NEWS AND VIEWS

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Utilization of triplet excited states in organic semiconductors

Song Guo[1], Shujuan Liu[1], Kenneth Yin Zhang[1], Wei Huang[1, 2], and Qiang Zhao[1, †]

[1]Key Laboratory for Organic Electronics & Information Displays (KLOEID) and Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications (NUPT), Nanjing 210023, China

[2]Shaanxi Institute of Flexible Electronics (SIFE), Northwestern Polytechnical University (NPU), Xi'an 710072, China

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Organic optoelectronics is an emerging research field, which has attracted extensive interests in the last few decades owing to its practical applications, like organic light-emitting diodes (OLEDs), organic memory devices, organic photovoltaic (OPV), sensors, and organic field-effect transistors[1, 2]. Organic semiconductors play a crucial role in this field. Compared to the traditional inorganic semiconductors, organic semiconductors open a fascinating research direction because of some unique advantages, such as flexible design, low cost, and rich optical and electronic properties. In organic optoelectronics, the excited states greatly determine the photoelectronic properties and application areas as shown in Fig. 1. Based on the electron spin in the molecule, the excited states of organic semiconductors include singlet and triplet states. As we know, the radiative transitions of singlet and triplet excited states are always accompanied by fluorescence and phosphorescence emission, respectively. However, because of the spin-forbidden transitions from the singlet excited states to the triplet excited states, it is often difficult to utilize the triplet excited states directly. Meanwhile, the theoretical basis of the triplet states is also relatively deficient. Thus, most of researches only focused on the regulation of the singlet states. In fact, effective utilization of the triplet excited states will be beneficial to significantly improve the performance of organic optoelectronic devices. To date, it still remains challenges to modulate and utilize the triplet excited states effectively for organic optoelectronic area. Great efforts have been devoted to solving this problem, and a series of functional materials and devices based on the triplet organic semiconductors have been explored.

Organic light-emitting diodes

OLEDs possess several outstanding advantages, like ultrathin and flexible display, self-illumination and rapid response speed, which have been demonstrated to be a promising solid-state lighting and display technology[3–5]. In the process of electroluminescence, both singlet and triplet excitons can be generated with the population ratio of 25% : 75%. However, conventional OLEDs mainly adopted fluorescent materials, which limited the device efficiency. Up to now, several methods have been proposed to utilize the triplet excitons. For example, transitional metal atoms (like Ir, Pt, etc) can be introduced into the molecules to enhance spin-orbit coupling (SOC) constants and boost the ISC, which can utilize both singlet and triplet excitons effectively. Additionally, numerous thermally activated delayed fluorescence (TADF) materials have been successfully explored. These materials have the capacity of reverse intersystem crossing from the triplet excited states to the singlet excited states. Theoretically, 100% excitons can be harvested to realize highly efficient emission in these material systems.

Organic memory devices

Triplet organic semiconductors possess rich charge transfer states. For example, triplet transition-metal complexes have metal-to-ligand charge transfer transition, ligand-to-ligand charge transfer transition, metal-to-ligand-ligand charge-transfer transition, etc. Generally, these triplet charge transfer states are very sensitive to the external environments. Slight stimulus can result in changes in the optoelectronic properties, including absorption spectra, emission spectra, emission lifetimes, and conducting states. Hence, these triplet organic semiconductors can be utilized as multimode information storages or encryption media, which can effectively increase the storage density and security[6–8].

Organic photovoltaic

Solar energy is a kind of renewable and clean energy. The efficient utilization of solar energy has always been a hot subject. OPV is one of the practical devices for the conversion from solar energy to electrical energy. The mechanism of OPV contains the following processes: the generation, diffusion and dissociation of the excitons, the transport and collection of the charge carriers. Triplet organic semiconductors have unique advantages in this field, because it can increase the migration distance of the excitons and is beneficial to improve the performance of the solar cells[9].

Diagnosis and treatment of diseases

With the continuous development of life science, increasing requirements have been put forward for disease detection and diagnosis technology. Optical detection with good selectivity, high sensitivity and short response time has gradually become a convenient detection method in biological area. Triplet exciton transitions in organic semiconductors are accompanied by phosphorescent emission with long luminescence lifetime. Utilizing this characteristic, time-resolved luminescence techniques can be used for the optical detection, which could effectively reduce the disturbance from the short-lived fluorescent signals and enhance the sensitivity and signal-to-noise ratio in complicated system. Additionally, triplet excited

† Correspondence to: Q Zhao, iamqzhao@njupt.edu.cn

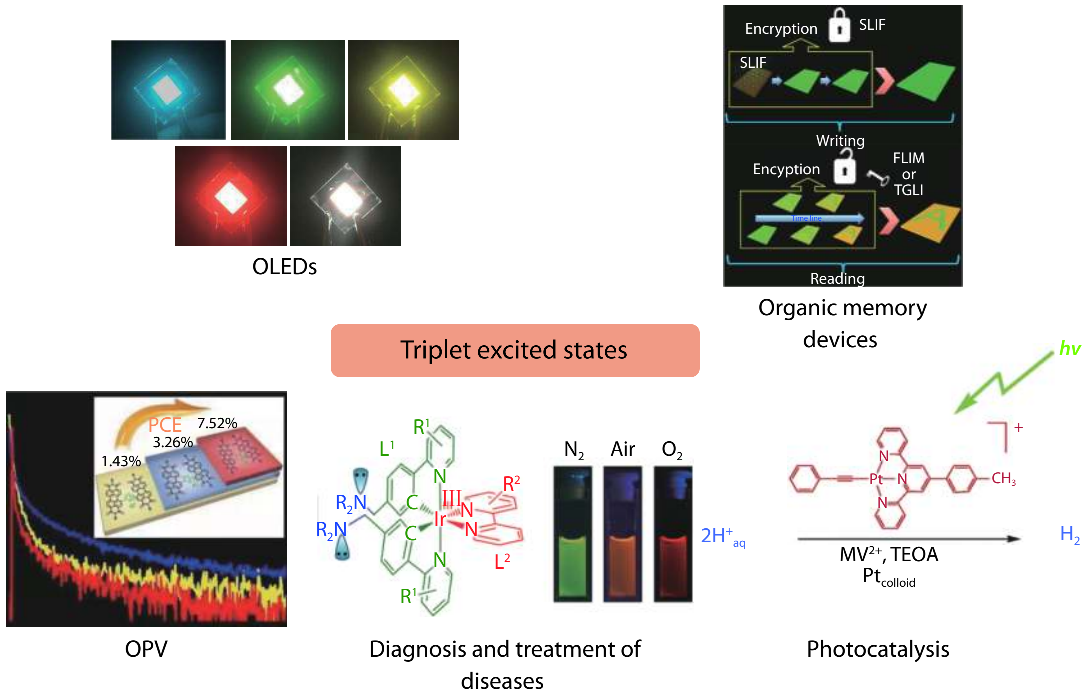

Fig. 1. (Color online) Utilization of triplet excited states in organic semiconductors. Copyright 2019 Chem Rec[5]. Copyright 2014 Nat Commun[6]. Copyright 2018 Angew Chem Int Ed[9]. Copyright 2018 J Am Chem Soc[10]. Copyright 2006 J Am Chem Soc[15].

states can be easily quenched by O_2, which can generate singlet oxygen. Thus, triplet organic semiconductors can also be rationally designed as photosensitizers for photodynamic therapy[10–13].

Photocatalysis

Hydrogen evolution via photocatalytic water splitting under visible light is considered as one of the promising strategies to solve the challenges of energy shortage and environmental crisis. It is an important subject to select appropriate photosensitizers for efficiently achieving the photocatalytic water splitting. Ideal photosensitizers should have the following features: large absorption coefficient in visible range, good stability, proper redox potential, long-lived excited states, etc[14, 15]. Triplet organic semiconductors, particularly transition-metal complexes (Ir(III), Ru(II), Pt(II), Pd(II) and Re(I) complexes), can meet the above requirements well, especially for their long-lived excited states and excellent photochemical stability.

Conclusion

Although numerous organic semiconductors for efficient utilization of triplet excited states have been designed along with the appropriate mechanisms, there still remain several challenges. For example, the deep blue and near-infrared OLEDs based on phosphorescent transition-metal complexes or TADF materials are of poor stability and short device lifetime. To overcome these obstacles, new material systems should be exploited. Meanwhile, the fabrication of devices should be also optimized rationally. The mechanisms of organic memory are not completely understood up to now, and the solar photovoltaic conversion efficiency needs to be improved. In addition, the application fields of these organic semiconductors are limited and new applications should be explored. In summary, great progress has been made in the researches for utilizing the triplet states, and more efforts will be dedicated to exploring the new organic semiconductors based on triplet states, such as purely organic room-temperature phosphorescent materials.

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