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A New Entry to Purely Organic Thermally Activated Delayed Fluorescence Emitters Based on Pyrido[2,3-b]pyrazine–Dihydrophenazasilines Donor–Acceptor Dyad

Tsuyoshi Goya,*[a] Paola Zimmermann Crocomo*[b] Takumi Hosono,[c] Satoshi Minakata,[c] Leonardo Evaristo de Sousa,[d] Piotr de Silva,*[d] Przemyslaw Data,*[b] and Youhei Takeda*[c]

Abstract: A new family of thermally activated delayed fluorescence (TADF) emitters based on a twisted donor–acceptor (D–A) dyad scaffold comprising of dihydrophenazasiline (D) and pyrido[2,3-b]pyrazine (A) has been developed, and their properties have been investigated. Time-resolved spectroscopic analysis in matrices revealed the detailed photophysical properties of the D–A compounds. These D–A compounds serve as the emitter for organic light-emitting diodes (OLEDs), showing a moderate external quantum efficiency (EQE) up to 9% in CBP matrix. Furthermore, theoretical calculations uncovered the excited states nature of the developed TADF emitters.

Introduction

Over the last decade, organic compounds that can display thermally activated delayed fluorescence (TADF) have rapidly attracted much attention as the emitter for efficient organic light-emitting diodes (OLEDs), as they can harvest electrically generated triplet excitons and convert into the emissive singlet excitons through reverse intersystem crossing (rISC) to achieve theoretically 100% internal quantum efficiency (IQE).[1,2] In addition to OLEDs, the high capability of harvesting triplet excited states allows for diverse applications of TADF-active organic compounds, spanning from time-resolved bio-imaging[3–5] to organic photoredox catalysis.[6] Therefore, the development of new TADF organic compounds and investigation of their photophysical properties contributes to the further understanding of underlying principles and the advancement of materials science.

As our research program on the development of organic materials, we have developed a variety of photofunctional organic compounds based on a dibenzo[aux]phenazine (DBPHZ)-cored donor–acceptor–donor (D–A–D) or donor–acceptor–donor (D–A–D–A) scaffold,[7] which are featured with efficient TADF,[8,9] room-temperature phosphorescence (RTP),[10] TADF/RTP-active mechanochromism,[11,12] and hydrochromism,[13] for instance. A significant finding through the structure-relationship studies of the series of D–A type compounds includes that the photophysics of the D–A–D compounds are highly affected by the donor conformation and bridging heteroatoms on the donor units. Based on these findings, we decided to explore a new D–A system that can show TADF, by applying a much simpler system. We focused on the use of electron-deficient azaromatic scaffold in place of DBPHZ unit. Pyrido[2,3-b]pyrazine (PYPZ) unit was selected as the electron-acceptor (A), as the skeleton has multiple sp2-hybridized nitrogen atoms in the conjugated backbone and thereby guarantees the high electron-affinity. Also, the PYPZ family is readily prepared through a simple condensation protocol between 2,3-diaminopyridines and benzil derivatives. Owing to the multiple embedded N(sp2) atoms in the naphthalene skeleton, the triplet state of PYPZ is (n,n*) state.[14] Therefore, if this electron-deficient core is connected with an appropriate electron-donor (D), intramolecular charge transfer (ICT) in the exited state would occur and the CT states should become the first singlet excited state (S1). Additionally, mixing of the intrinsic (n,n*) nature of the electron-acceptor core and CT(n,n*) excited states would allow for relaxing the El-Sayed rule[15] by increasing the spin-orbit coupling (SOC) between the excited singlet and triplet states. As for donor pet, we selected dihydrophenazasiline (DHPAzSi), as DHPAzSi compounds serve as a moderate...
electron donor, due to the operation of $\sigma^{*}$(C-Si)–π hyperconjugation, thereby allowing for the 1CT state in proximity to a higher triple excitation state (T1) to undergo (reverse) intersystem crossing via T2 state. Although D–A type organic photophysical materials containing the pyrido[2,3-b]pyrazine as the acceptor have recently been developed by several groups, TADF emitters based on the pyrido[2,3-b]pyrazine-acceptor and dihydrophenazasiline donor have been unknown. Herein, we disclose the synthesis and photophysical properties of a new family of D–A type purely organic TADF emitters 1–3 (Figure 1), using the dihydrophenazasiline as the donor and pyrido[2,3-b]pyrazine as the acceptor.

**Figure 1. The chemical structures of investigated materials.**

**Results and Discussion**

**Materials Synthesis**

The synthetic routes to 1–3 are shown in Scheme 1. The 7-bromo-2,3-diphenylpyrido[2,3-b]pyrazine (4) and 10-bromo-acenaphth[1,2-b]pyrido[2,3-e]pyrazine (6) were easily prepared through the condensation between 2,3-diamino-5-bromopyrazine with benzil and phenanthrene-9,10-dione, respectively, according to the procedures in literature. D–A compounds 1–3 were synthesized in good yields through the Pd-catalyzed Buchwald–Hartwig amination of 4/6 with the corresponding DHPAZS derivative (Scheme 1, and the detailed procedures and the spectroscopic data of the products are described in the Supporting Information).

**Scheme 1. Synthesis of D–A compounds 1–3.**

**Time-Resolved Spectroscopic Analysis**

To investigate the photophysical properties of compounds 1–3, time-resolved luminescence spectroscopic analysis was conducted in a non-polar polymer matrix Zeonex® (Figure 2), and in small molecule hosts, 4,4′-bis(N-carbazolyl)-1,1′-biphenyl (CBP) (Figure S4) and tris[4-(9H-carbazolyl-9-yl)phenyl]amine (TCTA) (Figure S5). In all of the cases, compounds 1–3 exhibited emissions in two distinct time regions (Figure 2b, d, and f). The first component, decaying with a lifetime in the nanosecond time delay is the prompt fluorescence (PF) from the singlet excited state (S1), and the second components decaying in micro to millisecond time delay are the delayed emissions (Figure 2, S4, and S5). When we look at the spectra more closely, all three compounds display more resolved prompt emission in Zeonex® matrix than in CBP and TCTA, and the emission spectra in CBP and TCTA are broader at and the longer wavelength region, when compared with in Zeonex® matrix. This phenomenon should be caused by the change in nature of the lowest singlet excited state in non-polar matrix (Zeonex®), the observed emission is radiated from the locally excited state (1LE) (Figure 2a, c, and e), while in CBP and TCTA hosts, the emission comes from charge-transfer excited state (1CT) (Figure S4a, c, e, Figure S5a, c, and e).

**Figure 2. Time-resolved PL spectra and photoluminescence decay profiles (intensity vs. delay time) of 1–3 in Zeonex® matrix. The energies are estimated from to the maximum emission peaks.**

Depending on the experimental temperature, we observed the change in spectra and emission intensity in the microsecond time delay, whereas the prompt emission appeared to be unchanged. The reason why such phenomenon was observed would be that delay emission is mainly contributed from the triplet excited states. At low temperature (10 K) and millisecond time delay, the phosphorescence was observed (spectra in red), and emission intensity decreased with the rise of temperature. On the other hand, the triplet excited states are transferred to...
the singlet excited states, due to the thermal activation of reverse intersystem crossing (rISC) causing TADF emission with the rise of temperature (Figure 2). In all the cases, at room temperature, only delayed emission through TADF mechanism was observed. Specifically, the TADF emission is very intense in Zeonex® matrix with a DF/PF ratio above 3 (Table 1), which correspond to almost 100% of recycling triplet excited state. When we look closely to the transient decays, the compound 1 exhibits the fastest decay profile (lower amount of ISC/rISC cycling) which together with high DF/PF ratio resulted high triplet conversion and TADF contribution. The fusion of the adjacent two phenyl units (compound 2) enlarges the overall π-conjugation, which resulted in a slight decrease in singlet and triplet energy when compared to compound 1 (Figure 2). Also, the expansion of π-conjugation (compound 2) drastically decreases the overall photoluminescence quantum yield (Table 1). When the isopropyl groups on the Si center of the donor were replaced with phenyl groups (compound 3), additional decrease of efficiency and delayed fluorescence intensity was observed (Figure 2 and Table 1). This was mostly attributed to the steric hindrance to restrict the oscillation between the donor and acceptor moieties and thereby decrease the efficiency of intramolecular charge transfer process. The photoluminescence spectra were shifted to the lower energy region in CBP and TCTA matrix, which allows for stabilizing the CT state by more polar nature, when compared with Zeonex®. Although the CT state is stabilized, the single-triplet energy gap ΔEST appeared to be independent from CT state energy, which may be the variation in the triplet excited state (T1) energy (Table 1). Intriguingly, the rISC process decreased, and the DF/PF ratio dropped more than half of values in Zeonex® (Table 1).

### Table 1. Summary of the general photophysical properties of 1–3.

| Compound | Host | λem (nm)[a] | φPL[b] | ππ (nm)[c] | τπ (μs)[d] | DF/PF[e] | E0 [eV][g] | S1 [eV][g] | T1 [eV][g] | ΔEST [eV][g] |
|----------|------|-------------|--------|------------|------------|---------|----------|----------|----------|------------|
| Zeonex®  | 527  | 0.25        | 13.24 ± 1.18 | 9.45 ± 0.98 | 6.08       | 0.024   | 2.46     | 2.27     | 0.19     |
| 1        | CBP  | 555         | 0.34    | 25.28 ± 1.06 | 1.06 ± 0.11 | 1.57    | 0.031   | 2.24     | 2.12     | 0.12     |
|          | TCTA | 555         | 0.26    | 32.29 ± 0.57 | 2.10 ± 0.44 | 1.20    | 0.026   | 2.25     | 2.07     | 0.19     |
| Zeonex®  | 521  | 0.08        | 8.68±0.09 | 0.7 ± 0.059 | 5.16       | 0.062   | 2.37     | 2.26     | 0.11     |
| 2        | CBP  | 553         | 0.29    | 17.67±0.18  | 2.7 ± 0.24  | 1.99    | 0.033   | 2.28     | 2.05     | 0.22     |
|          | TCTA | 551         | 0.14    | 26.81±0.83  | 3.92 ± 0.32 | 1.14    | 0.037   | 2.26     | 2.05     | 0.21     |
| Zeonex®  | 507  | 0.06        | 7.27±0.32 | 6.90 ± 0.76 | 3.15       | 0.061   | 2.44     | 2.34     | 0.10     |
| 3        | CBP  | 535         | 0.20    | 11.84±0.42  | 10.92 ± 0.66 | 0.78    | 0.036   | 2.33     | 2.07     | 0.27     |
|          | TCTA | 529         | 0.10    | 32.45±1.23  | 5.20 ± 0.71 | 1.17    | 0.034   | 2.34     | 2.09     | 0.25     |

[a] The maximum wavelength of photoluminescence spectra. [b] Photoluminescence quantum yield in degassed. [c] Prompt fluorescence lifetime. [d] Delayed fluorescence lifetime. [e] The ratio of delayed fluorescence (DF) to prompt fluorescence (PF). [f] Activation energy of the triplet to singlet transfer. Error ± 0.01 eV. [g] Singlet and triplet energy in. Error ± 0.03 eV. [h] Energy splitting. Error ± 0.05 eV. All parameters were estimated at 300 K.

**OLEDs Fabrication and Characterization**

To fabricate the OLEDs using the materials 1–3, the thermal stability of the compounds was investigated by the thermogravimetric analysis (TGA, Figure S1 and S2). All the compounds have a high degradation temperature Td (5 wt% loss under N2 gas) above 300 °C in the order of 3 (405 °C) > 2 (359 °C) > 1 (338 °C), which is consistent with the number of aromatic rings included in molecule and molecular rigidity. These values implied the feasibility of the fabrication of OLED devices through vacuum thermal evaporation (VTE) technique. Furthermore, the investigation of the glass transition temperature (Tg) of emitters 1–3 with differential scanning calorimetry (DSC) revealed the relatively high Tg [1: 92 °C, 2: 110 °C, 3: 113 °C] (Figure S3), which allow for morphological stability in OLED devices. The Tg values are comparable with those of similar PYPZ-based D–A compounds.[18]

To evaluate the possible use of emitters in OLED structure, the electrochemical analysis was conducted. All compounds exhibited a reversible reduction and an irreversible oxidation process (Figure S6). The estimated ionization potential (IP)/electron affinity (EA) of 1–3 determined with the CV experiments are 5.78 eV/3.35 eV, 5.79 eV/3.44 eV, 5.88 eV/3.47 eV, respectively (Figure S6). Compounds 1 and 2 share the same donor, and the IP energy values are similar. Also, a similar situation for the EA values of compounds 2 and 3 applies, where they share the same acceptor unit. These facts imply that the D–A systems in all the compounds are highly twisted and the HOMO and LUMO is distinctly separated to allow for small ΔEST values.

To evaluate the possibility of the use of the developed compounds as TADF-OLED emitters, devices were fabricated through co-evaporation technique (for the details, see the Supporting Information). The fabricated device structures are as follows: Devices 1–3 ITO/NPB [N,N-di(1-naphthyl)-N,N-diphenyl-(1,1'-biphenyl)-4,4'-diamine] (40 nm)/TSBPA [4,4’-(diphenylsilyl)bis(N,N-diphenyl)aniline] (10 nm)/10%, 1, 2 or 3 in CBP (30 nm)/TPBi [2,2’,2’’-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)] (50 nm)/LiF (1 nm)/Al (100 nm); Devices 4–6 ITO/NPB (40 nm)/TAPC [4,4’-cyclohexyldiethynebis(N,N-bis(4-methylphenyl)benzenamine)] (10 nm)/10%, 1, 2 or 3 in TCTA (30 nm)/TPBi [2,2’,2’’-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)] (50 nm)/LiF (1 nm)/Al (100 nm) (Figure 3). All fabricated devices present a low turn-on voltage between 2.0 V and 3.0 V (Figure 3a). There is significant influence of the donor
unit: compounds 1 and 2 formed much more efficient devices than 3 (Figure 3b). The highest external quantum efficiency (EQE) was achieved with device 1, which is fabricated with compound 1 in CBP host (EQE = 9.09%, Figure 3b). Those results are associated with photophysical results, where compound 1 exhibited the highest TADF contribution and photoluminescence quantum yield in comparison to the other compounds. The structural change in the acceptor unit did not affect EQE that much (device 2, Figure 3b) in CBP host. Nevertheless, in TCTA, there is twice decrease in efficiency for more π-conjugated acceptor derivative (compound 2, devices 4,5) when compared to compound 1. In contrast, the change in the Si-substituents on the donor connected to acenaphtho[1,2-b]pyrido[2,3-e]pyrazine acceptor (compound 3) significantly decreased the EQE (3.68%, Device 3, 6 Figure 3b) in both of the host. The highest luminance was observed in device 4 fabricated with compound 1 in TCTA host, up to 42,000 cd m⁻² (Figure 3c and d). Change of the acceptor unit in compound 1 (compound 2) resulted in the decrease of the luminance to 15,000 cd m⁻² (Device 5, Figure 3c and d), and change of the donor (compound 3) decreased down to 7,700 cd m⁻² (device 6, Figure 3c and d).

![Figure 3](image-url)

**Figure 3.** The characteristics of the OLED devices. a) Current-density-bias characteristics. b) EQE-current density characteristics. c) Luminance-current density characteristics. d) EQE-luminance characteristics.

**Theoretical Calculations**

Electronic structure calculations allow us to understand further the mechanisms responsible for the observed photophysical behavior. Here we employ density functional theory (DFT) with the long-range corrected functional LC-uPBE along with the 6-31G(d,p) basis set. The long-range separation parameter of the functional was tuned for all molecules according to the procedure described in reference, and the results are shown in Table S1. Excited state calculations employed the Tamm-Dancoff approximation (TDA) which avoids issues of triplet instability and has been shown to be appropriate for spectrum simulations. Solvent effects were accounted for by means of the polarizable continuum model (PCM) associated with a perturbative state specific solvent approach using parameters for toluene. Finally, spectrum simulations and all rate estimates were calculated using the nuclear ensemble approach as implemented in the NEMO software. A total of 500 geometries were sampled for each case and the QChem 5.0 software was used throughout.

We started our computational analysis by investigating conformational preferences for the three compounds. For this purpose, we performed geometry optimizations at the ground (S₀), S₁ and T₁ states using as initial geometries structures for which the donor and acceptor fragments are orthogonal and parallel to each other. We identified these two arrangements as the equatorial and axial conformations, respectively. Our results show that in the ground state, the equatorial conformation is more stable than the axial one for all compounds (Table S2–S4). However, the energy difference between the two conformers is low, such that the calculation of Boltzmann populations at 300 K indicates that axial conformers are expected to represent 36%, 25% and 38% of the total for compounds 1, 2, and 3, respectively (Table S2–S4). In the excited states, however, the picture is different. As seen in Tables S2–S4, the three compounds show overwhelming preference for the equatorial conformation in the S₁ state, where the donor and the acceptor are almost perpendicular. In the equatorial conformation, the S₁ state displays distinct charge transfer (CT) character from the donor to the acceptor (see NTOs in Figure 4), which is further stabilized under solvation. On the other hand, the T₁ state is more stable in the axial conformation, with the exception of compound 1, whose T₁ state is energetically lower in the equatorial conformation (Table S2–S4).

Once conformational preferences have been established, we moved on to predicting the photophysics of the three compounds. Fluorescence spectrum simulations can be seen in Figure S7, which show considerable overlap in the spectra of the three compounds. However, peak position shifts from 660 nm for compound 1 to 625 nm for compound 2 and 547 nm for compound 3. These are qualitatively in good agreement with the experimental results. Estimated fluorescence rates are rather low, ranging from 1.4 × 10⁶ s⁻¹ for compound 3 to 4.6 × 10⁶ s⁻¹ for compound 2 (detailed values and error estimates can be found in Table S5). These low values result from the strong CT character of their S₁ states, as transitions from CT states are known to display low oscillator strengths. Yet, these fluorescence rates still outcompete the phosphorescence rates from the triplet excited states, T₁ and T₂ (Table S6), which is in good agreement with the fact that only TADF was observed in matrices (Figure 2).

To determine the dynamics of excited states in these compounds, in addition to estimating fluorescence rates, we calculated intersystem crossing (ISC) rates using S₁ as the initial state. These estimates are shown in Table S7, and the data revealed that, for all the compounds, ISC rates can be significantly higher than fluorescence rates. By calculating the ratio between the rates of each process and the sum of ISC and fluorescence rates, we may estimate the probability of each individual process taking place. For compounds 1 and 2, the highest probabilities are associated with ISC transfers from S₁ to T₁ and T₂, with T₂ being the most probable one. For compound 3, however, ISC rates from S₁ to T₁ are much lower than that for T₂.
which is by far the preferred outcome. Prompt emission in the
three compounds, in contrast, is expected in less than 1% of
cases as a result of the weakly allowed S1 CT transitions. Given
the significant TADF emission in matrices, the triplet recycling
through ISC and rISC is very efficient for these molecules.

ISC transfers to triplet states above T2 also display
significant probability (ranging from 10% to 20%, Figure S9). As
such, it is worth looking into the energy gaps between the
different triplet states, as internal conversion between these
states is expected to be the preferred mechanism of relaxation.
Table S10 shows the average gap between triplet states
calculated from the 500 geometries sampled for use by the
nuclear ensemble method. It can be seen that the average gaps
between triplet states above T2 are between 0.2 and 0.3 eV. In
contrast, T2-T1 gaps range from 0.4 to 0.5 eV. These results
suggest that molecules that undergo ISC to T3 or higher triplets
are likely to suffer internal conversion back to the T2 state,
whereas the high T2-T1 gap may prevent efficient internal
conversion back to T1. This means that it is necessary to
analyze ISC and phosphorescence rates from both T1 and T2
states.

The estimation of rates for reverse ISC (rISC) from the T1
state to S0 states are shown in Tables S8. We focused on
compounds 1 and 2, that as mentioned above, are expected to
have the T1 state populated by means of ISC from S1. Comparing these two molecules, we observed that compound 1
shows orders of magnitude higher rISC (Table S8) than compound 2. This difference can be attributed to the fact that the
T1 state is more stable in the equatorial conformation for
compound 1, whereas it is more stable in the axial conformation
for compound 2. One key difference between these two
conformations that accounts for the difference in rates is that
reorganization energies for T1 to S1 transfers in the axial
conformation are much higher (~0.50 eV) than in the equatorial
one (~0.25 eV). On the other hand, phosphorescence energies
for the three compounds do not differ so significantly (ranging
from 670 nm to 725 nm) and the T1 phosphorescence spectra
(shown in Figure S8) show strong overlap. In addition to the
difference in rates, T1 states in compounds 1 and 2 have
different expected behaviors as well. In the case of compound 1,
rISC transfers to S1 dominate, whereas for compound 2 there is
an almost even split between phosphorescence and rISC. However, since the rates in question are very low, the T1 states in
compound 2 are good candidates for non-radiative deexcitation.

Finally, we turned to the estimation of rISC rates from the
T2 state. These can be seen in Tables S9. The rISC rates from
T2 to S0 states are larger than those from T1 for all three
compounds, but the rISC rates from T2 to S1 are much larger
than other transitions and are expected to be the dominant
mechanism of T2 depopulation followed by TADF pathway.
As such, following the previous discussion, we expect a continuous
interconversion between S1 and T2 states (also T1 in the case of
compounds 1 and 2) followed by delayed emission (TADF) from
the S1 state (Figure 4). The low fluorescence rates combined
with this continuous interconversion of triplets and singlets also
provide many opportunities for non-radiative decay other than
TADF channel, from which we expect to observe low
luminescence quantum yields for all three compounds. This
would be the reason why these molecules show moderate TADF
efficiency. In terms of emission wavelength, T2 phosphorescence spectrum simulations (shown in Figure S9)
differ significantly among the three compounds, with emission
peaks being evaluated at 548 nm, 484 nm and 596 nm for
compounds 1, 2 and 3, respectively.

Figure 4 summarizes the calculation results discussed
above by showing the most relevant mechanisms expected to
take place for each of the 3 compounds, namely ISC from S1 to
T1 and T2 followed by rISC back to S1 from where delayed
emission is observed. For compound 3, a similar mechanism is
presented, with the exception that ISC from S1 to T1 is expected
to be much less efficient than ISC from S1 to T2. As such, only
rISC from T2 collaborates to the repopulation of singlet states
and the consequent delayed emission.

Conclusion

In summary, we have successfully developed a new family of
TADF emitters, utilizing the D–A scaffold comprising of
polyyazaaromatics, i.e., pyrido[2,3-b]pyrazines, and dihydrophenazasilines as the donor. The time-resolve spectroscopic analysis revealed that these compounds show TADF in matrices. Furthermore, the OLEDs fabricated with developed D–A molecules achieved a high external quantum efficiency (EQE) up to 9%, exceeding the theoretical maximum of those fabricated with prompt fluorescence emitters (5%). Furthermore, theoretical calculations revealed the importance of the high triplet excited state (T₃) as the intermediate of efficient rISC process to yield TADF within the D–A scaffold.

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A new family of twisted donor–acceptor type thermally activated delayed fluorescence (TADF) emitters comprising of pyrido[2,3-b]pyrazine as the acceptor and dihydrophenazasilines as the donor has been developed. The organic light-emitting diodes fabricated the developed emitters achieved a high external quantum efficiency up to 9%. Theoretical calculations implied the intermediacy of a high triplet excited state for efficient TADF.

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