2-6-1. Thermally Activated Delayed Fluorescence (TADF)

Overview

In addition to fluorescence and phosphorescence, which are the basic luminescent functions of organic molecules, thermally activated delayed fluorescence (TADF) has attracted much attention in recent years since it enables 100% current-to-light conversion in OLEDs. Many TADF molecules have been reported based on donor-acceptor structures, and they are now being developed into multi-resonance and negative-gap materials.

Current Status and Frontiers

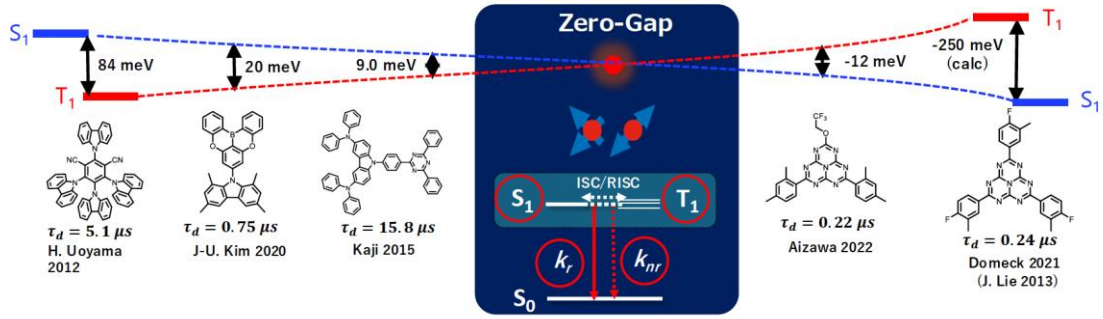
In OLEDs (organic light emitting diodes), if the thermal activation delayed fluorescence (TADF) process can be used, upconversion of triplet excitons generated by current excitation to singlet excitons would, in principle, enable 100% internal EL efficiency, It has been studied due to its interest as a fundamental phenomenon in photochemistry, and eosin Y and fluorescein were the targets of research, and were classified into E-type (delayed fluorescence) and P-type (triplet-triplet annihilation). Subsequently, benzophenone derivatives, tin polyphyrin compounds, and Cu complexes were reported, but no molecular structures were developed with clear applications in mind.

In 2009, the world's first delayed EL under current excitation was reported by an OLED using a tin porphyrin compound as the emission layer.[1] Subsequently, after 2010, external EL quantum efficiencies exceeding 5-10% were reported in donor-acceptor (D-A) type compounds containing triazine and indolocarbazole, and expectations for TADF were quickly raised. Then, in 2012, almost 100% internal EL efficiency was achieved using 4CzIPN, establishing TADF molecules as the third OLED emitting material.[2]

The significant advantage of TADF molecules is that they have a molecular structure similar to that of ordinary fluorescent molecules, allowing unlimited molecular design freedom, and a variety of molecular structures have been reported so far. Currently, in addition to exciplexes and CT complexes based on the D-A type, a wide variety of materials are under development, including multiple resonance structures[3] and proton-transfer types. In addition to RGB, TADF molecules that emit yellow and near-infrared light have also been developed. In particular, shortening the delayed fluorescence lifetime of TADF molecules offers many advantages, including suppressing rolloff (decrease in luminescence brightness) at high current density and improving device durability. There is a clear correlation between ΔE_{ST} and k_{RISC} of TADF molecules developed so far, and k_{RISC} improves as ΔE_{ST} decreases.[4]

Furthermore, negative-gap materials based on heptadine frameworks have recently been reported.[5] From quantum chemical considerations, the excited singlet and excited triplet energy difference ΔE_{ST} is given by the sum of the electron exchange energy (E_x) and the electron correlation energy (E_c). By considering two-electron excited states, E_c

takes a negative value, allowing the formation of a negative gap. Although heptadine derivatives have long been predicted from quantum chemical calculations to exhibit a negative gap, in many cases their luminescence efficiency was low, and their potential as luminescent molecules was considered unlikely. In 2021, by performing exhaustive quantum chemical calculations, many heptazine derivatives were found to exhibit negative-gap properties: a heptazine derivative (HAP-3MF) published in 2014 showed short-lived luminescence of 240 ns, and theoretical calculations have now shown it to be a −240 meV negative-gap material.[6] It is important to note here that the formation of a negative gap does not mean that the activation energy (ΔE_a) is zero. Recently, the introduction of various heteroatoms has been effective in improving SOC, and high k_{RISC} values of ~10^8 have been reported.[7] The improvement of k_{RISC} is an important factor because it leads to device stability in OLEDs.Δ Improving SOC, along with reducing ΔE_{ST}, is key. Although current TADF molecules have high efficiency and durability in the green region, there are still many issues with photo- and electrochemical stability in the blue and other colors, and the development of molecular skeletons with high durability remains needed.



References

1. A. Endo, M. Ogasawara, A. Takahashi, D. Yokoyama, Y. Kato, C. Adachi, *Adv. Mater.*, **21**, 4802–4806 (2009).
2. H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature*, **492**, 234–238 (2012).
3. M. Mamada, M. Hayakawa, J. Ochi, T. Hatakeyama, *Chem. Soc. Rev.*, **53**, 1624–1692 (2024).
4. H. Nakanotani, Y. Tsuchiya, C. Adachi, *Chem. Lett.*, **50**, 938–948 (2021).
5. N. Aizawa, Y.-J. Pu, Y. Harabuchi, A. Nihonyanagi, R. Ibuka, H. Inuzuka, B. Dhara, Y. Koyama, K. Nakayama, S. Maeda, F. Araoka, D. Miyajima, *Nature*, **609**, 502–506 (2022).
6. A. L. Sobolewski, W. Domcke, *J. Phys. Chem. Lett.*, **12**, 6852–6860 (2021).
7. I. S. Park, H. Min, T. Yasuda, *Angew. Chem. Int. Ed.*, **61**, e202205684 (2022).

Future Perspectives and Directions

Issues to be solved/realized by 10 years: For OLEDs, improving the transition rates of emitter materials will improve device performance, including reducing device degradation. If further improvements in the RISC rate and k_r can be achieved, it is expected that an ideal OLED that does not degrade can be developed.

(Author: Chihaya Adachi)