

## Exploration of the Photocatalytic Cycle for Sacrificial Hydrogen Evolution by Conjugated Polymers Containing Heteroatoms

Andrew W. Prentice and Martijn A. Zwijnenburg\*

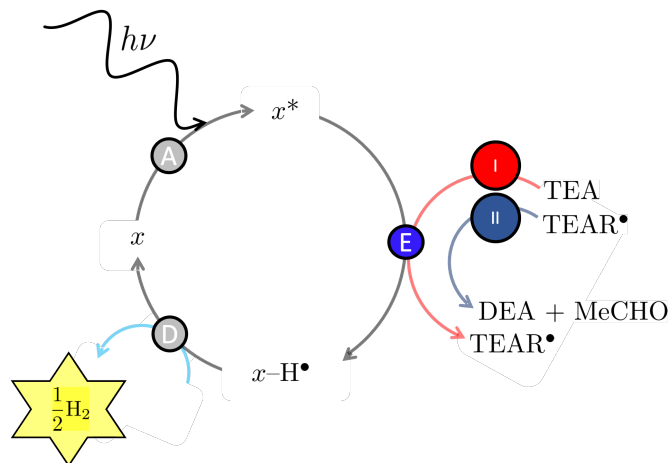
Department of Chemistry, University College London, London, WC1H 0AJ, United Kingdom.

E-mail: [m.zwijnenburg@ucl.ac.uk](mailto:m.zwijnenburg@ucl.ac.uk)

### Supplementary Information

For the fine details relating to the calculations, we direct the readers' attention to Section 2 of the main text. All D3-B3LYP/cc-pVTZ optimized geometries, in both water and triethylamine (TEA), used to construct the reaction profile and of the different hydrogen adsorption sites are available in the associated ZIP file (*geometries.zip*). The nomenclature of these files is as follows *a\_b\_c*. The specific polymer is given by *a*, with *b* describing either the charge state of the system (ground state ( $S_0$ ), lowest-energy excited state ( $S_1$ ), one-electron reduced (e) and one-electron oxidized (h)) or the specific hydrogen adsorption site. For the latter we also indicated the specific sub-unit the hydrogen is adsorbed onto. Finally, *c* is either water or TEA describing the specific dielectric continuum used in the calculations. In addition, we provide all of the structures used to construct the reaction profiles.

## S1 Synchronous Proton and Electron Transfer Cycle



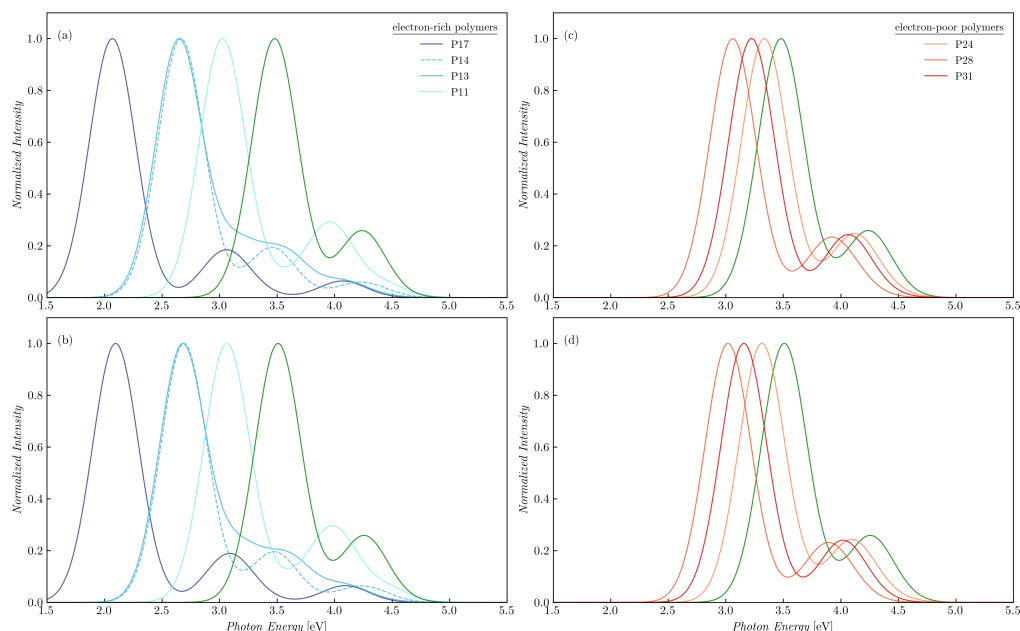
**Figure S1:** Proposed catalytic cycle for the case of synchronous proton and electron transfer.

## S1 Generation of Absorption Spectra

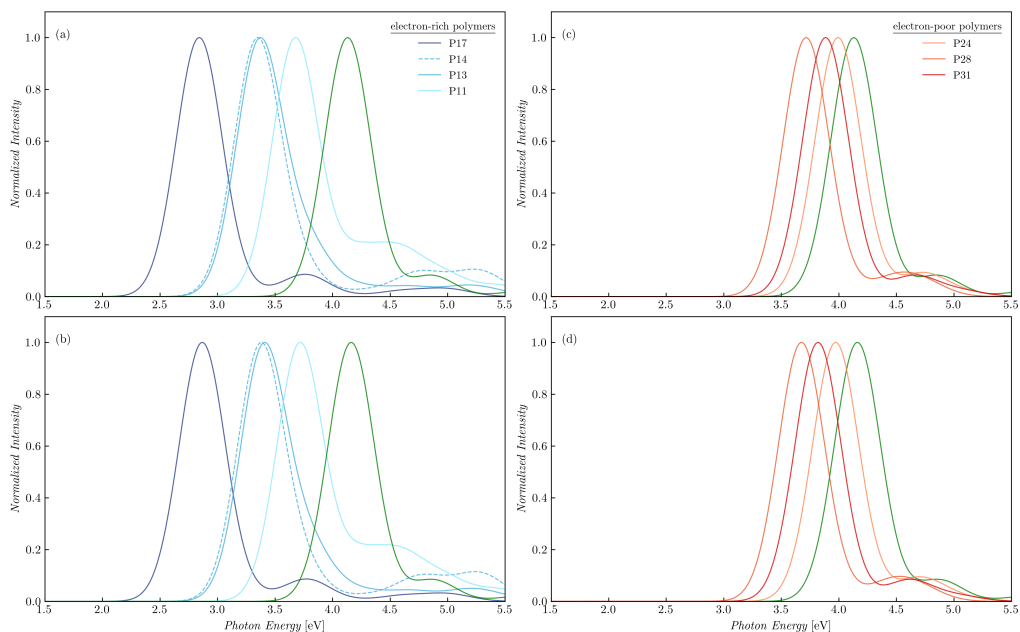
The vertical excitation energies (VEE) and oscillator strengths ( $f$ ) predicted by time-dependent density functional theory were used to generate an absorption spectrum, simulating the effect of peak broadening. In each calculation the 15 lowest-energy singlet states were computed. The spectral intensity at each photon energy ( $E_p$ ) is obtained as a sum of Gaussian functions, see equation 1, each of which is centered on the excitation energy of the specific state ( $VEE_j$ ) and weighted by the corresponding oscillator strength ( $f_j$ ). A  $\sigma$  value 0.2 eV was used, corresponding to a full width at half maximum of 0.5 eV. The  $E_p$  values considered ranged from 1.5 to 5.5 eV in 0.01 eV increments. The simulated absorption spectra of the oligomers in a water and TEA dielectric continuum are provided in figures S2 (D3-B3LYP/cc-pVTZ) and S3 (D3-CAM-B3LYP/cc-pVTZ), while figure S4 compares the spectra of the crosslinked and non-crosslinked oligomers. To observe

differences in the shape of the spectra, and not necessarily the height of the bright-absorption band, the spectral intensity of each point is divided by the maximum spectral intensity across the range of 1.5 to 5.5 eV.

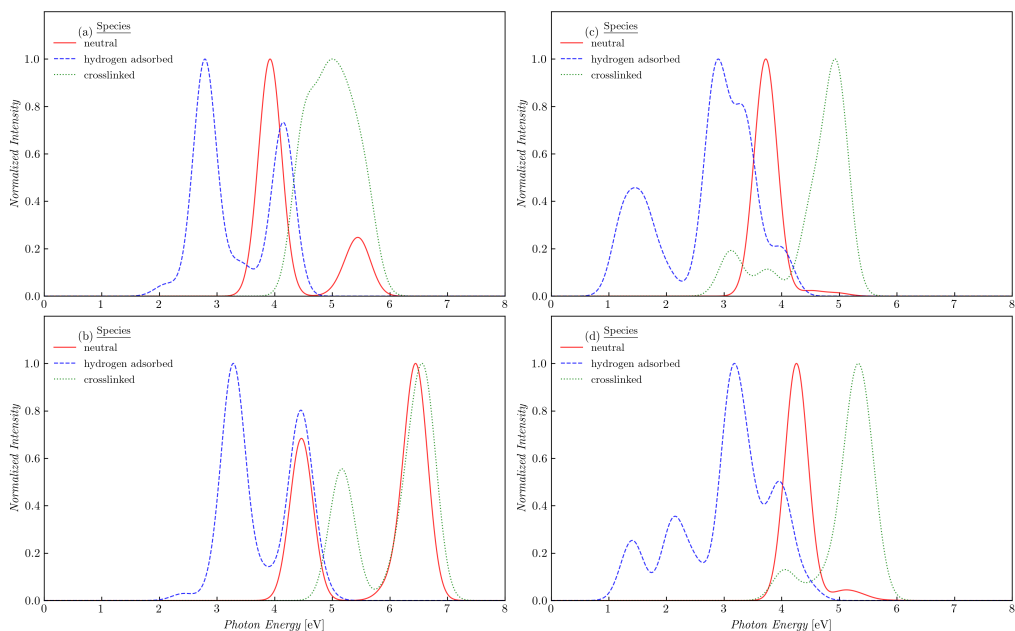
$$I(E_p) = \sum_{j=1}^{15} f_j e^{\left[ -\frac{1}{2} \left( \frac{E_p - VEE_j}{\sigma} \right)^2 \right]} \quad \text{Equation 1}$$



**Figure S2:** Predicted absorption spectra for electron-rich materials within a dielectric continuum representing water (a) and triethylamine (b). Predicted absorption spectra for electron-poor materials within a dielectric continuum representing water (c) and triethylamine (d). For reference the P1 spectrum was added to each subplot (green). All values predicted using D3-B3LYP/cc-pVTZ and all spectra containing 15 excited states.



**Figure S3:** Predicted absorption spectra for electron-rich materials within a dielectric continuum representing water (a) and triethylamine (b). Predicted absorption spectra for electron-poor materials within a dielectric continuum representing water (c) and triethylamine (d). For reference the P1 spectrum was added to each subplot (green). All values predicted using D3-CAM-B3LYP/cc-pVTZ and all spectra containing 15 excited states.



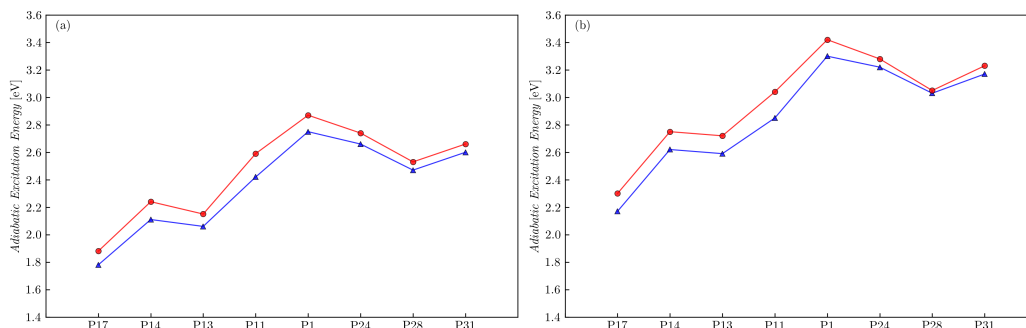
**Figure S4:** Predicted absorption spectra for the crosslinked P1 dimer (green dotted line) within a dielectric continuum representing water predicted using D3-B3LYP/cc-pVTZ (a) and D3-CAM-B3LYP/cc-pVTZ (b). For comparison we include the spectra of the neutral tetramer (red solid line) and the neutral tetramer with a single hydrogen adsorbed (blue dashed line). Predicted absorption spectra for the crosslinked P31 dimer (green dotted line) within a dielectric continuum representing water predicted using D3-B3LYP/cc-pVTZ (c) and D3-CAM-B3LYP/cc-pVTZ (d). For comparison we include the spectra of the neutral tetramer (red solid line) and the neutral tetramer with a single hydrogen adsorbed (blue dashed line).

## S2 Adiabatic Excitation Energy

The adiabatic excitation energy (AEE), see equation 2, is defined as the energy (E) difference between the lowest-energy singlet excited state after geometry relaxation ( $S_1$ ) and the ground state ( $S_0$ ). The AEE of the polymers in both dielectric environments are provided in figure S5, where sub-plot (a) shows results predicted using D3-B3LYP/cc-pVTZ and (b) using D3-CAM-B3LYP/cc-pVTZ.

$$AEE = E(S_1) - E(S_0)$$

Equation 2



**Figure S5:** The predicted adiabatic excitation energy for each polymer within a dielectric continuum representing water (blue triangles) and triethylamine (red circles). All values predicted using D3-B3LYP/cc-pVTZ(a) or D3-CAM-B3LYP/cc-pVTZ (b).

## S3 Ionization Potential and Electron Affinity

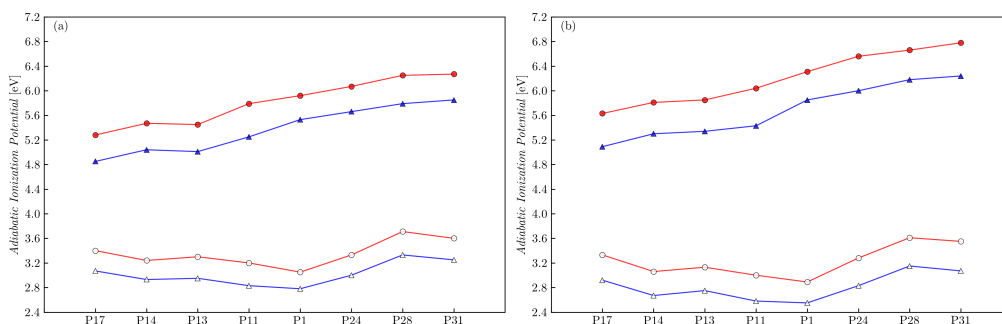
The ionization potential (IP), see equation 3, is defined as the energy difference between one-electron oxidized species ( $h^+$ ) and  $S_0$ . The excited-state IP ( $IP^*$ ) is similar, however,  $S_0$  is replaced with  $S_1$ . The IP and  $IP^*$  of the polymers in both dielectric environments are provided in Figure S6, where sub-plot (a) shows results predicted using D3-B3LYP/cc-pVTZ and (b) using D3-CAM-B3LYP/cc-pVTZ.

$$IP = E(h^+) - E(S_0)$$

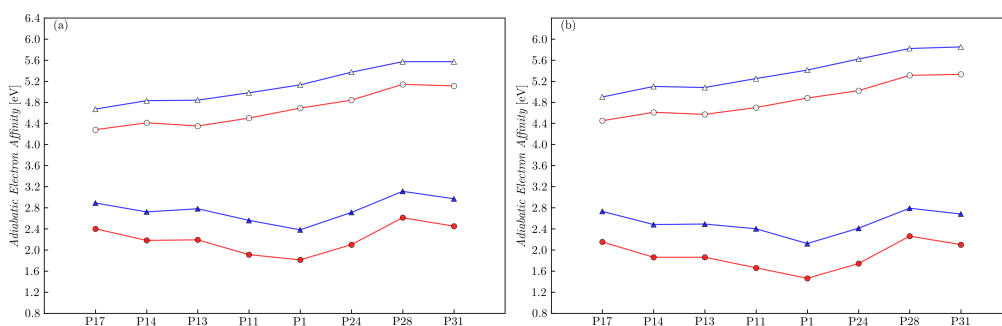
Equation 3

The electron affinity (EA), see equation 4, is defined as the energy difference between  $S_0$  and the one-electron reduced species ( $e^-$ ). The excited-state EA ( $EA^*$ ) is once again obtained by replacing  $S_0$  with  $S_1$ . The EA and  $EA^*$  of the polymers in both dielectric environments are provided in figure S7, where sub-plot (a) shows results predicted using D3-B3LYP/cc-pVTZ and (b) using D3-CAM-B3LYP/cc-pVTZ.

$$EA = E(S_0) - E(e^-) \quad \text{Equation 4}$$



**Figure S6:** The predicted ground (filled) and excited-state (hollow) ionization potential for each polymer within a dielectric continuum representing water (blue triangles) and triethylamine (red circles). All values predicted using D3-B3LYP/cc-pVTZ (a) or D3-CAM-B3LYP/cc-pVTZ (b).



**Figure S7:** The predicted ground (filled) and excited-state (hollow) electron affinity for each polymer within a dielectric continuum representing water (blue triangles) and triethylamine (red circles). All values predicted using D3-B3LYP/cc-pVTZ (a) or D3-CAM-B3LYP/cc-pVTZ (b).

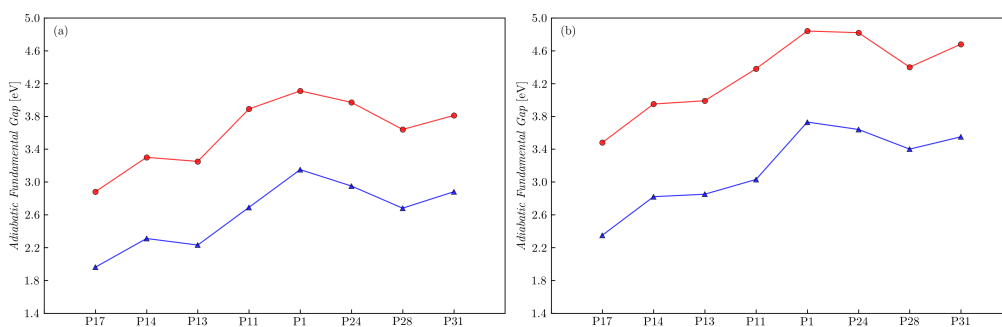
### S3 Adiabatic Fundamental Gap and Adiabatic Exciton Binding Energy

The adiabatic fundamental gap (AFG), see equation 5, is defined as the energy difference between IP and EA. The AFG of the polymers in both dielectric environments are provided in figure S8, where sub-plot (a) shows results predicted using D3-B3LYP/cc-pVTZ and (b) using D3-CAM-B3LYP/cc-pVTZ.

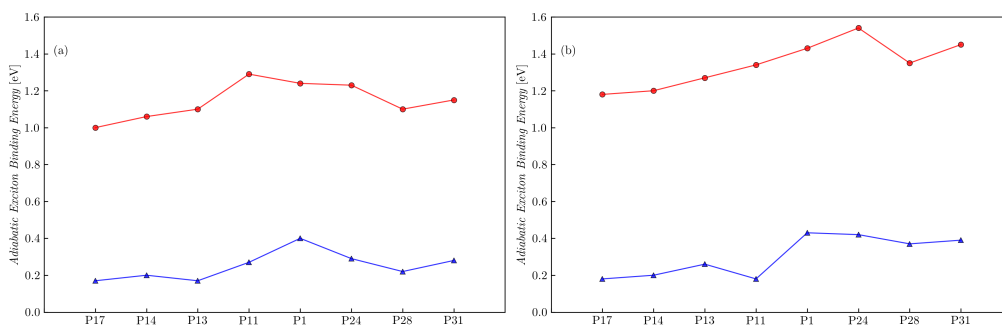
$$\text{AFG} = \text{IP} - \text{EA} \quad \text{Equation 5}$$

The adiabatic exciton binding energy (AEBE), see equation 6 is defined as the energy difference between AFG and AEE. The AEBE of the polymers in both dielectric environments are provided in figure S9, where sub-plot (a) shows data predicted using D3-B3LYP/cc-pVTZ and (b) using D3-CAM-B3LYP/cc-pVTZ.

$$\text{AEBE} = \text{FG} - \text{AEE} \quad \text{Equation 6}$$

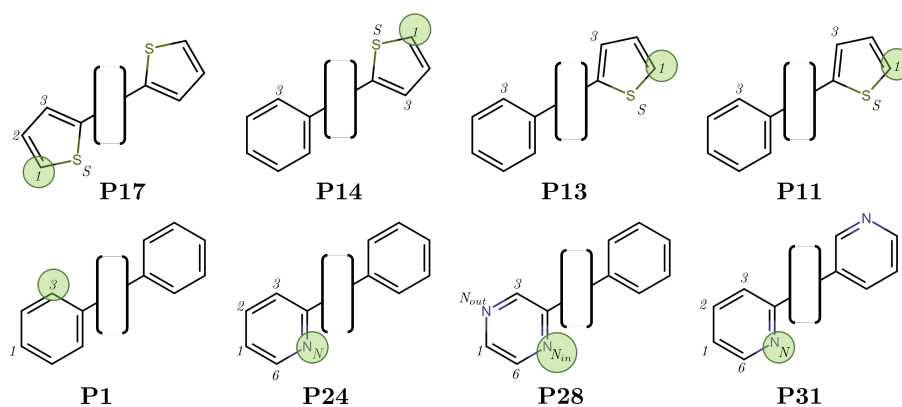


**Figure S8:** The predicted adiabatic fundamental gap for each polymer within a dielectric continuum representing water (blue triangles) and triethylamine (red circles). All values predicted using D3-B3LYP/cc-pVTZ(a) or D3-CAM-B3LYP/cc-pVTZ (b).



**Figure S9:** The predicted adiabatic exciton binding energy for each polymer within a dielectric continuum representing water (blue triangles) and triethylamine (red circles). All values predicted using D3-B3LYP/cc-pVTZ(a) or D3-CAM-B3LYP/cc-pVTZ (b).

## S5 Hydrogen Absorption Sites



**Figure S10:** Labels of the hydrogen absorption sites considered herein, with the lowest-energy site shown with a green circle. Only the outer units of the polymer are illustrated.



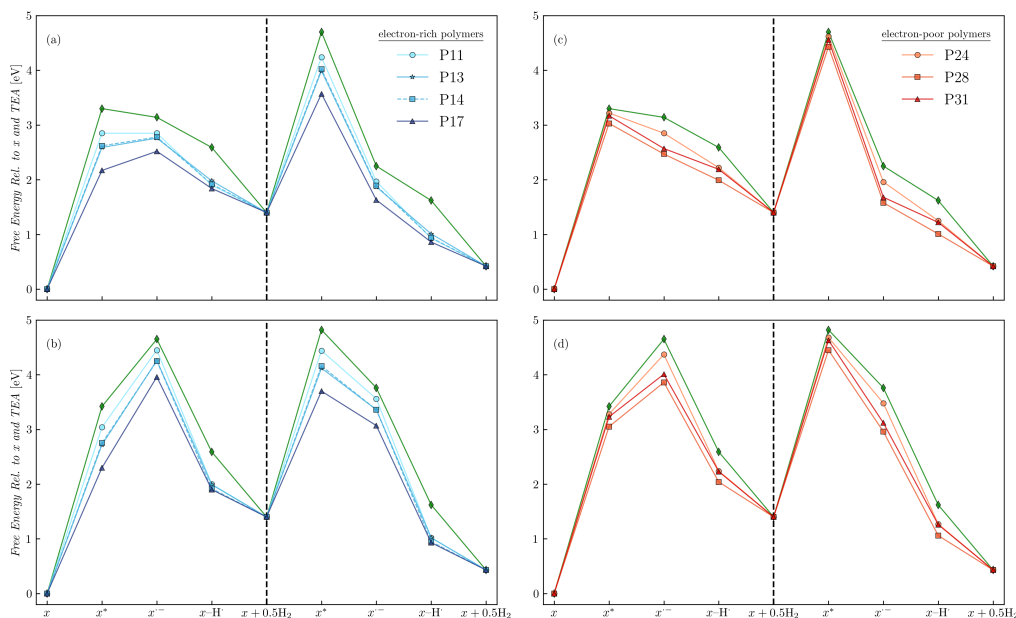
**Table S1:** Free energy difference for the different hydrogen absorption sites of each polymer of interest within a dielectric continuum representing water. All free energy differences are in terms of eV and are provided relative to the lowest energy site for the specific polymer. For an illustration of the hydrogen sites please see Figure S8.

x-water	Phenyl		Thiophene				Pyridine					Diazine				
D3-B3LYP	C <sub>1</sub>	C <sub>3</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	S	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	N	C <sub>6</sub>	C <sub>1</sub>	N <sub>in</sub>	C <sub>3</sub>	N <sub>out</sub>	C <sub>6</sub>
P17	-	-	0.00	0.78	0.28	1.91	-	-	-	-	-	-	-	-	-	-
P14	-	0.66	0.00	-	0.28	1.89	-	-	-	-	-	-	-	-	-	-
P13	-	0.52	0.00	-	0.33	1.87	-	-	-	-	-	-	-	-	-	-
P11	-	0.58	0.00	-	0.35	1.87	-	-	-	-	-	-	-	-	-	-
P1	0.00	0.00	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P24	-	-	-	-	-	-	0.33	0.60	0.36	0.00	0.58	-	-	-	-	-
P28	-	-	-	-	-	-	-	-	-	-	-	0.48	0.00	0.51	0.07	0.70
P31	-	-	-	-	-	-	0.42	0.70	0.45	0.00	0.69	-	-	-	-	-
D3-CAM-B3LYP																
P17	-	-	0.00	0.76	0.26	2.04	-	-	-	-	-	-	-	-	-	-
P14	-	0.67	0.00	-	0.27	2.02	-	-	-	-	-	-	-	-	-	-
P13	-	0.50	0.00	-	0.31	1.96	-	-	-	-	-	-	-	-	-	-
P11	-	0.61	0.00	-	0.35	2.00	-	-	-	-	-	-	-	-	-	-
P1	0.00	0.00	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P24	-	-	-	-	-	-	0.28	0.54	0.31	0.00	0.52	-	-	-	-	-
P28	-	-	-	-	-	-	-	-	-	-	-	0.45	0.00	0.49	0.02	0.64
P31	-	-	-	-	-	-	0.32	0.58	0.35	0.00	0.57	-	-	-	-	-

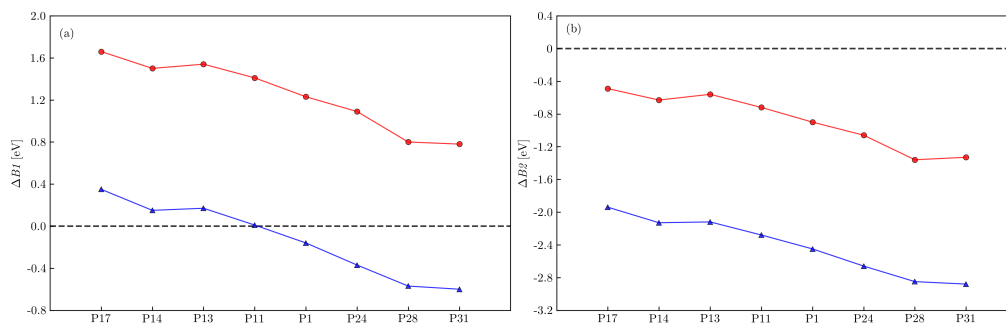
**Table S2:** Free energy difference for the different hydrogen absorption sites of each polymer of interest within a dielectric continuum representing triethylamine. All free energy differences are in terms of eV and are provided relative to the lowest energy site for the specific polymer. For an illustration of the hydrogen sites please see Figure S8.

<i>x</i> -TEA	Phenyl		Thiophene				Pyridine					Diazine				
D3-B3LYP	C <sub>1</sub>	C <sub>3</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	S	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	N	C <sub>6</sub>	C <sub>1</sub>	N <sub>in</sub>	C <sub>3</sub>	N <sub>out</sub>	C <sub>6</sub>
P17	-	-	0.00	0.78	0.27	1.93	-	-	-	-	-	-	-	-	-	-
P14	-	0.66	0.00	-	0.29	1.92	-	-	-	-	-	-	-	-	-	-
P13	-	0.50	0.00	-	0.32	1.88	-	-	-	-	-	-	-	-	-	-
P11	-	0.59	0.00	-	0.38	1.90	-	-	-	-	-	-	-	-	-	-
P1	0.01	0.00	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P24	-	-	-	-	-	-	0.31	0.58	0.33	0.00	0.55	-	-	-	-	-
P28	-	-	-	-	-	-	-	-	-	-	-	0.44	0.00	0.45	0.06	0.66
P31	-	-	-	-	-	-	0.33	0.58	0.38	0.00	0.57	-	-	-	-	-
D3-CAM-B3LYP																
P17	-	-	0.00	0.72	0.26	2.04	-	-	-	-	-	-	-	-	-	-
P14	-	0.67	0.00	-	0.26	2.03	-	-	-	-	-	-	-	-	-	-
P13	-	0.50	0.00	-	0.32	1.73	-	-	-	-	-	-	-	-	-	-
P11	-	0.62	0.00	-	0.33	1.98	-	-	-	-	-	-	-	-	-	-
P1	0.01	0.00	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P24	-	-	-	-	-	-	0.27	0.52	0.29	0.00	0.48	-	-	-	-	-
P28	-	-	-	-	-	-	-	-	-	-	-	0.39	0.00	0.41	0.02	0.59
P31	-	-	-	-	-	-	0.28	0.52	0.31	0.00	0.50	-	-	-	-	-

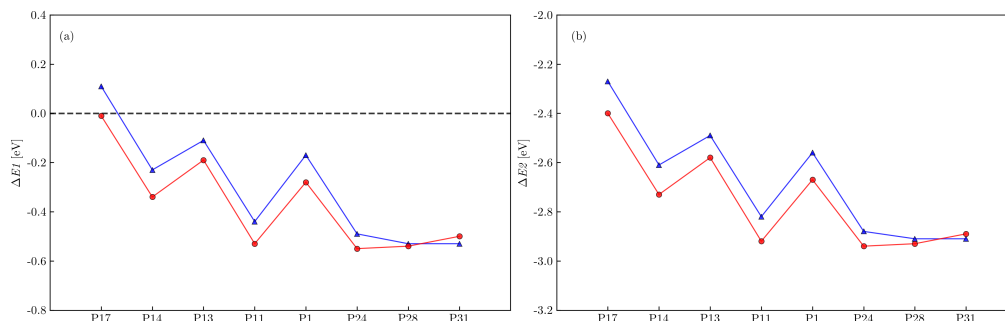
## S6 Free Energy Profiles



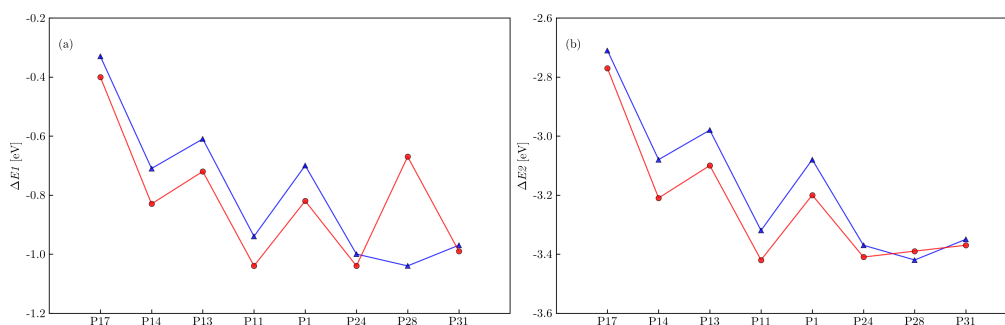
**Figure S11:** The predicted free energy profiles for sub-cycle I and II, left and right of the dashed line respectively, for oligomers of electron-rich materials immersed in water (a) and triethylamine (b), and for oligomers of electron-poor materials immersed in water (c) and triethylamine (d). In all panels P1 has been added for reference (green diamonds). All values predicted using D3-CAM-B3LYP/cc-pVTZ and are relative to the neutral polymer and triethylamine. The x-axis labels omit any reference to triethylamine or the degradation products.



**Figure S12:** The predicted free energy difference for electron transfer to the photoexcited polymer from triethylamine (a) and dehydrogenated triethylamine (b) within a dielectric continuum representing water (blue triangles) and triethylamine (red circles). All values predicted using D3-CAM-B3LYP/cc-pVTZ.



**Figure S13:** The predicted free energy difference for hydrogen atom transfer to the photoexcited polymer from triethylamine (a) and dehydrogenated triethylamine (b) within a dielectric continuum representing water (blue triangles) and triethylamine (red circles). All values predicted using D3-B3LYP/cc-pVTZ. The lowest-energy hydrogen absorption site was used, see Figure S8 and Tables S1 and S2 for the illustration and free energies of these sites, respectively.



**Figure S14:** The predicted free energy difference for hydrogen atom transfer to the photoexcited polymer from triethylamine (a) and dehydrogenated triethylamine (b) within a dielectric continuum representing water (blue triangles) and triethylamine (red circles). All values predicted using D3-CAM-B3LYP/cc-pVTZ. The lowest-energy hydrogen absorption site was used, see Figure S8 and Tables S1 and S2 for the illustration and free energies of these sites, respectively.

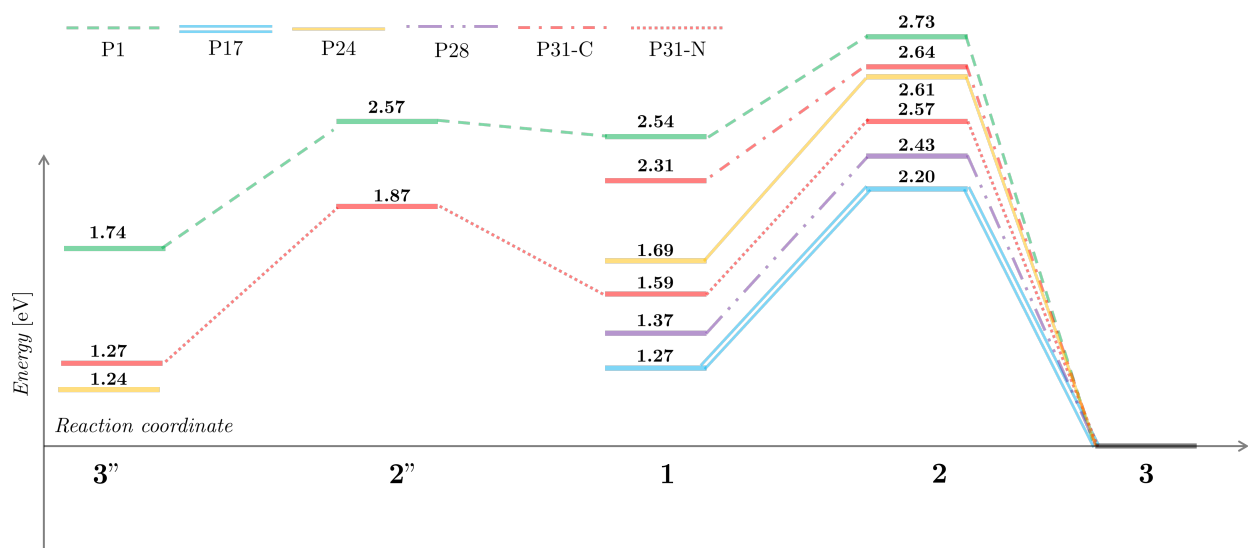
**Table 3:** Predicted back reaction energetics for polymers of interest within a dielectric continuum representing water. All energy differences are in terms of eV and pertain to free-energy differences

x-water	GD3-B3LYP		GD3-CAM-B3LYP	
	$x^{\bullet-} + \text{TEA}^{\bullet+} \rightarrow x + \text{TEA}$	$x^{\bullet-} + \text{TEAR}^+ \rightarrow x + \text{TEAR}^{\bullet}$	$x^{\bullet-} + \text{TEA}^{\bullet+} \rightarrow x + \text{TEA}$	$x^{\bullet-} + \text{TEAR}^+ \rightarrow x + \text{TEAR}^{\bullet}$
P17	-2.30	-0.06	-2.52	-0.23
P14	-2.47	-0.23	-2.78	-0.49
P13	-2.41	-0.17	-2.76	-0.48
P11	-2.64	-0.39	-2.85	-0.57
P1	-2.81	-0.57	-3.14	-0.85
P24	-2.49	-0.24	-2.85	-0.56
P28	-2.09	0.16	-2.47	-0.18
P31	-2.22	0.02	-2.57	-0.28

**Table 4:** Predicted back reaction energetics for polymers of interest within a dielectric continuum representing triethylamine. All energy differences are in terms of eV and pertain to free-energy differences.

x-TEA	GD3-B3LYP		GD3-CAM-B3LYP	
	$x^{\bullet-} + \text{TEA}^{\bullet+} \rightarrow x + \text{TEA}$	$x^{\bullet-} + \text{TEAR}^+ \rightarrow x + \text{TEAR}^{\bullet}$	$x^{\bullet-} + \text{TEA}^{\bullet+} \rightarrow x + \text{TEA}$	$x^{\bullet-} + \text{TEAR}^+ \rightarrow x + \text{TEAR}^{\bullet}$
P17	-3.65	-1.38	-3.96	-1.67
P14	-3.88	-1.61	-4.25	-1.96
P13	-3.86	-1.59	-4.26	-1.96
P11	-4.14	-1.88	-4.45	-2.16
P1	-4.24	-1.97	-4.65	-2.36
P24	-3.95	-1.68	-4.37	-2.08
P28	-3.44	-1.17	-3.86	-1.56
P31	-3.60	-1.33	-4.01	-1.72

## S7 Transition Barriers.



**Figure S15:** The predicted free energy reaction profile of hydrogen formation (structure **1-3**) for P17 (cyan double line), P1 (green dashed line), P24 (yellow solid line), P28 (purple dashed double dotted line) and P31 immersed in water, starting in all cases from the most stable hydrogen adsorption site. For P31 we include two different adsorption sites either position  $C_1$  or N. The competing crosslinked reaction pathway (structure **1-3''**) has also been provided for P1-water and P31-water. All values predicted using D3-B3LYP/cc-pVTZ, given in terms of eV and relative to two neutral polymers and molecular hydrogen, structure **3** (in contrast to figure 5 in the main text that shows the reaction profiles relative to structure **1**).

## S8 Free-Energy Raw Data

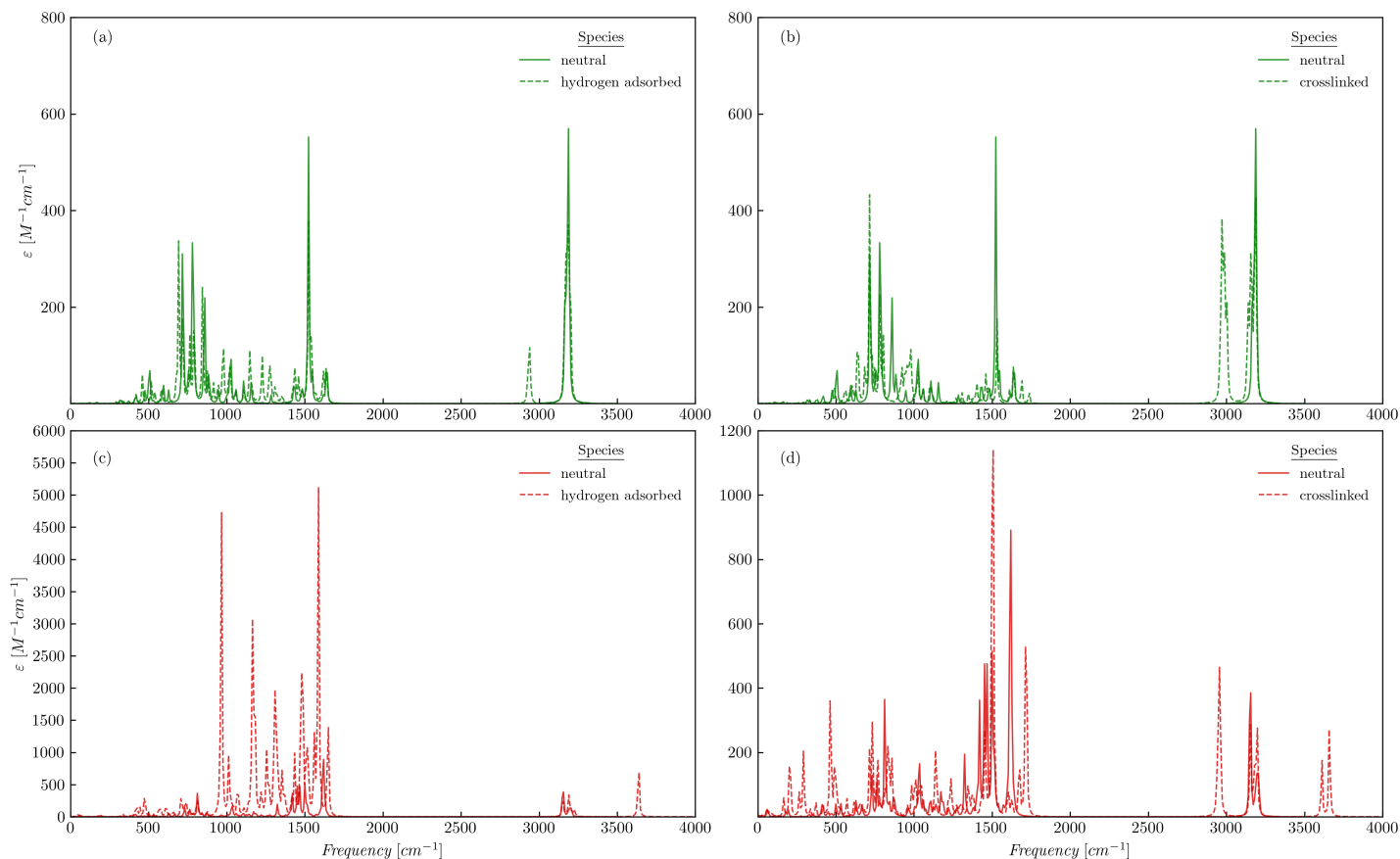
**Table S5:** Predicted energetics for polymers of interest within a dielectric continuum representing water. All energy differences are in terms of eV and pertain to free-energy differences except for VEE which is in terms of electronic energies. The lowest-energy hydrogen absorption site was used, see Figure S8 and Table S1 for the illustration and free energies of these sites, respectively.

x-water																
D3-B3LYP	VEE( <i>f</i> )	AIP	AEA	AIP*	AEA*	AFG	AEBE	AEE	$\Delta B1$	$\Delta B2$	$\Delta C1$	$\Delta C2$	$\Delta E1$	$\Delta E2$	$\Delta D$	H bind
P17	2.07(2.78)	4.85	2.89	3.07	4.67	1.96	0.17	1.78	0.52	-1.73	-0.41	-0.55	0.11	-2.27	-0.55	1.57
P14	2.66(2.73)	5.04	2.72	2.93	4.83	2.31	0.20	2.11	0.36	-1.88	-0.59	-0.73	-0.23	-2.61	-0.54	1.58
P13	2.65(2.58)	5.01	2.78	2.95	4.84	2.23	0.17	2.06	0.35	-1.89	-0.46	-0.60	-0.11	-2.49	-0.62	0.98
P11	3.03(2.66)	5.25	2.56	2.83	4.98	2.69	0.27	2.42	0.22	-2.03	-0.65	-0.79	-0.44	-2.82	-0.65	1.48
P1	3.48(3.05)	5.53	2.38	2.78	5.13	3.15	0.40	2.75	0.06	-2.19	-0.23	-0.37	-0.17	-2.56	-1.24	0.88
P24	3.34(3.09)	5.66	2.71	3.00	5.37	2.95	0.29	2.66	-0.17	-2.42	-0.32	-0.46	-0.49	-2.88	-0.83	1.29
P28	3.06(3.13)	5.79	3.11	3.33	5.57	2.68	0.22	2.47	-0.38	-2.63	-0.15	-0.28	-0.53	-2.91	-0.60	1.52
P31	3.22(3.14)	5.85	2.97	3.25	5.57	2.88	0.28	2.60	-0.37	-2.62	-0.16	-0.30	-0.53	-2.91	-0.73	1.39
D3-CAM-B3LYP																
P17	2.84(2.91)	5.09	2.73	2.92	4.90	2.35	0.18	2.17	0.35	-1.94	-0.68	-0.77	-0.33	-2.71	-0.44	1.66
P14	3.34(2.88)	5.30	2.48	2.67	5.10	2.82	0.20	2.62	0.15	-2.13	-0.86	-0.95	-0.71	-3.08	-0.52	1.58
P13	3.36(2.91)	5.34	2.49	2.75	5.08	2.85	0.26	2.59	0.17	-2.12	-0.78	-0.87	-0.61	-2.98	-0.58	1.01
P11	3.68(2.89)	5.43	2.40	2.58	5.25	3.03	0.18	2.85	0.01	-2.28	-0.95	-1.04	-0.94	-3.32	-0.50	1.60
P1	4.13(3.93)	5.85	2.12	2.55	5.41	3.73	0.43	3.30	-0.16	-2.45	-0.54	-0.63	-0.70	-3.08	-1.20	0.90
P24	3.99(3.91)	6.04	2.41	2.83	5.62	3.64	0.42	3.22	-0.37	-2.66	-0.63	-0.71	-1.00	-3.37	-0.82	1.28
P28	3.72(3.84)	6.18	2.79	3.15	5.82	3.40	0.37	3.03	-0.57	-2.85	-0.48	-0.57	-1.04	-3.42	-0.59	1.51
P31	3.89(3.88)	6.24	2.68	3.07	5.85	3.55	0.39	3.17	-0.60	-2.88	-0.38	-0.47	-0.97	-3.35	-0.79	1.31

**Table S6:** Predicted energetics for polymers of interest within a dielectric continuum representing triethylamine. All energy differences are in terms of eV and pertain to free-energy differences except for VEE which is in terms of electronic energies. The lowest-energy hydrogen absorption site was used, see Figure S8 and Table S2 for the illustration and free energies of these sites, respectively.

$\alpha$ -TEA																
D3-B3LYP	VEE(f)	AIP	AEA	AIP*	AEA*	AFG	AEBE	AEE	$\Delta B1$	$\Delta B2$	$\Delta C1$	$\Delta C2$	$\Delta E1$	$\Delta E2$	$\Delta D$	H bind
P17	2.10(2.77)	5.28	2.40	3.40	4.28	2.88	1.00	1.88	1.77	-0.49	-1.78	-1.90	-0.01	-2.40	-0.53	1.60
P14	2.69(2.72)	5.47	2.18	3.24	4.41	3.30	1.06	2.24	1.64	-0.63	-1.98	-2.10	-0.34	-2.73	-0.55	1.57
P13	2.68(2.57)	5.45	2.19	3.30	4.35	3.25	1.10	2.15	1.71	-0.56	-1.89	-2.01	-0.19	-2.58	-0.62	1.56
P11	3.06(2.64)	5.79	1.91	3.20	4.50	3.89	1.29	2.59	1.55	-0.72	-2.08	-2.21	-0.53	-2.92	-0.72	1.40
P1	3.51(3.05)	5.92	1.81	3.05	4.69	4.11	1.24	2.87	1.37	-0.90	-1.65	-1.77	-0.28	-2.67	-1.24	0.88
P24	3.31(3.11)	6.07	2.10	3.33	4.84	3.97	1.23	2.74	1.21	-1.06	-1.76	-1.88	-0.55	-2.94	-0.85	1.27
P28	3.02(3.19)	6.25	2.61	3.71	5.14	3.64	1.10	2.53	0.91	-1.36	-1.46	-1.58	-0.54	-2.93	-0.64	1.48
P31	3.16(3.20)	6.27	2.45	3.60	5.11	3.81	1.15	2.66	0.94	-1.33	-1.44	-1.56	-0.50	-2.89	-0.82	1.30
D3-CAM-B3LYP																
P17	2.87(2.92)	5.63	2.15	3.33	4.45	3.48	1.18	2.30	1.66	-0.63	-2.06	-2.14	-0.40	-2.77	-0.50	1.60
P14	3.37(2.86)	5.81	1.86	3.06	4.61	3.95	1.20	2.75	1.50	-0.79	-2.33	-2.41	-0.83	-3.21	-0.52	1.58
P13	3.40(2.91)	5.85	1.86	3.13	4.57	3.99	1.27	2.72	1.54	-0.75	-2.26	-2.34	-0.72	-3.10	-0.59	1.00
P11	3.72(2.88)	6.04	1.66	3.00	4.70	4.38	1.34	3.04	1.41	-0.88	-2.46	-2.54	-1.04	-3.42	-0.59	1.51
P1	4.16(3.94)	6.31	1.46	2.89	4.88	4.84	1.43	3.42	1.23	-1.06	-2.06	-2.14	-0.82	-3.20	-1.19	0.91
P24	3.97(3.94)	6.56	1.74	3.28	5.02	4.82	1.54	3.28	1.09	-1.20	-2.13	-2.21	-1.04	-3.41	-0.84	1.26
P28	3.68(3.89)	6.66	2.26	3.61	5.31	4.00	1.35	3.05	0.80	-1.49	-1.82	-1.90	-0.67	-3.39	-0.63	1.47
P31	3.82(3.93)	6.78	2.10	3.55	5.33	4.68	1.45	3.23	0.78	-1.51	-1.78	-1.86	-0.99	-3.37	-0.83	1.27

## S9 Predicted IR spectra



**Figure S16:** The predicted B3LYP-D3/cc-pVTZ infrared spectra of the neutral tetramer, the neutral tetramer with a hydrogen adsorbed and the crosslinked dimer of P1 (a,b) and P31 (c,d).

P1: For the tetramer with a hydrogen adsorbed, the peak just under 3000  $cm^{-1}$  corresponds to the symmetric and asymmetric stretching of both CH bonds on the carbon with the adsorbed hydrogen atom. For the crosslinked dimer, the peak just under



3000  $\text{cm}^{-1}$  contains the symmetric and asymmetric stretching of the CH bonds and also modes involving the now  $\text{sp}^3$  hybridised carbons. This peak is not observed in the neutral tetramer.

P31: For the tetramer with a hydrogen adsorbed, the highest energy peak around 3600  $\text{cm}^{-1}$  is the NH stretching mode which is not present for the neutral tetramer as no NH bonds are present. For the crosslinked dimer, the peaks around 3600  $\text{cm}^{-1}$  involve stretching of each of the NH modes. The peak just under 3000  $\text{cm}^{-1}$  consists of modes involving the now  $\text{sp}^3$  hybridised carbons.

S10: B3LYP predicted spin densities of  $x\text{-H}^\bullet$

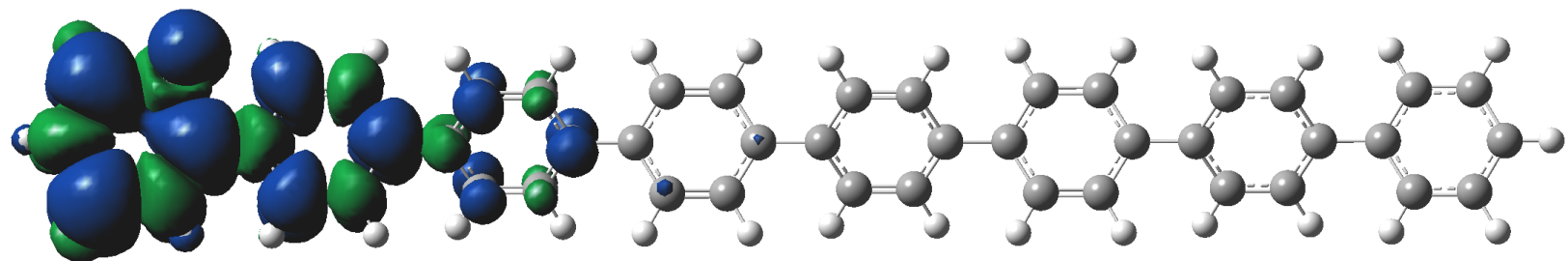


Figure S17: *The predicted B3LYP-D3/cc-pVTZ spin density for P1-H<sup>•</sup>*

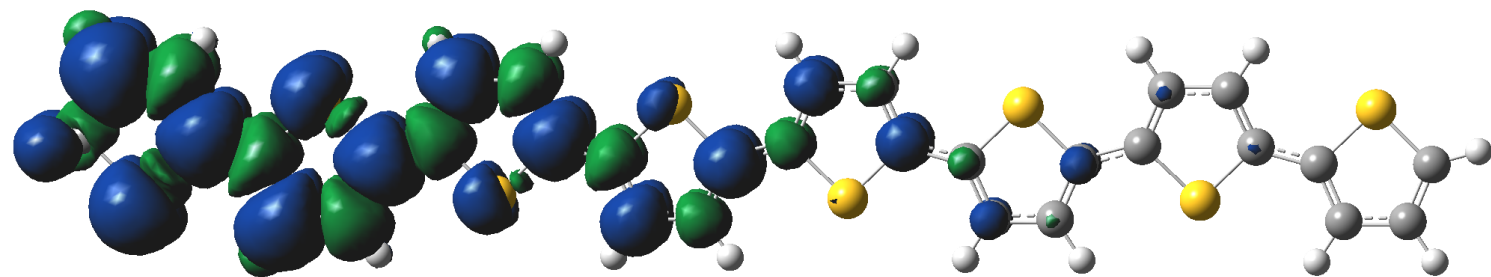
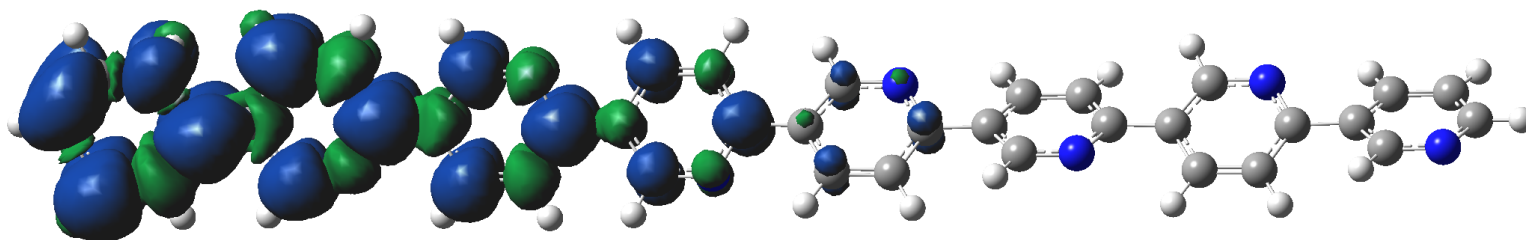


Figure S18: *The predicted B3LYP-D3/cc-pVTZ spin density for P17-H<sup>•</sup>*



**Figure S19:** *The predicted B3LYP-D3/cc-pVTZ spin density for P31-H<sup>+</sup>*