Why do sulfone-containing polymer photocatalysts work so well for sacrificial hydrogen evolution from water?

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ABSTRACT: In recent years, many of the highest performing polymer photocatalysts for hydrogen evolution from water have contained dibenzo[*b*,*d*]thiophene sulfone units in their polymer backbones. However, the reasons behind the dominance of this building block are not well understood. We use a new set of processable materials, in which the sulfone content is systematically controlled, to understand how the sulfone unit affects the three key processes involved in photocatalytic hydrogen generation in this system: light absorption; transfer of the photogenerated hole to the hole scavenger triethylamine (TEA); and transfer of the photogenerated electron to the palladium metal co-catalyst that remains in the polymer from synthesis. Using transient absorption spectroscopy and electrochemical measurements, and combined with molecular dynamics and density functional theory simulations, we find that the sulfone unit has two primary effects. On the picosecond timescale, it dictates the thermodynamics of hole transfer out of the polymer. The sulfone unit attracts water molecules such that the average permittivity experienced by the solvated polymer is increased, and we demonstrate here that TEA oxidation is only thermodynamically favourable above a certain permittivity threshold. On the microsecond timescale, we present experimental evidence that the sulfone unit acts as the electron transfer site out of the polymer, with the kinetics of electron extraction to palladium dictated by the ratio of photogenerated electrons to the number of sulfone units. For the highest performing, sulfone-rich material, hydrogen evolution appears to be limited by the photogeneration rate of electrons rather than their extraction from the polymer.

Introduction

Power generation from solar radiation is a compelling low carbon alternative to the burning of fossil fuels. However, the intermittent nature of solar photovoltaic energy supply requires current technologies to rely on energy storage systems to match supply to demand. One solution is to engineer the direct conversion of solar energy to chemical energy by using photocatalytic water splitting to generate hydrogen gas. For several decades, this field has focused almost exclusively on either inorganic or metal-organic catalysts^{1–3}. An alternative and relatively new approach is to use an organic photocatalyst. The chemical structures of organic semiconductors are easily modified, allowing for facile tuning of properties such as the optical band gap. Further, they typically have strong absorption coefficients, can be processed more easily and at lower temperatures, and can be made from Earthabundant non-toxic elements^{4–6}. Their processability is particularly advantageous for scale-up as inorganic materials are typically hard and brittle, making them unsuitable for low-cost coating techniques⁷. In the last few years, a wide range of organic photocatalysts have been studied, including carbon nitrides^{8–11}, covalent organic frameworks^{12–14}, covalent triazine-based frameworks^{15–17}, conjugated microporous polymers^{18–20} and linear conjugated polymers^{21–23}. In almost all cases, these



Figure 1. Chemical structures of PFO, FS1 to FS4, and FS5.

	Dibenzo[<i>b,d</i>]thiophene sulfone feed (y)ª	Palladium content ^b / ppm	Dispersion HER ^c / µmol g ⁻¹ h ⁻¹	Film HER ^d / µmol g ⁻¹ h ⁻¹	AQY at 420 nm ^e / %
FS1	0.03	1131	5	42	0.04
FS2	0.06	1232	18	80	0.25
FS3	0.13	2145	15	193	0.28
FS4	0.25	1619	238	436	1.09
FS5	0.50	290	1370	5885	2.07

Table 1. Hydrogen evolution rates and apparent quantum yields of polymers **FS1 to FS5**. (a) Dibenzo[*b,d*]thiophene sulfone content of the polymers based on monomer feed ratios. (b) Palladium content in parts per million, measured by ICP-OES. (c) Hydrogen evolution rates of 25 mg polymer dispersed in 22.5 mL 1:1:1 vol.% water:methanol:TEA, illuminated with visible light ($\lambda > 420$ nm, 300 W Xe light source). (d) Hydrogen evolution rates of polymer films drop-casted onto rough glass substrates (thickness of order 100s of nanometres) in water:methanol:TEA, illuminated with visible light. (e) Apparent quantum yields of the polymers in dispersion in water:methanol:TEA, illuminated with a 420 nm LED.

materials only produce hydrogen when immersed in water containing a sacrificial electron donor (SED) due to their low water oxidation activity. Organic photocatalysts have also been reported for overall water splitting, either in so-called Zschemes, in which hydrogen evolution occurs at the organic photocatalyst while oxygen evolution occurs on a metal oxide^{24,25}, or in single particulate organic photocatalyst systems enabled by suitable cocatalysts^{26,27}. However, the overall efficiencies of these systems are low, leaving significant room for advances in materials design and understanding.

Despite substantial increases in the activities of organic photocatalysts over the last five years, few studies have attempted to deconvolute the many factors (structural, optical, and electronic) that affect photocatalytic performance^{4–6}. Linear conjugated polymers are ideal materials for this task since their chemical structures – and hence their photocatalytic properties - can be tuned in a systematic manner, allowing for more controlled studies of structure-function relationships in organic photocatalysts. In our previous work, we showed that the inclusion of a dibenzo[b,d]thiophene sulfone unit in the backbone of a series of linear

polymers improved the hydrogen evolution rate (HER) in the presence of the SED triethylamine (TEA)^{28,29}. Since then, numerous research groups have synthesised series of photocatalysts in which sulfone-containing materials have outperformed sulfone-free materials³⁰⁻⁴². Sulfone-containing photocatalysts have rapidly reached impressive apparent quantum efficiencies of 29.3% at 420 nm⁴³, 18% at 500 nm⁴⁴ and 13.6% at 550 nm⁴⁰ when paired with hole scavengers. Despite the popularity of the sulfone monomer building block, few studies have shed further light on precisely why the sulfone unit improves performance in such a wide range of different materials. This is in part because of the insolubility of most sulfone-containing photocatalysts, which requires researchers to study dispersed polymer systems in which key optical and physical parameters are difficult to define. In this work we use a new series of processable linear conjugated polymers, in which we vary the amount of sulfone in the polymer backbone in a systematic manner, to elucidate the role of the sulfone unit in the hydrogen evolution process. The ability to make films allows us to carry out more quantitative studies of structurefunction-performance relationships relative to



Figure 2. (a) Hydrogen evolution rates as a function of sulfone content, on a logarithmic scale. (b) Attenuation coefficients and normalised photoluminescence spectra (360 nm excitation, 450 nm normalisation) of **FSn** thin films. Attenuation coefficients were estimated by relating the optical depth of spin-coated thin films to their physical thickness (**Figure S-12**).

polymer dispersions with ill-defined particle sizes. We find, as expected, that the amount of sulfone in the polymer correlates with its hydrogen evolution rate for both dispersions and films. We then use a combination of computational, spectroscopic and electrochemical characterisation techniques to examine the effect of the sulfone unit on the two redox reactions involved in these systems: the oxidation of TEA and the reduction of water.

<u>Results</u>

Materials, reaction mechanism and optoelectronic properties

Materials. The five photocatalysts studied in this work, **FS1-5**, are shown in **Figure** 1. These are co-polymers comprising different ratios of dibenzo[b,d]thiophene sulfone (v) and 9.9-di-nhexyl-fluorene (1-y) monomer units. The sulfone feed used in the synthesis of each polymer is assumed to be representative of their final molar composition. FS1-4 are statistical polymers, whilst FS5 is strictly alternating. Poly(9,9di-n-octyl-9H-fluorene) (PFO) was also included in hydrogen evolution experiments as a sulfone-free control material. The polymers were synthesised using a Suzuki-Miyaura-type polycondensation in the presence of a palladium catalyst. Details of the synthesis procedure can be found in the Supporting Information. In the studied systems, polymers are immersed into a 1:1:1 by volume water:methanol:triethylamine mixture. The methanol is included to facilitate mixing between the water and the

triethylamine (TEA) and there is no evidence that it is involved in the reaction mechanism⁴⁵. All HERs are measured under visible light, with a λ > 420 nm filter used to remove UV light from a Xenon lamp. Apparent quantum yields (AQYs) were measured using a 420 nm LED. The mass-normalised hydrogen evolution rate (HER) and the AQY both increase with increasing sulfone content (**Table 1**, **Figure 2a**). **PFO** was found to be effectively inactive during a 5-hour photocatalysis experiment (**Figure S-15**). Films perform better than their dispersed analogues, most likely due to their improved specific light absorption and solvent access.

Reaction mechanism. To understand the role of the sulfone, we will consider in turn the three major steps in the reaction mechanism^{23,29}: first, the polymer absorbs light to form excitons; second, the excitonic hole is scavenged by the TEA in less than 100 ps, causing the formation of an electron polaron in the polymer backbone⁴⁶; third, the electron polaron is used to reduce protons in the water. The formation of hydrogen from protons is most likely catalvsed by palladium clusters which exist in the organic material as a by-product of the polymers' synthesis route, with charges being transferred from polymer to palladium on the microsecond timescale⁴⁷⁻⁴⁹. Table 1 shows there is no obvious relationship between palladium content and HER in this series of materials. This is consistent with previous HER measurements on the glycolated analogue of FS5, FS-TEG, in which Pd loadings beyond approximately 250 ppm did not substantially improve performance^{50,51}. The nature of the palladium



Figure 3. (a) Molecular dynamics simulations of **PFO**-like and **FS5**-like oligomers in 1:1:1 vol.% water:methanol:TEA, with extracted solvent volume fractions within a 4 nm radius. TEA is shown in blue, water in red and methanol in yellow. Simulations of **FS3**-like and **FS4**-like oligomers can be found in the Supporting Information (**Figures S-57-60**). (b) Contact angles of **FSn** films with 1:1:1 vol.% water:methanol:TEA as a function of sulfone content. (c) -log(transmittance) spectra of 0.02 mg mL⁻¹ **FSn** dispersions in 1:1:1 vol.% water:methanol:TEA.

and the mechanism by which it reduces protons are beyond the scope of this work, and we merely note here that this is the assumed reaction pathway when interpreting electron kinetics within the photocatalysts.

Optoelectronic properties. Thin films of all five materials exhibit a ground state absorption peak in the 380 - 400 nm range (**Figure 2b**) with tails extending into the visible such that they are photocatalytically active under $\lambda > 420$ nm light. They have relatively similar optical band gaps (2.84 - 2.98 eV or 436 - 416 nm, **Figure S-14**) and attenuation coefficients around 2.5 × 10⁵ cm⁻¹ at their absorption peaks. The redshift in the absorption edge as the sulfone content increases from **FS1** to **FS5** does cause the absorption coefficient to increase by a factor of approximately 2 at 420 nm, however this difference is still small relative to the hundred-fold

difference in HER for the films and fifty-fold difference in AQY at 420 nm for the dispersions (Table 1). These data suggest that differences in the intrinsic optical properties of these materials are not responsible for the large difference in photocatalytic performance across this series of materials. The photoluminescence spectra show that increasing the sulfone content increases the emission ratio at 470 nm relative to 450 nm, whilst a further shoulder at 510 nm also becomes gradually more prominent (Figure 2b). The FS5 film emission exhibits stronger vibronic structure than the randomly copolymerised **FS1-4** films, which may be due to its strictly alternating monomer structure. Normalised absorption and photoluminescence spectra of FSn solutions in chloroform show similar red-shifts with increasing sulfone content and can found in Figures S-8 and S-9.

Influence of the sulfone on the local liquid environment

We first consider how the liquid environment surrounding the polymers is influenced by the polymers' chemical structures. We use molecular dynamics (MD) simulations of oligomers suspended in 1:1:1 water:methanol:TEA to determine the average volume fraction of the three solvents within 4 nm of the polymer backbone. Octamers (*i.e.* 16 fused benzene rings) containing zero, one, two and four sulfone units were used to represent the polymers **PFO**, **FS3**, **FS4** and **FS5**. The remaining monomer units were made up of the same 9,9-di-*n*-hexyl-9*H*-fluorene units used in the synthesised polymers. The octamers were equilibrated using an NVT ensemble for 10 ns before being run in an NPT ensemble for a minimum of 40 ns.

We find that the presence of the polar sulfone unit preferentially attracts polar water and methanol molecules at the expense of TEA, such that the volume of water close to the FS5-like octamer backbone is significantly higher than the volume of water close to the PFO-like oligomer (17% vs 11%, Figure 3a). The non-polar PFO-like oligomer instead draws more of the relatively non-polar TEA close to its backbone than the FS5-like oligomer. The MD simulations only use single oligomers and therefore do not include any macroscopic effects such as polymer aggregation, which would likely change the effective wettability of the dispersions in water:methanol:TEA. However, the simulated nanoscale affinity of the polymer for water can be seen on the macroscopic scale through the wettability of the polymer with water. Figure 3b shows that the contact angles of droplets of 1:1:1 water:methanol:TEA on the surfaces of FSn films get smaller with increasing sulfone content. Contact angles of water on FSn films also decrease as a function of sulfone content (Table S-7, Figure S-28), with all five polymers exhibiting high contact angles (> 90°) due to the non-polar fluorene side chains and the high surface tension of water.

Further evidence for the sulfone's affinity for polar media can be seen by comparing the films' absorption coefficients (**Figure 2b**) to the transmittance of dispersions in 1:1:1 water:methanol:TEA (**Figure 3c**). Whilst films of all five materials have similar absorbances, sulfone-rich polymer dispersions have higher attenuations when dispersed. This suggests that polymers with higher sulfone content form smaller particle sizes in the reaction mixture. Static light scattering (SLS) measurements suggest that all five polymer dispersions in water:methanol:TEA are highly polydisperse. Most of the polymer mass is likely contained within large particles (order of micrometres), although sulfonerich polymers appear to form larger numbers of smaller particles (diameter 100 - 1000 nanometres, **Figure S-24**).

The MD simulations, contact angles and SLS measurements all indicate that the affinity of the polar sulfone towards high dielectric solvents aids polymer dispersion in water:methanol:TEA. However, the correlation between HER and sulfone content is still strong when the polymers are cast as thin films with similar absorbance (**Table 1**, **Figure 2**). This indicates that any differences in dispersion particle sizes do not change the overall relationship between sulfone content and activity in this series.

Influence of the local liquid environment on TEA oxidation

The divergence of the polymers' local liquid environment from the bulk mixture has significant ramifications when considering the energetics of the redox reactions occurring in this system. To quantify this, we first use MD simulations alongside an effective medium model to estimate the permittivity experienced by excited species residing on single polymer chains when immersed in the water:methanol:TEA reaction mixture. Briefly, this involves finding the volume fraction of water, methanol and TEA that lie within 4 nm of the oligomer backbone in an MD simulation snapshot and then averaging over that region to estimate the relative permittivity experienced by the **PFO**-like and **FS5**-like oligomers. The cut-off of 4 nm is chosen as it encompasses approximately one shell of solvent molecules. In our model, species in the PFO-like oligomer (used herein as a conceptual model for the **FS1** polymer) experience a relative permittivity of 4.4 whilst species in FS5 experience an average of 7.2. The full radial dependence of the relative permittivity found using the MD is shown in Figure S-60 for PFO, FS3, FS4 and FS5. The estimated permittivities are likely overestimates as the simulated single chains allow more high-permittivity solvent molecules to get close to the polymer backbone than might be expected in an aggregated structure.

We next explore the impact of solvent permittivity on the oxidation potentials of **FS1** and **FS5** solutions using differential pulse voltammetry (DPV). These



Figure 4. Estimations of the driving force for TEA oxidation by **PFO/FS1** and **FS5** as a function of solvent permittivity. (a) Estimations of the ionisation potentials (IP) and excitonic hole potentials (EA*) of **FS1** and **FS5**, calculated from DPV (**Figure S-34**), as a function of THF vol. %. EA*s are estimated by assuming that the exciton binding energy approaches zero at infinite permittivity, and that this binding energy is inversely proportional to solvent permittivity (**Figure S-35**). (b) Simulated potentials involved in TEA oxidation as a function of solvent permittivity. The circled points on the potential plots for **PFO** (red) and **FS5** (green) indicate the relative permittivity at a distance of 4 nm from the polymer centre of mass (**Figure S-60**).

oxidation potentials are assumed to be approximately equal to (or at least, linearly dependent on) the polymers' ionisation potentials (IPs). The solvent permittivity was varied by incrementally increasing the volume ratio of tetrahydrofuran (THF, ε_r = 7.58) from 0% to 40% relative to toluene (ε_r = 2.38). These solvents were chosen since they are able to dissolve the polymers whilst also straddling the permittivities which **FS1** (ε_r =4.4) and **FS5** (ε_r =7.2) are simulated to experience in the water:methanol:TEA mixture. All solutions also contain 500 mM tetraoctylammonium tetrafluoroborate; experimental details can be found in the Supporting Information. As the permittivity of the solution is increased (i.e., the THF concentration is increased relative to toluene), the ionisation potentials shift to shallower (less negative) potentials vs vacuum by approximately 0.3 V (Figure 4a, solid lines; raw data in Figure S-34). The shift in IP as a function of solvent permittivity can be used to estimate the potentials of species involved in the reaction mechanism: namely excitonic holes (EA*) for TEA oxidation and electron polarons (EA) for proton reduction. EA* potentials were calculated from the measured IP potentials assuming that the binding energy of the initially photogenerated exciton approaches zero in an infinitely polar medium, and that this binding energy is inversely proportional to the dielectric constant of the solvent at high THF concentrations (See Supporting Information for calculation details, also Figure S-35). The calculated

EA* potentials for **FS1** and **FS5** are shown as a function of THF volume percentage in **Figure 4a** (dotted lines). The IP* and EA potentials were also estimated from the IP and EA* potentials using the polymers' optical band gaps. All four potentials (IP, IP*, EA, EA*) are shown together in **Figure S-36**.

Figure 4a shows that oxidation of FS5 occurs at deeper (more negative) potentials than **FS1** in all solvent mixtures, indicating that the inclusion of sulfone units into the polymer backbone deepens the IP regardless of solvent choice. Comparing across the solvent mixtures, we find that the permittivity of the polymer's liquid environment can critically affect the relevant polymer redox potentials in two ways: firstly, both polymers have shallower IPs when surrounded by the higher permittivity THF (akin to being surrounded primarily by water). The redox potentials then change non-linearly as the solvent mixture's polarity is lowered, with the most rapid change occurring at low polarity. Secondly, the high permittivity of the solvent environment stabilises the polymers' excited state, such that the excitonic hole and electron energies (EA* and IP*) converge towards the polaronic IP and EA potentials (Figure 4a, Figure S-36) - in other words, the excitonic binding energy is significantly decreased when the polymer is surrounded by a higher permittivity medium. A comparison of absorbance spectra in THF and toluene shows that the effect of solvent permittivity on these polymers' optical band gaps is effectively zero (Figure S-13).

DFT calculations were used to estimate the IP, IP*, EA and EA* potentials of **FS1** (again using the **PFO**like oligomer) and **FS5**, along with the oxidation potential of TEA to its charged radical, as a function of solvent permittivity. Potentials were calculated in pure THF and toluene using the b3lyp functional with the 6-311+g(d,p) basis set alongside an SMD polarisable continuous medium (PCM)⁵². A Bruggeman effective medium model was then used to estimate the permittivities of the THF-toluene mixtures at different THF concentrations. Finally, the potentials in the solvent mixtures were interpolated from those in the pure solvents assuming a reciprocal relationship between energy and permittivity (See Supporting Information for details).

The simulated EA* and TEA oxidation potentials are shown in **Figure 4b**. The EA* values qualitatively agree with the experimental data (**Figure 4a**), becoming asymptotically deeper with increasing permittivity (i.e. with THF concentration). The EA* potentials are more strongly affected by the presence of THF in the experimental data relative to the simulated data. This behaviour may be because the concentration of THF around the polymer is higher than the bulk mixture. The presence of the electrolyte will also increase the solvent mixture permittivities and as such the estimated experimental solvent permittivities are lower bounds on the true values; however, this will not affect the overall trends seen in this work.

We next consider the calculated potentials in THF:toluene in the context of the water:methanol:TEA system. As potential changes in this SMD model are primarily influenced by solvent permittivity, we assume that the relationship between potential and permittivity in Figure 4 is approximately the same in THF:toluene and water:methanol:TEA. As TEA acts as an exciton quencher in this system, determining whether a photoexcited polymer is thermodynamically able to oxidise TEA requires the EA* potential (excitonic hole potential) to be deeper than the TEA oxidation potential. Figure 4b shows that the driving force for TEA oxidation changes as a function of solvent permittivity. The simulations in Figure 3 suggested that **FS1** sits primarily in a low permittivity environment when immersed in water:methanol:TEA (ε_r = 4.4 for the **PFO**-like oligomer, circled in red): Figure 4b suggests that in this local solvent environment, the EA* potential is too shallow to drive TEA oxidation. By contrast, FS5 sits in a higher permittivity solvent when immersed

in water:methanol:TEA such that excitonic holes have a driving force for TEA oxidation ($\varepsilon_r = 7.2$, circled green). Noteably, if **FS5** experienced a permittivity of $\varepsilon_r = 4.4$ like **FS1**, it would also be unable to oxidise TEA. This is in part because the local solvent environment strongly affects the TEA oxidation potential as well as the polymers' EA* potential. We therefore conclude that the sulfone's ability to increase the local solvent permittivity is critical to its ability to oxidise TEA.

Influence of TEA oxidation driving force on electron generation

The analysis in the previous section suggests that the environment-dependent shift in the excitonic hole potential EA* critically affects the driving force for hole transfer from polymer to TEA and thus critically affects the formation of electron polarons in sulfone-containing polymers. Femtosecond transient absorption spectroscopy (fs-TAS) was employed to probe the formation of electrons in the materials with the highest and lowest sulfone content: FS1 and FS5. We used global analysis based on a genetic algorithm to deconvolute the data into spectral features differentiated by their different kinetic behaviours. This approach has the advantage of not requiring any sort of model: spectra and kinetics are extracted without any a priori assumptions. Details of all components and their physical assignments can be found in the Supporting Information.

Figure 5a and Figure 5b show the temporal evolution of the FS5 and FS1 absorption difference spectra when the polymers are dispersed in the water:methanol:TEA mixture. Both spectra exhibit a negative feature which peaks in the 500 nm region, which we assign to stimulated emission due to their similarities to the photoluminescence spectra in **Figure 2b**. The positive absorption features at > 620 (FS5) and > 700 nm (FS1) are of maximal size at < 1 ps after excitation and have almost completely decayed by 100 ps, suggesting they are caused by singlet exciton absorption. Similar features have been observed in fluorene-based polymers⁵³⁻⁵⁵. Global analysis suggests that the exciton absorption comprises two overlapping components with halflives of 0.9-1.2 ps and 5-6 ps, which might be suggestive of the presence of both hot excitons and vibrationally relaxed excitons (Figures S-39, S-40).

For both **FS1** and **FS5**, a third spectral component which features a positive peak centred at 600 nm can be extracted from the global analysis (**Figure**



Figure 5. (a, b) Femtosecond visible transient absorption spectra of the (a) **FS5** and (b) **FS1** 0.2 mgml⁻¹ dispersions in 1:1:1 vol.% water:methanol:TEA. The colour scale is measured in picoseconds after excitation with 420 nm light. (c) Normalised deconvoluted spectral components containing a 600 nm peak for **FS1** and **FS5**, assigned to the presence of CT states for **FS1**, and to CT states and electron polarons for **FS5**. The other spectral components can be found in **Figures S-39** and **S-40**. (d) Deconvoluted CT state/electron polaron transient absorption kinetics for **FS1** and **FS5**, extracted from the data in **Figure 5a-b** using global analysis. The time axis is linear from -1 to 1 ps.

5c). In the case of FS1, the peak is superimposed on top of a broad emission feature. Figure 5d shows the kinetics associated with these 600 nm peaks. The amplitude of the FS1 decay is adjusted to exclude the contribution from the stimulated emission. The component containing the 600 nm peak seen in FS1 is formed within a picosecond of excitation and decays continually over the course of the measurement. We observe the decay of a near-identical spectral component when FS5 is measured in a water:methanol mixture (i.e. in the absence of TEA, Figure S-41). By contrast, the 600 nm peak seen when FS5 is measured in water:methanol:TEA has far less associated emission, with a relatively small negative feature being present at < 530 nm. Crucially, this component also exhibits two distinct kinetic peaks: one formed in < 1 ps which decays quickly, akin to FS1 in water:methanol:TEA and FS5

in water:methanol, and a second which rises from approximately 5 ps before peaking 50-100 ps after excitation.

Considering the observations above and the nature of TEA as a hole scavenger, we suggest that the 600 nm feature formed in < 1 ps is an intermediate excited state such as a charge transfer (CT) state, whilst the rise in the 600 nm peak amplitude at > 5 ps is caused by the formation of electron polarons as holes are used up in the TEA oxidation reaction. The latter assignment is consistent with previous measurements on sulfone-containing polvmers^{45,56,57}, as well as with measurements on polyfluorenes⁵³⁻⁵⁵. It has previously been shown that CT states and polarons can have similar absorption spectra^{58,59}. The data in **Figure 5d** suggest that FS5 can transfer excitonic holes to TEA, with a substantial population of electrons being formed from 5 ps. By contrast, **FS1** has no rise in amplitude at > 5 ps, indicating that it does not generate electron polarons in detectable quantities on the picosecond timescale. This is consistent with the results from the previous section, which suggest that **FS5** has a driving force for TEA oxidation whilst **FS1** does not. Finally, we note that the reduced emission associated with the 600 nm feature in the presence of TEA suggests that polaron formation in **FS5** is at least partially caused by interactions between the TEA and the CT state.

Microsecond transient absorption (us-TA) spectra of FS1-5 dispersions in water:methanol:TEA all exhibit the same 600 nm polaronic absorption peak as the sole feature when photoexcited (Figure 6a, Figure S-44). An FS5 dispersion in water:methanol showed no transient absorption features on the microsecond timescale, again conveying the necessity of TEA for substantial electron generation (Figure S-45). The electron polaron absorption amplitudes increase with increasing sulfone content (Figure S-46), even when accounting for differences in ground state absorption (Figure 6b). DFT calculations suggests that the electron polaron absorption coefficients in the visible for FS1 and FS5 are likely similar (Figure S-61). The 600 nm absorption difference observed in the transient spectra can therefore be considered roughly proportional to the number of photogenerated electrons in the materials. FS1 photogenerates a small number of detectable electron polarons on the microsecond timescale, despite the lack of obvious TEA oxidation on the picosecond timescale. This could be because the number of polarons generated on picosecond timescales is too low to be measured, or it could be indicative of an alternate reaction pathway in which excitonic holes are transferred to residual palladium on the nanosecond timescale, as seen in a similarly lowpolarity F8BT polymer photocatalyst⁶⁰.

The electron absorption amplitudes correlate well with the HERs across the series (**Figure 6c**). The EA potentials calculated from the earlier electrochemistry experiments (**Figure S-34**) indicate there is a strong (> 1.5 V) driving force for proton reduction for all 5 materials (**Figure S-37**). The trend of electron density with HER in the absence of substantial differences in driving force across the series is consistent with the idea that the HERs in these materials may be limited by the electron generation rate of the material.

To determine whether performance could be linked to charge transport, we also carried out



Figure 6. (a) Microsecond TA spectrum of a 0.02 mg mL⁻¹ **FS5** dispersion in water:methanol:TEA, shown at different times after photoexcitation. (b) Kinetics of the 600 nm transient absorption signal for 0.02 mg mL⁻¹ **FSn** dispersions in water:methanol:TEA, normalised by the 420 nm ground state absorption of the dispersion. (c) Hydrogen evolution rates of the **FSn** 1.1 mg mL⁻¹ dispersions versus the magnitude of the 0.02 mg mL⁻¹ dispersions' 600 nm absorption feature 100 μ s after 420 nm excitation.

OFET measurements on three polymers with different sulfone content (**FS1**, **FS3** and a variant of **FS5** in which the hexyl side chain is replaced with a dodecyl side chain to improve processability). We find that hole polaron mobilities get lower as the sulfone content increases, showing that HE performance is not positively correlated to charge transport in these materials (**Figure S-56**).

Influence of the sulfone on palladium reduction

Having shown that the sulfone unit is critical to the polymers' ability to oxidise TEA and generate electrons, we now consider the impact of the sulfone unit on the polymers' ability to transfer electrons to an electron acceptor. We assume a mechanism in which electrons are transferred to residual palladium metal on the micro- to millisecond timescale, with hydrogen evolution catalysed by the metal on the same or longer timescales^{60,61}. In this work, we focus completely on the removal of the electron from the polymer, making no assumptions or claims as to the nature of the metal. In particular, we note that palladium likely also acts as a recombination site, although this becomes increasingly less likely as the polymers' sulfone content is increased since holes are increasingly scavenged by the TEA⁶¹.

Polaron lifetimes are often heavily dependent on the polaron density in the material, whilst a relationship between particle size and polaron kinetics has also previously been observed in F8BT nanoparticles⁶¹. However, the vast difference in particle sizes present across the FSn series of dispersions makes it difficult to accurately compare electron lifetimes across the series of materials. Instead, polaron kinetics are compared using FSn films with thicknesses of 150 - 250 nm (Figure S-47). Studying films allows us to control parameters such as charge density far more carefully: by exciting the films at different fluences, in line with the different film thicknesses, we can ensure that the photogenerated electron density (600 nm absorbance change) at 4 μ s post-excitation is approximately the same (4 μ s is the fastest reliable time response for these data). This allows us to isolate the effect of sulfone concentration on electron kinetics from effects caused by differences in dispersion particle size and absorbance. Figure 7a shows that the lifetime of the electron on the polymer decreases drastically with increasing sulfone content: electrons in sulfone-poor FS1 exhibit a half-life of 3.5 ms, whilst the sulfone-rich FS5 exhibits an electron half-life of 52 µs at the same charge density. Up to a few



Figure 7. (a) Normalised 600 nm electron absorption kinetics in the dropcast **FSn** films, excited such that the electron density at 4 μ s in each film is approximately the same (1.3-1.9 μ AA/d). (b,c): Normalised 600 nm kinetics in (b) **FS1** and (c) **FS5** films with different photogenerated electron densities. All measurements are in water:methanol:TEA. Δ A = absorbance change of the kinetic trace at 4 μ s, prior to normalisation. Films thicknesses (d) are estimated in nanometres from ground state absorbances.

milliseconds, these kinetics are well fitted by power law decays $\Delta A \propto t^{-\beta}$, with exponent β gradually decreasing from **FS1** ($\beta = 0.10$) to **FS5** ($\beta = 0.28$) (**Figure S-48**). The observation of power law kinetics with $\beta < 1$ suggests that these materials are energetically disordered, with the observed dispersive behaviour caused by trapping/detrapping of electrons in trap states^{62,63}.

Recent work on the sulfone homopolymer P10 has shown that the microsecond kinetics of electrons in these polymers are shortened with the addition of a metal co-catalyst, implying that electron transfer to the residual palladium occurs on this timescale⁶⁰. We therefore interpret the trend in electron lifetimes to mean that electron transfer to the residual palladium is more efficient in sulfonerich materials. Using the absorbance change density $(\mu\Delta A/d, d = film thickness)$ as a proxy for charge density, steady-state photoinduced absorption measurements on an FS5 film were used to estimate that the charge density photogenerated under the hydrogen evolution conditions used in this study is approximately 0.6 $\mu\Delta A/d$ (Figures S-53, 54). We therefore suggest that the differences in kinetics shown in Figure 7a are a good descriptor of the differing electron transfer efficiencies occurring under hydrogen evolution conditions in the FSn films.

We note that as there is no relationship between palladium content and sulfone content across the **FSn** series (**Table 1**), it is unlikely that the relationship in **Figure 7a** is caused by differences in palladium concentration. Further, we found no evidence to suggest that the relationship between sulfone content and electron kinetics is caused by possible differences in water flux into the films. A comparison of μ s-TAS electron kinetics in an **FS5** film immersed in water:methanol:TEA and in pure TEA (likely containing traces of water) showed that the presence of water does not quicken the electron kinetics (**Figure S-49**).

Figure 7a suggests that electrons are donated to the palladium acceptor via sulfone "transfer sites". To test this hypothesis, the electron kinetics of similarly thick **FS1** and **FS5** films were probed at a range of electron densities, achieved by varying the excitation fluence. **Figure 7b** shows that the electron lifetimes in **FS1** are insensitive to the electron density in the film, with all kinetics exhibiting similar behaviour. By comparison, **Figure 7c** shows that electron kinetics in **FS5** are dependent on the

electron density, with electron lifetimes becoming longer as the charge density is increased. At the highest charge densities (associated absorbances of $\mu\Delta A/d = 7.8, 8.5$), the electron lifetimes in **FS5** "saturate" towards those seen in FS1 (See also Figure **S-51**). These observations are unusual: charge decay kinetics often get faster at higher excitation fluences due to increased rates of bimolecular recombination, in contrast to the retardation observed here for FS5. The observed fluence-lifetime relationship, combined with the shape of the kinetics, suggests that bimolecular recombination does not dominate over electron transfer to the metal on the microsecond timescale. Instead, the "electron saturation" in FS5 suggests that electron transfer out of the polymer is inefficient at high charge densities. Given that the number of electrons observed in these measurements is much lower than the number of sulfone units in the materials, we suggest that the inefficient transfer seen in **Figure 7Figure 7** is not caused by electron saturation of the sulfone transfer sites. Instead, assuming that only a subset of the sulfone transfer sites have a sufficiently close palladium acceptor site, we propose that the lifetime lengthening with electron density is caused by electron saturation of the available palladium in these "palladium coupled sulfone sites". The efficiency of electron extraction can then be increased either by having more sulfone transfer sites (Figure 7a), which gives access to more palladium acceptors, or by reducing the electron density such that palladium saturation is no longer limiting performance (Figure 7c). This implies that the hydrogenevolving ability of palladium may limit future higher-performing polymers which rely solely on residual palladium for their activity.

The effect of charge density on charge lifetime in FS5 can be replicated by adjusting the film thickness rather than the amount of photogenerated charge (Figure S-52): here, the number of generated electrons in the films are similar but the film thicknesses vary by an order of magnitude. As in Figure 7c, the film with higher charge density (the thinner film) exhibits a longer electron lifetime. The charge density $(\Delta A/d)$ dependent saturation effect can therefore be observed both by changing the excitation fluence (i.e., the electron population ΔA) and by changing the film thickness (d). This is a good indication that the saturation effect is not specific to a given film thickness. This in turn suggests that this effect is universal to all microstructures including dispersions - for these polymers.

The spectroscopic data in Figure 7 suggest that the sulfone unit is the active site for electron transfer from polymer to palladium. To further study this hypothesis, DFT calculations, performed using the CHELPG atomic charge calculations scheme⁶⁴, were carried out on "PFO" and "FS5" oligomers to determine the effect of the sulfone unit on charge distribution and separation. The PFO oligomer comprised 3 fluorene monomers, whilst the FS5 oligomer contained a dibenzo[b,d]thiophene sulfone monomer flanked by two fluorene monomers. By calculating the difference between the neutral and anionic case, we can see where the excess electronic charge localises in the radical anion compared to the neutral state. We do this for different PCM solvent environments: in vacuum; in TEA; in water; and in TEA with a single explicit free water molecule (Figure S-62, Tables S-9 and S-**10**). The key results are summarised in **Figure** 8. In all four cases, the electron localises more strongly on the central monomer of the FS5 oligomer than on that of the PFO oligomer (full lines). This shows that the sulfone acts as a clear localisation area for significant amounts of the electronic charge, in agreement with other work^{38,39}. Notably, this electron localisation is considerably more pronounced when the polymer is surrounded by water: when the FS5 oligomer anion is in pure water, 75% of the electron localises in the central monomer and 21% is localised at the SO₂ unit. When in vacuum, the central monomer and SO₂ unit host 51% and 10% respectively. Furthermore, we can see from the introduction of the explicit water molecule that, like in the MD simulations, a hydrogen bond between the water molecule and the sulfone group is formed (Figure S-62).

Overall, the DFT calculations and the spectroscopic data show that the electron localises at the sulfone and that the sulfone unit improves charge extraction. Taken together, we suggest that electron transfer from polymer to palladium occurs primarily at the sulfone unit.

Discussion

The **FSn** series show a positive correlation between sulfone content and photocatalytic activity, in good agreement with other work³⁴⁻ ^{42,45,51,65}. We suggest that the higher performance of sulfone-rich materials is due to two factors: their higher thermodynamic driving force for



Figure 8. Summary of the calculated partial charge localisation in trimer anions, as a function of the environment. Solid lines: charge found on the central monomer unit (CH_2 or SO_2 inclusive). Dashed lines: charge found solely on the CH_2/SO_2 unit.

TEA oxidation and their faster electron extraction rates for palladium reduction.

TEA oxidation

Femtosecond transient absorption spectroscopy (Figure 5) shows that a significant electron population is photogenerated in the FS5 water:methanol:TEA dispersion, whilst the effectively inactive FS1 does not obviously form a measurable polaron population. This indicates that **FS1** is not able to oxidise an appreciable number TEA of molecules, whilst FS5 can. The effect of this is seen in the µs-TAS experiments: the inability of FS1 to transfer holes to TEA results in a smaller electron polaron population existing on the timescales that proton reduction is expected to occur (Figure 6). Across the entire **FSn** series, the correlation between the density of photogenerated electrons on the micro-millisecond timescale and the hydrogen evolution rate indicates that the formation of polymer anions is essential for proton reduction to occur.

We propose that there are two reasons for the difference in the polymers' ability to oxidise TEA. Firstly, the sulfone unit clearly deepens the 'intrinsic' EA* potential of the polymers. This can be seen in the optoelectronic and electrochemical measurements, and also in the DFT simulations. Secondly, the MD and DFT simulations suggests that the sulfone increases the permittivity of the solvent environment surrounding the polymer (**Figure 3**), which in turn further deepens the EA* potential in sulfonerich polymers (**Figure 4**). The simulations also suggest that the oxidation potential of TEA has a strong dependence on the local solvent permittivity. The combination of these three effects results in **FS5** having a thermodynamic driving force for TEA oxidation, whilst **FS1** has no driving force. The permittivity dependence of TEA oxidation highlights the importance of a polymer's ability to influence its local solvent environment in these systems: if TEA molecules are surrounded primarily by other TEA molecules, neither **FS1** nor **FS5** has a driving force for TEA oxidation.

These experimental and theoretical data allow us to introduce the concept of a local solvent "permittivity threshold": polymers must be hydrophilic enough to attract water and exceed this threshold if they are to oxidise TEA. To the best of our knowledge, such a concept has not been demonstrated before in the context of sacrificial water splitting. Notably, the permittivity threshold is not very high in FS5 relative to typical aqueous solvent permittivities, but it is high for a typical dry polymer ($\varepsilon_r \approx 3$). This highlights an important challenge for sacrificial polymer photocatalysts: careful design is required as the intrinsic hydrophobicity of carbon-based semiconductors (as e.g., seen in organic photovoltaic systems) may make it difficult to utilise the permittivity of the solvent.

Palladium reduction

The DFT simulations summarised in Figure 8 strongly suggest that electrons localise on the sulfone units, with a higher amount of electronic partial charge localising both on the dibenzo[b,d]thiophene sulfone monomer unit and on the SO₂ bridge head when compared to a fluorene (CH₂ bridge head) control. This is most likely due to the strong dipole that exists across the sulfone monomer unit⁴⁵. The model suggests that localisation is even more pronounced when the polymer sits in higher permittivity environments. Taken together, these observations suggest that the sulfone's 'intrinsic' electron acceptor nature is enhanced by its ability to attract water, with both the sulfone and its local environment contributing to the localisation effect.

The data in **Figure 7a** imply that the presence of the sulfone unit quickens the kinetics of electron transfer to the residual palladium cocatalyst on the microsecond timescale. The experimentally-estimated EA potentials for the series suggest that all 5 materials have a large driving force for proton reduction. This driving force is slightly smaller in FS5 than in FS1 (Fig**ure S-37**): the differences in electron extraction efficiency are therefore unlikely to be driven by differences in thermodynamics. Instead, the preferential localisation of the electron at the sulfone unit implies that electron transfer from polymer to palladium occurs at the sulfone unit. We propose that the electron transfer kinetics in Figure 7a are limited by the number of available sites where a sulfone unit and a palladium acceptor are in close proximity ("palladium coupled sulfone sites"). FS5 has more than 10 times as many sulfone units as FS1. For the same charge density, electrons can more easily find these sites in FS5 than in FS1, and so the electron transfer kinetics are faster in the sulfonerich polymers. To the best of our knowledge, this is the first direct experimental evidence of this concept.

This proposed mechanism is further corroborated by the fluence dependence of the electron kinetics in FS1 and FS5 films, which show that the electron kinetics are dictated by the ratio of electron density to sulfone density: FS1 is unable to efficiently extract electrons at all measured electron densities as it doesn't have enough palladium coupled sulfone transfer sites (Figure 7b). Electrons remain trapped in the polymer and exhibit longer lifetimes. By comparison, FS5 has enough palladium coupled sulfone units to efficiently extract charge at low electron densities. Photoinduced absorption measurements suggest that **FS5** operates in this high-transfer-efficiency regime when under hydrogen evolving conditions. At higher electron densities, electron extraction in FS1 and FS5 is similarly slow. The implied relative inability of the fluorene units to effectively transfer electrons to palladium suggests that designing polar donor-acceptor photocatalysts might be a worthwhile strategy in the future.

<u>Outlook</u>

The ability of the TEA to quickly separate photogenerated excitons (< 100 ps) is critical to the performance of these polymers. Materials that quench excitons via electron transfer to a metal co-catalyst, for example, often do so on the much slower nanosecond timescale: as a result,

the number of harvested excitons is much lower and the HERs for these single material photocatalysts are typically orders of magnitude smaller⁶¹. However, the positive correlation between microsecond electron density and HER in this series of materials (Figure 6) suggests that photocatalytic performance is still limited by the generation of electrons on the picosecond timescale. This implies that the primary advantage of the sulfone in these materials is its ability to encourage TEA oxidation. In the context of water splitting, where long-term system design involves phasing out sacrificial reagents, future studies should be wary of designing materials which may be optimising a sacrificial reaction rather than proton reduction. However, the sulfone unit does clearly also improve the kinetics of electron transfer to the palladium cocatalyst, and the high performance of sulfonerich materials is not solely tied to TEA oxidation: recent studies has demonstrated that sulfone-containing materials can be used without TEA either by loading them with IrO₂⁵⁷ or FeOOH⁶⁶, or by combining it in a Z-scheme with BiVO₄²⁴. Sulfone-containing polymers have also been shown to evolve hydrogen when using ascorbic acid as a scavenger^{39,40,43,44}.

This work also highlights the importance of characterising the solvent environment surrounding polymer photocatalysts. We have shown that the potentials of these materials are significantly affected by the presence of the polarisable medium they reside in. Therefore, simulations performed in vacuum may not always be a helpful estimation of the potentials that are relevant to catalysis. We suggest that future polymer photocatalyst design should consider that distortions in the composition of mixed-solvent systems close to the polymer may substantially affect redox reactions of interest. Further, in the systems presented here TEA oxidation is governed by the driving force from the EA* potential – the excitonic hole potential – and not from the IP/HOMO/oxidation potential. Designing materials based on their expected HOMO potentials rather than their EA* potentials may not always, therefore, lead to high performing systems. Finally, we note that characterising the relevant redox potentials in the appropriate dielectric media is important when designing any mixed-solvent photocatalyst system. This may include Z-schemes for water splitting involving

redox mediators as well as heterogeneous photocatalysis of other organic transformation reactions⁶⁷. In these systems, understanding the interaction between the mixed-solvent liquid environment and the photocatalyst will be critical.

Conclusions

We have presented a new series of processable materials in which the sulfone content in the polymer backbone is shown to correlate strongly with hydrogen evolution performance. This relationship holds for films as well as for dispersions, showing that differences in dispersion absorbance (i.e. particle size) are not the primary reason for differences in the HERs. Instead, we suggest two reasons to explain why these materials have outperformed most others over the last five years: the sulfone unit improves both the thermodynamics of hole transfer to the scavenger on the picosecond timescale and the kinetics of electron transfer to the metal co-catalyst on the microsecond timescale.

Overall, the correlation between HER and photogenerated electron density suggests that performance in this series of materials is limited by the generation of the electrons rather than their transfer to the water. This implies it is the polymers' ability to oxidise TEA which most affects their hydrogen evolution performance, even though this ability is linked to the polymers' hydrophilicities. Future photocatalyst design must be wary of optimising scavenger reactions that do not produce value products.

ASSOCIATED CONTENT

Supporting Information: General methods, NMR data, GPC data, PXRD data, UV-vis and PL spectra, hydrogen evolution experiments, SLS data, BET data, TGA data, contact angle measurements, DLS data, electrochemistry data, TAS data and global analysis methodology, FET data, MD and DFT calculations. This material is available free of charge via the Internet.

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Author Contributions

SAJH, JN and RSS conceptualized the study. Experimental data and subsequent analysis was carried out by SAJH (spectroscopy, electrochemistry, contact angles); RSS and DW (synthesis and characterisation); WYS and XS (OFETs). The ab-initio calculations were performed by DP and supervised by JN. JN, JD and AC supervised the study. The work was visualised and written by SAJH, RSS and JN. All authors have reviewed and given approval to the final version of the manuscript.

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