask and refluxed at 140 °C under a nitrogen atmosphere overnight. The solution was allowed to cool to room temperature to make the precipitate occur. The mixture was filtered through a funnel to obtain the crude product and further washed with water and n-hexane to afford ICTBr (0.98 g, 2.09 mmol, yield 83.6%).\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 8.65 (d, \(J = 3.5\) Hz, 2H), 8.62 (s, 1H), 8.42 (d, \(J = 9\) Hz, 1H), 8.20 (d, \(J = 9\) Hz, 1H), 8.13–8.11 (m, 2H), 7.89 (d, \(J = 9\) Hz, 1H), 7.84 (d, \(J = 4\) Hz, 2H) and 7.57 (d, \(J = 4\) Hz, 2H). \textsuperscript{13}C NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 187.15, 158.47, 143.68, 141.23, 138.41, 138.00, 137.82, 137.76, 135.30, 135.74, 131.70, 130.47, 128.50, 127.37, 126.71, 125.22, 123.10, 113.67, 72.03 and 29.70. HRMS (FD): calc for C\textsubscript{13}H\textsubscript{8}Br\textsubscript{2}N\textsubscript{2}OS: 443.8568 [M\textsuperscript{+}], found: m/z 443.8573.

**Synthesis of IDMFTBr**

IDMBr (0.26 g, 0.8 mmol), 5-bromo-2-thiophenecarboxaldehyde (0.23 g, 1.2 mmol), and acetic anhydride (4.8 ml) were added to a reaction flask and heated at 100 °C under a nitrogen atmosphere for 3 h. The solution was allowed to cool to room temperature and poured into a huge amount of water to make the precipitate occur. The mixture was filtered through a funnel and washed with n-hexane to obtain the crude product and further recrystallized with chloroform and n-hexane to afford IDMFTBr (0.305 g, 0.619 mmol, yield 77.4%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 8.08 (s, 1H), 7.89 (d, \(J = 9\) Hz, 1H), 8.86 (s, 1H), 8.73 (s, 1H), 8.61 (s, 1H), 8.48–8.45 (m, 2H), 8.35 (d, \(J = 9\) Hz, 1H), 7.99 (d, \(J = 4\) Hz, 2H) and 7.21 (d, \(J = 4\) Hz, 2H). \textsuperscript{13}C NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 188.87, 188.54, 188.06, 143.08, 142.46, 144.40, 141.80, 140.28, 138.96, 138.38, 138.78, 138.23, 138.78, 138.41, 137.80, 137.76, 135.30, 135.74, 131.70, 130.47, 128.50, 127.37, 126.71, 125.22, 123.10, 113.67, 72.03 and 29.70. HRMS (FD): calc for C\textsubscript{13}H\textsubscript{8}Br\textsubscript{2}O\textsubscript{3}S: 395.8545 [M\textsuperscript{+}], found: m/z 395.8461. \textsuperscript{35} 36
9 Hz, 1H), 7.95–7.90 (m, 2H), 7.36 (d, J = 4 Hz, 2H) and 7.20 (d, J = 4 Hz, 2H). 13C NMR (500 MHz, CDCl3): δ 160.05, 159.59, 159.08, 158.70, 139.51, 139.48, 138.99, 138.21, 137.98, 137.94, 136.31, 134.83, 134.76, 134.74, 132.54, 130.76, 130.32, 129.10, 128.66, 128.42, 127.05, 126.27, 125.77, 125.70, 112.84, 112.69, 112.48, 112.26, 112.15, 79.25, 78.47, 73.22, 72.47, 31.54, 22.61 and 14.08. HRMS (FD): calcd for C20H8Br2N4S: 491.8680 [M]+, found: m/z 491.8685.

**General procedure for Suzuki–Miyaura coupling polymerization**

A mixture comprising monomers, K2CO3, Pd(PPh3)4, dimethylformamide, and water was subjected to nitrogen degassing for 30 minutes and subsequently heated to 130 °C for a duration of 24 hours. After cooling to 25 °C, the mixture was poured into MeOH. The resulting precipitate underwent Soxhlet extraction with MeOH, hexane and chloroform to eliminate by-products and unreacted materials. The polymers were then collected and subjected to vacuum pressure drying.

**Hydrogen evolution test**

First, 2 mg of polymers and 1 ml of NMP were charged into a reaction glass and sonicated for 20 min. Next, 9 ml of water, 3 wt% H2PtCl6, and 1 M ascorbic acid (AA) were added to the glass and the pH value was adjusted to 4.00 using 10 M KOH. In the Pd content experiment, we added additional Pd(PPh3)4 solution as the Pd source. Moreover, the mixture was degassed with argon, and illuminated using a 350 W xenon lamp equipped with a visible light filter (380–780 nm) at room temperature, and the irradiance intensity was adjusted to 1000 W m−2. Finally, the amount of hydrogen produced was measured by gas chromatography with a thermal conductivity detector and standard hydrogen gas as a reference.

**Transient absorption spectroscopy**

Transient absorption spectroscopy was used to reveal the molecular dynamics and interactions of the polymers at the sub-picosecond timescale. The primary light source employed in this setup is a commercially available Yb:KGW laser system known as Pharos with a central wavelength of 1030 nm, an energy level of 800 mJ, and a repetition rate of 1 kHz. Each pulse of 190 fs duration has an energy of 800 μJ. To generate two identical pulses, a low group delay dispersion (GDD) 50/50 beam splitter is utilized. Pulse compression is accomplished using multiple plate compression (MPC). By employing this technique, the two pulse replicas achieve a final spectrum ranging the span from 550 nm to 980 nm. The compressed pulses, with a full width at half maximum (FWHM) duration of 3.2 fs, are characterized using a polarization-gating frequency-resolved optical gating (PG-FROG) system, ensuring accurate pulse duration measurements. A broadband half-wave plate and a wire-grid polarizer were employed to minimize nonlinear effects. Additionally, a linear translation stage (DL325, Newport) facilitates adjustments to the probe delay time, providing a delay range of up to approximately 2.2 ns. The transient absorption signal is obtained by spatially separating the transmitted probe pulse and guiding it into a designed spectrometer featuring a high-speed linear array camera that captures each probe pulse, exploiting the modulation of the pump pulses to generate the ΔT/T signal (setup detailed in the ESIF). Each of the sample solutions was placed into a cuvette of 2 mm thickness and three successive measurements were conducted to improve the data quality.

**Results and discussion**

**Photocatalyst synthesis and characterization**

Fig. 1 and S1† illustrate the synthetic pathways and structures of the indanone-based monomers and conjugated polymers investigated in this study. Derived from the precursor 4-bromomophthalic anhydride, we synthesized 5-bromo-1H-indene-1,3(2H)-dione (ICBrF). Subsequently, we produced two monomers with varying numbers of malononitrile substitutions, labeled as ICBR and IDMBr. These monomers were synthesized through carefully optimized Knoevenagel condensation, utilizing precise quantities of malononitrile, specific reaction times and controlled temperatures, all starting from ICBRF. Subsequently, we performed aldol condensation reactions involving these three monomers and 5-bromo-2-thiophenecarboxaldehyde. This process led to the creation of compounds compatible with Suzuki coupling in the following step, referred to as ICFBr, ICTBr, and IDMTBr. All monomers underwent comprehensive characterization and verification using 1H and 13C nuclear magnetic resonance spectroscopy (NMR) as well as high-resolution mass spectrometry (HRMS), as detailed in Fig. S2–S19.† Notably, certain monomers, including ICBR, ICTBr, and IDMBr, displayed two distinct pairs of signals in their 1H NMR spectra due to the presence of isomers. In the case of 13C NMR, monomers containing ketone groups, such as ICFBr and ICBR, exhibited signals in the range of 180–200 ppm, whereas IDMBr and IDMTBr, in which the ketone groups were substituted with malononitrile structures, lacked the ketone signal. The Fourier transform infrared spectroscopy (FTIR) results further corroborated the accurate identification of these monomers (Fig. 2a). Specifically, ICBRF displayed a characteristic C=O signal at 1700 cm−1, IDMBr showed a C≡N signal at 2222 cm−1, and ICBR presented both signals simultaneously. Density functional theory (DFT) was employed to predict the energy levels of these monomers. As illustrated in Fig. S20,† the incorporation of varying numbers of malononitrile groups allows the monomers to attain lower energy levels. This observation implies that the degree of malononitrile substitution could significantly impact the thermodynamic driving forces for the reduction of oxonium ions (H2O−) in the context of PHP. These monomers were integrated into a 3,7-bis(4,4,5,5-tetramethyl-1,3-dioxaborolan-2-yl)dibenzo[9,10,34,39-polysulfonyl] system, which was synthesized using the palladium (Pd)-catalyzed Suzuki-Miyaura coupling polymerization technique. The palladium catalyst, typically known as Pharos with a central wavelength of 1030 nm, an energy level of 800 mJ, and a repetition rate of 1 kHz, is utilized. Each pulse of 190 fs duration has an energy of 800 μJ. To generate two identical pulses, a low group delay dispersion (GDD) 50/50 beam splitter is utilized. Pulse compression is accomplished using multiple plate compression (MPC). By employing this technique, the two pulse replicas achieve a final spectrum ranging the span from 550 nm to 980 nm. The compressed pulses, with a full width at half maximum (FWHM) duration of 3.2 fs, are characterized using a polarization-gating frequency-resolved optical gating (PG-FROG) system, ensuring accurate pulse duration measurements. A broadband half-wave plate and a wire-grid polarizer were employed to minimize nonlinear effects. Additionally, a linear translation stage (DL325, Newport) facilitates adjustments to the probe delay time, providing a delay range of up to approximately 2.2 ns. The transient absorption signal is obtained by spatially separating the transmitted probe pulse and guiding it into a designed spectrometer featuring a high-speed linear array camera that captures each probe pulse, exploiting the modulation of the pump pulses to generate the ΔT/T signal (setup detailed in the ESIF). Each of the sample solutions was placed into a cuvette of 2 mm thickness and three successive measurements were conducted to improve the data quality.
Miyaura coupling method. Given the asymmetrical structure of the monomers, the resulting polymers, namely ICFTDB, ICTDB, and IDMTDB, are expected to be statistical polymers. Fig. S21† illustrates all possible coupling schemes for ICFTDB, ICTDB, and IDMTDB, encompassing different directions of polymerization and different forms of monomers. For the sake of simplicity, the polymers will be discussed in the form depicted in Fig. 1. Magic-angle spinning solid-state $^{13}$C NMR was employed to confirm the structure of these polymers. The NMR spectra of all polymers display remarkable similarities, with peaks appearing between 120 and 140 ppm, corresponding to aromatic carbons, $C=O$ bonds, or $C\equiv N$ bonds. Additionally, each polymer exhibits broad peak signals, a typical characteristic of polymers, further confirming their high degree of polymerization. Thermogravimetric analysis (TGA) was employed to evaluate the thermal stability of the photocatalysts by measuring weight loss as a function of increasing temperature (Fig. 2c and Table 1). The TGA results demonstrated that the polymers exhibited remarkable thermal stability under a nitrogen atmosphere, with decomposition temperatures ($T_d$) of 301 °C, 472 °C and 366 °C, respectively. Despite variations in thermal stability among the polymers, it can be concluded that all of them are expected to remain thermally stable without undergoing decomposition during their intended applications. Powder X-ray diffraction (PXRD) analysis reveals low crystallinity, as evidenced by the weak and broad diffraction peaks at around $2\theta = 25^\circ$ for all three polymers, indicating the amorphous nature of the materials (Fig. 2d). The diffraction peaks in this region are commonly associated with $\pi-\pi$ stacking within polymer structures, a phenomenon frequently discussed in the literature. $^{40}$ Additionally, the presence of peaks at $2\theta = 40^\circ$ and $2\theta = 47^\circ$ in all samples corresponds to the XRD pattern of palladium nanoparticles. $^{41}$ These peaks are attributed to catalyst residues from the Suzuki coupling reaction. Brunauer–Emmett–Teller (BET) analysis of polymers indicates that the polymers did not show a porous structure. (Fig. S22†) The light absorption properties of the polymers were assessed using ultraviolet-visible spectroscopy (UV-vis). The optical band gap ($E_g$) was determined from the Tauc plot based on the UV-vis data. As shown in Fig. 2e, S23† and Table 1, the calculated $E_g$ values for ICFTDB, ICTDB and IDMTDB were found to be 2.42, 2.54, and 2.52 eV, respectively, indicating their ability to absorb visible light effectively. The blue wavelength peaks in ICFTDB are attributed to $\pi-\pi^*$ transitions, $^{42-44}$ in contrast to the peak at around 500 nm, which is associated with charge transfer (CT). Cyclic voltammetry (CV) was employed to measure the HOMO and LUMO levels of the photocatalysts and additional information regarding the calculation process can be found in the ESI. (Fig. S24†) By combining these values with the $E_g$, the HOMO and LUMO levels were calculated. As shown in Table 1, the HOMO/LUMO energy levels of ICFTDB, ICTDB and IDMTDB were determined to be $-5.37/-2.95$ eV, $-5.44/-2.90$ eV and $-5.49/-2.97$ eV, respectively. These results indicate that all three polymers can facilitate hydrogen production in the presence of ascorbic acid. Notably, the polymers ICTDB and IDMTDB, which incorporate electron-withdrawing malononitrile substitutions, exhibited lower-lying HOMO levels compared to ICFTDB, consistent with the DFT simulation results. We use Pt as a cocatalyst in the hydrogen evolution experiment. In the catalytic reaction involving metals and semiconductors, understanding the energy level matching between the metal and the materials is crucial. $^{45}$ The results indicate that Pt has a sufficiently large work function ($\sim 4$ eV) to accept photoelectrons from the photocatalysts. $^{46}$

**Photocatalytic hydrogen evolution**

To refine the conditions for optimizing hydrogen evolution, a series of systematic experiments were performed. The polymerization of ICTDB through Suzuki coupling was executed using different solvent systems, including toluene/H$_2$O and DMF/H$_2$O systems. Notably, the HER of ICTDB was found to be notably superior when the DMF/H$_2$O system was employed. (Fig. S25†) Additional optimization experiments were also carried out to choose appropriate sacrificial agents. Fig. S26† presents the HER results for ICTDB utilizing triethanolamine (TEOA), triethylamine (TEA), and AA as sacrificial agents. The results show that the HER values for ICTDB with AA were higher than those with the other two sacrificial agents. Consequently, subsequent hydrogen evolution measurements were conducted using polymers synthesized in the DMF/H$_2$O system, with AA chosen as the sacrificial agent. Fig. 3a displays the hydrogen evolution rate (HER) results from a 5-hour test conducted under visible light excitation conditions (AM 1.5, 1000 W m$^{-2}$, $\lambda$ = 380–780 nm), with N-methyl pyrrolidine (NMP) as the cosolvent and ascorbic acid (AA) as the sacrificial agent, and adding 3 wt% of H$_2$PtCl$_6$. We added H$_2$PtCl$_6$ to provide the system with a cocatalyst. Under light irradiation, Pt metal will deposit on the surface of the material, facilitating the hydrogen production reaction. We further verified the presence of Pt(0) metal in the solid powder of ICTDB post hydrogen evolution using X-ray photoelectron spectroscopy (XPS) data (Fig. S27†). The results from X-ray absorption spectroscopy (XAS) allowed us to measure the signal of L$_3$-edge Pt in the HER solution, confirming that the oxidation state of Pt becomes more reduced after light irradiation (Fig. S28†). These HER outcomes reveal an intriguing trend, characterized by an initial increase followed by a subsequent decline, as the number of malononitrile substitutions increases (Fig. 3b). Notably, the photocatalyst ICTDB, featuring a single malononitrile substitution, exhibited a remarkable HER of 30.0 mmol g$^{-1}$ h$^{-1}$, representing a 11.5-fold increase compared to ICFTDB, which lacks malononitrile substitution. However, the introduction of a second malononitrile moiety into the photocatalyst did not further enhance the HER. Instead, it led to a reduction in the HER to 7.77 mmol g$^{-1}$ h$^{-1}$, which is approximately one-fourth of the performance achieved by ICTDB. These results underscore the substantial potential of IC-based polymers as promising photocatalysts. A more comprehensive discussion of these observations follows below. Control experiments were conducted to reveal the factors influencing photocatalytic activity. These results demonstrated that the kinetic curve of photocatalytic activity remained inert in the absence of water, light, and photocatalysts, emphasizing the indispensable roles played by these components in facilitating
the HER (Fig. S29†). Long-term photocatalytic cycling for hydrogen evolution demonstrated the remarkable photo stability and durability of ICTDB. As depicted in Fig. 3c, even after continuous photocatalytic hydrogen evolution for 16 hours (4 cycles), the HER value exhibited only a modest 14.7% decrease compared to the initial cycle. This result highlights the potential of ICTDB as a stable and enduring photocatalyst for prolonged hydrogen production applications. The apparent quantum yield (AQY) experiment for ICTDB aimed to establish a correlation between the HER and the visible light absorption. This investigation involved utilizing a light source equipped with bandpass filters at specific wavelengths (\(\lambda = 420, 460, 500, \) or 550 nm). The AQY values were determined by dividing the number of electrons involved in the hydrogen production process by the number of incident photons. Assuming that a complete reaction is a two-electron process, the details of the calculation are attached in the ESI†. The AQY values were found to be 8.35% and 5.77% at wavelengths of 420 nm and 460 nm, respectively. These results showcased a remarkable concordance between the AQY values and the UV-visible absorption spectrum (Fig. 3d). The literature has indicated that residual Pd from Suzuki coupling reactions can act as a cocatalyst in

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Fig. 1  Synthesis steps and structures of the indanone-based monomers and polymers.

Fig. 2  (a) FTIR of the monomers, (b) \(^{13}\)C NMR of the polymers, (c) TGA of the polymers, (d) XRD of the polymers, (e) UV-vis spectrum of the polymers, and (f) energy levels of the polymers.
hydrogen production reactions. In order to understand the residual amount of Pd in the three polymers, we employed inductively coupled plasma optical emission spectrometry (ICP-OES). The results unveiled a residual Pd content of 0.60 wt%, 1.04 wt%, and 0.86 wt% for ICFDTDB, ICTDB and IDMTDB, respectively. Previous studies have suggested that, at the scale of Pd content considered, there is no direct correlation between the HER and the quantity of Pd residues. Furthermore, as depicted in Fig. S30, the trend in hydrogen production remained consistent with the original findings at consistent Pd content levels. This suggests that the Pd content is not a decisive factor.

Discussion of hydrogen evolution

The hydrogen evolution performance of materials with various sacrificial agents could be influenced by the relative band positions. Sacrificial agents with an optimal thermodynamic driving force relative to materials tend to show improved performance. Fig. S31 illustrates the relative band positions of sacrificial donors and the photocatalyst. The oxidation potential becomes shallower from AA to TEA, resulting in a moderate thermodynamic driving force for transferring holes from the HOMO level of a photocatalyst to the sacrificial donor. To comprehend the distinction in the photophysics governing the photocatalytic activities between the AA system and the TEA system, we conducted photoluminescence measurements on ICTDB. Fig. S32 reveals that the photoluminescence intensity of ICTDB in the TEA system is considerably higher than that in the AA system. This suggests that the recombination of photo-generated electron–hole pairs in the AA system was more effectively suppressed compared to that in the TEA system. The hydrophilicity of the polymers was assessed using the sessile drop method, involving the measurement of water contact angles after coating the polymers onto glass substrates. As shown in Fig. S33, the results revealed that all three polymers exhibited water contact angles in the range of 60° to 65°, indicating a consistent level of hydrophilicity among them. All polymers exhibited significant hydrophilicity, a property that could potentially enhance their performance in the HER. Nevertheless, it’s important to recognize that factors beyond hydrophilicity play a more dominant role in influencing the HER performance of these photocatalysts. To elucidate the structural relationships among the polymers, we employed density functional theory (DFT) calculations to predict the optimal geometries and dihedral angles of the indanone-based pentamers. The dihedral angles between the indanone unit and the thiophene unit were found to be 0.21°, 0.27°, and 14.7°, for ICFDTDB, ICTDB and IDMTDB, respectively. These findings suggest that the introduction of the malononitrile substitution has a minimal impact on material planarity. Despite the substantial steric hindrance associated with the malononitrile structure, the initial substitution has a relatively minor effect on planarity due to the linear C=N group with sp hybridization. In contrast, subsequent malononitrile substitutions introduce significant strain and twist the polymer structure. A smaller dihedral angle compared to IDMTDB, as observed in ICTDB, contributes to better planarity. This enhanced planarity potentially facilitates faster electron and hole transfer, thereby enhancing charge transfer efficiency.

To assess the extent of particle aggregation in the hydrogen evolution solution, we employed fluorescence microscopy (FM) to analyse particle sizes. FM offers the advantage of exciting polymers with various wavelengths of light sources and capturing images of aggregates in their native state. As depicted in Fig. 4b, all three polymers exhibited aggregation sizes in the micron-scale range within the hydrogen evolution solutions. Notably, ICTDB displayed the smallest aggregation size, measuring approximately 20 μm, in contrast to ICFDTDB and IDMTDB. This reduced aggregation size suggests a larger reactive surface area, which has the potential to enhance
photocatalytic activity. Various characterization techniques were employed to investigate the charge generation and transfer dynamics of the photocatalysts upon irradiation. Electrochemical impedance spectroscopy (EIS) yielded semicircular curves, with ICTDB exhibiting a smaller Nyquist circular diameter and $R_{ct}$ compared to ICFTDB and IDMTDB (Fig. 4c and S34†). This observation implies that the incorporation of the IC structure enhances the charge transfer ability, providing the polymer with a more favorable interface for charge transfer in the photocatalytic hydrogen production reaction. Time-resolved

**Fig. 4** (a) Calculated dihedral angles of the polymers, (b) fluorescence microscope images of the polymers, (c) EIS of the polymers, (d) time-resolved photoluminescence (TRPL) spectrum of the polymers, and (e) photocurrent measurement of the polymers.

**Fig. 5** (a) TAS spectra of ICFTDB, (b) TAS spectra of ICTDB, (c) TAS spectra of IDMTDB, (d) comparison of amplitude average lifetime of the three polymers in HER solution ($\Delta$OD is normalized from the data ranging from 0.5 to 1800 ps), (e) comparison of ICTDB in the AA system and TEA system, and (f) schematics for the electron quenching pathways of the polymers.
photoluminescence (TRPL) measurements, including instrument response function curves, were conducted to determine the average photoluminescence lifetimes (Fig. 4d). Among the three polymers, ICTDB displayed the shortest lifetime, signifying its rapid charge transfer capability.\(^{50-61}\) Additionally, photocurrent measurements were employed to investigate the photo-response of all polymers (Fig. 4e). Notably, ICTDB exhibited the highest photocurrent response, indicating the most effective separation of photo-induced electrons and holes, as well as the fastest charge mobility. These results consistently align with the HER performance.

### Transient absorption spectroscopy

In order to investigate the transient charge carrier dynamics within the photocatalysts, we employed femtosecond to nanosecond transient absorption (TA) spectroscopy in this study. Fig. 5a–c display the TA spectra of all three polymers, spanning delay times from 1 ps to 1.8 ns, for ICTDB, ICTDB, and IDMTDB upon 430 nm excitation in the HER solution. In all cases, a positive signal emerged beyond 700 nm, indicating the presence of photoinduced absorption (PIA) associated with the absorption of singlet excitons.\(^{64-66}\) To elucidate the origins of the PIA signal, we conducted kinetic decay and fitting analyses on the curves displaying the highest PIA signals, as detailed in Fig. S35† and Table 2. Fitting the data with three-exponential functions revealed that all three photocatalysts exhibited two short-lived components and one long-lived component in their decay profiles.\(^{11,67-69}\) The short-lived components \(\tau_1\), within the picosecond timescale, are likely to signify electron transfer to Pt sites. Conversely, the long-lived component \(\tau_3\) is attributed to charge carrier recombination.\(^{11,68-70}\) Among the three photocatalysts, ICTDB exhibits the highest proportion \(\tau_1\) lifetime component, accounting for 82.2% of the total, signifying exceptionally rapid transfer of photoexcited electrons to the Pt sites in ICTDB. Although the \(\tau_1\) of IDMTDB is slightly shorter than that of ICTDB, the proportion of the \(\tau_1\) component is significantly smaller than that of ICTDB, indicating inefficient ultrafast charge transfer compared with ICTDB. Furthermore, we examined the ultralong lifetime component \(\tau_3\). ICTDB exhibited the shortest \(\tau_3\) lifetime (0.12 ns), followed by ICTDB (0.37 ns) and IDMTDB (0.45 ns). This ultralong lifetime is associated with photoluminescence resulting from charge carrier recombination, and it aligns with the similar timescales and results obtained from TRPL measurements. Notably, ICTDB displayed a \(\tau_3\) proportion of only 3.1%, indicating minimal recombination effects. In contrast, ICTDB and IDMTDB had a \(\tau_3\) proportion of 31.9% and 21.5%, respectively, suggesting that these two polymers might experience significant charge carrier recombination after pump excitation. We also calculated the amplitude average lifetime, revealing that ICTDB exhibited the shortest lifetime at 10.3 ps, followed by IDMTDB (85.9 ps) and ICTDB (148.4 ps), as summarized in Fig. 5d and Table 2. Additionally, we measured TA spectra of ICTDB in both the AA and TEA systems. As depicted in Fig. 5e, the PIA in the TEA group is comparatively weaker, and its long-lived component \(\tau_3\) has a higher proportion, indicating a more pronounced recombination effect in ICTDB in the TEA system compared to the AA system. (Fig. S36†) This observation aligns with the PL results, suggesting that due to the mismatch in energy levels, electrons generated in the TEA system are more prone to recombination rather than undergoing ultrafast transfer to Pt sites. We depicted the electron quenching pathway within the polymers in Fig. 5f. Excitons are promptly generated and dissociate into free electrons and holes within a few femtoseconds of excitation. Subsequently, the photogenerated electrons follow mainly three decay pathways. First, they can readily be captured by the Pt cocatalyst at the material interface and utilized for hydrogen production. It’s noteworthy that this electron trapping process has a relatively short lifetime, occurring within a few picoseconds. Concurrently, the photogenerated holes transfer to a deeper “hole-trapped state,” where they can persist for an extended duration.\(^{71-72}\) Consequently, the second electron quenching pathway, characterized by a timescale of tens of picoseconds, involves the recombination of photogenerated electrons with these trapped holes. The slowest electron quenching process is the recombination of electrons in the LUMO and holes in the HOMO, occurring on a timescale consistent with the lifetimes measured in the TRPL results. Based on these analyses, we can conclude that all three polymers, when subjected to visible light illumination, undergo excitation and generate charge carriers. Importantly, ICTDB, with its relatively larger \(\tau_1\) lifetime component, demonstrates the fastest electron transfer ability, along with the least impact of charge recombination among the three photocatalysts.\(^{11,65-67,69,70,73-74}\) These findings are consistent with the HER performance of these polymers and underscore the superior charge transfer capability of ICTDB as a photocatalyst.

### Conclusions

In conclusion, we have successfully designed and synthesized novel indanone-based monomers, which served as building blocks for the creation of indanone-based conjugated polymers.
for photocatalytic hydrogen evolution. Importantly, the incorporation of malononitrile functionalities introduced a pull-push effect, enhancing charge transfer capabilities. Among these polymers, ICTDB, featuring a single malononitrile substitution, exhibited exceptional performance with a HER of 30.0 mmol g\(^{-1}\) h\(^{-1}\) under visible-light illumination. This outstanding result surpassed that of ICFTDB, a polymer without malononitrile substitution, by a factor of 11.5. The improvement can be attributed to several factors, including reduced aggregation size, improved charge transfer properties, and enhanced photocurrent response. However, the introduction of a second malononitrile moiety led to a structural twist, resulting in a decreased HER performance of 7.77 mmol g\(^{-1}\) h\(^{-1}\). Furthermore, our investigation through transient absorption spectroscopy provided concrete evidence supporting the enhanced ultrafast electron transfer capabilities of ICTDB towards Pt sites while concurrently minimizing recombination effects. Our study not only introduced novel indanone moieties as a platform for water-splitting photocatalysts but also laid a promising foundation for the future application of IC-based polymers in this field.

Author contributions

T.-F. Huang (conceptualization: equal, data curation: lead, formal analysis: lead, investigation: lead, methodology: lead, software: equal, visualization: equal, writing – original draft: lead, and writing – review and editing: lead); Y.-R. Zhuang (data curation: equal, formal analysis: lead, and supervision: support); C.-L. Chang (methodology: equal, software: support, supervision: lead, and validation: lead); C.-L. Huang (investigation: support, methodology: equal, lead, validation: support, and writing – review and editing: support); W. C. Lin (methodology: support, supervision: support, and validation: support); Z.-C. Jiang (data curation: equal, formal analysis: equal, investigation: equal, methodology: equal, software: equal, validation: support, and visualization: support); L.-Y. Ting (methodology: support, supervision: support, and validation: support); I. M. A. Mekhemer (methodology: support and validation: support); Y.-E. Sun (supervision: lead, and writing – review and editing: support); Y. T. Lin (methodology: equal, project administration: support, resources: lead, and supervision: support); Y.-T. Tseng (supervision: lead, and validation: support); Y.-H. Wu (methodology: support, supervision: support, and validation: support); B.-H. Li (supervision: support); S.-D. Yang (project administration: support, resources: lead, and supervision: support); Y.-J. Cheng (methodology: equal, project administration: support, resources: lead, and supervision: support); H.-H. Chou (conceptualization: lead, formal analysis: support, funding acquisition: lead, methodology: equal, project administration: lead, resources: lead, supervision: lead, validation: lead, writing – original draft: support, and writing – review and editing: support).

Conflicts of interest

There are no conflicts to declare.

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Notes and references