



FRONTIERS ARTICLE

Intramolecular radiationless transitions dominate exciton relaxation dynamics



Chanelle C. Jumper^a, Jessica M. Anna^a, Anna Stradomska^b, Juleon Schins^c, Mykhaylo Myahkostupov^d, Valentina Prusakova^e, Daniel G. Oblinsky^a, Felix N. Castellano^d, Jasper Knoester^b, Gregory D. Scholes^{a,*}

^a Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada

^b Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

^c Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

^d Department of Chemistry, North Carolina State University, Raleigh, NC 27695, USA

^e Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403, USA

ARTICLE INFO

Article history:

Received 31 January 2014

In final form 4 March 2014

Available online 12 March 2014

ABSTRACT

Reports of long-lived exciton coherences have lead researchers to expect that model dimer systems inevitably generate exciton superposition states observable by two-dimensional electronic spectroscopy. Here we report a careful photophysical characterization of a model dimer system, a diacetylene-linked perylene-3,4,9,10-tetracarboxylic diimide dimer to examine that issue. The absorption spectrum of the dimer shows molecular exciton splitting, indicating that excitation is delocalized. The assignment of exciton states was supported by other photophysical measurements as well as theoretical calculations. Ultrafast two-dimensional electronic spectroscopy was employed to identify and characterize excitonic and vibrational features, as they evolve over time. Population transfer between the two exciton states is found to happen in <50 fs, thus preventing the sustainment of exciton coherences. We show that such fast radiationless relaxation cannot be explained by coupling to a solvent spectral density and is therefore missed by standard approaches such as Redfield theory and the hierarchical equations of motion.

© 2014 Published by Elsevier B.V.

1. Introduction

The flow of energy through the exciton manifolds of natural light harvesting complexes and synthetic molecular assemblies after photoexcitation is a topic of fervent research involving a variety of state-of-the-art experimental and theoretical approaches [1–23]. One of the motivations for these studies is to pursue an understanding of the underlying molecular level mechanisms that govern the energy transfer dynamics in photosynthetic light harvesting complexes. The initial light harvesting stage of photosynthesis involves the transfer of excitation energy across chromophores before reaching a reaction center for charge separation and ultimately leading to energy storage. This process often involves transfer of excitation among excitonically coupled chromophores. Gaining a deeper understanding of the details of energy transfer and the role of molecular excitons supports the ultimate goal of improving the design and development of artificial solar energy-driven technologies [24–29].

In photosynthesis, the protein structure determines the pigment orientations, which are often found in pairs of electronically

coupled dimers, as well as higher order assemblies. Generalized Förster theory [30–33] or modified Redfield theory [34–38] is the currently accepted framework, which describes a ‘hopping’ type energy transfer occurring between coherently delocalized donor and acceptor states. Recent studies have suggested that additional coherent superpositions between donor and acceptor exciton states in several photosynthetic complexes [39–47] may play a role in coherent light harvesting [7,8]. As a result, it is sometimes assumed that such coherences should be easily demonstrated in isolated dimer systems of the corresponding coupling regime in a solvent environment. However, ultrafast exciton relaxation observed for various systems, including the chlorosome of green sulfur bacteria [48] and protein-supported chromophoric systems [49–54], may compete with the sustenance of exciton superposition states. It is the balance of these two processes that we wish to pursue in this Letter.

To obtain a better understanding of these interdependent photophysical processes, both theoretical [55–57] and experimental studies [57–61] began to address ideal model systems. For a photosynthetic exciton, the ideal system would comprise a pair of rigidly linked chromophores in an appropriate solvent environment, where the electronic couplings between the chromophoric units and the surrounding environment are comparable. A study

* Corresponding author.

E-mail address: greg.scholes@utoronto.ca (G.D. Scholes).

of such a heterodimeric system has recently been reported and evidence for long-lived electronic coherences was uncovered [60]. However, the ultrafast relaxation among excitonic states has also been observed in solvent suspended homodimers [61–63]. In the present contribution, we employ ultrafast two-dimensional electronic spectroscopy (2DES) to explore the photophysics of a model perylenediimide (PDI) homodimer and its corresponding monomer in order to understand the interplay between electronic coherences and energy equilibration.

2DES is a significant advance of pump-probe spectroscopy for elucidating ultrafast dynamics, including signatures of coherences, in complex condensed phase systems [39,64–68]. 2DES spreads the information contained in a pump-probe spectrum over two frequency axes and the resulting spectra can be thought of as frequency-frequency correlation map. The time dependent amplitude changes of the peaks within this map give detailed information on coherences and energy flow through the system. Coherences are flagged by the modulation of peaks at the difference frequency of the states in superposition. Careful metrics are additionally applied to characterize the coherence as either vibrational or electronic in character [46,69]. Population transfer between states is signified by a decrease in amplitude of the diagonal peak of the first state and a corresponding increase in amplitude of the off-diagonal peak located at the energy coordinates of the two states in question [56].

In this Letter, our aim is to examine a simple and carefully characterized model dimer system in order to compare the competition between excitonic coherences and population relaxation. Thus, we use a combination of 2DES, steady-state measurements, and theoretical modeling to carefully characterize our model dimer system, a homodimer consisting of two strongly coupled perylenediimide units linked by a diacetylene bridge [70]. This dimer has clear exciton splitting determined by the angle between the two transition dipole moments, collinear with the long C_2 axis of each (unsubstituted) monomeric unit [71,72]. In combination with intermediate-strength coupling to high-frequency vibrations, this PDI dimer is a good candidate for the study of exciton dynamics from coherences to population relaxation.

The manuscript is organized as follows. In the first part, we describe a systematic experimental characterization of the dimer, including the assignment of the linear spectrum and confirmation of the presence of molecular exciton states. This is further corroborated by calculations used to characterize ground and excited states of the dimer and reproduce the linear spectrum. In the second part, we explore the ultrafast exciton dynamics following photoexcitation via 2DES. These reveal ultrafast dephasing of excitonic superposition states dominated by an ultrafast population relaxation on the sub-50 fs timescale. This observation suggests that the dynamics are controlled by a passage through a conical intersection, which results in the rapid deactivation of the upper exciton population.

2. Experimental

2.1. Synthesis

The synthesis of the PDI monomer and dimer has been described elsewhere [70].

2.2. Sample preparation for room temperature measurements

PDI monomer or PDI dimer were individually diluted in dichloromethane (DCM) to an optical density (OD) at the absorption maximum of 0.24 for absorption experiments (/1 cm) and for non-linear two-dimensional spectroscopy (/1 mm), and to an OD of <0.05 for fluorescence experiments (/1 cm).

2.3. Sample preparation for measurements at 10 K

Dilute solutions of PDI monomer or dimer were mixed with a DCM solution of the matrix polymer poly(ethyl methacrylate). The solution was dispensed by pipette onto microscope coverslips with a final OD of <0.05. The thickness of the film was on the order of ~ 100 nm.

2.4. Steady-state spectroscopy

Room temperature absorption spectra were recorded using a CARY 100 Bio UV–visible spectrophotometer. Fluorescence emission and excitation spectra were recorded on a Fluorolog-3 (Horiba) spectrometer in a 90° mode, with a xenon arc light source and an R928 photomultiplier tube. To obtain room temperature two-dimensional photoluminescence (2DPL), the emission wavelength was stepped by 2 nm from 550 to 700 nm while recording excitation scans from 400 to 600 nm by 1 nm steps. The resulting data were combined in a two-dimensional plot. To obtain 2DPL at 10 K, prepared PEMA films containing PDI monomer or dimer were mounted at a 45° angle and cooled to 10 K with a Cryodyne[®] model 22C He cryostat (CTI-Cryogenics). Emission wavelength was stepped by 1 nm in 500–700 nm spectral window, while scanning the excitation as above, generating a corresponding 2D map. To obtain anisotropy data, excitation scans were recorded at four polarization combinations: VV, HH, VH, HV with respect to emission set to 600 nm, the maximum of the $S_1 \rightarrow S_0^{(0-0)}$ transition. Anisotropy values were calculated as follows [73]:

$$\langle r \rangle = \frac{I_{VV} - G * I_{VH}}{I_{VV} + 2 * G * I_{VH}} \quad (1)$$

where the 'G factor', which normalizes a polarization-dependent instrument response, is defined as:

$$G = \frac{I_{HV}}{I_{HH}} \quad (2)$$

Data were recorded with excitation and emission slits set to a 2.5 nm bandpass.

2.5. Time-resolved fluorescence and quantum yield measurements

Photoluminescence lifetimes were measured using the gated second-harmonic (4 MHz repetition rate, ~ 1 nJ/pulse) output of a tunable ultrafast Ti-sapphire oscillator (Coherent, ~ 120 fs) as an excitation source and a time-correlated single photon counting (TCSPC) detection system (LifeSpec II, Edinburgh Instruments, ~ 150 ps IRF). The excited state lifetimes were obtained from the first-order decay fit of single wavelength emission transients using Origin 8.0 software. Fluorescence quantum yields were measured using an absolute PL quantum yield spectrometer (C11347, Hamamatsu).

2.6. Coherent two-dimensional electronic spectroscopy

The experimental set-up has been described in detail elsewhere [46]. Briefly, three incoming pulses (Supplemental Figure S2) arrive at the sample position arranged in a box geometry, leading to a signal emission in the background free direction determined by the wavevectors of the incoming fields [64]. A fourth electric field, the local oscillator (E_{LO}), is combined with the signal such that both real and imaginary components can be extracted through spectral interferometry. According to the box geometry, one phase-matching condition leads to the generation of a non-linear spectroscopic signal occurring in the direction of the local oscillator. Two time orderings give rise to the rephasing and nonrephasing spectra with wavevector combinations as follows: $k_{s, R} = -k_1 + k_2 + k_3$ and

Download English Version:

<https://daneshyari.com/en/article/5380972>

Download Persian Version:

<https://daneshyari.com/article/5380972>

[Daneshyari.com](https://daneshyari.com)