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Covalently Locked Donor–Acceptor Block Copolymer Nanoparticles Enable Efficient, Stable and Reproducible Photocatalytic Hydrogen Evolution

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ABSTRACT

Organic photocatalysts with tailored properties and unique processability offer a sustainable route to solar hydrogen. To maximize light harvesting and charge generation, donor and acceptor materials are usually physically mixed to form D:A heterojunction nanoparticles (NPs). However, weakly constrained interactions can promote phase segregation, morphological evolution, and limited reproducibility. Here, we introduce an all-conjugated donor–acceptor block copolymer, PBDB-T-*b*-PYT, in which covalent linkage between PBDB-T and PYT segments constrains nanoscale donor–acceptor organization and promotes intramolecular charge transfer. Compared with nanoparticles prepared from a physical PBDB-T:PYT blend, PBDB-T-*b*-PYT nanoparticles exhibit stronger photoluminescence quenching, more persistent charge-associated transient absorption features, and improved photoelectrochemical charge extraction. As a result, hydrogen evolution reaction (HER) rates exceeding 120 mmol cm^{−2} g^{−1} h^{−1} (>450 μmol h^{−1}) are achieved with low Pt loading (<3 wt.%). PBDB-T-*b*-PYT NPs retained 95% of the initial HER rate after 96 h of photocatalysis. Conversely, NPs prepared from physically mixed PBDB-T and PYT show lower activity and faster deactivation, consistent with morphology-driven losses. PBDB-T-*b*-PYT also maintains high performance across polymer batches, improving reproducibility. These results establish all-conjugated donor–acceptor block copolymers as a promising design strategy for combining high activity, operational stability, and reproducibility in organic nanoparticle photocatalysis.

1 | Introduction

Hydrogen gas (H₂) is a pivotal energy carrier in the transition toward carbon neutrality, producing only water as a by-product when combusted or used in fuel cells [1]. As global hydrogen

demand grows, the development of sustainable and carbon-free production routes becomes imperative. Water electrolysis provides a green route for H₂ production, particularly when powered by renewable electricity, but the high capital and operational costs hamper large-scale deployment [2]. Photocatalysis (PC)

Alexandre Holmes and Qiaonan Chen contributed equally to this work.

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provides an alternative route that converts solar energy directly into chemical energy in the form of H_2 . In contrast to electrocatalysis, particulate PC operates without an external bias, offering a potentially favorable energy balance and simplified device requirements [3]. In this approach, semiconductor nanoparticles (NPs) are dispersed in water to maximize the photocatalytic surface and light harvesting [4].

Inorganic photocatalysts such as TiO_2 or $ZnCdS$ pioneered advances in hydrogen evolution reaction (HER) [5–7]. However, their absorption is often limited to the UV range, which constitutes less than 5% of the solar spectrum. Organic photocatalysts offer broad absorption ranges, tailored energy levels, and excellent processability [8]. A common strategy to maximize light absorption and charge generation relies on the physical blending of electron donor (D) and electron acceptor (A) materials within single NPs [9, 10], ultimately yielding remarkable performance [11].

However, the physical mixing of donor and acceptor materials in D:A heterojunction NPs remains limited by several challenges. The internal D:A distribution, i.e. NP morphology, must be controlled to avoid unfavorable architectures such as core-shell that can lead to poor charge generation and extraction [12–15]. The internal D:A morphology is affected by the NP size, promoting higher performance by reducing the likelihood of charge recombination [16–21]. Finally, photocatalytic performance can suffer from operational instability, owing to phase segregation within NPs during operation [22]. Together, these considerations constitute the central bottleneck for the development of efficient, durable and reproducible photocatalysts.

Over the past decade, several strategies have been developed to address the morphological issue of D:A heterojunction NPs. Preparation techniques, semiconductor engineering, and surfactant selection have emerged as effective tools to achieve suitable morphologies, while allowing the NP size to be fine-tuned [23–26]. Yet, the vast majority of D:A heterojunction NPs suffer from limited morphological stability, which constrains long-term activity [11]. Through the design of ternary blends or double-cable architectures, morphological changes can be mitigated [22, 27]. However, such strategies tend to achieve lower performances in addition to displaying a strong system dependency. Together, these studies highlight a fundamental trade-off between efficiency and stability.

To overcome these issues linked to D:A heterojunction NPs, we designed a covalently bonded all-conjugated donor-acceptor block copolymer. Our strategy relies on the covalent linkage between donor and acceptor segments, ensuring i) nanoscale intermixed donor and acceptor phases, ii) high morphological stability and iii) resilience to NP size variations. Covalently connected donor-acceptor architectures have proven effective in organic photovoltaics (OPV) [28–35], but remain largely unexplored, particularly for photocatalytic applications.

We demonstrate the benefits of all-conjugated block copolymers for photocatalytic hydrogen production, through the design of PBDB-T-*b*-PYT NPs. The covalent linkage between donor and acceptor blocks promotes the formation of highly intermixed NPs, enabling efficient charge generation. As a result, PBDB-T-*b*-PYT

NPs exhibit a HER rate exceeding $120 \text{ mmol cm}^{-2} \text{ g}^{-1} \text{ h}^{-1}$ ($450 \text{ } \mu\text{mol h}^{-1}$) with only 3 wt.% of Pt cocatalyst, owing to improved charge generation and extraction properties, supported by spectroscopic and photoelectrochemical measurements. Moreover, they display exceptional stability, retaining 94% of their initial activity after 40 h under a standard solar simulator, and 95% after 96 h under LED irradiation. In contrast, the NPs prepared under the same conditions from a physical blend of PBDB-T and PYT show much lower efficiencies, around $20 \text{ mmol cm}^{-2} \text{ g}^{-1} \text{ h}^{-1}$, and poor stability, retaining only 69% of the initial HER rate after 40 h. Together, these results position all-conjugated block copolymers as a promising class of materials that combines high photocatalytic performance and outstanding operational stability.

2 | Synthesis and Characterizations of PBDB-T-*b*-PYT

Two benchmark conjugated polymers widely used in OPV, PBDB-T and PYT, with complementary absorption spectra, were selected as electron donor and acceptor segments, respectively, to construct the block copolymer PBDB-T-*b*-PYT (Figure 1a). PBDB-T-*b*-PYT was synthesized via a one-pot sequential polymerization, starting with the PBDB-T block followed by the addition of PYT precursors [28]. Detailed synthetic procedures are provided in the Supplementary Information (Schemes S1 and S2 and Figure S1). The synthesis was designed to target approximately a 1:1 donor:acceptor (D:A) mass ratio. After purification, the dominant chloroform-soluble fraction was obtained in high yield (>85%), and the main and lower-molecular-weight fractions exhibited comparable relative spectral signatures (Figure S2), consistent with a D:A composition close to the targeted value. Accordingly, unless otherwise stated, physically blended PBDB-T:PYT nanoparticles were prepared at a 1:1 mass ratio as the primary reference for evaluating the block-copolymer approach.

The favorable energetic alignment of PBDB-T and PYT is expected to promote exciton dissociation within the all-conjugated backbone of PBDB-T-*b*-PYT, thereby facilitating charge separation and subsequent HER (Figure 1b and Figure S3) [9]. Both the block copolymer PBDB-T-*b*-PYT and the physical blend of PBDB-T:PYT exhibited suitable energy levels to drive both proton reduction ($2 \text{ H}^+ + 2 \text{ e}^- = \text{H}_2$) and ascorbic acid (AA) oxidation to dehydroascorbic acid ($\text{AA} = 2 \text{ e}^- + 2 \text{ H}^+ + \text{DHA}$) [36].

Owing to the complementary absorption of the two building blocks, PBDB-T-*b*-PYT displayed a broad absorption spectrum spanning from the visible to the near-infrared region (Figure 1c). Compared to pristine PBDB-T or PYT, the corresponding absorption features of PBDB-T-*b*-PYT are slightly blue shifted (Table S1). This shift likely arises from increased disorder due to the covalent interaction of PBDB-T and PYT blocks and/or the relatively shorter block lengths that directly affect the conjugation length ($M_w = 33.8 \text{ kg mol}^{-1}$, $\bar{D} = 2.1$). In comparison, pristine PBDB-T ($M_w = 119.8 \text{ kg mol}^{-1}$, $\bar{D} = 2.8$) and PYT ($M_w = 27.2 \text{ kg mol}^{-1}$, $\bar{D} = 2.6$) present redshifted absorption, consistent with extended conjugation length and/or improved order. Nevertheless, the broad absorption of PBDB-T-*b*-PYT maximizes light harvesting properties, which is expected to ensure high photocatalytic activity.

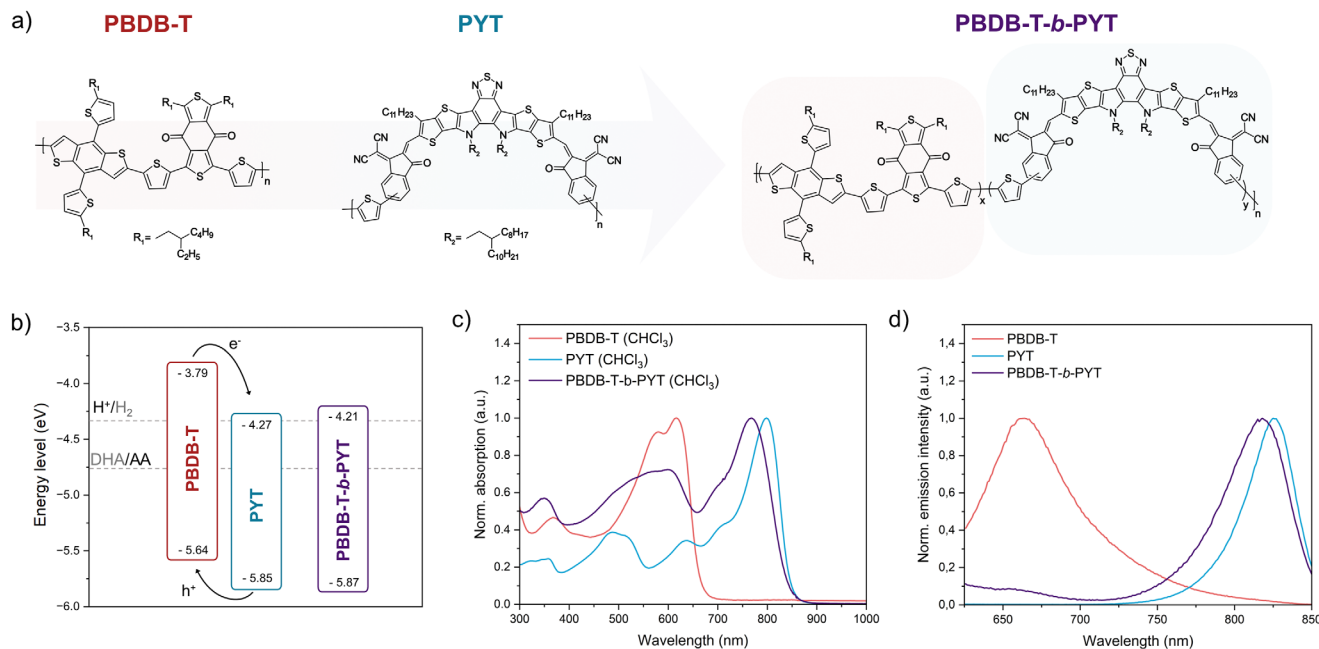


FIGURE 1 | (a) Chemical structure of PBDB-T, PYT and PBDB-T-b-PYT. (b) Energy levels vs vacuum for PBDB-T, PYT, and PBDB-T-b-PYT calculated from cyclic voltammetry. Reduction potential of H^+/H_2 and the two-hole oxidation potential of ascorbic acid (AA) to dehydroascorbic acid (DHA) at pH of 2.5 [37]. (c) Normalized absorption spectra of PBDB-T, PYT and PBDB-T-b-PYT in chloroform solution. (d) Normalized emission spectra ($\lambda_{exc} = 564$ nm) of PBDB-T, PYT, and PBDB-T-b-PYT in chloroform solution.

Photoluminescence (PL) measurements in dilute solution show a single emission at 818 nm for PBDB-T-b-PYT, close to that of pristine PYT (825 nm) (Figure 1d). Notably, the emission feature characteristic of PBDB-T around 670 nm is absent, consistent with efficient intramolecular quenching following photoexcitation of the donor segment. In contrast, a physical mixture of PBDB-T and PYT in solution retained emission features from both components, indicating limited quenching due to negligible charge transfer under these conditions (Figure S4). Time-Dependent Density Functional Theory (TD-DFT) calculations further support spatial separation of the frontier orbitals, with a strong delocalization of hole and electron density on PBDB-T and PYT blocks, respectively (Figures S5–S7). Together, these results are consistent with an efficient intramolecular charge transfer in the case of PBDB-T-b-PYT, promoting efficient charge formation, which we hypothesize to be beneficial for photocatalytic hydrogen evolution, as discussed in the following section.

3 | Preparation and Characterizations of PBDB-T-b-PYT NPs

All-conjugated block copolymers are expected to yield intermixed morphologies [38], however, it remains necessary to ensure the formation of percolation pathways to promote efficient charge transport to the NP surface, where photocatalytic reactions occur. Therefore, PBDB-T-b-PYT NPs were prepared by miniemulsion to promote the formation of a thermodynamically stable morphology (Figure S8) [39]. First, PBDB-T-b-PYT was dissolved in chloroform, and mixed with an aqueous phase containing hexadecyltrimethylammonium bromide (C_{16} TAB). A cationic surfactant was selected owing to its ability to enhance charge sep-

aration and transfer, alongside suppressing charge recombination [11]. After stirring, the emulsion was subjected to ultrasonication to form a miniemulsion. Ultimately, chloroform was removed from the mixture through heating, leading to the formation of PBDB-T-b-PYT NPs stabilized by C_{16} TAB. The relatively long nanoparticle formation process (from a few minutes to hours) facilitates the formation of ordered domains and partial phase segregation. PBDB-T NPs, PYT NPs and PBDB-T:PYT blend NPs were prepared under the same conditions. For PBDB-T:PYT blend NPs, a mass ratio of 1:1 was used to match the feed ratio used for the synthesis of PBDB-T-b-PYT.

In aqueous dispersions, PBDB-T-b-PYT NPs exhibited absorption profiles comparable to those of PBDB-T and PYT NPs (Figure 2a and Figure S9). In contrast, PBDB-T:PYT blend NPs exhibited redshifted features that might either indicate the formation of larger domains or be linked to their larger molecular weight. The unbalanced contribution in absorption between PBDB-T and PYT in the physical blend likely arises from different absorption coefficients, correlated with the lower molecular weight of PYT and different degree of crystallization. In addition, all dispersions presented comparable sizes: 87 ± 6 nm for PBDB-T-b-PYT NPs and 81 ± 6 for PBDB-T:PYT blend NPs (Figure S10).

To probe the intermixing of PBDB-T-b-PYT NPs, PL experiments were conducted. Upon excitation at 564 nm, thereby mostly related to the absorption of the PBDB-T block, a fluorescence quenching (η_Q) above 80% was achieved, consistent with enhanced electron transfer from PBDB-T to PYT domains (Figure 2b). Furthermore, the selective excitation of PYT at 770 nm is consistent with more efficient hole transfer from PYT to PBDB-T segments, with η_Q up to 72% (Figure S11). In contrast,

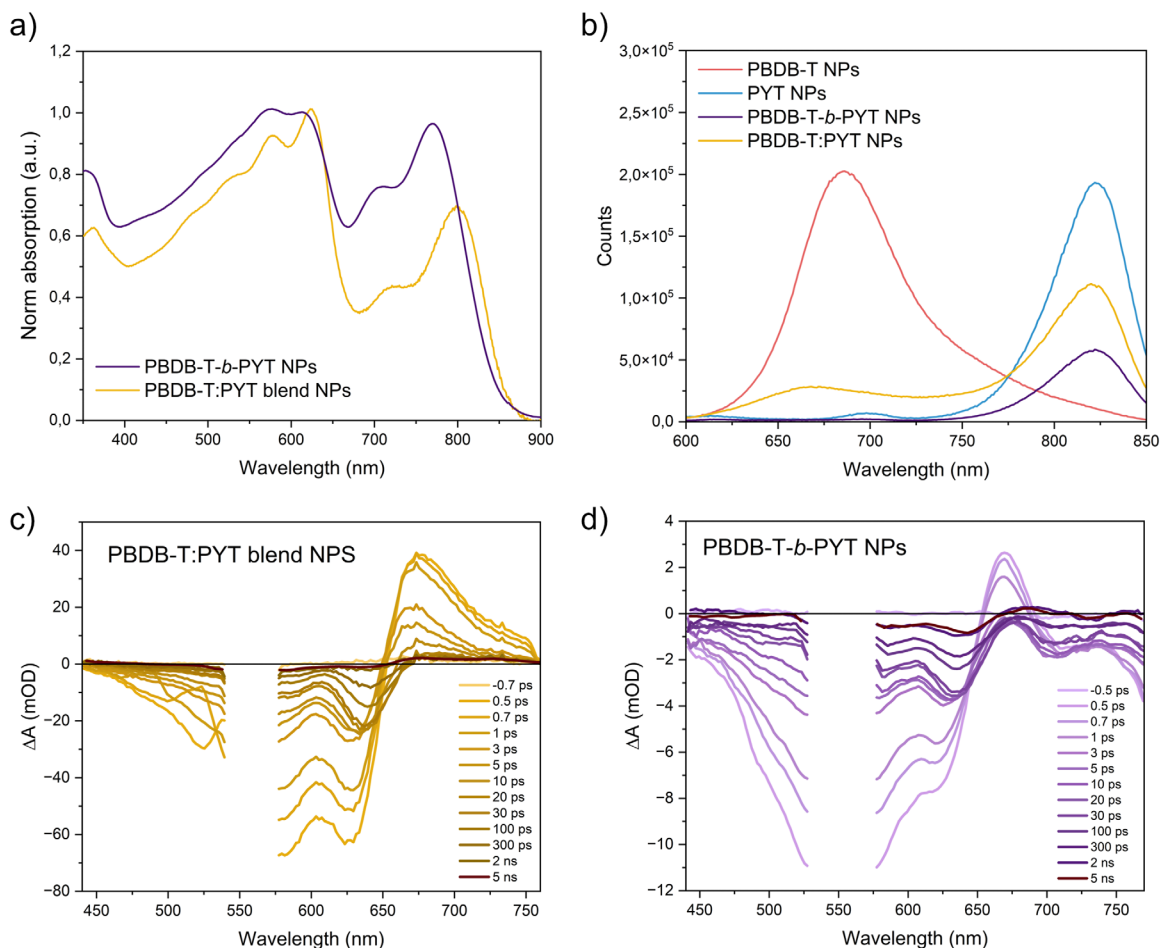


FIGURE 2 | (a) Normalized absorption spectra and (b) emission spectra of PBDB-T-b-PYT NPs and PBDB-T:PYT blend NPs. For emission spectra, pristine PBDB-T NPs and PYT NPs emissions are used as reference to compare fluorescence quenching when excited at $\lambda_{\text{exc}} = 564$ nm and with a fixed concentration of active materials (0.01 mg mL^{-1}). TA spectral evolution of (c) PBDB-T:PYT blend NPs and (d) PBDB-T-b-PYT NPs after excitation at 550 nm.

upon excitation at 564 nm, the PL quenching of PBDB-T:PYT blend NPs was limited to 54%, indicating less efficient donor–acceptor coupling and/or reduced interfacial area accessible to excitons, particularly for processes initiated in the acceptor-rich regions. Interestingly, recombination is most likely predominant within PYT domains, as PBDB-T emission was almost fully quenched (Figure 2b) [40]. In addition, selective excitation of PYT domains yielded η_Q of about 30%, consistent with the reduced hole-transfer previously reported (Figure S11) [9].

To further elucidate the mechanism behind charge generation, we conducted time-resolved photoluminescence (TR-PL) and femtosecond transient absorption (TA) measurements. The fluorescence decay kinetics were probed by selectively exciting the acceptor at 750 nm (Figure S12). The fluorescence lifetime of PYT NPs ($\tau_{\text{avg}} = 1.3$ ns) is quenched both in the case of the block copolymer and the blend, which can be associated to hole transfer. The faster decay in PBDB-T-b-PYT NPs ($\tau_{\text{avg}} = 53$ ps) than in PBDB-T:PYT blend NPs ($\tau_{\text{avg}} = 95$ ps) could suggest a more efficient hole transfer (Table S2), in agreement with steady-state PL measurements, though contributions from trap-assisted or aggregation-related non-radiative relaxation cannot be fully excluded.

TA measurements were conducted by excitation at 550 nm, which mainly excites PBDB-T, to evaluate charge transfer from donor to acceptor within block copolymer and blend nanoparticles. PBDB-T shows a broad ground state bleaching (GSB) band from 450 nm to 650 nm along with excited state absorption (ESA) peaking around 675 nm, while PYT shows GSB below 540 nm and above 620 nm and ESA in the region 540–620 nm (Figure S13). In the spectral region above 650 nm, PBDB-T shows a positive ESA feature whereas PYT shows negative GSB. In the blend and block copolymer, 550 nm mainly excites the donor sites, after which energy and/or electron transfer to the acceptor sites can take place (Figure 2c,d). Following donor excitation, PBDB-T:PYT blend NPs mostly displayed features corresponding to PBDB-T, with almost superimposable features at 5 ps delay time (Figure S14a). At long delay times (2 ns, Figure S14b) both PBDB-T and PBDB-T:PYT blend NPs display a broad, red-shifted ESA feature between 670 and 750 nm compared to ESA at earlier times peaking at 675 nm. In the fluorinated PBDB-T analogue PM6, a similar long-lived ESA has been assigned to the formation of PM6 hole polarons [41–43].

On the other hand, PBDB-T-b-PYT NPs displayed features that can be attributed to both donor and acceptor, with an

additional GSB signal around 675 nm (Figure 2d), attributed to a charge/energy transfer from donor to acceptor. At delay times <1 ps, the spectra show a positive ESA from the donor peaking at around 670 nm, whereas at later delay times, the signal turns negative and resembles the GSB of the acceptor. This indicates ultrafast (≤ 5 ps) charge/energy transfer from the donor to the acceptor in the block copolymer. In the case of PBDB-T:PYT blend NPs, such observation is far more discrete and can suggest that charge/energy transfer occurs at a lesser extent when compared to the block copolymer. Furthermore, at 2 ns delay time, PBDB-T-*b*-PYT NPs display a positive TA signal at 680 nm but still retain a negative feature around 730 nm (Figure S14b). The resulting spectrum is likely the result of a competition between the PBDB-T hole polaron ESA, and the PYT GSB. Furthermore, in similar systems a positive feature around 680 nm has been associated with electroabsorption, arising from the induced electric field upon polaron formation [44–46]. The potential hole polaron ESA and electroabsorption features together with the remaining GSB of PBDB-T (525–650 nm) are consistent with the persistence of charge-separated or polaron-associated states in PBDB-T NPs, PBDB-T:PYT blend NPs and PBDB-T-*b*-PYT NPs. As a complementary, empirical measure of signal persistence, we compare the TA signal amplitude at 630 nm at 0.5 ps and 2 ns. About 4%, 3%, and 13% of the initial magnitude was preserved after 2 ns for PBDB-T, PBDB-T:PYT blend, and PBDB-T-*b*-PYT NPs, respectively, consistent with the more persistent spectral features described above. We note that this comparison reflects the overall magnitude of the transient signal rather than a quantified population of a specific species.

A phenomenological analysis of the TA kinetics was performed by using the sum of three exponential decay components (Figure S15 and Table S3). PBDB-T:PYT blend NPs displayed decay kinetics faster than neat PBDB-T ($\tau_1 = 1.2$ ps, $\tau_2 = 5.9$ ps and $\tau_3 = 19$ ps), supporting energy/charge transfer from PBDB-T to PYT. On the other hand, PBDB-T-*b*-PYT NPs exhibited significantly different kinetics: a short component characterized by a time constant of $\tau_1 = 1.1$ ps and a positive amplitude ($A_1 = 0.80$) followed by two slower components with negative amplitudes ($\tau_2 = 52$ ps, $A_2 = -0.12$ and $\tau_3 = 2.6$ ns, $A_3 = -0.08$). The negative amplitude is likely describing the decay of PYT GSB as well as the emergence of a positive signal that could be related to the formation of PBDB-T hole polaron and electroabsorption. Furthermore, the 2.6 ns time constant is the longest obtained in any sample, and dynamics on the ns timescale have previously been attributed to the recombination of polarons in similar systems [46, 47]. The covalent link within PBDB-T-*b*-PYT increases donor-acceptor population transfer and produces a larger and longer-lived spectral component. The kinetic analysis therefore provides quantitative evidence of excited state dynamics substantially differ between the block copolymer and its constitutional counterparts (PBDB-T NPs and PYT NPs, see Figure S15) and their physical mixture (PBDB-T:PYT blend NPs).

To further investigate the internal morphology of PBDB-T-*b*-PYT NPs, we conducted Scanning Transmission Electron Microscopy combined with Energy Dispersive X-ray Spectroscopy (STEM-EDX) measurements (Figure 3) [48, 49]. To ensure enough resolution on individual NPs with minimal surfactant contamination, we modified the synthetic procedure (more details in the Supporting Information).

STEM-EDX images were collected with a pixel resolution of 4×4 nm². For organic semiconductor nanoparticles presenting diameters around 50–150 nm, this threshold provides a high-fidelity overview of the nanoscale morphology and domain distribution. However, it is important to mention that molecular-level intermixing and sub-nanometer fluctuations cannot be identified by STEM-EDX. Additionally, elemental mapping represents 2D projections of 3D volumes, which can complicate spatial mapping. Importantly, PYT contains nitrogen whereas PBDB-T does not; therefore, the N–K map serves as a selective marker for PYT-rich regions. In contrast, C, O, and S are present in both components and are used primarily as reference/structural maps and for overlays rather than as unique compositional identifiers.

As displayed in Figure 3a,b and Figures S16–S20, both PBDB-T-*b*-PYT NPs and PBDB-T:PYT NPs exhibit a broadly distributed N–K signal across the particle cross-section, indicating that the PYT segment is not confined to a localized core or shell region but is instead distributed throughout the nanoparticle volume. The overlay maps (N–K + S–K and O–K + S–K) further support nanoscale co-distribution of acceptor-associated nitrogen with the sulfur/oxygen signals that track the polymer framework, within the resolution of 4×4 nm² accessible by STEM-EDX.

Compositional fluctuation mappings were compared to evaluate the internal phase morphology for PBDB-T-*b*-PYT NPs and PBDB-T:PYT NPs. In the case of the physical blend, while macro-phase separation is avoided with nanoscale phase distribution, localized variations and uncoupled elemental trends are observed across individual nanoparticle volumes (Figures S21–S23). Conversely, block copolymer nanoparticles exhibit synchronized cross-correlation between the sulfur and nitrogen profiles across a wide range of nanoparticles, consistent with improved nanoscale distribution throughout the nanoparticle bulk (Figures S24–S27).

This structural picture aligns with the improved PL quenching observed for PBDB-T-*b*-PYT under both donor- and acceptor-selective excitation, and more persistent TA features following donor excitation. We expect that the direct covalent linkage between donor and acceptor blocks may constrain the extent of phase separation, which results in a more intimate donor-acceptor contact for efficient exciton dissociation when compared to usual physical blends, such as PBDB-T:PYT NPs. Overall, STEM-EDX is consistent with the formation of heterojunction NPs with distributed D:A domains for both systems under our processing conditions, while indicating a slightly more uniform acceptor distribution for the all-conjugated block copolymer.

4 | Photocatalytic Activity

Photocatalytic HER experiments were conducted in the presence of H₂PtCl₆ salts as a cocatalyst precursor (3 wt.% Pt) and AA as sacrificial electron donor (SED), with the resulting hydrogen evolution displayed in Figure 4a. To ensure photodeposition of Pt and comparable results, photocatalytic experiments were conducted over 8 h. A concentration of photocatalyst NPs of 25 $\mu\text{g mL}^{-1}$ was selected to conduct photocatalytic experiments, and the impact of different concentration will be discussed more in detail in the last section of this article.

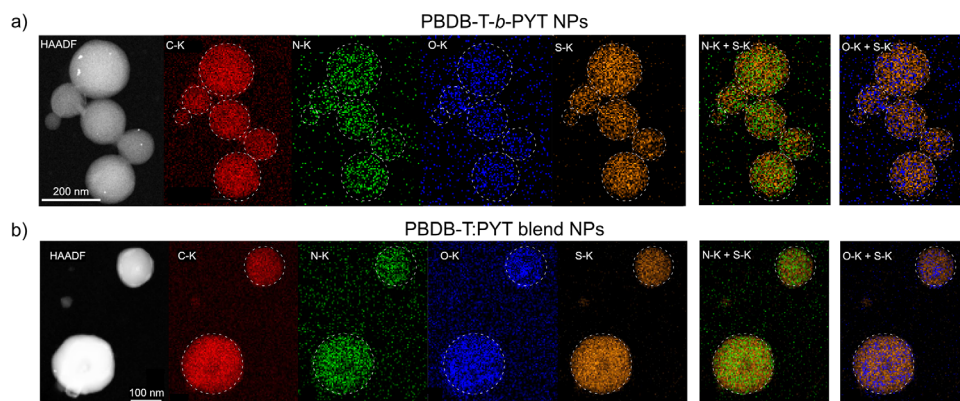


FIGURE 3 | STEM-EDX maps of (a) PBDB-T-b-PYT NPs and (b) PBDB-T:PYT blend NPs showing C-K, N-K, O-K and S-K maps. In addition, combined maps are provided: N-K and S-K, O-K and S-K.

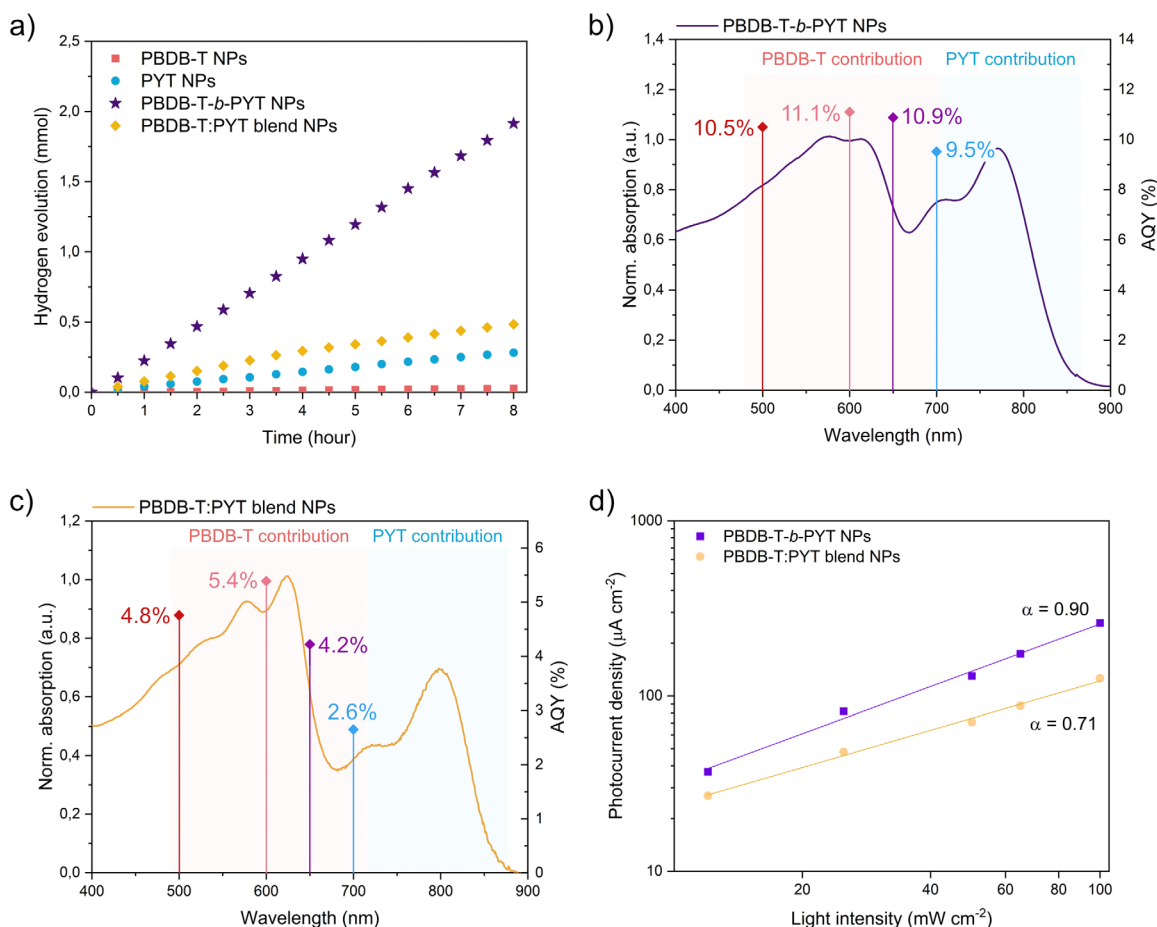


FIGURE 4 | (a) Hydrogen evolution of PBDB-T NPs, PYT NPs, PBDB-T-b-PYT NPs and PBDB-T:PYT blend NPs. Apparent quantum yield of (b) PBDB-T-b-PYT NPs and (c) PBDB-T:PYT blend NPs at different wavelengths. (d) Photocurrent density as a function of light intensity for PBDB-T-b-PYT NPs and PBDB-T:PYT blend NPs. For all photocatalytic experiments: 0.75 mg (panel a) and 0.375 mg (panels b, c) of photocatalyst NPs were dispersed in 30 mL of water, in the presence of 3 wt.% of Pt, and ascorbic acid at 0.1 M. The irradiation surface was fixed to 10 cm^2 and the light intensity to 100 mW cm^{-2} . Experiments were conducted at 6°C and under reduced pressure (1.2 kPa).

To ensure a transparent and clear quantification of photocatalytic performance, we emphasize the importance of reporting metrics [50]. Both photocatalyst loading and irradiation area constitute the primary factors that can influence the apparent photocat-

alytic performance. Therefore, these two parameters should be accounted for when expressing performance to ensure cross-laboratory comparability. By following the reporting guideline in a recent perspective [50], we utilized the dual normalization

of area and mass (in $\text{mmol cm}^{-2} \text{g}^{-1} \text{h}^{-1}$) for $\text{HER}_{\text{A,M}}$ rates. Furthermore, we also report the widely used HER rates ($\mu\text{mol h}^{-1}$) for comparison.

Overall, PBDB-T-*b*-PYT performed the best and achieved a high HER rate of $32 \text{ mmol cm}^{-2} \text{g}^{-1} \text{h}^{-1}$ ($239 \mu\text{mol h}^{-1}$), exhibiting a steady and stable hydrogen evolution (Figure 4a). This performance was 4 times higher than that of PBDB-T:PYT blend NPs, which achieved a HER rate of $8.1 \text{ mmol cm}^{-2} \text{g}^{-1} \text{h}^{-1}$ ($61 \mu\text{mol h}^{-1}$). These results are in good agreement with TR-PL and TA observations, which revealed reduced charge generation and lifetime in the case of PBDB-T:PYT blend NPs, consistent with their lower photocatalytic performances. It should be noted that D:A blend NPs usually suffer from strong D:A ratio dependence, with improvements usually achieved using unbalanced D:A ratio (typically 7:3 or 2:8) [9]. However, such conditions are not representative of the D:A ratio present in the block copolymer and therefore not considered further in this work. Nevertheless, both PBDB-T-*b*-PYT NPs and PBDB-T:PYT blend NPs achieved much higher performances as compared to the pristine PBDB-T NPs and PYT NPs, with HER rates of 0.4 and $4.7 \text{ mmol cm}^{-2} \text{g}^{-1} \text{h}^{-1}$, respectively.

We further explored whether the difference in molecular weight between PBDB-T:PYT blend NPs and PBDB-T-*b*-PYT NPs could be responsible for the lower performance. For instance, PBDB-T in the physical blend PBDB-T:PYT showed a significantly higher molecular weight ($\text{Mw} = 119.8 \text{ kg mol}^{-1}$) than PBDB-T-*b*-PYT ($\text{Mw} = 33.8 \text{ kg mol}^{-1}$). Therefore, PBDB-T:PYT NPs were prepared with two additional PBDB-T batches with lower molecular weight of 10.8 and 59.0 kg mol^{-1} (Figure S28). Upon reduction of Mw, lower HER rates of 4.2 and $7.8 \text{ mmol cm}^{-2} \text{g}^{-1} \text{h}^{-1}$ were achieved, respectively (Figure S29). This trend was confirmed when preparing PBDB-T-*b*-PYT NPs with a low molecular weight fraction ($\text{Mw} = 14.8 \text{ kg mol}^{-1}$) (Figures S30 and S31). These observations support the idea that higher Mw polymers might be beneficial for HER, in agreement with previously reported work [51]. Therefore, the higher performance achieved by PBDB-T-*b*-PYT is unlikely to arise from a difference in PBDB-T Mw.

PBDB-T-*b*-PYT was synthesized using a one-pot approach, with successive polymerization of the donor and acceptor building blocks. However, it remains unclear whether the resulting performance in HER can be solely attributed to the alternance of donor and acceptor blocks. Therefore, a fully random copolymer PBDB-T-*r*-PYT was synthesized by introducing all four monomers at the same time during the polymerization (Scheme S3). Surprisingly, despite a comparable nanoparticle size and the presence of both donor and acceptor features (Figure S32), PBDB-T-*r*-PYT NPs achieved rather low HER performance ($0.6 \text{ mmol cm}^{-2} \text{g}^{-1} \text{h}^{-1}$). The low HER activity of the random copolymer PBDB-T-*r*-PYT supports the importance of block architecture. However, the exact impact of backbone architecture toward performance for block copolymers cannot yet be isolated and requires further investigation.

Next, we explored how PBDB-T and PYT contribute to the photocatalytic reaction through apparent quantum yield (AQY) measurements (Figure 4b,c). For these experiments, the concentration of photocatalyst used was $12.5 \mu\text{g mL}^{-1}$. We selected specific wavelengths to probe PBDB-T (500 and 600 nm) and PYT

(650 and 700 nm) contributions. While PYT absorption partially overlaps with PBDB-T, we assumed that these wavelengths (500 and 600 nm) will be dominated by PBDB-T absorption, displaying higher absorption coefficients.

PBDB-T-*b*-PYT NPs displayed AQYs about 10% across 500, 600, 650, and 700 nm, which rank among the highest reported to date at these wavelengths, especially considering the low Pt content [11, 52]. On the other hand, PBDB-T:PYT blend NPs exhibited a main contribution from PBDB-T (5.4% at 600 nm), with a sharp decrease for PYT contribution (2.6% at 700 nm). These results are in excellent agreement with previous PL measurements, highlighting that in the case of PBDB-T-*b*-PYT NPs, comparable contribution can be achieved owing to excellent electron and hole transfer properties. However, in the case of PBDB-T:PYT blend NPs, the overall AQY remained lower. In addition, the contribution of PYT in the photocatalytic process appeared limited when compared to PBDB-T and could arise from a lower absorption coefficient combined with a lower hole transfer efficiency.

To resolve the charge carrier dynamics, complementary transient photocurrent response (TPR) measurements were performed (Figure S33). Under chopped illumination, PBDB-T-*b*-PYT NPs exhibited significantly higher photocurrent density (J_{ph}) than PBDB-T:PYT blend NPs across all light intensities (from 12.5 to 100 mW cm^{-2}). The evaluation of photocurrent as a function of light intensity (I), related by the law $J_{\text{ph}} \propto I^\alpha$, can reveal the preferential recombination pathways following the slope α . PBDB-T-*b*-PYT NPs displayed an α value of 0.90, consistent with efficient charge carrier extraction dominated by first-order recombination (Figure 4d). However, the physical blend showed a lower α value of 0.71, highlighting stronger bimolecular recombination losses [53]. Then, we conducted TPR measurements with selective excitation of donor and acceptor materials (Figure S34). PBDB-T-*b*-PYT NPs maintained well-balanced photocurrents, with incident photon-to-current efficiencies (IPCE) of 0.54% and 0.46% at 520 and 700 nm, respectively. In contrast, PBDB-T:PYT blend NPs showed more imbalanced IPCE values of 0.27% and 0.20%, in line with AQY results where PYT contributions remain lower.

This observation correlates with open-circuit transient photovoltage (OTP) measurements, where PBDB-T-*b*-PYT NPs achieved a larger absolute photovoltage (-330 mV against -240 mV for the blend), indicating higher driving force from enhanced quasi-Fermi level splitting (Figure S35). Furthermore, PBDB-T:PYT blend NPs exhibited a slower photovoltage build-up upon illumination, indicating charge trapping that acts as a kinetic bottleneck.

To investigate whether the differences in HER rates could be linked to differences in Pt photodeposition quality, we conducted STEM measurements following photocatalysis. Pt appeared to be homogeneously distributed across the surface of both PBDB-T-*b*-PYT NPs and PBDB-T:PYT NPs, with comparable loading densities (Figure S36). Highly dispersed Pt clusters of approximately 2.3 nm were observed in the case of PBDB-T-*b*-PYT NPs, against 2.5 nm for PBDB-T:PYT NPs (Figure S37). Through a colorimetry assay, we quantified that about $2.6 \pm 0.1 \text{ wt.}\%$ and $2.7 \pm 0.1 \text{ wt.}\%$ of Pt was photodeposited onto PBDB-T-*b*-PYT NPs and PBDB-T:PYT NPs, respectively (Figures S38–S42 and Table

S4). This corresponds to approximately 86%–90% of the targeted 3 wt.% Pt loading. In comparison, previous reports usually reported photodeposition yields below 50% [54, 55]. However, they tend to rely on higher initial feed (>10 wt.%) and anionic surfactants that could limit interactions with H_2PtCl_6 salts due to electrostatic repulsions. Overall, the comparable Pt loading between both PBDB-T-*b*-PYT NPs and PBDB-T:PYT NPs, within experimental uncertainty, suggests that the differences in HER rates are unlikely to arise from different Pt loadings.

An important step in photocatalytic HER is the transfer of photogenerated electrons from the semiconductor to the Pt cocatalyst. In D:A heterojunction nanoparticles, electrons are expected to preferentially reside on the acceptor phase and subsequently be extracted by Pt [55]. Here, PBDB-T-*b*-PYT and PBDB-T:PYT NPs exhibit essentially identical total Pt loadings (2.6 ± 0.1 and 2.7 ± 0.1 wt.%, respectively). Although STEM-EDX does not allow us to establish preferential localization of Pt on specific donor- or acceptor-rich domains, the more constrained nanoscale compositional variation of PBDB-T-*b*-PYT may provide more effective electronic connectivity between acceptor segments and accessible Pt sites. This could facilitate electron extraction to the cocatalyst and thereby contribute to the enhanced HER activity of the block copolymer relative to the physical blend. We emphasize that this remains a mechanistic interpretation, as the spatial relationship between Pt clusters and individual acceptor-rich domains cannot be directly resolved by the present measurements.

5 | Photocatalytic Stability

We then investigated the photocatalytic stability of PBDB-T-*b*-PYT NPs and PBDB-T:PYT blend NPs by conducting hydrogen evolution experiments over 40 h (10 h for each cycle). PBDB-T-*b*-PYT NPs displayed a remarkably stable activity, retaining 94% of the initial HER rate after 40 h (Figure 5a). The second and third cycles displayed enhanced HER rates, which might be correlated to a change in photocatalyst concentration during cycling, as discussed in the next section. The decrease in HER rate over time was associated with a partial loss of photocatalysts attributed to the deposition on the reactor's window upon cycling (Figure S43). Nevertheless, both absorption and emission profiles of PBDB-T-*b*-PYT NPs remained identical over time showcasing a high resilience toward photocatalytic experiments (Figure 5b and Figure S44). Their stability was further confirmed with additional stability investigation under LED light, with more than 95% of the initial HER rate retained after 96 h of activity (Figures S45 and S46), placing PBDB-T-*b*-PYT NPs among the most efficient and stable organic photocatalysts reported to date (Table S7) [56].

In contrast, PBDB-T:PYT blend NPs showed a rapid decline in HER rate, ultimately retaining only 69% of their initial HER rate after 40 h. This loss in performance is correlated with pronounced change in absorption profiles (Figure 5c and Figure S47). After photocatalytic experiments, a highly unbalanced $\lambda_{0-0}^{\text{PBDB-T}}/\lambda_{0-0}^{\text{PYT}}$ ratio can be observed, increasing from 1.43 to 1.94 after 40 h (Table S5). This is also correlated with the strong changes in the emission profile observed upon photocatalytic experiments (Figure S48).

The origin of such change in absorption profile could arise from several factors, including photobleaching or colloidal aggregation. However, the evolution of the nanoparticle size upon photocatalytic experiments was also comparable to that of PBDB-T-*b*-PYT NPs, therefore unlikely to be the only factor linked to a decrease in performance (Figure S49).

We then investigated the chemical stability of both PBDB-T-*b*-PYT NPs and PBDB-T:PYT blend NPs during photocatalytic experiments. After 40 h of photocatalysis, chloroform was used to recover the photocatalyst from the dispersions. ATR-FTIR and UV-vis measurements confirmed the chemical robustness of PBDB-T-*b*-PYT, PBDB-T, and PYT, with no apparent degradation (Figures S50 and S51).

Next, we explored if a change in morphology could be the origin of the decreased photocatalytic activity in the case of the physical mixture. In D:A blends, phase segregation can be thermally activated and the rearrangement of D:A domains can be followed by UV-vis spectroscopy [57]. Upon heating to 80°C for 15 h, no evolution of the absorption profile could be observed in the case of PBDB-T-*b*-PYT NPs (Figure S52). However, PBDB-T:PYT blend NPs displayed spectral changes that resemble those observed upon photocatalytic experiment (Figure S53).

Similarly, STEM-EDX measurements performed after 16 h of photocatalysis revealed comparable nitrogen distribution across the nanoparticle for PBDB-T-*b*-PYT NPs, also confirmed by compositional fluctuation analysis (Figures S54–S56). However, slight variation in nitrogen mapping could be observed in the case of PBDB-T:PYT blend NPs, resulting in more unbalanced distribution within the nanoparticles (Figures S57–S59).

Overall, these results highlight the intrinsic instability of D:A blend NPs over extended photocatalytic experiments, and our observations tend to indicate a correlation with lower morphological stability. On the other hand, we showcased the exceptional strength of PBDB-T-*b*-PYT block copolymers to unite high efficiency and long-term stability [11, 23]. While phase segregation is not proven to be fully suppressed, block copolymers present a higher resilience than physical blends, which strongly benefits photocatalytic performances over extended times.

To provide a clearer mechanistic framework, Figure 6 summarizes a multiscale working model linking the molecular architecture of the photocatalysts to their nanoscale organization, excited-state dynamics, and photocatalytic performance. At the molecular level, TD-DFT and NTO (Figures S5–S7) calculations suggest spatial separation of frontier orbitals in PBDB-T-*b*-PYT that could be attributed to intramolecular charge transfer enabled by the covalent linkage between donor and acceptor blocks [58]. In contrast, PBDB-T and PYT are separate macromolecules in the physical blend, and charge separation therefore requires intermolecular donor-acceptor contact. Because of the short exciton diffusion length, the quality of intermolecular donor-acceptor contact will significantly affect recombination rates and potentially translate to HER performance.

At the nanoparticle level, we propose that covalent linkage between the two blocks limits large-scale compositional rearrangement and helps maintain donor and acceptor segments

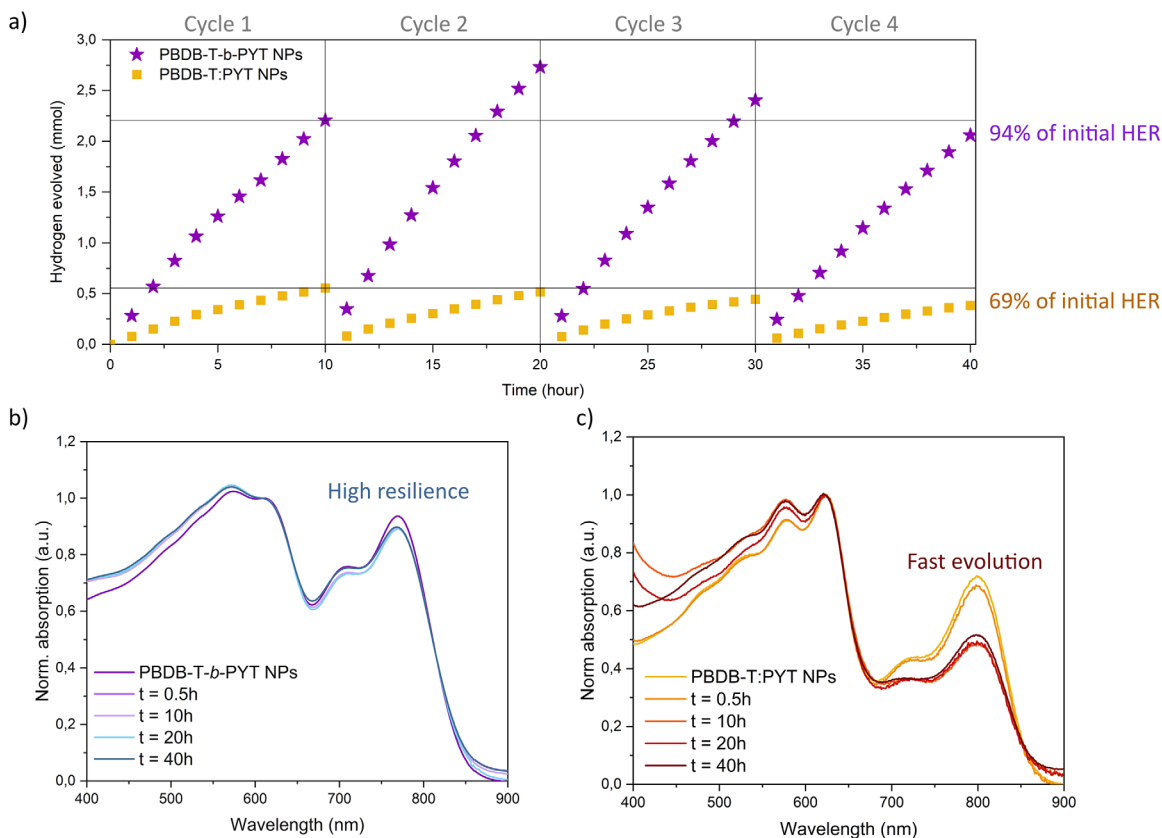


FIGURE 5 | (a) Hydrogen evolution of PBDB-T-b-PYT NPs and PBDB-T:PYT NPs stabilized by C_{16} TAB over 40 h of photocatalysis. The initial HER rate was calculated by considering the first 10 h of photocatalysis. After 10 h, the amount of ascorbic acid consumed was re-inserted in the reactor. For all photocatalytic experiments: 0.75 mg of photocatalyst NPs were dispersed in 30 mL of water, in the presence of 3 wt.% of Pt, and ascorbic acid at 0.1 M. The irradiation surface was fixed to 10 cm² and the light intensity to 100 mW cm⁻². Experiments were conducted at 6°C and under reduced pressure (1.2 kPa). Absorption spectra of (b) PBDB-T-b-PYT NPs and (c) PBDB-T:PYT blend NPs before, and after 0.5, 10, 20, and 40 h of photocatalytic experiments.

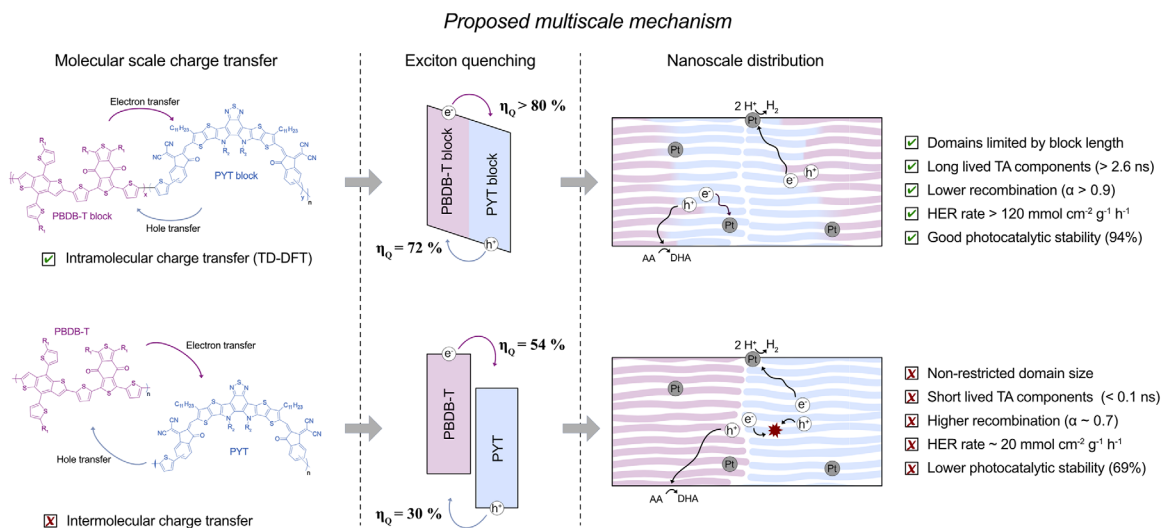


FIGURE 6 | Proposed multiscale model for PBDB-T-b-PYT NPs and PBDB-T:PYT NPs.

in closer spatial proximity. In contrast, in the physical blend, PBDB-T and PYT chains are not covalently constrained and can undergo greater independent aggregation and phase rearrangement, potentially leading to larger-scale phase separation.

STEM-EDX (Figure 3) does not directly resolve molecular-scale intermixing, but the compositional analysis indicates a somewhat more uniform nanoscale distribution for PBDB-T-b-PYT than for the physical blend. We emphasize that the domain morphology

depicted in Figure 6 is illustrative, based on STEM-EDX compositional correlation rather than direct imaging. This interpretation is consistent with the substantially stronger photoluminescence quenching observed for PBDB-T-*b*-PYT under both donor- and acceptor-selective excitation, indicating more effective electronic communication between the two components (Figure 2b). TA kinetics reveal a long-lived spectral component in the case of PBDB-T-*b*-PYT that is not observed for the physical blend. This enhanced charge lifetime is consistent with the lower recombination rate within PBDB-T-*b*-PYT (Figure 4d).

Furthermore, we quantified a comparable Pt cocatalyst loading for both systems. Therefore, differences in total Pt loading are unlikely to account for the large difference in HER activity, although we cannot exclude a possible contribution from differences in the spatial localization of Pt. Moreover, the proposed relationships between morphology, charge dynamics and HER represent a working interpretation supported by collective observations rather than direct proof of causality. In this context, our data and observations support a model in which the block-copolymer architecture constrains nanoscale compositional variation, facilitates donor-acceptor electronic coupling, and is associated with more persistent charge-separated states and reduced recombination losses. These features are consistent with the higher HER activity and improved operational stability observed for PBDB-T-*b*-PYT NPs.

6 | Performance Robustness and Reproducibility Across Size and Operating Conditions

A persistent challenge in NP photocatalysis is limited reproducibility: small variations in the miniemulsion process (shear force applied, concentration in the organic phase, surfactant content) often affect the NP size distribution [16], and HER rates can change substantially with NP size in conventional D:A blend systems [23, 59]: in blends, changing NP size frequently alters the effective donor-acceptor interfacial area and the extent of internal phase segregation, so activity becomes tightly coupled to self-assembly outcomes rather than intrinsic material properties.

A key novelty of the all-conjugated block copolymer approach is that covalent donor-acceptor linkage constrains domain formation, which should reduce sensitivity to NP size and improve batch-to-batch robustness. To evaluate this hypothesis, we prepared PBDB-T-*b*-PYT NPs spanning a wide diameter range from 29 to 114 nm (Figure S60). The change in NP size was achieved by changing the initial PBDB-T-*b*-PYT concentration in the chloroform solution (Table S6). Unlike typical D:A blends—where smaller NPs often maximize interfacial area and therefore outperform larger ones—PBDB-T-*b*-PYT exhibits consistently high activity across this broad size range. However, while nanoparticles larger than 70 nm presented comparable performance, further reduction in size resulted in a decrease of HER rate, from 30 mmol cm⁻² g⁻¹ h⁻¹ down to 20 mmol cm⁻² g⁻¹ h⁻¹ (Figure 7a and Figure S61). The gradual decrease at smaller sizes correlates primarily with reduced optical absorption (Figure S62) and signatures of lower structural order, as indicated by the blue-shifted features and lower η_Q (Figures S63 and S64).

Furthermore, a reduction in nanoparticle size is associated with an increase in specific surface area, requiring a larger amount of surfactant to stabilize the same mass of photocatalyst. This increased surfactant loading can severely impact surface recombination by acting as an insulating barrier that hinders efficient electron transfer to the Pt cocatalyst and hole extraction to the ascorbic acid donor. Previous works highlighted the negative impact of excessive surfactant usage on charge extraction from organic nanoparticles [60, 61].

Therefore, all-conjugated block copolymer nanoparticles can decouple the impact of size on efficiency, but to a limited extent, as interfacial properties remain mostly driven by surfactants. To confirm the reliability of HER measurements, we repeated photocatalytic experiments from the same PBDB-T-*b*-PYT NPs dispersion. As presented in Figure S65, comparable results were obtained, highlighting that differences in performance do not arise from the Pt photodeposition step.

Furthermore, we investigated the reproducibility of the synthetic approach. Three individual batches of PBDB-T-*b*-PYT were synthesized through the one-pot approach. The resulting polymers showed comparable absorption profiles both in chloroform solution and nanoparticle dispersion in water (Figure S66). Furthermore, the dispersions presented extremely comparable nanoparticle size, ranging from 87 to 91 nm (Figure S67). More importantly, these three individual polymer batches showcased an average HER rate of 39 ± 1 mmol cm⁻² g⁻¹ h⁻¹, with less than 4% variability, demonstrating that the block-copolymer strategy supports high batch-to-batch reproducibility across both polymer synthesis and nanoparticle preparation (Figure 7b and Figure S68).

Building on the robustness of PBDB-T-*b*-PYT NPs, we further optimized key reaction parameters. First, an increase in the concentration of AA to 0.2 M resulted in an improved HER rate of 37 mmol cm⁻² g⁻¹ h⁻¹ (Figure S69). Pt loading was then tuned rationally: activity increased with Pt content up to 5 wt.% (47 mmol cm⁻² g⁻¹ h⁻¹) and eventually led to lower efficiencies at 10 wt.%. These observations are consistent with previous reports [9], and likely arise from the formation of large Pt clusters rather than small and well-distributed Pt clusters. However, the benefits on HER rate by loading 5 wt.% were minimal when compared to the initial HER rate achieved at 3 wt.% (only a 1.5-fold improvement while almost doubling the content of Pt). Therefore, we identified 3 wt.% Pt as the best compromise between efficiency and precious-metal usage (Figure S70) [52]. It was also noticed that in the absence of cocatalyst, almost no photocatalytic activity was achieved (0.2 mmol cm⁻² g⁻¹ h⁻¹), indicating the necessity of the use of cocatalyst.

Finally, we investigated how the concentration of NPs impacts the final performance, when using optimized conditions of 0.2 M of ascorbic acid and 3 wt.% of Pt cocatalyst. The initial concentration of NPs investigated was 25 μ g mL⁻¹ and achieved a HER rate as high as 38 mmol cm⁻² g⁻¹ h⁻¹ (287 μ mol h⁻¹). By reducing the concentration of photocatalyst to 12.5 μ g mL⁻¹, a 1.6-fold increase in hydrogen evolved was achieved (450 μ mol h⁻¹), yielding a normalized HER rate superior to 120 mmol cm⁻² g⁻¹ h⁻¹ (Figure 7c and Video S1). Similarly, PBDB-T:PYT blend NPs showed improved HER rate up to 20 mmol cm⁻² g⁻¹ h⁻¹

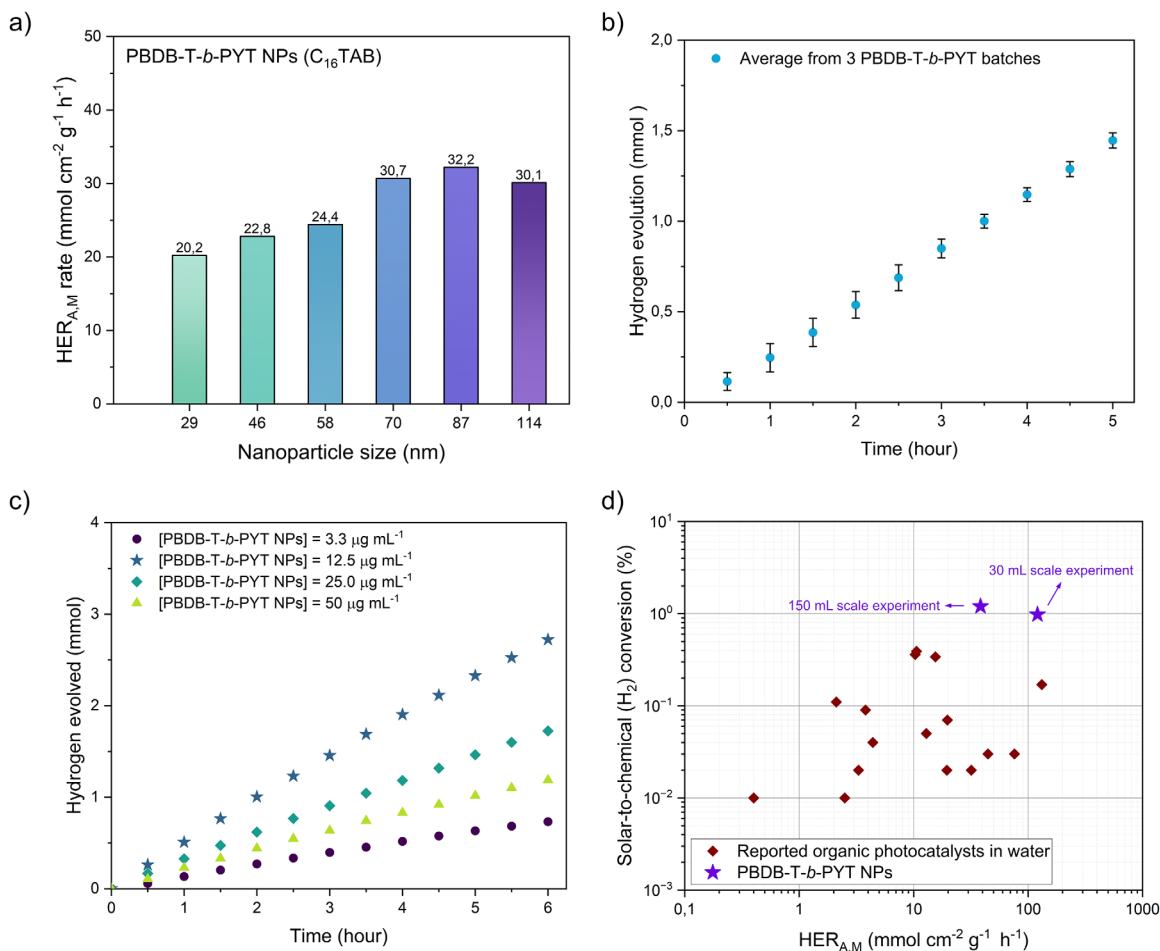


FIGURE 7 | (a) Area- and mass-normalized hydrogen evolution rate of PBDB-T-*b*-PYT NPs with different nanoparticle sizes. (b) Hydrogen evolution of three individual PBDB-T-*b*-PYT batches prepared in the same conditions. (c) Hydrogen evolution of PBDB-T-*b*-PYT NPs at different concentrations for optimized conditions, detailed in Table S8. More details can be found in Table S7. For all photocatalytic experiments: 0.75 mg of photocatalyst NPs were dispersed in 30 mL of water (if not specified), in the presence of 3 wt.% of Pt, and ascorbic acid at 0.1 M (panel a) and 0.2 M (panel b, c). The irradiation surface was fixed to 10 cm². Experiments were conducted at 6°C and under reduced pressure (1.2 kPa).

(74 μmol h⁻¹) at a lower concentration (12.5 μg mL⁻¹), but remained significantly less efficient than that of PBDB-T-*b*-PYT (Figure S71).

To understand the reason behind such behavior, we conducted sequential photocatalytic experiments (Figure S72): PBDB-T-*b*-PYT NPs at an initial concentration of 50 μg mL⁻¹ were sequentially diluted to 25 and 12.5 μg mL⁻¹ along photocatalytic experiments. The enhanced activity observed at lower NP concentrations is consistent with improved light penetration, reduced scattering and/or interparticle recombination at lower concentrations, increasing the fraction of photoactive material effectively activated by the light field [62]. For instance, at a concentration of 12.5 μg mL⁻¹, 50% of the incident light over 1 cm path was absorbed (Figure S73). Upon dilution, the transmittance increases, allowing for more exposed photocatalysts which ultimately benefits HER. We further confirmed that this conclusion is independent of the scale of photocatalytic experiment. For instance, by increasing the reaction volume from 30 to 150 mL, the same trend was observed (Figure S74). By varying the loading of photocatalyst from 0.5 mg (3.3 μg mL⁻¹) to 5 mg (33 μg mL⁻¹), an optimum HER rate of

1153 μmol h⁻¹ was achieved for a loading of 1.5 mg (10 μg mL⁻¹) (Video S2).

Finally, we benchmarked our block copolymer approach against recently reported state-of-the-art organic photocatalysts. As discussed, apparent HER rates can be severely affected by variations in reactor geometries and light intensity in different laboratories. Therefore, in addition to the HER_{A,M} rate (in mmol cm⁻² g⁻¹ h⁻¹), we calculated the solar-to-chemical efficiencies SCC_(H₂) of PBDB-T-*b*-PYT NPs [50]. This complementary metric directly quantifies the amount of incident light energy converted into chemical bonds stored as hydrogen gas, thereby accounting for light intensities that the widely used HER rates often neglect. As illustrated in Figure 7d and Table S7, PBDB-T-*b*-PYT NPs displayed excellent performance, with a HER_{A,M} rate of 120 mmol cm⁻² g⁻¹ h⁻¹, and a SCC_(H₂) of 0.98%. To ensure reproducibility and transparency, all parameters of the most efficient system are reported in Table S8. However, it is important to note that SED, such as ascorbic acid or triethylamine, can contribute to hydrogen generation and should be considered for cross-study comparison of photocatalyst efficiency [63].

7 | Conclusion

This study demonstrates that all-conjugated donor-acceptor block copolymers provide a robust materials design route to improve activity, operational stability, and reproducibility in organic nanoparticle photocatalysis. By covalently integrating PBDB-T (donor) and PYT (acceptor) into a single macromolecule, PBDB-T-*b*-PYT constrains donor-acceptor organization within the NP, enabling efficient charge generation while reducing the sensitivity of photocatalytic hydrogen evolution to nanoscale morphology. Under optimized conditions, PBDB-T-*b*-PYT NPs achieved a HER rate exceeding $120 \text{ mmol cm}^{-2} \text{ g}^{-1} \text{ h}^{-1}$ ($450 \mu\text{mol h}^{-1}$), outperforming PBDB-T:PYT blend NPs ($20 \text{ mmol cm}^{-2} \text{ g}^{-1} \text{ h}^{-1}$, $74 \mu\text{mol h}^{-1}$). Importantly, we demonstrated an outstanding photocatalytic stability for PBDB-T-*b*-PYT NPs, with more than 94% of the initial HER rate retained after 40 h of photocatalytic experiments, against 69% for the physical blend of PBDB-T and PYT. More than 95% of the initial HER rate was retained after 96 h under LED light. Furthermore, we showcased that all-conjugated block copolymers benefit from improved batch-to-batch reproducibility, with less than 4% of variability across 3 different PBDB-T-*b*-PYT batches.

This work pioneers the use of block copolymer NPs for photocatalytic applications, tackling the major stability issue of usual donor:acceptor physical blends: by constraining donor:acceptor domains through covalent linkage, intermixed morphologies are promoted and can ensure long-lasting performances. In practice, we expect that the block-copolymer strategy should be extendable to other high-performing OPV-derived donors and non-fullerene acceptors. Future efforts will focus on expanding this platform toward lower- or precious-metal-free cocatalysts, while further correlating nanoscale morphology with long-term activity under operationally relevant conditions.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File 1: aenm71708-sup-0001-SuppMat.pdf.

Supporting File 2: aenm71708-sup-0002-VideoS1.mp4.

Supporting File 3: aenm71708-sup-0003-VideoS2.mp4.