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Review

Aggregation structures of organic conjugated molecules on their optoelectronic properties

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ABSTRACT

The intimate connection between stacking modes and optoelectronic properties of organic conjugated materials has been discussed from the viewpoints of developing microscopic models and further understanding of their functions and potential applications. In particular, three basal dimer configurations (cofacial configuration, staggered configuration, and crossed configuration) and their respective optical (including radiative and non-radiative) and electrical properties are expatiated in detail. Eventually, we put forward the perspective on achieving the promising laser material that features high fluorescence quantum yield and charge mobility.

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1. Introduction

In the research field of organic optoelectronics, π -functional molecules and polymers act as the great potential in the appliances of organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs) and organic field-effect transistors (OFETs), due to their tunable optical and electrical properties owing to the majority of organic molecules and the variety of molecular stacking modes. The performance of the devices mentioned above strongly rely on the understanding of the behaviours of excitons, or the tight-binding electron-hole pairs to be exact, in organic materials, which is rather complex and different to that in the inorganic counterpart. The models on exciton were earlier developed by Frenkel and Davydov *et al.* [1], and recently were systematically discussed by Bredas and Spano *et al.* [2] through building more complex models. Radiative transition from excited molecules generates fluorescence when an electron relaxes from the excited singlet state to its ground state. However, the defects widely existing in most amorphous organic systems may quench fluorescence due to the trapping of excitons. Thus, the crystalline material usually presents the specific molecular stacking with very low content of impurities, making it precise to construct the relationship between the molecular stacking mode and the optoelectronic properties.

The highly long-range ordered molecular arrangement induces the higher charge mobility [3], and at the same time, single crystal itself also could be highly efficient fluorescent material in solid [4].

There is still confusion on understanding the mobility of π -conjugated materials, but the consensus on designing of rigid structure with strong intermolecular interaction enables to achieve excellent performance [5]. According to the simplified Marcus theory which provides direct insight into the charge hopping between adjacent molecules, the charge transfer rate k is given by the following equation:

$$k = \left(\frac{4\pi^2}{h}\right)t^2(4\pi\lambda RT)^{-0.5} \exp\left(\frac{-\lambda}{4RT}\right) \quad (1)$$

where λ is the internal reorganization term and t is transfer integral. Thus, smaller reorganization energy and larger transfer integral are of great benefit for the hopping rate. In fact, it is the stacking mode (the latter term), rather than intramolecular factor, that dramatically motivates changes in bandgap, especially results in a strong dispersion in the conduction band according to the one dimensional tight-binding model. A π - π distance of around 3.5 Å admittedly and 4 Å estimated in theoretical analysis implies the strong intermolecular electronic coupling, which consists with neighbouring molecules distance in most π stacking modes.

Herein, this short review will summarize how the stacking mode affects the optoelectronic functions of π -conjugated materials in the following three typical aggregation models including cofacial configuration (H-aggregation), staggered

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configuration (J-aggregation), and crossed configuration (X-aggregation), and probes into how to realize the balance of high solid state luminous efficiency and charge carrier mobility in one material.

2. The relationship between molecular stacking modes and optoelectronic functions of organic crystalline materials

According to molecular excitation model [6], the molecular excitation leads to transition dipole moment along the polarization axis. To a certain extent, the sign of the solvatochromism depends on the polarity in dipole moment of the molecule between its ground state and excited state. If the intermolecular overlap is large enough for units to abandon their individuality, it is well established that the primary photophysics in the bound dipoles, which is possibly coupled to a local lattice distortion of the conjugated cores in the orderly fashion [7]. The molecular stacking modes, indeed the relative spatial orientation of transition dipoles, do work in the energy splitting (so-called Davydov splitting) state of optically allowed transitions. The fluorescence usually originates from the decay of the lowest excited state, and as the result, H- and J-aggregation (parallel stacking mode) induce obvious spectral evolution while X-aggregation (cross stacking mode) keeps similar spectrum as single molecule, which is attributed to the spatial orientation of transition dipoles (Fig. 1). Kasha *et al.* concluded that the exciton state energy level diagrams are given by a succinct equation:

$$\Delta E_{\text{agg}} = \Delta E_{\text{mono}} + \Delta E_{\text{dv}} \pm \varepsilon \quad (2)$$

where ΔE_{agg} and ΔE_{mono} represent for the upper energy levels of aggregate and monomer respectively; ΔE_{dv} is the van der Waals term, which works prominently in the bound systems; and ε is the splitting energy dependent on the dipoles moment, which is related to the centre-to-centre distance and relative spatial geometry between adjacent molecules. The orientation factor, κ , is usually used to describe the dimer geometry, actually in

proportion to the splitting energy. In the dimer system, upon the parallel stacking mode, κ is given by $\kappa_{\parallel} = 1 - 3 \cos^2 \theta$, which reflects that the upper state splitting for dimers with parallel transition moments varies the inclined angle θ . As a result, it could be optically distinguished through typical bathochromic shift of the J-aggregate band and hypsochromic shift of the H-aggregate band in the absorption spectra. Upon the crossed stacking mode, κ is given by $\kappa_{\times} = \cos \alpha$ (for the neglected intermolecular slippage, in other words, $\theta = 90^\circ$), which reflects that the upper state splitting for dimers with crossed transition moments varies the rotational angle α . As contrasted with parallel stacking mode, crossed stacking pattern exhibits simultaneously bathochromic and hypsochromic shift as the small rotational angle leads to both allowable splitting transition, while the large rotational angle makes the similar property of monomer. Thus in general, large intermolecular slippage ($\theta < 54.7^\circ$) and large intermolecular rotation are classified as J-aggregation and X-aggregation respectively, while the smaller slippage ($\theta > 54.7^\circ$) or smaller rotation is classified as H-aggregation. This classification is better understood and distinguished optically. Of cause, in the planar lattice system, the splitting energy increases as the aggregated length increases, which is corrected by a constant (relative to the number of interacting molecules), indicating the further narrowed bandgap of crystal.

On the other hand, the non-radiative transition is also considered in the fluorescence yield in solid, especially the long-range Förster energy transfer process. The structural factor, κ^2 , ranges from 0 to 4, is one of the crucial parameters to control the energy transfer efficiency (Fig. 2) [8]. The energy transfer rate k_{ET} is described as follows:

$$k_{\text{ET}} = \frac{9000(\ln 10)\kappa^2\varphi}{128\pi^5n^4N_A\tau R^6}J_c \quad (3)$$

where φ is the quantum yield; n is the refractive index; N_A is the Avogadro constant; τ is the lifetime and J_c is the spectral overlap

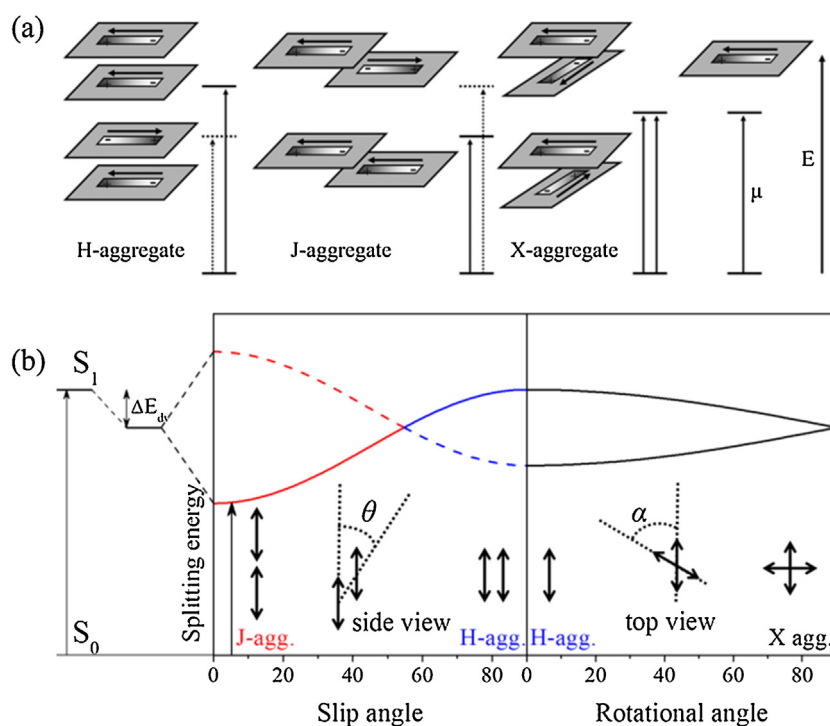


Fig. 1. (a) Schematic representation of optically allowed transitions of molecular monomer and splitting in a cofacial configuration (H-aggregate), staggered configuration (J-aggregate) and crossed configuration (X-aggregation). (b) Splitting energy in the parallel and crossed stacking dimer systems in the framework of exciton model.

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