Multidimensional coherent spectroscopy of excitons in \( \pi \)-conjugated polymer

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The photophysics of \( \pi \)-conjugated polymers has been of considerable interest over the last three decades because of their organic semiconductor properties. Primary photoexcitations, Frenkel excitons, can be probed optically by means of numerous linear spectroscopies, providing a wealth of information on the strength of excitonic coupling, the exciton coherence length, and on the nature of the disordered energy landscape. Nonetheless, there are intrinsic limitations in the information that can be obtained with linear spectroscopy compared to non-linear coherent techniques. Examples of this are the separation of homogeneous and inhomogeneous broadening contributions to the total exciton spectral lineshape, the detailed spectral structure of exciton-vibrational coupling, and correlations between optical excitations, including exciton-charge and exciton-exciton correlations. In the present work, we discuss the role of two-dimensional coherent excitation spectroscopy and review its applications towards unravelling the basic photophysics of \( \pi \)-conjugated polymers as well as polymer:fullerene blends, and we argue that these techniques are now valuable mainstream materials optical probes.

10\textsuperscript{th} Anniversary Statement

The influence of the Journal of Materials Chemistry C in the development of the basic science of conjugated polymers is substantial, and C.S.A. has published some of his key contributions to the photophysics of these materials in the journal. It is his firm conviction that advanced optical probes are now at the point of maturity that they are to be considered as valuable techniques within the materials characterization toolbox, much like “standard” techniques such as linear absorption and emission techniques. The readership of the journal is broad, spanning all aspects of research on conjugated polymers, ranging from synthesis, processing, physical characterization, and engineering of their technologies, and this contribution to the 10\textsuperscript{th} Anniversary Issue is aimed at the entire community. The authors therefore hope to stimulate further use of nonlinear coherent spectroscopies in the research of excitonic properties of conjugated polymer materials and their devices by connecting the ultrafast spectroscopy and materials science communities.
1 Introduction

The optical properties of \( \pi \)-conjugated polymers are governed by the nature of their primary photoexcitation, which are Frenkel excitons. These are strongly bound quasiparticles with binding energies \( \gg 10k_B T \) at ambient temperature. Excitonic properties in organic semiconductors in general provide a window into their materials physics, and have always been investigated as a key probe of their electronic landscape. The solid-state absorption spectra of conjugated polymers, while encoding signatures of photophysical aggregates of molecular chromophores along the polymer backbone, are often dominated by static disorder, and the large inhomogeneous linewidth obscures details of the rich spectral structure. The seminal work of Spano on excitons in conjugated polymers, of which Refs. [19–34] are a subset, involved implementation of Holstein Hamiltonians that treat excitonic coupling, vibronic coupling, energetic disorder, and charge-transfer components when describing push-pull materials, incorporating all of these contributions on equal footing. This has presented a formal way to interpret absorption and photoluminescence lineshapes to quantify excitonic parameters such as free-exciton bandwidth and the nature of their disordered energy landscape, which has been tremendously impactful in semiconductor-polymer materials science over the past decade. The main observables that enter the linear lineshape interpretation are relative 0–0 and 0–1 peak intensities, which quantify excitonic coupling in the absorption spectrum \([19,21,22]\), with additional information on the correlated nature of the energetic disorder via photoluminescence \([24,26]\). To go beyond this effective exciton model, more detailed analysis of the spectral structure is desirable, and techniques such as resonance Raman spectroscopy, for example, are valuable \([15,30]\). Many details of the many-body excitonic structure that dominates solid-state behaviour of conjugated polymers are not readily extracted from the broad, convoluted linear optical lineshapes, and it is advantageous to measure nonlinear lineshapes, which resolve rich structure within inhomogeneously broadened spectra beyond linear lineshapes \([39,44]\). Furthermore, many-body excitonic details central to the photophysical aggregate behaviour are not readily identifiable from linear lineshapes; although these states are localized within a chromophore, at sufficiently high densities, exciton-exciton interactions start to dominate the optical properties of organic solids \([43]\). For example, the spontaneous formation of strongly coupled light-matter quantum condensates in organic materials depends fundamentally on the details of exciton-exciton interactions \([45]\), how are two-quantum interactions manifested in spectral lineshapes of Frenkel excitons? We have found in early work that both charges and triplet excitons are produced on ultrafast timescales due to multi-quantum interactions in conjugated polymers \([37,39]\), but no detail on these can be derived by linear excitation lineshapes. Furthermore, we have found that prompt charge separation occurs via what we have interpreted as charge-transfer states that appear to be intrinsic in these systems \([50,53]\), and fundamental electronic couplings that give rise to these is of fundamental relevance.

Our objective for this article is to discuss two-dimensional coherent spectroscopy as a non-linear optical probe that contributes...
to the understanding of excitons in π-conjugated polymer materials, to discuss how this approach is now to be considered a mainstream materials characterization tool in this field, and to review what we consider to be key contributions of this class of techniques to the semiconductor polymer materials science.

We first discuss the information that can be discerned from two-dimensional coherent optical lineshapes, and then we review contributions to the understanding of exciton and biexciton structure in neat polymer films, as well as charge separation in heterostructures with electron acceptors designed for photovoltaic applications. We highlight how some photocurrent-detected implementations are particularly valuable in optoelectronic devices.

2 Two-Dimensional Coherent Spectroscopy

In optical spectroscopy, the interaction between light and matter produces an induced mesoscopic polarization $\tilde{P}(t)$ that depends on time according to the electric field component of the driving electromagnetic waves. According to the laws of electrodynamics, this time-varying polarization serves itself as a source of electromagnetic waves, resulting in emission of radiation (measurable signal) with a well-defined wavevector ($\vec{k}$) that respects momentum conservation of the incident excitation source, meaning it has a distinct spatial orientation (see Fig. 1 and Ref. [54] for an example of this experimental implementation). If the excitation source is coherent, due to laser excitation, this signal has, in principle, a well defined phase relationship with respect to the excitation source, and the dissipation of this coherence limits the optical linewidth. Quantum mechanics establish that the induced polarization is the expectation value of the quantum dipole operator $|\vec{P}|$, in which the electric fields drive transitions between quantum states of the system. It is common to expand the induced polarization in a power series of the incident electric field, taking into account successive light-matter interactions:

$$P(t) = \varepsilon_0 \left( \chi^{(1)} E_A(t) + \chi^{(2)} E_A(t) \cdot E_B(t) \right. + \left. \chi^{(3)} E_A(t) \cdot E_B(t) \cdot E_C(t) + \ldots \right),$$

with the nonlinear susceptibilities $\chi^{(i)}$ (which are tensors), $\varepsilon_0$ the vacuum permittivity, and $E_j(t)$ the electric field of the wavepackets of the individual laser pulses that are used to induce the successive light-matter interactions. In the first order of this expansion, the polarization is proportional to the incident electric field, which corresponds to the linear response of the sample. All higher orders are considered to be the non-linear response of the material. The most common way to explore the non-linear response is to have multiple electric field interactions with the material. This involves using light pulses with strict time control (inter pulse delay), well-defined phase, and frequency control (pulse spectrum),

Fig. 2 Example of a 2D spectra of a system with two excited levels $|a\rangle$, $|b\rangle$ and a ground state $|g\rangle$. (a) The spectrum is symmetric along the diagonal since the states share a common ground, (b) the states are decoupled, (c) coupling of the b and a states leads to relaxation of b towards a, which translates to an asymmetric amplitude of the off-diagonal peaks. Insets show the energy diagrams of the excited state couplings. Modulus of a rephasing 2D spectrum for an inhomogeneous system. (d) Each resonant frequency is decoupled from the others and is represented by a red circle. The homogeneous width of each emitter, represented by the size of the circle, is measurable along the anti-diagonal. (e) The total signal forms an elongated peak along the diagonal (inhomogeneous broadening). (f) Pulse sequence used to perform a MDCS measurement involving 3rd order polarization.
with a typical experimental geometry as depicted in Fig. 1. This is one implementation of multi-dimensional coherent spectroscopy (MDCS), but we note that there are a diversity of MDCS; we direct the reader to Ref. 56 for an excellent overview of the diversity of techniques. The \( n \) number of light pulses employed corresponds to the \( n^{th} \) non-linear order, e.g. interaction of three light pulses corresponds to the \( 3^{rd} \) order non-linear response of the material, five light-matter interactions correspond to the \( 5^{th} \) order non-linear response, and so on. The work on conjugated polymers has been limited to probing the third order response, and we thus limit our discussion on this order of nonlinear spectroscopy.

In MDCS, the non-linear signal contains information regarding ultrafast dynamics of electronic and vibrational phenomena of a system. Some advantages over linear spectroscopy techniques are the ability to resolve homogeneous and inhomogeneous broadening of the spectral features independently from each other, the separation of interaction pathways as well as the identification of correlations (coupling) between exited states of the system. Additionally, the signal detection is not limited only to coherent light, but in can also be implemented in order to detect incoherent emission, photocurrent, steady-state photoinduced absorption, or transient absorption.

For the case of isotropic media the second order MDCS signal vanishes, consequently the most common measurement is of third order susceptibility \( \chi^{(3)} \) in equation 1. Three light pulses are required in order to obtain a third order non-linear response, with geometry as depicted in Fig. 1(a), and again in Fig. 2(f). The first pulse, creates a coherent superposition between the ground and an excited state of the system, also known as coherence. The phase of this coherence oscillates at the frequency difference between the ground and excited states during a time \( \tau_1 \), and mesoscopically, a coherent polarization is generated. The second pulse creates a population state that evolves during a time \( \tau_2 \). Depending on the experiment, instead of population, the second pulse can create further coherences between higher excited states. Finally, the third pulse creates a new coherence between ground and excited states, which radiates the measured signal after a time \( \tau_3 \). This is represented in Figs. 1(b), 1(c), and 2(f).

A MDCS experiment records the phase oscillations of the coherences created by pulse 1 and measured with pulse 2, as a function of the delay time \( \tau_1 \). Subsequently, a 2D spectrum is extracted using a Fourier transform along that time variable. The axis related to the Fourier domain of \( \tau_1 \) is referred to as excitation (or absorption) energy. The spectral amplitude and phase of the coherent signal emitted by the nonlinear material response is measured with a spectrometer and heterodyne detection (spectral interferometry) with the LO pulse, and this spectral axis is referred to as the emission energy, and these spectral interferograms are mea-
sured as a function of $\tau_1$, usually at fixed $\tau_2$, but alternatively in the case of two-quantum coherence measurements, at fixed $\tau_1$ and as a function of $\tau_2$ (Fig. 1(a)). Fig. 2 shows a simulation of typical MDCS 2D maps considering a system of two excited states. The features along the diagonal correspond to optical transition autocorrelations, which reproduce the structure of a common linear absorption spectrum. Off diagonal features (cross-peaks) are created when different excited states share a common ground state (Fig. 2(a)), meaning that it is an intrinsic feature of the material and not an indication of sample inhomogeneity. The absence of cross peaks (Fig. 2(b)) reflects two uncorrelated optical transitions. Variations in the intensity and shape of these cross-peaks provides information on the coupling (correlation) strength between the exited states (Fig. 2(c)).

Measurements can be classified as N-quantum depending on the difference in the number of quanta separating the two states involved in the generated coherences. The most common example is a one-quantum (1Q) measurement where the ground and excited state are separated by one quantum of the incident photon energy. In this case the MDCS 2D map probes directly the optical transitions related to absorption and photoluminescence phenomena of the sample.

To probe excited states lying two-quantum above the ground state arising from e.g. biexcitons, it is necessary to perform two-quantum (2Q) measurements. Depending on the MDCS experiment, when having a non-collinear beam configuration, it is possible to isolate two-quantum coherent signals by using a specific pulse sequence as depicted in Fig. 1(c). While, for a collinear beam configuration this can be achieved by doing a second harmonic lock-in demodulation. This experiment has demonstrated to be sufficiently sensitive to probe biexciton states in a polymeric system.

The 2D spectra measured with MDCS provides us with the ability to separate the homogeneous and inhomogeneous broadening contributions of the spectral linewidth, in contrast to linear spectroscopy techniques, where the spectral features are a combination of both types of broadening. The homogeneous linewidth is directly related to the time decay of the coherence generated by the light-matter interaction (also known as dephasing time). Meanwhile, in the case of inhomogeneous broadening, the linewidth is the result of the contributions from the distribution of resonant frequencies, brought on by sample inhomogeneities, defects, Doppler broadening, etc.

Figs. 2(d), (e) show an example of a 2D spectra where a distribution of decoupled emitters, each one with its own homogeneous width (red circles), leads to the emergence of a spectral feature with inhomogeneous (homogeneous) broadening corresponding to the diagonal (cross-diagonal) width of the measured peak, in the limit of strong inhomogeneity. Typically, the way in which the inhomogeneous (homogeneous) linewidths are obtained is by measuring the peak width along a cut in the diagonal (cross-diagonal) of the 2D spectra. However, this procedure is not entirely accurate in the limit in which inhomogeneous broadening is not the dominant contribution. As Siemons et al. showed, there is coupling between the diagonal and cross-diagonal spectral lineshapes, i.e. an increase of the inhomogeneous broadening will also lead to a slight elongation in the cross-diagonal direction, and vice versa. The authors demonstrate a method, using projection-slice theorem, to extract the absolute homogeneous and inhomogeneous linewidth of the spectra. They considered a Markovian approximation for the homogeneous broadening (resulting in an exponential decay with a dephasing rate $\gamma$), and a Gaussian envelope of with $\sigma$ for the inhomogeneous broadening.

Conjugated polymers referred to in this work are typically in an inhomogeneous broadening limit. This means that the intrinsic homogeneous (inhomogeneous) broadening can be obtained by performing a zero-time rephasing experiment, and measuring the Lorentzian (Gaussian) width of the cross-diagonal (diagonal) feature. In this type of measurement, the phase evolution of the coherence during $\tau_1$ and $\tau_3$ are opposite, so any non-intrinsic inhomogeneous dephasing that occurs during $\tau_1$ is cancelled by a mirror-opposite rephasing during time $\tau_3$. If the population time is set as $\tau_2 = 0$, then the measurement is referred to as photon-echo. We will consider below an example of a 2D coherent spectral lineshape that is not indicative of dominant inhomogeneous broadening, although this would not have been evident from linear spectral lineshape analysis.

We highlight that in spite of efforts by some members of the MDCS community to establish conventions, there are currently none for displaying MDCS plots, as different authors display such spectra in different ways. (Even the current authors have adopted different conventions over time.) The published data displayed in this review reflect that sociology.

3 Excitons in neat polymers

3.1 Linear optical signatures of excitons in photophysical aggregates

The photophysics of conjugated polymer assemblies can be understood in the context of Kasha theory. In this model Kasha et al. describe the role of optically generated excitations in the absorption and fluorescence of small chromophore aggregates. Briefly, Coulombic coupling is mediated via dipole-dipole interactions between polymer chromophores, leading to the formation of excitonic states. If the coupling term is negative, the neigh-
bouring polymer chains have a head-to-tail orientation and are referred to as J-aggregates. On the other hand, if the coupling term is positive, the chain arrangement is side-by-side and the polymer is known as H-aggregate.

Excitons have different physical traits depending on the geometric arrangement of the chains. In J-aggregates (along the chromophore chain), excitons are of Wannier-Mott characteristics, meaning they can be separated over several repeated units. For H-aggregates (across the chains), the excitons have more Frenkel-like properties, where the separation is limited to neighbouring chains.

Extensions to the Kasha model include the effect of intramolecular vibrations on the spectra of exciton states. These vibrations are often referred to as progression-building due to the characteristic succession of peaks that appear in the absorption/emission spectra, as shown in Fig. 4 for poly(3-hexylthiophene) (P3HT) films. Because of this, P3HT has been used as model platform to develop the physical understanding of vibrational coherence and electron transfer dynamics in organic photovoltaics. Its semi-crystalline nature gives rise to the previous mentioned vibrational structure, and its strong coupling with optical excitons are visible in the absorption/emission spectra.

P3HT aggregates formed from good solvents are mostly H-like (see Fig. 4), favoring interchain interactions. This is likely due to the abundance of aggregates with low conjugation lengths, consequence of a high level of disorder brought on by fabrication processes (rapid solvent evaporation, spin-casting films, etc.).

The underlying differences between J- and H-aggregates are reflected in the features of the absorption and photoluminescence (PL) spectra of the polymers. The clearest example is the Frank-Condon vibronic progression resulting from coupling between the vinyl-stretching modes of the π-conjugated backbone and the optical exciton $S_0 \rightarrow S_1$ transition. Understanding this vibrational structure of the absorption and PL spectra has been a key approach to explain structure-property relations. Any distortion on the vibronic progression upon aggregation helps predict the effect on the spectral features due to disorder, temperature and molecular assembling.

Regarding the PL spectrum, it is considered that the emission occurs from the lowest energy exciton following Kasha’s rule. In the absence of disorder, this corresponds to an exciton with wavevector equal to zero and vibrational quanta $\nu = 0$ (labeled as 0-0 in Figure 3). Subsequent spectral peaks are referenced according to the total number ($\nu$) of vibrational quanta. The relative intensity of the 0-0 peak with respect to the rest of the vibronic progression is directly related to the exciton coherence length (distance over which an exciton maintains wavelike behaviour).

Specifically in J-aggregates, higher exciton coherence lengths lead to constructive interference between the emitting dipoles resulting in an enhancement of the 0-0 peak, whilst for H-aggregates, the interference is destructive, causing a suppression of the 0-0 spectra peak. Therefore, an ideal H-aggregate has a PL spectrum formed by a vibronic progression without the 0-0 peak, whereas the PL spectrum of a J-aggregate is also a modified Frank-Condon progression, dominated by a superradiant 0-0 peak.

The PL spectra is also sensitive to the amount of disorder in the conjugate. In P3HT, this disorder comes in the form of structural (packing) defects, chemical impurities (oxidized defects), torsional defects. In H-aggregates, where the 0-0 peak is suppressed, the introduction of disorder allows for 0-0 emission. Meaning that the strength ratio between 0-0 and 0-1 emission is direct probe for disorder.

Another defining difference between J- and H-aggregates is observable in the absorption spectrum. The ratio of the $A_1$ and $A_2$ absorption peaks is related to the nearest-neighbor interchain Coulomb coupling, which is directly proportional to the exciton bandwidth. In the case of J-aggregates, an increasing ratio reflects an increase in the exciton bandwidth as well as a redshift of the main peak ($A_1$). For H-aggregates, the behaviour is opposite, i.e., the increase ratio of the $A_1$ and $A_2$ correlates to a decrease in the exciton bandwidth and a blue-shift of the spectrum.

Previous studies have found that the exciton bandwidth depends on the interchain Coulomb coupling, which at the same time depends on the conjugate chain length $L$. Once $L$ exceeds the intermolecular separation, the interchain coupling goes down as a function of $L$, i.e., shorter chains lead to stronger interchain interaction and more H-like behaviour.

In an ideal case where the chains are infinitely long, the interchain interaction vanishes. This indicates that the absorption spectra can directly probe the interchain coupling and intrachain order. In practice, one has to take into account concurrently inter- and intra-chain interactions in the calculations. Therefore a realistic picture of a polymer aggregate is one that has both a J- and H-characteristics, meaning the polymer is a 2D excitonic system containing delocalized excitons along the polymer chain as well as between the chains. Despite the valuable information that can
be extracted from absorption and photoluminescence spectra, the
details on how excitons interact with their environment cannot
be obtained from the linear spectra. This is mainly because the
homogeneous and inhomogeneous line broadening cannot be se-
lectively extracted from the total spectral width. In this context,
MDCS has been an important tool to disentangle these broaden-
ing contributions.

In the following sections we will discuss results regarding the
photoexcited dynamics of neat polythiopehenes, and their blends,
as well as population effects on the spectral linewidths probed via
MDCS experiments.

3.2 2D coherent excitation lineshape of HJ aggregates

We start our discussion of spectral lineshapes by considering
MDCS measurements on a relatively rigid polythiophene deriva-
tive. The 2D coherent rephasing spectrum of [poly(2,5-bis(3-
hexadecylthiophene-2-yl)thieno[3,2-b]thiophene)] a conju-
gated polymer in the polythiophene family, at zero population-
waiting-time, i.e. \( \tau_2 = 0 \) in Fig. 2(f), is displayed in Fig. 5. Part
(a) displays the norm of the spectrum, while parts (b) and (c) dis-
play the real and imaginary spectra, respectively. In this sample,
the linear lineshape (top panel) is very similar to that of P3HT in
Fig. 4(a), and is indicative of dominant H-aggregate behaviour.

The diagonal 0–0 feature in Fig. 5(a) is suppressed with respect
that corresponding to 0–1, consistent with the lineal lineshape.
Cross peaks between the 0–0 and 0–1 diagonal peaks are also ob-
erved, as expected for a vibronic progression, which is the situa-
tion depicted in Fig. 2(a). The real and imaginary spectra, how-
ever, show structure in the (0–1/0–0) cross peak, with clear evi-
dence of an excited-state absorption superimposed with the cross
peak, a feature not observed in the (0–0/0–1) cross peak. This
excited-state absorption is associated with two-quantum transi-
tions, which will be discussed in Section 4 below. Furthermore,
the norm of the spectrum, shown in Fig. 5(a), displays highly
symmetric lineshape of the 0–0 and 0–1 diagonal peaks, which
is indicative of moderate inhomogeneity, a regime depicted in
Figs. 3(b) and diagonal and anti-diagonal cuts in Fig. 3(e). From
this lineshape, the homogeneous and inhomogeneous linewidths
have been extracted, and it was concluded that the importance
of the homogeneous contribution to the total linewidth is indicative
of the importance of dynamic disorder in this polymer system.
The nonlinear coherent lineshape thus reveals richer information
than available via the linear spectrum.

3.3 Homogeneous dephasing and exciton delocalization

Single-molecule spectra of conjugated aggregates differs appre-
ciably from its solid state counterparts, in such manner that the
spectral lineshape is not due solely to a distribution of inhomo-

genous resonators. Previous studies on isolated P3HT chains at low temperature (4 K) showed that the PL spectrum spans over a large spectral range in the visible region, with a linewidth ranging from \(~10-30\) meV and almost invariant line shapes. Thiessen et al. suggested that the inhomogeneous broadening of the PL emission of solution P3HT arises from the conformational disorder at the single chain level. They hypoth-

![Graph](https://via.placeholder.com/150)

**Fig. 5** (a) Absolute rephasing 2D coherent spectrum of PBT TT at zero-
population-waiting time, measured at 5 K. The 0–0 and 0–1 diagonal
peaks, as well as their cross peaks, are indicated in the figure. (b) Real
and (c) imaginary components of the spectrum in part (a). Top: absorp-
tion spectrum of PBT TT and spectrum of the femtosecond pulses used
in the measurement. Previously unpublished data.
esized that intrachain torsional disorder gives rise to a distribution of chromophore energies through exciton delocalization and electron-hole polarization. Consequently, this energetic disorder is responsible for the variability in the spectral range of the emission spectra, leading to a large inhomogeneous linewidth. This is in contrast to bulk films, where the line shapes are very strongly dependent on the film microstructure. The authors of Ref. [109] argued that the emission spectral lineshape in the bulk is composed of a distribution of single-chain emission spectra that are distributed throughout the entire visible range, and not dictated by the aggregate mode of Spanj,

That report highlighted the need to experimentally isolate the homogeneous spectral linewidth of P3HT in the solid state.

In a subsequent study, Gregoire et al. [83] measured simultaneously the homo/inhomogeneous excitation linewidth of a P3HT bulk film and compared them to those obtained by single-molecule measurement, in order to determine the validity of aggregate excitonic models and the effects of aggregation. They employed an MDCS variant referred to as two dimensional photoluminescence (2DPL), where the measured nonlinear response is the time-integrated PL intensity. The authors demonstrated that the homogeneous linewidth was an order of magnitude larger compared to single polymer chains (at 8 K). This can be seen in Fig. 6(a), which presents the modulus of a 2D rephasing spectra. Fig. 6(b) shows the extracted homogeneous linewidth (blue dots) compared with simulations performed with a homogeneous dephasing rate of $2\gamma = 90$ meV (black line). The obtained dephasing rate is close to an order of magnitude larger than the lower limit reported for isolated chains. [109] This establishes unambiguously that the bulk spectral lineshape is not due to a distribution of non-interacting single-chain spectra, but by solid-state, aggregate dispersion that results in more rapid homogeneous dephasing.

In addition, Gregoire et al. [83] reported numerical simulations of the 2D rephasing and nonrephasing spectra, both with homogeneous dephasing rates of $2\gamma = 30$ meV and $2\gamma = 90$ meV (see Fig. 7). The authors demonstrated that a homogeneous linewidth of $2\gamma = 30$ meV, which would correspond to an upper limit of the single-chain linewidth [109], leads to a significantly narrower 2D spectra compared to the measurements. The simulations considered an inhomogeneous linewidth of $\sigma = 130$ meV which corresponds to the disorder widths previously used to model absorption and PL lineshapes in P3HT [25]. The authors suggested that the additional homogeneous broadening seen in the bulk film comes from interchain photophysical aggregate effects, which consists of fluctuations in excitonic coupling between $\pi$ electrons across chains [22], increasing the dephasing rate and promoting H-aggregate-like signatures in the spectra.

### 3.4 Exciton population dynamics in P3HT

MDCS has been shown to be a powerful method to study the sub picosecond time evolution of electronic and vibrational coherences, specifically in conjugated polymers, where strong correlation and population dynamics can affect exciton delocalization [113,118] vibrational relaxation [119,122], electron trans-
Fig. 8 Representative absorptive 2D spectra of P3HT film with a population time $\tau_2 = 200$ fs, along with the linear absorption and photoluminescence spectra to illustrate the peak positions. Figure extracted from Ref. [84].
Fig. 9 (a) Real part of the MDCS 2D maps of a P3HT film at different population times $\tau_2$. (b)-(d) Time traces of the amplitudes of one diagonal peak (with excitation and detection wavelengths at 564 nm) and two cross peaks (with excitation wavelength at 614 nm (or 564 nm) and detection wavelength at 564 nm (or 674 nm)). Time traces from the rephasing spectra (absolute value, cross), nonrephasing spectra (absolute value, empty circle), and the 2D spectra (absolute value, empty square) are shown. (e) and (f) Correspond to the Fourier transforms of the time traces of two diagonal peaks (with excitation and detection wavelengths at 564 nm (or 614 nm)) along the population time axis. Figure extracted from Ref. 84.
Fig. 10 Two-dimensional coherent photoluminescence excitation (2D-PLE) spectroscopy. (A) Schematic of the experimental pulse sequence. Here $\phi_i$ is the phase of pulse $i = 1, 2, 3, 4$. The inter-pulse delays are $\tau_{21}$ (coherence time), $\tau_{32}$ (population waiting time), and $\tau_{43}$ (coherence time). The phase-modulation reference waveforms for phase-sensitive detection are generated optically at frequencies $\Omega_{21}$ and $\Omega_{43}$, at which the relative phase $\phi_{21} = \phi_2 - \phi_1$ and $\phi_{43} = \phi_4 - \phi_3$ oscillate, respectively.

In this work, time and spectrally integrated photoluminescence (PL) intensity is demodulated by phase-sensitive detection at the reference frequency $f_{\text{ref}} = \Omega_{43} + \Omega_{21}$ and $\Omega_{43} + 2\Omega_{21}$ for the one- and two-quantum correlation spectra, respectively, shown in Fig. 11. We outline in Supplemental Material that the 2D-PLE lineshape can contain contributions from nonlinear incoherent population dynamics over the entire exciton lifetime, and that all spectral lineshapes presented in Fig. 11 are free from this undesired contribution under the excitation conditions of this experiment. (B) Double-sided Feynman diagrams of the two most important two-quantum response terms that couple a ground state ($|0\rangle$), a single exciton state ($|1\rangle$), and a two-exciton state ($|2\rangle$). (C) Schematic representation of the 2D-PLE expected spectrum for two correlated optical transitions at energies $\hbar \omega_a$ and $\hbar \omega_b$. The spectral axes $\hbar \omega_{21}$ and $\hbar \omega_{43}$ are obtained by Fourier transform of the 2D coherent PL decay function along time variables $\tau_{21}$ and $\tau_{43}$ at fixed $\tau_{32}$. (D) Schematic representation of a two-quantum 2D-PLE correlation spectrum. The two-quantum energy $\hbar \omega_{21,2Q}$ corresponds to the two quantum coherences involving pulses 1 and 2. The diagonal line represents $\hbar \omega_{21,2Q} = 2\hbar \omega_{43}$.

Fig. 11 2D-PLE spectra measured at 5K and $\tau_{32} = 30$ fs. (A) The real part of the one-quantum non-rephasing ($f_{\text{ref}} = \Omega_{43} + \Omega_{21}$) spectrum. (B) The real part of the two-quantum ($f_{\text{ref}} = \Omega_{43} + 2\Omega_{21}$) spectrum. (C) Spectral cuts along $\hbar \omega_{21,2Q} - \hbar \omega_{\text{diag}}$ spectral axis at fixed $\hbar \omega_{43} = 2.06$ (blue), 1.99 (fuscia), and 1.94 eV (red) for the spectrum in B. Here $\hbar \omega_{\text{diag}}$ is the $\hbar \omega_{21,2Q} = 2\hbar \omega_{43}$ two-quantum diagonal energy, corresponding to zero net two-quantum correlation energy (neither binding nor repulsion). We chose to measure 2D coherent spectra with $\tau_{32} = 30$ fs in order to avoid ambiguous time ordering at $\tau_{32} = 0$. Due to the highly transient nature of the two-quantum coherence signal, it would not be possible to measure with $\tau_{32} \gg 30$ fs.
4.1 Two-quantum coherence measurements in PBT TT

We have recently explored the spectral structure of Frenkel biexcitons in PBT TT, with a nonlinear spectral lineshape already discussed in the context of Fig. 5 by means of two-quantum coherence measurements. Such measurements can directly identify biexciton resonances via two-quantum coherences. They can therefore quantify the biexciton binding energy. In that work, we constructed the coherent two-dimensional excitation spectrum via incoherent measurement of the time-integrated photoluminescence (PL) intensity due to a fourth-order excited-state population arising from the interference of wavepackets produced by a sequence of four light-matter interactions, allowing the measurement of the spectral correlations between resonance involving pulses 1 and 2 and those corresponding to pulses 3 and 4 in Fig. 10A. This is the same technique as was used for the homogeneous linewidth measurements of P3HT reported in Fig. 6. This technique uses phase sensitive detection to construct the 2D coherent spectrum by modulating the relative phase of each pulse pair in the four-pulse sequence, and demodulating the total photoluminescence signal at a side band of the two phase modulation reference waveforms. However, in Ref. 80 we implemented the demodulation at the second harmonic of the signal relative to the phase modulation function of the first two pulses. The two energy axes are constructed by Fourier transformation of the two-dimensional coherence decay function along time variables t_{21} and t_{43} at a fixed population time t_{32}. Accordingly, the spectral correlation along resulting energy axes (hω_{21}, hω_{43}) involves single-quantum (|0⟩→|1⟩) and two-quantum (|0⟩→|2⟩) transitions, represented schematically in the left of Fig. 10B. The two principal coherent pathways involving the correlations between one- and two-quantum coherences under this detection scheme are depicted by the double-sided Feynman diagrams in Fig. 10B. We also display schematic diagrams of the one- and two-quantum 2D-PLE coherent spectra for two correlated transitions in Figs. 10C and 10D respectively. These may be correlated, for example, via a common ground state such as H-like and J-like states in a HJ aggregate, each evident in the diagonal of the 2D-PLE spectrum (hω_{21} = hω_{43}). In the two-quantum correlation spectrum, a signal along the two-quantum diagonal (hω_{21} = 2hω_{43}) signifies two non-interacting excitons, while a signal above or below the diagonal signifies binding interactions with repulsive or attractive character, depending on the signs of the excitonic coupling (H- or J-like coupling), respectively. In Fig. 10A, the lower energy diagonal peak displays 2J biexcitons (the two-quantum energy is higher than twice the one-quantum energy), while the higher-energy resonance displays structure corresponding to 2H biexcitons (in which the two-quantum energy is less than twice the one-quantum energy).

The 2D spectrum in Fig. 11A is dominated by a symmetric diagonal peak centered at hω_{21} = hω_{43} ≈ 2.06 eV, corresponding to the 0–0 peak energy. We also observe a weak diagonal signal centered at ≈ 1.99 eV, with even weaker structure identified at lower energy. These features display intense cross peaks with the (0–0) resonance. The rich spectral structure displayed at the low-energy tail of the 2D-PLE spectrum demonstrates the existence of distinct states at the low-energy edge of the 0–0 absorption peak. We note that the energy of the weak diagonal feature corresponds to the 0–0 absorbance peak energy found in PBT TT J-aggregates induced when blending this semiconductor with a polar commodity plastic. We thus hypothesize that these are weak signatures of J-aggregate macromolecular conformations bearing effects of interactions with static dipoles. We present in Ref. 80 the linear absorption spectrum of the same batch of PBT TT in a blend with an ionic liquid, processed such that the J-aggregate dominates the lineshape, which supports the assignment in Fig. 11A. The 0–0 absorption peak in that film is at 1.96 eV, consistent with the spectrum reported in ref. 138, which supports the assignment of the weak, low-energy diagonal feature as the origin of the J-aggregate progression.

We observe in Fig. 11B a broad distribution along the two-quantum energy axis hω_{21,2Q} centered at the one-quantum energy hω_{43} = 2.06 eV (the 0–0 excitation maximum), with the peak of the distribution below the two-quantum diagonal, i.e., below the energy at which hω_{21,2Q} = 2hω_{43}. Thereby, the spectrum cuts through the diagonal line, with a tail extending to the high-energy side of the diagonal. We also observe two-quantum peaks for the features at lower energy than the 0–0 peak in Fig. 11A. These are both centered at higher energy than the diagonal; meaning that the two-quantum correlation is predominantly repulsive for the low-energy features. In Fig. 11C, we display cuts of the two-quantum excitation spectrum at fixed one-quantum energies hω_{43}. The cuts are along hω_{21,2Q} relative to the two-quantum diagonal energy hω_{diag}. This is a good reference because signal on the diagonal corresponds to the energy of two excitons that coexist without interaction. Importantly, we notice, on the one hand, that the 0–0 absorption peak, assigned to the vibronic progression of an H aggregate, forms biexcitons with attractive interactions with E_{21,1b} = −64 ± 6 meV. On the other hand, the low-energy resonances, which we hypothesize to correspond to J-aggregate resonances, display predominantly repulsive two-quantum correlations, peaked at E_{21,1b} = +106 ± 6 and +233 ± 6 meV, respectively. This supports the hypothesis that both attractive and repulsive biexciton binding coexist within the inhomogeneously broadened 0–0 linear absorption peak.

A key finding of Ref. 80 is that that interchain H-like excitons are associated with intrachain exciton-exciton couplings. In contrast, interchain J-like excitons are paired by intrachain exciton-exciton couplings. In either case, the biexciton binding energy is related to the exciton-exciton contact interaction and the inter-site hopping (excitonic coupling) energy, which are intrinsic molecular parameters quantified by quantum chemistry.
and that are expected to be controllable via chemical design and polymer assembly.

4.2 Biexciton stability and exciton-backbone coupling

We generally think of bound states as arising from an attractive interaction between two particles. However, in Ref. [80] as described in the proceeding section, we reported both attractive and repulsive biexciton binding; we reported further theoretical analysis in Ref. [139] where we discussed that in J-aggregate systems, 2J-biexcitons can arise from repulsive dipolar interactions with energies $E_{2J} > 2E_J$ while in H-aggregates, 2H-biexciton states $E_{2H} < 2E_H$ corresponding to attractive dipole exciton-exciton interactions. According to our model[139], Frenkel biexcitons mix J-like and H-like character in terms of their collective quantum behavior with the requirement that the ratio of the exciton/exciton interaction and the perpendicular hopping term be $U/t > 0$, with $t = -\hbar^2 / 2\mu J$ and $U < 0$ a contact interaction potential, which gives rise to localized biexciton states in the perpendicular direction.

We understand this in the context of a textbook-level model for a biexciton state interacting with a deformable lattice. Adopting a relative coordinate between the two excitons, we write the biexciton Schrödinger equation as

$$\tau\psi'' + U\delta(x)\psi = E\psi,$$

(2)

where $U$ is the contact interaction between the two excitons. For bound states, $\psi(x)$ must vanish as $x \to \pm\infty$, giving that

$$\psi(x) = \begin{cases} \sqrt{\kappa} e^{-\kappa x} & x > 0 \\ \sqrt{\kappa} e^{\kappa x} & x < 0, \end{cases}$$

(3)

where $\kappa = U/2t$ is a positive constant and $E = t\kappa^2$. In general, we take $t = -\hbar^2 / 2\mu J$ and $U < 0$ for an attractive potential giving rise to a bound state energetically below the continuum for the scattering states.

Generally, interactions with the lattice phonons produce an additional stability to the reorganization of the system about the bound state. However, in the case of the 2J bi-exciton, reorganization of the lattice can actually destabilize the state by pulling it back into the continuum of unbound states. To see this, we append to the 1D impurity model a term coupling the biexciton to the lattice as per the Davydov model[140][149] such that resulting equations of motion read

$$i\hbar\dot{\psi}(x) = (t\nabla^2 + U\delta(x) + (E_o + 2\chi \nabla u(x)))\psi(x) + \kappa \psi(x),$$

(4)

where $u(x)$ is the lattice deformation, $\chi$ is the linear coupling between the biexciton and the lattice, $m$ is the mass of the lattice “atoms” and $k$ is the elastic modulus. The bound-states are invariant under Galilean transformation and one can find a closure relation

$$\nabla u = \frac{2\chi}{k} |\psi|^2$$

(5)

that gives us a non-linear Schrödinger equation

$$i\hbar\dot{\psi} = (t\nabla^2 + g|\psi|^2 + U(x))\psi,$$

(6)

where $g = -4\chi^2 / k$. Note that $E_0$ is a constant given by

$$E_0 = E - 2t + \frac{1}{2} \int_{-\infty}^{\infty} (m\dot{u}^2 + k\ddot{u}^2) dx$$

(7)

that we can ignore for purposes of this analysis. The $\delta$-function potential implies the wave function should have the form in Eq. [3] Taking $\kappa$ as a variational parameter and minimizing the total energy, one obtains

$$\kappa = \frac{U}{2t} \frac{g}{8t}.$$ 

(8)

$\kappa > 0$ is necessary to produce a localized state and from above $U/t > 0$ and $g < 0$ from its definition above, we have a stability requirement that if $U > 0$ and $t > 0$, then $-g < 4U$. Solving for the binding energy,

$$E_B = \frac{(4U + g)^2}{64t}.$$ 

(9)

We obtain a straight-forward estimate of the contribution of both the lattice and the exciton/exciton coupling to the biexciton binding.

In Fig. [12] we plot the biexciton binding energy versus the non-linearity parameter, $g$. For the attractively bound 2H, lattice reorganization is expected to stabilize the biexciton state by further localizing the state ($\kappa$ increases as $g$ increases in magnitude). On the other hand, for the 2J state, increasing the magnitude of $g$ decreases $\kappa$ and destabilizes the otherwise bound 2J state by ef-
effectively pulling it back into the continuum of unbound (scattering) biexciton states. When $-g = 2U$ the state is fully delocalized and further increases in the lattice coupling lead to unbound solutions. We rationalize the biexciton spectral structure observed in Fig. 11 by the dependence of the biexciton binding energy on $g$ as reported in Fig. 12.

5 Photocurrent-detected spectroscopy in operating diodes

Two-dimensional photocurrent excitation spectroscopy (2D-PCE) is an MDCS experiment, where the detection mechanism probes the photocurrent generated by a sequence of four ultrashort laser pulses, akin to the photoluminescence-detected variant of the experiment in Fig. 11. 2D-PCE has been a key approach in the research of photocharge generation dynamics, not only because of the unique detection sensitivity but also due to the ability to probe the correlation between optical excitations and photocarriers in polymer semiconductors. These correlations are identifiable through cross-peaks in 2D spectral maps, and are of the utmost importance to study materials in which photocarrier precursors, such as excitons in molecular semiconductors, are the primary photoexcitations. A special case are materials for photovoltaic applications, such as solar cells based on PCDTBT:PCBM blends (Fig. 13(a)). This is a polymer:fullerence benchmark system that has been shown to yield solar-power conversion efficiencies as high as 7%\(^{150,151}\). The photocurrent excitation spectrum of this system is displayed in Fig. 13(b).

Importantly, Vella et al.\(^{72}\) demonstrated that illumination using an ultrafast pulse sequence such as that depicted in Fig. 11 at sufficiently low fluence, produces J-V curves that match those under standard solar (AM 1.5G) illumination, shown in Fig. 13(c),
where the current density (as a function is applied voltage) is compared between both types of illumination. This result suggests that the current densities probed by 2D-PCE experiments are comparable to those of a functioning solar cell, which is critical in establishing that these advanced optical probes probe dynamics in regimes that are relevant in the optoelectronic device.

Additionally, as a result of 2D-PCE measurements, Vella et al. suggested a tunneling process from an exciton state to a current producing charge-separated state. Consequently, the authors stated that the timescale of this process would be dominated by fluctuations due to interaction with the bath ensemble, predicting dephasing times \( \leq 20 \) fs. In order to test their prediction, the authors extracted the optical dephasing time by taking the antidiagonal cut of the 2D spectra, as shown in Fig. 14. The measured peak was fit to a Lorentzian function with a full-width-at-half-maximum (FWHM) of 100±1 meV. This represents the homogeneous linewidth of the main exciton transition from the donor polymer, and corresponds to a dephasing time of 13 fs 12.

A concurrent 2D-PCE study by Li et al. 57 on PCDTBT:PCBM, similar to that of Vella et al. 72 but with larger bandwidth of the ultrafast pulse, revealed an inhomogeneously broadened spectrum, and suggested structure of charge-transfer excitons and photocarriers. Fig. 15 was extracted from this study, and it shows the 2D maps corresponding to the rephasing (a,b), non-rephasing (c,d) and total spectrum (e,f). In addition, the authors demonstrated that the 2D spectra from photocurrent excitation (2D-PCE), photoluminescence excitation (2D-PLE), and photoinduced absorption (2D-PIA) all yield similar features, indicating that charge-transfer excitons, probed via photoluminescence, photocarriers via photocurrent, and polarons generally via quasi-steady-state photoinduced absorption, can all be probed using the same excitation pulsetrain sequence. This work further confirmed the polaronic nature of the photocarriers and charge-transfer excitons in PCDTBT:PCBM.

6 Perspective

Given the work that we have highlighted in this review, in this section we provide our vision of where MDCS can make further impact in the understanding of excitons in \( \pi \)-conjugated polymers.

6.1 Coherent optical lineshapes of photophysical aggregates

Besides disentangling the homogeneous and inhomogeneous contributions to the total spectral width, and thereby quantifying the optical dephasing processes in materials, MDCS can reveal a very well defined spectral structure as shown in Fig. 5, which displays the absolute, real, and imaginary spectra of the rephasing signal of a PBTTT film at 5 K and at a population waiting time \( \tau_2 = 0 \) fs. If we observe carefully Fig. 5(b) and Fig. 5(c), the real part of the 0–0 peak at \( \sim 2.06 \) eV displays absorptive lineshape in the real component, but dispersive character in the imaginary component; a diagonal peak in the real part and a derivative feature about the diagonal in the imaginary part. This is what is expected for non-interacting chromophores. However, the 0–1 diagonal feature at \( \sim 2.21 \) eV displays inverted behaviour: the real part displays apparently dispersive lineshape while the imaginary part displays apparently absorptive lineshape. This behaviour evolves over the first few hundred femtoseconds (data not shown here) such that this character inverts between 0–0 and 0–1 diagonal peaks: 0–0 in the real part evolves from absorptive to dispersive character in the real spectrum and vice-versa in the imaginary one. This behaviour encodes the quantum dynamics of the photophysical aggregates. It is well understood now that the 0–0 feature encodes the many-body behaviour of the aggregate 29. It will be highly insightful to describe this type of MDCS lineshape evolution by simulation of the quantum dynamics that include all of the aggregate many-body details, lattice reorganization, and energetic disorder. Our groups are currently focused in this work.

It was also highlighted in Section 3.2 that the absolute spectrum in Fig. 5(a) display highly symmetric diagonal 0–0 and 0–1 diagonal peaks. This reflects a comparable values of the homogeneous and inhomogeneous linewidths, which we interpret as indicative of dynamic disorder governing the disordered landscape in PBT. On the other, P3HT is clearly in an inhomogeneously broadened limit, as shown in Fig. 6. The linear absorption spectrum of both materials, however, displays similar total width, and it would not have been possible to differentiate between the two materials purely from linear spectroscopy. This presents an opportunity to investigate more technologically relevant families of conjugated polymers that have varying degree of backbone rigidity, and that span from flexible polymers such as P3HT to “hairy-rod” materials 152, for example.

Another opportunity for MDCS is to address lineshapes in push-
pull materials. There are already reports of these techniques applied to this class of materials. MDCS approaches are well suited to address the structure of inter-chromophore coupling effects due to charge-transfer interactions, and we consider that there is still much to understand in structure-property relations in this realm.

6.2 Two-quantum spectral structure of Frenkel biexcitons

The rich spectral structure revealed in Fig. 11 is intriguing in that it reveals the role of both attractive and repulsive binding in conjugated polymer hybrid HJ aggregates. We rationalized this observation by considering the geometry of two-quantum correlations along and between chains, but there is tremendous scope to understand this further with microscopic detail, and we consider that there is substantial scope for the electronic structure community to push the development of first-principle methods that account for many-body correlations to explore our reports of biexciton binding in PBTTT. On the same token, stochastic effects that drive many-body quantum dynamics need to be incorporated in the theoretical treatment of Frenkel biexcitons. Finally, we consider that the series of materials families that will be relevant for 2D coherent lineshape analysis in the context of the discussion in Section 6.1 should be studied with the double-quantum coherence techniques developed in Ref. 80, and the measurement should be executed beyond two-quantum correlations — how many Frenkel excitons correlate in the series of conjugated polymers of technological interest, and what does this imply for their potential in classical and quantum photonics?

6.3 MDCS in operating optoelectronic devices

Fig. 13 addresses a general criticism of ultrafast spectroscopy, which affirms that the excitation conditions and resulting excitation densities are beyond the regimes that are relevant in the operation of polymer-based optoelectronic devices. With photocurrent detection and using the phase-sensitive detection techniques developed originally by Tekavec et al., it is possible to measure nonlinear responses of the polymer semiconductor in a diode with current-voltage characteristics that are in the regime of solar power conversion. We consider that there is ample scope to expand the studies to address contemporary high-efficiency systems involving non-fullerene acceptor systems, in which the spectral structure of interchromophore couplings will play a crucial role in the understanding of device operation. One unexplored direction is in electrolytic cells. We have been able to carry out incoherent ultrafast experiments in conjugated-polymer-based electrochemical cells, and there are clear opportunities to extend such studies with the photocurrent/photovoltage spectroscopies discussed in this review. Nevertheless, the role of unexpected incoherent nonlinear population dynamics may be an issue in organic devices, and methods to decouple this background signal from the nonlinear coherent response will be required. However, this also presents an opportunity to develop methods to measure concurrently nonlinear population dynamics between multiple excitations, and the nonlinear coherent response of the material.

Author contributions

EGM and AVF gathered most of the material described in this review article, and led the early drafts of the manuscript. CSA and ERB led the intellectual development of the article. All authors participated in the redaction of the manuscript.

Conflicts of interest

There are no conflicts of interest to declare by any of the authors.

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