Topical Review

Exciton dynamics in 2D organic semiconductors

Ankur Sharma, Md Mehedi Hasan and Yuerui Lu

School of Engineering, College of Engineering and Computer Science, The Australian National University, Canberra, ACT 2601, Australia

E-mail: yuerui.lu@anu.edu.au

Received 16 August 2022, revised 8 September 2022
Accepted for publication 13 September 2022
Published 28 September 2022

Abstract

Two-dimensional (2D) semiconducting materials have been studied extensively for their interesting excitonic and optoelectronic properties arising from strong many-body interactions and quantum confinement at 2D limit. Most of these materials have been inorganic, such as transition metal dichalcogenides, phosphorene, etc. Organic semiconductor materials, on the other hand, have been investigated for their excellent electrical conductivity and low dielectric coefficients for similar applications in the thin film or bulk material phase. The lack of crystallinity in the thin film and bulk phases has led to ambiguity over the excitonic and electronic/optical band gap characteristics. The recent emergence of 2D organic materials has opened a new domain of high crystallinity and controlled morphology, allowing for the study of low-lying excitonic states and optoelectronic properties. They have been demonstrated to have different excitonic properties compared with the Wannier–Mott excitons in inorganic 2D materials. Here we present our recent experimental observations and analysis of 2D organic semiconductor materials. We discuss the role of high-crystalline and morphology-controlled growth of single-crystalline materials and their optoelectronic properties. The report explains the Frenkel (FR) and charge-transfer (CT) excitons and subsequent light emission and absorption properties in organic materials. The true nature of low-lying excitonic states, which arises from the interaction between CT and FR excitons, is experimentally studied and discussed to reveal the electronic band structure. We then discuss the pure FR behaviour we observed in J–type aggregated organic materials leading to coherent superradiant excitonic emissions. The supertransport of excitons within the organic materials, facilitated by their pure FR nature, and the delocalization of excitons over a large number of molecules are also demonstrated. Finally, we discuss the applications and our vision for these organic 2D materials in fast organic light-emitting diodes, high-speed excitonic circuits, quantum computing devices, and other optoelectronic devices.

Keywords: excitonic, organic, semiconductors, two-dimensional

* Author to whom any correspondence should be addressed.

Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Future perspectives
The understanding of the low-lying excitonic states made possible due to high-crystalline two dimensional (2D) organic materials has led to various applications because of superradiant, narrow linewidth, and coherent emissions. In organic materials, we can achieve coherent emission at RT without coupling the 2D material to an optical cavity. This can lead to ultra-narrow linewidth lasers and high quantum yield organic light emitting devices. Also, utilising the supertransport (ST) of Frenkel excitons the organic 2D materials can act as building blocks for superfast excitonic circuit applications. The operation of excitonic circuits is based on the control of exciton fluxes by an external voltage and can have either excitonic or photonic inputs or outputs. Excitonic circuits based on organic materials will be able to provide high interconnection speeds between electronic and optical communication and signal processing devices. They can eliminate the delay between signal processing and optical communication. The demonstrated speed can be as quick as 0.2 ns and with ST reported in pentacene, it can be even higher. Second, organic 2D materials offer scalability and compactness. A field-effect transistor (FET) device made of organic 2D material is in principle like an electronic FET device, but with much faster-operating speeds. We have already demonstrated that optical emission can be externally controlled using a back gate voltage in an organic FET device. This opens avenues to make excitonic circuits and bridges between inorganic-organic electronic and photonic circuits. The major challenges for excitonic devices are finite excitonic lifetimes and limited binding energies. The excitons as demonstrated here can travel up to 1.5 µm with a lifetime of up to 3 ns in wetting layer and over 0.6 µm in 1L with much faster exciton diffusion coefficients compared to quasi-1D system. This makes these organic materials ideal candidates for excitonic device applications in FET devices, etc.

1. Introduction

Atomically thin two-dimensional (2D) materials and their hetero-structures have emerged as promising candidates and drawn great attention for future optoelectronic devices [1–6]. Compared with bulk materials, those atomically thin layers provide an ideal platform to investigate the strong many-body [7] interactions arising from the highly enhanced quantum confinement and reduced dielectric screening in atomic layers [8–12]. The majority of the 2D materials investigated so far, semi-metallic graphene [13], insulating hexagonal boron nitride (h-BN) [14, 15], transition metal dichalcogenides (TMDCs) [16–20], and phosphorene [21] are inorganic crystals having strong in planes of covalent chemical bonds. On the contrary, organic crystals are bonded by weak van der Waals (vdW) cohesive forces and lead to applications in photovoltaic energy generation, high-speed excitonic circuits, quantum computing, etc [22–24]. Materials like anthracene, tetracene, and pentacene show high charge carrier mobilities in crystal phase, making them excellent candidates for field effect transistors [25–27]. Pentacene, specifically promotes outstanding singlet fission crucial for improving solar cell efficiencies above the Shockley Queisser limit [28, 29]. Various studies have been done to demonstrate the optical and electrical properties of these organic materials and polymers in thin film and single crystal phases [1, 22, 30, 31]. The exciton, an excited electron–hole pair bound by Coulomb attraction, plays a key role in the photo-physics of organic molecules and drives practically important phenomena. Recently, it was demonstrated that using vdW epitaxy, high-quality organic materials like pentacene with controlled thickness could be grown on h-BN or graphene [32, 33], which was earlier possible only in the thin film phase. Though some studies have reported the nature of excitonic states in thin film organic states, there has been a long-standing ambiguity over the role of excitons and energy states in organic semiconductor materials due to a lack of experimental observations. Highly ordered single crystals provide the best platform to show the predictive structure-function relations of any material because of their high degree of structural order and chemical purity.

In this review, we establish the true nature of low-lying energy exciton states in organic molecular crystals, which were experimentally detected and studied in novel 2D organic materials. We review the role of Frenkel (FR) and charge transfer (CT) excitons and their coupled and decoupled states in determining the optoelectronic properties of these organic 2D semiconductor materials. We demonstrate how they are truly different from their inorganic counterparts such as TMDCs, which have the Wannier–Mott excitons defining their optoelectronic properties. In section 2 we describe the difference between crystal structure, energy states, and excitonic configuration between inorganic 2D, organic thin film, and organic 2D materials. This section further explains the role and optimised conditions of high-crystalline growth of organic molecular crystals on their intrinsic exciton energy states and hence the light emission and optoelectronic properties. Section 3 describes the detailed excitonic characteristics in these 2D materials and the emergence of orientation dependent optoelectronic properties classifying them into H and J-type aggregates with different energy states. The coupling of CT-FR excitonic energy levels lead to characteristic photoluminescence (PL) signatures in organic 2D materials, which have been described in detail in this section. Section 4 demonstrates the experimental observation of decoupled pure and quantified FR excitonic state emission reported from highly crystalline 2D organic materials, which have critical applications in coherent emissions-based applications. Section 5 builds on the coherent FR excitonic emissions and describes the phenomenon of superradiance (SR) and supertransport (ST) of coherent excitons in organic 2D materials establishing them as ideal candidates for high-speed excitonic circuit applications. Section 6 describes our vision and potential application areas for these organic 2D materials that make use of their novel excitonic properties and light emissions.

2. Optoelectronic properties of organic 2D materials

Organic semiconductors as a class of semiconductor materials have a characteristic advantage as they combine the advantages of semiconductor materials with the chemical and mechanical benefits of organic compounds and molecules [34]. They provide great flexibility to tailor emission wavelengths...
by changing their manufacturing, are light, flexible, and can be produced easily on a large scale. Organic semiconductors have been studied to be of three major types, including amorphous films, molecular crystals, and polymer films. They all have their semiconducting properties originating from the nature of π electrons in the overlapped molecular orbitals and the coupling of molecules in the solid crystal resulting from strong coulombic interactions, as detailed in this section.

2.1. Optoelectronic properties and band structures of organic and inorganic materials

There have been several organic semiconductors studied over the last few decades in various forms. They are very different from other inorganic semiconductors, which have a band gap in the visible wavelength range. Traditional semiconductors such as germanium, GaAs, and silicon have low band gaps from 0.6 eV – 1.4 eV at room temperature. Thus, free charges in them can be created by excitation from a valence band to a conduction band, and they have large dielectric constants. In contrast, organic semiconductor materials and their conductivity result from doping or photogenerated e-h pairs, which are bound by mutual coulomb interaction as their dielectric coefficients are low and hence a much larger binding energy of excitons is expected. Figure 1 shows the key difference between the inorganic, organic thin film, and 2D organic materials. The concept of a single band gap between valence and conduction bands to explain the inorganic semiconductors does not apply to organic semiconductors. Organic semiconductors have various energy bands formed due to the molecular overlap of π electrons, and each band has its energy, bandwidth, and photo-physical properties which are critically affected by their growth conditions, molecular orientation within the crystal, and degree of purity. The inorganic 2D materials such as MoSe$_2$ and WSe$_2$ have a covalently bonded crystal lattice which results in a one characteristic band gap separation between conduction and valence bands as shown in figures 1(a) and (b). Wannier–Mott excitons are commonly found here, which can be represented by hydrogen like functions. The mean e-h distance is large as compared to the lattice constant, which is made possible due to a lower effective mass resulting from weak coulombic interaction and large
atomic orbitals overlapping in inorganic materials as shown in figure 1(c). On the other hand, in organic thin films or bulk materials, the coulomb attraction is much stronger due to lower dielectric coefficients, and the excitons are much smaller in size as shown in figures 1(d)–(f). The band structure is formed because of hybrid p-orbitals in the carbon atom a sit binds with other atoms. Thus, electrons no longer belong to one atomic orbital but instead are shared between two molecular orbitals. This generates a complex energy state defined between the highest occupied molecular π orbital and lowest unoccupied π* molecular orbital as shown in figure 1(e). The transitions between π and π* orbitals are mostly in the visible range which makes them suitable candidates for semiconducting applications. Thus, organic semiconducting materials have much smaller FR and CT excitons. This makes the excitonic nature of organic crystals more complex than that of inorganic solid-state semiconductors. The FR exciton is a neutral excited state in which the electron and hole are placed on the same molecule. They show characteristic large short-range coupling and high radiative efficiencies, enabling potential applications in lasing and organic light-emitting diode (OLED) applications. Whereas, the CT exciton consists of a pair of charge carriers localized at different molecules, enabling long-range coulombic coupling and low recombination suitable for organic solar cells and singlet exciton fission applications. A lot of studies have demonstrated the role of CT-FR excitonic states in determining the resultant and emission properties of organic semiconductors as their energies are very close and interact with each other as explained later in section 3. Several theoretical studies have been presented recently which show the role of coupled CT and FR states and explain the broad PL emission and absorption spectra that are commonly reported from organic materials. In recently demonstrated organic 2D materials as shown in figure 1(g), the morphology of each layer can be precisely controlled in the growth process of organic molecules over a substrate. The resultant band structure shows the emergence of clear and decoupled FR and CT excitonic states and hence the resultant light emission is also critically impacted. Figure 1(h) shows the coupled and decoupled FR-CT band structure in monolayer and multilayer organic material samples as reported by Sharma et al [33]. Figure 1(i) shows the physical schematic diagram of a true FR exciton where the e− and h+ reside on the same molecular unit as opposed to a CT exciton where they are shared by two nearby molecular orbitals.

2.2. Effect of crystallinity on the optoelectronic properties

The optical properties of organic materials are heavily influenced by large molecular π orbital overlaps and complex molecular structures. Hence, the degree of crystallinity and molecular orientation, both of which can be controlled during the growth phase, determine the optical properties in this case [35]. This was first demonstrated in tetracene monomers and thin film samples, as shown in figure 2(a) [24]. The monomer state demonstrates PL spectra similar to the neutral state FR excitons. The clear difference in optical emission and absorption of the monomer versus the crystalline thin
film showed the effect of crystallinity on the optical properties. The characterization of excitons in bulk organic crystals such as polymers is particularly complicated and challenging because of the large number of disorders and interfacial states in bulk samples [36–38]. Limited experimental evidence exists to identify the nature of intrinsic excitons in organic semiconductors because direct measurement of absorption is challenging due to difficulties in growing high-quality ordered optically transparent single crystal samples [24]. Fluorescence spectroscopic results are distorted due to high self-absorption, wave guiding from total internal reflection, and depolarization due to crystal birefringence [24]. This was experimentally demonstrated when bulk thin film pentacene samples with varied crystallinity degrees (controlled by changing growth conditions) were grown on hBN substrates as shown in figure 2(b). The resultant PL spectra at both room and low temperatures were broad PL spectra, which is characteristic of organic semiconductor thin films (figure 2(c)). But, as the thickness was controlled and the degree of crystallinity was improved, the emergence of sharp PL features like the ones demonstrated in figure 2(a) started appearing, demonstrating the impact of crystallinity on the optical properties (figure 2(d)).

This was further optimized, and recent studies probed the intrinsic excitonic nature of atomically thin organic 2D semiconductors grown using vdW epitaxy over h-BN substrates as shown in figures 2(e) and (f). On an h-BN surface with atomic smoothness and well-defined crystal facets, single-crystal pentacene (figure 2(e)) was epitaxially formed layer by layer. A recent report describes the layer-dependent arrangement of pentacene and associated electrical transport characteristics on h-BN. Figure 2(f) shows the layers of the pentacene sample where the wetting layer (WL) was the first pentacene layer and the next layer developed over WL was classified as 1L (thickness of 1.1 nm). The next layer grown on 1L was designated as 2L with a measured thickness of 1.6 nm, which is almost similar to the thin film phase [39]. In comparison to bulk organic and thin film samples, monolayer pentacene, which is an ultraclean system with high crystallinity and minimal interfacial states, enables the decoupling of anisotropic FR excitons from isotropic CT excitons. Due to the absence of high crystallinity, scattering, and the existence of disorders and interfacial states, mixed states are seen in most bulk and thin film organic semiconductors [36, 38]. This allowed to probe the intrinsic excitonic transitions in organic crystals at the quantum limit.

3. Excitonic characteristics of 2D organic materials

3.1. Orientation dependent optoelectronic properties (H and J aggregates)

Apart from the degree of crystallinity, the orientation of the molecules in the growth of organic semiconductors also critically affects the recombination energy distribution and excitonic states. The effect of molecular packing on excitonic states was first reported by Kasha [41], who extended the geometry-related FR exciton treatment by Davydov [42]. The crystallinity and molecular aggregation as simulated and predicted by Hestand et al [43] divided the aggregation into H and J-type. Studies have reported that the H-type aggregation causes broadening or weaker PL emission as compared to J-type aggregation, where the herringbone structure allows for aggregated and balanced molecular coupling leading to high mobility and high emission simultaneously. This was also confirmed by our experiments on pentacene layers that were epitaxially grown on h-BN substrates. The highly clean and sharp crystalline system allowed us to first identify the strongly aggregation-sensitive intrinsic excitonic emissions from the same type of organic materials at the atomic scale. From our temperature-dependent and angle-resolved PL measurements [33], H-type WL pentacene showed broad PL spectra as compared to a narrow PL emission from a J-type 1L sample as shown in figures 3(a) and (b). The orientation of the transition dipole moment (TDM) demonstrated by red arrows is different in H- and J-type. The resultant band structure is shown in figures 3(c) and (d). Only excited state bands with \( k = 0 \), where \( k \) is the quantum number of the wave vector representing the excitonic states, are permitted optical transitions from and to the ground state. The total TDMs in a group of molecules determine the oscillator strength of an optical transition. If the Coulombic attraction is larger than the Coulombic repulsion, the value of \( J > 0 \) and small total TDM, resulting in an optically forbidden lowest excited state (\( S_1 \)) [44]. If the Coulombic attraction is larger than the Coulombic repulsion, then value of \( J \) is negative (\( J < 0 \)) and a large total TDM, resulting in an optically allowed \( S_1 \). When \( J > 0 \), molecular aggregates are considered as H-type, and when \( J < 0 \), they are considered as J-type. Moreover, \( J > 0 \) is produced by side-by-side molecule orientations, whereas \( J < 0 \) is produced by head-to-tail molecular orientations.

Yamagata et al [45] also showed that the charge transfer has a significant impact to determine the H- and J-type behaviour which in turn is a direct consequence of molecular packing in oligoacenes. This was further confirmed by simulations using first principal Hamiltonian equations, as shown in figure 3(e). In 1L, the TDMs of each molecule (red arrow) are packed head-to-tail, but in WL, the TDMs are packed side by side. \( J \) denotes the excitonic interaction between local FR exciton states at nearest-neighbour molecules. The study found that \( J \) is negative in 1L (corresponding to J-type aggregation), resulting in a positive total TDM value along the ‘b’ axis of the pentacene unit cell (as
Figure 3. Orientation dependent optoelectronic properties and energy states. (a, b) Schematic diagram of the molecular arrangement in WL (a) and 1L (b) pentacene samples grown on hBN substrate and the orientation of the net dipole moment- head to tail (1L) and side by side in WL. (c, d) Schematics showing the excited states in an ideal H-type (c) and J-type (d) monomer. Orange arrows indicate the spin of electrons in each state. (e) TDMs at each molecule (red arrows) follow a head-to-tail packing in 1L, whereas TDMs in WL are packed side by side. The Coulombic contact force between nearby molecules is shown by pink arrows. Reproduced from [33]. CC BY 4.0.

shown by the purple arrow), allowing for emission from 1L, whereas $J$ is positive in WL (corresponding to H-type aggregation), resulting in very little emission from WL at 0 K. Thus, H- and J-type behaviour in WL and 1L viz. is a consequence of the molecular packing in these layers plus the columbic charge coupling.

3.2. Coupling of CT and FR excitonic states in organic thin film semiconductors

The FR exciton is a neutral excited state in which the electron and hole are placed on the same molecule. Frenkel excitons have large short-range Coulombic interactions and
high radiative efficiencies, making them suitable for use in OLEDs and laser devices [24, 45]. Whereas the CT exciton consists of a pair of charge carriers localized at different molecules. CT excitons exhibit long-range Coulombic interactions and low recombination rates, which makes them suitable for organic solar cells and singlet exciton fission applications [24, 45]. When the energy difference between CT and FR excitons is small enough, the excitons can interact and generate new FR–CT mixed states. Because of the absence of high crystallinity and the presence of disorders and interfacial states [36–38], most bulk and thin film organic semiconductors exhibit mixed states [46]. Figure 4(a) shows the coupled state of FR–CT states where the FR state is the low-lying state and that results in multiple new energy states in organic thin films and polycrystalline samples [47]. The energy of the CT and FR states can be reversed by deepening the packing style (face to face or herringbone). This was confirmed by theoretically calculating the contribution of CT excitons in the energy bad dispersion of pentacene sample by Hestand et al [43] as shown in figure 4(b). The model demonstrated the strong contribution of up to 45% of CT excitons in the b-polarized PL component of pentacene. The PL emissions, including their vibronic sidebands were discovered to consist of complex FR and two-particle CT excitonic states. The spectrum polarized along b displayed J-aggregate (FR exciton dominated) while the spectrum polarized orthogonal to b displayed H-aggregate (CT exciton dominated) [48]. Similar in PTCDA, the absorption and PL emission were identified to have a CT and FR coupled combination, determining the overall broad spectra as shown in figure 4(c) [49]. Hence, the strong FR–CT coupling results in the lack of feasibility of organic bulk thin film semiconductors to be ideal candidates to have applications in excitonic devices based on organic semiconductor materials. To limit FR–CT mixing and observe SR emission, we need to precisely control the crystallinity and molecular aggregation into H- and J-type, as predicted theoretically by Spano et al.

4. Decoupling of CT and FR excitonic states in organic 2D materials

Molecular organisation and aggregation are crucial for organic electrical devices. First, as explained in section 3, molecule
orientation affects charge carrier transit, light absorption efficiency, and other properties due to molecular packing. The second is due to packing-induced electronic energy levels, such as orientation-dependent ionisation energies, which impact energy level alignment and hence effect the charge injection barrier, charge transfer, charge transport, and exciton dissociation in organic semiconductor devices. As a result, having strong control over the molecular orientation and crystallinity of organic thin films is the first step toward making high-performance organic single crystal (OSC) devices. Since the molecular packing also causes the change in FR and CT contributions as discussed earlier, to truly decouple the FR and CT excitons, growing highly crystalline and morphology controlled monolayer samples with minimal defects is essential. This was demonstrated recently in both pentacene [33] and PTCDA [50] where monolayers of each were grown in a controlled and optimised growth condition. In pentacene, the WL and 1L samples showed very different PL emission spectra, as shown in figure 4(d). The WL (H-type) showed broad PL spectra dominated by CT excitons whereas, the 1L (J-type) showed only a narrow peak, which is characteristic of FR excitons.

Because of the reduced defect, disorder, and interfacial states in the monolayer domain, we were able to witness long-range coherent super-transport from FR excitons that were de-localized over hundreds of pentacene molecules. WL pentacene samples with H-type molecular aggregation demonstrated in-plane isotropic emissions dominated by CT excitons. In contrast, anisotropic PL emission peak emission was seen in 1L pentacene with J-type molecular aggregation. The WL has a substantially wider PL spectrum for strong couplings between FR and CT excitons [24]. The wide PL spectrum is linked to different band energy levels produced in pentacene as a result of vibronic interaction between the FR and CT states [51]. 1L, on the other hand, has a single peak centred at about 680 nm which is primarily FR excitonic emission, as previously discussed. This is a true experimental demonstration of decoupled FR and CT excitonic emissions from organic 2D material, which were further confirmed by temperature dependent, and polarization resolved PL experiments. The results match well with H- and J-type tendencies confirming the role of highly crystalline samples in decoupling the FR and CT states in 2D pentacene. In PTCDA/Me-PTCDI [50] 1L samples, the lack of π−π stacking in 1L resulted in minimal electronic coupling and CT-FR exciton coupling. The resulting band structure in 1L compared with multilayer samples is shown in figure 4(e). This demonstrates the emergence of a single narrow linewidth peak from 1L samples which is dominated by FR emission, in contrast to a broad PL emission from multilayer samples which do not cause the decoupling of FR and CT states, as shown in figure 4(f). Both these studies [33, 50] confirmed the FR excitonic emission from 1L sample using low temperature PL measurements which showed the PL emission increased sharply with reducing temperature and narrowing of the linewidth pointing towards true FR excitonic emissions from a clean, defect-free high crystalline 2D organic sample.

5. Superradiance and ST of FR excitons in 2D organic materials

Coherent excitonic systems have been established to affect the optical emission properties and photon-charge conversion efficiency in semiconductor materials. They are critical not only for improved photon-charge conversion efficiency but also for achieving Bose–Einstein condensates and are less likely to be perturbed during transport as compared to other single-particle/quasi-particle states-important for ultra-fast optoelectronic devices. There is a renewed interest in utilising the transport and emission of coherent excitons in solid state semiconductor materials and molecular systems as well as stable Bose–Einstein condensates at room temperature. Spontaneous collective coherent emission from a system of several non-interacting dipole active atoms (excitons) was defined as Superradiance by Dicke as shown in figure 5(a) [52]. In SR, interactions between TDM of each unit allow coherent emission across multiple sites.

While coherent states have been demonstrated in 2D materials such as TMDCs coupled with an optical cavity, it is difficult to maintain robust coherence without the confinement inside an optical cavity, due to relatively short excitonic lifetime and loss in coherence due to defects, disorders, and scattering effects and phononic interactions. 2D organic semiconductor materials offer a suitable platform for excitons to delocalised over multiple unit cells by coherent superposition of their base states, even without electronic coupling. Excitonic coherence in organic molecular crystals is a direct function of constructive interference of individual TDM. This is made possible in organic 2D materials due to the high order of crystallinity and ordered growth of each unit cell, as demonstrated in J-type aggregation in figure 2 earlier in conjunction with the de-coupling of FR and CT excitonic states. Recently superradiant emission was reported by Sharma et al [33] from 1L pentacene samples which are highly crystalline and had J-type molecular aggregation. Figure 5(b) shows the temperature dependent PL emission from the 1L pentacene sample, which shows a sharp rise in the PL intensity and narrow linewidth emission with reducing temperature, which are features of SR emission. The cluster of molecules \(N_N\) over which the exciton is delocalised was also experimentally determined to be around 135 molecules. Similar SR emissions from 1L PTCDA molecules were also reported. To experimentally confirm SR radiance, exciton lifetime measurements are conducted, as the excitonic lifetime reduces by a factor of \(N_N\) in superradiant emissions. Figures 5(c) and (d) shows the reduced lifetime of FR excitons from 1L Pentacene at 77 K using time-resolved PL and pump probe experimental techniques. The two experiments confirmed that the lifetime reduces to around 4.2 ps at 77 K from FR exciton emissions of 1L pentacene sample as compared to 1200 ps from pentacene thin film sample grown similarly on h-BN. The significant reduction in lifetime coupled with the sharp increase in PL emission and reduced full-width half maximum substantiate the SR emission. Similar observations of a reduced lifetime were also reported from 1L PTCDA as shown in figure 5(e).
The coherent delocalisation of excitons over multiple sites in highly crystalline organic 2D materials leads to an analogous phenomenon called ST. The enhanced oscillator strength coupled with delocalisation over large molecular unit cells leads to large-scale and super-fast FR exciton transport. This was experimentally determined by Sharma et al. [33] using direct near-field imaging and spatially resolved temporal mapping techniques as shown in figures 5(f) and (g). The excitons in 1L and WL samples of pentacene diffused across the crystalline organic 2D pentacene with diffusion coefficients $354.5 \pm 50.1 \text{ cm}^2 \text{s}^{-1}$ and $3.5 \pm 0.2 \text{ cm}^2 \text{s}^{-1}$, respectively at 77 K. The spatial-temporal measurements confirmed these values from 1L and WL with reported diffusion coefficients of $306.8 \pm 14.1 \text{ cm}^2 \text{s}^{-1}$ and $3.3 \pm 1.1 \text{ cm}^2 \text{s}^{-1}$, respectively, as obtained from the slope in figure 5(g). The value of diffusion coefficient reported from 1L pentacene samples is about one order of magnitude higher than previously reported values from even quasi-1D systems such as carbon nanotubes (CNTs) and nanowires [53]. The reason for that is threefold: 1L pentacene has strong intermolecular coupling resulting in strong oscillator strength and hence an enhanced TDM causing superradiant emissions. Within each of these delocalised patches of molecules, the energy transfer occurs at ballistic speeds in contrast to diffusive-hopping based Förster Energy transfer mechanism. Second, these 2D organic samples are highly crystalline and with minimum defect interfaces causing large delocalisation and long-range diffusion lengths for excitons. The correlation between crystallinity, growth conditions and diffusion length has been explained in detail by Sharma et al. [33] in organic 2D materials. Third, the quantum confinement at the 2D limit further enhances the oscillator strength of FR excitons providing additional support for long range ultra-fast exciton transport.

6. Conclusions and prospects

The understanding of the low-lying excitonic states made possible due to high-crystalline 2D organic materials has led to various applications of these materials for high-speed excitonic device applications. In figure 6(a), we show our vision of the devices that can utilise the superradiant, narrow linewidth, and coherent emissions that we have experimentally now observed from 2D organic materials. There have been some reports that talk about the device application possibilities using SR emission. But with organic materials, we can achieve coherent emission at room temperature without coupling the 2D material to an optical cavity. This can lead to ultra-narrow linewidth lasers and high quantum yield organic light emitting devices [50] in figure 6(b). Also, utilising the ST of FR excitons the organic 2D materials can act as building blocks for superfaster excitonic circuit applications [54]. The operation of excitonic circuits is based on the control of exciton fluxes by an external voltage. The devices can have either excitonic or
Excitonic circuits based on organic 2D materials will be able to provide high interconnection speeds between the electronic and optical communication and signal processing devices, which is critical for the integration of novel optoelectronic devices using photons as compared to conventional electron-based signal processing devices. They can eliminate the delay between signal processing and optical communication. The demonstrated speed can be as quick as 0.2 ns and with ST reported in pentacene, it can be even higher. Second, organic 2D materials offer scalability and compactness. A FET device made out of organic 2D material, as shown in figure 6(c) is in principle similar to an electronic FET device, but with much faster-operating speeds. We have already demonstrated that optical emission can be externally controlled using a back gate voltage in an organic FET device, as shown in figure 6(d). This opens avenues to make excitonic circuits and bridges between inorganic organic electronic and photonic circuits. The diffraction limit for excitonic circuits is given by the exciton de Broglie wavelength and is comparatively much smaller than light wavelength limited photonics devices which are closer to 10 nm at room temperature. The major challenges for excitonic devices are finite excitonic lifetimes and limited binding energies. In regular band-gap semiconductors, the exciton can only travel very limited distances before it recombines, and this has been a long-standing challenge for excitonic devices. The excitons as demonstrated in figure 5 can travel up to 1.5 µm with a lifetime of up to 3 ns in WL and over 0.6 µm in 1L with much faster exciton diffusion coefficients compared to any 1D or quasi-1D system. This makes these organic materials ideal candidates for excitonic device applications in FET devices, etc.

To address the issue of binding energy limitation, Sharma et al. have demonstrated anisotropic emission and super-fast anisotropic transport of excitons from 1L organic material such as pentacene (figures 6(e) and (f)). The anisotropic emission points to the fact that excitons can be further confined in a quasi-1D space in a 2D system which can lead to enhanced binding energies of FR excitons as have been reported in a similar quasi-1D system such as phosphorene. The Dichroic ratio which is the term used to estimate the anisotropy of optical transitions, estimated from our
experimental observations in pentacene is as high as 9.5, which is even higher than what is reported from phosphorene [58]. Thus, highlights the fact that FR exciton binding energy can be very high and can be harnessed to overcome the limitations of earlier excitonic and photonic circuits. Thus, devices with long-range ultra-fast exciton transport from organic 2D material-based devices can be made possible due to the high anisotropy of FR excitonic emissions.

In conclusion, the true nature of low-lying excitonic and energy states in single crystal organic molecules was comprehensively detailed due to the novel growth of organic 2D materials. The decoupling of FR and CT states in high crystalline organic 2D materials has led to experimentation and demonstration of coherent and delocalised SR emissions and long-range superfast transport of excitons across the 2D organic materials. This article provided a comprehensive review of the key excitonic properties affecting the optoelectronic properties in organic 2D materials, which have critical applications in high-speed excitonic circuits, quantum computing devices, narrow linewidth emission lasers, fast OLEDs, and other optoelectronic bridges and devices.

**Acknowledgments**

We thank Robert Halbich of the School of Engineering, The Australian National University, for helpful discussions. The authors also acknowledge the funding support from the ANU PhD student scholarship, the Australian Government RTP scholarship, the Australian Research Council (ARC; Nos. DP220102219, DP180103238 and LE200100032) and the National Heart Foundation (ARIES ID: 35852).

**Conflict of interest**

The authors declare that they have no competing financial interests.

**ORCID iD**

Md Mehedi Hasan [https://orcid.org/0000-0003-1548-6579](https://orcid.org/0000-0003-1548-6579)

**References**

[1] Zhang L *et al* 2021 2D organic single crystals: synthesis, novel physics, high-performance optoelectronic devices and integration Mater. Today *50* 442–75

[2] Zhu Y, Sun X, Tang Y, Fu L and Lu Y 2020 Two-dimensional materials for light emitting applications: achievement, challenge and future perspectives *Nano Res.* *14* 1912–36

[3] Zhu Y, Li Z, Zhang L, Wang B, Luo Z, Long J, Yang J, Fu L and Lu Y 2018 High-efficiency monolayer molybdenum ditelluride light-emitting diode and photodetector *ACS Appl. Mater. Interfaces* *10* 43291–8

[4] Zhang L *et al* 2018 Efficient and layer-dependent exciton pumping across atomically thin organic-inorganic type-I heterostructures *Adv. Mater.* *30* e1803986

[5] Yildirim T, Zhang L, Neupane G P, Chen S, Zhang J, Yan H, Hasan M M, Yoshikawa G and Lu Y 2020 Towards future physics and applications via two-dimensional material NEMS resonators *Nanoscale* *12* 22366–85

[6] Zhang L *et al* 2020 2D materials and heterostructures at extreme pressure *Adv. Sci.* *7* 2002697

[7] Pei J, Yang J, Yildirim T, Zhang H and Lu Y 2019 Many-body complexes in 2D semiconductors *Adv. Mater.* *31* e1706945

[8] Mak K F, He K, Lee C, Lee G H, Hone J, Heinz T F and Shan J 2013 Tightly bound trions in monolayer MoS2 Nat. Mater. *12* 207–11

[9] Yang J, Xu R, Pei J, Myint Y W, Wang F, Wang Z, Zhang S, Yu Z and Lu Y 2015 Optical tuning of exciton and trion emissions in monolayer phosphorene *Light Sci. Appl.* *4* e312

[10] Xu R *et al* 2016 Exciton brightening in monolayer phosphorene via dimensionality modification *Adv. Mater.* *28* 3493–8

[11] Shang J, Shen X, Cong C, Peimyoo N, Cao B, Eginligil M and Yu T 2015 Observation of excitonic fine structure in a 2D transition-metal dichalcogenide semiconductor *ACS Nano* *9* 647–55

[12] Ugeda M M *et al* 2014 Giant bandgap renormalization and excitonic effects in a monolayer transition metal dichalcogenide semiconductor *Nat. Mater.* *13* 1091–5

[13] Bonaccorso F, Sun Z, Hasan T and Ferrari A C 2010 Graphene photonics and optoelectronics *Nat. Photon.* *4* 611–22

[14] Constantinescu G, Kuc A and Heine T 2013 Stacking in bulk anthracene thin films *Science* *342* 41165–77

[15] Vogl T, Doherty M W, Buchler B C, Lu Y and Lam P K 2019 Atomic localization of quantum emitters in multilayer hexagonal boron nitride *Nano Lett.* *19* 22366–85

[16] Lopez-Sanchez O *et al* 2013 Ultrashort excitons in monolayer MoS2 Nat. Mater. *12* 1912–36

[17] Zeng H, Dai J, Yao W, Xiao D and Cui X 2012 Valley polarization in MoS2 monolayers by optical pumping *Nat. Nano* *7* 490–3

[18] Zhu Y, Wang B, Li Z, Zhang J, Tang Y, Torres J F, Lipinski W, Fu L and Lu Y 2021 A high-efficiency wavelength-tunable monolayer LED with hybrid continuous-pulsed injection Adv. Mater. *33* e2101375

[19] Pei J *et al* 2017 Front biaxial excitons in atomically thin MoSe2 *ACS Nano* *11* 7468–75

[20] Sharma A, Zhu Y, Halbich R, Sun X, Zhang L, Wang B and Lu Y 2022 Engineering the dynamics and transport of excitons, trions, and biaxial excitons in monolayer WSe2 *ACS Appl. Mater. Interfaces* *14* 41165–77

[21] Zhang S *et al* 2014 Giant bandgap renormalization and excitonic effects in a monolayer transition metal dichalcogenide semiconductor *Adv. Mater.* *13* 1091–5

[22] Sierringhaus H, Tessler N and Friend R H 1998 Integrated optoelectronic devices based on conjugated polymers *Science* *280* 1741–4

[23] Rogers J A 2001 Toward paperlike displays *Science* *291* 1502–3

[24] Bardeen C J 2013 Excitonic processes in molecular crystalline materials MRS Bull. *38* 65–71

[25] Ahn T-S, Müller A M, Al-Kaysi R O, Spano F C, Norton J E, Beljonne D, Brédas J-L and Bardeen C J 2008 Experimental and theoretical study of temperature dependent exciton delocalization and relaxation in antracene thin films *J. Chem. Phys.* *128* 054505

[26] de Boer R W I, Gershenson M E, Morpurgo A F and Podzorov V 2004 Organic single-crystal field-effect transistors *Phys. Status Solidi R Lett.* *201* 3102–31

[27] de Boer R W I, Jochensen M, Klapwijk T M, Morpurgo A F, Niemax J, Tripathi A K and Pflaum J 2004 Space charge limited transport and time of flight measurements in tetracene single crystals: a comparative study *J. Appl. Phys.* *95* 1196–202
[28] Congreve D N, Lee J, Thompson N J, Hontz E, Yost S R, Reusswig P D, Bahlke M E, Reineke S, Van Voorhis T and Baldo M A 2013 External quantum efficiency above 100% in a singlet-exciton-fission-based organic photovoltaic cell Science 340 334–7

[29] Rao A, Wilson M W B, Hodgkiss J M, Albert-Seifried S, Bässler H and Friend R H 2010 Exciton fission and charge generation via triplet excitons in pentacene/C60 bilayers J. Am. Chem. Soc. 132 12698–703

[30] Sirringhaus H 2005 Device physics of solution-processed organic field-effect transistors Adv. Mater. 17 2411–25

[31] Jiang H and Hu W 2020 The emergence of organic single-crystal electronics Angew. Chem., Int. Ed. Engl. 59 1408–28

[32] He D et al 2014 Two-dimensional quasi-freestanding molecular crystals for high-performance organic field-effect transistors Nat. Commun. 5 5162

[33] Sharma A et al 2020 Supertransport of excitons in atomically thin organic semiconductors at the 2D quantum limit Light Sci. Appl. 9 116

[34] Köhler A and Bässler H 2015 Electronic Processes in Organic Semiconductors: An Introduction (New York: Wiley)

[35] Podzorov V 2013 Organic single crystals: addressing the fundamentals of organic electronics MRS Bull. 38 15–24

[36] Lee K et al 2010 Interfacial trap density-of-states in pentacene-and ZnO-based thin-film transistors measured via novel photo-excited charge-collection spectroscopy Adv. Mater. 22 3260–5

[37] Chua L-L, Zaussmell J, Chang J-F, Ou E C-W, Ho P K-H, Sirringhaus H and Friend R H 2005 General observation of n-type field-effect behaviour in organic semiconductors Nature 434 194

[38] Podzorov V, Menard E, Borissov A, Kiryukhin V, Rogers J A and Gershenson M E 2004 Intrinsic charge transport on the surface of organic semiconductors Phys. Rev. Lett. 93 086602

[39] Zhang Y et al 2016 Probing carrier transport and structure-property relationship of highly ordered organic semiconductors at the two-dimensional limit Phys. Rev. Lett. 116 016602

[40] Lim S-H, Bjorklund T G, Spano F C and Bardeen C J 2004 Exciton delocalization and superradiance in tetracene thin films and nanoaggregates Phys. Rev. Lett. 92 107402

[41] Kash A 1963 Energy transfer mechanisms and the molecular exciton model for molecular aggregates Radiat. Res. 20 55–70

[42] Davydov A 1971 Theory of Molecular Excitations vol 7 (New York: Plenum Press) pp 387–94

[43] Hestand N J, Yamagata H, Xu B, Sun D, Zhong Y, Harutyunyan A R, Chen G, Dai H-L, Rao Y and Spano F C 2015 Polarized absorption in crystalline pentacene: theory vs experiment J. Phys. Chem. C 119 22137–47

[44] Spano F C and Silva C 2014 H-and J-aggregate behavior in polymeric semiconductors Annu. Rev. Phys. Chem. 65 477–500

[45] Yamagata H, Maxwell D S, Fan J, Kittilstved K R, Brisen A L, Barnes M D and Spano F C 2014 HJ-aggregate behavior of crystalline 7,8,15,16-tetraazaterrylene: introducing a new design paradigm for organic materials J. Phys. Chem. C 118 28842–54

[46] Zhu X Y, Yang Q and Muntwiler M 2009 Charge-transfer excitons at organic semiconductor surfaces and interfaces Acc. Chem. Res. 42 1779–87

[47] Yamagata H, Norton J, Hontz E, Olivier Y, Beljonne D, Bredas J L, Silbey R J and Spano F C 2011 The nature of singlet excitons in oligoacene molecular crystals J. Chem. Phys. 134 204703

[48] Qi D, Su H, Bastjian M, Jurchescu O D, Palstra T M, Wee A T S, Rübhausen M and Rusydi A 2013 Observation of Frenkel and charge-transfer excitons in pentacene single crystals using spectroscopic generalized ellipsometry Appl. Phys. Lett. 103 113303

[49] Hoffmann M, Schmidt K, Fritz T, Hasche T, Agranovich V M and Leo K 2000 The lowest energy Frenkel and charge-transfer excitons in quasi-one-dimensional structures: application to MePTCDI and PTCDCA crystals Chem. Phys. 258 73–96

[50] Zhao H et al 2019 Strong optical response and light emission from a monolayer molecular crystal Nat. Commun. 10 5589

[51] Spano F C and Yamagata H 2011 Vibronic coupling in J-aggregates and beyond: a direct means of determining the exciton coherence length from the photoluminescence spectrum J. Phys. Chem. B 115 5133–43

[52] Cong K, Zhang Q, Wang Y, Noel G T, Belyanin A and Kono J 2016 Dicke superradiance in solids J. Opt. Soc. Am. B 33 C80–101

[53] Sharma A, Khan A, Zhu Y, Halbich R, Ma W, Tang Y, Wang B and Lu Y 2019 Quasi-line spectral emissions from highly crystalline one-dimensional organic nanowires Nano Lett. 19 7877–86

[54] Grosso G, Graves J, Hammers M A T, High A A, Butov L V, Hanson M and Gossard A C 2009 Excitonic switches operating at around 100 K Nat. Photon. 3 577–80

[55] High A A, Hammers M A T, Butov L V, Hanson M and Gossard A C 2007 Exciton optoelectronic transistor Opt. Lett. 32 2466–8

[56] High A A, Novitskaya E E, Butov L V, Hanson M and Gossard A C 2008 Control of exciton fluxes in an excitonic integrated circuit Science 321 229–31

[57] Wakita K 2013 Semiconductor Optical Modulators (New York: Springer)

[58] Sharma A, Yan H, Zhang L, Sun X, Liu B and Lu Y 2018 Highly enhanced many-body interactions in anisotropic 2D semiconductors Acc. Chem. Res. 51 1164–73