

Development of TADF/RTP-Active Multi-Photofunctional Organic Emitters

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ABSTRACT

In 2014, we discovered a skeletal rearrangement of BINAMs to provide dibenzo[*a,j*]phenazines (DBPHZs). By making use of DBPHZs, we have succeeded in developing multi-photofunctional organic emitters based on DBPHZ-cored twisted D–A type molecules, displaying efficient thermally activated delayed fluorescence, high-contrast conformation-dictated multi-color-changing mechanochromic luminescence, and room-temperature phosphorescence.

1 Introduction

Organic emitters that display multiple photofunctions with a single molecular component can find many applications in optoelectronics, sensing, imaging fields, and much more.¹ Therefore, the development of multi-photofunctional organic emitters is a fundamentally important research topic to enable future technologies. Recently, heavy-metal-free organic emitters that can harvest electrically-generated triplet excitons and convert into light in an efficient manner have attracted much attention as the next-generation emitters and sensitizers for efficient organic light-emitting diodes (OLEDs). From the viewpoint of materials design, twisted or resonant donor-acceptor (D–A) π -conjugated emissive compounds have emerged as promising candidates for thermally activated delayed fluorescence (TADF) materials, due to distinct HOMO/LUMO separation to reduce the singlet/triplet energy splitting in the excited states (ΔE_{S-T}) and thereby accelerate reverse intersystem crossing (rISC).

In 2014, we discovered an oxidative skeletal rearrangement of 1,1'-binaphthalene-2,2'-diamines (BINAMs) to provide U-shaped diazaacenes, dibenzo[*a,j*]phenazines (DBPHZs), otherwise impossible to access by precedent reactions.^{2,3} By making use of the unique physicochemical properties and molecular structures of DBPHZs,^{3,4} we have succeeded in developing unique multi-photofunctional organic emitters based on DBPHZ-cored twisted D–A–D triads and D–A–D–A macrocycles, displaying efficient thermally activated delayed fluorescence (TADF), high-contrast conformation-dictated multi-color-changing mechanochromic luminescence (MCL), and room-temperature

phosphorescence (RTP) (Figure 1).⁵

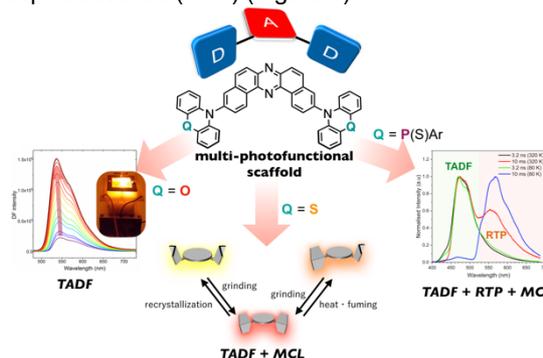


Figure 1.

2 Experiment & Results

Focusing on the high electron-accepting abilities and luminescent properties of DBPHZs, we have succeeded in developing an organic emissive material that shows efficient orange TADF with a twisted donor-acceptor-donor (D–A–D) structure, where two phenoxazine (POZ) electron-donors are directly linked to the DBPHZ unit with almost the right angle (Figure 2).

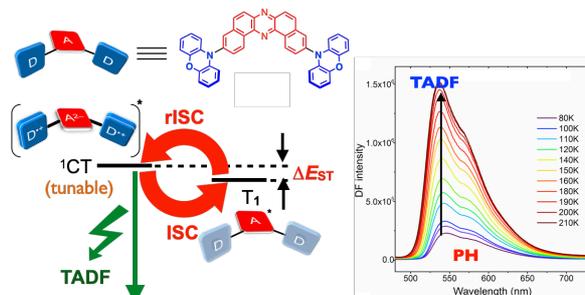


Figure 2

Detailed time-resolved spectroscopic measurements revealed that the TADF is generated through an efficient reverse intersystem crossing (rISC) from the locally excited triplet state (3LE_A) to the intramolecular charge-transfer excited singlet state (1CT).⁶ Furthermore, by employing the D–A–D molecule as the emitting material in OLEDs, we achieved the maximum theoretical external quantum efficiency of an OLED as high as 16%, which surpasses the maximum

theoretical external quantum efficiency (5%) of that with a conventional fluorescent material. Also, the utilization of our TADF material with blue- and green-light-emitting TADF materials allowed for the realization of a highly efficient all-TADF white-light-emitting OLED, which would find promising flexible light applications.⁷ Furthermore, we have developed the first macrocyclic structured TADF material, by utilizing the U-shaped structure of DBPHZ,⁸⁻¹⁰ which will open up the new avenue for supramolecular light-emitting materials.

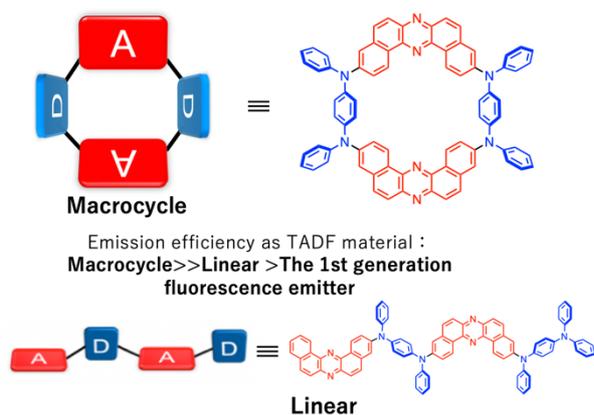


Figure 3

Molecules that can change their luminescence color in response to external stimuli such as mechanical force, temperature, and organic vapor (i.e., luminescent mechanochromism) can find many potent applications such as in security inks, thermo- and chemical sensors. However, the design principle for the luminescent mechanochromic materials that can show high color contrast and can show multi-color luminescence has not yet been established. Furthermore, given TADF-active molecules are endowed with a luminescence function apart from TADF, hitherto-unexplored applications such as host-free OLEDs, and 3D displays with a single emissive material can be realized.¹ To develop value-added TADF materials, we focused on the utilization of phenothiazine (PTZ) as the electron donors in our original twisted D–A–D scaffold. PTZ is conformationally more flexible than POZ, owing to the larger sulfur atom, and thereby the resulting D–A–D molecule can take varied conformations with different excited state energies. Indeed, the D–A–D compound showed high contrast and multiple color change in yellow to deep-red region in response to various external stimuli such as grinding, heating, and fuming with organic solvent vapor (Figure 4).¹¹ From the X-ray structure analysis and time-resolved spectroscopic measurement, we found out that the drastic change in emission color is caused by the change in photophysical processes (TADF, room temperature phosphorescence, and a mixture of the them) that are related to different conformations.¹² The generality of this molecular design

has also been proven by the single crystal-to-single crystal (SCSC) phase transition of a D–A–D molecule, which has a phosphorus bridge in the electronic donors.¹³ It should be also noted that the phosphorus-containing D–A–D molecule exhibited not only TADF but also room temperature phosphorescence (RTP), providing a new design guideline for purely organic RTP materials. This finding led us to the success in the development of heavy-metal-free RTP OLED material composed of abundant elements such as C, H, N, and Si.¹⁴

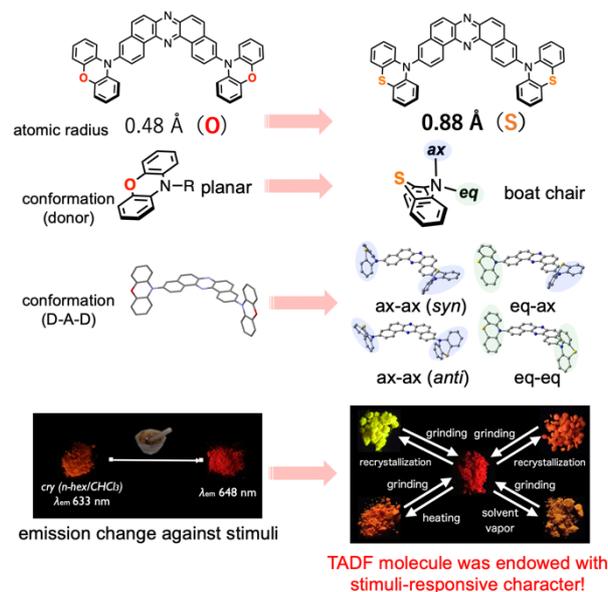


Figure 4

3 Conclusions

In conclusion, we have explored and established a new materials design concept for multi-photofunctional organic emitters, based on the integrated strategy utilizing “molecular shape” and “element intrinsic character”. This would pave the way toward the development of value-added organic emitters that enables smart display technologies in the future.

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