SUPPORTING INFORMATION

Pursuing the Holy Grail of Thermally Activated Delayed Fluorescence Emitters: A

Molecular Strategy for Reducing Energy Gap and Enhancing Spin-Orbit Coupling

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Determination of the photophysical constants

The parameters of photophysical processes were determined using equations outlined in the literature.^{S1,S2} PL decay curves were fitted with the multiexponential equation:

$$I(t) = A_0 + \sum_{i=1}^{n} A_i exp\left(-\frac{t}{\tau_i}\right),$$
(S1)

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

$$\tau_{PF, DF} = \sum_{i=1}^{n} f_i \tau_{i'}$$
(S2)

where f_{i} is fractional contribution of *i*-th component expressed as:

$$f_i = \frac{A_i \tau_i}{\sum_{i=1}^n A_i \tau_i}.$$
(S3)

The ratio of DF and PF quantum yields $\varphi_{DF}/\varphi_{PF}$ was determined as following:

$$\frac{\varphi_{DF}}{\varphi_{PF}} = \frac{A_{DF}\tau_{DF}}{A_{PF}\tau_{PF}},\tag{S4}$$

where ${}^{A_{DF}}$ and ${}^{A_{PF}}$ are pre-exponential factors of delayed and prompt fluorescence, respectively. Rate constants of radiative $({}^{k_{r}})$ and nonradiative $({}^{k_{nr}})$ decay and intersystem crossing $({}^{k_{ISC}})$ were given by equations:

$$k_r = \frac{\varphi_{PF}}{\tau_{PF}},\tag{S5}$$

$$k_{ISC} = \frac{\varphi_{DF}}{\varphi \tau_{PF}},\tag{S6}$$

$$k_{nr} = \frac{1}{\tau_{PF}} - \left(k_r + k_{ISC}\right),\tag{S7}$$

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

$$\varphi_{ISC} = k_{ISC} \tau_{PF}, \tag{S8}$$

$$\varphi_{rISC} = \frac{1 - \varphi_{PF}/\varphi}{\varphi_{ISC}}.$$
(S9)

Finally, rate constant for rISC (k_{rISC}) was calculated as

$$k_{rISC} = \frac{\varphi_{rISC}}{\tau_{DF}} \left(\frac{\varphi}{\varphi_{PF}} \right).$$
(S10)

Additional results of spectroscopic investigations



Figure S1. Dependence of the absorption maxima on ortho-Hammet constants.^{S3}



Figure S2. PL spectra in ZNX films at RT on air: (A) emission spectra and (B) excitation spectra.

Figure S3 presents the comparison of emission spectra of ZNX and DPEPO films doped with varying concentrations of DMAC-Cl-DPStB. The PL maximum gradually red-shifts with increasing concentration. DPEPO, being a more polar medium, provides further red-shifted PL_{max} compared to ZNX.



Figure S3. Emission spectra of DMAC-Cl-DPStB in different hosts and varying concentrations.

Experimental estimation of E_a and SOC values using Arrhenius and Marcus-Hush theories

The analysis of PL decays in the 298 – 140 K range (Fig. 3 and Fig. S4, S5, SI) enabled calculation of k_{rISC} constant rates at various temperatures in ZNX and DPEPO films. To determine the energy barriers E_a for rISC, the Arrhenius law equation was applied:

$$k_{rISC} = A \cdot \exp\left(-\frac{E_a}{k_{\rm B}T}\right),\tag{S11}$$

where k_B stands for Boltzmann constant, T - temperature and A is pre-exponential constant. In order to estimate SOC values, the Marcus-Hush equation was used:

$$k_{rISC} = \frac{V^2}{\hbar} \sqrt{\frac{\pi}{k_B T \lambda}} exp \left[-\frac{\left(\Delta E_{ST} + \lambda\right)^2}{4k_B T \lambda} \right],$$
(S12)

where *V* is SOC constant, \hbar is reduced Planck's constant, λ is reorganization energy for respective transition, ΔE_{ST} is the energy gap between singlet and triplet state. This semiclassical expression is connected with the Arrhenius equation (S1) by the following relations:

$$A = \frac{V^2}{\hbar} \sqrt{\frac{\pi}{k_{\rm B} T \lambda}},\tag{S13}$$

$$E_a = \frac{\left(\Delta E_{ST} + \lambda\right)^2}{4\lambda}.$$
(S14)

Consequently, by matching the ΔE_{ST} and λ parameters to satisfy both relations, where E_a and A are derived from Arrhenius plot, it was possible to estimate empirical SOC values V for each transition, as it is presented in Table S1.

Table S1. Values of activation energies and spin-orbit coupling constants determined using experiential $k_{rISC}(T)$ dependences.

Cmpd	Ea	[eV]	SOC [cm ⁻¹]				
	ZNX	DPEPO	ZNX	DPEPO			
Н	0.082	0.079	0.13	0.29			
F	0.070	0.022	0.18	0.07			
Cl	0.061	0.031	0.28	0.14			

Analysis of time resolved emission spectra (TRES). In an attempt to analyze the interplay of S_1 and T_1 states, TRES were measured at 10K (Fig. S3). In the PF regime in both media, fluorescence spectra show gradual bathochromic shift caused by different rate of emission of various θ -rotamers.^{S4} Exclusively, DMAC-H-DPStB in both media shows red-shifted emission at the millisecond regime which can be attributed to phosphorescence (Fig. S3A and B). TRES of DMAC-F-DPStB measured with a 10 ms delay are identical to the late PF (in the ZNX film, Fig. S3C) or show slight blue shift (in the DPEPO film, Fig. S3D). Very similar behavior is observed for Cl and Br derivatives (Fig. S3E-H), but most of their delayed emission appears faster – within tens of microseconds up to few milliseconds most likely due to increased SOC. This data does not allow to distinguish either long-lifetime emission is the delayed fluorescence or phosphorescence. However, it evidences the vanishing difference between S₁ and T₁ states under the introduction of a halogen substituent.

DMAC-Cl-DPStB, which presents the highest contribution of the second, 385 nm band, in ZNX shows some vibronic structure of millisecond emission (Fig. S3E), which can be explained by the contribution of phosphorescence of the bent-DMAC isomer.^{S5}



Figure S4. Time-resolved emission spectra in ZNX and DPEPO films at 10 K.



Figure S5. PL decay curves in DPEPO film 10% at various temperatures: (A) DMAC-H-DPS, (B) DMAC-Cl-DPS, (C) DMAC-F-DPS. Respective photophysical parameters are given below.

Compound	<i>T</i> [K]	τ _{PF} [ns]	τ _{DF} [μs]	k _{ISC} [10 ⁶ s ⁻¹]	$k_{ m rISC}$ [10 ⁴ s ⁻¹]
DMAC-H- DPStB	140 180 200 260	14.4 14.1 14.1 14.1	205.4 92.1 61.1 23.3	38.6 40.2 40.5 40.1	1.1 2.6 3.8 12.2
DMAC-F- DPStB	140 180 200 260	20.4 20.3 20.2 20.2	19.4 14.5 12.5 9.7	34.8 32.1 33.6 31.2	16.1 21.8 24.8 33.8
DMAC-Cl- DPStB	140 180 200 260	14.1 14.2 14.3 13.4	19.1 13.2 9.4 4.6	54.5 54.3 51.6 51.5	22.2 32.8 40.1 70.2



Figure S6. PL decay curves in ZNX films 0.5% at different temperatures: (A) DMAC-H-DPS, (B) DMAC-Cl-DPS, (C) DMAC-F-DPS. Respective photophysical parameters are placed below.

Compound	<i>T</i> [K]	τ _{PF} [ns]	τ _{DF} [μs]	k _{ISC} [10 ⁶ s ⁻¹]	k _{rISC} [10 ⁴ s ⁻¹]
DMAC-H- DPStB	160 210 240 270	12.5 11.2 10.7 10.7	1048.6 364.4 212.8 93.4	41.6 55.8 55.1 53.1	0.19 0.73 1.1 2.3
DMAC-F- DPStB	160 210 240 270	19.8 19.8 19.8 19.2	296.4 77.8 68.2 31.7	32.7 32.2 32.2 34.4	0.96 3.6 4.1 9.2
DMAC-Cl- DPStB	160 210 240 270	12.9 12.9 12.9 12.5	56.4 21.3 11.9 8.8	50.1 54.1 51.0 50.1	5.1 15.6 24.7 33.0

TD-DFT/B3LYP/LanL2DZ level of theory



Figure S7. Distribution of energy gap between pure ³CT and ¹CT states



Molecular orbitals in optimized geometries

T₂ state* *red circles indicate electronic desnity on a halogen



Figure S8. Molecular orbitals involved in the formation of S_1 , T_1 , and T_2 states; level of theory: B3LYP/def2-SVP.

Additional details on molecular modeling procedures and results within the dynamic



approach

Figure S9. CT numbers of the T_1 state in the modeled nuclear ensemble. Level of theory M06-2X/Def2-SVP.

Electronic structure calculations. DFT geometry optimizations were carried out using the Turbomole 7.7 package. The conformational space of the T_1 state was explored by optimizing geometries at the PBE0-D3BJ/def2-SVP level of theory. For all compounds, two distinct low-energy minima were identified. The first one is a conventional twisted intramolecular charge transfer (TICT) structure, where the two linked groups are twisted relative to each other. The second minimum corresponds to a bent structure, in which the second phenyl ring of the DPS forms weak interaction with the DMAC moiety.

The calculated reorganization energies for the three compounds are 0.267 eV, 0.269 eV, 0.217 eV, and 0.224 eV for R = H, F, Cl, and Br, respectively. Although the smallest reorganization energy for DMAC-Cl-DPStB favors faster rISC, numerical tests reveal that

variations in reorganization energy are not the dominant factor driving the trends, considering that λ values are relatively similar for all compounds. These values were obtained for optimal geometries and were used for calculations of rISC rates of whole ensemble.



Twisted (left) and bent (right) T_1 structures of DMAC-F-DPStB, as optimized with PBE0-D3BJ/Def2-SVP in vacuum.

Bent Conformers and Their Role in High-Energy Emission. T₁ minima for twisted and bent structures are approximately isoenergetic (energy difference in vacuum 0.1 eV or smaller, in moderately polar DCM solvent below 0.04 eV). Nevertheless, the bent conformer exhibits distinct photophysical properties. The rISC rates for the bent conformers are significantly lower compared to the twisted conformers due to the larger ΔE_{ST} gaps. For example, the calculated rates are 2.7×10^3 s⁻¹ for DMAC-H-DPStB, 4.8×10^4 s⁻¹ for DMAC-F-DPStB, and 4.4×10^4 s⁻¹ for DMAC-Cl-DPStB, which are at least an order of magnitude lower than those of the twisted conformers. The primary factor limiting rISC in bent conformers is the consistently larger ΔE_{ST} gaps (Fig. S9A), which never approach values close to zero, unlike the twisted structures. Despite their smaller degree of charge separation (bent conformers exhibit a weaker CT character in both the S₁ and T₁), which enhances SOC to some extent (Fig. 9B), these do not compensate for the unfavorable S-T gap distribution. Finally, the calculated reorganization energies (based on TDDFT M06-2X-D3/Def2-SVP optimizations) are 0.296 eV, 0.268 eV and 0.235 eV for H, F and Cl substituents, respectively.

While the theory suggests that both conformers coexist across various environments, the bent conformer likely appears in trace amounts in experiments. The presence of the bent conformer provides a plausible explanation for the high-energy vibronic band observed in DMAC-Cl-DPStB in ZNX films. This low-intensity emission band, centered at 375 nm, is absent in other emitters and nearly vanishes in DPEPO films (Fig. 2B, main text). Time-resolved emission spectroscopy confirms that this band is associated with fast (<5 ns) emission from the bent conformer (Fig. S3, SI). Excitation spectra further support this assignment, showing distinct behavior from the dominant 460 nm band of the twisted conformer (Fig. S2, SI).

Notably, the bent conformer appears TADF inactive due to its inefficiency in facilitating rISC. This conclusion aligns with its low rISC rates and large ΔE_{ST} gaps from computational analysis. The experimental evidence, including the temperature-dependent appearance of the high-energy band and its vibronic structure, corroborates the computational findings. The coexistence of the bent conformer in trace amounts highlights its limited but noticeable influence on the photophysical behavior of DMAC-Cl-DPStB in specific environments, such as the ZNX host matrix.

In summary, the bent conformer provides a non-TADF emission channel characterized by high-energy, short-lived luminescence. This feature is prominent in DMAC-Cl-DPStB due to its steric and electronic properties but is largely suppressed in other emitters or alternative host environments. These findings underscore the importance of host selection and molecular conformation in controlling emission properties, particularly for halogen-substituted blue emitters.



Figure S10. Results of molecular modeling calculations for bent isomers: distribution of ΔE_{ST} (**A**), and SOCME (**B**) of the S₁-T₁ transitions; calculated for T₁ geometry at the M06-2X/Def2-SVP level of theory.

Table S2. Representative natural transition orbitals for the electrnic transitions within three groups of conformations found within the modeled molecular ensemble.

	Norn	nal group	Mixed	group	Inverted group			
	HONTO	LUNTO	HONTO	LUNTO	HONTO	LUNTO		
S ₁								
T ₁								
T ₂								



Figure S11. Structures (top and side views) and the analysis of linker ring conformations (red lines and histogram of valence angle deviations) of several molecular geometries within the Normal (N), Mixed (M), and Inverted (I) groups (Table S2).

Spectral properties in liquid solutions

To obtain gradual change of PL_{max} and E_{S1} , solvatochromic investigations were performed for DMAC-H-DPStB, DMAC-F-DPStB, and DMAC-Cl-DPStB in various solvents under room temperature: hexane, toluene-hexane 1/3 (ν/ν) mixture, toluene, chlorobenzene, dichloromethane (DCM), 1,2-dichloroethane (DCE), and dimethylsulfoxide (DMSO). For this reason set of solvents differs slightly for each emitter. The obtained spctra, emission dcay curves, rate constants and their dependencs are given below (Fig. S10, S11, S12, and Table S3)



Figure S12. Steady-state PL spectra of (A) DMAC-H-DPStB, (B) DMAC-F-DPStB, and (C) DMAC-Cl-DPStB in various solutions.



Figure S13. PL intensity decay curves in (A) toluene and (B) DCM.



Figure S14. The dependencies of the natural logarithm of k_r (A) and k_{ISC} (B) on the energy of S₁ state (E_{S1}) in solutions. The dependence of $\ln(k_{rISC})$ (C) on k_r in solutions with different polarity. Linear regression parameters for all above mentioned dependencies are presented in Table S2.

Compound	Parameter	Figure 5	Fig. S10 A	Fig. S10 B	Fig. S10 C
name		$\ln k_{rISC}$ vs. E_{SI}	$\ln k_r$ vs. E_{SI}	$\ln k_{\rm ISC}$ vs. E_{SI}	$\ln k_{rISC}$ vs. k_{r}
DMAC-H-	Slope	-3.88 ± 0.34	3.26 ± 0.35	-3.69 ± 0.26	-1.47 ± 0.15
DPStB	Intercept	25.75 ± 0.99	6.05 ± 1.02	27.99 ± 0.77	23.22 ± 1.25
	R-Square	0.97	0.96	0.98	0.96
	(COD)				
DMAC-F-	Slope	-5.36 ± 0.27	1.38 ± 0.21	-4.55 ± 0.61	-4.49 ± 0.79
DPStB	Intercept	30.71 ± 0.75	11.74 ± 0.61	30.19 ± 1.74	17.87 ± 0.49
	R-Square	0.99	0.91	0.92	0.91

Table S3. Linear regression parameters for each plot on Figures 5 (main text) and S10 (SI).

	(COD)				
DMAC-Cl-	Slope	-6.06 ± 0.59	3.3 ± 0.3	-1.38 ± 0.19	-2.71 ± 0.19
DPStB	Intercept	32.19 ± 1.67	6.34 ± 1.02	21.7 ± 0.5	17.33 ± 0.12
	R-Square	0.97	0.95	0.92	0.99
	(COD)				

Table S4. Selected spectral and photophysical parameters of DMAC-H-DPStB, DMAC-F-DPStB, and DMAC-Cl-DPStB in toluene and DCM solutions.

Compound	$\lambda_{\rm abs}$ [nm]	PL _{max} [nm]	PL.	E_{S1}	PLQY [%]	τ _{PF} [ns]	τ _{DF} [μs]	k _r	<i>k</i> _{nr}	$k_{\rm ISC}$ s ⁻¹]	k _{rISC}
			[nm / eV]						L- •	- 1	
Toluene											
DMAC-H-	362	456	406	3.05	30	20	1.2	1.1	2.6	1.3	0.113
DPStB											
DMAC-F-									1.50		0.115
DPStB	365	476	419	2.96	26	23	1.9	0.5	1.50	2.3	0.115
DMAC-Cl-	275	481	125	2 02					17		0.35
DPStB	3/5	401	423	2.92	32	13	0.84	0.8	1./	5.0	0.55
					DCM						
DMAC-H-	255	510	128	2 82	40	21	1 /	0.5	0.7	2.5	0.20
DPStB	333	510	430	2.05	40	21	1.4	0.5	0.7	5.5	0.29
DMAC-F-	262								0.040	5.0	0.5
DPStB	363	525	440	2.82	36	20	0.78	0.02	0.040	5.0	0.5
DMAC-Cl-	272								15		0.85
DPStB	372	521	450	2.76	25	14	0.43	0.5	1.5	5.3	0.85

¹H-NMR spectra of target emitters





DMAC-F-DPStB



DMAC-Cl-DPStB



DMAC-Br-DPStB











¹³C-NMR spectra







DMAC-F-DPStB











DMAC-Br-DPStB



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HRMS spectra



DMAC-H-DPStB



DMAC-F-DPStB



DMAC-Cl-DPStB



DMAC-Br-DPStB

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