Twisted Carotenoids Do Not Support Efficient Intramolecular Singlet Fission in the Orange Carotenoid Protein

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Abstract

Singlet exciton fission is the spin-allowed generation of two triplet electronic excited states from a singlet state. Intramolecular singlet fission has been suggested to occur on individual carotenoid molecules within protein complexes, provided the conjugated backbone is twisted out-of-plane. However, this hypothesis has only been forwarded in protein complexes containing multiple carotenoids and bacteriochlorophylls in close contact. To test the hypothesis on twisted carotenoids in a 'minimal' one-carotenoid system, we study the orange carotenoid protein (OCP). OCP exists in two forms: in its orange form (OCPo), the single bound carotenoid is twisted, whereas in its red form (OCPr), the carotenoid is planar. To enable room-temperature spectroscopy on canthaxanthin-binding OCPo and OCPr without laser-induced photoconversion, we trap them in trehalose glass. Using transient absorption spectroscopy, we show that there is no evidence of long-lived triplet generation through intramolecular singlet fission, despite the canthaxanthin twist in OCPo.

TOC Graphic
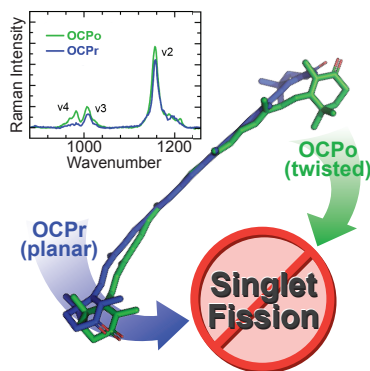
Singlet exciton fission (SF) is the conversion of a spin-0 singlet exciton[1] (or excited singlet state) into a pair of spin-1 triplet excitons.[2–5] This multiexciton generation process has been studied over the past decade primarily because of its promise to improve solar cell efficiency;[6–10] one high-energy photon creates two low-energy excited states, which could be harvested by conventional photovoltaic devices in a process minimizing energetic losses due to thermalization. SF has other potential applications for non-linear optics,[11–13] OLEDs[14] or even quantum technologies[15–18] by taking advantage of the virtue that a single photon creates a pair of spin-entangled quantum states. However, despite promising results,[19,20] practical applications have yet to be realized, in part due to the limited library of materials that undergo SF, none of which is yet ideal.[4,7]

In the search for other SF materials, the polyenes, 'class III' SF materials according to Smith and Michl's categorization,[2] form an intriguing materials class. In these materials, the lowest-lying singlet excited state (S_1) has dominant triplet-pair character, denoted $^1(TT)$ (see Refs.[3,21,22]) and thus demonstrates negligible one-photon absorption from the ground-state. S_1 is instead accessed by internal conversion following excitation to the strongly absorbing S_2 state.

This SF class includes conjugated polymers such as polydiacetylene,[23–25] poly(alkyl-thienylenevinylene),[26–28] a new generation of donor-acceptor singlet fission polymers,[29–32] quinoidal thiophenes,[33–37] carbene-based diradicaloids[38] and antiaromatic core-structured molecules.[39,40] The polyene family also includes the carotenoids, a large class of over 1000 naturally occurring molecules,[41,42] represented here by canthaxanthin (CAN) which forms the subject of this work (see structure in Fig. 1a).

In comparison with better-studied 'class I' SF materials,[2,46–49] mostly based on molecules such as pentacene[50,51] or tetracene,[52–55] SF in polyenes is less well understood. This is attributable in part to their complex manifold of low-lying triplet-pair states[56–58] and strong vibronic coupling,[59,60] and also partly due to the sensitivity of the photophysics to conjuga-
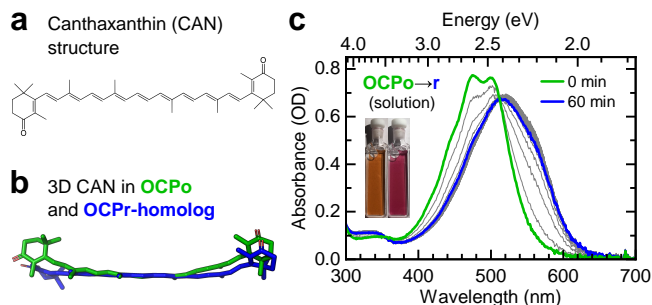
Figure 1: **The orange carotenoid protein (OCP) photoswitches from orange (OCPo) to red (OCPr) forms with different carotenoid conformations.** The OCP studied here binds a single CAN carotenoid whose skeletal structure is shown in panel (a). The bound CAN conformation depends on the OCP form, as shown in panel (b): when CAN is bound in OCPo (green, data from X-ray diffraction structure PDB 4XB5[43,44]) it has a twisted conformation; when bound in an OCPr N-terminal homolog (blue, data from X-ray diffraction structure of red carotenoid protein, RCP: PDB 4XB4[43,45]) it is planar. (c) In solution, OCPo converts to OCPr under white-light illumination (1600 µmol photon m^{-2} s^{-1}) resulting in a change in color (see inset) and absorbance spectrum (main panel). The spectra were taken in 1 min intervals under constant white-light illumination. In the dark, OCPr converts back to OCPo (see SI Fig. S1). The optical path length for solution measurements was 1 mm.

tion length and molecular geometry. In polyenes, the lowest-lying ^{1}(TT) state that makes up the dominant contribution of S_1[21,22,61,62] contains tightly-bound triplets that are unlikely to easily separate into free triplets,[63] without additional energy.[56]

Indeed, while intramolecular singlet fission (iSF) has been observed in a variety of long-chain polyenes in solution,[23–32] the triplet-pairs in polyenes decay rapidly (ps-ns) to the S_0 ground-state,[3] unlike the recently designed 'class I' iSF systems.[47–49,64] Even in carotenoid aggregates, where intermolecular SF occurs between neighboring chromophores,[65–70] the majority of triplet excited states decay to S_0 surprisingly quickly (within a nanosecond).[3,65,70] In isolated carotenoids in solution, the dominant deactivation channel from the photoexcited S_2 state is internal conversion to S_1. To our knowledge, there is no evidence that isolated carotenoids in solution demonstrate intramolecular SF (iSF).

Nevertheless, similarly to recent reports that torsion or twisting along a molecular backbone can allow both rapid iSF and formation of long-lived triplets in 'class I' SF materials,[48,64] iSF along a single *twisted* carotenoid chain to produce long-lived (µs) triplets has

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been suggested to occur in some photosynthetic light-harvesting complexes (LHCs).[71–75] In these systems, the protein binds the carotenoid so that it is constrained in a twisted geometry. This twist reportedly stabilizes a triplet at either end of the molecule.[71,73]

This hypothesis was initially proposed to explain the presence of SF in the light-harvesting antenna (LH1) from *Rhodospirillum rubrum*, because of the large intermolecular distances between neighboring carotenoids (>10 Å).[71] More recently, Yu *et al.*[73] observed a correlation between the presence of SF and the so-called ν_4 resonance Raman peak (~ 980 cm^{-1}) in LHCs (LH1-RC and LH2) from *Thermochromatium tepidum* and *Rhodobacter sphaeroides* 2.4.1. The intensity of ν_4 is related to carotenoid backbone twisting,[73,76] so this finding led to the conclusion that backbone twisting of the carotenoid is the 'structural determinant' that enables iSF.[73]

To test the hypothesis that singlet fission (SF) can occur along a single twisted carotenoid chain, we examine a protein that binds a single carotenoid: the orange carotenoid protein (OCP). In OCP the protein exists in two forms, orange and red (OCPo and OCPr) with the carotenoid in either a twisted or planar conformation, respectively (see Fig. 1). By studying both forms with the protein fixed in a trehalose-sucrose glass, we demonstrate that a twisted backbone is not sufficient to enable iSF in a protein-bound carotenoid. In light of recent work understanding magnetic field effects (MFEs) in SF systems,[77,78] we also discuss published reports of MFEs in LHCs from purple bacteria[79–84] and find that the reported MFEs are also inconsistent with iSF. Overall, we conclude that iSF is not supported on carotenoids bound to the OCP and unlikely to occur in LHCs.

In this study, the OCP was produced in *Escherichia (E.) coli* by virtue of a dual plasmid system comprised of pET28a with the *Synechocystis* sp. PCC 6803 OCP gene (slr1963) and pAC-CANTHipi, which provides near-100% accumulation of CAN.[85] Carotenoid-containing protein was isolated according to the method described in SI Section S1.1.

In solution, upon illumination with white light, the dark-adapted OCPo form undergoes a conformational switch to the OCPr form, with a concomitant red-shift of its steady-

state absorbance spectrum due to the effective conjugation length extension of the bound carotenoid,[76,86–88] see Fig. 1c. The change is reversible, with back-conversion from OCPr to OCPo occurring in the dark, see SI Fig. S1.

Previously published X-ray diffraction structures by Leverenz, Sutter, and co-workers[43] show that the conjugated backbone of the bound carotenoid is twisted out of the plane of conjugation in OCPo (PDB 4XB5[44]), while in OCPr N-terminal domain homologs such as red carotenoid protein (RCP) it is relatively planar (PDB 4XB4[45]). The difference between the two conformations of CAN is depicted in Fig. 1b using data from X-ray diffraction structures.[43] The different protein conformations containing a twisted and non-twisted form of CAN provide an uncomplicated model system to study the role of carotenoid geometry on iSF.

To avoid the problems associated with using spectroscopy to probe a light-activated conformational switch, we prevent the conformational change by trapping the protein in either its OCPo or OCPr conformations in a trehalose-sucrose glass as previously described.[70] This glass matrix prevents OCPo $\rightleftharpoons$ OCPr conversion, as demonstrated in Fig. 2(a,b), and allows us to probe each conformation in isolation at room temperature, without altering its conformation or photophysics.[89]

To confirm the twisted/planar conformations of CAN in OCPo/OCPr glass films, we turn to resonance Raman spectroscopy. As described above,[73,76] the presence of a so-called ν_4 peak at $\sim$980 cm^{-1} in the resonance Raman spectrum of carotenoids (due to out-of-plane C$-$H wagging modes[90]) is generally associated with a backbone twist of the carotenoid.[73,76] Fig. 2c shows the resonance Raman spectrum of OCPo (blue) and OCPr (green). Consistent with previous measurements on an echinenone-binding OCP,[76] we observe a larger twist-induced ν_4 peak in OCPo than in OCPr, confirming native geometry is maintained in trehalose-encapsulated OCPo and OCPr.

Having established that the CAN backbone is more twisted in OCPo than OCPr, we test the suggestion that such a twist is the determinant for iSF reactivity.[72,73,75] Picosecond
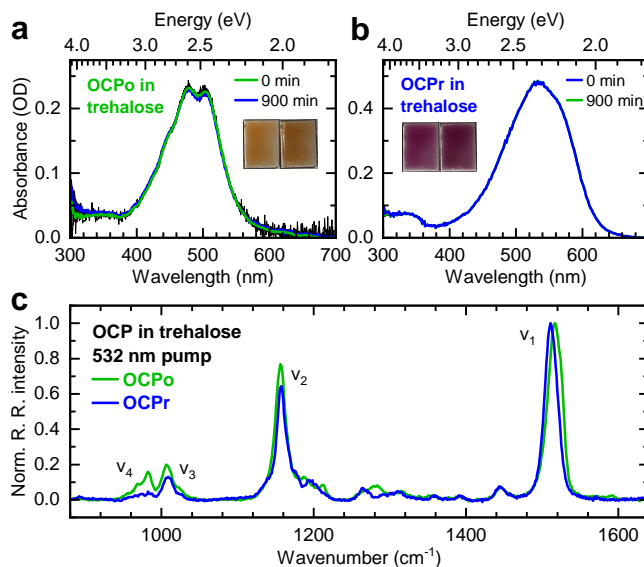
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Figure 2: **OCPo and OCPr trapped in trehalose glass films.** The steady-state absorbance spectra of the OCPo film (a) were taken in 1 min intervals under constant white-light illumination (1600 µmol photon m^{-2} s^{-1}) and the spectra of the OCPr film (b) were taken in 1 min intervals at 22 °C in darkness. No changes in spectra were observed over 900 min. (c) The resonance Raman spectra of OCPo (green) and OCPr (blue) films in trehalose glass show vibrational peaks typical of carotenoids, labelled following convention.[73,76] The spectra show a significant difference in the intensity of the ν_4 vibrational peak between OCPo and OCPr and a shift of the ν_1 peak. The Raman measurements were performed using a 532 nm laser. Data is averaged from two successive scans, and normalized to the peak ν_1 intensity.

transient absorption spectroscopy spectra and dynamics are shown in Figs. 3 and 4. Global lifetime analysis of the data is shown in SI Figs. S5 and S6, but simply from inspection of the raw data in Fig. 3, we see that all spectral features in both OCPo (green) and OCPr (blue) decay to <1% of the initial population within 30 ps. Importantly, we observe no obvious formation of SF-generated triplets. Instead both OCPo and OCPr broadly demonstrate the expected isolated carotenoid behavior characterized by rapid internal conversion from S_2 to S_1 (evidenced by the instrument-limited decay of an excited-state absorption (ESA) in the near infrared region), and subsequent decay of S_1-like states to the ground-state. Therefore, a twist along the carotenoid backbone is not sufficient to enable iSF.

The lack of intramolecular singlet fission (iSF) in the protein-twisted carotenoid in OCPo appears to question the currently accepted hypothesis that the determinant for intramolecular singlet fission (iSF) in carotenoids is a twist along its backbone.[73] Indeed,
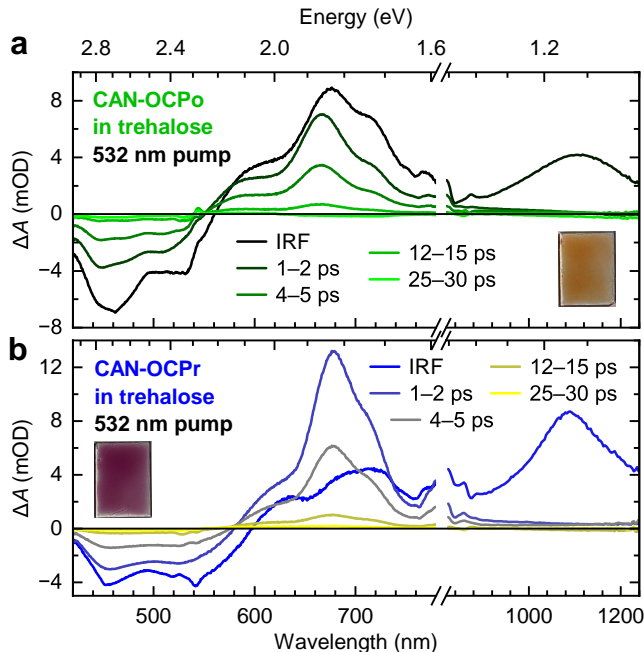
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Figure 3: **Transient absorption spectra of CAN-binding OCPo (a) and OCPr (b) trapped in trehalose films.** The spectral timeslices have been averaged between the times indicated in the legends and are consistent with an $S_2 \rightarrow S_1 \rightarrow S_0$ decay scheme in both cases, with no discernible long-lived features (see also global lifetime analysis of the data in SI Section S4.2). The films were excited with 532 nm, 5 kHz, $\sim$100 fs, 200 µJ cm^{-2} pump pulses.

while the carotenoid environment in OCP and photosynthetic complexes is very different, the carotenoids in OCPo and light-harvesting complexes (LHCs) seem to demonstrate similar backbone twists (see SI Fig. S2 and SI text for further comparison).[73] Therefore, the lack of iSF in OCPo suggests it would be worth revisiting the mechanism of SF in purple bacterial LHCs, particularly considering recent work on the nature of intermediate triplet-pair states involved in SF, as probed by magnetic-field-dependent measurements.[77,78] We therefore return to the original studies of SF in these LHC systems and discuss them in light of this recent work.[77,78]

Singlet fission in LHCs was first observed in a series of experiments that probed their magnetic field-dependent fluorescence.[79–81] Representative data for oxidized cells from *Rhodobacter sphaeroides* 2.4.1 from Ref.[79] are reproduced in Fig. 5; similar behavior has been reported for whole cells and isolated LHCs from several strains of purple bacteria.[79–81,84] The shape
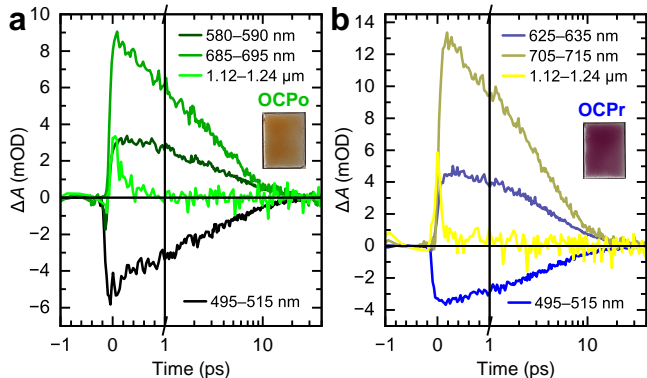
Figure 4: **Transient absorption dynamics of CAN-binding OCPo (a) and OCPr (b) in trehalose glass.** The dynamics have been averaged between the wavelengths indicated in the legends and demonstrate that no discernible long-lived features are seen. The films were excited with 532 nm, 5 kHz, ~100 fs, 200 µJ cm^{-2} pulses. Note the plots have a linear time-axis up to 1 ps, and subsequently logarithmic up to 40 ps.

of the magnetic field effect (MFE in Fig. 5), with an initial dip in fluorescence as the field increases from 0 to 40 mT, and then a rise in fluorescence to saturation beyond 100 mT, is a characteristic signature of SF.

This behavior is very well described by the kinetic model of SF by Johnson and Merrifield,[51,91–94] published in the 1960s and 70s. Recent work shows[77,78] that this low-field Merrifield-type MFE behavior can only be observed when the inter-triplet exchange interaction J is negligible, or more precisely when $J \ll D$,[95] where D is the intra-triplet dipolar zero-field splitting parameter. In carotenoids, and indeed most organic chromophores, D is relatively small, on the order of 4–10 µeV.[96,97] If J increases beyond D, the MFE has a different behavior, showing dips in fluorescence at much higher field strengths.[77,78,98,99] Therefore, to determine whether SF along a single carotenoid chain is capable of producing the measured MFEs in LHCs, we must estimate the values of J and D.

Before doing so we make several observations about the carotenoids involved in SF in LHCs of purple bacteria: (1) the $S_0 \rightarrow S_2$ absorbance spectra of the carotenoids in light-harvesting antenna are similar to their all-*trans* forms in organic solvent and depend sensitively on carotenoid conjugation length.[74,100] A full break in conjugation along the chain would lead to a dramatic blue-shift of the carotenoid absorption feature that is not observed.
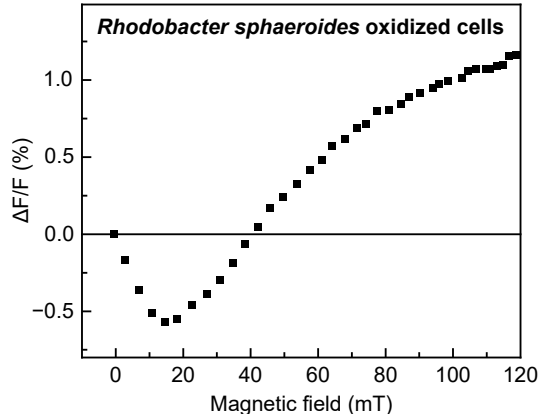
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Figure 5: **Magnetic field effect (MFE) of *Rhodobacter sphaeroides*.** Data reproduced from Ref.[79] and used with permission from Elsevier. The data is plotted as the normalized change in fluorescence $\Delta F/F$ (detected at 890 nm) as a function of the magnetic field strength upon 515 nm excitation in oxidized cells of *Rhodobacter sphaeroides* 2.4.1, with 1 mM $K_3Fe(CN)_6$ added. $A_{850-960} = 0.35$; optical path length 2 mm.

(2) The carotenoid $T_1{\to}T_n$ excited-state absorption feature seen in transient absorption of LHCs[71,72,74,75] is very similar to that seen in aggregated carotenoids of comparable conjugation lengths forming triplets by intermolecular SF.[65–67,70] The $T_1{\to}T_n$ feature is also sensitive to carotenoid conjugation length,[74,101,102] and a conjugation break along the chain would similarly lead to a blue-shift that is not observed. (3) The dipolar D and E parameters of the SF-generated triplets in LHCs from transient electron parametric resonance (EPR) spectroscopy are similar to full-chain triplet D and E parameters, rather than to their half-chain alternatives.[84] These observations suggest that the conjugation along the chain is not broken, even in the LHC antenna protein, and therefore that the triplets at either end of the chain maintain orbital overlap and, presumably, non-negligible J.

The exchange interaction, J, between triplets within a pair is equal to one sixth of the energy difference between the pure singlet triplet-pair, denoted $^1(TT)$, and the pure quintet, $^5(TT)$.[3] In addition, to first approximation, the energy of $^5(TT)$ is equal to twice the free triplet energy.[3,56,103] In carotenoids, as described above, the lowest energy singlet state (S_1) is predominantly a pure singlet $^1(TT)$ state. Therefore, comparison between twice the energy of a triplet on half a chain against the energy of S_1 on a full chain provides an indication of

the exchange interaction.

Recent high-level density matrix renormalization group (DMRG) calculations of the Pariser-Parr-Pople-Peierls Hamiltonian[56] calculate that $2 \times E(\mathrm{T}_1)$ for a half chain is higher in energy than S_1 ($\approx {}^1(\mathrm{TT})$) for a full chain at all conjugation lengths. This is supported by experimentally determined energies: for diphenylhexatriene with $N = 5$ conjugated double bonds, $2 \times E(\mathrm{T}_1) = 3.02 \pm 0.1$ eV,[101,104] while for spheroidene with twice the number of double bonds ($N = 10$), $E(\mathrm{S}_1) = 1.77$ eV.[105] This would indicate an exchange interaction of $J = 0.2$ eV, which is orders of magnitude larger than the dipolar parameter $D \sim 4\text{--}10$ µeV.[96,97] These energies indicate that the triplets within ${}^1(\mathrm{TT})$ should be strongly exchange coupled.

The triplets within a single carotenoid chain are therefore strongly exchange coupled ($J \gg D$), even in a protein that twists the carotenoid backbone,[73] as no breaks in conjugation along the carotenoid chain have been observed (*i.e.* no observable shifts in absorption spectra[74] or changes in dipolar D and E parameters[84]). Therefore, MFEs such as those reproduced in Fig. 5, that were the initial proof of SF in purple bacteria, cannot be explained with an intramolecular model of SF. We speculate that the mechanism for singlet fission in light-harvesting complexes must be intermolecular, possibly occurring *via* the neighboring bacteriochlorophyll *a* molecules in the protein complex.

We conclude that singlet fission (SF) to produce long-lived triplets does not occur along a single twisted carotenoid chain in the OCP and is unlikely to occur on a single carotenoid chain in purple bacterial light-harvesting complexes (LHCs), contrary to the current notion.[71–75] We conclude this because (1) immobilized OCPo – an uncomplicated, minimal carotenoprotein – shows similar twisted carotenoid geometry to LHCs, but shows no evidence of SF, and (2) the MFEs that identified SF in purple bacteria are irreconcilable with iSF without a significant break in conjugation (which is not observed in LHCs). These findings therefore call into question the mechanism of SF that is observed in LHCs.

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Author contributions: G.A.S. conceived the study. G.A.S., J.P.P., S.W. and J.C. designed the experiments. G.A.S., M.S.P. and A.H. prepared protein samples under the supervision of M.P.J. and C.N.H. Absorbance measurements were performed by G.A.S. Resonance Raman measurements were performed by H.K.H.L. under the supervision of W.C.T. Transient absorption was conducted by J.P.P. and S.W. within the Lord Porter Laser Facility, with D.C. providing facility management. J.P.P. and G.A.S. analyzed the data. J.P.P., G.A.S. and J.C. wrote the manuscript and prepared the figures with input from all authors.

Supporting Information Available

- **Supplementary information (SI):** Experimental methods are detailed, including canthaxanthin-binding OCP production, OCPo and OCPr in sugar glasses preparation, spectroscopic setups, and data analysis procedures. A figure showing backconversion of solution OCPr to OCPo in the dark is included. A figure comparing the resonance

Raman spectra of OCPo and OCPr of this work against previously published spectra of purple bacterial LHCs is included and discussed. A resonance Raman spectrum of blank trehalose is included. A figure showing a transient absorption pump spectrum is included. The results of global lifetime analysis on the transient absorption data is detailed.

- Data will be available on the University of Sheffield's repository, ORDA, once the paper has been accepted for publication.

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