

## Supporting Information

# Targeted Design of Organic Janus Particles for Improved Photocatalytic Hydrogen Evolution

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## Videos

**Video S1:** A thin Janus film of Pt/PCDTBT:PCBM, spin-coated on a glass slide, is immersed at the bottom of a beaker in an aqueous solution containing 0.2M ascorbic acid and irradiated with light. Bubbles are preferentially generated on the right side of the film where platinum nanoparticles are located.

**Video S2:** Aqueous solution containing 0.2M ascorbic acid and 0.1mg of pure PCDTBT:PC<sub>61</sub>BM nanoparticles under light irradiation. Almost no hydrogen bubbles are generated.

**Video S3:** Aqueous solution containing 0.2M ascorbic acid and 0.1mg of Pt/PCDTBT:PC<sub>61</sub>BM nanoparticles modified by simple photodeposition. Under illumination, some hydrogen bubbles are produced.

**Video S4:** Aqueous solution containing 0.2M ascorbic acid and 0.1mg of Janus nanoparticles Pt/PCDTBT:PC<sub>61</sub>BM. In the presence of light, significant hydrogen evolution is observed.

## Experimental Section

### Chemicals

Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4,7-di-2-thienyl-2',1',3'-benzothiadiazole] (PCDTBT) was provided by PCAS Canada and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) by Solaris Chem. Sodium dodecyl sulfate (SDS), dichlorobenzene, chloroform, ascorbic acid (AA), hexachloroplatinic acid hydrate (>99.9%, H<sub>2</sub>PtCl<sub>6</sub>·H<sub>2</sub>O), gold (III) chloride trihydrate (>99.9%, HAuCl<sub>4</sub>·3H<sub>2</sub>O), palladium (II) sulfate (98%), ammonium chloride (99.99% NH<sub>4</sub>Cl) and agarose (low gelling temperature) were purchased from Sigma Aldrich. The metal deposition solution was prepared with milliQ water (resistivity =18 MΩ cm)

### Methods

#### Thin film Preparation

To prepare a thin film of the organic polymer, glass substrates were used. The substrates were first cleaned with distilled water. They were then subjected to ultrasonic cleaning in a sequence of neutral detergent, deionized water for three times, acetone and isopropanol, with each step lasting 15 minutes. A solution of PCDTBT and PC<sub>61</sub>BM was prepared using dichlorobenzene as the organic solvent, with concentrations of 7 mg/ml for PCDTBT and 16.1 mg/ml for PC<sub>61</sub>BM stirred for 24 h at 60 °C in a nitrogen-filled glovebox. Then, a thin film, with a thickness of approximately 100 nm, was deposited via spin-coating at 1000 rpm for 60 seconds, followed by drying at 120°C for 10 minutes.

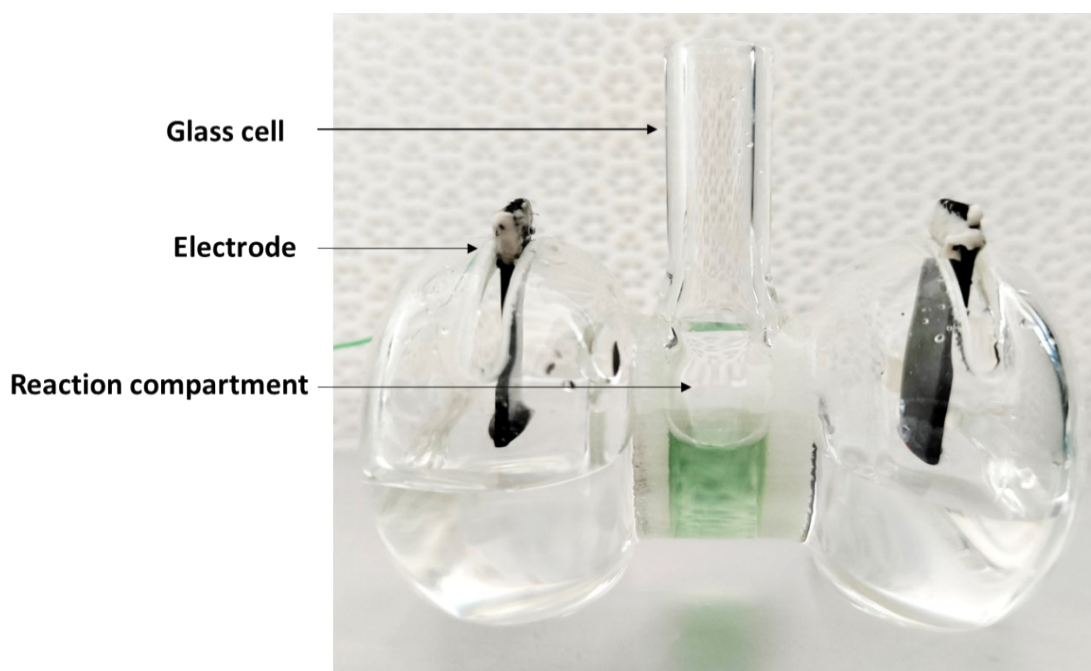
#### Particle Synthesis

Particles were prepared using a miniemulsion process to obtain water-based inks. For the organic phase, a 28 mg/ml donor/acceptor mixture (1:1.2 wt%) was dissolved in chloroform and stirred for 24 hours at 60°C in a nitrogen-filled glovebox. The aqueous phase was prepared by dissolving 5 mg/ml of SDS surfactant in deionized water, followed by 30 minutes of stirring at room temperature. The organic phase was then added to the aqueous phase in a 1:5 volume ratio, and the mixture was stirred for 1 hour at 40°C (1000 rpm) to form a macroemulsion. The miniemulsion was obtained by sonicating the macroemulsion using a BRANSON Digital Sonifier 450 in an ice-water bath for 2 minutes at 17% power. Chloroform was then evaporated by stirring the miniemulsion for 3 hours at 70°C with the lid open. To remove the excess of

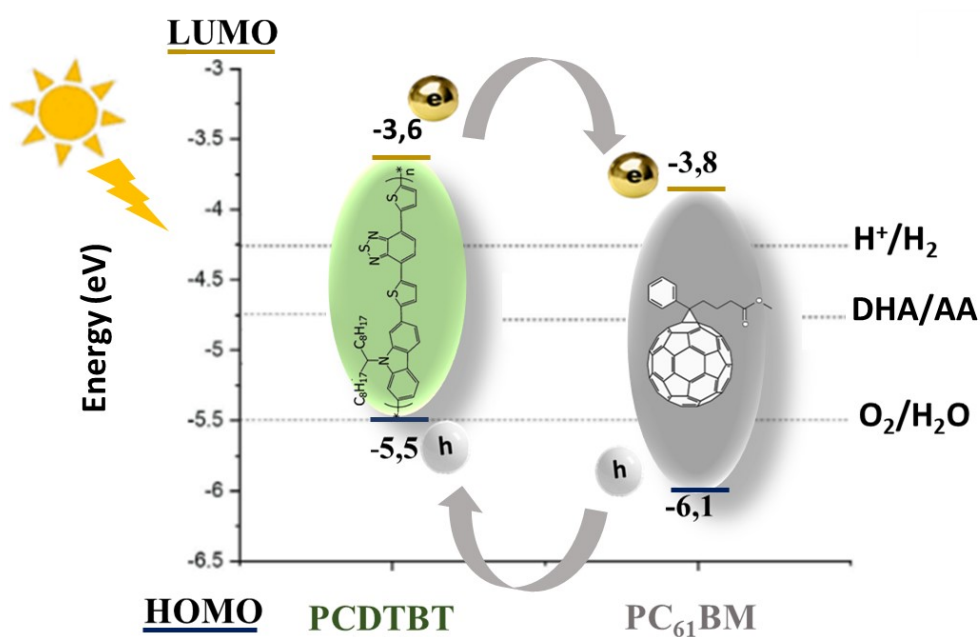
surfactant, the samples were centrifuged using an Amicon Ultra-15 centrifuge filter (100 kDa cut-off) and a Hettich Universal 320 centrifuge. Six centrifugation cycles were performed at 2200 rpm for 6 minutes, with the sediment being redispersed in 15 ml with deionized water between each step. It was observed that for more than six washing steps, aggregation occurred, leading to a significant loss of material due to excessive surfactant removal. It is worth mentioning that the dispersions remained stable and could be stored in the dark for several months without aggregation or degradation of the active materials.

### **Asymmetric deposition of metal nanoparticles (Pt, Au and Pd) on PCDTBT:PC<sub>61</sub>BM thin films and particles**

The bipolar electrodeposition experiments were carried out using a DC high-voltage supply (Heinzinger, PNC 10000-200POS), and light was generated by a LC8, HAMAMATSU 200W mercury xenon lamp (62 mW/cm<sup>2</sup>). The experimental setup involved a custom-made glass cell, composed of three compartments, open at the top to allow light irradiation. The central chamber, where the substrates and reagents were placed, was separated from the two electrode compartments by two Nafion membranes (N115, thickness 0.005), positioned in front of the glassy carbon feeder electrodes to prevent interference from bubbles generated at the electrodes. In the central reaction chamber, the glass substrate with the thin film was placed in an aqueous solution of 1 mM H<sub>2</sub>PtCl<sub>6</sub>.xH<sub>2</sub>O. In the case of particles, PCDTBT:PC<sub>61</sub>BM particles were dispersed in an agarose gel (1.4% w/v in Milli-Q water) containing varying concentrations of different metal salts: 1 mM and 5 mM HAuCl<sub>4</sub>.3H<sub>2</sub>O, 1 mM H<sub>2</sub>PtCl<sub>6</sub>.xH<sub>2</sub>O, or 1 mM PdSO<sub>4</sub>. The electrode compartments were filled with a 1 mM NH<sub>4</sub>Cl aqueous solution. Gels were prepared by mixing the ingredients, followed by ultrasound treatment to ensure a perfectly homogeneous dispersion. Subsequently, light and an electric field with different intensities were applied.



**Figure S1:** Glass cell used for light-assisted bipolar electrodeposition

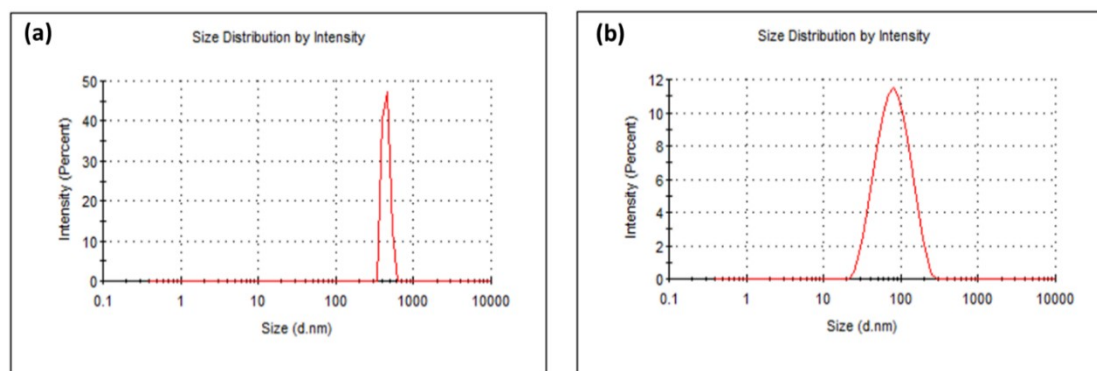


**Figure S2:** Schematic representation of energy levels, as well as electron and hole transfer in a PCDTBT:PC<sub>61</sub>BM heterojunction (at pH = 3).

For SEM experiments, which were performed with a TESCAN VEGA3 SBH instrument, the synthesis process was slightly modified (concentration of SDS and organic phase and the power and the time of the sonicator) to produce larger particles, enabling an easier observation of their morphology. For the organic phase, 40 mg/ml of donor/acceptor (wt% of 1:2.5) mixture was first dissolved in chloroform and stirred for 24 h at 60 °C in a nitrogen-filled glovebox. The aqueous phase was obtained by preparing 1 mg ml<sup>-1</sup> of SDS in deionized water and stirred for 30 min at RT. The organic phase was injected into the aqueous phase (ratio 1:5) and then stirred at 1000 rpm at room temperature for 1 h to obtain the macroemulsion. The miniemulsion was obtained by sonicating the macroemulsion with a BRANSON Digital Sonifier 450 in an ice-water bath for 1 min at 10% of the maximum power. Chloroform was evaporated by stirring the miniemulsion for 3 h at 70 °C with the lid open. Finally, in order to eliminate the excess SDS, six centrifugation cycles were carried out at 2200 rpm for 6 min. The Z-average size of the particles was determined by dynamic light scattering (DLS) as shown in the following table:

<b>PCDTBT :PC<sub>61</sub>BM Concentration (mg/mL)</b>	<b>SDS Concentration (mg/mL)</b>	<b>Particle size (nm)</b>
28	5	67
40	1	525

**Table S1.** Size of the PCDTBT: PC<sub>61</sub>BM particles synthesized under different experimental conditions



**Figure S3:** Size distribution of (a) particles prepared with 1 mg/mL SDS and (b) 5 mg/mL SDS, measured by Dynamic Light Scattering (DLS).

### X-ray photoelectron spectroscopy analysis

The oxidation states of the noble metals (Au, Pt and Pd), deposited asymmetrically by bipolar electrochemistry on PCDTBT:PC<sub>61</sub>BM particles, were determined by XPS using a Thermo Fisher Scientific K-ALPHA spectrometer. XPS powder samples were prepared by placing the particles on a thin piece of conductive indium foil positioned in a stainless-steel holder. The survey spectra (0-1100 eV) were recorded with a 400  $\mu$ m X-ray spot size using a constant pass energy of 200 eV, while high-resolution spectra were recorded with a continuous pass energy of 40 eV. Charge neutralization was applied during the analysis. High-resolution spectra (i.e. Au 4*f*, Pd 3*d* and Pt 4*f*) were quantified and/or fitted using the AVANTAGE software provided by ThermoFisher Scientific (Scofield sensitivity factors used for quantification).

The survey spectra of the Metal/PCDTBT:PC<sub>61</sub>BM Janus particles show the emission characteristic for carbon (C 1s), nitrogen (N 1s), oxygen (O 1s) and sulfur (S 2p) stemming from the core PCDTBT:PC<sub>61</sub>BM particles along with those for gold (Au 4*f*), platinum (Pt 4*f*) or palladium (Pd 3*d*) species. These data are therefore consistent with the expected chemical composition of the prepared heterostructures. To get further information about the oxidation

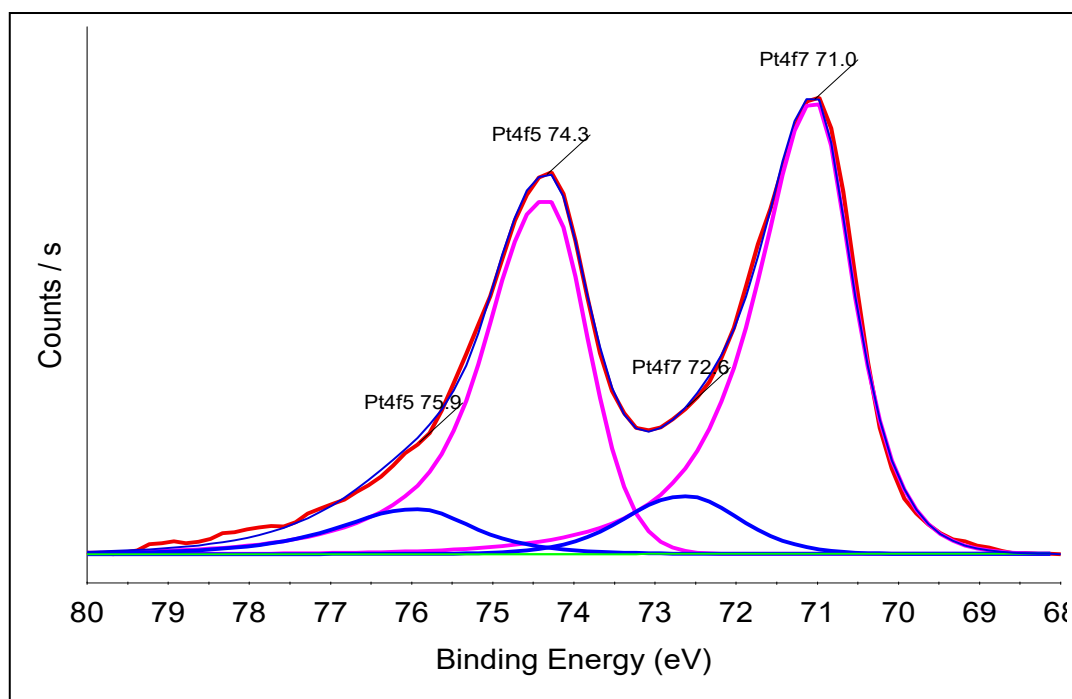
states of the metallic species, adequate peak deconvolution of the Au 4f, Pt 4f or Pd 3d regions was achieved by considering two different oxidation states for each metal.

First of all, peak fitting of the Pt 4f region led to two contributions for Pt 4f<sub>7/2</sub> and Pt 4f<sub>5/2</sub> emission lines, a main one (87.5 at%) at 71.0 and 74.3 ± 0.1 eV, and a minor one (12.5 at%) at 72.6 and 75.9 ± 0.1 eV (Figure S4). In both cases the spin-orbit splitting was found to be 3.3 ± 0.1 eV which is typical for the Pt 4f region. The main contribution was assigned to Pt 4f<sub>7/2</sub> and Pt 4f<sub>5/2</sub> features of Pt<sup>0</sup> sites, while the minor one can be attributed to Pt<sup>II</sup> sites <sup>1,2</sup>. The absence of chlorine in the survey spectrum suggests the formation of small amounts of PtO species.

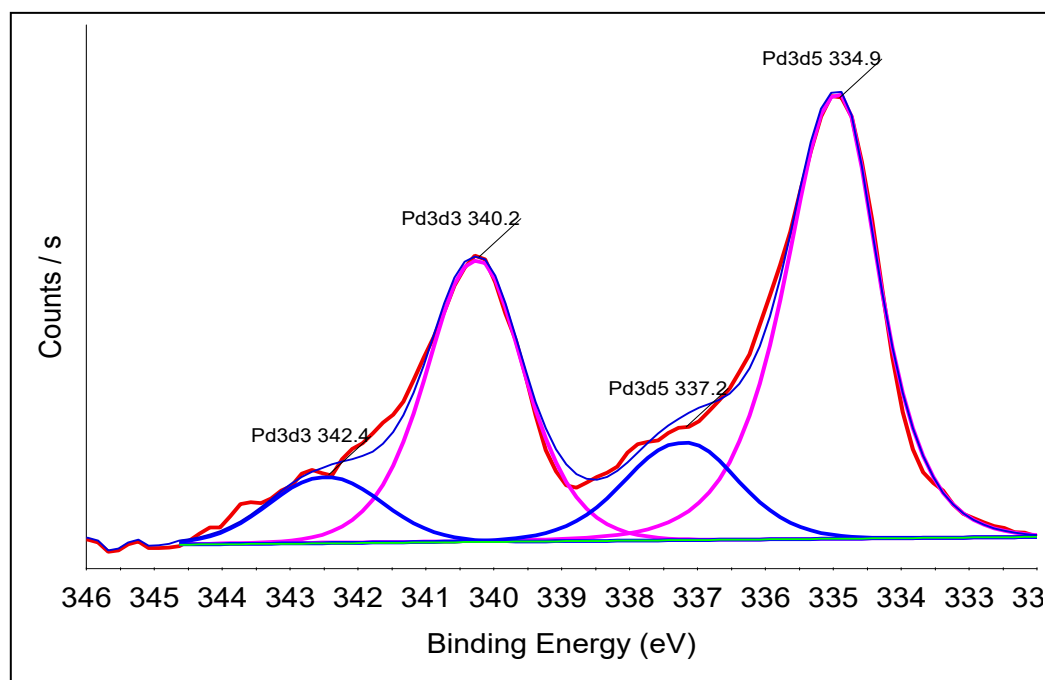
A similar analysis carried out for the Au 4f region yielded two doublets for Au 4f<sub>7/2</sub> and Au 4f<sub>5/2</sub> emission, a main one (92 at%) at 84.0 and 87.7 ± 0.1 eV, and a minor one (8 at%) at 86.6 and 90.4 ± 0.1 eV (Figure S5), both spin-orbit splitting, i.e., 3.7-3.8 ± 0.1 eV, being characteristic for the Au 4f region. Moreover, the main doublet was assigned to Au 4f<sub>7/2</sub> and Au 4f<sub>5/2</sub> features of Au<sup>0</sup> sites while the minor one could be attributed to Au<sup>III</sup> sites indicating the presence of few remaining unreduced species <sup>3,4</sup>. No evidence of Au<sup>I</sup> species could be found in the spectra <sup>5</sup>.

Finally, the analysis of the Pd 3d region gave two contributions for Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> emission features, a main one (80 at%) at 334.9 and 340.2 ± 0.1 eV, and a minor one (20 at%) at 337.2 and 342.4 ± 0.1 eV (Figure S6), both spin-orbit splitting, i.e., 5.2 ± 0.1 eV being characteristic for the Pd 3d region. The main contribution was assigned to Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> features of Pd<sup>0</sup> sites, while the minor one can be attributed to Pd<sup>II</sup> sites, likely PdO species <sup>[6, 7]</sup>.

In summary, despite the minor presence of remaining unreduced or partially reduced species, XPS data clearly demonstrate the efficiency of bipolar electrodeposition in achieving precise metal deposits on the organic particles.

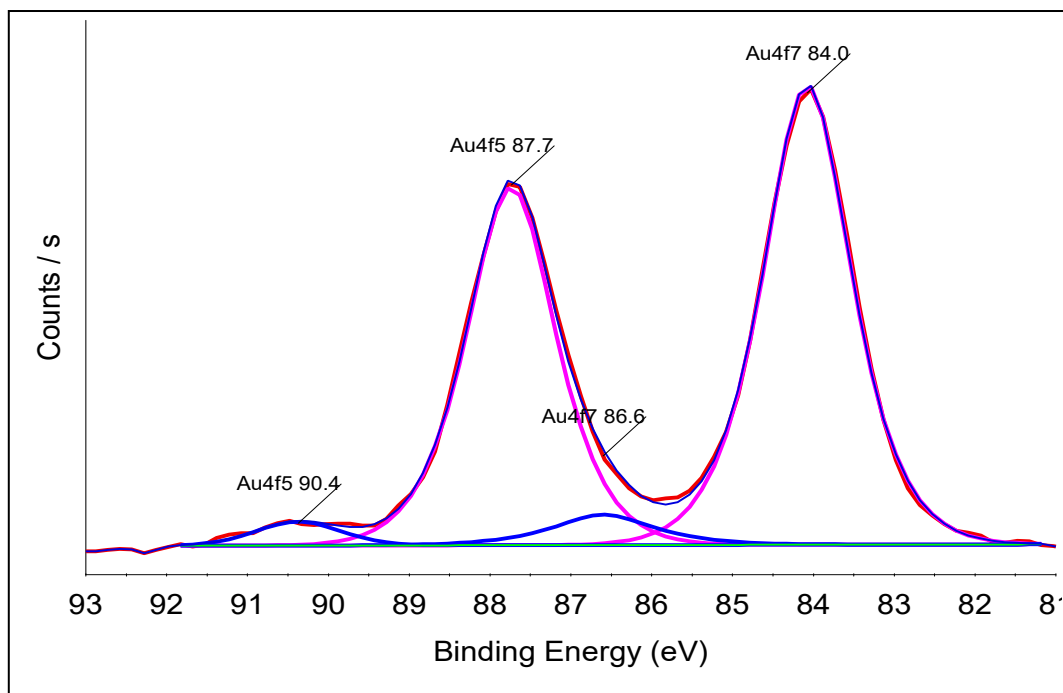


**Figure S4:** Experimental (red), and fitted XPS spectra (total fit, blue thin line), fit for Pt<sup>0</sup> sites (pink), fit for Pt<sup>II</sup> sites (blue, thick line)) Pt 4*f* of Pt/PCDTBT: PC<sub>61</sub>BM Janus particles.



**Figure S5:** Experimental (red), and fitted XPS spectra (total fit, blue thin line), fit for Pd<sup>0</sup> sites (pink), fit for Pd<sup>II</sup> sites (blue, thick line)) Pd 3*d* of Pd/PCDTBT: PC<sub>61</sub>BM Janus particles.





**Figure S6:** Experimental (red), and fitted XPS spectra (total fit, blue thin line), fit for Au<sup>0</sup> sites (pink), fit for Au<sup>III</sup> sites (blue, thick line)) Au 4f of Au/PCDTBT:PC<sub>61</sub>BM Janus particles.

## Experimental setup for hydrogen measurement

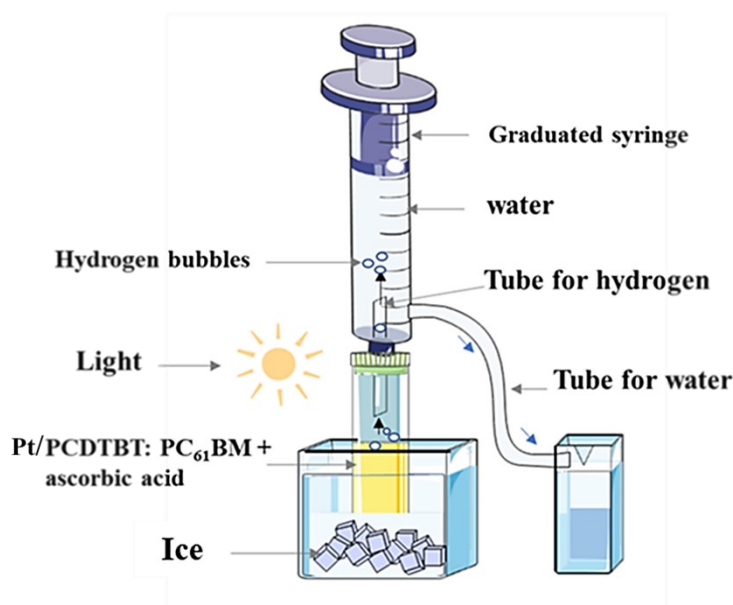
### Hydrogen evolution experiments

**PCDTBT:PC<sub>61</sub>BM thin films:** A thin film, supported on glass, of pristine or metal-modified PCDTBT:PC<sub>61</sub>BM was immersed in deionized water with 0.2 M ascorbic acid as the sacrificial electron donor. The solution was then illuminated with a UV-visible light (Mercury Xenon source) to initiate the photocatalytic reaction.

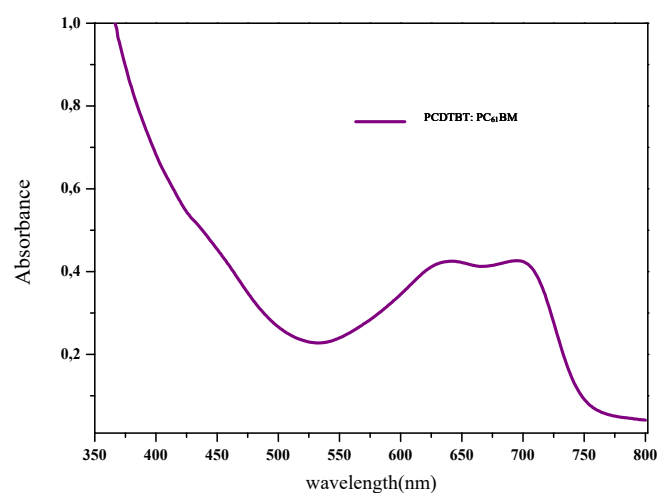
**PCDTBT:PC<sub>61</sub>BM nanoparticles:** For the particle-based system, 0.1 mg of pure or Pt-decorated PCDTBT:PC<sub>61</sub>BM nanoparticles were added to 2.5ml of an aqueous solution containing 0.2M ascorbic acid (pH=3). These suspensions were illuminated under exactly the same conditions for one hour, to drive the photocatalytic hydrogen evolution process.

**Figure S7** illustrates the set-up used to quantify the amount of produced hydrogen. A suspension of the selected particles was introduced into a cuvette filled with water and ascorbic acid, which served as a sacrificial electron donor. The cuvette containing the suspension was irradiated by UV-visible light (Mercury Xenon source) under stirring to initiate the water-

splitting reaction, leading to the generation of hydrogen bubbles. Due to buoyancy, the formed hydrogen bubbles rise towards the graduated syringe filled with water. The pressure generated by the rising bubbles displaces the water in a tube connected to a syringe and is further pushed into a collection vessel, enabling the measurement of the amount of displaced water, being directly correlated to the volume of produced hydrogen. To prevent overheating of the particle suspension during the water-splitting reaction, ice was placed under the cuvette to maintain a stable temperature. For one hour reaction time, Janus particles demonstrated the highest efficiency, producing 650  $\mu\text{L}$  of hydrogen which corresponds to a rate of 270 mmol/h/g, while pure PCDTBT:PC<sub>61</sub>BM particles produced only 50  $\mu\text{L}$  of hydrogen with a rate of 20.8 mmol/h/g and particles randomly covered with platinum nanoparticles generated 150  $\mu\text{L}$  of hydrogen, corresponding to a rate of 62.4 mmol/h/g.



**Figure S7:** Scheme and picture of the employed hydrogen collection system



**Figure S8:** UV-Visible spectrum of an aqueous suspension of PCDTBT:PC<sub>61</sub>BM nanoparticles (67nm)

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