Experimental and Theoretical Study of an Efficient Polymer Nano-Photocatalyst for Hydrogen Evolution

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1. Materials
Semiconducting polymer Poly[9,9-dioctylfluorenyl-2,7-diyl]-co-(1,4-benzo-2,1',3'-thiadiazole)] (F8BT, 1) was purchased from Ossila, UK. PFODTBT polymer (2) and Poly[9,9-dioctylfluorenyl-2,7-diyl]-alt-co-(bithiophene)] (F8T2, 3) were purchased from Solaris. The co-polymer, polystyrene grafted with ethylene oxide and carboxyl groups (PS-
PEG-COOH, back bone chain MW 8500, graft chain MW 4600, total chain MW 36500), was purchased from Polymer Source Inc., Canada. All other reagents were purchased from Sigma-Aldrich (Sweden) and used as received unless indicated otherwise. All experiments and measurements were carried out at room temperature unless indicated otherwise.

2. Preparation of Pdots

Pdots in aqueous solution was prepared by using a modified nano-precipitation method. The first step is to prepare stock solutions of polymer 1 or 3 and PS-PEG-COOH both in tetrahydrofuran (THF) with the same concentration of 1.0 mg/mL. Then, 2.5 mL of the PFBT (F8T2) solution and 0.5 mL of the PS-PEG-COOH solution were mixed and diluted to 50 mL THF. The mixture was sonicated to ensure homogeneity. This 50 mL solution was quickly poured into 100 mL distilled water in an ultrasonic bath, yielding a clear and light green solution. Finally, the THF in the mixture was removed by argon stripping while the solution was being sonicated, followed by filtration through a 0.45 μm syringe filter. A clear Pdots 1 or 3 dispersion was obtained, which remains clear and stable for months without any signs of aggregation.

In case of polymer 2 we prepared 4 different concentrations (25 µg/ml, 50 µg/ml, 75 µg/ml and 100 µg/ml) and always keep the ratio between polymer and co-polymer 5:1 (w/w). In this case solubility of this polymer is not so nice so maintaining concentration of 1.0 mg/mL is quite difficult. In this case first we dissolved the polymer in minimum solvent and co-polymer solution was added to that then the mixture was diluted to 50 ml. The final amount of polymer in Pdots solution in water was determined from UV-Vis experiment after removing water and re-dissolving in THF (Figure S2).

![Scheme S1](image-url). Schematic drawing of preparation of Pdots for photocatalysis test.
3. **DLS Measurements.**
The hydrodynamic diameter was measured by Zetasizer Nano-S from Malvern Instruments Nordic AB.

4. **Hydrogen Generation.**
Hydrogen was detected using a Unisense microsensor or GC (PerkinElmer Clarus 500, using Ar as carrier gas). The sensor was calibrated by injecting different volumes of hydrogen-saturated water in a calibration chamber with fixed amount of water (Ar purged). The sensor was polarized at +1000 mV until reaching a stable value before every measurement. A typical measurement is, the reaction cuvette was charged with the Pdots solution (3.0 mL) containing ascorbic acid (0.2 M, with pH adjusted to 4.0 with 1.0 M NaOH solution), and sealed with a septum. pH of the mixture was adjusted to 4 with NaOH in order to eliminate the proton source coming from ascorbic acid ($\text{pKa}_1 = 4.01$). The resulted reaction mixture was degassed by bubbling before illumination. A LED PAR38 lamp (17 W, 5000K, Zenaro Lighting GmbH, $\lambda > 420$ nm) was used as the light source. The light intensity of LED lamp is similar to the light intensity of visible light region in standard 1 sun. It is verified by solar cell.

5. **SEM and EDX**
Powder polymer were placed on conductive carbon tape on a sample holder disk, and coated using an Au -sputter coating for 30 sec. A Zeiss 1550 with AZtec EDX instrument was used for acquiring images using a 5 kV energy source under vacuum.

6. **Deuterium Labelling Experiment**
Pdots in $\text{D}_2\text{O}$ instead of $\text{H}_2\text{O}$ was prepared by using a same preparation method. Gas detection was done in the microwave vial with the Pdots solution (10.0 mL) containing ascorbic acid (0.2 M, with pH adjusted to 4.0 with 1.0 M NaOD solution). The resulted reaction mixture was degassed by Ar bubbling before illumination. A LED PAR38 lamp (17 W, 5000K, Zenaro Lighting GmbH, $\lambda > 420$ nm) was used as the light source and the solution was illuminated for 4 h. Gas analysis was carried out with a HPR-20 benchtop gas analysis system (HIDEN Analytical) using Ar as carry gas.

7. **Quantum Yield Measurements**
Apparent quantum yield was determined under the same catalytic conditions stated above, with light source of different wavelength. 300 watt Xe lamp (AULTT CEL-HXF300/CEL-HXUV300) was used as light source equipped AM1.5 filter and different band pass filters (CEAULIGHT, 450, 500, 550, 600, 650 and 700 nm) were used to select particular wavelength. The light intensity was measured with a Coherent LabMax_T0 sensor for visible range. The apparent quantum yields ($\Phi$) were estimated using the following equations:

$$\Phi_{\text{H}_2} = 2 \times \frac{\text{moles of hydrogen}}{\text{moles of incident photons}}$$
\[ n_p = \frac{It\lambda}{N_Ahc} \]

where \( n_p \) represents the moles of incident photons, \( I \) is the radiant power (assuming all of the input light has been absorbed in our case), \( \lambda \) is the light wavelength, \( t \) is the irradiation time (excluding the induction time), \( h \) is the Planck constant, \( N_A \) is the Avogadro constant, \( c \) is the speed of light.

8. Pd poisoning experiment

**CO poisoning:** CO was purged to the Pdots solution in water, taken in sealed microwave vial for 20 min. Then the excess CO was removed by Ar purging for a time period of 20 min. Then the Pdots solution subjected to the hydrogen evolution measurement through Unisense microsensor by following the same procedure as we discussed previously. **CAUTION! CO is an odorless, colorless and tasteless gas, and it is EXTREMELY toxic. The CO purging experiment should be done in well-equipped fume hood!**

**EDTA:** 1.2 mg of EDTA (to maintain 1 mM concentration) was added to the reaction cuvette containing 4.0 mL of Pdots solution and ascorbic acid (0.2 M, with pH adjusted to 4.0 with 1.0 M NaOH solution), and sealed with a septum. The resulted reaction mixture was degassed by bubbling before illumination. A LED PAR38 lamp (17 W, 5000K, Zenaro Lighting GmbH, \( \lambda > 420 \text{ nm} \)) was used as the light source. Hydrogen evolution measurement through Unisense microsensor was carried out by following the same procedure as we discussed previously.

9. DFT Calculation

All density functional theory calculations were performed using Gaussian 09 program package. The geometry optimizations and frequency calculations were carried out with the B3LYP hybrid functional and 6-31G* basis set while the electronic total energies were computed with additional single-point correction at B3LYP/6-311G** theory level. The average hydrogen adsorption free energies, for \( n \) adsorbed atoms, have been calculated as follows:

\[ \Delta G_H = (G_{\text{oligomer,H}} - G_{\text{oligomer}} - (n/2)G_{\text{hydrogen_molecule}})/n, \quad (1) \]

where \( G_{\text{oligomer,H}} \), \( G_{\text{oligomer}} \) and \( G_{\text{hydrogen_molecule}} \) are the Gibbs free energies of the hydrogenated oligomer, pristine oligomer and \( H_2 \), respectively, with \( G = U + PV - TS \). The vibrational, rotational and translational contributions (statistical mechanics contributions) were included in the calculation of internal energy (U) and entropy (S), i.e., for instance, \( U = E_{\text{elect}} + \text{ZPE} + U_{\text{vib}} + U_{\text{rot}} + U_{\text{trans}} \), where ZPE and \( U_{\text{vib}} \) are the zero-point energy and vibrational contribution at finite temperature T, respectively.

10. Steady State Absorption/Emission Measurements.

A PerkinElmer Lambda 750 UV–vis spectrophotometer was used for steady state UV–vis measurements. The instrument of fluorescence measurement used was a Fluorolog 3-222.
emission spectrophotometer (Horiba Jobin-Yvon) together with the FluorEssence software. All the emission spectra were measured on samples at right angle with respect to the excitation light using standard 1 cm quartz cuvettes.

11. Gas-MS Measurements.
Gas analysis was carried out with a HPR-20 benchtop gas analysis system (HIDEN Analytical) using Ar as carry gas.

12. Time-correlated Single Photon Counting (TCSPC) Measurements.
TCSPC measurements were carried out by using a pulsed diode laser source (Edinburgh Instruments EPL470) operating at 470.4 nm with a pulse FWHM of ca. 87.3 ps. A neutral density filter was used to attenuate the beam to obtain photon counts of approx. 1% or less of the incoming light intensity. The detector used was a Hamamatsu MCP-photomultiplier tube R3809U-51 (cooled to ca. -40 °C). The signal was passed to a discriminator (Ortec 9307) and then into a TAC (Ortec 566, 50 ns time range used). The electrical trigger signal from the laser was also passed through a discriminator (Tennelec TC454) and on to the TAC (Ortec 566). The TAC output was read by a DAQ-1 MCA computer card using 4096 channels and collected with Horiba Jobin Yvon DataStation 2.3 software. All measurements were done in reverse mode at 20 MHz and under magic angle polarization. A cut-off filter was used to block the scattered excitation light. The instrument response function (IRF) was obtained by using a blank microscopy glass slide. Fluorescence lifetimes were obtained by iterative reconvolution of the IRF and the collected decay curves, by fitting to a multiexponential decay model using either in-house scripts or with the help of the SpectraSolve 2.01 software.

13. Electrochemical Measurements.
Cyclic voltammetries were measured by an Autolab potentiostat with a GPES electrochemical interface (EcoChemie), using glassy carbon (diameter 3 mm) as the working electrode, Ag/AgCl electrode (saturated KCl aqueous solution) as the reference electrodes, and a platinum column as the counter electrode.

14. Raman Spectroscopy
Raman spectroscopy measurements were performed on the Pdots in water, polymer in THF and polymer film using a Renishaw in Via Raman spectrometer with 1 cm⁻¹ resolution between 1200 and 1750 cm⁻¹. The samples were subjected to two different laser excitations of 532 nm and 785 nm in order to have resonance and off-resonance conditions, respectively. A 50x and a 20x objectives with 1-3 μm diameter laser spot and 0.7-9.5 mW laser power were used depending on the measurement method. The measurements of the polymer films were carried out in air while the liquid samples were in a sealed quartz cell during the measurements. All the Raman spectroscopy measurements were done at room temperature.
15. Estimation of the band gap of Pdots.

The optical bandgap $E_g$ of Pdots, was estimated by zero-zero transition energy ($E_{0,0}$), which is calculated by $E_{0,0} = \frac{hc}{\lambda} = \frac{1240}{\lambda}$. Where $h$ is Plank’s constant, $c$ is the speed of light and $\lambda$ is the wavelength.

16. Supporting Figures and Tables

Table S1. The electron orbital distribution of different states of different polymers.

| Polymers | Ground State | Reduced State |
|----------|--------------|---------------|
|          | HOMO | LUMO | HOMO |
| 1        | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| 2        | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| 3        | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |

The electrons of polymer 1 and 2 are concentrated on BT units after reduction, which facilitate the hydrogen bonding with N atoms. However, the electrons of polymer 3 are delocalized along with the whole skeleton.

Table S2. Hydrogen generation activities of some documented organic polymer based photocatalysts.

| Catalysts                      | Hydrogen generation rate \(a\) | Apparent Quantum yield/Quantum yield | Conditions                  | Reference                      |
|--------------------------------|---------------------------------|-------------------------------------|-----------------------------|--------------------------------|
| g-C$_3$N$_4$ (3.0 wt% Pt)      | 0.1 mmol h$^{-1}$g$^{-1}$       | 0.1 %                               | 10 vol% Triethanolamine $\lambda > 420$ nm | Nat. Mater. 2009, 8, 76-80     |
| g-C$_3$N$_4$ (3.0 wt% Pt)      | 15 mmol h$^{-1}$ g$^{-1}$      | 50.7% (405 nm)                      | Triethanolamine             | ACS Catal. 2016, 6, 3921–3931. |
| hydrazone-based COF (Pt-modified) | 1.9 mmol h$^{-1}$g$^{-1}$    | 2.2 %                               | 10 vol% Triethanolamine $\lambda > 420$ nm | Chem. Sci., 2014, 5, 2789–2793 |
| azine hydrazone-based COF (0.68 wt% Pt) | 1.5 mmol h$^{-1}$g$^{-1}$     | ---                                 | 10 vol% Triethanolamine $\lambda > 420$ nm | Nat. Commun. 2015, 6.           |
| Covalent Triazine Frameworks (1.0 wt% Pt) | 0.2 mmol h$^{-1}$g$^{-1}$ | 2.4 %                               | 12.5 vol% Triethanolamine $\lambda > 420$ nm | Macromol. Rapid Commun. 2015, 36, 1799–1805 |
| Heptazine-Based Microporous Polymer (3.0 wt% Pt) | 0.12 mmol h$^{-1}$g$^{-1}$ | ---                                 | 10 vol% Triethanolamine $\lambda > 420$ nm | Macromol. Rapid Commun. 2013, 34, 1008–1013 |
| Microporous organic nanorods (50 wt% TiO$_2$–Pt) | 1.25 mmol h$^{-1}$g$^{-1}$ | 4.5 %                               | 10 vol% Triethanolamine $\lambda > 420$ nm | J. Mater. Chem. A, 2014, 2, 7656 |
| Phenyl-triazine oligomers (2.2 wt% Pt) | 0.12 mmol h$^{-1}$g$^{-1}$ | 5.5 %                               | 10 vol% Triethanolamine $\lambda > 420$ nm | Energy Environ. Sci., 2015, 8, 3345–3353 |
| Triazine-based Carbon          | 4.9 mmol h$^{-1}$g$^{-1}$      | 3.4 %                               | 10 vol%                     | Angew. Chem. Int. Ed.          |
Nitrides (2.3 wt% Pt)

| Conjugated poly(azomethine) (3.0 wt% Pt) | 0.07 mmol h⁻¹g⁻¹ | --- | 10 vol% Triethanolamine λ > 420 nm | 2013, 52, 2435 –2439 |
| Porous Conjugated Polymers (2.0 wt% Pt) | 0.17 mmol h⁻¹g⁻¹ | 1.8 % | water/Methanol/triethylamine mixture λ > 420 nm | Chem. Commun., 2010, 46, 8932–8934 |
| Conjugated Polynorbornene (3.0 wt% Pt) | 2.9 mmol h⁻¹g⁻¹ | 4.0 % | water/Methanol/triethylamine mixture λ > 420 nm | Angew. Chem., Int. Ed. 2016, 55, 1792 –1796 |
| Conjugated copolymer | 0.18 mmol h⁻¹g⁻¹ | 4.2 % | 20 vol% diethylamine λ > 420 nm | J. Am. Chem. Soc. 2015, 137, 3265–3270 |
| Planarized Conjugated Polymer | 5.8 mmol h⁻¹g⁻¹ | 2.3 % | water/Methanol/triethylamine mixture λ > 420 nm | Angew. Chem. Int. Ed. 2016, 55, 1792 –1796 |
| PFODTBT Pdots (0.1% Pd) | 50.0 mmol h⁻¹g⁻¹ | 0.6 % (550 nm) | Pure aqueous λ > 420 nm | Angew. Chem. Int. Ed. 2016, 55, 12306 –12310 |

**Figure. S1.** Absorption spectra of polymers (1, 2 and 3) in THF and Pdots (1, 2 and 3) solution.

(a) The values are calculated according to the reported data in literatures.
Figure S2. Absorption spectra of Pdots 2 prepared from different concentration of polymer 2.
Figure. S3. The TCSPC curves and fitting data of different polymers in THF and Pdots in aqueous solution.

Figure. S4. Cyclic voltammetry of Pdots 2 and 3 in pH 4.5 buffer solution.

Figure. S5. The Raman spectra of Pdots 2 in water, polymer 2 in THF and polymer 2 film measured under resonance (532 nm) and non-resonance (785 nm) conditions.
Figure S5 a and b show the Raman spectra of the polymer film, polymer in THF and Pdots in water for the resonance and non-resonance conditions, respectively. Under the 532 nm excitation of the polymer film, the vibrational modes were in good agreement with the Raman spectra of a similar polymer F8TBT in literature. The vibrations at 1445, 1542 and 1603 cm\(^{-1}\) were also seen for the low concentration of the polymer in water. This effectively showed the vibrational signature is kept under resonance conditions (i.e. electronic excitation of the polymer) when the polymer was dispersed in water as well. However, the strong fluorescence effect in the Raman spectrum of the THF solution hidden the Raman signal. For the off-resonance condition with the 785 nm laser, weaker signals were naturally seen. However, the strongest vibration band at 1444 cm\(^{-1}\) as well as a weak feature at 1605 cm\(^{-1}\) were in consistence with the resonance condition. Here, the absence of strong fluorescence effect in THF revealed the 1445 cm\(^{-1}\) band but also a distinct shoulder indicated a change of interactions in the THF solution. From a vibrational perspective, the results thus indicated that the polymer structure was more or less the same in solid phase as in water but not certified in the case of THF. In addition, in both conditions, either resonance or non-resonance, the Pdots did not influence the vibrational features, indicating a low interaction between the polymers in the aggregated Pdot state.

Figure S6. Optimization of the concentration polymer 2 in Pdots solution.

It is very interesting to evaluate the influence of Pdots concentration on hydrogen evolution. The best active polymer (2) is used for this study. Four different stoichiometric mixture of polymer 2 (25 µg/ml, 50 µg/ml, 75 µg/ml and 100 µg/ml) and co-polymer were used to prepare Pdots. The concentration of pdots in water increases upon increase of polymer concentration from 25 µg/ml to 75 µg/ml. Further increasing to 100 µg/ml led to big particle formation during THF removal and seriously precipitates out from the solution. Figure S6
depicts that the concentration of the polymer play important role in amount of polymer after formation of Pdots. Then photocatalytic hydrogen generation was tested with these various Pdots samples (Figure S6). There is dramatically increment in hydrogen generation upon polymer concentration in Pdots from 4 µg/ml to 8 µg/ml, but further increasing the concentration does not contribute so much in the hydrogen evolution.

Table S3. The concentration data and hydrogen evolution rate of different samples.

| Pdots | Polymer amount (µg/ml) | copolymer amount (µg/ml) | Polymer in Pdots (µg/ml) | H₂ (mmol/g) | H₂* (mmol/g.h) |
|-------|------------------------|--------------------------|--------------------------|-------------|---------------|
| 1     | 25                     | 5                        | 17                       | 4           | 8             |
| 2     | 25                     | 5                        | 4                        | 35          | 20            |
| 2     | 50                     | 10                       | 8                        | 62          | 50            |
| 2     | 75                     | 15                       | 13                       | 63          | 47            |
| 2     | 100                    | 20                       | 9                        | 60          | 48            |
| 3     | 25                     | 5                        | 19                       | 0.2         | 0.1           |

*Initial rate
**Figure. S7.** The GC data with injection of 100 µL headspace gas after 1 h light illumination for 25 mL Pdots 2 solution (13 µg/ml).

From the GC calibration data, we can conclude there is 5% H$_2$ in headspace of our reaction vial. The total amount of H$_2$ produced is 17 µmol.

**Figure. S8.** SEM image and EDX of polymer 1.

**Figure. S9.** SEM image and EDX of polymer 2.
**Figure. S10.** SEM image and EDX of polymer 3.

**Table S4.** The Pd amount determined by EDX in different polymer samples

| Polymers | 1     | 2     | 3     |
|----------|-------|-------|-------|
| Pd (w/w) | 0.1%  | 0.1%  | 0.5%  |

Polymer 3 has more residual Pd, but its Pdots did not show any photocatalytic reactivity for proton reduction, although it has similar band gap to polymer 1 and suitable reduction potential to reduce proton. As a conclusion, we don’t think the residual Pd from these polymers plays a crucial role in photocatalytic proton reduction.

![Graph](image)

**Figure. S11.** Pd poisoning experiments of Pdots 2 with EDTA and CO.

![Graph](image)

**Figure. S12.** Gas mass experiment with three times injection of equal amount (0.5 mL) of air.

The injection of air was to check the influence of pressure on the signal of gas mass spectra. We can see the pressure change due to injection of 0.5 mL gas every time shows negligible
influence of signal. We observed much less H\textsubscript{2} generated from D\textsubscript{2}O experiment than that from H\textsubscript{2}O experiment. However, we indeed detected D\textsubscript{2} as main product from D\textsubscript{2}O experiment. For H\textsubscript{2}O experiment, there was negligible signal from D\textsubscript{2} which should be mainly from pressure change.

**Figure S13.** Optimized structures of polymer 1 (a), 2 (b) and 3 (c). Level of theory: B3LYP/6-31G*, Gaussian code.

**Figure S14.** Energy profile for the H\textsubscript{2} formation from interacting hydrogen atoms present at the same BT (a) and at different polymer units (b). The values are referred to the ground-state geometry. The insets indicate the structures of the initial, transition and final states (i-iii, respectively).
Solvation Calculations

- PCM solvation model;
- B3LYP-6-311G** with SP.
- Freq-B3LYP/6-31G*.

| System       | $\Delta G$ a.u. | $\Delta G$ (eV) | $\Delta G$ a.u. | $\Delta G$ (eV) |
|--------------|-----------------|-----------------|-----------------|-----------------|
| pf2t-H (S-site) | 0.083           | 2.264        | 0.083           | 2.264        |
| Pfbt-H (S-site)  | 0.078           | 2.110        | 0.073           | 1.990        |
| Pfbt-H (N-site)    | 0.024           | 0.657        | 0.022           | 0.599        |
| pfdbt-H (S-site)   | 0.082           | 2.218        | 0.081           | 2.217        |
| pfdbt-H (N-site)    | 0.026           | 0.711        | 0.023           | 0.632        |
| pfdbtt-2H (cis,N-site) | 0.020      | 0.272        | 0.017           | 0.235        |
| pfdbtt-3H (cis,N-site) | 0.045     | 0.408        | 0.039           | 0.357        |

$1/2G (\text{H}_2) = -0.5905$ hartrees

**Figure S15.** Solvation effect calculation within the PCM approach (B3LYP/6-311G*)

In order to check the solvation effect, the calculation is also conducted within the PCM approach (B3LYP/6-311G*). The obtained trend (see Figure 15) remains the same and the changing on the binding energies is minor for all studied systems. For instance, for Hydrogen interacting on the S-site of PFBT (polymer 1) the binding energy changed from 2.11 eV to 1.99 eV; while for Hydrogen interacting on the N-site of the same polymer the solvation shifted the energy from 0.657 eV to 0.599 eV. Therefore, we concluded that the calculations performed in the gas phase suffice for our analysis.

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