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RESEARCH HIGHLIGHTS

Improving reverse intersystem crossing of MR-TADF emitters for OLEDs

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Thermally activated delayed fluorescence (TADF) emitter is a promising organic light-emitting diode (OLED) material due to low cost, wide luminous color gamut and 100% exciton utilization efficiency[1]. To achieve high TADF performance, a feasible strategy is to construct a twisted donor–acceptor (D–A) unit, decreasing the overlap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and minimizing the energy gap ($\Delta E_{\rm ST}$) between the lowest singlet (S_1) and triplet (T_1) states[2, 3]. However, this long-range charge transfer feature is often disadvantageous for achieving high oscillator strengths (f) and radiative transition rates ($k_{\rm r}$)[4] (Fig. 1(a)). Moreover, common TADF emitters always display broad electroluminescence spectra, whose full-widths at half-maximum (FWHMs) are 70–100 nm[5]. Therefore, it is necessary to realize a narrow-band emission system, which can improve the display quality greatly, with high $k_{\rm r}$ and high rate constant of reverse intersystem crossing ($k_{\rm RISC}$).

In 2015, Hetakeyma *et al.* developed a rigid polycyclic aromatic framework based on B/N system with opposite multiple-resonance (MR) effect for the first time, offering narrow-band emission and efficient TADF performance[6] (Fig. 1(b)). In the emitter DABNA-1 with a highly rigid framework, the cofacial backbone resulted in short-range charge transfer, giving a high PLQY of 88% and a small FWHM of 30 nm in doped film. The corresponding OLEDs with 1 wt% doping offered a maximum external quantum efficiency ($\rm EQE_{max}$) of 13.5% and a FWHM of 28 nm. Through modifying peripheral benzene ring and diphenylamine, the emission peak of DABNA-2 was slightly red-shifted and the OLEDs exhibited a FWHM of 28 nm and an $\rm EQE_{max}$ of 20.2%. In terms of device efficiency and color purity, it is superior to previous commercial blue emitters[7], and it also has potential to replace current commercial blue fluorescent materials as the core of OLEDs. Although MR-TADF emitters have achieved nearly full-color emission, this class of materials tends to exhibit poor $k_{\rm RISC}$ values (~10^4 $\rm s^{-1}$) and severe efficiency roll-off at high current densities[8].

The strategies for alleviating the efficiency roll-off in MR-TADF OLEDs are as follows: (1) hyperfluorescence sensitization (HFS) by using TADF materials with high $k_{\rm RISC}$; (2) introducing "heavy atoms" like S or Se into the skeleton; (3) extending charge delocalization by fusing rigid skeleton. In 2019, Adachi *et al.* designed HFS OLEDs based on ν-DABNA[9] and hetero-donor-type TADF material (HDT-1) with accelerated S_1 energy transfer process[10]. A high $k_{\rm RISC}$ (9.2×10^5 $\rm s^{-1}$) was obtained in doped ternary film. Compared with host-guest type devices, sensitized pure-blue TADF OLEDs showed higher EQE and small efficiency roll-off, and the EQE reached 32% at 1000 cd/m^2. Later, Duan *et al.* fused aza-aromatics into B/N skeleton and synthesized a pure-green AZA-BN emitter ($\lambda_{\rm PL}$ = 522 nm, FWHM = 28 nm)[11] (Fig. 1(c)). Benefitting from efficient HFS mechanism, HFS OLEDs displayed a higher $\rm EQE_{max}$ of 31.6% and smaller efficiency roll-off than non-sensitized devices[12]. Obviously, through the intervention of TADF sensitizer, the ternary emitting layer showed a more efficient triplet-exciton up-conversion rate.

According to Fermi's golden rule, the $k_{\rm RISC}$ in TADF systems mainly depends on spin-orbit coupling (SOC) and energy splitting between S_1 and T_1 states, as expressed in equation: $k_{\rm RISC} \propto |<S_1|\hat{H}_{\rm SOC}|T_1>/\Delta E_{\rm ST}|^2$ [13]. Recently, Yasuda group developed a fused-nonacyclic π-system (BSBS-N1), embedded with B, N, and S atoms. With "heavy atom" S[14], BSBS-N1 exhibited a big $<S_1|\hat{H}_{\rm SOC}|T_1>$ value of 0.31 $\rm cm^{-1}$ and a high $k_{\rm RISC}$ of 1.9×10^5 $\rm s^{-1}$. The corresponding OLEDs offered smaller efficiency roll-off than BBCz-SB LEDs[8]. Similarly, the strategy of using S to improve SOC was further confirmed by Yang *et al.*[15] $k_{\rm RISC}$ over 10^5 $\rm s^{-1}$ was obtained in toluene solution and MR-TADF OLEDs showed smaller efficiency roll-off. To intuitively reflect the influence of heavy atom on RISC, Yasuda *et al.* doped Se atom into MR-TADF emitter (CzBSe)[16], yielding a record $k_{\rm RISC}$ exceeding 10^8 $\rm s^{-1}$ (Fig. 2(a)). Benefitting from its ultrafast triplet-exciton up-conversion, OLEDs with CzBSe offered an $\rm EQE_{max}$ of 23.9%, with narrow blue emission ($\lambda_{\rm EL}$ = 481 nm, FWHM = 33 nm) and significantly alleviated efficiency roll-off.

Extending charge delocalization by fusing rigid skeleton is an effective approach to solve efficiency roll-off of MR-TADF OLEDs. By fusing hole-transport units (carbazole, dibenzofuran) into B/N framework, Zheng *et al.* achieved two π-extended MR-TADF emitters (NBO and NBNP), peaking at 487 and 500 nm with narrow FWHMs of 27 and 29 nm in toluene solutions[17], respectively. $\Delta E_{\rm ST}$ were reduced (0.12 eV for NBO, 0.09 eV for NBNP) *via* charge delocalization of frontier orbitals. Meanwhile, SOC values were further improved due to the introduction of O and N heteroatoms. As results, $k_{\rm RISC}$ for NBO and NBNP are nearly an order of magnitude higher than

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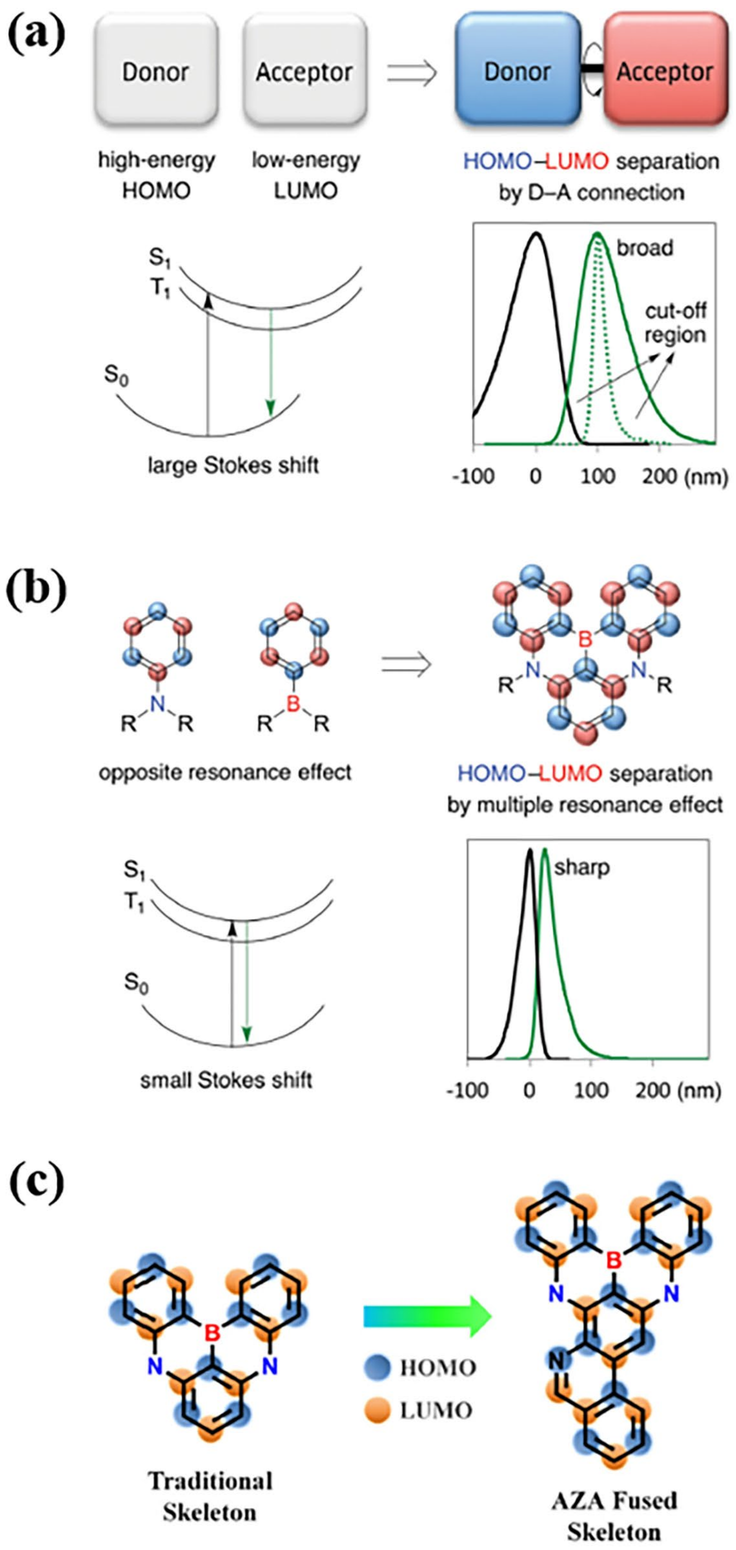

Fig. 1. (Color online) (a) Traditional design strategy for TADF. Reproduced with permission[6], Copyright 2016, Wiley-VCH. (b) Design strategy for MR-TADF. Reproduced with permission[6], Copyright 2016, Wiley-VCH. (c) New MR-TADF skeletons with fused aza-aromatics. Reproduced with permission[11], Copyright 2020, Wiley-VCH.

that of BBCz-SB. Consequently, NBO- and NBNP-based OLEDs showed EQE_{max} of 26.1% and 28.0%, with low efficiency roll-off. To further enhance the CT state of MR-TADF emitters, Zheng *et al*. adopted double resonance unit superposition strategy and obtained two green MR-TADF emitters (VTCzBN and TCz-VTCzBN) based on indolo[3,2,1-*jk*]carbazole (ICz) unit and B/N skeletons[18] (Fig. 2(b)), and the emissions peaked at 496 and 521 nm with FWHMs of 34 and 29 nm, respectively. Benefitting from thorough charge delocalization within frontier molecular orbitals, ΔE_{ST} values were close to 0 eV and large $<S_1|\hat{H}_{SOC}|T_1>$ values were obtained. As a result, high k_{RISC} values were also achieved, and VTCzBN and TCz-VTCzBN-based OLEDs showed EQE_{max} of 31.7% and 32.2%, with low efficiency roll-off, respectively. D-TCz-VTCzBN displayed ultrapure green CIE of (0.22, 0.71), consistent with the green display standard of the National Television System Committee.

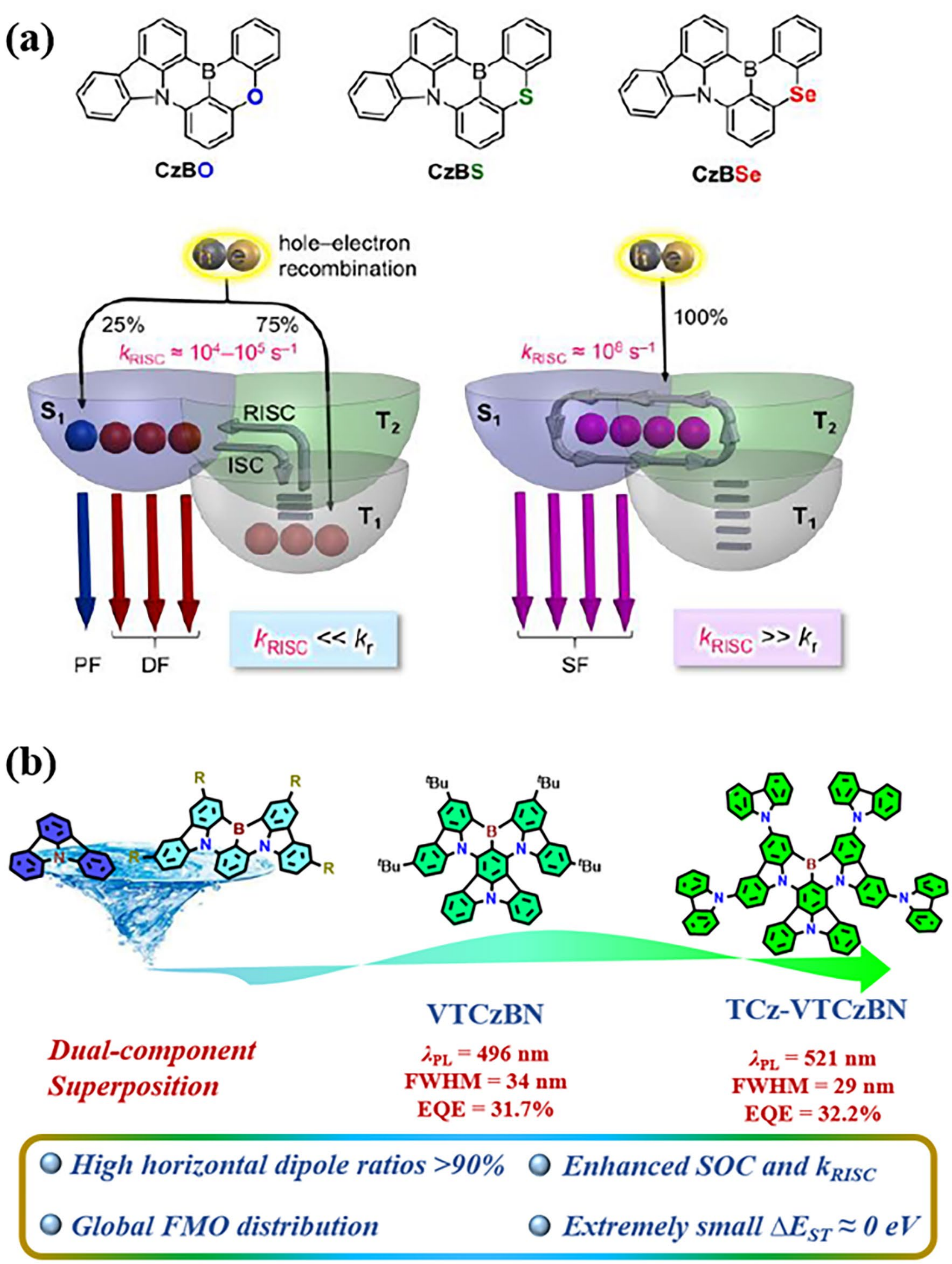

Fig. 2. (Color online) (a) Molecular structures of CzBO, CzBS, and CzBSe with different chalcogens, conventional TADF mechanism and ideal superimposed fluorescence (SF) mechanism. Reproduced with permission[16], Copyright 2022, Wiley-VCH. (b) Double resonance unit superposition strategy. Reproduced with permission[18], Copyright 2022, Wiley-VCH.

In short, enhancing k_{RISC} of MR-TADF emitters is crucial for reducing efficiency roll-off of OLEDs. Some strategies are highlighted, like TADF sensitization, heavy atom introduction, extending charge delocalization. More efforts are needed to develop MR-TADF OLEDs with high EQE, low efficiency roll-off and narrow emission.

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References

[1] Uoyama H, Goushi K, Shizu K, et al. Highly efficient organic light-emitting diodes from delayed fluorescence. Nature, 2012, 492, 234

[2] Yang Z, Mao Z, Xie Z, et al. Recent advances in organic thermally activated delayed fluorescence materials. Chem Soc Rev, 2017, 46, 915

[3] Ren B, Zuo C, Sun Y, et al. Intramolecular spatial charge transfer enhances TADF efficiency. J Semicond, 2021, 42, 050201

[4] Notsuka N, Nakanotani H, Noda H, et al. Observation of nonradiative deactivation behavior from singlet and triplet states of thermally activated delayed fluorescence emitters in solution. J Phys Chem Lett, 2020, 11, 562

[5] Kaji H, Suzuki H, Fukushima T, et al. Purely organic electroluminescent material realizing 100% conversion from electricity to light. Nat Commun, 2015, 6, 8476

[6] Hatakeyama T, Shiren K, Nakajima K, et al. Ultrapure blue thermally activated delayed fluorescence molecules: efficient HOMO-LUMO separation by the multiple resonance effect. Adv Mater, 2016, 28, 2777

[7] Jung H, Kang S, Lee H, et al. High efficiency and long lifetime of a fluorescent blue-light emitter made of a pyrene core and optimized side groups. ACS Appl Mater Interfaces, 2018, 10, 30022

[8] Yang M, Park I S, Yasuda T. Full-color, narrowband, and high-efficiency electroluminescence from boron and carbazole embedded polycyclic heteroaromatics. J Am Chem Soc, 2020, 142, 19468

[9] Kondo Y, Yoshiura K, Kitera S, et al. Narrowband deep-blue organic light-emitting diode featuring an organoboron-based emitter. Nat Photonics, 2019, 13, 678

[10] Chan C Y, Tanaka M, Lee Y T, et al. Stable pure-blue hyperfluorescence organic light-emitting diodes with high-efficiency and narrow emission. Nat Photonics, 2021, 15, 203

[11] Zhang Y, Zhang D, Wei J, et al. Achieving pure green electroluminescence with CIEy of 0.69 and EQE of 28.2% from an aza-fused multi-resonance emitter. Angew Chem Int Ed, 2020, 59, 17499

[12] Huang T, Wang Q, Xiao S, et al. Simultaneously enhanced reverse intersystem crossing and radiative decay in thermally activated delayed fluorophors with multiple through-space charge transfers. Angew Chem Int Ed, 2021, 60, 23771

[13] Kim J U, Park I S, Chan C Y, et al. Nanosecond-time-scale delayed fluorescence molecule for deep-blue OLEDs with small efficiency rolloff. Nat Commun, 2020, 11, 1765

[14] Nagata M, Min H, Watanabe E, et al. Fused-nonacyclic multi-resonance delayed fluorescence emitter based on ladder-thiaborin exhibiting narrowband sky-blue emission with accelerated reverse intersystem crossing. Angew Chem Int Ed, 2021, 60, 20280

[15] Liu F, Cheng Z, Jiang Y, et al. Highly efficient asymmetric multiple resonance thermally activated delayed fluorescence emitter with EQE of 32.8% and extremely low efficiency roll-off. Angew Chem Int Ed, 2022, 61, e202116927

[16] Park I S, Min H, Yasuda T. Ultrafast triplet-singlet exciton interconversion in narrowband blue organoboron emitters doped with heavy chalcogens. Angew Chem Int Ed, 2022, 61, e202205684

[17] Luo X F, Ni H X, Ma H L, et al. Fused π-extended multiple-resonance induced thermally activated delayed fluorescence materials for high-efficiency and narrowband OLEDs with low efficiency roll-off. Adv Opt Mater, 2022, 10, 2102513

[18] Luo X F, Song S Q, Ni H X, et al. Multiple-resonance-induced thermally activated delayed fluorescence materials based on indolo[3,2,1-*jk*]carbazole with an efficient and narrowband pure-green electroluminescence. Angew Chem Int Ed, 2022, in press

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