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Asymmetric thermally activated delayed fluorescence (TADF) emitters with 5,9-dioxa-13*b*-boranaphtho[3,2,1-*de*]anthracene (OBA) as acceptor and highly efficient blue-emitting OLEDs

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A series of new organic emitters have been prepared through introducing various donors (D) to the *meta*-position of the boron atom in central phenyl ring in the acceptor (A) of 5,9-dioxa-13*b*-boranaphtho[3,2,1-*de*]anthracene (OBA). Their thermal, photophysical, electrochemical and electroluminescent (EL) properties have been characterized in detail. The photophysical results have revealed that these OBA-based molecules adopting D-A configuration can exhibit efficient thermally activated delayed fluorescence (TADF) properties with reverse inter-system crossing constant (k_{Risc}) in the order of 10⁵ s⁻¹. It has been shown that introducing –Br group to the OBA acceptor can increase k_{Risc} by 2 to 3 times. Importantly, deep-blue TADF emitter **OBA-O** can show high photoluminescent quantum yield (PLQY) of 0.84, while the blue analog **OBA-BrO** with –Br group can possess even high PLQY of 0.92 in the doped film. Benefitting from their high PLQYs as blue-emitting TADF emitters, the doped organic light-emitting diodes (OLEDs) based on these OBA-based TADF emitters can achieve attractive electroluminescent (EL) performances. The blue-emitting OLEDs with CIE (0.17. 0.17) can show the maximum external quantum efficiency (η_{ext}) of 17.8%, current efficiency (η_{L}) of 33.2 cd A⁻¹ and power efficiency (η_{e}) of 34.2 Im W⁻¹, while the data for the bluish-green device are 22.5%, 49.2 cd A⁻¹ and η_P of 56.9 Im W⁻¹. The great potential of these TADF emitters based OBA acceptor has been clearly indicated by these EL data. In addition, these asymmetric OBA-based molecules will enrich structural diversity of this kind of TADF emitters.

Introduction

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After being demonstrated by Adachi,¹⁻⁵ thermally activated delayed fluorescence (TADF) emitter have received substantial research endeavors, since they can harness both singlet and triplet excitons in the electroluminescent (EL) process without the aid of precious metal ions through reverse intersystem crossing (RISC).^{6, 7} With these new-generation emitters, the organic light-emitting diodes (OLEDs) can still fulfill high EL efficiencies without costly Pt(II) and Ir(III) phosphorescent complexes.^{8, 9} To maintain highly efficient RISC process, TADF emitters possess typically small energy difference (ΔE_{ST}) between the first singlet excited state (S₁) and the first triplet excited state (T₁).¹⁰⁻¹² To meet this purpose, TADF molecules

generally adopt D–A-type or D–A–D-type (D = electron donor, A = electron acceptor) configuration to promote the RISC procedure by reducing ΔE_{ST} .^{13, 14} Therefore, on this basis, various TADF emitters have been successfully developed by employing donors, such as acridine,¹⁵⁻¹⁷ phenoxazine¹⁸⁻²⁰ and phenothiazine^{21, 22} etc. as well as acceptors including aromatic nitrogen heterocyclic units,²³⁻²⁵ sulphonyl groups,^{26, 27} aromatic ketones,^{28, 29} aryl phosphine oxide (APO) groups³⁰⁻³² and so on. With these novel TADF emitters, highly efficient OLEDs have been constructed with diverse EL wavelengths required to make Red(R)-Green(G)-Blue(B) full-color displays and white OLEDs (WOLEDs).^{12, 33-36} All these encouraging results have clearly indicated the great potential of these TADF molecules in the field of OLEDs.

Recently, organic borons have been employed as acceptors for the TADF molecules,³⁷⁻³⁹ especially for the blue emitters. For example, $B(Mes)_{2}$,^{37, 40} 10*H*-phenazaborin⁴¹ and 10*H*phenoxaborin^{37, 42} have exhibited great potential of furnish high EL efficiencies to the concerned TADF emitters. More importantly, some advanced rigid polycyclic boron-containing aromatic skeletons were introduced into TADF molecules which can bring highly efficient blue-emitting OLEDs showing good color quality. For example, Lee and coworkers had adopted 5,9-dioxa-13b-boranaphtho[3,2,1-*de*]anthracene



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⁺ Electronic supplementary information (ESI) available: Synthetic details for intermediate compounds, CV curves and some EL data.

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(OBA)-type acceptor to develop high-performance blueemitting TADF molecules through attaching carbazole-based donor to the central phenyl ring of OBA unit on the paraposition of the boron atom, showing extremely high external quantum efficiency (η_{ext}) of 38.15% and color coordinates of (0.15, 0.28). Deep-blue emission can also be achieved by one of this OBA-type emitters with $\eta_{\rm ext}$ of 21.50% and attractive color coordinates of (0.15, 0.06).43 Recently, Peng and Wang et al have introduced acridine moiety to different positions of each of the two terminal phenyl rings in OBA unit.⁴⁴ The OLEDs with these OBA-based TADF emitters can achieve very higher $\eta_{\rm ext}$ of 20.5%. ⁴⁴ Clearly, the great potential of boron-containing units as acceptors of the TADF molecules can be seen. Unfortunately, this kind of acceptors is still remained unexplored compared other type acceptors aforementioned. Hence, developing new TADF molecules with boron-containing acceptors should be of great importance for bringing high EL efficiencies.

In this contribution, a series of new TADF molecules adopting asymmetric configuration have been reported with OBA-type acceptor and phenoxazine or phenothiazine as donor. Different from all the reported symmetric TADF molecules with the OBA-type acceptor, the donors in these new OBA-based TADF molecules have been introduced to the central phenyl ring of OBA unit on *meta*-position of the boron atom. Clearly, this substitution mode and molecular structure will definitely enrich structure-activity relationship information for the OBA-based TADF molecules. Critically, based on these new OBA-based emitters, highly efficient blue-emitting OLEDs have been constructed with CIE (0.17. 0.17), η_{ext} of 17.8%, η_{L} of 33.2 cd A⁻¹ and η_{P} of 34.2 lm W⁻¹. In addition, even higher EL performances have been furnished in bluish green devices with EL efficiencies of 22.5%, 49.2 cd A⁻¹ and η_{P} of 56.9 lm W⁻¹.

Experimental

General information

Commercial chemicals were used without further purification. All reactions were carried out under nitrogen atmosphere. Prior to use, solvents were carefully dried and distilled from appropriate drying agents. All reactions were monitored by thin-layer chromatography (TLC) from Merck & Co., Inc. Column chromatography and preparative TLC was conducted by using silica gel from Shenghai Qingdao (300-400 mesh). ¹H and $^{13}\mbox{C}$ NMR spectra were recorded in \mbox{CDCl}_3 or DMSO on a Bruker Avance 400 or 600 MHz spectrometer. The chemical shifts were quoted on the solvent residual peak at δ 7.26 ppm for ¹H and 77.0 ppm for ¹³C NMR. Fast atom bombardment mass spectrometry (FAB-MS) spectra were obtained on a Finnigan MAT SSQ710 system. UV-vis spectra were recorded Shimadzu UV-2250 spectrophotometer. on а The photoluminescent spectra and lifetimes of these OBA-based emitters were measured on Edinburgh Instruments FLS920 spectrophotometer. The photoluminescent quantum yields (PLQYs) were determined in toluene solutions with an integrating sphere. With a scan rate of 100 mV s⁻¹, cyclic Page 2 of 14

voltammetry measurements were carried out on A Rrinceton Applied Research model 2273 A potentiostal through through through through through through through through the second s

Synthesis

The key intermediate compounds OBr, SBr, OBA, OB, and SB were synthesized according the literature method⁴⁵⁻⁴⁹ with the synthetic details presented in Electronic Supplementary Information (ESI).

General procedure for synthesis of OBA-Br and OBA-2Br

N-Bromosuccinimide (NBS) (1.2 equiv, 0.395 g, 2.221 mmol) for the synthesis of **OBA-Br** or (2.5 equiv, 0.823 g, 4.627 mmol) for the synthesis of **OBA-2Br** was added to a solution of OBA (1.0 equiv, 0.500 g, 1.851 mmol) in THF (10 mL) at room temperature under nitrogen atmosphere. After the mixture was stirred at room temperature for 3 h, it was cooled to 0 °C and added to water, the reaction mixture was extracted with CH_2CI_2 . The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure, then purified by column chromatography over silica gel using petroleum ether as the eluent. A white solid of the title compound was obtained.

OBA-Br. Petroleum ether (PE); Yield: 67%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.70 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 1H), 7.78–7.71 (m, 2H), 7.68 (d, J = 4.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.45–7.39 (m, 2H), 7.17 (d, J = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 176.8, 160.3, 153.1, 137.7, 134.6, 134.5, 134.0, 133.9, 123.4, 123.1, 118.8, 118.5, 110.1, 100.8; FAB-MS (m/z): 348, 350 [M]⁺; Anal. Calcd for C₁₈H₁₀BBrO₂: C, 61.95; H, 2.89; found: C, 61.85; H, 2.78.

OBA-2Br. Petroleum ether (PE); Yield: 56%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.70 (dd, J = 7.6, 1.2 Hz, 2H), 8.24 (s, 1H), 7.80-7.76 (m, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.45 (t, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.4, 156.4, 133.1, 132.3, 128.4, 127.3, 121.8, 120.5, 117.5, 110.7; FAB-MS (m/z): 428 [M]⁺; Anal. Calcd for C₁₈H₉BBr₂O₂: C, 50.53; H, 2.12; found: C, 50.39; H, 2.18.

General synthetic procedure for the asymmetric OBA-based emitters

Under a nitrogen atmosphere, **OBA-Br** (1.0 equiv, 0.10 g, 0.287 mmol)/**OBA-2Br** (1.0 equiv, 0.1 g, 0.235 mmol), **OB/SB** (1.3 equiv), and Pd(PPh₃)₄ (0.033 g, 0.029 mmol) were added to degassed toluene (10 mL) and K₂CO₃ (3 mL, 2 M). The reaction mixture was heated to 110 °C and stirred for 18 h. After cooling to room temperature, the mixture was extracted into CH₂Cl₂ and dried with anhydrous Na₂SO₄. After evaporated to dryness, the residue was purified by column chromatography over silica gel using proper eluent.

OBA-O. CH_2Cl_2 /petroleum ether (1:5, v:v); Yield: 62%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.12 (d, J = 7.2 Hz, 2H), 7.86 (d, J = 7.2 Hz, 2H), 7.41 (dd, J = 8.0, 4.4 Hz, 3H), 7.35–7.16 (m, 6H), Published on 03 September 2019. Downloaded on 9/4/2019 12:19:32 AM

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6.97 (d, J = 8.4 Hz, 1H), 6.70-6.60 (m, 6H), 6.07 (d, J = 9.2 Hz, 2H); 13 C NMR (100 MHz, CDCl₃): δ (ppm) 158.7, 158.5, 157.5, 154.3, 144.0, 138.8, 137.0, 134.6, 133.2, 133.0, 132.6, 132.0, 130.3, 130.2, 128.5, 128.4, 123.8, 123.3, 123.1, 122.9, 122.1, 121.2, 117.1, 115.6, 115.4, 113.4, 110.0; FAB-MS (m/z): 527 [M]^+; Anal. Calcd for $C_{36}H_{22}BNO_3$: C, 81.99; H, 4.20; N, 2.66 found: C, 81.89; H, 4.11; N, 2.55.

OBA-S. CH₂Cl₂/petroleum ether (1:5, v:v); Yield: 54%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.12 (d, J = 7.2 Hz , 2H), 7.87 (d, J = 8.4 Hz, 2H), 7.43 (dd, J = 11.2, 1.6 Hz, 3H), 7.31 (td, J = 8.8, 1.6 Hz, 2H), 7.2-7.1 (m, 4H), 7.02 (dd, J = 7.2, 1.6 Hz, 2H), 6.97 (d, J = 8.4 Hz, 1H), 6.89 (t, J = 7.6 Hz, 2H). 6.81 (t, J = 7.6 Hz, 2H). 6.39 (dd, J = 8.0, 0.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 160.5, 160.3, 157.6, 153.7, 139.2, 139.1, 138.1, 136.1, 134.8, 134.7, 134.1, 134.0, 132.8, 132.4, 132.1, 130.6, 130.4, 123.4, 122.6, 122.3, 120.4, 118.8, 118.7, 117.7, 109.5; FAB-MS (m/z): 543 [M]⁺; Anal. Calcd for C₃₆H₂₂BNO₂S: C, 79.57; H, 4.08; N, 2.58 found: C, 79.49; H, 4.05; N, 2.47.

OBA-BrO. CH_2CI_2 / petroleum ether (1:3, v:v); Yield: 58%. ¹H NMR (400 MHz, CDCI₃): δ (ppm) 8.13 (d, J = 7.2 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.63 (s, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.32 (t, J = 6.8 Hz, 3H), 7.22–7.13 (m, 3H), 6.70–6.61 (m, 6H), 6.06 (d, J = 9.2 Hz, 2H); ¹³C NMR (100 MHz, CDCI₃): δ (ppm) 158.3, 158.2, 153.3, 153.2, 144.0, 137.6, 137.4, 134.4, 133.1, 133.0, 132.9, 132.0, 130.3, 128.5, 128.4, 123.4, 123.3, 123.2, 121.2, 117.4, 117.0, 115.4, 113.4, 102.5; FAB-MS (m/z): 605, 607 [M]⁺; Anal. Calcd for C₃₆H₂₁BBrNO₃: C, 71.32; H, 3.49; N, 2.31 found: C, 71.19; H, 3.37; N, 2.18.

OBA-BrS. CH₂Cl₂/petroleum ether (1:3, v:v); Yield: 46%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.12 (d, J = 7.2 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.66 (s, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.35-7.15 (m, 6H), 7.03 (dd, J = 7.6, 1.6 2H), 6.90(t, J = 7.6 Hz, 2H), 6.82 (t, J = 7.6Hz, 2H), 6.38 (dd, J = 8.0, 0.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 160.2, 160.0, 152.8, 152.6, 139.0, 138.6, 136.0, 134.6, 134.3, 134.2, 134.1, 132.7, 132.3, 132.0, 131.8, 130.5, 130.2, 126.9, 123.6, 123.4, 122.6, 122.2, 118.8, 118.7, 117.5, 116.7, 101.5; FAB-MS (m/z): 621, 623 [M]⁺; Anal. Calcd for C₃₆H₂₁BBrNO₂S: C, 69.48; H, 3.40; N, 2.25 found: C, 69.36; H, 3.31; N, 2.19.

Results and discussion

Synthesis and structural characterization

The synthetic strategies for the asymmetric OBA-based TADF emitters are outlined in Scheme 1 and the synthetic details for the literature compounds are provided in ESI. From Scheme 1, the preparation of the designed TADF emitters is fulfilled by Suzuki cross-coupling between the compound of boronic acid pinacol ester containing donor group **OB** or **SB** and the corresponding brominated OBA derivative **OBA-Br** or **OBA-2Br** Chemical structures of these asymmetric OBA-based TADF emitters have been characterized by NMR spectroscopies, mass spectrometry and elemental analyses. A characteristic doublet signal at δ ca. 8.1 ppm for all the OBA-based TADF emitters can be assigned to the two protons attached to the carbon atoms adjacent to the boron-bonded carbon atoms in the OBA unit. The doublet resonance peak at δ *ca.* 7.9 ppm can be ascribed to the two protons close to the OBA unit on phenyl ring between OBA acceptor and corresponding donor. For **OBA-BrO** and **OBA-BrS**, the singlet signal at δ ca. 7.6 ppm should be induced by the proton in between -Br group and donor on the OBA unit. The other several sets of resonance peaks after ca. 7.1 ppm can be safely assigned to the protons on phenoxazine or phenothiazine groups. These NMR spectral data have clearly confirmed the chemical structures of these OBA-based TADF emitters (Figure S1-4).

Different from the substitution pattern employed by literature analogs,^{43,44} introducing donors to the *meta*-position of the boron atom in the central phenyl ring of OBA unit can facilitate the synthesis of these OBA-based TADF emitters with diverse structures at the same time providing new information about structure-property relationship of this type of TADF emitters.

Thermal and photophysical properties

Under nitrogen flow, thermal properties of these asymmetric OBA-based emitters had been characterized by both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Indicated by the TGA data (Figure S5), all the OBA-based emitters can show good thermal stability with decomposition temperature (T_d) ranging from 362 to 393 °C (Table 1). Introducing –Br group, **OBA-BrO** and **OBA-BrS** can possess higher T_d than **OBA-O** and **OBA-S** (Table 1), which should be ascribed to the conjugation effect between –Br group and OBA ring to stabilize C-B bond. The DSC traces reveal no glass transition process for these asymmetric OBA-based emitters to benefit their EL application, indicating their high phase stability induced by their twist structures due to introducing donor to the *meta*-position of the boron atom in the central phenyl ring of OBA unit.

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Scheme 1 Synthesis of the OBA-based TADF emitters.

 Table 1. Photophysical and thermal data of these asymmetric OBA-based emitters

Compounds	Absorption ^a λ_{abs} (nm)	Emission $\lambda_{ m em}$ (nm)	PLQY	T _d ^f (°C)
OBA-O	283 (4.69), 299 (3.92), 309 (4.57), 338 (4.15), 386 (4.27)	444 ^b /450 ^c	0.76 ^d /0.84 ^e	362
OBA-S	283 (4.74), 300 (4.54), 310 (4.58), 342 (4.03), 387 (4.30)	456 ^b /470 ^c	0.63 ^d /0.75 ^e	385
OBA-BrO	282 (4.34), 301 (4.13), 312 (4.18), 385 (3.93), 391 (3.95)	470 ^b /476 ^c	0.84 ^d /0.92 ^e	393
OBA-BrS	282 (4.60), 301 (4.36), 312 (4.41), 385 (4.15), 392 (4.17)	478 ^b /470 ^c	0.53 ^d /0.55 ^e	391

^{*a*} Measured at a concentration of *ca*. 10⁻⁵ M in toluene at room temperature and log ε values in parentheses are presented. ^{*b*} Measured in toluene at 293 K. ^{*c*} Measured in doped mCP film (doping ratio: 10 wt.%) at 293 K. ^{*d*} Absolute PL quantum yield (PLQY) in toluene measured with an integrating sphere at room temperature. ^{*e*} Absolute PL quantum yield (PLQY) in doped mCP film (doping ratio: 10 wt.%) measured with an integrating sphere at 293 K. ^{*f*} *T*_d is the decomposition temperature.

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Fig. 1 UV–vis absorption (a) and PL (b) spectra for these asymmetric OBA-based emitters in toluene at 293 K.

Figure 1a shows UV-vis absorption spectra of these asymmetric OBA-based emitters in toluene at 293 K and the corresponding data have been summarized in Table 1. For all these asymmetric OBA-based emitters, they typically exhibit two major absorption bands (Figure 1a). The high-energy strong absorption bands before 350 nm should be assigned to the $\pi \rightarrow \pi^*$ transitions in aromatic systems in both OBA unit and donor groups. However, besides these high-energy absorption bands, these asymmetric OBA-based emitters can show a relatively weaker absorption band around 390 nm with broad structureless spectral line (Figure 1a). These broad structureless low-energy absorption bands should be induced by the charge-transfer (CT) process in these asymmetric OBA-based emitters, regarding as a character to show TADF behavior based on

literature results.^{38, 50-54} With –Br group, the low-energy absorption bands for **OBA-BrO** and **OBA-BrS** can show slight bathochromic effect compared with those from **OBA-O** and **OBA-S** without –Br group (Figure 1a).

In order to get deep insight into the absorption feature of these asymmetric OBA-based emitters, key front molecular orbitals (MOs) have been obtained by theoretical calculation based on their ground states (S_0) (Figure 2). From the MO pattern of these OBA-based emitters, obvious separation between their highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) can be seen clearly (Figure 2). It indicates that the lowest energy transition processed in these asymmetric OBA-based emitters originate from π orbitals of the donor groups to the π^* orbitals of the acceptor group of OBA unit, exhibiting obvious intra-molecular charge transfer (CT) feature. Thus, the low-energy structureless broad absorption bands of OBA-O, OBA-S, OBA-BrO and OBA-BrS should be induced by the intra-molecular charge transfer transition process. In addition, the CT feature of their low-energy absorption has been indicated by the structureless broad spectral line-shape (Figure 1a). Obviously, introducing electron-withdrawing -Br group to the acceptor OBA unit will definitely facilitate the intra-molecular CT process in these asymmetric OBA-based emitters to stabilize their CT states. Hence, the low-energy CT absorption bands of OBA-BrO and OBA-BrS can show bathochromic effect compared with those of OBA-O and OBA-S free of -Br group (Figure 1a). Clearly, the experimental results are consistent well with the theoretical results, indicating the validity of the theoretical calculations.

Photoluminescent (PL) spectra of these asymmetric OBAbased emitters are shown in Figure 1b. Generally, these asymmetric OBA-based emitters can show PL spectra in blue light region with broad spectral line-shape (Figure 1b). The broad spectral lines without fine structure also indicate the CT features of their emission behavior. Owing to the stronger donating ability associated with phenothiazyl group, OBA-S (ca. 456 nm) and OBA-BrS (ca. 478 nm) can show longer emission wavelength than their corresponding analogs OBA-O (ca. 444 nm) and OBA-BrO (ca. 470 nm) with phenoxazyl donor (Figure 1b and Table 1). Based on the optimized structures of these asymmetric OBA-based emitters, the phenoxazyl group can adopt perfect planar configuration (Figure 2), showing higher rigidity than the nonplanar phenothiazyl group. The highly rigid phenoxazyl group should show advantage of restraining the nonradiative processes in OBA-O and OBA-BrO.²⁰ Hence, OBA-O possesses higher PLQY than OBA-S and so does OBA-BrO than OBA-BrS (Table 1).

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Fig. 2 Molecular orbital patterns (isocontour value = 0.025) for the asymmetric OBA-based emitters based on their optimized S_0 geometries. (a) **OBA-O**, (b) **OBA-S**, (c) **OBA-BrO** and (d) **OBA-BrS**.

Table 2. TADF data of these asymmetric OBA-based emitters

Compound	S ₁ (eV) ^a	7 ₁ (eV) ^a	∆E _{s⊤} (eV) ^b	τ _{ΡF} (ns) ^c	τ _{DF} (μs) ^c	$oldsymbol{\Phi}_{PF}$ (%) d	$oldsymbol{\Phi}_{DF}$ (%) ^d	k _{PF} (10 ⁷ s ⁻¹) ^е	k _{DF} (10 ⁵ s⁻¹) ^e	k _{ISC} (10 ⁶ s ⁻¹) ^f	k _{RISC} (10 ⁵ s ⁻¹) ^f
OBA-O	3.15	3.06	0.09	90.7	4.14	27.0	57.0	0.30	1.38	2.02	4.28
OBA-S	3.17	3.08	0.09	77.9	4.80	27.1	48.0	0.35	1.01	2.22	2.76
OBA-BrO	3.25	3.21	0.04	33.1	3.74	19.8	72.2	0.60	1.93	4.70	8.97
OBA-BrS	3.19	3.12	0.07	47.8	0.81	24.5	30.5	0.51	3.75	2.84	8.41

^{*a*} Experimental data were determined from onsets of the fluorescence and phosphorescence (77 K) spectra in doped mCP film (doping ratio: 10 wt.%). ^{*b*} $\Delta E_{ST} = E_{S1} - E_{T1}$. ^{*c*} The prompt fluorescence lifetime (τ_{PF}) and delayed fluorescence lifetime (τ_{DF}) were measured in doped mCP film at 300 K. ^{*d*} The prompt fluorescence quantum yields (Φ_{PF}) and delayed fluorescence quantum yields (Φ_{DF}) were estimated according to the prompt and delayed proportions in transient decay curves. ^{*e*} The rate constants of PF and DF (k_{PF} and k_{OF}) evaluated according to experimental data: $k_{PF} = \Phi_{PF} / \tau_{PF}$ and $k_{DF} = \Phi_{DF} / \tau_{DF}$. ^{*f*} The rate constants of intersystem crossing and reverse (k_{ISC} and k_{RISC}) are further estimated according to $k_{ISC} = \Phi_{DF} k_{PF} / (\Phi_{PF} + \Phi_{DF})$ and $k_{RISC} = k_{DF} k_{PF} / (\Phi_{PF})$.

TADF behaviors

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Adopting D- π -A configuration facilitating their TADF behavior, all these asymmetric OBA-based emitters should possess TADF ability. In order to characterize their TADF behavior, the transient decay curves have been obtained in both doped film in mCP and degassed toluene at different temperature (Figure 3). Clearly, in both mCP doped film and toluene, two decay processes can be observed. The prompt decay processes show short lifetimes in the order of dozens of nanoseconds, while the delayed decay processes can show much longer lifetimes in the order of microsecond which is shortened with increasing of temperature (Figure 3 and Table 2). All these characteristic phenomena have indicated the TADF feature for the emission behavior of these asymmetric OBA-based emitters. Critically, even at 77 K, they still can maintain the delayed decay process (Figure 3), indicating their efficient reverse intersystem crossing (RISC) process even at very low temperature.

With the aim to interpret their different TADF behavior, natural transition orbital (NTO) patterns for both $S_0 \to S_1$ and

 $S_0 \rightarrow T_1$ transitions based on the optimized S_1 and T_1 geometries of these asymmetric OBA-based TADF emitters have been obtained through theoretical calculations (Figure 4). Due to the fact that both HOMO and LUMO patterns are obtained on the basis of the S_0 state,^{41, 43-45} NTOs based on excited states should be reasonably employed to interpret their TADF behavior involving the excited states of these OBA-based emitters. From the NTO patterns for both $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ transitions, there is a distinct separation between hole and particle orbitals of these asymmetric OBA-based emitters (Figure 4). Furthermore, the large twisting angle > 90° between donor and acceptor OBA group can also furnish distinct separation of the NTOs as well (Figure 4). For sure, these characters associated with the asymmetric OBA-based emitters should definitely favor their TADF behaviors.

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Fig. 3 Transient PL decays for these asymmetric OBA-based emitters doped in mCP film (doping ratio: 10 wt.%). The inset shows the temperature dependence of transient PL decay in degassed toluene. (a) OBA-O, (b) OBA-S, (c) OBA-BrO and (d) OBA-BrS,

Based on the photophysical results, critical parameter ΔE_{ST} has been obtained for these asymmetric OBA-based emitters. Clearly, all the experimental ΔE_{ST} values are less than 0.1 eV (Table 2), which is also supported by the theoretical results (Figure 4). The small ΔE_{ST} values associated with these asymmetric OBA-based emitters will also furnish high TADF ability. With -Br group, OBA-BrO and OBA-BrS can show higher rate constants of intersystem crossing (k_{ISC} , 4.70 × 10⁶ s⁻¹ and 2.84×10^6 s⁻¹, respectively) compared with **OBA-O** (2.02×10^6 s⁻¹) and **OBA-S** ($2.22 \times 10^6 \text{ s}^{-1}$) due to the heavy-atom effect induced by -Br group (Table 2). Also, owing to the heavy-atom effect, OBA-BrO and OBA-BrS can possess shorter prompt fluorescence lifetime (τ_{PF}) than **OBA-BO** and **OBA-BS** (Table 2). It should be noted that introducing -Br group can bring even small ΔE_{st} values. The ΔE_{st} values are 0.09 eV for **OBA-O** and OBA-S, while those for OBA-BrO and OBA-BrS are 0.04 and

0.07 eV, respectively (Table 2). Owing to their smaller ΔE_{ST} values, OBA-BrO and OBA-BrS can show higher kRISC values of $8.97 \times 10^5 \text{ s}^{-1}$ and $8.41 \times 10^5 \text{ s}^{-1}$ than **OBA-O** (*ca.* $4.28 \times 10^5 \text{ s}^{-1}$) and OBA-S (ca. 2.76 × 10⁵ s⁻¹) (Table 2). Reasonably, electronwithdrawing -Br group on OBA acceptor will promote separation of the MOs of these asymmetric OBA-based TADF emitters, which will favor the TADF procedure of OBA-BrO and **OBA-BrS**. Hence, they can possess higher k_{RISC} value as aforementioned. In addition, the OBA-based TADF emitters OBA-O and OBA-BrO with rigid phenoxazyl group can possess higher k_{RISC} values compared with their analogs **OBA-S** and OBA-BrS with phenothiazyl group, respectively (Table 2). This result might be ascribed to the fact that the rigidity associated with the phenoxazyl group in OBA-O and OBA-BrO can reduce the chance of competition with RISC process from the nonradiative procedure due to the molecular flexibility. ²⁰

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Fig. 4 Natural transition orbital patterns (isocontour value = 0.025) for both $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ excitations based on the optimized S_1 and T_1 geometries, respectively, together with the S_0 geometry showing twisting angle between donor and acceptor.

Electrochemical properties

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Electrochemical data of these asymmetric OBA-based TADF emitters had been measured through cyclic voltammetry (CV) with ferrocene as the internal standard. In the anodic scan, all the OBA-based TADF emitters can exhibit reversible oxidation processes (Table 3 and Figure S6). The reversible oxidation processes with oxidation potential (E_{pa}) in the range from 0.32 to 0.35 V can be ascribed to the oxidation the donor groups in these OBA-based TADF emitters (Table 3). There is an irreversible reduction process observed for all these asymmetric OBA-based TADF emitters (Table 3 and Figure S1). This reduction process can be safely assigned to the reduction of the acceptor OBA group. Owing to the electron-withdrawing –Br group on the OBA unit, **OBA-BrO** and **OBA-BrS** can show reduction potentials (E_{pc}) of -2.37 V and -2.46 V, less negative than those of **OBA-O** (*ca.* -2.49 V) and **OBA-S** (*ca.* -2.52 V), respectively (Table 3). Due to the stronger electron-donating ability of sulfur atom than oxygen atom, the phenothiazyl group make the OBA acceptor in **OBA-S** and **OBA-BrS** more difficult to be reduced. Hence E_{pc} of -2.52 V for **OBA-S** is lower than E_{pc} of -2.49 V for **OBA-O**. Comparing with the E_{pc} s of **OBA-BrO** and **OBA-BrS**, the same trend can be observed.

Table 3. Redox properties of these asymmetric OBA-based emitters

	-				
Compound	E _{pa} (V)	$E_{\rm pc}$ (V)	E _{HOMO} (eV) ^c	E _{LUMO} (eV) ^d	$E_g^{CV}(eV)^e$
OBA-O	0.35 ^{<i>a</i>} ,0.49 ^{<i>a</i>}	-2.49 ^b	-5.15	-2.31	2.84
OBA-S	0.34 ^{<i>a</i>}	-2.52 ^b	-5.14	-2.28	2.86
OBA-BrO	0.33 ^{<i>a</i>}	-2.37 ^b	-5.13	-2.43	2.70
OBA-BrS	0.32 ^{<i>a</i>}	-2.46 ^b	-5.12	-2.34	2.78

^{*a*} Reversible. The value was set as $E_{1/2}$. ^{*b*} Irreversible. The value was derived from the cathodic peak potential. ^{*c*} $E_{HOMO} = -(4.8 + E_{pa})$ eV. ^{*d*} $E_{LUMO} = -(4.8 + E_{1,pc})$ eV, $E_{1,pc}^1$: First reduction potential. ^{*e*} CV energy gap $E_g^{cv} = LUMO - HOMO$.

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Electroluminescent ability

Inspired by the blue emission and high PLQY of these asymmetric OBA-based emitters, their doped OLEDs had been constructed with device configuration of ITO/ HATCN (5 nm)/ TAPC (40 nm)/x-wt% Emitter : mCP (20 nm)/ TmPyPB (40 nm)/ LiF (1 nm)/ Al (100 nm) (Figure 5). Considering practical application, well-known functional materials have been employed to make the devices. Dipyrazino[2,3-f:2',3'h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN) and di-[4-(*N*,*N*-ditolylamino)phenyl]cyclohexan (TAPC) serve as hole injector and hole transporter. 1,3-Bis(carbazol-9-yl)benzene is the host material. 1,3,5-Tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) has been employed to serve the function of both hole-blocking and electron-transporting, while LiF and Al are used as the electron injection layer (EIL) and cathode, respectively.

When adding a proper driving voltage to the OLEDs, EL emission can be recorded (Figure 6). The EL spectra (Figure 6) of the optimized OLEDs exhibit great resemblance to the PL spectra of the involved OBA-based TADF emitters with bathochromic effect. From the energy diagram involved in these OLEDs, these asymmetric OBA-based TADF emitters should be mainly excited by energy-transfer from mCP host to the TADF guests. The current density-voltage-luminance (*J-V-L*) curves and efficiency-luminance relationship of the devices are shown in Figures 7, 8 and ESI (Figure S7, S8 and S9) respectively. The EL data are tabulated in Table 4.

Compared with the PL spectra (Table 1), the EL wavelength (Table 4) exhibits red-shift effect compared with the corresponding PL wavelength. Furthermore, magnitude of the red-shift effect is in proportion to the PL wavelength (Table 1 and 4). This result can be ascribed to the exciton stabilization effect from the polar host mCP molecules. For TADF emitter with D-A structure, the emitter with longer emission wavelength can generate excitons with higher polarity with larger dipole-moment, which can interact strongly with polar mCP molecules and hence induce much stronger exciton stabilization effect to effectively lower energy-level of the excitons. As a result, compared with analog with shorter emission wavelength, the emitter with longer emission wavelength should generate EL with much longer wavelength compared with its PL wavelength obtained in low polar toluene. Hence, larger red-shift effect from PL to the corresponding EL spectrum can be observed for the emitter with the longer emission wavelength.

With **OBA-O** as the emitter, the device **A2** emitting the bluest color of 446 nm with CIE (0.17, 0.17) can be turned on at a very low voltage of 2.7 eV. Importantly, device **A2** can achieve maximum η_{ext} of 17.8%, η_{L} of 33.2 cd A⁻¹ and η_{P} of 34.2 lm W⁻¹ with maximum luminance (L_{max}) of 6785.2 cd m⁻² at 13.2 V (Figure 8a and Table 4). The device **C2** based on **OBA-BrO** can also show attractive EL ability with η_{ext} of 22.5% and η_{L} of 49.2 cd A⁻¹ respectively (Figure 8c and Table 4). With low turn-on voltage ($V_{turn-on}$) of 2.7 V, the highest η_{P} of 56.9 lm W⁻¹ can be afforded by device **C2**. Despite of its inferior EL performances with respect to those of devices **A2** and **C2**, device **D2** based on **OBA-BrS** still show much higher EL efficiencies with η_{ext} of

9.2%, $\eta_{\rm L}$ of 20.3 cd A⁻¹ and $\eta_{\rm P}$ of 20.9 lm W⁻¹ than, device, **B2** with **OBA-S** as emitter (Figure 8 and Table 14). Obviously, devices based on **OBA-O** and **OBA-BrO** can show much higher EL efficiencies than the ones with **OBA-S** and **OBA-BrS** (Figure 8 and Table 4). This result might be ascribed to the higher PLQY for **OBA-O** (*ca.* 0.84) and **OBA-BrO** (*ca.* 0.92) than that of **OBA-S** (*ca.* 0.75) and **OBA-BrS** (*ca.* 0.55) (Table 1). All these encouraging EL data should indicate the great potential of the OBA moiety in developing highly efficient TADF emitters.



Fig. 5 Device structure of the vacuum evaporated OLEDs together with energy level diagram and molecular structures of the materials employed in the fabricated OLEDs.



Fig. 6 EL spectra for the optimized OLEDs based on these asymmetric OBA-based emitters at *ca.* 5 V.

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Fig. 7 Current density-voltage-luminance (*J-V-L*) characteristics for the optimized OLEDs based on these asymmetric OBA-based emitters.



Fig. 8 Relationship between EL efficiencies and luminance for the optimized devices. (a) Device A2, (b) Device B2, (c) Device C2 and (d) Device D2

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Table 4. EL performance of these asymmetric OBA-based TADF emitters.

Table 4. E	EL performance of these a	asymmetric	: OBA-based TADF e	emitters.			DOI: 10.1	View Article Online .039/C9TC04115J
Device	Dopant	V _{turn-on} (V)	Luminance L _{max} (cd m ⁻²) ^a	η _{ext} (%)	η _L (cd A ⁻¹)	$\eta_{ extsf{P}}$ (Im W ⁻¹)	λ_{\max} (nm) d	
A1	OBA-O (3.0 wt %)	3.1	4735.3 (13.2)	14.1 (3.1) ^a 11.7 ^b 5.8 ^c	26.2 (3.1) 22.7 10.7	27.0 (3.1) 21.2 6.6	446 (0.17, 0.17)	
A2	OBA-O (5.0 wt %)	2.7	6785.2 (13.2)	17.8 (3.1) ^a 15.5 ^b 8.5 ^c	33.2 (3.1) 28.3 16.3	34.2(3.1) 26.5 11.7	446 (0.17, 0.17)	
A3	OBA-O (7.0wt %)	3.1	4763.0 (13.6)	10.8 (3.1) ^a 5.8 ^b 2.9 ^c	20.0 (3.1) 11.3 5.4	20.6 (3.1) 9.5 3.1	446 (0.17, 0.17)	
B1	OBA-S (3.0 wt %)	3.4	3051.9 (14.6)	1.7 (3.7) <i>ª</i> 0.6 ^b 0.5 ^c	2.4 (3.4) 0.8 0.7	2.2 (3.4) 0.5 0.2	488 (0.20, 0.31)	
B2	OBA-S (5.0 wt %)	3.4	3582.6 (14.2)	4.4 (3.4) ^a 1.3 ^b 0.7 ^c	6.3 (3.4) 1.7 1.0	5.8 (3.4) 1.2 0.3	488 (0.20, 0.31)	
B3	OBA-S (7.0wt %)	3.1	3525.6 (14.2)	3.4 (3.4) ^a 0.95 ^b 0.6 ^c	4.9 (3.4) 1.4 0.8	4.5 (3.4) 0.9 0.3	488 (0.20, 0.31)	
C1	OBA-BrO (3.0 wt %)	3.1	1618.7 (11.5)	12.1 (3.1) ^a 4.1 ^b 0.8 ^c	26.4 (3.1) 9.1 1.6	27.5 (4.1) 27.1 4.3	500 (0.21, 0.38)	
C2	OBA-BrO (5.0 wt %)	2.7	1694.8 (10.2)	22.5 (2.7) ^a 12.5 ^b 3.1 ^c	49.2 (2.7) 26 7.1	56.9 (2.7) 22.5 4.3	500 (0.21, 0.38)	
С3	OBA-BrO (7.0 wt %)	2.7	1621.4 (9.2)	17.7 (2.7) <i>°</i> 10.5 ^b 2.2 ^c	38.7 (2.7) 22.5 4.8	44.8 (2.7) 18.6 2.7	500 (0.21, 0.38)	
D1	OBA-BrS (3.0 wt %)	3.1	891.6 (14.2)	7.6 (3.1) ^a 0.7 ^b	16.8 (3.1) 1.6	17.3 (3.1) 0.8	520 (0.29, 0.46)	
D2	OBA-BrS (5.0 wt %)	2.7	959.4 (14.2)	9.2 (3.1) ^a 0.8 ^b	20.3 (3.1) 1.7	20.9 (3.1) 0.9	520 (0.29, 0.46)	
D3	OBA-BrS (7.0 wt %)	2.7	908.6 (13.9)	8.2 (3.1) ^a 0.8 ^b	18.1 (3.1) 1.8	18.7 (3.1) 1.0	520 (0.29, 0.46)	

^a Maximum values of the devices. Values in the parentheses are the voltages at which they were obtained. ^b Values collected at 100 cd m². ^c

Values collected at 1000 cd m⁻². ^d Values were collected at 7 V and CIE coordinates (x, y) are showed in parentheses.

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Conclusions

Through attaching donor groups to the meta-position of 5,9dioxa-13b-boranaphtho[3,2,1-de]anthracene (OBA) unit, four novel organic TADF emitters with asymmetric configuration have been developed with the highest k_{RISC} of 8.97×10⁵ s⁻¹. It has been found that introducing –Br group to the OBA unit can enhance the TADF ability of these asymmetric OBA-based TADF emitters. Importantly, deep-blue TADF emission at 440 nm can be achieved in these asymmetric OBA-based TADF emitters with very high PLQY of ca. 0.84 in doped film. In addition, with these novel OBA-based TADF emitters, the doped OLEDs can exhibit attractive EL performances in blueemitting OLEDs with a maximum η_{ext} of 17.8%, η_{L} of 33.2 cd A⁻¹, $\eta_{\rm P}$ of 34.2 lm W⁻¹ and EL maximum 448 nm associating CIE (0.17, 0.17). In addition, the bluish green OLEDs can achieve even higher EL performances with a maximum η_{ext} of 22.5%, η_{L} of 49.2 cd A⁻¹, η_P of 56.9 lm W⁻¹. All these promising results not only provide critical information of structure-activity relationship for OBA-based emitters, but also indicate the great potential of the OBA moiety as acceptor group to develop TADF emitters with advanced EL capacity.

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Conflicts of interest

There are no conflicts to declare.

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TOC

Asymmetric thermally activated delayed fluorescence (TADF) emitters with 5,9-dioxa-13*b*boranaphtho[3,2,1-*de*]anthracene (OBA) as acceptor and highly efficient blue-emitting OLEDs †

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With 5,9-dioxa-13*b*-boranaphtho[3,2,1-*de*]anthracene (OBA) as acceptor, thermally activated delayed fluorescence (TADF) emitters adopting asymmetric configuration can achieve highly efficient blue-emitting OLEDs.

