1-2-1. Organic Molecules

Overview

When an organic molecule in the ground singlet state (S_0) is photoexcited, an excited singlet state molecule is first formed, by keeping the original spin multiplicity. These singlet excited states are numbered from the lowest energy state as S_1, S_2, etc. Generally, S_2 and the higher states are called as "higher excited states", and they rapidly undergo internal conversion to form S_1 (Kasha's rule). Furthermore, molecules in the excited singlet state can undergo intersystem crossing (ISC) via spin inversion, to form molecules in the excited triplet states (T_1, T_2, etc). Based on their electronic structure, the excited states are classified as π-π*, n-π*, and, and charge-transfer (CT) states (Fig. 1). Controlling the electronic structure of excited states is the basis for the practical applications, including light-emitting materials, photochemical reactions, and thermally activated delayed fluorescence.

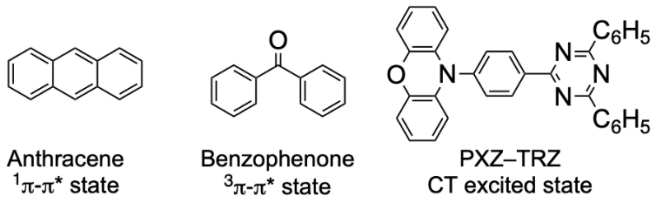

Figure 1. Examples of organic molecules possessing respective electronic structures upon photoexcitation.

Current Status and Frontiers

Not only fundamental interests but also application aspects, the electronic structure of excited-state molecules has been widely studied. Many researchers in Japan have led this field since the 1970s. Recently, significant progress in controlling electronic structure of organic molecules has been made to achieve unique photochemical reactions, development of luminescent materials, exemplified as below.

1. Photochemical reactions that do not follow the Kasha's rule

Generally, molecules excited to the higher excited states (S_2 or higher) rapidly undergo internal conversion to S_1. Thus, fluorescence, non-radiative decay, and chemical reactions occur from the S_1 state, which is widely accepted

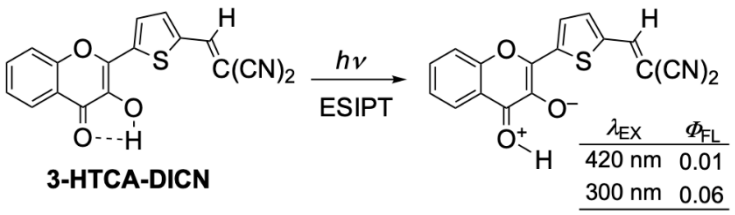

Figure 2. ESIPT fluorescence of **3-HTCA-DICN** exhibiting anti-Kasha behavior.

as “Kasha's rule”. However, some examples are known as anti-Kasha phenomena, that do not follow Kasha's rule owing to various reasons. Chou *et al.* demonstrated that the excited-state intramolecular proton transfer (ESIPT) fluorescence properties of the hydroxychromene derivative **3-HTCA-DICN** (Fig. 2) exhibit a significant excitation wavelength dependence.[1] Excitation of **3-HTCA-DICN** by 420-nm light provides the S_1 state and red fluorescence with quantum yield (Φ_{FL}) of 0.01. On the other hand, 300-nm excitation provides the higher excited state (S_n) and an increased Φ_{FL} of 0.06. Time-resolved spectroscopic measurements revealed that the activation energy of the ESIPT process in the S_n state was reduced due to the high n-π* characteristics owing to the carbonyl group. This anti-Kasha behavior is well explained by the difference in the electronic structure between the S_1 and S_n states.

2. Electronic structures of charge-transfer excited states and S–T inversion

Excitation of molecules composed of electron donors and acceptors forms charge-transfer (CT) excited states. CT-excited molecules have a small energy gap between S_1 and T_1 (ΔE_{ST}), thereby exhibiting thermally activated delayed fluorescence (TADF, see Section 2-6-1). While ΔE_{ST} is generally positive, Aizawa *et al.* reported that a heptazine derivative **$HzTFEX_2$** (Fig. 3) is a ST-inverted molecule possessing negative ΔE_{ST}.[2] As a result, the ST-inverted molecule has a large k_{RISC}, which can be expected as an efficient emitter for organic light-emitting diodes. This phenomenon can be explained by contribution of two-electron-excited states to the S_1 and T_1 states.

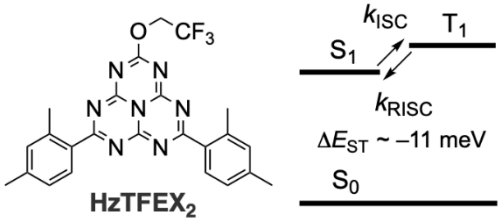

Figure 3. **$HzTFEX_2$** possessing negative ΔE_{ST}.

References

1. H.-W. Tseng, A. P. Demchenko, P.-T. Chou, et al., *Chem. Sci.* **7**, 655–665 (2016).
2. N. Aizawa, Y.-J. Pu, Miyajima, et al., *Nature*, **609**, 502–506 (2022).

Future Perspectives and Directions

Challenges to be resolved or realized within 5 years: Accurate estimation of electronic structures using high-level quantum chemical calculations

Challenges to be resolved or realized within 10 years: Application to photoenergy conversion including artificial photosynthesis

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