Time-Resolved Resonance Raman Spectroscopy of a Water Splitting Photocatalyst

Contact *acowan@liverpool.ac.uk*

C. Li

Stephenson Institute for Renewable Energy and Department of Chemistry, University of Liverpool, UK

O. Thwaites

Stephenson Institute for Renewable Energy and Department of Physics, University of Liverpool, UK

A. M. Gardner

Early Career Laser Laboratory, Stephenson Institute for Renewable Energy, and Department of Chemistry, University of Liverpool, UK

I. V. Sazanovich

Central Laser Facility
STFC Rutherford Appleton Laboratory, Harwell Campus, Didcot, UK

A. J. Cowan

Stephenson Institute for Renewable Energy and Department of Chemistry, University of Liverpool, UK

Introduction

Photocatalytic water splitting offers a sustainable way to produce green hydrogen, potentially at a low cost. Organic materials such as linear conjugated polymers have become a highly active field of research with photocatalytic activity for sacrificial hydrogen evolution [1], water oxidation [2] and even complete water splitting being recently reported [3,4].

A major attraction of polymer photocatalysts is that they are synthetically tunable and the community can draw from a wide existing literature of known light absorbing polymers from the organic photovoltaic community [5]. But to benefit from this synthetic flexibility it is important that structure function relationships are developed so that the synthetic chemists are able to design the next generation of photocatalysts in a rational manner. Transient (UV/Vis) absorption spectroscopy (TAS) has been used extensively to study charge carrier kinetics in organic photocatalysts [6] and we have recently summarized key studies and provided guidelines for experimentalists considering such works [7]. Transient absorption spectroscopy in the UV/Vis spectral window provides important information on the kinetics and electronic states but it is hard to identify the structural nature of intermediates [8]. Transient IR absorption spectroscopy is limited in application due to the presence of water in excess whilst conventional Raman spectroscopy can be hampered by the emissive nature of many polymers of interest.

Recently we demonstrated that Time-Resolved Resonance Raman (TR^3) using an optical Kerr gate could be used to measure the spectrum of an electron polaron of a commonly studied polymer P10 (poly(dibenzo-[*b,d*]thiophene sulfone) [9]. In that first study we were able to assess the mechanism of charge separation but the signal to noise ratio of spectra was relatively low and a limited spectral window was addressed (600-1450 cm^{-1}). Density functional calculations indicated that at higher frequencies strong Raman modes exist at ~1600 cm^{-1}, which are sensitive to local charge densities. Here we report new data over an expanded spectral window to confirm our original assignment. We also study a modified P10 polymer that contains an IrO$_x$ water oxidation co-catalyst. Recently P10-IrO$_x$ has been shown to be active for complete water splitting making its analysis of interest to the community. [4]

Results and discussion

P10 is a yellow polymer with an absorption onset at 400 nm. TR^3 using a Kerr gate at the ULTRA facility are measured in a manner previously reported [9]. Briefly here we measure the Raman scatter (Raman probe 630 nm, 2 ps, 4 mW, 10 kHz) of transient species formed following 400 nm excitation (2 ps, 5 mW, 10 kHz) of P10 and P10 with IrO$_x$ added. A 630 nm Raman probe is chosen as our past TAS UV/Vis measurements show this is on resonance

with the proposed electron polaron species [9]. As P10 is highly emissive a 2 ps 800 nm gating pulse (2.4 W at 10 kHz) is used to induce a transient optical anisotropy in a CS$_2$ Kerr medium. During the period of the laser pulse the Kerr gate is "opened" as incident linearly polarized light is rotated by 90° allowing to pass through a cross polarizer into the spectrometer. In this way photoluminescence contributions can be temporally gated out allowing for detection of the weaker Raman scatter.
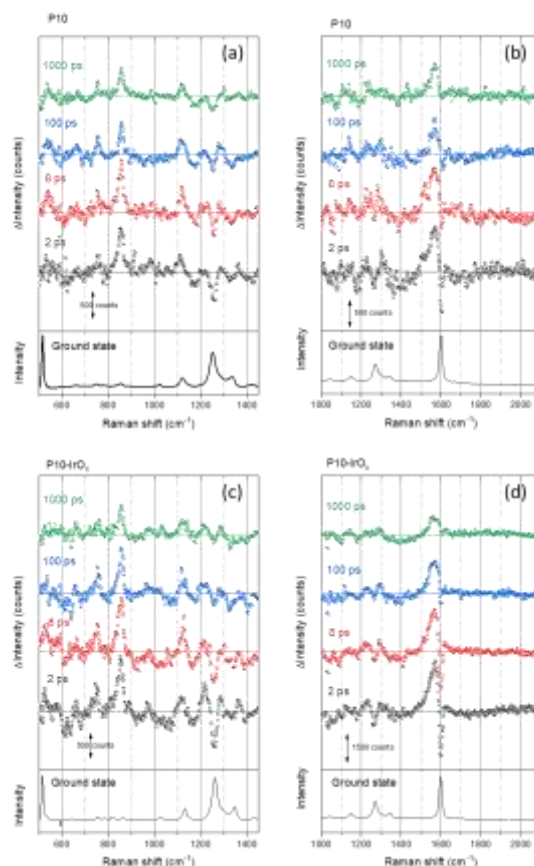

Figure 1. Kerr gated TR^3 spectra and ground state spectra (all 630 nm probe) recorded of P10 and P10-IrO$_x$ following 400 nm excitation.

Figure 1a shows that following 400 nm excitation of P10 bleaching of the ground state Raman bands occurs and new transient Raman bands appear at 988, 855 and 753cm^{-1} and in the region of 1210 and 1110 cm^{-1}. We have previously assigned these to an electron polaron or an exciton with polaronic character. In-line with our past DFT calculations (Figure 2) we can find that

extending the Raman probe window leads to detection of a new, intense and broad band, around 1570 cm^{-1}, figure 1b. Interestingly DFT calculations indicate that the hole will have a band, close to 1600 cm^{-1} which displays a negligible shift compared to the ground electronic state of P10 (Figure 2). The wavenumber of the transient ~1570 cm^{-1} band is in excellent agreement with that calculated for the P10 electron polaron, and of the Raman spectrum of P10 obtained under steady state illumination (Figure 2). [9] This allows conclusive assignment of the 630 nm band observed in our transient (UV/Vis) spectra to the electron polaron, in agreement with the long-lived nature of this transient signal in the presence of sacrificial electron donors.[1,3]
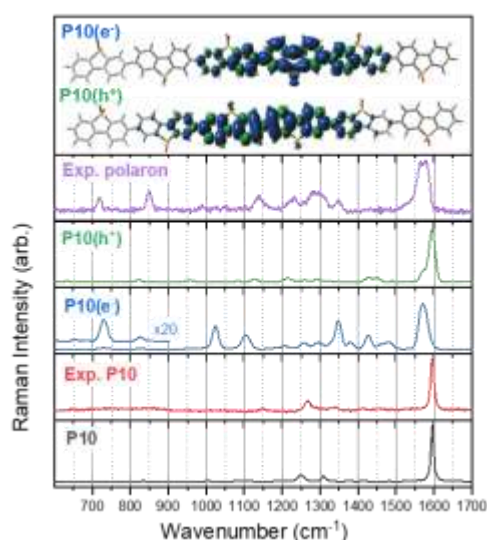

Figure 2. DFT calculated spectra and schematic of polaron localization on a P10 hexamer (theory level ωB97XD/cc-pVDZ). Also included is a Raman spectrum recorded under steady state illumination conditions which we assign to the P10 (electron) polaron. Figure reproduced from J. Phys. Chem. Lett. 2021, 12, 10899−10905.

Addition of IrO_x to P10 enables complete water splitting and using TAS we found that this was due to an increased yield of charge separation (electron polaron formation) due to fast hole transfer to the IrO_x catalyst (within 1-3 ps). [4] The TR[3] spectra of P10-IrO_x show similar behavior to the unmodified P10 further supporting the conclusion that the transient Raman spectra do not show a significant hole contribution. In both P10 and P10-IrO_x the electron polaron exists for > 1 ns indicating that electron transfer during hydrogen evolution is slower than this. From our past works it may be anticipated that the rate of electron polaron formation would increase when IrO_x is present but the process is shown elsewhere to occur on timescales similar to the instrument resolution here. [4] Interestingly oxidized IrO_x centres are known to have an absorption band at 650 nm, which overlaps with the Raman probe used here. Past Raman spectroelectrochemistry of IrO_x [10] shows that water splitting intermediates have Raman modes between 600-850 cm^{-1} but careful inspection of figure 1c and 1a shows no clear differences in this spectral region. The low IrO_x levels present (0.45 wt. %) make identifying bands of this species challenging in our current Raman experiment and future efforts will explore methods to increase the signal to noise ratio in this spectral region.

Conclusions

Here we have reported new TR[3] data for the linear polymer photocatalyst P10 and identified a new strong Raman mode of the P10 electron polaron. Interestingly experiments with P10 samples loaded with an IrO_x water oxidation catalyst also show clear evidence for long-lived electrons. The photoelectrons generated persist for >1 ns with no clear changes in the Raman spectra indicating that electron transfer to the catalytic sites of hydrogen evolution is slow. In the absence of sacrificial electron donors charge-recombination within the P10 polymer outcompetes electron transfer to catalytic sites. Future ns-ms TR[3] studies could explore this potential kinetic bottleneck, and how co-catalysts, such as the IrO_x studied here, which show remarkably fast h^+ transfer, providing mechanistic insight, which can be used to not only extend the polymer localized electron polaron lifetime, but provide routes for rationale design of complete water-splitting polymer based photocatalysts.

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