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Hydrogen evolution by polymer photocatalysts; a possible photocatalytic cycle†

Andrew W. Prentice and Martijn A. Zwijnenburg*

Abstract: We propose, supported by ab-initio calculations, a possible photocatalytic cycle for hydrogen evolution by a prototypical polymer photocatalyst, poly(p-phenylene), in the presence of a sacrificial electron donor. As part of that cycle we also introduce a family of related sites on the polymer that in the absence of a noble metal co-catalyst can facilitate the evolution of molecular hydrogen when the polymer is illuminated. The bottlenecks for hydrogen evolution, electron transfer from the sacrificial electron donor and hydrogen-hydrogen bond formation, are discussed, as well as how they could potentially be improved by tuning the polymer properties and how they change in the presence of a noble-metal co-catalyst.

1 Introduction

The constant depletion of fossil fuels and natural gas sources, not to mention their detrimental effect on the environment and the ever-growing demand for energy, has led to development and application of low-CO₂, in some instances CO₂-free, renewable-energy sources such as bio-mass, solar, wind, tidal and geothermal. Solar energy is by far the most promising of the renewable sources as the hypothetical energy attained from incident light on 1 % of the earth’s surface at an 10 % conversion efficiency (105 TW) considerably out-weighs the predicted energy demand for 2050. To put the importance of solar energy into perspective the cumulative upper bound energy output of bio-mass, wind, tidal and geothermal is one-fifth of that of the aforementioned solar energy output.

The role of molecular hydrogen (H₂) as an energy carrier has also been extensively studied and garnered significantly interest in recent times because of the high energy content (141.9 MJ kg⁻¹) when compared to other known fuels such as methane (55.5 MJ kg⁻¹) and gasoline (47.5 MJ kg⁻¹). However, the use of molecular hydrogen has been hindered by the difficulty of finding a low-cost renewable synthetic route, as well as a convenient way of subsequently storing the produced hydrogen. One possible synthetic route is photocatalytic water-splitting, see Eq. 1, first demonstrated in the form of photoelectrolysis using a TiO₂ photoanode by Fujishima and Honda in 1972.

\[ \text{H}_2\text{O}(l) + \text{Photocatalyst} + h\nu \rightarrow \text{H}_2(g) + \text{O}_2(g) \] (1)

Traditionally, metal oxides containing transition metals such as titanium, gallium and tantalum are employed as water-splitting photocatalysts. However, organic materials such as carbon nitrides, conjugated linear polymers, conjugated microporous polymers (CMPs) and covalent organic frameworks (COFs) have been shown to be able to drive proton reduction, see Eq. 2, and/or water oxidation, see Eq. 3, in the presence of sacrificial electron donor (SED) and acceptor (SEA) species, respectively. Carbon nitride was the first organic material to evolve both hydrogen and oxygen in the presence of these sacrificial species, as well as the first organic material reported to perform overall water splitting. Compared to their inorganic counterparts, organic photocatalysts have the advantage of facile tunability of the photocatalyst’s properties through co-polymerisation and chemical functionalisation as well as being based on generally more earth-abundant elements.

\[ 2\text{H}^+_{(aq)} + 2e^- \rightarrow \text{H}_2(g) \] (2)

\[ \text{O}_2(g) + 4\text{H}^+_{(aq)} + 4e^- \rightarrow \text{H}_2\text{O}(l) \] (3)

Despite a significant uptake of interest in organic materials the exact relationship between their (opto-)electronic/structural properties and the observed hydrogen (HER) and oxygen evolution reaction (OER) rates still remains far from clear. Previously, we demonstrated that empirically the variation in HER/OER rates between polymers can be described in terms of (i) the thermodynamic driving force for proton reduction and water oxidation, controlled by the ionisation potential (IP) and electron affinity (EA) of the neutral polymer, in both the ground state and in the presence of an excited electron-hole pair (exciton) (ii) the onset of light absorption and (iii) the dispersability of the polymer particles in suspension. The dispersability of a polymer probably depends both on the size (distribution) of the polymer particles in suspension and the inherent wettability of the polymer or its sidegroups. Our empirical observations are in line with a classical semiconductor microscopic model where the exciton formed through the absorption of light either (i) spontaneously falls apart and the free electron and hole formed in the process reduce protons/SEA and oxidise water/SED, respectively, or (ii) more likely due to the large exciton binding energy relative to k_B T in polymers, drives one of the two solution half-reactions and the free-electron/hole formed in the process the other. Transient spectroscopy of polymers un-
under hydrogen evolution conditions\cite{25,28} indeed suggest the presence of electron polarons, though the exact catalytic cycle and nature of the sites responsible for HER/OER for this semiconductor-like model, and the role played by transition or noble metal co-catalyst is less clear. McCulloch and co-workers demonstrated that upon removal of Pd from polymers prepared via Suzuki coupling the HER rates drop to effectively zero\cite{29,30} but other authors report HER by polymers that contain negligible noble metals and/or are prepared via a non noble-metal route.\cite{31,32} Domcke, Sobolewski and co-workers have proposed an alternative microscopic HER mechanism, based on ab-initio calculations on hydrocarbon bonded pyridine,\cite{33} acridine,\cite{34} heptazine,\cite{35,36} and triazine-water complexes,\cite{37,38} which does not involve heterolytic exciton dissociation and the formation of free-carrier charges. Instead photon absorption induces an electron driven proton transfer, i.e. proton coupled electron transfer (PCET) or hydrogen atom transfer (HAT), from water to the photoexcited organic molecule, resulting in the formation of an hydrogenated organic molecule and an hydroxyl radical, essentially homolytic rather than heterolytic exciton dissociation. The evolution of molecular hydrogen can then proceed through a dark reaction involving the combination of two hydrogenated radicals or via absorption of another photon populating a bond dissociative pathway, either directly through vibronic coupling or excited state absorption.

Here we propose, supported by density functional theory (DFT) and correlated wave function calculations, a possible photocatalytic cycle for HER by a prototypical polymer photocatalyst, poly(p-phenylene) (PP$_n$) oligomers of different length $n$. These oligomers are then embedded in H$_2$O or TEA to model a polymer strand near the polymer-H$_2$O and polymer-TEA interface, respectively, where the chemistry takes place. The effect of solvent in these calculations is described by a continuum solvation model, which recovers the main dielectric effect of solvation on the (electronic) properties of these relatively hydrophobic polymers. While essentially a minimal model of polymer particles, such models are successfully used to calculate the potentials of charge-carriers and excitons in polymers,\cite{39,40,41,42,43,44,45,46,47} as well as previously shown to predict accurate potentials when compared with available experimental photoelectron spectroscopy data.\cite{25,28}

## 2 Computational Details

### 2.1 Computational Model

The poly(p-phenylene) polymer is described in this study as single p-phenylene (PP$_n$) oligomers of different length $n$. These oligomers are then embedded in H$_2$O or TEA to model a polymer strand near the polymer-H$_2$O and polymer-TEA interface, respectively, where the chemistry takes place. The effect of solvent in these calculations is described by a continuum solvation model, which recovers the main dielectric effect of solvation on the (electronic) properties of these relatively hydrophobic polymers. While essentially a minimal model of polymer particles, such models are successfully used to calculate the potentials of charge-carriers and excitons in polymers,\cite{39,40,41,42,43,44,45,46,47} as well as previously shown to predict accurate potentials when compared with available experimental photoelectron spectroscopy data.\cite{25,28}

### 2.2 Density Functional Theory

All density functional theory calculations were performed with Gaussian 16 (Revision A.03)\cite{49} employing a polarisable continuum model (PCM)\cite{50,51} to account for the reaction field, specifically the integral equation formalism (IEF-PCM)\cite{52} In order to explore the excited state landscape we utilise the time-dependent extension to DFT (TD-DFT)\cite{53} All structures were confirmed as stationary points on the multi-dimensional potential energy surface and further validated to be local minima by analytic frequency calculations, displaying positive curvature along all vibrational modes. The (free) energy differences for all process considered are adiabatic, i.e. the structure of all species are the relevant local minima with the solvent fully equilibrated for each structure, this is also extended to the $S_1$ state. However, for the vertical absorption profiles we use the non-equilibrium approach which only takes into account solvent polarization from the shift in electron density upon photoexcitation maintaining the cavity shape which was optimal for the ground state density. We utilize either H$_2$O ($\varepsilon = 78.36$) or TEA ($\varepsilon = 2.38$) PCM models to simulate the interface between the polymer and the solvent, denoted herein as PP$_n$-H$_2$O or TEA, respectively. The free energy (G) is obtained via corrections to the electronic energy (E) and calculated using the standard ideal gas, rigid rotor and harmonic oscillator statistical models to the translation, rotational and vibrational energy levels of the molecule at a temperature of 298.15 K. The B3LYP\cite{54,55} CAM-B3LYP\cite{56,57} and MN15\cite{58} approximations to the exchange-correlation functional were used in conjunction with the cc-pVTZ basis set. To account for dispersion interactions we include Grimme’s D3 dispersion correction\cite{59} to the B3LYP and CAM-B3LYP electronic energies and forces.

### 2.3 Second Order Algebraic Diagrammatic Construction

All second order Møller-Plesset (MP2) and algebraic diagrammatic construction (ADC(2)) computations were performed using TURBOMOLE V7.4.1\cite{60,61} and MN15 approximations to the exchange-correlation functional were used in conjunction with the cc-pVTZ basis set, we include the conductor-like screening model (COSMO)\cite{62} solely in the former calculations as gradients are not implemented within TURBOMOLE V7.4.1 for ADC(2) and compute the SCS-MP2 energy using the solvated Hartree-Fock (HF) molecular orbitals.\cite{63} Once again we use H$_2$O and TEA implicit solvent models. For the adiabatic excitation energy a single point calculation using the larger cc-pVTZ basis-set was then performed in which the correlated density of the ground or excited state is self consistent with the reaction field. For the vertical excitation spectra we once again use the cc-pVTZ basis-set and the correlated density to generate the reaction field, computing the non-equilibrium response of each state.
2.4 Coupled Cluster Theory

All single point coupled cluster singles and doubles (CCSD) calculations were performed in Gaussian 16 (Revision A.03) employing an IEM-PCM solvation model to account for the polymer-H_2O interface, as well as invoking the frozen core approximation. The effect of solvation when calculated using the Hartree-Fock (HF) or CCSD densities was found to be very similar, with the adiabatic excitation energy and electron affinity differing by 0.01 and 0.04 eV, respectively, as computed with the cc-pVDZ basis set. For excited states the equation of motion (EOM) extension to CCSD was employed. Taking into account the much larger computational cost of the latter, as this involves an additional CCSD self-consistent cycle, we use the former for all (EOM-CCSD results we discuss below. These calculations use the larger cc-pVTZ basis-set and geometries obtained from ADC(2) or DFT.

3 Results

3.1 Proposed Photocatalytic Cycle and Overview of Reactions

We begin with an overview of the proposed catalytic cycle, which is illustrated in Fig. 1(B). Initially, PP_n undergoes excitation after absorption of a photon generating an exciton. After this vertical excitation (VE) into any excited singlet state, the system is exothermic (exergonic) reactions.

\[
G(P_{PP_n}^+) = G(P_{PP_n}) - AIP(PP_n) + ET(P_{PP_n}) = AIP(PP_n) - AE(AEA(PP_n))
\]

The next step would involve the transfer of a proton (PT) for which we have multiple possible scenarios: (i) PT between TEA and TEA (step J), (ii) PT between TEA and PP_n (step C + G), (iii) PT between TEA-H and PP_n (step C + H), (iv) TEAR and TEA (step K) and (v) PT between TEAR and PP_n (step C + I). The final step of the cycle would involve de-hydrogenation of [PP_n-H]^*, resulting in the formation of H_2 for every 2 molecules of [PP_n-H]^* (step D + L), thus completing the proposed catalytic cycle.

Instead of sequential electron and proton transfer upon excitation of the polymer, concerted electron-proton transfer, and thus effectively hydrogen atom transfer, could take place, analogous to the mechanism discussed by Domcke and co-workers for water oxidation.

3.2 Excited State Landscape

We begin with an exploration of the vertical absorption spectra as a function of increasing oligomer length using both (TD-)DFT and SCS-ADC(2). In order to reduce some of the computational strain we employ symmetry within the SCS-ADC(2) calculations, namely D_2 and C_2v for even and odd oligomer lengths, while in the (TD-)DFT equivalent no symmetry was enforced (i.e. C_1). Despite being one of the simplest possible conjugated materials, it has been noted in previous studies that there is a disagreement between correlated wave function methods and (TD-)DFT when predicting the nature of the vertical excited states for small PP oligomers. It is discussed further within the supporting information (see Section S1). The simulated absorption spectra for the largest and smallest oligomers using CAM-B3LYP and SCS-ADC(2) are provided in Fig. 2(A) and Fig. 2(C) (see Section S2 for the peak broadening parameters and Fig. S2 for all other predicted absorption spectra). As expected upon extension of the oligomer length a clear red shift of the lowest energy bright absorption band is observed. This lowest energy bright state corresponds to a \( ^1\pi\pi^* \) transition and can be described by a single particle-hole transition from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. The red-shift with oligomer length is most prominent for B3LYP with the VEE changing from 4.87 to 3.53 eV (1.34 eV) for PP_2 to PP_7-H_2O. For SCS-ADC(2), CAM-B3LYP and MN15 we observe shifts of 5.40 to 4.28 eV (1.12 eV), 5.24 to 4.17 eV (1.07 eV) and 5.02 to 3.82 eV (1.20 eV), respectively. We observe a good agreement between both SCS-ADC(2) and CAM-B3LYP for the VEE of the optically bright state, with a maximum deviation of 0.16 eV. For B3LYP and MN15 the excitation energy of this absorption band is significantly underestimated when compared to the aforementioned methods. Upon switching from the high dielectric H_2O environment to low dielectric TEA we observe a small increase in the VEE of the bright state, with a maximum blue shift of 0.08 eV.

We now turn our attention to the S_1 AEE for each oligomer
length and theoretical method combination. The AEE for each oligomer length is shown in Fig. 2(B) and Fig. 2(D) for the case of the PP$_n$-H$_2$O and TEA interface, respectively. As a result of relaxation of the oligomer and/or solvent the AEE is significantly lower than the VEE, the difference between which may potentially be dissipated to the environment as heat and thus lost. For SCS-ADC(2) upon transition from PP$_2$ to PP$_7$-H$_2$O the AEE decreased from 4.59 to 3.69 eV and from 4.32 to 3.45 eV for CAM-B3LYP. For B3LYP and MN15 the AEE ranged from 4.08 to 2.92 eV and from 4.20 to 3.20. For PP$_2$-H$_2$O the CCSD AEE was calculated to be 4.76 eV, larger than the ADC(2) equivalent by 0.17 eV. At the TEA interface the AEE are again blue shifted when compared to the high dielectric environment, with a maximum blue shift of 0.18 eV, which was observed for PP$_2$. The SCS-ADC(2) AEE on the other hand were essentially the same in both environments, maximum blue shift of 0.02 eV for PP$_6$, which may be the result of neglecting the effect of solvation in the SCS-ADC(2) structural optimizations.

### 3.3 Exciton Dissociation and Electron Transfer

In inorganic materials the exciton binding energy (EBE) is normally a few tens of meV or less and excitons thus spontaneously dissociates into free-charge carriers. In contrast, the $S_1$ exciton in polymer photocatalysts is normally still bound at room temperature as a result of the much larger EBE in organic conjugated materials, as well as the fact that excitons in polymers

**Fig. 2** (A,C) The simulated absorption spectra for PP$_2$ (blue) and PP$_7$ (brown) calculated using TD-CAM-B3LYP at the polymer-water and polymer-TEA interface, respectively. The SCS-ADC(2) equivalent is given as a solid or dashed black line for PP$_2$ and PP$_7$, respectively. (D) The predicted AEE as a function of oligomer length for CAM-B3LYP (green triangles), SCS-ADC(2) (blue stars), B3LYP (orange circles) and MN15 (red squares) at the polymer-water and polymer-TEA interface, respectively.
self-trap, i.e. localise by distorting the polymer geometry. As shown in Fig. 3(C) the adiabatic EBE, the EBE when also considering self-trapping, can be obtained from the difference between the adiabatic fundamental gap (AFG) and the AEE, the former quantity itself is the difference between the AIP and AEA of the material. At the interface with water the adiabatic EBE of the polymer is calculated to be approximately 0.4 eV for each of the exchange-correlation functionals considered, essentially independent of oligomer length (see Table S5). However, at the interface with TEA the adiabatic EBE is significantly larger; over 1.2 eV for all oligomer lengths (see Table S6). This increase can be attributed to the increased stabilization of the charged species in the high-dielectric environment, schematically shifting down the energy of the arbitrary h• and e− PES in Fig. 3(C), thus providing smaller AIPs and larger AEA associated with TEA. As mentioned previously the AEE is only slightly blue shifted in TEA therefore the increase in EBE is dominated by the difference of the AFG in both environments.

We now turn our attention to the electron transfer process (step B) from the SED to the photoexcited polymer. As discussed earlier the degradation pathway of TEA means that this electron may come from this species directly (step E) or from the dehydrogenated TEAR radical (step F). As the oligomer length increases AEA(PPn) increases, resulting in a lower thermodynamic driving force for this ET. For the H2O solvated systems ET using TEA as the SED is moderately thermodynamically favorable for small oligomer lengths (see Fig. 4), with free energy values ranging from -0.65 eV for PP2 and -0.19 eV for PP7 when using CAM-B3LYP. For B3LYP and MN15 the dependence with oligomer length is similar, however, for PP8 and PP7 the ET is predicted to be slightly endergonic. Using CCSD the electronic energy difference of the ET process for PP2 was calculated to be -1.01 eV, somewhat more exothermic than that predicted by DFT (-0.52 eV and -0.61 eV for B3LYP and CAM-B3LYP, respectively). For ET involving TEAR we predict that ET is highly exergonic for all oligomer lengths. For PPn-TEA the increased AIP of TEA coupled with the decreased AEA values of the polymer results in ET being endergonic for all oligomer lengths (see Fig. 3B). Once again ET from TEAR is exergonic for all oligomer lengths, though with a lower driving force than in H2O.

3.4 Proton Transfer and H2 Generation

The next step of the proposed catalytic cycle then involves the protonation of the one-electron reduced polymer (step C). The various proton sources have been outlined above in Section 3.1 and Fig. 3(B). For PP2 to PP3-H2O using DFT we have studied each unique adsorption site on the photocatalyst, see Fig. 3(A) for the carbon atom labels for non-equivalent carbon atoms. For all oligomer lengths we find that the lowest energy adsorption sites are those corresponding to aromatic -CH- sites with adsorption of the proton on the sites linking the phenyl units being considerably less favourable (see Table S7 for the specific free energy differences for each polymer length). All the different aromatic -CH- sites lie within 0.03 eV (<1 kcal mol−1), therefore below we only discuss the case for the C3 position, which was the lowest free energy adsorption site. As outlined in Fig. 4 for all oligomers we observe that PT is exergonic with the driving force once again decreasing with an increase in the oligomer length. The PT step is far more exergonic at the TEA interface (cf. -0.24 and -1.68 eV for PP-7-H2O and TEA when using TEA+ as the proton source, respectively). As PPn-H+ is neutral both solvents will stabilize this species to a similar extent, therefore, the low-dielectric environment will essentially gain back the energy differential of the preceding ET step. The reaction profile for PT is similar for the three proton sources considered, see Fig. 4(A) and (B) for TEA and TEAR*, respectively. For PT with [TEA-H]+ as the proton source we observe that PT is exergonic with the driving force once again decreasing with an increase in the oligomer length.

Fig. 4 Predicted free energy of proton transfer at the polymer-H2O (A) and polymer-TEA (B) interface as a function of oligomer length, when TEA (upward triangle) and TEAR* (downward triangle) is the source of protons. B3LYP results in orange and CAM-B3LYP results in green, with respect to C3 hydrogenated polymer.

The final step of the catalytic cycle then involves the regeneration of the original photocatalyst and the release of the molecular hydrogen (step D + L). We find in both environments that this reaction is considerably exergonic, ~ 1.2 eV, and practically does not change when going from PP2 to PP7 (see Table S5 and Table S6). We also observe no apparent difference between the reaction energetics at the different solvent interfaces. The binding free energy between the polymer and a hydrogen atom was calculated to be approximately 0.8 eV for all oligomers and once again unaffected by the specific solvent model employed. Using CCSD the reaction energetics for PP2-H2O are similar with a PT reaction energy of ~0.9 eV. The hydrogen binding energy was calculated to be 1.41 eV using CCSD, 0.6 eV larger than the DFT predicted values. Both bond dissociation energies for PPn-H+, calculated by
DFT and CCSD, are far smaller than the experimental $\sigma_{C-H}$ bond dissociation energy for benzene at 298 K (4.9 eV)\(^2\). Finally, to probe the barrier to H\(_2\) evolution we performed a constrained optimization, starting from a fully optimized tail-to-tail cluster of two PP\(_2\)-H* molecules, where we step-by-step stretch the $\sigma_{C-H}$ bonds decreasing the H-H distance. We keep the two phenyl rings furthest away from the forming H\(_2\) molecule fixed at all points along the scanning coordinate. The result of this constrained optimization can be seen in Fig. 5. The approximate barrier height that we obtain in this way is 0.79 eV relative to the cluster of the two PP\(_2\)-H* molecules, which serves as an upper estimate of the true barrier height for hydrogen evolution starting from two H* atoms adsorbed on nearby polymer chains. As there are no formally charged species in this process we would expect the barrier at the polymer-TEA interface to that observed at the H\(_2\)O interface. This value is significantly smaller than that predicted for hydrogen evolution from H* adsorbed on benzothiadiazole units of adjacent chains of a benzothiadiazole-thiophene co-polymer (1.32 eV) by Pati and co-workers\(^2\), using a similar computational set-up, but considerably larger than that measured experimentally for platinum (0.1 – 0.2 eV depending on the surface).\(^2\)

**Fig. 5** The energy of each geometry along the constrained optimization scan, all values computed with B3LYP/cc-pVTZ at the polymer-H\(_2\)O interface.

**Discussion**

Fig. 5 shows the B3LYP free energy profile starting from TEA and PP\(_n\), going round the cycle once, producing TEAR* and 1/2 H\(_2\), and twice, the subsequent oxidation of TEAR* to DEA and MeCHO and producing another 1/2 H\(_2\), regenerating PP\(_n\) at the end of each cycle. Fig. 5(A) and (C) are the profiles for the polymer-H\(_2\)O interface and (B) and (D) for the equivalent polymer-TEA case. As can be seen for both environments HER driven by the absorption of two photons, with the electrons provided by the overall oxidation of TEA, is thermodynamically favourable. In the case of the polymer-H\(_2\)O interface, cycles starting with TEA and TEAR* after excitation by light are both downhill. The free-energy profile for the latter case is considerably steeper, as TEAR* is a stronger oxidant than TEA (see Fig. 3A), while for the former case the top of the profile flattens for longer oligomers, as for these oligomers ET and PT are approximately iso-energetic. The CAM-B3LYP free-energy profile is provided in Fig. S3, for which the flattening is not as apparent as the ET for large oligomer lengths is still exergonic. In contrast, for the polymer-TEA interface, the first step of the cycle after excitation is uphill by ~1 eV when oxidising TEA, because ET from TEA to the polymer in TEA is endergonic (see Fig. 3B). Based on our calculations we cannot rule in or out that proton and electron transfer happens simultaneously via PCET or HAT rather than sequentially. If proton and electron transfer is coupled then that would have the largest influence for the polymer-TEA interface as it would allow the mechanism to side-step the uphill ET step, making the free-energy profile, just like for the polymer-H\(_2\)O case, all down-hill. We also have considered inverting the order of ET and PT steps, first transferring a proton to form PP-H* and TEA* from PP* and TEA, and then transferring an electron to form PP-H* and TEAR*. This was, however, considerably worse from an energetic perspective. PT is strongly exergonic in that scenario (1.46 and 3.18 eV for PP\(_2\) near the polymer-H\(_2\)O and polymer-TEA interface, respectively as predicted by B3LYP) and while ET would be more favourable (-2.79 and -4.63 eV, respectively), in this case there would even be an even greater free-energy barrier to climb over, even in the case of the polymer-H\(_2\)O interface, ruling out this order of events.

**Fig. 6** (A-B) The free energy profile for each step of the investigated catalytic cycle using PP\(_n\) and TEA as the reactants, modeled within a H\(_2\)O and TEA dielectric continuum, respectively. (C-D) The free energy profile for each step of the investigated catalytic cycle using PP\(_n\) and TEAR* as the reactants, modeled within a H\(_2\)O and TEA dielectric continuum, respectively. Data shown for $n=2$ (blue triangles), 4 (green squares), 6 (purple stars) and 7 (brown diamonds), calculated using B3LYP and provided relative to PP\(_n\) and TEA.

From a thermodynamic perspective hydrogen evolution, and 2-hole oxidation of TEA, is thus exergonic under illumination at both the polymer-H\(_2\)O and polymer-TEA interface. The uphill ET step for the case of the polymer-TEA interface, when oxidising TEA for the first of two loops around the cycle, gives rise to a thermodynamic barrier of ~ 1 eV when the ET and PT steps are sequential, that would be absent in the case of concerted PCET/HAT. Illumination is essential as in the absence of the 2-photon bias, nothing would happen as the ground state of the polymer, in contrast to its excited state counterpart, cannot extract an electron from TEA/TEAR*.

Poly(p-phenylene) and re-
lated polymers are sufficiently hydrophobic resulting in the mixtures of H$_2$O and TEA (and methanol), used experimentally as SEDs, phase-segregating in solution. Molecular dynamics simulations suggest that the environment close to the polymer is TEA-rich and as such the environment of the polymer will lie somewhere in between the two extreme cases in terms of the dielectric environment modeled here. This means, that if ET and PT are not concerted, there will likely be a free-energy barrier due to the uphill ET-step with an activation energy somewhere between the 0.79 eV barrier of the molecular hydrogen formation step. The ET step will also be competing with the ground-state back reaction (step M) where the electron is transferred back to TEA and the polymer returns to its electronic ground state, a process that due to fact that ground state adiabatic electron affinity is so much smaller than its excited state counterpart is more exergonic than proton transfer. Other side reactions such as proton transfer between TEA$^+$ and TEAR$^+$ with TEA, see Fig. 1, would also be in competition with the polymer-SED$^+$ PT steps (see Table S8). A polymer such as poly(p-phenylene) should thus be able to evolve hydrogen when illuminated but in practice the HER rates will be low due to a combination of the the barriers and the back reaction.

Next we can investigate the effect of adding a noble metal cocatalyst such as platinum or palladium nanoparticles. Assuming that also in the presence of such a co-catalyst the exciton falls apart by accepting an electron from TEA/TEAR$^+$ when on the polymer, in line with the observation with a signal in transient absorption spectroscopy that has been assigned as arising from an electron-polaron on the polymer, the effect of the co-catalyst is in this case mainly to lower the barrier for the molecular hydrogen formation step. Even in the presence of the co-catalyst the issue of the thermodynamic barrier due to the uphill ET step and the ground-state back reaction than remain. This together, combined with the fact that poly(p-phenylene) only starts absorbing light on the edge between visible and ultraviolet light might explain why even in the presence of platinum or palladium particles poly(p-phenylene) is not a very active hydrogen evolution photocatalyst.

The calculations also suggest that polymers with a more positive excited state electron affinity than poly(p-phenylene), i.e. more electron-poor polymers, probably will be more active. A positive shift in the excited state electron affinity will make ET in general more favourable, reducing the uphill nature of ET for the polymer-TEA interface (step M) where the electron is transferred back to TEA and the polymer returns to its electronic ground state, a process that due to fact that ground state adiabatic electron affinity is so much smaller than its excited state counterpart is more exergonic than proton transfer. Other side reactions such as proton transfer between TEA$^+$ and TEAR$^+$ with TEA, see Fig. 1, would also be in competition with the polymer-SED$^+$ PT steps (see Table S8). A polymer such as poly(p-phenylene) should thus be able to evolve hydrogen when illuminated but in practice the HER rates will be low due to a combination of the the barriers and the back reaction.

Finally, as already mentioned above, the mechanism proposed by Domcke and co-workers, where the exciton on the polymer dissociates homolytically rather than heterolytically, i.e. by forming two neutral rather than two oppositely charged fragments, and a hydrogen atom is transferred between the molecule that gets oxidised and the polymer, is a special case of the mechanism discussed here. This assumes that electron and proton transfer happen simultaneously and that the proton and electron by definition come from the same source. Domcke and co-workers typically only consider water oxidation but it appears trivial to extend their mechanism to instances where the source of the electron and proton is a SED, such as TEA.

5 Conclusions

A potential photocatalytic cycle for hydrogen evolution by poly(p-phenylene), a prototypical polymer photocatalyst, in the presence of triethylamine as a sacrificial electron donor has been proposed and the thermodynamics of the cycle explored via ab-initio calculations, using both density functional theory and correlated wave-function methods. As part of the cycle a series of related sites on the polymer, the aromatic -CH- atoms, have been found to be able to adsorb hydrogen atoms and to facilitate hydrogen-hydrogen bond formation and thus molecular hydrogen evolution, even if with a considerably larger barrier than for on noble-metals such as platinum.

To evolve one molecule of H$_2$ in the presence of TEA the proposed cycle has to be traversed twice. In the first loop TEA gets oxidised to TEAR$^+$, its one-electron counterpart that has lost one hydrogen atom to the polymer, while during the second loop TEAR$^+$ gets oxidised to DEA and MeCHO. In each case, TEA or TEAR$^+$ transfers one electron and one proton to the polymer resulting in an adsorbed hydrogen atom. This electron and proton transfer can take place sequentially or synchronously. Finally, two hydrogen atoms adsorbed on adjacent or the same polymer chain combine to make molecular hydrogen. For polymers particles surrounded by H$_2$O all steps are predicted to be downhill, however, for polymer particles surrounded by TEA, electron transfer from TEA to the polymer excited by the absorption of light is predicted to be uphill. As previous molecular dynamics simulations on similar types of hydrophobic polymers immersed in a mixture of H$_2$O, TEA and methanol, used experimentally as reaction solution, show that the environment around these polymers become locally enriched in TEA, with the mixture phase-segregating, under experimental conditions electron transfer from TEA is likely uphill and will form a thermodynamic barrier. As experimental transient absorption spectroscopy suggests that even in the presence of noble metal co-catalysts electron transfer and exciton dissociation still takes place on the polymer, this thermodynamic barrier is also likely there in the presence of such co-catalysts. The thermodynamic barrier combined with the fact that poly(p-phenylene) only starts absorbing light on the edge between visible and ultraviolet light probably explains why even in the presence...
of platinum or palladium particles poly(p-phenylene) is not a very active hydrogen evolution photocatalyst.

Based on the proposed cycle, polymers that have more positive excited state and ground state electron affinity values than poly(p-phenylene) are likely more active. The positive shift in the excited state electron affinity reduces how uphill the electron transfer step is in the presence of TEA and thus under experimental conditions, while shifting the ground state electron affinity to more positive values reduces how thermodynamically favourable the undesired back reaction is, where after electron transfer to the excited polymer the electron is returned to TEA and the energy of the light absorbed dissipated in the form of heat. The ground state electron affinity of the polymer probably controls how strong hydrogen atoms adsorb on the polymer and by extension likely the barrier height for the hydrogen-hydrogen bond formation.

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Conflicts of interest
There are no conflicts to declare.

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Hydrogen evolution by polymer photocatalysts; a possible photocatalytic cycle

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Supplementary Information
S1 Exploration of Excited States

As mentioned in the main text there is a disagreement between time-dependent density functional theory (TD-DFT) and correlated wave function methods in the ordering of the excited states for small oligomers of poly(p-phenylene), PP\textsubscript{n}, where \( n \) represents the oligomer length. The chemical structure of the PP oligomers and Cartesian coordinate system used is shown in Fig. S1, with even and odd oligomer lengths exhibiting \( D_2 \) and \( C_{2h} \) symmetry, respectively. Fukada and co-workers\textsuperscript{1} showed that when using the symmetry-adapted cluster configuration interaction method on PP\textsubscript{2}, \textit{in vacuo}, the lowest adiabatic excitation is of \( 1^1B_3 \) symmetry, disagreeing with TD-DFT calculations employing the PBE0 functional which instead have the optically bright \( 1^1B_1 \) as the lowest energy transition. The gas-phase excited state landscape of PP\textsubscript{2} to PP\textsubscript{8} has also been investigated previously in Ref. 2 using both RI-CC2 and TD-B3LYP. This also showed a disagreement between the ordering of the vertically excited electronic states when using B3LYP and RI-CC2 which was especially apparent for \( n = 2, 3 \) and 4. For \( n \geq 5 \) the nature of the lowest vertical transition was in agreement between both methods.

Figure S1: Chemical structure of PP\textsubscript{5} with specific numbering of non-equivalent carbon atoms and the Cartesian coordinate system used.

For each oligomer length of poly(p-phenylene) our TD-DFT calculations predict that the lowest excited state, both in terms of the adiabatic and vertical excitation, is the optically bright state. The vertical transition is described by a single particle-hole transition from the highest occupied to lowest unoccupied molecular orbital, see Table SS1 and Table SS2 for the adiabatic/vertical excited state energies at both the polymer-water and polymer-TEA interface, respectively. For SCS-ADC(2) the vertical excitation energies for each symmetry are provided in Table SS3 and Table SS4 at both the polymer-water and polymer-TEA
interface, respectively. The excited state which matches the ground state symmetry, A and A_g for odd and even oligomer lengths, respectively, has been excluded as it is expected that this state will not be (one of) the lowest energy state(s). In terms of the vertical excitation energies the picture is somewhat analogous to that in Ref. 2 in which they perform RI-CC2 calculation exclusively in vacuo. For PP_2 the 1^1B_2 and 1^1B_3 states are quasi-degenerate, with the optically bright 1^1B_1 state lying at almost 0.6 eV higher in energy. As we increase the oligomer length the bright state drastically lowers in energy when compared to 1^1B_2/1^1B_g and 1^1B_3/1^1B_u states. For PP_4 the energy spanned by the three states is small at 0.06 eV. For PP_5 and longer chain lengths the optically bright state is the lowest vertical excited state. We then turned out attention to the adiabatic excitation energy (AEE) of each symmetry for ADC(2). For PP_2–H_2O the lowest ADC(2) AEE is the 1^1B_3 state (4.588 eV) in agreement with Ref. 1 despite the inclusion of the implicit solvent environment. The higher-lying 1^1B_2 and 1^1B_1 states are located at 4.709 and 4.818 eV, respectively. This disagrees with all DFT calculations which has this as the optically bright state. However, for PP_3 and PP_4 the lowest AEE for ADC(2) corresponds to the optically bright 1^1A_u and 1^1B_1 state, respectively, now in agreement with the density functional theory equivalent calculations. Therefore, for n ≥ 5 it was sufficient to only optimise the 1^1A_u/1^1B_1. The adiabatic excited energies for each symmetry for n = 2, 3 and 4 and for the bright state for n ≥ 5 are provided in Table S3. Analogous findings were observed for for SCS-ADC(2) at the PP_n–TEA, see Table S4.
Table S1: The vertical excitation energy, oscillator strength and the adiabatic excitation energy as a function of oligomer length modeled at the PP\_n-H\_2O interface for each of the exchange-correlation functionals considered. All values are in terms of eV with the exception of the oscillator strength which has arbitrary units.

| oligomer-H\_2O | B3LYP | CAM-B3LYP | MN15 |
|----------------|-------|-----------|------|
|                | VEE   | f         | AEE  | VEE   | f         | AEE  | VEE   | f         | AEE  |
| PP\_2-H\_2O    | 4.87  | 0.57      | 4.08 | 5.24  | 0.56      | 4.32 | 5.02  | 0.59      | 4.20 |
| PP\_3-H\_2O    | 4.25  | 1.07      | 3.49 | 4.73  | 1.16      | 3.84 | 4.45  | 1.15      | 3.67 |
| PP\_4-H\_2O    | 3.92  | 1.52      | 3.21 | 4.47  | 1.72      | 3.63 | 4.16  | 1.69      | 3.42 |
| PP\_5-H\_2O    | 3.73  | 1.92      | 3.05 | 4.32  | 2.28      | 3.52 | 3.99  | 2.21      | 3.30 |
| PP\_6-H\_2O    | 3.61  | 2.30      | 2.96 | 4.23  | 2.83      | 3.48 | 3.89  | 2.72      | 3.23 |
| PP\_7-H\_2O    | 3.53  | 2.68      | 2.92 | 4.17  | 3.38      | 3.45 | 3.82  | 3.24      | 3.20 |

Table S2: The vertical excitation energy, oscillator strength and the adiabatic excitation energy as a function of oligomer length modeled at the PP\_n-TEA interface for each of the exchange-correlation functionals considered. All values are in terms of eV with the exception of the oscillator strength which has arbitrary units.

| oligomer-TEA | B3LYP | CAM-B3LYP | MN15 |
|--------------|-------|-----------|------|
|              | VEE   | f         | AEE  | VEE   | f         | AEE  | VEE   | f         | AEE  |
| PP\_2-TEA    | 4.87  | 0.58      | 4.26 | 5.25  | 0.58      | 4.50 | 5.03  | 0.61      | 4.37 |
| PP\_3-TEA    | 4.26  | 1.09      | 3.67 | 4.74  | 1.17      | 4.01 | 4.48  | 1.15      | 3.84 |
| PP\_4-TEA    | 3.94  | 1.53      | 3.37 | 4.49  | 1.74      | 3.78 | 4.18  | 1.71      | 3.58 |
| PP\_5-TEA    | 3.75  | 1.93      | 3.20 | 4.34  | 2.29      | 3.66 | 4.01  | 2.22      | 3.44 |
| PP\_6-TEA    | 3.64  | 2.30      | 3.10 | 4.26  | 2.84      | 3.60 | 3.91  | 2.73      | 3.36 |
| PP\_7-TEA    | 3.56  | 2.67      | 3.04 | 4.20  | 3.39      | 3.58 | 3.85  | 3.24      | 3.32 |
Table S3: The vertical excitation energy, oscillator strength and the adiabatic excitation energy as a function of oligomer length for each excited state symmetry, modeled at the PP$_n$-H$_2$O interface with SCS-ADC(2). All values are in terms of eV with the exception of the oscillator strength which has arbitrary units.

| oligomer-H$_2$O | $1^1B_1/1^1A_u$ | $1^1B_2/1^1B_g$ | $1^1B_3/1^1B_u$ |
|-----------------|-----------------|-----------------|-----------------|
| PP$_2$-H$_2$O   | 5.40 0.68 4.71  | 4.83 0.00 4.82  | 4.82 0.00 4.59  |
| PP$_3$-H$_2$O   | 4.85 1.36 4.19  | 4.79 0.00 4.75  | 4.63 0.00 4.42  |
| PP$_4$-H$_2$O   | 4.60 1.94 3.93  | 4.65 0.00 4.58  | 4.59 0.00 4.36  |
| PP$_5$-H$_2$O   | 4.40 2.51 3.80  | 4.61 0.00 4.54  | 4.54 0.00       |
| PP$_6$-H$_2$O   | 4.38 3.13 3.72  | 4.58 0.00 4.58  | 4.58 0.00       |
| PP$_7$-H$_2$O   | 4.28 3.73 3.69  | 4.55 0.00       |                 |

Table S4: The vertical excitation energy, oscillator strength and the adiabatic excitation energy as a function of oligomer length for each excited state symmetry, modeled at the PP$_n$-TEA interface with SCS-ADC(2). All values are in terms of eV with the exception of the oscillator strength which has arbitrary units.

| oligomer-TEA  | $1^1B_1/1^1A_u$ | $1^1B_2/1^1B_g$ | $1^1B_3/1^1B_u$ |
|---------------|-----------------|-----------------|-----------------|
| PP$_2$-TEA    | 5.41 0.69 4.71  | 4.82 0.00 4.82  | 4.82 0.00 4.60  |
| PP$_3$-TEA    | 4.88 1.37 4.20  | 4.79 0.00 4.75  | 4.64 0.00 4.43  |
| PP$_4$-TEA    | 4.65 1.95 3.94  | 4.65 0.00 4.58  | 4.61 0.00 4.38  |
| PP$_5$-TEA    | 4.48 2.52 3.81  | 4.63 0.00 4.58  | 4.58 0.00       |
| PP$_6$-TEA    | 4.41 3.10 3.74  | 4.58 0.00 4.61  | 4.61 0.00       |
| PP$_7$-TEA    | 4.34 3.66 3.71  |                 | 4.58 0.00       |
S2 Generation of Absorption Spectra

The vertical excitation energies and oscillator strengths obtained via TD-DFT and SCS-ADC(2) computations were transformed to an absorption spectrum, by simulating the effect of peak broadening. The absorption intensity (I) at each photon energy (E_p) is obtained as a sum of Gaussian functions, see Eq. 1, centred on the excitation energy of the specific state (E_i) and weighted by the corresponding oscillator strength (f_i). A σ value of 0.2 eV was used, corresponding to a full width at half maximum of 0.5 eV. The E_p was ranged from 3.00 to 7.00 eV in 0.01 eV steps. The absorption spectra for each oligomer length employing various theoretical methods are provided in Fig. S2. To observe differences in the shape of the spectra, and not solely the size of the height of the absorption peaks, each intensity is divided by the maximum intensity (I_{max.}) at a particular E_p (Γ'), and plotted with respect to E_p, see Eq. 2.

\[ I(E_p) = \sum_{i} f_i e^{-\frac{(E_p - E_i)^2}{2\sigma}} \]  
\[ \Gamma'(E_p) = \sum_{p=3.00}^{7.00} \frac{1}{I_{max.}(E)_p} (E)_p \]
Figure S2: (A,B) The simulated absorption spectra for PP$_n$ as a function of oligomer length calculated using SCS-ADC(2) at the polymer-water and polymer-TEA interface, respectively. (C,D) The simulated absorption spectra for PP$_n$ as a function of oligomer length calculated using TD-CAM-B3LYP at the polymer-water and polymer-TEA interface, respectively. (E,F) The simulated absorption spectra for PP$_n$ as a function of oligomer length calculated using TD-B3LYP at the polymer-water and polymer-TEA interface, respectively. (G,H) The simulated absorption spectra for PP$_n$ as a function of oligomer length calculated using MN15 at the polymer-water and polymer-TEA interface, respectively.
## S3 Reaction Energetics

Table S5: Various reaction energetics of interest within the catalytic cycle, modeled within a water continuum model for each of the exchange correlation functionals. All values relate to free energies and are in terms of eV. In all cases the hydrogen binding site was taken to be the C3 position.

|          | B3LYP |          |          |          |          |          |          |          |          |          |          |
|----------|-------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|          | oligomer | AEE | AIP(PP\textsubscript{n}) | AE\textsubscript{A}(PP\textsubscript{n}) | AIP(PP\textsubscript{n}) | AIP(PP\textsubscript{n}) | AFG | EBE | ET(TEA) | ET(TEA\textsuperscript{(*)}) | PT(TEA\textsuperscript{(*)}) | PT([TEA-H\textsuperscript{+}]) | PT(TEA\textsuperscript{(*)}+H\textsubscript{2}O) | H\textsubscript{2} gen. | H bind. |
| PP\textsubscript{2}-H\textsubscript{2}O | 3.93 | 6.11 | 1.83 | 5.76 | 2.18 | 4.28 | 0.35 | -0.57 | -2.82 | -0.76 | -0.75 | -0.90 | -1.26 | 0.86 |
| PP\textsubscript{2}-H\textsubscript{2}O | 3.35 | 5.82 | 2.09 | 5.44 | 2.47 | 3.74 | 0.38 | -0.25 | -2.49 | -0.53 | -0.51 | -0.66 | -1.24 | 0.88 |
| PP\textsubscript{2}-H\textsubscript{2}O | 3.08 | 6.65 | 2.24 | 5.32 | 2.61 | 3.45 | 0.37 | -0.12 | -2.37 | -0.38 | -0.36 | -0.51 | -1.24 | 0.88 |
| PP\textsubscript{2}-H\textsubscript{2}O | 2.92 | 5.61 | 2.30 | 5.22 | 2.69 | 3.31 | 0.39 | -0.03 | -2.28 | -0.32 | -0.30 | -0.46 | -1.24 | 0.89 |
| PP\textsubscript{2}-H\textsubscript{2}O | 2.84 | 5.57 | 2.34 | 5.18 | 2.73 | 3.23 | 0.39 | 0.01 | -2.23 | -0.27 | -0.25 | -0.41 | -1.25 | 0.88 |
| PP\textsubscript{2}-H\textsubscript{2}O | 2.78 | 5.55 | 2.37 | 5.14 | 2.77 | 3.19 | 0.41 | 0.05 | -2.20 | -0.24 | -0.22 | -0.38 | -1.25 | 0.87 |

|          | CAM-B3LYP |          |          |          |          |          |          |          |          |          |          |          |
|----------|-----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|          | oligomer | AEE | AIP(PP\textsubscript{n}) | AE\textsubscript{A}(PP\textsubscript{n}) | AIP(PP\textsubscript{n}) | AIP(PP\textsubscript{n}) | AFG | EBE | ET(TEA) | ET(TEA\textsuperscript{(*)}) | PT(TEA\textsuperscript{(*)}) | PT([TEA-H\textsuperscript{+}]) | PT(TEA\textsuperscript{(*)}+H\textsubscript{2}O) | H\textsubscript{2} gen. | H bind. |
| PP\textsubscript{2}-H\textsubscript{2}O | 4.18 | 6.26 | 1.72 | 5.90 | 2.08 | 4.55 | 0.36 | -0.65 | -2.93 | -0.92 | -0.86 | -1.01 | -1.21 | 0.88 |
| PP\textsubscript{2}-H\textsubscript{2}O | 3.70 | 6.03 | 1.93 | 5.63 | 2.34 | 4.10 | 0.40 | -0.38 | -2.67 | -0.73 | -0.66 | -0.82 | -1.19 | 0.91 |
| PP\textsubscript{2}-H\textsubscript{2}O | 3.50 | 5.92 | 2.02 | 5.52 | 2.42 | 3.90 | 0.40 | -0.27 | -2.56 | -0.64 | -0.57 | -0.73 | -1.19 | 0.91 |
| PP\textsubscript{2}-H\textsubscript{2}O | 3.40 | 5.89 | 2.08 | 5.48 | 2.49 | 3.81 | 0.41 | -0.22 | -2.51 | -0.59 | -0.52 | -0.68 | -1.19 | 0.91 |
| PP\textsubscript{2}-H\textsubscript{2}O | 3.34 | 5.86 | 2.10 | 5.45 | 2.52 | 3.76 | 0.42 | -0.20 | -2.48 | -0.55 | -0.49 | -0.64 | -1.20 | 0.90 |
| PP\textsubscript{2}-H\textsubscript{2}O | 3.32 | 5.84 | 2.12 | 5.45 | 2.51 | 3.71 | 0.39 | -0.19 | -2.48 | -0.54 | -0.47 | -0.62 | -1.20 | 0.90 |

|          | MN5 |          |          |          |          |          |          |          |          |          |          |          |
|----------|-----|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|          | oligomer | AEE | AIP(PP\textsubscript{n}) | AE\textsubscript{A}(PP\textsubscript{n}) | AIP(PP\textsubscript{n}) | AIP(PP\textsubscript{n}) | AFG | EBE | ET(TEA) | ET(TEA\textsuperscript{(*)}) | PT(TEA\textsuperscript{(*)}) | PT([TEA-H\textsuperscript{+}]) | PT(TEA\textsuperscript{(*)}+H\textsubscript{2}O) | H\textsubscript{2} gen. | H bind. |
| PP\textsubscript{2}-H\textsubscript{2}O | 4.05 | 6.26 | 1.77 | 5.82 | 2.21 | 4.49 | 0.44 | -0.47 | -2.91 | -0.89 | -0.82 | -0.82 | -1.27 | 0.81 |
| PP\textsubscript{2}-H\textsubscript{2}O | 3.53 | 6.01 | 2.03 | 5.56 | 2.48 | 3.99 | 0.45 | -0.20 | -2.64 | -0.63 | -0.56 | -0.56 | -1.27 | 0.81 |
| PP\textsubscript{2}-H\textsubscript{2}O | 3.30 | 5.90 | 2.18 | 5.48 | 2.60 | 3.72 | 0.42 | -0.13 | -2.57 | -0.47 | -0.41 | -0.41 | -1.27 | 0.81 |
| PP\textsubscript{2}-H\textsubscript{2}O | 3.18 | 5.85 | 2.21 | 5.39 | 2.67 | 3.64 | 0.46 | -0.04 | -2.47 | -0.45 | -0.38 | -0.38 | -1.26 | 0.81 |
| PP\textsubscript{2}-H\textsubscript{2}O | 3.11 | 5.83 | 2.24 | 5.35 | 2.72 | 3.59 | 0.48 | 0.00 | -2.43 | -0.41 | -0.34 | -0.34 | -1.27 | 0.80 |
| PP\textsubscript{2}-H\textsubscript{2}O | 3.08 | 5.81 | 2.27 | 5.35 | 2.73 | 3.53 | 0.45 | 0.00 | -2.44 | -0.37 | -0.31 | -0.31 | -1.27 | 0.80 |
Table S6: Various reaction energetics of interest within the catalytic cycle, modeled within a TEA continuum model for each of the exchange correlation functionals. All values relate to free energies and are in terms of eV. In all cases the hydrogen binding site was taken to be the C3 position.

| oligomer | B3LYP | CAM-B3LYP | MN15 |
|----------|-------|-----------|------|
|          | AEE   | AIP(PP_n) | AEA(PP_n) | AEEA(PP_n) | AIP(PP_n) | AFG | EBE | ET(TEA) | ET(TEAR*) | PT(TEA*) | PT([TEA-H]^+) | PT(TEA*+H_2O) | H_2 gen. | H bind. |
| PP_2-TEA | 4.06  | 6.79      | 0.98    | 5.04 | 2.73 | 5.81 | 1.75 | 1.02 | −1.25 | −2.47 | −2.47 | −2.59 | −1.26 | 0.86 |
| PP_3-TEA | 3.52  | 6.38      | 1.38    | 4.90 | 2.86 | 5.00 | 1.48 | 1.15 | −1.11 | −2.09 | −2.09 | −2.21 | −1.24 | 0.88 |
| PP_4-TEA | 3.24  | 6.18      | 1.61    | 4.85 | 2.94 | 4.57 | 1.33 | 1.20 | −1.07 | −1.86 | −1.87 | −1.99 | −1.23 | 0.89 |
| PP_5-TEA | 3.05  | 6.07      | 1.69    | 4.74 | 3.02 | 4.38 | 1.33 | 1.31 | −0.96 | −1.78 | −1.79 | −1.90 | −1.24 | 0.88 |
| PP_7-TEA | 2.97  | 6.00      | 1.76    | 4.72 | 3.03 | 4.24 | 1.28 | 1.33 | −0.94 | −1.71 | −1.71 | −1.83 | −1.24 | 0.8 |
| PP_9-TEA | 2.91  | 5.93      | 1.78    | 4.69 | 3.02 | 4.15 | 1.24 | 1.36 | −0.90 | −1.68 | −1.68 | −1.80 | −1.25 | 0.88 |
Table S7: The free energy of PP<sub>n</sub>-H<sub>2</sub>O for each non-equivalent carbon binding site, all values are given with respect to C3. For comparison we include equivalent data at the PP<sub>2</sub>-TEA interface.

|        | B3LYP | CAM-B3LYP |
|--------|-------|-----------|
| oligomer | C1    | C2    | C3    | C4    | C5    | C6    | C7    | C8    | C9    | C10   |
| PP<sub>2</sub>-H<sub>2</sub>O | 0.01  | 0.15  | 0.00  | 0.27  |       |       |       |       |       |       |
| PP<sub>3</sub>-H<sub>2</sub>O | 0.00  | 0.17  | 0.00  | 0.29  | 0.17  | 0.03  |       |       |       |       |
| PP<sub>4</sub>-H<sub>2</sub>O | 0.00  | 0.17  | 0.00  | 0.30  | 0.15  | 0.03  | 0.02  | 0.18  |       |       |
| PP<sub>5</sub>-H<sub>2</sub>O | 0.01  | 0.18  | 0.00  | 0.30  | 0.14  | 0.03  | 0.02  | 0.17  | 0.16  | 0.02  |
| PP<sub>2</sub>-TEA    | 0.01  | 0.14  | 0.00  | 0.27  |       |       |       |       |       |       |
| PP<sub>3</sub>-H<sub>2</sub>O | 0.00  | 0.12  | 0.00  | 0.24  |       |       |       |       |       |       |
| PP<sub>4</sub>-H<sub>2</sub>O | 0.01  | 0.14  | 0.00  | 0.26  | 0.16  | 0.03  |       |       |       |       |
| PP<sub>5</sub>-H<sub>2</sub>O | 0.01  | 0.14  | 0.00  | 0.27  | 0.15  | 0.03  | 0.02  | 0.16  |       |       |
| PP<sub>2</sub>-TEA    | 0.00  | 0.11  | 0.00  | 0.23  |       |       |       |       |       |       |
Table S8: The free energy difference for competing electron transfer reactions, step J and step K, for each of the exchange-correlation functionals used in the presence of an H$_2$O and TEA dielectric continuum.

|           | H$_2$O                  |                  |                  |                  |
|-----------|-------------------------|------------------|------------------|------------------|
| Reaction  | GD3-B3LYP               | GD3-CAM-B3LYP    | MN15             |
| Step J    | $-$0.02                 | $-$0.07          | 0.07             |
| Step K    | $-$0.16                 | $-$0.16          | 0.00             |

|           | TEA                     |                  |                  |                  |
| Reaction  | GD3-B3LYP               | GD3-CAM-B3LYP    | MN15             |
| Step J    | 0.00                    | $-$0.05          | $-$0.04          |
| Step K    | $-$0.12                 | $-$0.13          | 0.02             |
Figure S3: (A-B) The free energy profile for each step of the investigated catalytic cycle using PP$_n$ and TEA as the reactants, modeled within a H$_2$O and TEA dielectric continuum, respectively. (C-D) The free energy profile for each step of the investigated catalytic cycle using PP$_n$ and TEAR$^\bullet$ as the reactants, modeled within a H$_2$O and TEA dielectric continuum, respectively. Data shown for $n = 2$ (blue triangles), 4 (green squares), 6 (purple stars) and 7 (brown diamonds), calculated using CAM-B3LYP and provided relative to PP$_n$ and TEA.

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