Supporting information

Decisive Role of Heavy-Atom Orientation for Efficient Enhancement of Spin-Orbit Coupling in Organic Thermally Activated Delayed Fluorescence Emitters

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Table of contents

Section S1: Photophysical measurements
Section S2: Quantum chemical calculations
Section S3: NMR spectra of target emitters
Section S4 Determination of photophysical parameters
Section S1: Photophysical measurements

Steady-State PL (6% CBP)

A

Normalized PL Intensity

Wavelength [nm]

600 700 800 900

Steady-State PL (10% CBP)

C

Normalized PL Intensity

Wavelength [nm]

500 600 700 800 900

Phosphorescence (6% CBP)

B

Normalized PL Intensity

Wavelength [nm]

500 600 700 800 900

Phosphorescence (10% CBP)

D

Normalized PL Intensity

Wavelength [nm]

500 600 700 800 900

Steady-State PL (6% CBP)

E

Normalized PL Intensity

Wavelength [nm]

450 500 550 600 650 700 750 800 850 900

Phosphorescence (6% CBP)

F

Normalized PL Intensity

Wavelength [nm]

450 500 550 600 650 700 750 800 850 900
**Figure S1.** Steady-State PL spectra of investigated compounds: 6% (A, E) and 10% (C) CBP with onsets and phosphorescence spectra measured in 10K, 6% (B, F) and 10% (D) CBP.

**Table S1.** Experimental determination of $^1$CT, $^3$CT and $^3$LE - onset values.

| w\textsubscript{X/CBP} | Fluorescence | Phosphorescence | Phosphorescence |
|-------------------------|--------------|----------------|-----------------|
|                         | $\lambda$\textsubscript{onset} | $^1$CT energy | $\lambda$\textsubscript{onset} | $^3$CT energy | $\Delta E_{^{1}\text{CT}$-$^{3}$CT} | $\lambda$\textsubscript{onset} | $^3$LE energy | $\Delta E_{^{1}$CT-$^{3}$LE} |
| ZNX 0.1%                | [nm]         | [eV]           | [nm]            | [eV]           | [eV] | [nm]         | [eV] | [eV]          |
| H 6%                    | 597          | 2.07           | 608             | 2.04           | 0.04 | 552          | 2.25 | -0.18         |
| H 10%                   | 600          | 2.07           | 609             | 2.04           | 0.03 | 552          | 2.25 | -0.07         |
| 1Br 6%                  | 569          | 2.18           | 589             | 2.10           | 0.08 | 552          | 2.25 | 0.00          |
| 1Br 10%                 | 579          | 2.14           | 595             | 2.08           | 0.06 | 552          | 2.25 | 0.00          |
| 2Br 6%                  | 552          | 2.25           | 585             | 2.12           | 0.13 | 552          | 2.25 | 0.00          |
| 2Br 10%                 | 560          | 2.21           | 585             | 2.11           | 0.10 | 552          | 2.25 | 0.13          |
| 3Br 6%                  | 521          | 2.37           | 571             | 2.17           | 0.20 | 552          | 2.25 | 0.13          |
| 3Br 10%                 | 527          | 2.35           | 575             | 2.16           | 0.19 | 552          | 2.25 | 0.13          |

**Figure S2.** Phosphorescence spectra of investigated compounds dispersed in ZNX, measured in 10K under excitation wavelength $\lambda_{\text{exc}} = 370$ nm with a 20ms delay after excitation pulse.
Figure S3. PL spectra of H (A), 1Br (B), 2Br (C), and 3Br (D) in 6% CBP, taken at different time delays.

Figure S4. PL intensity decays of investigated compounds (10% CBP) measured in vacuum under excitation wavelength $\lambda_{exc} = 330$ nm.
Section S2: Quantum chemical calculations

Theoretical rate constants of rISC were calculated using Marcus-Hush equation:

\[ k_{(r)ISC} = \frac{V^2}{\hbar} \sqrt{\frac{\pi}{k_B T \lambda}} \exp \left[ \frac{(\Delta E_{ST} + \lambda)^2}{4k_B T \lambda} \right], \]  

(S1)

where \( V \) is SOC constant, \( \hbar \) is reduced Planck constant, \( \lambda \) is sum of internal \( \lambda_{int} \) and external \( \lambda_{solv} \) reorganization energies for respective transition (in our calculations we assumed \( \lambda_{solv} = 0.3 \text{ eV} \) \( \Delta E_{ST} \) is the energy gap between singlet and respective triplet state, \( k_B \) stands for Boltzmann constant, \( T \) is temperature.

Relative contribution of \( i \)-th rotamers in \( \text{H, 1Br, 2Br and 3Br} \)-rotamers was calculated using Boltzmann distribution law:

\[ \mu_i[\%] = \frac{\exp \left( -\frac{\Delta E_i}{k_B T} \right)}{\sum_{i=1}^{N} \exp \left( -\frac{\Delta E_i}{k_B T} \right)}. \]  

(S2)

where \( N \) is the number of existing isomers (for \( \text{H, 1Br 2Br and 3Br} \)-rotamers \( N = 2, 16, 16 \) and 32, respectively), \( \Delta E_i \) denotes the energy difference between \( i \)-th rotamer and most stable rotamer (with lowest energy). Procedure for theoretical prediction rate constants described in details in [1].
Figure S5. Calculated electronic parameters of all H, 1Br and 2Br – rotamers. In main text, key rotamers (depicted in Figure 5, Table 3) from each group: H-rotamers: 1 (as H-1) and 2 (as H-2); 1Br-rotamers: 3 (as 1Br-endo) and 12 (as 1Br-exo); 2Br-rotamers: 5 (as 2Br-syn) and 9 (as 2Br-anti).
Calculated electronic parameters of all 3Br rotamers. In main text, key rotamers (depicted in Figure 5, Table 3) from 3Br-rotamers group: 32 (as 3Br-C$_{3v}$), 17 (as 3Br-A), 21 (as 3Br-A), 12 (as 3Br-B), 1 (as 3Br-C).
Table S2. Calculated values of different geometry (dihedrals $\theta_a$, $\theta_b$, and $\theta_h$) and electronic parameters (plotted in Figures S5 and S6) of all rotamers.

|        | 1     | 2     | $\chi^\circ$ |        | 1     | 2     | $\chi^\circ$ |        | 1     | 2     | $\chi^\circ$ |        |
|--------|-------|-------|--------------|--------|-------|-------|--------------|--------|-------|-------|--------------|--------|
| $\theta_a$ (\degree) | 0.05  | 0.08  | 0.06         |        | 0.05  | 0.08  | 0.06         |        | 0.05  | 0.08  | 0.06         |        |
| $\Delta f_{\text{ET-CT}}$ (eV) |        |        | 0.03         | 0.03   | 0.03  | 0.03   | 0.03         | 0.03   | 0.03  | 0.03  | 0.03         | 0.03   |
| $\epsilon_f$ (eV) | 0.10  | 0.11  | 0.109        | 0.109  | 0.109 | 0.109 | 0.109        | 0.109  | 0.109 | 0.109 | 0.109        | 0.109  |
| $\theta_h$ (\degree) | 0.18  | 0.17  | --           |        | 0.18  | 0.17  | --           |        | 0.18  | 0.17  | --           |        |
| $\sigma_{\text{S2}}$ | 67.2  | 52.8  | --           |        | 67.2  | 52.8  | --           |        | 67.2  | 52.8  | --           |        |
| $k_{\text{ISC}}$ (10^5 s^{-1}) |        |        | 0.16         | 0.30   | 0.20  |        | 0.16         | 0.30   | 0.20  |        | 0.16         | 0.30   |

- $\theta$ - rotation angles
- $\Delta f_{\text{ET-CT}}$ (eV) - Energy gap between $C^\prime$ and $C^\prime$ excited states
- $\epsilon_f$ (eV) - Oscillator strength
- $E_a$ (eV) - Activation energy
- $\mu$ [%] - Relative contribution estimated using Boltzmann distribution law - equation S2
- $k_{\text{ISC}}$ (10^5 s^{-1}) - Calculated rate constant for $C^\prime\rightarrow C^\prime$ transition
- $\theta_a$, $\theta_b$, $\theta_h$ - dihedral angles (Figure 3)
Calculations of the $^{3}\text{LE}\rightarrow^{1}\text{CT}$ rate constants. To verify whether $^{3}\text{LE}\rightarrow^{1}\text{CT}$ channel has an impact on rISC, we performed theoretical calculations of its rate constants ($k_{3\text{LE}-1\text{CT}}$) using Marcus-Hush equation (S1) and experimental $\Delta E_{3\text{LE}-1\text{CT}}$ values. Since we consider two triplet states from which rISC is potentially possible, at first, we estimated relative population of these levels using Boltzmann distribution law:

$$\chi_i[\%] = \frac{\exp\left(-\frac{\Delta E_i}{k_BT}\right)}{\sum_{i=1}^{N}\exp\left(-\frac{\Delta E_i}{k_BT}\right)},$$  \hspace{1cm} (S3)

where $\Delta E_i$ denotes the energy difference between lowest triplet state ($T_1$) and respective triplet state ($T_i$):

$$\Delta E_i = (T_i - T_1),$$  \hspace{1cm} (S4)

$$a_i = \exp\left(-\frac{(T_i - T_1)}{k_BT}\right).$$  \hspace{1cm} (S5)

Table S3. Theoretical constant rates $k_{3\text{LE}-1\text{CT}}$ with determined population of lowest triplet excited states of emitters.

| Alignment of triplet excited states: | CBP 10% |
|-------------------------------------|---------|
| $T_2 = ^{3}\text{LE(A)}$          |         |
| $T_1 = ^{3}\text{CT}$             |         |
| $^{3}\text{LE(A)}$                | $^{3}\text{CT}$ |

| $T_1$ | $T_2$ | $\Delta E_{T_2-T_1}$ | $a_1$ | $a_2$ | $\chi_{3\text{LE}(A)}$ | $\chi_{3\text{CT}}$ | $k_{3\text{LE}-1\text{CT}}$ | $\chi_{3\text{LE}(A)} k_{3\text{LE}-1\text{CT}}$ |
| [eV]  | [eV]  | [eV]                 |       |       | [%]                   | [%]               | [10^4 s^{-1}]    | [10^4 s^{-1}]    |
|-------|-------|----------------------|-------|-------|-----------------------|-------------------|------------------|------------------|
| H     | 2.03  | 2.25                 | 0.22  | 1     | 0.0003                | 0.03              | 99.97           | 186.2           | 0.04             |
| 1Br   | 2.08  | 2.25                 | 0.17  | 1     | 0.0018                | 0.18              | 99.82           | 24.4            | 0.03             |
| 2Br   | 2.11  | 2.25                 | 0.14  | 1     | 0.0070                | 0.70              | 99.30           | 1.1             | 0.01             |
| 3Br   | 2.16  | 2.25                 | 0.09  | 1     | 0.0281                | 2.92              | 97.08           | 3.8             | 0.10             |

From the results included in Table S3, it can be seen, that population of triplet states is strongly dominated by $^{3}\text{CT}$ state due to large difference in energies between $^{3}\text{CT}$ and $^{3}\text{LE}$ levels.

Next, values of $k_{3\text{LE}-1\text{CT}}$ for each emitter were calculated just as $k_{3\text{CT}-1\text{CT}}$, taking into account population of $^{3}\text{LE}$ state $\chi_{3\text{LE}(A)}$. Results are presented in Table S3 and Figure 4.

Since theoretical predictions of rISC constant rates based on exclusively $^{3}\text{LE}-^{1}\text{CT}$ channel did not showed a good correlation with experimental values, we conclude that $^{3}\text{LE}-^{1}\text{CT}$ channel has not considerable impact on rISC in most of the cases except for the rotamers with very low rates of $^{3}\text{CT}-^{1}\text{CT}$ transition as 2Br-anti ones.
Figure S7. Differences in the orbital transition moment of H rotamers. *note that contour value is 0.01 (high)

Figure S8. Natural transition orbitals for the S1-S0 and T1-S0 transitions for selected H, 1Br and 2Br rotamers. NTO indicate almost negligible role of bromine atoms in the electronic transitions.
Figure S9. Natural transition orbitals for the $S_1$-$S_0$ and $T_1$-$S_0$ transitions for selected 3Br rotamers. NTO indicate almost negligible role of bromine atoms in the electronic transitions.
Figure S10. Triplet spin density distribution (TSDD) maps
Section S3: NMR spectra of target emitters

$^1$H NMR spectrum of 3-((4-((2-bromo-4-methylphenyl)(p-tolyl)amino)phenyl)-dibenzo[a,c]phenazine-11,12-dicarbonitrile (1Br) in CDCl$_3$
$^1$H NMR spectrum of 3-(4-(bis(2-bromo-4-methylphenyl)amino)phenyl)dibenzo[$a,c$] phenazine-11,12-dicarbonitrile (2Br) in CDCl$_3$. 
$^1$H NMR spectrum of 3-((4-(bis(2-bromo-4-methylphenyl)amino)phenyl)dibenzo [$a,c$]phenazine-11,12-dicarbonitrile (3Br) in CDCl$_3$. 

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S15
$^1$H NMR spectrum of 3-(4-(bis(2-bromo-4-methylphenyl)amino)phenyl)phenanthrene-9,10-dione (2) in CDCl$_3$. 

$^1$H NMR spectrum of 3-(4-(bis(2-bromo-4-methylphenyl)amino)-3-bromophenyl)-phenanthrene-9,10-dione (3) in CDCl$_3$
Section S4: Determination of photophysical parameters

PL decay curves (presented in Figures 2F and S4) were fitted with the multiexponential equation:

\[ I(t) = A_0 + \sum_{i=1}^{n} A_i \exp\left(-\frac{t}{\tau_i}\right) \quad \text{(S6)} \]

where \(A_i\) is the pre-exponential factor, \(\tau_i\) is the decay time and \(I(t)\) is emission intensity. Average lifetimes of prompt (\(\tau_{PF}\)) and delayed fluorescence (\(\tau_{DF}\)) were determined using the following formula:

\[ \tau_{PF}, \tau_{DF} = \sum_{i=1}^{n} f_i \tau_i \quad \text{(S7)} \]

where \(f_i\) is fractional contribution of \(i\)-th component expressed as:

\[ f_i = \frac{A_i \tau_i}{\sum_{i=1}^{n} A_i \tau_i} \quad \text{(S8)} \]

The ratio of DF and PF quantum yields \(\varphi_{DF}/\varphi_{PF}\) was determined as follows:

\[ \frac{\varphi_{DF}}{\varphi_{PF}} = \frac{\sum_{i=1}^{n} \tau_{DF(i)} A_{DF(i)}}{\sum_{j=1}^{n} \tau_{PF(j)} A_{PF(j)}} \quad \text{(S9)} \]

where \(A_{DF(i)}\) and \(A_{PF(j)}\) is the pre-exponential factor of delayed and prompt fluorescence component, respectively; \(\tau_{DF(i)}\) and \(\tau_{PF(j)}\) is the lifetime of delayed and prompt fluorescence component, respectively. The rate constants of radiative (\(k_r\)) and nonradiative (\(k_{nr}\)) decay and intersystem crossing (\(k_{ISC}\)) are given by equations[S2]:

\[ k_r = \frac{\varphi_{PF}}{\tau_{PF}}, \quad \text{(S10)} \]

\[ k_{ISC} = \frac{\varphi_{DF}}{\varphi_{PF} \tau_{PF}}, \quad \text{(S11)} \]

\[ k_{nr} = \frac{1}{\tau_{PF}} - (k_r + k_{ISC}). \quad \text{(S12)} \]

where \(\varphi\) is PLQY (\(\varphi_{DF} + \varphi_{PF}\)). Further, the quantum yields for ISC and rISC were calculated as

\[ \varphi_{ISC} = k_{ISC} \tau_{PF}, \quad \text{(S13)} \]
\[ \varphi_{\text{rISC}} = \frac{1 - \varphi_{PF}/\varphi}{\varphi_{ISC}}. \] \hspace{1cm} \text{(S14)}

Finally, the rate constant of rISC \((k_{\text{rISC}})\) was calculated as

\[ k_{\text{rISC}} = \frac{\varphi_{\text{rISC}}}{\tau_{DF}} \left( \frac{\varphi}{\varphi_{PF}} \right). \] \hspace{1cm} \text{(S15)}

Thus obtained photophysical parameters are presented in Table 2 (main text).

References

[S1] M. Mońka, I. E. Serdiuk, K. Kozakiewicz, E. Hoffman, J. Szumilas, A. Kubicki, S. Y. Park and P. Bojarski, Mater. Chem. C. 2022, 10, 7925-7934.

[S2] Tao, Y.; Yuan, K.; Chen, T.; Xu, P.; Li, H.; Chen, R.; Zheng, C.; Zhang, L.; Huang, W. Thermally Activated Delayed Fluorescence Materials Towards the Breakthrough of Organoelectronics. Adv. Mater. 2015, 26, 7931 – 7958.