NB-Type Electronic Asymmetric Compounds as Potential Blue-Color TADF Emitters: Steric Hindrance, Substitution Effect, and Electronic Characteristics

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Supporting Information

ABSTRACT: This article is devoted to the theoretical study of the effects of a connection pattern and stereo hindrance of different π-bridges, nitrogen-containing donors, and boron-containing acceptors on the electrooptic properties of NB-type electronic asymmetric compounds in conventional D−π−A frameworks by the density functional theory (DFT) and time-dependent DFT (TD-DFT) approaches. By introducing three different connection groups (−O−, −CH2−, and −CMε2−) and guided by structural rationality, we formed 30 NB-type molecules, which have been classified into four types: D−π−A, D−π−X1−π−A, D−π−X1−π−X2−A, and D−π−X1−π−X2−A (Xn are connection groups). Then, the energy gaps (ΔE_ST) between the first singlet and triplet excited states were evaluated by TD-LC-ωPBE with the optimal values of ω*, as well as an approximate method, which only considers the interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). It is found that for the compounds with strong vibronic coupling, the calculated ΔE_ST defined as the difference of vertical excitation energies largely deviates from the experimental result. The consistency between the estimated and experimental values indicates that ΔE_ST is predominantly determined by the frontier molecular orbitals, which can be tuned by adjusting the modular overlap between HOMO and LUMO or the orientation of the donor and acceptor groups. Accompanied with the other electronic and optical properties, our study suggests that the interaction mode, D−π−X1−π−A, the modified D−π−A system with a rigidly fixed acceptor and a relatively free donor, can serve as a valuable molecular design pattern for new blue-colored thermally activated delayed fluorescence (TADF) emitters. Specifically, our calculations predict that ARD-BZN-2CMε2-PYN and its relatives might have excellent potential as TADF emitters.

1. INTRODUCTION

Thermally activated delayed fluorescence (TADF) materials have been intensively explored as one of the most promising third-generation electrofluorescent materials for applications in modern organic light-emitting diode (OLED) devices in recent years.1−10 An OLED is a light-emitting diode (LED) in which the emissive electroluminescent layer is a film of an organic compound that emits light in response to an electric current. Since the first big breakthrough of Tang and VanSlyke in 1987,11 the materials and efficiency of OLEDs have been improved profoundly.12−15 In recent years, OLEDs have been used to create digital displays in devices such as television screens, computer monitors, and portable systems such as mobile phones, handheld game consoles, and personal digital assistants.12,16

The functioning of OLED relies on the electrofluorescence process.16 Upon electronic injection, there is a 3:1 generation of triplet and singlet excitons in OLEDs.17 Owing to the spin-forbidden effect between the triplet excited state and singlet ground state, the triplet excitons get wasted as thermal energy; thus, only a maximum of 25% internal quantum efficiency (IQE) can be expected for conventional fluorescence material-based devices. Through exploitation of the spin−orbit interaction in rare transition metal organic complexes, the IQE of phosphorescent materials can surpass the 75% statistical limit in well-tuned devices. To break the limit of the spin statistics and achieve nearly 100% IQE, scientists have proposed two approaches, one is “singlet-trapping” and the other is “triplet-trapping.”12 The singlet-trapping method utilizes phosphorescence materials (typically, organometallic compounds with heavy transition metal centers) to convert the singlet excitons to triplet excitons through efficient intersystem crossing (ISC) induced by a strong spin−orbit coupling effect,18,19 so as to emit light from the emissive triplet excited state totally.16 However, the triplet-trapping method utilizes delayed fluorescence materials (typically, organic compounds
with very low singlet–triplet energy gaps) to convert the triplet excitons to singlet excitons through efficient reverse intersystem crossing (rISC) induced by thermal activation, so as to emit light from the emissive singlet excited state. Upon careful exploitation of these methods, near 100% IQE can be achieved.30

Full color and white-light displays need efficient OLEDs that emit three basic colors (red, green, and blue).12,16 Currently, high-performance blue-light OLEDs are the final piece to pursue for industrial applications of the technology. Considering the rareness and high cost of heavy transition metal complexes, though the electronics might not be so attractive. Therefore, the design and investigation of TADF emitters with a low energy gap and high emission energy (in blue color) are still in great need for future replacement of the expensive phosphorescence emitters in high-performance OLED devices.4 Basically, two classes of TADF-emitting materials have been intensively investigated, the first one is transition metal organic complexes bearing saturated d10 configuration to diminish the possible dπ−dπ* transition quenching loss, the other is pure organic polycyclic aromatic compounds.30−24

Through building models and performing numerical simulations, researchers have found that the vibronic coupling effect, the regio- and conformational isomerization, and the dynamic nature of excited states might play important roles in determining the fitness of TADF materials.25−27 Recently, 10H-phenoinoxaborin derivatives have been designed and tested as high-efficiency blue TADF materials in OLEDs,28,29 whose frameworks can be either asymmetric D−π−A (or D−A) or symmetric D−A−A−D. It has been observed that the steric hindrance arising from the hydrogen–hydrogen (H−H) interaction, as shown in Figure 1, is vital for such NB-type molecules as TADF emitters. The term “NB-type” indicates the intrinsic structural characteristic of the compound, which is basically composed of a nitrogen-containing donor and a boron-containing acceptor interconnected by a π-bridge. Through borylation of 1,3-phenyloxybenzene, and subsequently borylation of 1,3-phenyloxybenzene, and subsequently borylation of 1,3-phenyloxybenzene, and subsequently boron-containing acceptor interconnected by a

![Figure 1. Steric hindrance arising from the H–H interaction in an NB-type system.](image)

Figure 1. Steric hindrance arising from the H–H interaction in an NB-type system.

...time-dependent DFT (TD-DFT) method.34 Through introduction of three different connection groups (−O−, −CH2−, and −CMEO2−), and guided by structural rationality, 30 NB-type molecules, as shown in Figure 2, have been constructed, which can be classified into four types: D−π−A (1−2), D−X1−π−A (3−10), D−π−X1−A (11−26), and D−X1−π−X2−A (27−30), where Xn denotes connection groups. Their singlet−triplet energy gaps, ∆EST, will be evaluated by the range-separated DFT LC-ωPBE with the optimal value of ω.35−38 On the basis of ∆E_ST, absorption/emission energies, and corresponding oscillator strengths, the possibility of utilizing NB-type electronic asymmetric compounds as potential TADF materials was evaluated.

2. THEORETICAL METHODS

The TADF process proceeds by rISC from the triplet to singlet excited states and relies on relatively small energy differences between singlet and triplet excited states. Therefore, ∆E_ST and E_S are the basic quantities used to determine the quality of the compound to be viewed as potential TADF materials. Benchmark tests on existent delayed fluorescence molecules have shown that conventional DFT XC functionals (e.g., LDA, GGA, hybrid B3LYP, etc.) typically are not suitable to predict these excited-state properties correctly and consistently. However, through a fine tune of the range separation of the DFT exchange and pure Hartree–Fock exchange under the generalized Kohn–Sham framework, DFT becomes trustable to give a reliable prediction on the excited-state properties.36−38

In these long-range-corrected (LRC) DFT functionals, the amount of exact exchange is weighted according to the interelectron distance (r_{12}) as 1 = \frac{\text{erfc}(ωr_{12})}{\text{erf}(ωr_{12})} + \frac{\text{erf}(ωr_{12})}{\text{erf}(ωr_{12})}, where erf(x) = \frac{2}{\sqrt{π}} \int_0^x \exp(-t^2) dt and erfc(x) = 1 − erf(x). For a given system, the optimal ω value can be obtained without empirical fitting by minimizing the function

$$J = |ω\text{HOMO}(ω, N) + IP(ω, N)|$$

(1)

In donor−acceptor systems, it is useful to focus not only on the ionization potential (essentially related to the donor component) but also on the electron affinity (essentially related to the acceptor component). Electron affinity (i.e., in the absence of geometry relaxation) of the N electron system can be considered as the ionization potential of the N + 1 electron system. In this context, the tuning of the ω value can be done by minimizing the following equation

$$J^2 = \sum_{i=0}^{N} [ε_{\text{HOMO}}(ω, N + i) + IP(ω, N + i)]^2$$

(2)

Here, ε_{\text{HOMO}} and IP denote the highest occupied molecular orbital (HOMO) energy and ionization potential, respectively.

In this study, we then calculated ∆E_ST and E_S by TD-DFT/6-31+G(d,p) with the optimally tuned range-separated functional, LC-ωPBE, abbreviated as LC-ω*PBE. The Tamm–Dancoff approximation (TDA) to TD-DFT was adopted. TD-LC-ω*PBE with TDA had been benchmarked to be able to give reliable prediction for ∆E_ST in organic TADF emitters.42 The root-mean-square errors can be as low as 0.10 eV; this level of accuracy is crucial for the quantitative theoretical prediction of TADF molecules. Similarly, by using the tuned range-separated LC-BLYP functional at the TDA framework, Penfold demonstrated that the special tuned...
functional can give a rather trustable prediction of singlet−triplet gaps for TDAF molecules. For the applicability of TDA in predicting such excited state properties, refer to the prominent works of Peach et al. To show how to obtain the optimal range-separation parameter, $\omega^*$, we took ARD-BZN-2O-DPB (13) as an example to tune $\omega^*$, as shown in
The barycenters of the spatial regions defined by \( \rho_+(r) \) and \( \rho_-(r) \), referred in the following as \( R_+ \) and \( R_- \), can thus be defined as

\[
R_+ = \frac{\int \rho_+(r) \, dr}{\int \rho_+(r) \, dr} = (x_+, y_+, z_+) \tag{5}
\]

\[
R_- = \frac{\int \rho_-(r) \, dr}{\int \rho_-(r) \, dr} = (x_-, y_-, z_-) \tag{6}
\]

The spatial distance between the two barycenters of density distributions can thus be used to measure the CT excitation length, \( D_{CT} \).

The ground-state geometric optimizations of all of the studied systems in the gas phase were finished at the theoretical level of B3LYP/6-311G(d,p). To calculate the adiabatic excitation energies of some selected compounds, the geometries of \( T_1 \) and \( S_1 \) are required, which were obtained at theoretical levels of UoB97X-D/6-31+G(d,p) and TD-oB97X-
D/6-31+G(d,p), respectively. Owing to the CT characters of $S_1$, the LRC-DFT XC functional, $\omega$B97X-D, should be more suitable than the conventional hybrid functional, B3LYP. In addition, for some selected compounds, we also simulated their related electrooptic properties (including the vertical absorption and emission characteristics, etc.) in the solution phase, wherein the solvent effect was taken into account by the polarizable continuum model (PCM, solvent = toluene). All of the calculations were performed within the Gaussian 09 software package.

3. RESULTS AND DISCUSSION

As stated in Section 1, the main purpose of this study is to explore how the geometric and electronic characteristics affect the electrooptic properties (tuning the energy gap and first singlet excited energy) and eventually change the appropriateness of the compounds as TADF emitters. Indeed, we observed that the connection pattern and steric hindrance greatly affect the electrooptic properties of the studied systems. Thirty NB-type molecules have been constructed through the introduction of three different connection groups (−O−, −CH−, and −CMe−).

Figure 2 shows the classification of the compounds and the correspondence between structures and names. Because the IUPAC names are tedious and inconvenient to refer to, we denote them by shorthand names and ordinal numbers. Three symbols are used to denote donors (ARD, PXZ, and DPA), three symbols for acceptors (PXB, DPB, and PYN), symbol BZN for the central benzene ring, and symbols −O−, −CH−, and −CMe− for the connection groups.

3.1. $E_{S_1}$, $E_{T_1}$, and $\Delta E_{ST}$. $E_{S_1}$, $E_{T_1}$, $\Delta E_{ST}$, and $E_{S_i}$ are the basic quantities used to evaluate the quality of combined compounds as TADF emitters. Table 1 collects these two quantities as well as the corresponding oscillator strengths ($f$). Empirically, the energy gap is related to the efficiency to convert the triplet exciton to the singlet one through rISC induced by thermal activation, so as to emit light from the emissive singlet excited state to the ground state. This obeys the Arrhenius form, that is, the smaller the energy gap, the higher the efficiency. A very large $\Delta E_{ST}$ would correspond to a rather low-efficiency rISC and hence an unacceptable internal (and external) quantum efficiency. $E_{S_i}$ can provide a good estimate of the emission color, although it is
Table 2. Calculated Dipole Moments ($\mu$), Energies of HOMO and LUMO, HOMO–LUMO Gap ($E_{\text{H}}$, $E_{\text{L}}$, and $E_{\text{gap}}$), the Modular Overlap (A) and Average Separation Distance ($\Delta r_{\text{ST}}$) between HOMO and LUMO, the Estimated Singlet–Triplet Energy Gap ($\Delta E_{\text{ST}}$ (est)), and CT Quantities ($q_{\text{CT}}$ and $D_{\text{CT}}$) Corresponding to $S_0$ $\rightarrow$ $S_1$ at $S_0$ Geometries

| system               | $\mu$ (Debye) | $E_{\text{H}}$ (eV) | $E_{\text{L}}$ (eV) | $E_{\text{gap}}$ (eV) | $A$ | $\Delta r_{\text{ST}}$ (Å) | $\Delta E_{\text{ST}}$ (est) (eV) | $q_{\text{CT}}$ (c$^-$) | $D_{\text{CT}}$ (Å) |
|----------------------|---------------|----------------------|----------------------|------------------------|-----|-----------------------------|-----------------------------|----------------------|----------------------|
| ARD-BZN-PXB (1)      | 2.20          | -6.53                | -0.80                | 5.72                   | 0.066 | 14.34                       | 0.009                       | 1.236                | 3.178                |
| PXZ-BZN-PXB (2)      | 3.48          | -6.37                | -0.79                | 5.57                   | 0.065 | 14.73                       | 0.008                       | 1.212                | 3.322                |
| DPA-2CH$_2$-BZN-PXB (3) | 0.19         | -6.53                | -0.66                | 5.78                   | 0.269 | 11.96                       | 0.174                       | 0.809                | 2.754                |
| DPA-2CMe$_2$-BZN-PXB (4) | 0.19         | -6.47                | -0.71                | 5.75                   | 0.268 | 11.94                       | 0.173                       | 0.848                | 2.524                |
| DPA-2O-BZN-PXB (5)   | 0.33          | -6.41                | -0.69                | 5.72                   | 0.273 | 11.67                       | 0.184                       | 0.770                | 2.741                |
| ARD-2CH$_2$-BZN-PXB (6) | 0.08         | -6.25                | -0.75                | 5.50                   | 0.281 | 12.17                       | 0.187                       | 0.831                | 3.037                |
| ARD-2CMe$_2$-BZN-PXB (7) | 0.09         | -6.24                | -0.74                | 5.50                   | 0.282 | 12.13                       | 0.189                       | 0.886                | 2.854                |
| ARD-2O-BZN-PXB (8)   | 0.80          | -6.08                | -0.75                | 5.33                   | 0.289 | 11.77                       | 0.204                       | 0.721                | 2.446                |
| PXZ-2CMe$_2$-BZN-PXB (9) | 1.21         | -6.09                | -0.78                | 5.31                   | 0.278 | 12.58                       | 0.177                       | 0.816                | 2.823                |
| PXZ-2O-BZN-PXB (10)  | 0.95          | -6.35                | -0.74                | 5.61                   | 0.285 | 11.74                       | 0.199                       | 0.680                | 2.235                |
| ARD-BZN-2CH$_2$-DPB (11) | 1.29         | -6.47                | -0.93                | 5.54                   | 0.104 | 12.27                       | 0.025                       | 1.285                | 3.074                |
| ARD-BZN-2CMe$_2$-DPB (12) | 1.37         | -6.45                | -0.97                | 5.48                   | 0.106 | 12.15                       | 0.027                       | 1.338                | 2.908                |
| ARD-BZN-2O- DPB (13) | 2.14          | -6.53                | -0.90                | 5.63                   | 0.099 | 12.30                       | 0.022                       | 1.235                | 3.090                |
| PXZ-BZN-2CH$_2$-DPB (14) | 2.59         | -6.38                | -0.88                | 5.51                   | 0.104 | 12.64                       | 0.025                       | 1.249                | 3.175                |
| PXZ-BZN-2CMe$_2$-DPB (15) | 2.69         | -6.29                | -0.97                | 5.32                   | 0.103 | 12.53                       | 0.024                       | 1.304                | 3.006                |
| PXZ-2O-BZN- DPB (16) | 3.48          | -6.44                | -0.84                | 5.59                   | 0.093 | 12.65                       | 0.020                       | 1.217                | 3.120                |
| ARD-BZN-3CH$_2$-PYN (17) | 1.86         | -6.45                | -0.70                | 5.76                   | 0.101 | 12.40                       | 0.024                       | 1.258                | 3.067                |
| ARD-BZN-CMe$_2$-PYN (18) | 1.80         | -6.45                | -0.72                | 5.73                   | 0.096 | 12.51                       | 0.021                       | 1.287                | 3.040                |
| ARD-BZN-2CMe$_2$-PYN (19) | 1.89         | -6.45                | -0.75                | 5.70                   | 0.105 | 12.29                       | 0.026                       | 1.307                | 2.949                |
| ARD-BZN-3CMe$_2$-PYN (20) | 1.82         | -6.45                | -0.78                | 5.67                   | 0.100 | 12.39                       | 0.023                       | 1.335                | 2.927                |
| ARD-BZN-2O-PYN (21)  | 2.99          | -6.50                | -0.70                | 5.80                   | 0.105 | 12.24                       | 0.026                       | 1.240                | 3.019                |
| PXZ-BZN-3CH$_2$-PYN (22) | 3.16         | -6.37                | -0.64                | 5.73                   | 0.094 | 12.76                       | 0.020                       | 1.234                | 3.140                |
| PXZ-BZN-CMe$_2$-PYN (23) | 3.11         | -6.37                | -0.66                | 5.70                   | 0.093 | 12.86                       | 0.019                       | 1.249                | 3.140                |
| PXZ-BZN-2CMe$_2$-PYN (24) | 3.21         | -6.29                | -0.75                | 5.54                   | 0.097 | 12.66                       | 0.021                       | 1.282                | 3.019                |
| PXZ-BZN-3CMe$_2$-PYN (25) | 3.15         | -6.29                | -0.78                | 5.51                   | 0.096 | 12.76                       | 0.021                       | 1.297                | 3.025                |
| PXZ-2O-BZN-2PYN (26)  | 4.34          | -6.41                | -0.65                | 5.76                   | 0.100 | 12.58                       | 0.023                       | 1.212                | 3.081                |
| DPA-2CMe$_2$-BZN-2O- DPB (27) | 0.10         | -6.68                | -0.65                | 6.03                   | 0.364 | 10.33                       | 0.369                       | 0.653                | 1.143                |
| DPA-2O-BZN-2O- DPB (28) | 0.69          | -6.50                | -0.72                | 5.78                   | 0.396 | 9.49                        | 0.476                       | 0.739                | 2.432                |
| ARD-2CMe$_2$-BZN-2O- DPB (29) | 0.01         | -6.34                | -0.81                | 5.53                   | 0.414 | 10.08                       | 0.490                       | 0.787                | 2.490                |
| PXZ-2O-BZN-2O- DPB (30) | 0.65          | -6.36                | -0.77                | 5.59                   | 0.432 | 9.21                        | 0.583                       | 0.660                | 2.070                |
vertical energy gaps and are closer to the experimental data. Obviously, the adiabatic and vertical $\Delta E_{ST}$ can exhibit very distinctive behaviors for different patterns. For example, for several compounds (11 and 12, 14 and 15, and 19 and 20) belonging to D–\pi–X1–A, the adiabatic gaps are larger than the corresponding vertical ones. But the sizes of the gaps are typically lower than 0.20 eV. Thus, they have a great chance to fulfill the gap requirement of TADF emitters. Compound 16 in type D–\pi–X1–A is also an experimentally verified valid TADF emitter.\(^{30}\) However, for this compound, the calculated vertical $\Delta E_{ST}$ is 0.09 eV in the gas phase, agreeing well with the experimental value of 0.06 eV, indicating that for this one-side fixed class, D–\pi–X1–A, the difference between the calculated vertical and adiabatic energy gaps is relatively small, and the vertical $\Delta E_{ST}$ seems to be a reasonable estimation of the real $\Delta E_{ST}$.

For most of the studied compounds, their first singlet excited states mainly come from the electronic transitions from HOMO to lowest unoccupied molecular orbital (LUMO) and nearby frontier MOs (see Table S3), and they possess obvious CT characters, indicated by the difference of charge densities shown in Figure 3 and the charge distribution of HOMO and LUMO shown in Figure S2. For the first two compounds, their HOMOs and LUMOs occupy distinct spatial regions and have a very small overlap. However, for these two compounds, the contribution from HOMO → LUMO + 2 transitions is also significant. Through the connection between the donor and \pi-bridge, the compounds 3–5 in the D–X1–\pi–A series display a more extensive electron distribution in the HOMOs. The compounds 11–16, 19–21, and 24–26 in the D–\pi–X1–A series differ from those in D–X1–\pi–A, in that they bear more extensive distribution in the LUMOs. The overlap region for the compounds in the D–\pi–X1–A and D–\pi–A series is smaller than that for those in the D–X1–\pi–A series.

The orbital diagram is confirmed by the values of modular overlap $\Lambda$ shown in Table 2. $\Lambda$, defined as $\Lambda = \frac{\int \psi^*_H(r)\psi_L(r)\,dr}{\int \psi^*_L(r)\psi_L(r)\,dr}$, is the overlap between HOMO and LUMO. In addition, Table 2 also shows the average separation distance between HOMO and LUMO ($\Delta r_{HL} = |r_H - r_L|$ with $r_H/L = \frac{\int \psi^*_H(r)\psi_L(r)\,dr}{\int \psi^*_L(r)\psi_L(r)\,dr}$) and the estimated energy gaps denoted by $\Delta E_{ST}(\text{est})$. On the basis of $\Lambda$ and $\Delta r_{HL}$, $\Delta E_{ST}$ can be qualitatively estimated via $\Delta E_{ST}(\text{est}) = 28.8\frac{\Lambda}{\Delta r_{HL}}$ by following Chen et al.\(^{50}\) When $\Delta r_{HL}$ is in angstrom (Å), $\Delta E_{ST}(\text{est})$ would be in eV. The estimated energy gaps and calculated vertical $\Delta E_{ST}$ by TD-DFT are pictorially compared in Figures S3 and S4. A detailed analysis about the differences between the estimated and calculated energy gaps has been given in the SI.

The CT distance ($D_{CT}$) experiences small variations across the four classes. D–\pi–A bears relatively large values of ~14.0 Å, and D–X1–\pi–X2–A holds relatively small ones (~9.0 Å). This can be understood by the difference in conjugation (planar) and the electron–sufficient (or deficient) character. The CT charge ($q_{CT}$) gives a clear contrast among the four classes. The largest values exist for D–\pi–A and D–X1–\pi–X1–A (>120°), and the others hold low values (<90°).

To summarize this subsection: $\Delta E_{ST}$ and $S_i$ exhibit different behaviors across the four classes. The compounds in the D–\pi–X1–A series consistently display rather low $\Delta E_{ST}$ values of <0.30 eV, and the energy gap can be qualitatively understood by the difference in the modular overlap between HOMO and LUMO, because $S_i$ is predominately contributed by the electronic transitions from HOMO to LUMO.

3.2. Emission Characteristic. As fluorescence materials, their emission channel from $S_1$ to $S_0$ must open according to Kasha’s rule; thus, the corresponding oscillator strength should have considerable size. In Section 3.1, the assessment of the appropriateness as the TADF emitter candidate is based on the vertical excitation energy. Although the absorption and emission spectra usually have mirror symmetry for the molecules without the structure’s flexibity, in real systems, especially in the molecules whose geometries are flexible, the vibronic coupling usually is very strong and the emissive properties can be significantly different from the absorption...
properties. In principle, the best blue-color TADF emitter candidates should be those bearing possibly the smallest energy gap and the highest excitation energy, in addition to a large-enough oscillator strength. In reality, a trade-off between $\Delta E_{\text{ST}}$ and $f$ must be adopted. Considering the criteria of $\Delta E_{\text{ST}} < 0.30$ eV, only the compounds 1–2 and 11–26 in the D–π–A and D–π–X1–A series seem to have a chance. However, as shown in Table 1, the absorption oscillator strengths corresponding to $S_0 \rightarrow S_1$ transitions for the compounds in D–π–X1–A at $S_0$ geometries are essentially zero. Here, we thus examine the emission behaviors of these systems.

The common structural character for compounds 11–26 in the D–π–X1–A series is that they have a relatively free donor (ARD or PXZ) (see Figure 2), which has been confirmed by the geometric parameters shown in Table S1. In $S_0$ dihedral angles $D1$ of the compounds in D–π–X1–A typically are $\sim 90^\circ$, whereas those in $S_1$ are $\sim 70^\circ$. The reduction of $D1$ upon photoexcitation (or possibly electric excitation) enhances the conjugation of the compounds and should play a crucial role in their emission behaviors.

Table 3 shows the emission energy and the corresponding oscillator strength. Because $S_1$ possesses a CT character, TADF emission behaviors can be a dark state. Criteria to assess TADF emitters. It has been established that the geometries are essentially zero. Here, we thus examine the emission channel for the compounds in D–π–X1–A can have comparable emission energies to those in D–π–A, and can span a large energy range. The compounds with an ARD donor typically give a higher emission energy than those with PXZ. For the compounds with the same donor and acceptor in D–π–X1–A, the effect of connection group X1 on $E_{\text{emi}}$ is small.

(a) With the same geometries, different DFT functionals give apparently different emission energies, and the variation can be larger than 1 eV. Compared with the experimental data, the conventional hybrid functional, TD-B3LYP, seems to underestimate $E_{\text{emib}}$; TD-LC-oPBE tends to overestimate $E_{\text{emi}}$, and TD-oB97X and TD-LC-oPBE produce a more reasonable $E_{\text{emi}}$.

(b) Considering the results produced by TDA-LC-oPBE as the standard, the compounds in D–π–X1–A can have comparable emission energies to those in D–π–A, and can span a large energy range. The compounds with an ARD donor typically give a higher emission energy than those with PXZ. For the compounds with the same donor and acceptor in D–π–X1–A, the effect of connection group X1 on $E_{\text{emi}}$ is small.

(c) All TD-DFT methods predict that the emission channel for the compounds in D–π–X1–A is open, except for those with the connection –O–. The compounds in D–π–X1–A (11–26) and D–π–A (1 and 2) have relatively smaller oscillator strengths compared to those in D–π–A (3–5).

The calculated $f$ values of all of the compounds in type D–π–2O–A are zero. However, it is known that compound PXZ-BZN-2O-DPB (16) does emit light.30 The discrepancy between the theory and experiment might come from the neglecting of the non-Condon effect and the exclusion of the molecular environmental effect in the theoretical calculation. In the gas phase, the compounds in D–π–2O–A have a quasiorthogonal geometry in both $S_0$ and $S_1$ (D1 is near $90^\circ$). This type of molecular symmetry usually attributes $S_1$ to be a dark state.

The rate constant ($k_{\text{TADF}}$) of TADF emission is another criterion to assess TADF emitters. It has been established that there exist various radiative and nonradiative processes for the TADF emitter after electric excitation. Moreover, currently, the theoretical calculation of all of the related processes is not feasible especially for medium- to large-sized molecular systems. Nevertheless, under certain assumptions, $k_{\text{TADF}}$ can be estimated by the following equation:

$$k_{\text{TADF}} = \frac{2 \pi e^2 n^3}{e \mu c} \frac{1}{\omega^2 + 1 + 3 \exp(\Delta E_{\text{ST}}/k_B T)}$$

where $\epsilon$ is the elementary charge, $n$ is the refractive index of the material, $m_e$ is the mass of electron, $\omega$ is the speed of light in vacuum, $k_B$ is the Boltzmann constant, and $T$ is the temperature. Because the geometries of $S_1$ and $T_1$ might be close to each other, and the $T_1$ structure can be obtained via unrestricted optimization in the triplet manifold with relatively more cost compared to that in ground-state optimization, here we use $T_1$ geometries to replace those of $S_1$ in the calculation of $k_{\text{TADF}}$. The vertical excitation energy ($E_{S_0}(T_1)$) and the corresponding oscillator strength ($f(T_1)$) based on the optimized $T_1$ geometry, in addition to the estimated rate constants of $k_{\text{TADF}}$, have been tabulated in Table 4.

Table 4. Vertical Excitation Energy $E_{S_0}(T_1)$ and Oscillator Strength $f(T_1)$ of $S_0$ for Selected Compounds in the Gas Phase at the $T_1$ Optimized Geometry

| system                  | $E_{S_0}(T_1)$ | $f(T_1)$ | $\Delta E_{\text{ST}}$ | $k_{\text{TADF}}$ |
|-------------------------|----------------|----------|-------------------------|------------------|
| ARD-BZN-2CH$_2$-DPB    | 2.81           | 0.3017   | 0.014                   | 6.1              |
| ARD-BZN-2CM$_2$-DPB    | 2.84           | 0.3040   | 0.013                   | 6.5              |
| ARD-BZN-2O-DPB         | 2.99           | 0.1303   | 0.207                   | 2.0 $\times 10^{-3}$ |
| PXZ-BZN-2CH$_2$-DPB    | 2.73           | 0.2503   | 0.084                   | 3.7 $\times 10^{-1}$ |
| PXZ-BZN-2CM$_2$-DPB    | 2.71           | 0.2564   | 0.124                   | 3.7 $\times 10^{-1}$ |
| PXZ-BZN-2O-DPB         | 2.80           | 0.1022   | 0.089                   | 1.3 $\times 10^{-1}$ |
| ARD-BZN-2CM$_2$-PYN    | 3.02           | 0.3181   | 0.013                   | 7.7              |
| ARD-BZN-3CM$_2$-PYN    | 3.02           | 0.3214   | 0.013                   | 7.8              |
| ARD-BZN-2O-PYN         | 3.05           | 0.2228   | 0.099                   | 2.3 $\times 10^{-1}$ |
| PXZ-BZN-2CM$_2$-PYN    | 2.85           | 0.2560   | 0.131                   | 6.7 $\times 10^{-2}$ |
| PXZ-BZN-3CM$_2$-PYN    | 2.85           | 0.2395   | 0.124                   | 8.6 $\times 10^{-2}$ |
| PXZ-BZN-2O-PYN         | 2.86           | 0.1543   | 0.164                   | 1.1 $\times 10^{-2}$ |

$E_{S_0}(T_1)$ of D–π–X1–A compounds can span a range from 2.71 eV (PXZ-BZN-2CM$_2$-DPB) to 3.05 eV (ARD-BZN-2O-PYN), and this characteristic is valuable in realizing the appropriate emission color in devices. We also note that the introduction of –O– groups makes the emission energy blue-shifted weakly. All compounds have large emission strengths ($f(T_1) > 0.10$). The difference in $k_{\text{TADF}}$ is large and is predominately determined by $\Delta E_{\text{ST}}$. The lifetime of some compounds can be several hundreds of $\mu$s. The D–π–X1–A series display great contrast ($f$ vs $f(T_1)$) in Tables 1 and 4, which might be associated with the geometric change between the ground and excited states (the reduction of the dihedral D1).

Electronic properties such as ionization potential and electron affinity are important experimentally measurable quantities for optoelectronic materials. For computational details of these quantities, refer to Figure S5 and related contents in SL. They are calculated at the B3LYP/6-311G(d,p) level of theory. This level should be sufficient to give quantitative predictions. To account for the trade-off between
the energy gap and oscillator strength, we have included a scatterplot between the two quantities in Figure S6, where \( \Delta E_{ST} \) is the vertical energy gap in the gas phase (from Table 1), and \( f \) is the emission oscillator strength based on the T₁ structure (partly in Table 4). Obviously, there is no simple proportionality relationship between the two quantities. In accordance with our conceptual classification of the compounds into four classes, the D−π−X1−A class located in the left-lower corner of the region (small \( \Delta E_{ST} \) and acceptable \( f \)) seems to be in a good position overcoming the trade-off.

In a typical setup of an OLED device, the emitters are doped in the emission layer with a relatively low weight ratio (\( \sim 0.10 \)). Thus, the charge transportation mobility is vital for charge equilibrium in this guest–host emission layer. Crudely, the mobility is dominated by the electron extraction potential (EEP), hole extraction potential (HEP), hole recombination energy (\( \lambda_h \), and electron recombination energy (\( \lambda_e \)). We have tabulated these quantities in Table S4.

Because the studied compounds are very similar from a structural point of view, they exhibit comparable IP(v), IP(a), HEP, EA(v), EA(a), and EEP. The variation in \( \lambda_h \) and \( \lambda_e \) is also small, and they are comparable in size. Therefore, these systems would exhibit a good charge equilibrium, which is preferable for a realistic design of the emitters. For future comparison with experimental data, the simulated UV–vis absorption spectra of selected compounds in toluene at the B3LYP/6-31+G(d,p)/PCM level of theory have been provided in Figure S7.

To summarize, these D−π−X1−A compounds are predicted to be valid blue- (or green-) color emitters, given compounds 1 and 2 as the reference. Because they also obey other requirements of TADF emitters (low \( \Delta E_{ST} \), open emission channel), they might be potential candidates for applications in OLEDs. Specifically, our calculations predict that ARD-BZN-2CMC₂-PYN and its relatives might have excellent potential as TADF emitters.

### 3.3. Tuning \( \Delta E_{ST} \) via the Frontier Orbital Overlap and Group Substitution

As described in Section 3.1, the energy gap of \( \Delta E_{ST} \) is very much dependent on the overlap and energy levels of frontier MOs. It is thus possible to tune \( \Delta E_{ST} \) through altering the orientation of the donor and acceptor and through applying the group substitution of interacting H-atoms. For example, the notable difference between S₁ geometries for the compounds in the D−X1−π−A (3−10) and D−π−X1−A (11−26) series is that the former assumes mediate-size dihedral angle D2 (\( \sim 50^\circ \)) between the acceptor and π-bridge, whereas the latter holds quasiorthogonal dihedral angle D1 (\( \sim 90^\circ \)) between the donor and π-bridge (see Table S1). This small structural change has profound impact on the electrooptic properties of the compounds as shown above. We then vary the dihedral angles D1 (or D2) to check how \( \Delta E_{ST} \) and \( \Lambda \) vary with D1 (or D2).

Figure 4 shows the dependence for representative compound 4 in the D−X1−π−A series and compounds 12 and 24 in the D−π−X1−A series. The restricted optimization was used by starting from the full-optimized geometry and fixing the dihedral angle, D1 (or D2), from 30 to 90° with a step-size of 5°. For all of the compounds, \( \Delta E_{ST} \) decreases with the increase of D2 (or D1) from 30 to 90° at apparently different speeds, suggesting that one can tune the energy gap of the compound via tuning the orientation of the donor and the acceptor. \( \Delta E_{ST} \) values of compound 4 are always larger than 0.20 eV, whereas those of the latter two compounds are lower than 0.15 eV when D1 changes from 65 to 90°. A experiences a smooth drop for all of the three compounds. It is obvious that the compounds in the D−X1−π−A and D−π−X1−A series might exhibit very different performances as TADF emitters.

Considering that compounds 1 (ARD-BZN-PXB) and 2 (PXZ-BZN-PXB) are experimentally verified valid TADF emitters, it would be valuable to further explore new structures on the basis of them being potential TADF materials. It is repeatedly experienced that the electrooptic properties (especially the energy gap, \( \Delta E_{ST} \)) are rather sensitive to the changes on the basic frameworks, for example, a single nitrogen replacement on the linking benzene bridge would profoundly shift the excitation energy and markedly change the \( \Delta E_{ST} \). In the next subsection, we restrict to examine the changes introduced by group substitution of the interacting hydrogen atoms on two compounds, where only di-substitution at the same side via F, Cl, and OMe (methoxy group) was considered. The substitution positions, -a, -b, -c, and -d, have been used to distinguish them, where -a denotes the positions of two H atoms on the donor (ARD or PXZ), -b denotes the two H...
atoms on the benzene next to the donor, -c denotes the two H atoms on the benzene next to the acceptor (PXB), -d denotes the two H atoms on the acceptor.

The calculated optical and electronic properties of substituted ARD-BZN-PXB and PXZ-BZN-PXB in the gas phase have been presented in Table 5. From the data, we observed that:

(a) The energy gap, $\Delta E_{ST}$, exhibits very different behaviors across the four substitution positions (-a, -b, -c, and -d). This behavior holds for all three substitution groups without regard to their donor or acceptor character.

(b) With regard to different positions, substitution at the -b position always gives the lowest $\Delta E_{ST}$, and substitution at the -a position generally gives the highest $\Delta E_{ST}$.

(c) Consider all -b substituted compounds, Cl substitution gives the lowest energy gap, whereas F and OMe give comparable energy gaps.

(d) The decrease in energy gaps can be mainly associated with the drop in the singlet state energy, whereas the triplet state energy seems stable under such kind of substitutions.

In short, through simple substitution of interacting H atoms on the basic frameworks (ARD-BZN-PXB and PXZ-BZN-PXB), the electrooptic properties can be appropriately tuned to fit the requirement of TADF emitters. Hence, substitution at specific positions can be a valuable strategy to optimize TADF materials when lead compounds are available.

4. CONCLUSIONS

By using the DFT and TD-DFT approaches, we have investigated the effects of the connection pattern and stereo hindrance of different π-bridges, donors, and acceptors on the electrooptic properties of four classes of NB-type compounds (D−π−A, D−X1−π−A, D−π−X1−A, and D−X1−π−X2−A). On the basis of $\Delta E_{ST}$ as well as absorption/emission energies and properties, the possibility of utilizing NB-type electronic asymmetric compounds as potential TADF materials was evaluated. The following conclusions have been made.

(1) For compounds with strong vibronic coupling, the calculated $\Delta E_{ST}$ values by TD-DFT in the gas phase largely deviate from the experimental values. To reproduce the experimental value, the photo-induced geometrical changes and the realistic molecular environments should be taken into account.

(2) Qualitatively, the energy gap is predominately determined by the frontier MO overlap and energy levels. The dependence of the energy gap across different interaction modes can be mainly attributed to the difference in modular overlap between HOMO and LUMO, because the first singlet excited states arise basically by HOMO to LUMO transitions and possess considerable intramolecular CT character.

(3) The effect of the orientation of the donor and acceptor on the energy gap, $\Delta E_{ST}$, is significant. $\Delta E_{ST}$ varies with the torsion of the structural framework and group substitution. The basic structural frameworks might determine the quality and behavior of the combined compounds, and group substitution would further modify the quality in a small manner.

(4) The reduction of the dihedral angle ($D1$) between the donor and π-bridge in D−π−X1−A molecules from $\sim$90° in $S_0$ to $\sim$70° in $S_1$ increases the mixing of localized excitation and CT excitation and thus enhances the emissive rate.

To sum up, we suggest that the interaction mode, D−π−X1−A, the modified D−π−A system with a rigidly fixed acceptor and a relatively free donor, can serve as a valuable molecular design pattern for new blue-color TADF emitters. Specifically, our calculations predict that ARD-BZN-2CMe2-PY and its relatives might have excellent potential as TADF emitters.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00514.
the LC-ω*PBE/6-31+G(d,p) method; the transition character of \( S_1 \) and \( T_1 \) for selected compounds in the gas phase; the vertical and adiabatic ionization potential and electron affinity, EEP, HEP, hole recombination energy, and electron recombination energy for selected compounds in the gas phase (PDF)

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**Notes**
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