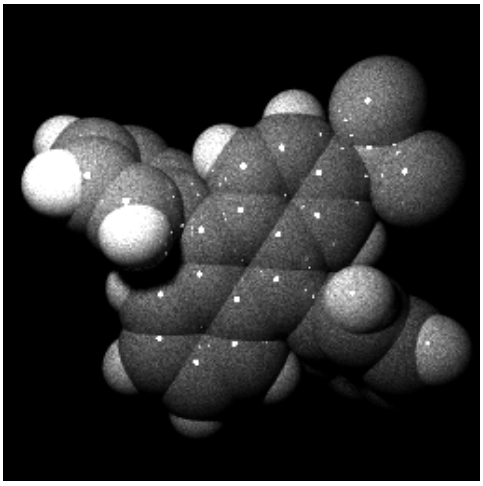

PHOTON UPCONVERSION IN AN IONIC LIQUID: A PRESSURE STUDY

INTERNSHIP REPORT

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Abstract

Photon upconversion presents a way to circumvent the Shockley-Queisser limit for solar cells by allowing sub-bandgap photons to be used for power generation. An ionic liquid capable of photon upconversion by triplet-triplet annihilation was characterized using spectroscopy, magnetic fields and hydrostatic pressure. The system was found to be more strongly electronically coupled under pressure, reflecting decreased intermolecular distances. The response of the upconversion to a magnetic field was surprisingly solid-like. The threshold intensity of upconversion was determined as $18.0\,\mathrm{mW\,cm^{-2}}$. Since efforts to determine the dependence of the threshold intensity on pressure were inconclusive, suggestions are given for further research.

Acknowledgements

I am indebted to my supervisor, Bruno Ehrler. Without him this project would not have been possible and he worked hard to make my internship at AMOLF as great as it could be. I also wish to thank TianYi Wang, who acted as my daily supervisor, for showing me the ropes in the lab with numerous techniques that were unknown to me. I wish to thank Albert Polman's group also for letting me use their cooled spectrometer and especially Nick Schilder for helping me personally with it. Similarly I wish to thank Jenny Kontoleta for sharing her green laser setup with me and for being a delightful person to work with. Special thanks to Shota Hisamitsu, Nobuhiro Yanai and Nobuo Kimizuka from Kyushu University are in order for kindly providing an extraordinary material as the subject of this study. Finally I want to thank my parents, who were always there for me throughout my adventure of an internship.

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Chapter 1

Introduction

1.1 Solar cells and the Shockley-Queisser limit

The world consumes vast amounts of energy, both as chemical fuels and electricity. The majority of this electricity is produced from fossil fuels, causing carbon dioxide emissions that are increasing global temperatures via the greenhouse effect. To limit global temperature rise while global energy demand still increases, a transition to more sustainable sources of energy is of vital importance. Photovoltaic technology offers the possibility to directly convert sunlight into electricity with no carbon dioxide emissions. The amount of solar power that impinges on the Earth is far greater than human power consumption [1]. The aim of solar cell research is to reduce the cost per watt and increase the power output per square meter of solar panels beyond what is available today, so that solar energy can play a larger role in global energy production.

In a photovoltaic device, light energy is converted into electrical energy. This conversion happens via the promotion of electrons from the valence band of a semiconductor to the conduction band by the absorption of photons [1]. By the increase in energy of the electrons, a voltage is generated. The energy range between the bands is termed the bandgap and represents energies that are forbidden. The presence of these forbidden states prevents excited electrons from decaying to the valence band immediately.

The efficiency of the photovoltaic process is bound by the detailed balance limit or Shockley-Queisser limit, which takes various thermodynamic effects, such as blackbody radiation from the device and radiative recombination, into account [2]. However the majority of energy losses are spectral losses: sunlight consists of a continuous spectrum and photons will either have energy below the bandgap and be entirely unable to excite an electron, or have energy above the bandgap and excite an electron while the excess energy is lost as heat.

Various techniques exist to combat these spectral losses. Perhaps the most widespread is the multijunction or tandem cell, where multiple photovoltaic junctions with different bandgaps are stacked together. By absorbing each photon in the widest bandgap that will accept it, spectral losses are reduced with each junction that is added.

1.2 Upconversion by triplet-triplet annihilation

Another technique to reduce spectral losses is photon upconversion. Here the aim is to convert long wavelength light to shorter wavelengths and thus allow sub-bandgap photons to be used for power generation, which is achieved by combining the energy from two photons into one in a specially engineered material. There are various processes that can achieve upconversion. One of these is frequency doubling in nonlinear optical crystals [3], which is best understood as a wave phenomenon and requires coherent light. It is useful for attaining certain laser wavelengths but cannot upconvert incoherent sunlight. Two-photon absorption in the f orbitals of lanthanides [4] is another possible upconversion route. As the name implies, the atom absorbs two photons at once and can then re-emit the energy as a single upconverted photon. Two-photon absorption does not require coherent light but works best at very high light intensities. Here we will focus on upconversion by triplet-triplet annihilation (TTA) in organic materials, which can upconvert incoherent light even at low intensities.

1.2.1 Singlet and triplet excited states in molecules

Unlike the energy bands of semiconductors like silicon, molecules have electron orbitals with discrete allowed energy values [5]. These orbitals can each be occupied by up to two electrons at a time. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) respectively correspond to the valence and conduction band of semiconductors. A photon can excite an electron from the HOMO to the LUMO, but the excitation remains localized to the same molecule.

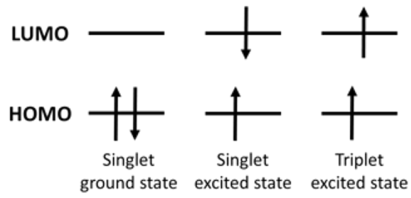


Figure 1.1: Different electronic states

Owing to their proximity, the spin orientation of the excited electron and the electron left behind (or equivalently, the electron hole) affects the properties of the exciton (electron-hole pair). While a single electron has one of two possible spin orientation states, for two electrons there are four distinct possible wavefunctions. One of them is antisymmetric under particle exchange, that is to say the sign of the wavefunction flips when the two electrons are swapped and is called the singlet state. The other three wavefunctions are symmetric under particle exchange and are called triplet states.

The Pauli exclusion principle dictates that two electrons can only occupy the same orbital if they form a spin singlet, so that the ground state of a molecule is usually a singlet. Because absorption and emission of light leave the electron spin unchanged, rapid photochemical reactions mostly involve singlet excited states.

1.2.2 Upconversion kinetics

The process of upconversion by TTA begins with the absorption of photons by a sensitizer species, initially exciting it to a singlet excited state. This species contains one or more atoms with highly charged nuclei that cause a strong spin-orbit coupling. The intrinsic spin

of the electron and its orbit around the nuclei both induce a magnetic dipole. The parallel and antiparallel orientations of these minute magnets have slightly different energies. The difference is proportional to the fourth power of the nuclear charge. A consequence of the spin-orbit coupling is a mixing of the singlet and triplet state, so that transitions between the two manifolds (intersystem crossing) become allowed. This can be understood as the transfer of a quantum of angular momentum from an electron's spin to its orbit. Through intersystem crossing (ISC in figure 1.2), the sensitizer species can produce triplet excitons from light.

These triplets are then transferred to an emitter species. Exchange of triplet excitons happens through the Dexter energy transfer mechanism, which involves the simultaneous transfer of the electron and hole from one species to another (TET in figure 1.2). The process is dependent on wavefunction overlap between molecules and thus the transfer rate decreases exponentially with distance. Because there is no strong spin-orbit coupling in the emitter, triplet excitons cannot easily decay to the ground state.

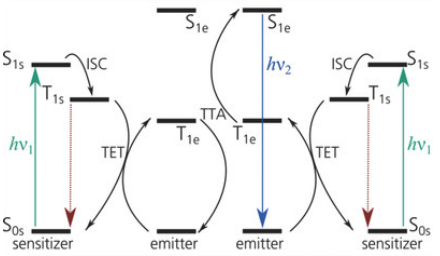


Figure 1.2: The various processes involved in upconversion by TTA, including intersystem crossing (ISC) and triplet energy transfer (TET). Image taken from [6].

Through Dexter transfer of triplets between emitters, and molecular diffusion of emitters if the system is in solution, two triplet excitons can collide. The emitter molecule is selected so that the energy of the first triplet state is approximately half that of the first singlet excited state. The electrons in two triplet excitons can rearrange to one singlet exciton and one singlet ground state while conserving total spin angular momentum, so the combination is spin-allowed as well as energetically favorable. The rearrangement proceeds through an intermediate bound pair of triplets [7], often denoted (TT) and termed a multiexciton. With the radiative decay of the resultant singlet exciton, emitting a higher-energy photon, the triplet-triplet annihilation is complete and photon upconversion is achieved.

The process of upconversion by TTA is characterized by two regimes [8]. At low light intensities and thus triplet concentrations, the probability that two triplets will meet and annihilate is a quadratic function of the triplet concentration, since the probability that a given triplet will collide with another before decaying increases linearly with triplet concentration. At higher intensities, the time before colliding with another triplet is significantly shorter than the triplet lifetime and the probability that a given triplet is upconverted no longer depends on the concentration. The rate law becomes first-order in this case, a linear function of the triplet concentration. Any loss mechanisms that affect either the triplet or the multiexciton can decrease the triplet lifetime or quantum efficiency, but only alter the overall quadratic and linear behavior if the loss mechanisms are concentration dependent.

While the transition between these two regimes is not sharp but rather continuous, a value known as the threshold intensity can be found by extrapolating the quadratic and linear regimes and finding the intersection point. The more desirable regime for operation in an upconverting solar cell is the high-intensity regime since the system is at its peak quan-

tum efficiency then. In particular, the threshold intensity should be lower than the intensity of sunlight in the spectral range where the upconverter operates. As such, the threshold intensity and linear quantum efficiency are important figures of merit for upconversion systems. When a system is in the quadratic regime, the quantum efficiency is sometimes divided by the excitation irradiance to provide a figure of merit that does not depend on the irradiance [6].

1.2.3 The nature of the multiexciton

The triplet and singlet excitons are named after their spin multiplicity, the number of distinct configurations or states that make up the excitation. When two triplets collide, there are therefore nine different scenarios for the individual wavefunctions of the electrons involved. It should be noted that the nine spin states of the multiexciton are not pure quantum states and will therefore interconvert when not observed, in a time-dependent way that is described by a probability matrix.

One of the nine states is the desired overall singlet. Three more form an overall triplet, and the remaining five states form a spin quintet. The overall triplet can decay to a (singlet) ground state and a triplet exciton. Because two triplets formed the multiexciton, this is a loss mechanism for upconversion as one exciton is effectively consumed. Because a quintet state requires at least two electrons to be excited, there are no lower-energy quintet states to which it can decay. The energies of these nine configurations as well as the mixing probability matrix depends strongly on the relative orientation of the colliding emitter molecules and thus on the liquid or solid state of the system. Since triplets and quintets have a net magnetic moment, a process such as upconversion by TTA is also sensitive to external magnetic fields.

1.2.4 Current research into upconversion

Many TTA upconversion systems have been prepared and characterized in recent years [6]. Various species are used as emitters and sensitizers, with the pairing of emitter diphenylanthracene (DPA) and sensitizer platinum or palladium octaethylporphyrin (PtOEP, PdOEP) being a commonly used model system. These chemicals are dissolved in a solvent, often toluene, to allow molecular diffusion to bring triplets together. The PtOEP absorption peak lies around $533\,\mathrm{nm}$ so that it can be excited with a readily available green laser [9], and the system has favorable triplet and singlet energy levels to strongly drive upconversion. Because a decrease in energy is employed to drive each step, the emission wavelength of around $450\,\mathrm{nm}$ is far from halved compared to the absorbed radiation.

While much-used in upconversion research, the DPA-PtOEP pairing has properties that make it undesirable for practical application in solar cells. Especially in combination with photovoltaic materials such as silicon and gallium arsenide that are optimal for single-junction operation and thus have narrow bandgaps, the photon energies involved in upconversion are too high. To remedy the mismatch, work has been done on upconverting molecules with more extended pi systems that can efficiently upconvert red and even infrared radiation [10]. One issue with these inevitably larger molecules is their lower solubility in liquids like toluene.

The generally liquid state of TTA upconversion systems is considered problematic for applications in solar cells that have to withstand outdoor conditions for decades. A solid-state system, where triplets would diffuse by Dexter energy transfer alone, is more desirable for solar cells, where it could be added as a solid film behind a transparent cell to absorb transmitted photons and be covered with a reflector to ensure all the upconverted light is directed back toward the solar cell. Various solid-state upconversion systems have been described [11–13].

A number of figures of merit have been used for TTA upconversion systems, all of which are subject to constant improvement. The quantum efficiency in the linear regime is perhaps the most commonly stated of these and the current state of the art is at least $13.6\,\%$ [14], achieved with a nonporphyrin platinum complex sensitizer and DPA emitter. A quantum efficiency of $50\,\%$ is the theoretical maximum on account of two photons being required to produce one upconverted photon. Confusingly, $100\,\%$ is sometimes taken as the maximum and the reported numbers doubled compared to the former convention. The total energy efficiency of upconversion is not typically reported, but is around $7.1\,\%$ for the aforementioned platinum complex system and around $8.3\,\%$ for a good DPA-PtOEP system in toluene [15]. The threshold intensity is also important. In particular, it must be low enough to allow effective upconversion of direct sunlight, and preferably lower intensity illumination also. Systems have been reported with threshold intensities as low as $3.0\,\mathrm{mW\,cm^{-2}}$ [16]. Comparing this with the solar irradiance of $100\,\mathrm{mW\,cm^{-2}}$ should be done with caution as only a small part of the solar spectrum will excite the system. Upconversion systems are also being combined with experimental solar cells and compared by power conversion efficiency and relative photocurrent enhancement of the upconversion process [17].

Besides the potential application in solar cells, upconversion systems also see use in light-activated medicine. Human tissue strongly absorbs and scatters light, but wavelengths between 650 and $1350\,\mathrm{nm}$ are less affected in what is called the near-infrared window. Thus, light can be used more effectively for targeted drug delivery when red or infrared light beams are used and upconverted *in situ* to radiation with high enough energy to effect chemical changes in the drug, activating it. These upconverting systems must be encapsulated in a biocompatible way and protected from the molecular oxygen and reactive oxygen species that are present in the body [18, 19].

1.3 An upconverting ionic liquid

In 2015, Hisamitsu et al. [16] reported the synthesis of an upconversion system based on an ionic liquid, with the diphenylanthracene sulfonate anion as the emitter. Because the DPA chromophore is bound covalently to the negatively charged sulfonate group, it has a strong energetic incentive to remain dispersed in the liquid. The counterion is a tetraalkylphosphonium structure whose tails act to keep the system liquid at room temperature. PtOEP is used

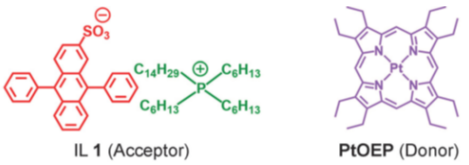


Figure 1.3: Molecules present in the ionic liquid

as the sensitizer and is dissolved in the liquid at a low concentration ($0.01\,\mathrm{mol}\,\%$). This approach circumvents problems with solubility limits of the emitter, which is usually a significant limiting factor. While not strictly a solid, the ionic liquid is highly viscous ($2760\,\mathrm{Pa\,s}$) and might be considered pseudo-solid state and a realistic form factor for a practical upconversion system. Considering the high viscosity and consequently slow molecular diffusion, Dexter transfer is the dominant mechanism in triplet diffusion, as was demonstrated by operating the system in frozen form.

The threshold intensity was remarkably low at $3.0\,\mathrm{mW\,cm^{-2}}$. The low value was proposed to be due to the formation of a bicontinuous structure in the liquid, with the alkyl tails of the cations and the DPA chromophores of the anions forming interlocking, contiguous structures. This densely packed arrangement of emitters would allow for easy transfer of triplets between adjacent molecules, while the continuous structure ensures that all triplets can reach one another. The driving force for the assembly of this structure would be the difference in cohesive energy between the aromatic diphenylanthracene and aliphatic alkyl chains, as well as the electrostatic attraction of the ions.

1.4 Motivation for this work

Much is still unknown about the upconversion in the ionic liquid. Its general characteristics are intermediate between solid-state and solution systems so that the operation mechanisms are not known exactly; research is needed especially into triplet diffusion in the liquid and the way it affects the TTA kinetics. Further confirmation of the proposed bicontinuous ordering in the liquid would be quite relevant to upconversion research, to validate and guide the further use of such self-assembled structures for upconversion.

To investigate the influence of intermolecular distances on processes such as triplet energy transfer from the sensitizer to the emitter and between emitters, one possible course of action is to alter the chemical structure of the system under study [20–22]. While effective, this approach requires the time-consuming synthesis and characterization of an entirely new compound. If multiple distances are to be measured then different compounds with different spacers are needed. With sufficiently high hydrostatic pressure, condensed matter can be compressed by several per cent, enough to measurably alter the optical, excitonic and electronic properties of the material [23–25].

In this work, the characteristics and upconversion photoluminescence (UCPL) of the very same ionic liquid as in ref. [16], of which samples were kindly provided by Kyushu University, are studied as a function of hydrostatic pressure up to $400\,\mathrm{MPa}$. The effect of a magnetic field on the upconversion process is also studied as a further characterization. An increase in magnetic field strength is predicted to affect the multiexciton state in a way that decreases the upconversion efficiency, but differently for solid-state and solution systems [26]. Of particular interest is the pressure dependence of the threshold intensity, which is also measured. This intensity is expected to decrease as the molecules are forced into closer proximity, thus enhancing triplet diffusion by Dexter transfer and allowing triplets to travel further before decaying.

Chapter 2

Methods

2.1 Sample preparation & Pressure application

All substrates were $15 \times 15\ \mathrm{mm}$ fused quartz slides that were sonicated in deionized water and detergent for 15 minutes, washed with deionized water, sonicated in acetone for 15 minutes, washed with isopropanol, and treated with oxygen plasma for 10 minutes. All cover slips used were $15 \times 15\ \mathrm{mm}$ borosilicate glass slips and were cleaned in the same manner. Sample preparation was done under an inert atmosphere.

For the UV-vis absorption measurements, the ionic liquid was used as received from Kyushu University and placed between two substrates using a needle. The thickness was reduced by pressing the slides together with $100\ \mathrm{N}$ of force for three hours, at a temperature of $70\ ^{\circ}\mathrm{C}$ under inert atmosphere. This approach was necessary due to dilution not being an option for studying the properties of the neat liquid. Both the pure ionic liquid and the ionic liquid with PtOEP were prepared this way.

For the magnetic field dependent upconversion photoluminescence (UCPL) measurements, the ionic liquid sample with PtOEP was used as received from Kyushu University. A droplet was applied to a substrate using a needle and covered with a cover glass.

For the pressure and intensity dependent UCPL, the sample of ionic liquid with PtOEP was redissolved in dichloromethane under inert atmosphere and dried by heating to $70\ ^{\circ}\mathrm{C}$ for 3 hours under vacuum before use, to avoid aggregation of the PtOEP. A droplet of the sample was then applied to a substrate using a needle and covered with a cover glass.

Pressure was applied to the samples using an ISS stainless steel pressure cell with sapphire windows and manual pump, using FC-72 (perfluorohexane) as the hydraulic fluid. After each pressure point was reached, the system was left to equilibriate for 10 minutes before starting the corresponding measurement. All pressures reported are gauge pressures, measured relative to ambient pressure.

2.2 UV-vis absorption

The sample was placed in the pressure cell, which was mounted in a PerkinElmer Lambda 750 UV-Vis-NIR absorption spectrometer. The absorption spectrum between 200 and 600 nm was measured with wavelength increments of 0.5 nm, at pressures between 0 and $400\,\mathrm{MPa}$ in $50\,\mathrm{MPa}$ increments on the up stroke and $100\,\mathrm{MPa}$ decrements on the down stroke to measure any hysteresis. This was done with both the pure ionic liquid and the ionic liquid with PtOEP added.

Spectra were further analyzed by fitting a system of five Gaussian peaks to the absorption structure between 300 and 450 nm, using photon energy rather than wavelength on the x-axis. The peak central energies, peak widths at half maximum (FWHM), and relative peak areas were compared at every pressure point.

2.3 Magnetic field dependence of upconversion photoluminescence

The sample was mounted between the poles of an electromagnet (GMW Magnet Systems, model 3470) and illuminated with a 532 nm laser (same as above) at 1.00 mW, which was focused onto the sample using a 100 mm focal length lens. The upconverted light was focused with a 30 mm focal length lens, passed through a 500 nm short pass filter and coupled into a multi-mode optical fiber. This fiber coupled the light into the spectrometer (same as above). The dependence of the magnetic field between the poles on the electric current applied to the magnet was determined using a gaussmeter (AlphaLab Inc., model GM-1-ST).

The current in the electromagnet was varied from 0 to 4 A in increments of 200 mA, and back to 0 A in decrements of 1000 mA. At each magnetic field strength, the upconversion spectrum was recorded with an integration time of 1 s.

The upconversion spectra were analyzed by background subtraction and by integrating the counts between 400 and 500 nm. This gave the UCPL intensity for every magnetic field strength.

2.4 Pressure and intensity dependence of upconversion photoluminescence

2.4.1 Experimental setup

The sample was placed in the pressure cell at 45 degrees to the excitation laser (532 nm, 147.5 mW, Laserglow Technologies), which was passed through a continuously variable optical density filter and focused onto the sample with a 100 mm focal length lens. The upconverted light from the sample was focused with a 30 mm focal length lens, passed through a 500 nm shortpass filter and coupled into a multi-mode optical fiber. This fiber coupled the light into the spectrograph (Princeton Instruments Acton SpectraPro 2300i) with liquid nitrogen cooled CCD sensor (Princeton Instruments LN/CCD).

2.4.2 Parameters

Due to clouding in the hydraulic fluid at pressures greater than 250 MPa, the upconversion spectra were recorded at pressures between 0 and 200 MPa in 25 MPa increments on the up stroke and 50 MPa decrements on the down stroke to measure any hysteresis. For each up stroke measurement, the excitation intensity was varied exponentially, doubling the intensity each time, between $0.5\,\mu W$ and $4096\,\mu W$ by adjusting the variable density filter and by adding and removing an additional neutral density filter with optical density 3.0. On the down stroke, the intensity was varied between $1\,\mu W$ and $4096\,\mu W$ with eightfold increments. The intensity was verified using an optical power meter (Thorlabs PM200) whose photodiode was on a flip mount between the neutral density filters and the focusing lens. To obtain suitable spectra across seven orders of magnitude of photoluminescence strength, the integration time on the CCD was varied from 200 s at 0.5 and $1\,\mu W$ of excitation power, to 20 s at 2 and $4\,\mu W$, to 2 s at 8 and $16\,\mu W$, to 200 ms between 32 and $256\,\mu W$, to 20 ms between 512 and $4096\,\mu W$.

2.4.3 Beam spot characterization

The beam spot was characterized after the measurement by removing the pressure cell and placing a CCD beam profiler (Thorlabs BC106N) in the beam line at the position of the image of the sample, considering the different refractive indices of air, sapphire and perfluorohexane. Dense media reduce the apparent depth of immersed objects proportionally to their refractive index when the interfaces are flat, so 6.4 mm of sapphire (n = 1.76 [27]) window appears the same as 3.64 mm of air. Similarly 11 mm of perfluorohexane (n = 1.25 [27]) appears as 8.8 mm of air. The apparent position of the sample is thus 4.96 mm closer to the entry window than the actual position and the beam profiler was placed at this apparent position. The effective spot diameter was then determined by the $1/e^2$ level of the marginal distributions of the beam power as in [16], while accounting for the elliptical shape of the spot due to the angle of incidence.

2.4.4 Analysis

The UCPL intensity was obtained from each spectrum by background subtraction and integration of the spectral range between 400 and 500 nm. These values were divided by the integration time to give a uniform measure of UCPL intensity. The threshold intensity was found by fitting linear functions of slope two and one respectively to the four lowest and highest values of the logarithms of the UCPL intensity and excitation intensity. For the measurements taken on the down stroke, instead the two lowest and highest values were taken. The intersection of the two linear functions gave the threshold intensity.

Chapter 3

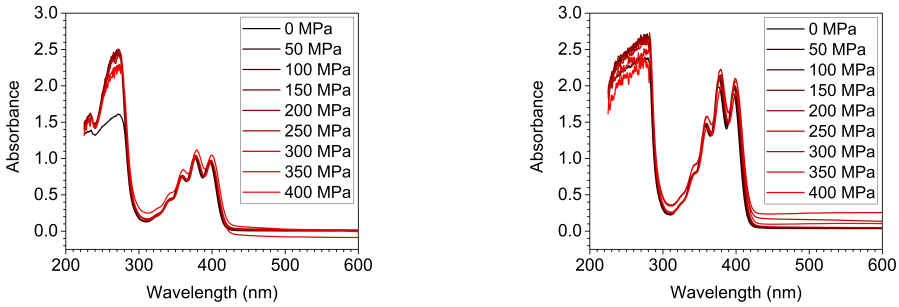
Results & Discussion

The ionic liquid was characterized by a range of spectroscopic techniques. The optically relevant components of the liquid, diphenylanthracene (DPA) sulfonate and platinum octaethyl porphyrin (PtOEP) are identified via UV-vis absorption spectroscopy and by using this technique with pressurized samples, the electronic coupling between molecules as a function of pressure are gauged. The following measurements are based on the upconversion photoluminescence (UCPL) from the system. First it is confirmed that upconversion by triplet-triplet annihilation (TTA) occurs in the sample from the UCPL spectrum. Then the UCPL spectrum and especially its integrated area are measured as a function of the strength of an applied magnetic field, to probe the spin statistics of the upconversion process, and finally as a function of both hydrostatic pressure and excitation intensity, to determine the threshold intensity of upconversion at different pressures and assess the influence on triplet diffusion rates.

3.1 UV-vis absorption

The absorption spectra for the ionic liquid both with and without PtOEP and at pressures up to 400 MPa can be seen in figure 3.1. The vibronic absorption peaks of DPA [28] are clearly visible between 300 and 450 nm. The different peaks in this structure represent the molecule being excited to the same electronic state (the first singlet excited state), but in different states of molecular vibration. The spectra are also in good agreement with the original work [16]. At increased pressure, a small but significant redshift can be seen in this structure. The peak between 200 and 300 nm represents a transition to a higher electronic excited state. The much lower height of this peak in the pure ionic liquid at 0 MPa is considered an artifact of measuring such high absorbance values as the detector is operating with very few photons then. The difference in peak heights between the two samples is due to variation in sample thickness, which was controlled only qualitatively.

At 350 and 400 MPa the absorption appears to increase at all wavelengths; the apparent increase is due to scattering caused by the partial solidification of the hydraulic fluid, nucleating the formation of a sol at these pressures. This clouding is deemed a minor effect



(a) Pure ionic liquid **(b)** Ionic liquid with PtOEP

Figure 3.1: UV-Vis absorption spectra at different pressures

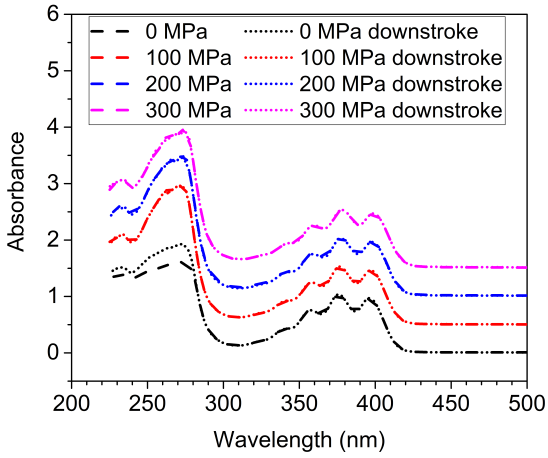
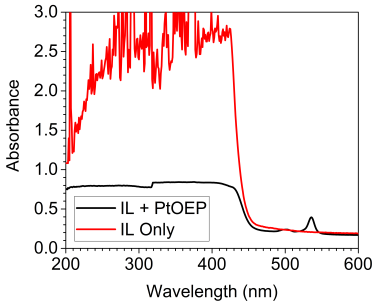
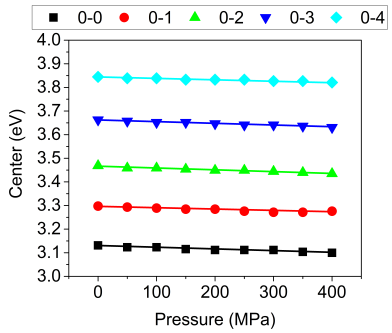


Figure 3.2: The (offset) absorption spectra of the pure ionic liquid at various pressures during the up stroke and down stroke



(a) Absorption spectra of thick samples of the pure ionic liquid (IL) and the ionic liquid with PtOEP



(b) Fitted peak center energy versus pressure for the ionic liquid sample with PtOEP

Figure 3.3

that does not invalidate the acquired spectra. Spectra taken on the down stroke (figure 3.2) confirmed that there is no significant hysteresis with respect to pressure and there was no significant degradation of the samples during measurement.

The main absorption peak of PtOEP around 530 nm [9] was detected in the sample in which it was present, but was only resolved in samples much thicker (around 1 mm) than the ones used for the pressure measurements owing to the low PtOEP concentration in the ionic liquid. These spectra can be seen in figure 3.3a. The presence or absence of PtOEP absorption was the only difference between the two samples; the absorption peaks of the DPA chromophore were unaffected. In these thicker samples, the absorption of the DPA chromophore was such that no appreciable amount of radiation shorter than 450 nm could reach the detector and a plateau appeared at those wavelengths. Even the valley around 300 nm was not detected. The different appearance of the plateaus in figure 3.3a is due to variance in sample geometry; the thicker samples were prepared without sandwiching and the ionic liquid formed droplets over time. The pure ionic liquid sample blocked the beam entirely while the sample with PtOEP obstructed the beam only partially, so that the measured absorbance values were lower and enough photons reached the detector to not appear as a noisy signal.

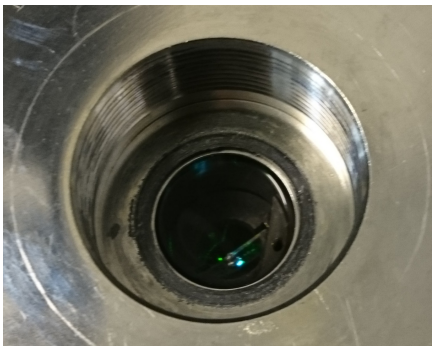
By modeling each spectrum as a system of Gaussian peaks, the effects of pressure can be quantified. The shoulder visible around 375 nm was consistently fitted as a peak and is known to correspond to a real vibronic transition [29], hence the decision to use a five-peak system. In figure 3.3b, the effect of pressure on these five peaks can be seen.

The central energy of each peak slightly but consistently decreases with pressure, with a slope that is similar for each peak as can be seen in table 3.1. Generally the slope is around $-70\,\mu\mathrm{eV}/\mathrm{MPa}$. The lack of sudden changes or other features in the relationship between energy and pressure is an indication that no phase changes are being caused by the high pressure and the intermolecular distances are being varied smoothly as intended.

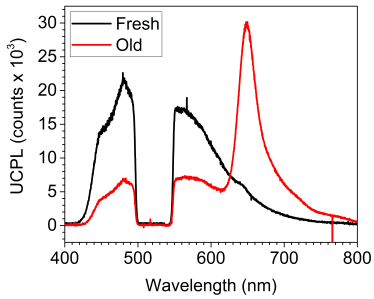
Crucially, the redshift is an indication that the strength of electronic coupling between the molecules is increased under pressure. In the liquid state or in a solvent, peaks from

Peak	Pure ionic liquid			Ionic liquid + PtOEP		
	Slope (μeV/MPa)	Slope error (μeV/MPa)	R^2 (-)	Slope (μeV/MPa)	Slope error (μeV/MPa)	R^2 (-)
0-0	-71.7858	4.0554	0.98	-70.4305	6.5851	0.93
0-1	-56.5826	7.9868	0.86	-65.2256	8.9651	0.87
0-2	-76.8789	6.3437	0.95	-75.2287	5.1207	0.96
0-3	-71.5728	4.9544	0.96	-75.0799	4.0547	0.98
0-4	-61.1671	9.7811	0.83	-51.3397	4.9508	0.93

Table 3.1: Details of fitting peak central energy



(a) Upconversion photoluminescence from a sample in the pressure cell



(b) Upconversion spectrum from a freshly prepared sample and a sample that was exposed to air for seven days

Figure 3.4

electronic transitions are typically redshifted compared to the vapor phase since excited states are electric dipoles and a polarizable medium acts to stabilize that dipole. With the excited state having lower energy, a redder photon can excite a molecule to that state. In this case, the smaller intermolecular distances at high pressure act to increase the stabilizing effect of the polarizability of the surrounding medium. The observed redshift is consistent with the observation in the original work that the absorption of the neat ionic liquid is redshifted compared to a solution of the ions in methanol, again indicating a stronger interaction of the chromophores. This observation was taken as indirect evidence of the bicontinuous structure of the liquid.

3.2 Upconversion photoluminescence spectroscopy

To the naked eye the UCPL appears cyan to white, as can be seen in figure 3.4a. The upconversion photoluminescence spectrum can be seen in figure 3.4b and has a strong component with shorter wavelengths than the excitation laser (532 nm). In the ionic liquid without the PtOEP sensitizer, excitation at the same wavelength caused no detectable photoluminescence, confirming that PtOEP is required to populate the system with triplets.

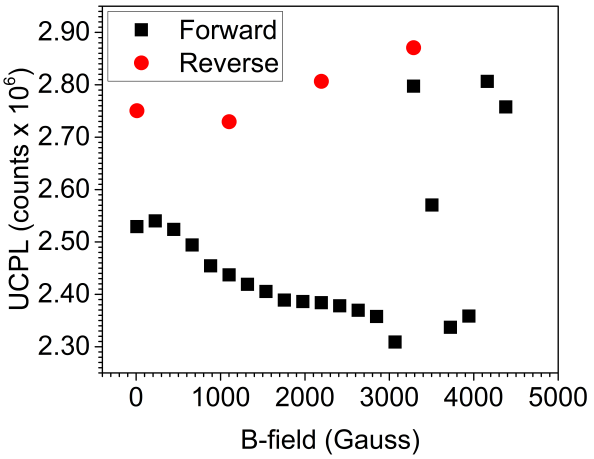


Figure 3.5: Intensity of upconverted light versus excitation irradiance, at different pressures

The spectra in figure 3.4b were composited from spectra taken with a 500 nm shortpass and 550 nm longpass filter, hence the exclusion of the wavelengths between those two values. In samples that had been exposed to air for several days, the color turned to magenta as an additional peak appeared in the spectrum around 650 nm, corresponding to the phosphorescence of PtOEP [30], and the upconversion photoluminescence decreased. The phosphorescence peak is also visible in the spectrum of the fresh sample as a small shoulder. The spectral shape is in good agreement with the original work [16]. This spectrum confirms that upconversion is occurring in the sample.

3.3 Magnetic field dependence of upconversion photoluminescence

To confirm that the upconversion proceeds via TTA, the influence of an external magnetic field on the intensity of upconversion photoluminescence was measured. The results of this measurement are plotted in figure 3.5. Around 3000 Gauss there is a disturbance that appears to have affected all subsequent measurements, including the reverse field scan. The issue was probably mechanical, knocking some lens out of alignment. Despite this, the measurements up to the disturbance appear to be valid and will be treated as such.

The overall shape of the curve up to the disturbance shows an initial slight increase in upconversion photoluminescence, followed by a sharper decrease and eventual saturation. This is consistent with triplet-triplet annihilation in crystalline solid films [26]. In such an ordered system, the multiexciton state can be interpreted in terms of wavefunction symmetry with respect to exchange of the two constituent triplets [31]. This separates the even states, which are overall singlets, quintets, and mixtures thereof, from odd states which are overall triplets. At zero field, three of the nine multiexciton states have singlet char-

acter and can participate in upconversion, while a magnetic field of intermediate strength mixes the singlet and quintet in such a manner that all six even states have singlet character. At high field strength, the singlet character is concentrated into two states so that the upconversion efficiency is reduced. The reduction at high field depends on the ratio of the dissociation rate and annihilation rate of the multiexciton, and is one third if annihilation is greatly favored.

Conversely, in solutions and glassy solids the molecules are oriented randomly and the exchange symmetry approach is no longer valid [26]. At zero field, all nine states have nonzero singlet character while at high field, the singlet character is again concentrated into two states. Thus solution systems show upconversion that decreases monotonically with an increase in magnetic field strength [32], where the maximum reduction is one ninth, again if annihilation is favored over dissociation. The initial increase seen in the ionic liquid indicates that while the system is a liquid, there is some preferred orientation to the DPA chromophores. Since this ordering is unlikely to be complete, the behavior probably lies between the two extremes of crystalline and disordered. Because the size of the initial increase depends not only on the degree of ordering but also the branching ratio between dissociation and annihilation, the degree of ordering cannot be determined exactly from this data.

3.4 Pressure and intensity dependence of upconversion photoluminescence

The dependence of the upconversion photoluminescence on the excitation power density can be seen in figure 3.6. The overall shape of the curves is as expected for a TTA upconversion system: quadratic at low intensity (appearing linear with slope two on a log-log plot), transitioning to linear at high intensity (linear with slope one). This shape is due to triplet-triplet annihilation being limited by triplet decay at low triplet densities and thus having bimolecular kinetics, but limited by formation of the singlet exciton from two bound triplets at high intensities and having unimolecular kinetics then.

There are some outliers in the data: the two lowest-intensity points at 0 MPa and the very lowest at 125 MPa. These are likely unphysical; given the low intensities and long integration times it is much more likely that some stray light reached the detector. These points were not included in the determination of the threshold intensity.

The overall intensity of the curves appears to decrease with increasing pressure, but the curves taken on the down stroke have lower intensity still. The mismatch between up stroke and down stroke measurements at the same pressures indicates an irreversible degradation of the upconversion system, probably due to photobleaching of the sensitizer during the high-intensity measurements despite efforts to minimize the exposure times. Degradation by oxygen is unlikely because the sample was prepared in an oxygen-free environment and was effectively protected from the atmosphere by immersion in the hydraulic fluid, as demonstrated in the absorption spectroscopy (figure 3.2).

Figure 3.7a details the process used to find the threshold intensities: the four lowest and the four highest intensity data points were used for fitting of linear functions (using the logarithms of both coordinates) of slopes two and one, respectively. The threshold

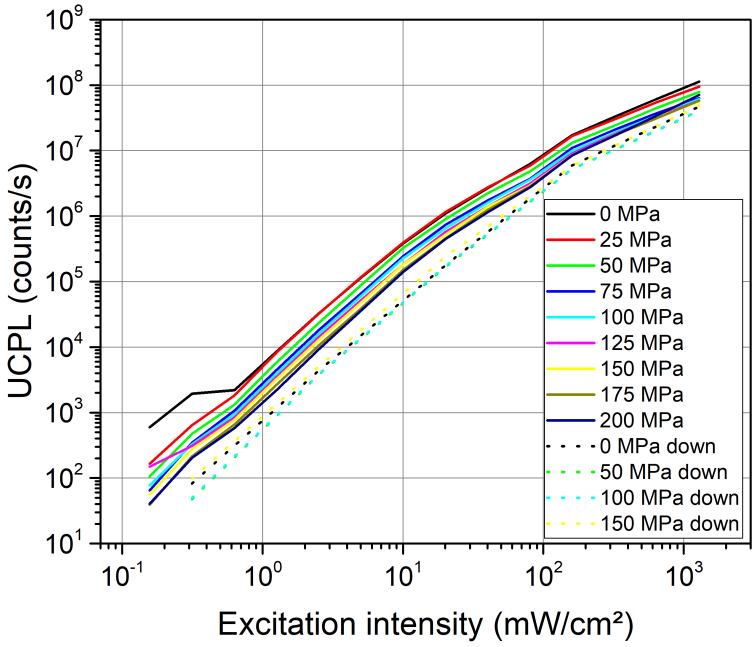
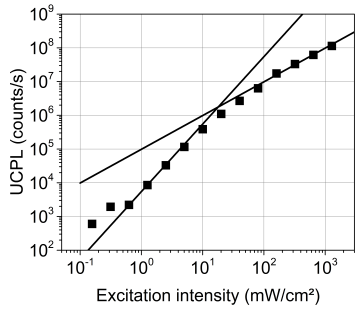
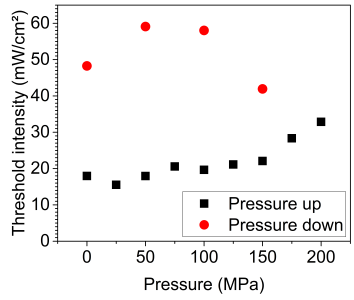


Figure 3.6: Intensity of upconverted light versus excitation irradiance, at different pressures



(a) Example of the construction used to find the threshold intensity



(b) Threshold intensity of the upconversion system versus pressure

Figure 3.7

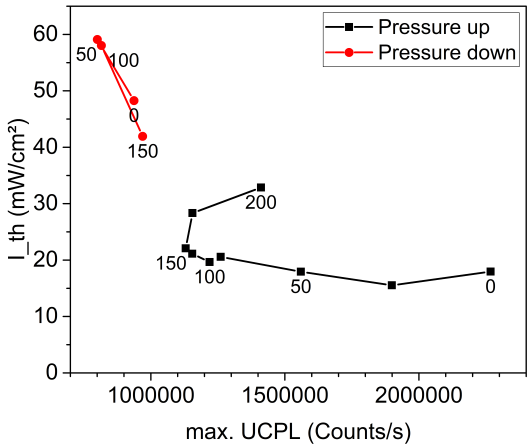


Figure 3.8: Relationship of calculated threshold intensity, UCPL at maximum excitation intensity ($1288\,\mathrm{mW\,cm^{-2}}$) and pressure

intensity was then given by the intersection of those functions. The threshold intensities at different pressures can be seen in figure 3.7b. At ambient pressure, the threshold intensity was determined at $18.0\,\mathrm{mW\,cm^{-2}}$. This is in rough correspondence with the original work [16], where the value was determined as $3.0\,\mathrm{mW\,cm^{-2}}$. The difference could be due to a number of causes, such as the triplet concentration being different at the same laser intensity due to a difference in sample thickness, or differences in the way the beam spot diameter was determined.

Just as the total photoluminescence decreased constantly during data acquisition, the threshold intensity appears to have mostly increased, with the down stroke measurement at 0 MPa being a notable exception. The magnitude of the disagreement between the up and down strokes appears to follow no easily identifiable pattern. As can be seen in figure 3.8, the measured UCPL intensity and threshold intensity roughly follow a negative correlation: points with lower UCPL intensity tend to have higher threshold intensity. The degradation during measurement makes it nontrivial to make reliable statements about the pressure-dependent behavior.

Through the effects of the degradation, the two lowest-pressure data points of the down stroke measurements suggest a possible upward trend in the threshold intensity with pressure, contrarily to what was predicted. Especially the data point at 0 MPa on the down stroke appears to validate this trend, having a lower threshold intensity than at 50 MPa despite the overall increase. In addition, the 50 MPa point itself has only a slightly higher threshold intensity than the 100 MPa point, and significantly lower than one might expect from the down stroke points at 200 and 150 MPa. To determine the behavior of the threshold intensity under pressure more conclusively, a more refined version of the experiment is necessary.

An increase in the threshold intensity at high pressure would imply that any decrease

in threshold intensity due to longer triplet diffusion length is offset by another pressure dependent phenomenon. One possibility is that hydrostatic pressure changes the relative orientations of the molecules in such a way that triplet diffusion is impeded or triplet decay is facilitated. It is also possible that the molecules are forced into a more ordered configuration, thus concentrating the singlet character into fewer states of the multiexciton and rendering annihilation to a singlet less likely. While no phase changes are thought to occur in the relevant pressure range, a continuous rearrangement is still a possibility, as happens in liquid water close to its freezing point.

A change of the ratio of the dissociation and annihilation of the multiexciton in favor of dissociation would also decrease the threshold intensity. This is possible if the overall triplet becomes less mixed with the singlet and quintet so that it is likely to decay to a single triplet or dissociate into a pair of triplets. Furthermore, the two triplets resulting from such a dissociation could remain entangled as an overall triplet for some time and be unable to annihilate on subsequent collisions [33]. Thus each triplet must travel further on average to find a suitable annihilation partner and the threshold intensity is increased.

Possibly the two lowest-pressure down stroke points are faulty; since the linear fit was done on the basis of two intensity measurements for the down stroke, a single measurement error could invalidate the value found for the threshold intensity. Furthermore these data points should be considered the least reliable of all as the sample was the most damaged for these measurements. Thus possibly the threshold intensity generally decreases with pressure. This would be more in line with expectations as the emitter molecules come into closer contact, as verified by the UV-vis spectroscopy, and Dexter transfer of triplet excitons between emitters is facilitated, thus increasing their diffusion length and requiring lower triplet concentration to reach the threshold.

Chapter 4

Conclusion

4.1 What was found

In this work, we studied an ionic liquid capable of photon upconversion by triplet-triplet annihilation [16] using hydrostatic pressure and magnetic fields. Pressure-dependent UV-vis absorption spectroscopy, magnetic field dependent spectroscopy of the upconversion photoluminescence, and pressure and intensity dependent spectroscopy of the upconversion photoluminescence were used to characterize the system and investigate its upconversion behavior.

The upconversion system was found to be more strongly electronically coupled at high pressures, with the absorption spectrum redshifting by around $70\,\mu\mathrm{eV\,MPa^{-1}}$ due to the molecules becoming more affected by the polarizability of their neighbors. This confirmed that by using hydrostatic pressure, the intermolecular distances in the liquid can be altered continuously.

The upconversion in the system was also found to have a solid-like response to a magnetic field, showing a slight increase in photoluminescence with magnetic field strength, followed by a stronger decrease and eventual saturation. This pattern implies high symmetry in the orientation of emitter molecules and thus a high degree of ordering in the structure of the material, despite it being able to flow as a viscous liquid.

At ambient pressure, the threshold intensity of upconversion, at which the dependence on incident light intensity transitions from quadratic to linear and the system reaches its peak quantum efficiency, was measured as $18.0\,\mathrm{mW\,cm^{-2}}$. This value is in rough correspondence with the original work, where $3.0\,\mathrm{mW\,cm^{-2}}$ was found. The measurements at increased pressure were largely rendered inconclusive by what appeared to be photobleaching damage. An increase in the threshold intensity at high pressure could be ascribed to the structure of the material becoming more ordered, thus leading to unfavorable spin statistics that would increase the probability of two bound triplets dissociating. Conversely, a decrease in the threshold intensity could be due to more efficient triplet diffusion, so that triplets travel further before decaying and are more likely to collide.

Overall the upconversion in the ionic liquid seems to be governed by its characteris-

tics that are intermediate between solid and liquid state; the response to magnetic fields is solid-like but the system has superior quantum efficiency and threshold intensity to typical solid upconversion systems. Moreover, the application of hydrostatic pressure was demonstrated to be a useful tool for probing these characteristics. More research is necessary to determine the solid or liquid character of the system at high pressure and its influence on the upconversion behavior.

4.2 Future work

4.2.1 Refinement of intensity plot

To determine the upconversion behavior under pressure more conclusively, the pressure and intensity dependence experiment is to be refined. Specifically, measures must be taken to limit the time the sample is exposed to the high-intensity excitation laser. Besides yielding reliable values for the threshold intensity, this refinement would allow the absolute photoluminescence curves to be compared and statements to be made about the efficiency of the system. Protection of the sample could be achieved using a mechanical shutter in the excitation beam line that would only open briefly for each measurement (in this work, blocking the beam was done manually). Another approach would be to move the beam spot across the sample between measurements, thus limiting the exposure of any particular parcel of ionic liquid to the beam.

4.2.2 Transient absorption

Transient absorption spectroscopy would provide a wealth of data about the system by effectively revealing the absorption spectrum of excited states, including triplet excitons and the multiexciton [7]. In addition to elucidating the upconversion mechanics at ambient conditions, the experiment could be done with the pressure cell to characterize how the mechanics change with pressure.

4.2.3 Magnets and pressure

Pressure was hypothesized to force the molecules in the liquid into a more ordered state, thus rendering the spin statistics of TTA more alike to a solid-state system. This could be confirmed by repeating the magnetic field dependence experiment under pressure and comparing the intensity curves. If the initial bump in the curve becomes more pronounced, that indicates more solid-like behavior and could offer an explanation for the possible increased threshold intensity at high pressure.

4.2.4 Structural studies

When reasoning about the bicontinuity of the liquid and the orientation of its molecules, a clear picture of the structure would be most helpful. Nuclear magnetic resonance (NMR) experiments might be able to provide this information. In NMR, the sample is subjected to a magnetic field sufficiently strong to affect the energies of the spin states of the atomic

nuclei and the degree of splitting of the energy levels is probed using radio waves. NMR experiments can assess the chemical structure and purity of compounds, as was done at Kyushu University to verify the successful synthesis of the components of the ionic liquid. A NOESY (nuclear Overhauser effect spectroscopy) experiment can reveal the proximity in real space of the different protons (hydrogen nuclei) in a given substance. This information could be used to determine the typical orientations that the DPA chromophores assume. In addition, there is precedent for NMR at pressure ranges similar to that used in this study [34] so that this structural information could be acquired for the entire pressure range and any changes in molecular ordering revealed.

Bibliography

[1] P. Würfel, *Physics of solar cells: from basic principles to advanced concepts*. John Wiley & Sons, 2016.

[2] W. Shockley and H. J. Queisser, "Detailed balance limit of efficiency of p-n junction solar cells," *Journal of applied physics*, vol. 32, no. 3, pp. 510–519, 1961.

[3] D. N. Nikogosyan, *Nonlinear optical crystals: a complete survey*. Springer Science & Business Media, 2006.

[4] F. Auzel, "Upconversion and anti-stokes processes with f and d ions in solids," *Chemical reviews*, vol. 104, no. 1, pp. 139–174, 2004.

[5] P. Atkins and J. De Paula, *Elements of physical chemistry*. Oxford University Press, USA, 2013.

[6] J. C. Goldschmidt and S. Fischer, "Upconversion for photovoltaics–a review of materials, devices and concepts for performance enhancement," *Advanced Optical Materials*, vol. 3, no. 4, pp. 510–535, 2015.

[7] C. K. Yong, A. J. Musser, S. L. Bayliss, S. Lukman, H. Tamura, O. Bubnova, R. K. Hallani, A. Meneau, R. Resel, M. Maruyama, *et al.*, "The entangled triplet pair state in acene and heteroacene materials," *Nature Communications*, vol. 8, 2017.

[8] A. Monguzzi, J. Mezyk, F. Scotognella, R. Tubino, and F. Meinardi, "Upconversion-induced fluorescence in multicomponent systems: Steady-state excitation power threshold," *Physical Review B*, vol. 78, no. 19, p. 195112, 2008.

[9] A.-K. Bansal, W. Holzer, A. Penzkofer, and T. Tsuboi, "Absorption and emission spectroscopic characterization of platinum-octaethyl-porphyrin (ptoep)," *Chemical physics*, vol. 330, no. 1, pp. 118–129, 2006.

[10] V. Yakutkin, S. Aleshchenkov, S. Chernov, T. Miteva, G. Nelles, A. Cheprakov, and S. Baluschev, "Towards the ir limit of the triplet–triplet annihilation-supported upconversion: Tetraanthraporphyrin," *Chemistry-A European Journal*, vol. 14, no. 32, pp. 9846–9850, 2008.

[11] R. R. Islangulov, J. Lott, C. Weder, and F. N. Castellano, "Noncoherent low-power upconversion in solid polymer films," *Journal of the American Chemical Society*, vol. 129, no. 42, pp. 12652–12653, 2007.

[12] R. Vadrucci, C. Weder, and Y. C. Simon, "Low-power photon upconversion in organic glasses," *Journal of Materials Chemistry C*, vol. 2, no. 16, pp. 2837–2841, 2014.

[13] M. Hosoyamada, N. Yanai, T. Ogawa, and N. Kimizuka, "Molecularly dispersed donors in acceptor molecular crystals for photon upconversion under low excitation intensity," *Chemistry-A European Journal*, vol. 22, no. 6, pp. 2060–2067, 2016.

[14] L. Liu, D. Huang, S. M. Draper, X. Yi, W. Wu, and J. Zhao, "Visible light-harvesting trans bis (alkylphosphine) platinum (ii)-alkynyl complexes showing long-lived triplet excited states as triplet photosensitizers for triplet–triplet annihilation upconversion," *Dalton Transactions*, vol. 42, no. 30, pp. 10694–10706, 2013.

[15] M. Penconi, F. Ortica, F. Elisei, and P. L. Gentili, "New molecular pairs for low power non-coherent triplet–triplet annihilation based upconversion: dependence on the triplet energies of sensitizer and emitter," *Journal of Luminescence*, vol. 135, pp. 265–270, 2013.

[16] S. Hisamitsu, N. Yanai, and N. Kimizuka, "Photon-upconverting ionic liquids: Effective triplet energy migration in contiguous ionic chromophore arrays," *Angewandte Chemie International Edition*, vol. 54, no. 39, pp. 11550–11554, 2015.

[17] Y. Y. Cheng, A. Nattestad, T. F. Schulze, R. W. MacQueen, B. Fückel, K. Lips, G. G. Wallace, T. Khoury, M. J. Crossley, and T. W. Schmidt, "Increased upconversion performance for thin film solar cells: a trimolecular composition," *Chemical Science*, vol. 7, no. 1, pp. 559–568, 2016.

[18] Q. Liu, B. Yin, T. Yang, Y. Yang, Z. Shen, P. Yao, and F. Li, "A general strategy for biocompatible, high-effective upconversion nanocapsules based on triplet–triplet annihilation," *Journal of the American Chemical Society*, vol. 135, no. 13, pp. 5029–5037, 2013.

[19] A. Turshatov, D. Busko, S. Baluschev, T. Miteva, and K. Landfester, "Micellar carrier for triplet–triplet annihilation-assisted photon energy upconversion in a water environment," *New Journal of Physics*, vol. 13, no. 8, p. 083035, 2011.

[20] C. Weinheimer, Y. Choi, T. Caldwell, P. Gresham, and J. Olmsted, "Effect of a steric spacer on chromophoric interactions of ruthenium complexes containing covalently bound anthracene," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 78, no. 2, pp. 119–126, 1994.

[21] M. T. Whited, P. I. Djurovich, S. T. Roberts, A. C. Durrell, C. W. Schlenker, S. E. Bradforth, and M. E. Thompson, "Singlet and triplet excitation management in a bichromophoric near-infrared-phosphorescent bodipy-benzoporphyrin platinum complex," *Journal of the American Chemical Society*, vol. 133, no. 1, pp. 88–96, 2010.

[22] R. Ziessel, B. D. Allen, D. B. Rewinska, and A. Harriman, "Selective triplet-state formation during charge recombination in a fullerene/bodipy molecular dyad (bodipy= borondipyrromethene)," *Chemistry-A European Journal*, vol. 15, no. 30, pp. 7382–7393, 2009.

[23] T. Wang, B. Daiber, J. M. Frost, S. A. Mann, E. C. Garnett, A. Walsh, and B. Ehrler, "Indirect to direct bandgap transition in methylammonium lead halide perovskite," *Energy & Environmental Science*, vol. 10, no. 2, pp. 509–515, 2017.

[24] R. Resel, M. Oehzelt, K. Shimizu, A. Nakayama, and K. Takemura, "On the phase-transition in anthracene induced by high pressure," *Solid state communications*, vol. 129, no. 2, pp. 103–106, 2004.

[25] M. Blanchard, M. Alfredsson, J. Brodholt, G. D. Price, K. Wright, and C. R. A. Catlow, "Electronic structure study of the high-pressure vibrational spectrum of fes2 pyrite," *The Journal of Physical Chemistry B*, vol. 109, no. 46, pp. 22067–22073, 2005.

[26] J. Mezyk, R. Tubino, A. Monguzzi, A. Mech, and F. Meinardi, "Effect of an external magnetic field on the up-conversion photoluminescence of organic films: The role of disorder in triplet-triplet annihilation," *Physical review letters*, vol. 102, no. 8, p. 087404, 2009.

[27] D. W. Rankin, *CRC handbook of chemistry and physics, edited by David R. Lide*. Taylor & Francis, 2007.

[28] D. Dzebo, K. Moth-Poulsen, and B. Albinsson, "Robust triplet–triplet annihilation photon upconversion by efficient oxygen scavenging," *Photochemical & Photobiological Sciences*, 2017.

[29] R. N. Jones, "The ultraviolet absorption spectra of anthracene derivatives.," *Chemical reviews*, vol. 41, no. 2, pp. 353–371, 1947.

[30] M. A. Baldo, D. O'brien, Y. You, A. Shoustikov, *et al.*, "Highly efficient phosphorescent emission from organic electroluminescent devices," *Nature*, vol. 395, no. 6698, p. 151, 1998.

[31] R. Merrifield, "Theory of magnetic field effects on the mutual annihilation of triplet excitons," *The Journal of Chemical Physics*, vol. 48, no. 9, pp. 4318–4319, 1968.

[32] T. Mani and S. A. Vinogradov, "Magnetic field effects on triplet–triplet annihilation in solutions: modulation of visible/nir luminescence," *The journal of physical chemistry letters*, vol. 4, no. 17, pp. 2799–2804, 2013.

[33] G. D. Scholes, "Correlated pair states formed by singlet fission and exciton–exciton annihilation," *The Journal of Physical Chemistry A*, vol. 119, no. 51, pp. 12699–12705, 2015.

[34] J. Jonas and A. Jonas, "High-pressure nmr spectroscopy of proteins and membranes," *Annual review of biophysics and biomolecular structure*, vol. 23, no. 1, pp. 287–318, 1994.