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Design of Materials for Organic Light-Emitting Diodes

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Highly efficient organic light-emitting diodes (OLEDs) containing a new emitter material named DACT-II are developed. DACT-II allows all the electrically excited triplet excitons, which are normally dissipated as heat, to be converted into singlet excitons by reverse intersystem crossing. In addition, photoluminescence quantum yield of DACT-II is 100%, which allows DACT-II-based OLEDs to realize an internal quantum efficiency of 100%. Although these features guarantee that DACT-II displays outstanding performance, DACT-II also has other advantages as an emitter for OLEDs, including favorable molecular orientation for effective light out-coupling, small roll-off, high thermal stability, and high performance over a wide temperature range. Results on boron-containing emitters, solution-processable emitters, and host-free solution-processable emitters are also described. In addition, recent results on charge transport simulation will be presented if time permits.

1. Introduction

People obtain information through sight, smell, touch, taste, and hearing. Among the senses we have, most information is gathered by sight, so displays and other visual aids are important for every scene of our daily life. After their pioneering work on the electroluminescence (EL) from organic materials,[1] Tang and VanSlyke[2] successfully fabricated organic light-emitting diodes (OLEDs) with an external EL quantum efficiency (EQE) of 1%. EQE is expressed as follows

$$EQE = IQE \times \eta_{out} = \beta \times \gamma \times \Phi_{PL} \times \eta_{out} \qquad (1)$$

where IQE is internal EL quantum efficiency, η_{out} is the light out-coupling factor, β is the exciton generation factor resulting in photons, γ is the carrier balance ratio of holes and electrons, and Φ_{PL} is the photoluminescence (PL) quantum yield (PLQY). Focusing on β, electronic excitation generates 25% lowest excited singlet excitons (S_1) and 75% lowest triplet excitons (T_1). Because T_1 normally result in heat, only S_1 can be converted into light in normal fluorescent OLEDs. Therefore, β is limited to 25%. Obviously, use of T_1 is a key to increase β. T_1 can be converted into light by introducing heavy atoms, typically Ir or Pt, into emitter materials to theoretically provide β of 100%.[3,4] However, these heavy atoms are unevenly distributed around the world, which may cause dispute. Recently, a new type of emitter with a theoretical β of 100% that functions through thermally activated delayed fluorescence

(TADF) has been reported by Adachi's group.[5] T_1 are converted into light via reverse intersystem crossing (RISC) from T_1 to S_1. Despite that, the TADF materials consist only of abundant atoms such as H, C, and N. Research on TADF is now snowballing, provoked by their successful results. Here, we present a design concept to develop efficient TADF materials. Recently developed TADF materials with excellent performance based on this concept are also introduced.

2. Molecular design concept

Effective up-conversion of T_1 to S_1 can be realized by minimizing the S_1-T_1 energy gap, ΔE_{ST}. When ΔE_{ST} becomes comparable to thermal energy (~26 meV at room temperature), T_1 are thermally activated to S_1, which then decay through delayed fluorescence rather than normal fluorescence from S_1 to S_0. This process is called TADF. ΔE_{ST} is expressed as

$$\Delta E_{ST} =$$
$$2 \left\langle \varphi_{HOMO}(\mathbf{x}_1)\varphi_{LUMO}(\mathbf{x}_2) \left| \frac{1}{|\mathbf{x}_2 - \mathbf{x}_1|} \right| \varphi_{HOMO}(\mathbf{x}_2)\varphi_{LUMO}(\mathbf{x}_1) \right\rangle$$
$$(2)$$

where $\mathbf{x}_1$ and $\mathbf{x}_2$ denote the coordinates of electrons in the HOMO and LUMO, respectively. Equation (2) indicates that spatial separation of HOMO and LUMO is effective to minimize ΔE_{ST}. Therefore, molecules in which electron-donating and -accepting moieties are chemically bonded are good candidates as efficient TADF materials. Inclusion of spacer groups and/or highly twisted conformation between the donor and acceptor decrease HOMO–LUMO overlap, further lowering ΔE_{ST}. However, following the RISC process from T_1 to S_1, TADF materials need to undergo radiative decay from S_1 to S_0. The rate constant for radiative decay, k_r, is related to the transition dipole moment from S_1 to S_0, μ_{10}, and μ_{10} is described by the HOMO and LUMO distributions as follows

$$\mu_{10} = \langle \varphi_{HOMO}(\mathbf{x})|-e\mathbf{x}|\varphi_{LUMO}(\mathbf{x})\rangle, \qquad (3)$$

where $\mathbf{x}$ is a coordinate in three-dimensional space. Equation (3) shows that well-separated HOMO–LUMO distributions make μ_{10} and k_r small; some overlap between the HOMO and LUMO is necessary to obtain large k_r. Therefore, the small ΔE_{ST} and large μ_{10} required for efficient TADF are seemingly in a trade-off relationship. However, the different dependence of ΔE_{ST} and μ_{10} on the HOMO–LUMO overlap allows us to reconcile these two factors.

3. Experimental procedure

To design new materials, the candidates should be synthesizable and not contain heavy atoms. When devices are fabricated by vacuum deposition, the candidates should vaporize before they decompose. When devices are fabricated by wet processes, the candidates should be soluble in organic solvents. Considering these factors, we designed new materials composed of donor and acceptor segments. ΔE_{ST} and μ_{10} are important parameters for designing TADF materials, as explained above. Therefore, the first screening was calculation of ΔE_{ST} and μ_{10}. We calculated ΔE_{ST} and μ_{10} for candidate materials composed of donor and acceptor segments. Not only the selection of the segments, but also their linkage is important; insertion of a spacer group (or not), how to link the segments (bonded at a *para*-, *meta*-, or *ortho*-position in the case of benzene rings), and torsion angles (by inserting bulky groups at the *ortho*-position) were considered. Only candidates with small ΔE_{ST} and large μ_{10} were selected for synthesis.

The second screening was experimental PLQY and TADF investigation of the synthesized candidates. We measured the PLQY of purified candidates. PLQYs of solutions and solids are normally different, and those of doped and neat films also differ. The PLQY of doped films (or neat films when the device is host-free) is one of the four factors in eq. (1), Φ_{PL}. TADF character was confirmed by transient PL decay measurements under O_2-free conditions. If delayed fluorescence was observed in addition to normal fluorescence and the intensity of delayed fluorescence increases with rising temperature, the material has TADF character; ΔE_{ST} is comparable to thermal energy at measured temperatures. For these materials, β in eq. (1) can exceed 25%; indeed, β of 100% was realized for several materials. We fabricated devices using such TADF materials.

4. Results and discussion

On the basis of the above molecular design concept, we developed a TADF material named DACT-II.[6] DACT-II is composed of electron-donating diphenylaminocarbazole (DAC) and electron-accepting triphenyltriazine (T) groups. The calculated torsion angle (α) for the chemical bond between these groups is 48°. The HOMO and LUMO of DACT-II are localized on DAC and T groups, respectively; such HOMO–LUMO separation results in small ΔE_{ST}, but the HOMO–LUMO overlap is still large enough to obtain large μ_{10}. As expected from quantum chemical calculations, experimentally obtained ΔE_{ST} and PLQY for doped films of DACT-II were 9 meV and 100%, respectively. ΔE_{ST} is much smaller than thermal energy at room temperature (26 meV), which allowed highly efficient RISC. These results suggested that DACT-II should be an excellent emitter for TADF OLEDs, so we fabricated devices based on DACT-II. A maximum EQE of 29.6% was obtained. With an out-coupling sheet, a device with a maximum EQE of 41.5% was achieved.

The high EQEs of DACT-II-based OLEDs confirmed that DACT-II is a leading TADF material. DACT-II has further excellent features as follows.
1) Composed only of C, H, and N.

2) Large PLQY of 100%, as described above.
3) Small ΔE_{ST} of 9 meV, as described above. The ΔE_{ST} is much smaller than thermal energy at room temperature of 26 meV, which allow highly efficient RISC of 100%.
4) Favorable molecular orientation. DACT-II tends to orient parallel to the substrate with an order parameter S of -0.3, even though DACT-II molecules in the emitter layer are in an amorphous state. Such molecular orientation increases light out-coupling, enhancing EQE.
5) Small roll-off. DACT-II-based OLEDs showed only slight roll-off, with EQEs of 26.9% and 21.8% even at 500 and 3,000 cd m^{-2}, respectively. With an out-coupling sheet, EQEs were 37.6% and 30.7% at 500 and 3,000 cd m^{-2}, respectively.
6) High thermal stability. The glass transition temperature of DACT-II thin films was 192 °C at a heating rate of 500 K s^{-1}.
7) High performance over a wide temperature range. The PLQY of DACT-II of 100% at room temperature is preserved even at low temperature; it is 98% at 200 K.
8) Of course, DACT-II has appropriate HOMO and LUMO energy levels that are compatible with those of standard surrounding materials.

Optical simulation indicated η_{out} of the DACT-II-based OLEDs without out-coupling sheets was 29.0±0.9%, indicating an IQE of 29.6/29.0×100≈100%. Our detailed analysis shows that diphenylamino groups play an important role in both the TADF character and molecular orientation of DACT-II. The equivalent molecule without diphenylamino groups does not exhibit TADF character and has random molecular orientation.

In addition to our development of TADF OLEDs containing DACT-II, we will present our results on boron-containing TADF molecules,[7] solution-processable TADF molecules,[8] and host-free solution-processable TADF molecules.[9] We will also describe our recent results on charge transport simulation[10] if time permits.

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