Supplementary Information (SI) for Journal of Materials Chemistry C.

SUPPORTING INFORMATION

Experimental evidences of the excited-state mixing in the blue emitter for organic light emitting diodes

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Contents

Section 1. Determination of photophysical parameters

The parameters of photophysical processes were calculated using equations described in the literature[S1,S2].

PL decay curves showed in Figure 4 (main text) were fitted with the multiexponential equation:

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

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:

$$\tau_{PF,\ DF} = \sum_{i=1}^{n} f_i \tau_i, \tag{S2}$$

where $f_i$is fractional contribution of i-th component expressed as:

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

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:

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

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

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

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

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

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

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

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

Thus obtained photophysical parameters are presented in **Table 1,** main text.

Section 2. Additional spectroscopic data

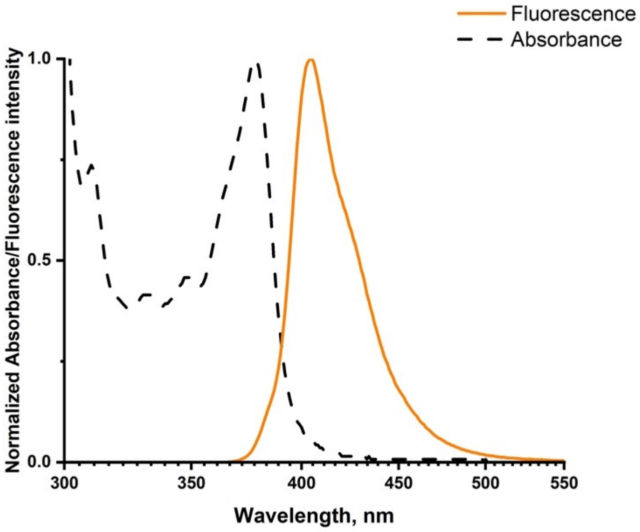

Figure S1. Absorbance and fluorescence spectra of TMCz-BO in methylcyclohexane (MCH) solution.

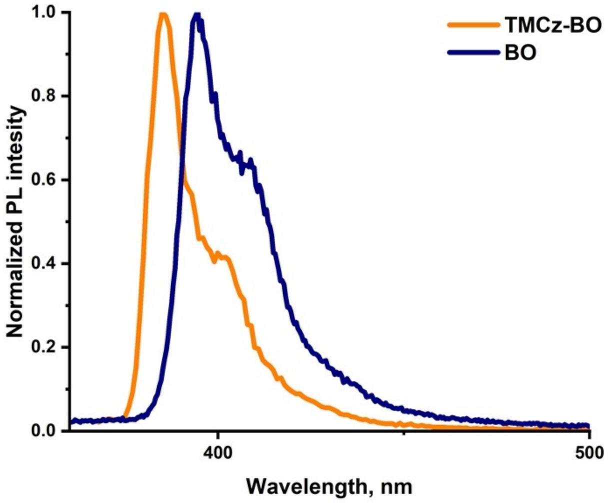

Figure S2. Fluorescence spectra of **TMCz-BO** and acceptor fragment **BO** in MCH solution at room temperature

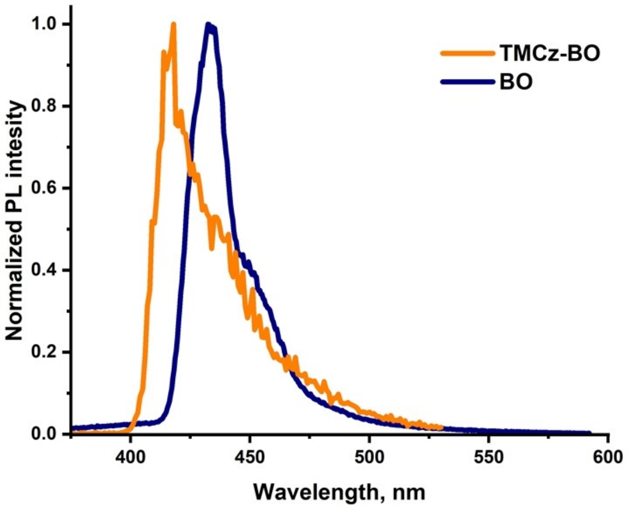

Figure S3. Phosphorescence spectra of **TMCz-BO** and the acceptor molecule **BO** in MCH frozen glass at 77K.

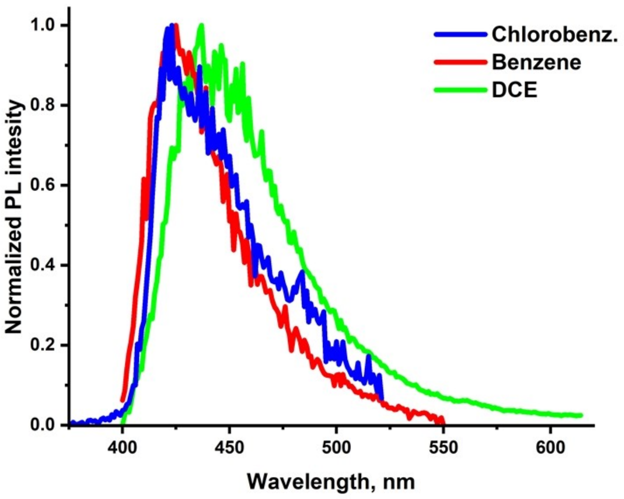

Figure S4. Phosphorescence spectra of TMCz-BO in chlorobenzene, benzene and DCE frozen solutions at 77K

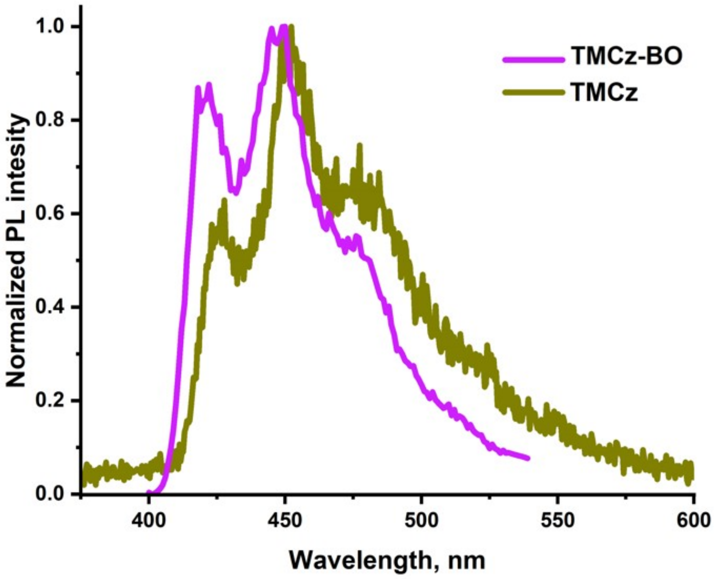

Figure S5. Phosphorescence spectra of **TMCz-BO** in frozen DMSO and the TMCz donor at 77K.

Table S1. Linear regression parameters for the fitted linear dependencies Figure 3, main text.

Parameter	**Plot B** lnk_r vs. E_{S1}	**Plot D** lnk_{rISC} vs. E_{S1}	**Plot C** lnk_{ISC} vs. E_{S1}	**Plot E** lnk_{rISC} vs. k_r	**Plot F** k_{ISC} vs. k_r
Slope	2.65 ± 0.34	-1.16 ± 0.09	-4.14 ± 0.87	-0.72 ± 0.07	-1.76 ± 0.27
Intercept	7.91 ± 1.01	18.34 ± 0.26	28.03 ± 2.59	15.45 ± 0.06	21.84 ± 2.16
R^2	0.953	0.984	0.882	0.97	0.933

Section 3. Computational determination of the nature of excited states

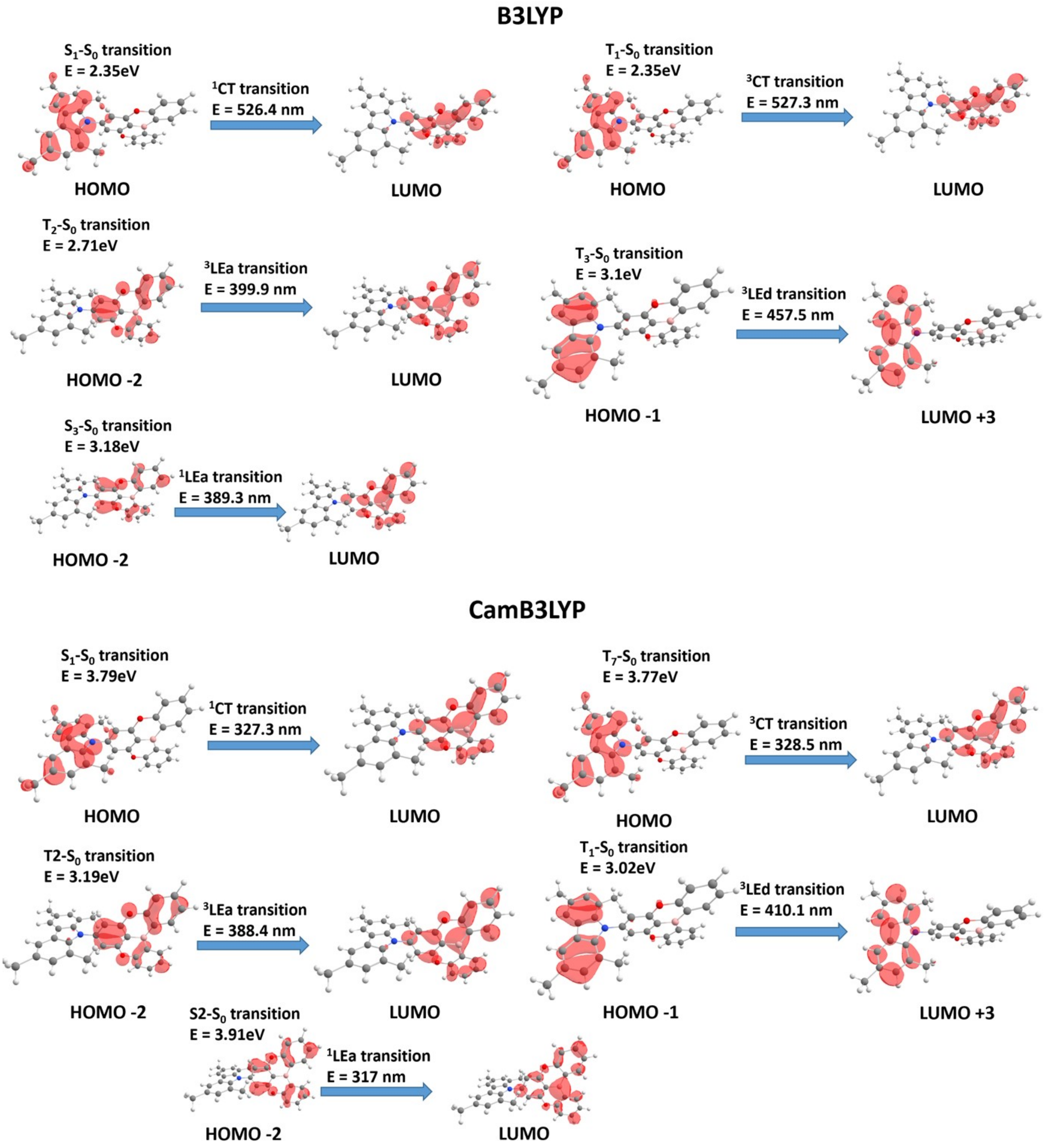

Figure S6. Profiles of molecular orbitals calculated using various levels of theory; for clarity only one sign of wave function is shown.

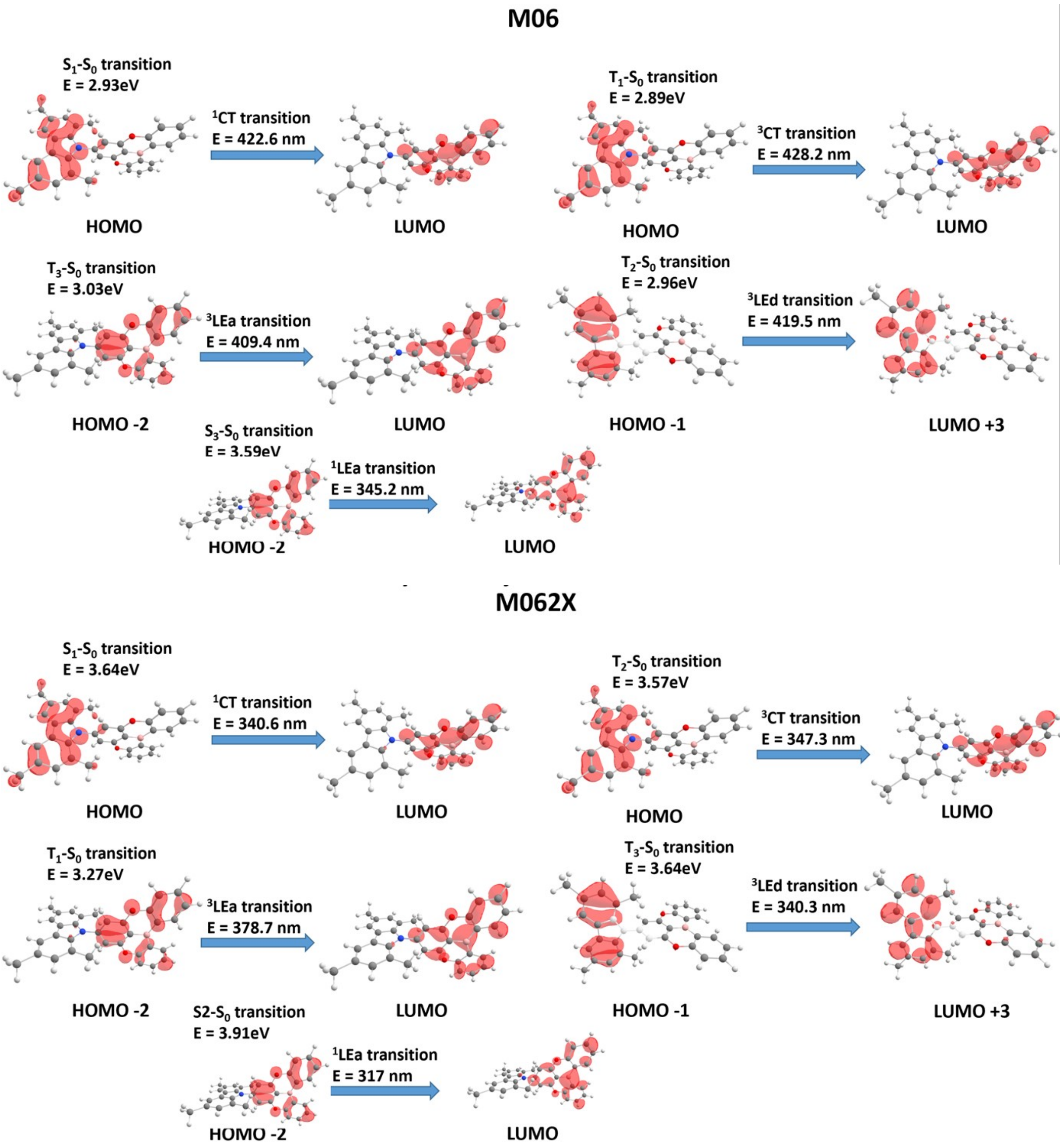

Figure S6. continued

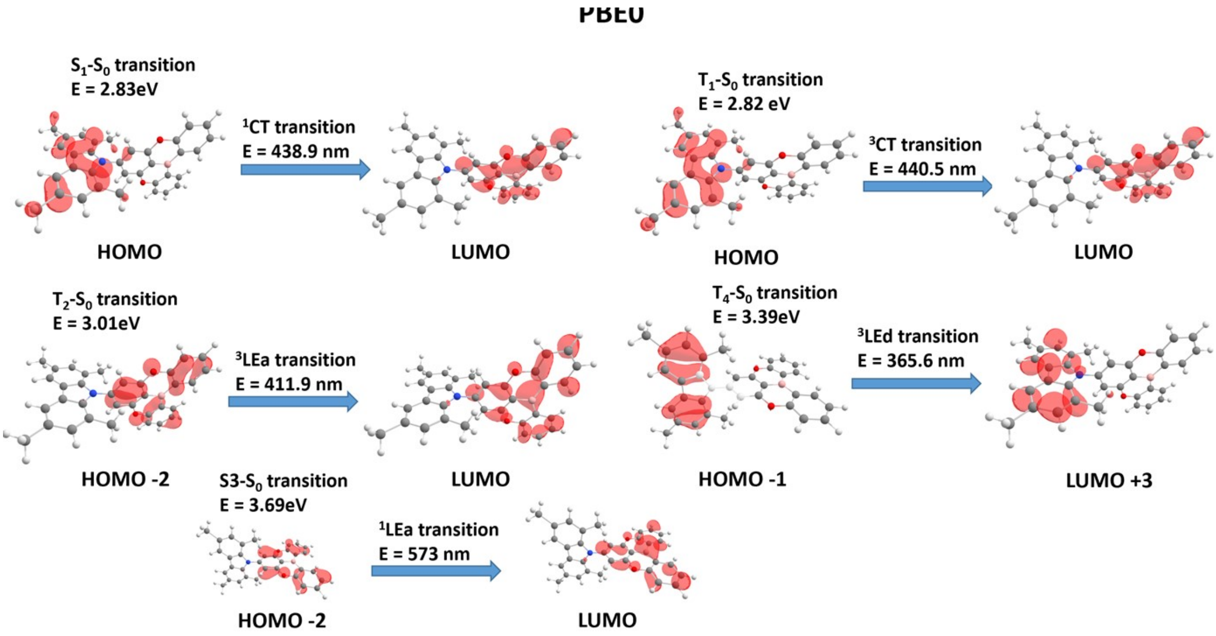

Figure S6. continued

Section 4. Time-resolved emission spectra

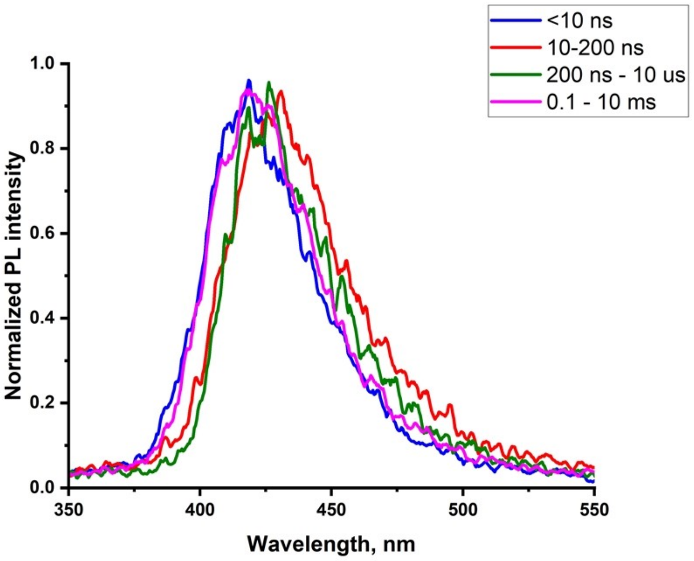

Figure S7. TRES of TMCz-BO in ZNX film (0.1%, *w/w*) at RT, vacuum.

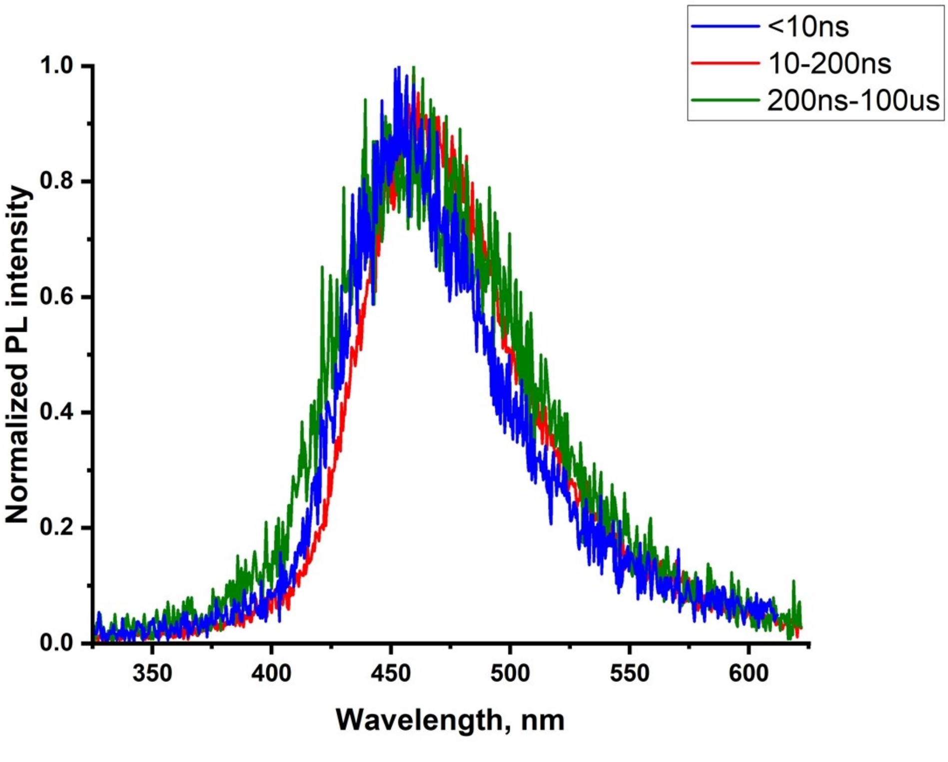

Figure S8. TRES of TMCz-BO in DPEPO film (10%, *w/w*) at RT, vacuum

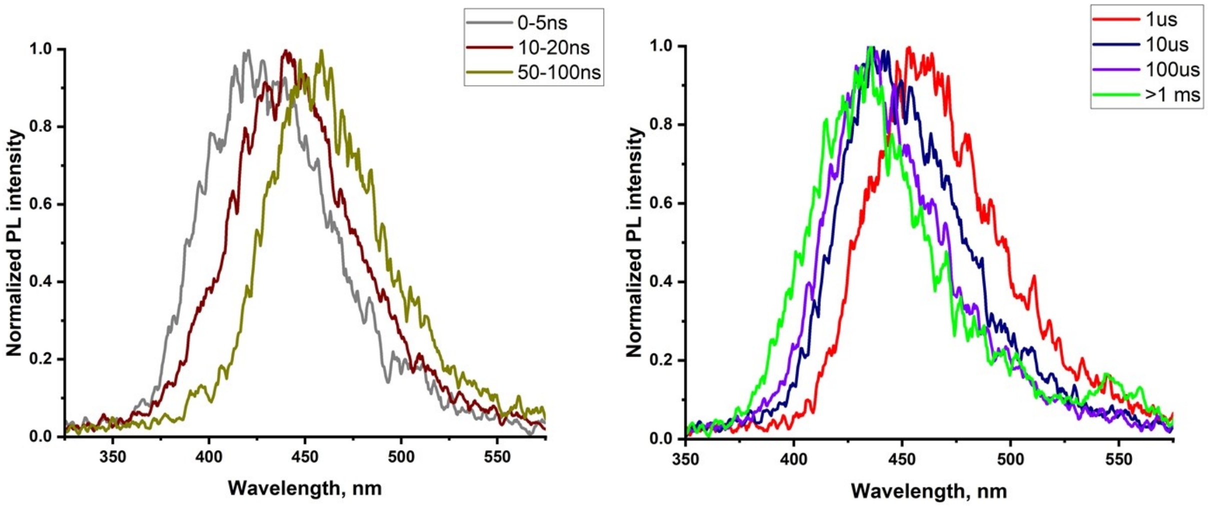

Figure S9. TRES of TMCz-BO in PMMA film (0.1%, *w/w*) at RT, vacuum.

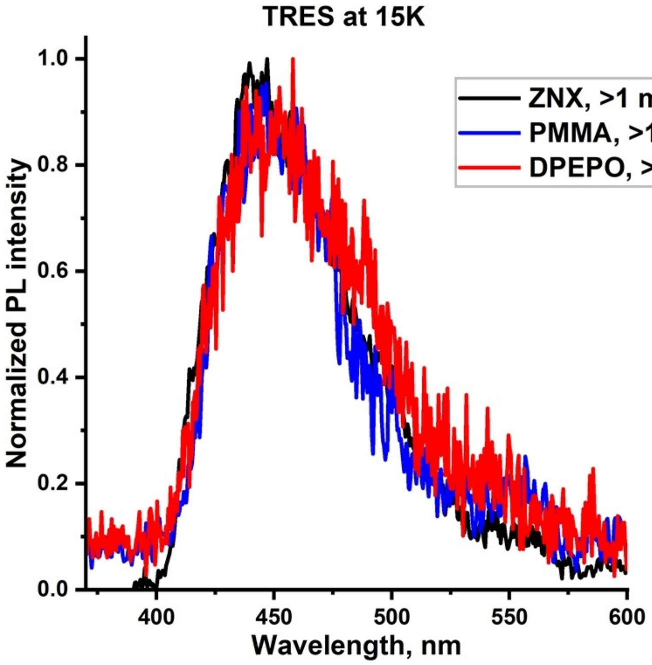

Figure S10. PL spectra of TMCz-BO in doped films at 15 K with a delay time of 1 ms.

Comparison of TMCz-BO spectra in the MCH solvent and ZNX host

Table S2. Full-width at half-maximum (FWHM) values in MCH solution and ZNX film

	Fluorescence		**Phosphorescence**	
	[nm]	[eV]	[nm]	[eV]
MCH	35	0.26	34	0.23
ZNX	41	0.29	66	0.41

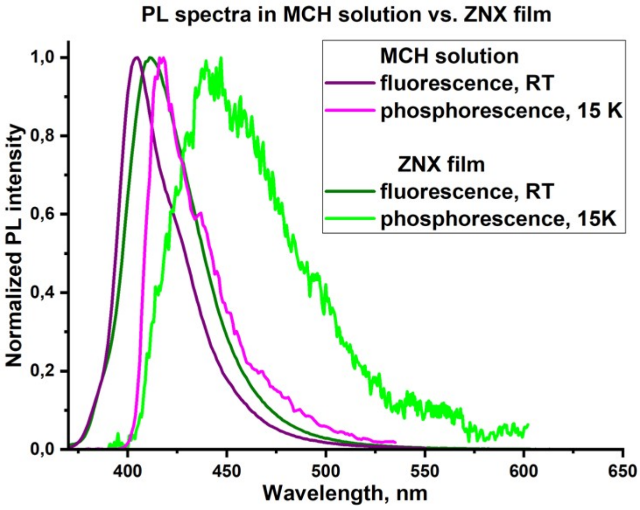

Figure S11. Fluorescence (RT) and phosphorescence (15K) spectra in MCH solution and ZNX film.

Section 5. Quantum Chemical Calculations

Calculations of electronic parameters and rISC values

For the calculations of k_{rISC} values Marcus-Hush equation [S3] was used

$$k = \frac{V^2}{\hbar}\sqrt{\frac{\pi}{k_{\mathrm{B}}T\lambda}}\exp\left[-\frac{(\Delta E_{\mathrm{ST}} + \lambda)^2}{4k_{\mathrm{B}}T\lambda}\right] \quad (1)$$

where:

k is a rate constant

V is the SOC constant

λ is the sum of internal and external (λ_{solv}) reorganization energies for the respective transition

ΔE_{ST} is an energy gap between singlet and triplet state

k_{B} is the Boltzmann constant

$\hbar$ is the reduced Planck's constant

T is the temperature (298.15 K).

On the B3LYP/cc-pVDZ level of theory, the value of the $\Delta E_{3\mathrm{CT}\rightarrow 1\mathrm{CT}}$ energy gap was predicted of 4.5 meV for the 90° rotamer. Deviation of θ from the optimal value causes the increase of $\Delta E_{3\mathrm{CT}\rightarrow 1\mathrm{CT}}$ values as shown in Table S6. To take this into account, the statistically weighted $\Delta E_{3\mathrm{CT}\rightarrow 1\mathrm{CT}}$ was calculated using population of each θ-rotamer given by Boltzmann distribution at room temperature using respective energies of species (Table S4, S5). To describe the rISC dynamics in solutions, θ-rotamer population in the T_1 (^{3}CT) state geometry was used. The statistically weighted $\Delta E_{(3\mathrm{CT}\rightarrow 1\mathrm{CT})\mathrm{w}}$ value of 7.8 meV was obtained as described below. The calculated reorganization energies (Table S7) and SOC constants (Table S8) at various θ are presented below.

The $\Delta E_{3\mathrm{CT}\rightarrow 1\mathrm{CT}}$ values in various solvents were estimated using the $k_{\mathrm{r}}(E_{\mathrm{S1}})$ dependence as described in [S2]. Specifically, DFT calculations predicted $\mathrm{PL}_{\mathrm{max}}$ of 526 nm matching well the experimental value of 519 nm obtained for the DCE solution (Table 1, main text). The abovementioned $\Delta E_{3\mathrm{CT}\rightarrow 1\mathrm{CT}}$ value of 7.8 meV was thus ascribed to the DCE medium. Taking into account linear dependence of k_{r} on the S_1 energy (Figure 3B) and $\ln(k_{\mathrm{rISC}})$ on k_{r} (Figure 3D), linear correlation between k_{r} and $\Delta E_{3\mathrm{CT}\rightarrow 1\mathrm{CT}}$ was assumed. Therefore, $\Delta E_{3\mathrm{CT}\rightarrow 1\mathrm{CT}}$ for other solvents were estimated by proportion using experimental k_{r} values (Table S3).

For each medium, statistically weighted $k_{3CT \to 1CT}$ rate constants were obtained (Table S3) using Marcus-Hush equation (1) for each θ-rotamer via three approaches. As described below, these approaches use different SOC constants, and the same set of $\Delta E_{(3CT \to 1CT)}(\theta)$ and $\lambda(\theta)$ for each medium.

Table S3. Summary of estimation of $\Delta E_{(3CT \to 1CT)w}$, $\ln(k_{T1\text{-}S1})_w$, and V_w for different media.

	E_{S1} [eV]	k_r [10^{-6} s^{-1}]	$\Delta E_{(3CT \to 1CT)w}$, meV	$\ln(k_{T1\text{-}S1})_w$ [a]			V_w variable,[d] [cm^{-1}]
				$V_w = V_{3CT\text{-}1CT}$	$V_w = 0.44$ cm^{-1}	exper. (V_w is a variable)	
Tol/Hex	3.19	11.0	15.6	13.01	14.39	14.7	0.051
Benz.	3.04	8.7	12.3	13.29	14.64	14.8	0.049
ClBenz.	2.99	8.4	11.9	13.33	14.68	14.9	0.048
DCE	2.86	5.5	7.8	13.75	15.11	15.1	0.045
DMSO	2.75	3.5	5.0	14.14	15.41	15.1	0.038

E_{S1} – energy of the S_1 state obtained experimentally from PL_{onset};

$\Delta E_{(3CT \to 1CT)w}$ – statistically weighted energy gap between ^{3}CT and ^{1}CT states obtained by DFT calculations (for DCM) or using proportion:

$$\Delta E_{(3CT \to 1CT)w}\ (i\text{-solvent}) = k_r(i)^* \Delta E_{(3CT \to 1CT)w}(\text{DCM}) \,/\, k_r(\text{DCM});$$

[a] statistically weighted rISC constants calculated using 1) $V_{3CT\text{-}1CT}$ predicted for each θ-rotamer (Approach 1); 2) V values giving a statistically weighted V_w value of 0.44 cm^{-1} (Approach 2), or 3) variable V values obtained from the reconstruction of experimental k_{rISC} values (Approach 3);

[b] statistically weighted variable V values obtained from the reconstruction of experimental k_{rISC} values using $\Delta E_{(3CT \to 1CT)w}$;

note that in all calculations, the external reorganization energy was equal to $\Delta E_{(3CT \to 1CT)}$ for each θ-rotamer.

Dependence of electronic parameters on the dihedral angle between donor and acceptor fragments (*θ*)

Table S4. Relative energies of the species with various θ value in various electronic states.

	Energies of electronic states relative to the optimal geometry in the same state [eV]					
θ [°]	**S_0**	**^{1}CT**	**^{1}LE$_A$**	**^{3}CT**	**^{3}LE$_A$**	**^{3}LE$_D$**
60	0.27	0.57	0.26	0.48	0.28	0.20
65	0.15	0.37	0.14	0.30	0.16	0.21
70	0.082	0.23	0.071	0.18	0.086	0.14
75	-	-	0.034	0.094	0.042	0.059
77	0.039	0.10	-	0.069	-	-
80	0.015	0.056	0.014	0.040	0.017	0.026
82	0.0091	0.034	-	0.025	0.010	0.013
84	0.0048	0.019	-	0.014	0.0054	0.0076
85	-	-	0.0036	-	-	-
86	0.0020	0.0078	-	0.0058	0.0020	0.0038
88	0.0008	0.0019	0.0	0.00	0.00019	0.0015
90	0.0000	0.0000	0.00030	0.0058	0.0	0.00
92	0.0008	0.0019	0.0	0.014	0.00019	0.0015
94	0.0020	0.0078	-	0.025	0.0020	0.0038
95	-	-	0.0036	-	-	-
96	0.0048	0.019	-	0.040	0.0054	0.0076
98	0.0091	0.034	-	0.069	0.010	0.013
100	0.015	0.056	0.014	0.094	0.017	0.026
103	0.039	0.10	-	0.18	-	-
105	-	-	0.034	0.30	0.042	0.059
110	0.082	0.23	0.071	0.48	0.086	0.14
115	0.15	-	0.14	-	0.16	0.21
120	0.27	-	0.26	-	0.28	0.20

Table S5. Population (*p*) of species with various *θ* value

	Population of rotamers, *p* [%]					
***θ* [°]**	**S_0**	**^{1}CT**	**^1LE_A**	**^{3}CT**	**^3LE_A**	**^3LE_D**
60	2.39×10^{-6}	3.14×10^{-11}	6.55×10^{-6}	9.54×10^{-10}	2.30×10^{-6}	5.46×10^{-5}
65	2.67×10^{-4}	9.03×10^{-8}	4.90×10^{-4}	1.18×10^{-6}	2.35×10^{-4}	2.44×10^{-5}
70	4.41×10^{-3}	2.47×10^{-5}	6.69×10^{-3}	1.40×10^{-4}	3.82×10^{-3}	1.08×10^{-3}
75	-	-	2.89×10^{-2}	3.63×10^{-3}	2.08×10^{-2}	1.19×10^{-2}
77	2.31×10^{-2}	2.76×10^{-3}	-	9.87×10^{-3}	-	-
80	5.85×10^{-2}	1.85×10^{-2}	6.33×10^{-2}	3.00×10^{-2}	5.58×10^{-2}	4.82×10^{-2}
82	7.38×10^{-2}	4.42×10^{-2}	-	5.36×10^{-2}	7.20×10^{-2}	6.86×10^{-2}
84	8.74×10^{-2}	7.97×10^{-2}	9.37×10^{-2}	8.35×10^{-2}	8.72×10^{-2}	9.06×10^{-2}
86	9.76×10^{-2}	1.21×10^{-1}	-	1.14×10^{-1}	9.95×10^{-2}	1.09×10^{-1}
88	0.1×10^{-1}	1.52×10^{-1}	1.08×10^{-1}	1.34×10^{-1}	1.07×10^{-1}	1.17×10^{-1}
90	1.05×10^{-1}	1.64×10^{-1}	1.06×10^{-1}	1.43×10^{-1}	1.08×10^{-1}	1.20×10^{-1}
92	1.02×10^{-1}	1.52×10^{-1}	1.08×10^{-1}	1.34×10^{-1}	1.07×10^{-1}	1.17×10^{-1}
94	9.76×10^{-2}	1.21×10^{-1}	9.37×10^{-2}	1.14×10^{-1}	9.95×10^{-2}	1.09×10^{-1}
96	8.74×10^{-2}	7.97×10^{-2}	-	8.35×10^{-2}	8.72×10^{-2}	9.06×10^{-2}
98	7.38×10^{-2}	4.42×10^{-2}	-	5.36×10^{-2}	7.20×10^{-2}	6.86×10^{-2}
100	5.85×10^{-2}	1.85×10^{-2}	6.33×10^{-2}	3.00×10^{-2}	5.58×10^{-2}	4.82×10^{-2}
103	2.31×10^{-2}	2.76×10^{-3}	-	9.87×10^{-3}	-	-
105	-	-	2.89×10^{-2}	3.63×10^{-3}	2.08×10^{-2}	1.19×10^{-2}
110	4.41×10^{-3}	2.47×10^{-5}	6.69×10^{-3}	1.40×10^{-4}	3.82×10^{-3}	1.08×10^{-3}
115	2.67×10^{-4}	-	4.90×10^{-4}	-	2.35×10^{-4}	2.44×10^{-5}
120	2.39×10^{-6}	-	4.64×10^{-6}	-	2.30×10^{-6}	5.46×10^{-5}

Table S6. Calculated singlet-triplet energy gaps between selected states as a function of θ.

	Energy gap [eV]		
θ [°]	**^{1}CT-^{3}CT**	**^{1}CT-^{3}LE$_A$**	**^{1}CT-^{3}LE$_D$**
60	0.10	0.30	0.20
65	0.074	0.21	0.15
70	0.053	0.14	0.11
77	0.028	0.082	0.070
80	0.019	0.036	0.033
82	0.013	0.023	0.020
84	0.0092	0.013	0.012
86	0.0065	0.0059	0.006
88	0.0048	0.0018	0.00017
90	0.0045	0.000074	0.0013
92	0.0048	0.0018	0.00017
94	0.0065	0.0059	0.0061
96	0.0092	0.013	0.012
98	0.013	0.023	0.020
100	0.019	0.036	0.033
103	0.028	0.082	0.070
110	0.053	0.14	0.11
115	0.074	0.21	0.15
120	0.10	0.30	0.20

Table S7. Calculated internal reorganization energies for selected spin-flip transitions in TMCz-BO and DMAC-TRZ as a function of *θ*.

	Internal reorganization energy [eV]				
θ [°]	**TMCz-BO**			**DMAC-TRZ**	
	^{1}CT-^{3}CT	^{1}CT-^{3}LE$_A$	^{1}CT-^{3}LE$_D$	^{1}CT-^{3}CT	^{1}CT-^{3}LE$_A$
60	0.0038	0.046	0.095	-	-
65	0.0025	0.079	0.080	0.15	0.23
70	0.0018	0.10	0.10	0.10	0.22
75	0.0011	0.12	0.12	0.062	0.22
80	0.00063	0.13	0.13	0.032	0.21
82	0.00047	0.13	0.13	0.023	0.21
84	0.00033	0.13	0.13	0.016	0.21
86	0.00021	0.14	0.14	0.011	0.21
88	0.00014	0.14	0.14	0.0076	0.21
90	0.0	0.14	0.14	0.0066	0.21
92	0.00014	0.14	0.14	0.0076	0.21
94	0.00021	0.14	0.14	0.011	0.21
96	0.00033	0.13	0.13	0.016	0.21
98	0.00047	0.13	0.13	0.023	0.21
100	0.00063	0.13	0.13	0.032	0.21
105	0.0011	0.12	0.12	0.062	0.22
110	0.0018	0.10	0.10	0.10	0.22
115	0.0025	0.079	0.080	0.15	0.23
120	0.0038	0.046	0.095	-	-

Table S8. Calculated SOC constants for various transitions and values.

	SOC [cm^{-1}]					
θ [°]	$^{1}\mathrm{CT}\rightleftarrows{}^{3}\mathrm{CT}$	$^{1}\mathrm{CT}\rightleftarrows{}^{3}\mathrm{LE}_{\mathrm{A}}$	$^{1}\mathrm{CT}\rightleftarrows{}^{3}\mathrm{LE}_{\mathrm{D}}$	$^{1}\mathrm{LE}_{\mathrm{A}}\rightleftarrows{}^{3}\mathrm{CT}$	$^{1}\mathrm{LE}_{\mathrm{A}}\rightleftarrows{}^{3}\mathrm{LE}_{\mathrm{A}}$	$^{1}\mathrm{LE}_{\mathrm{A}}\rightleftarrows{}^{3}\mathrm{LE}_{\mathrm{D}}$
60	0.11	0.18	0.10	0.18	0.019	0.040
65	0.10	0.16	0.15	0.18	0.014	0.030
70	0.090	0.13	0.16	0.17	0.0075	0.020
77	0.070	0.12	0.17	0.17	0.0025	0.0080
80	0.050	0.11	0.17	0.16	0.0	0.0060
82	0.040	0.11	0.17	0.16	0.0	0.0040
84	0.030	0.11	0.17	0.16	0.0	0.0030
86	0.020	0.11	0.17	0.16	0.0	0.0020
88	0.010	0.10	0.17	0.16	0.0	0.0
90	0.0	0.10	0.17	0.16	0.0	0.0
92	0.010	0.10	0.17	0.16	0.0	0.0
94	0.020	0.11	0.17	0.16	0.0	0.0020
96	0.030	0.11	0.17	0.16	0.0	0.0030
98	0.040	0.11	0.17	0.16	0.0	0.0040
100	0.050	0.11	0.17	0.16	0.0	0.0060
103	0.070	0.12	0.17	0.17	0.0025	0.0080
110	0.090	0.13	0.16	0.17	0.0075	0.020
115	0.10	0.16	0.15	0.18	0.014	0.030
120	0.11	0.18	0.10	0.18	0.019	0.040

Approach 1. V_w is constant equal to $V_{(3CT\rightarrow 1CT)w}$; V_w = 0.02 cm^{-1} (selected examples)

Medium: DCE. $\Delta E_{3CT\rightarrow 1CT}$ (θ) as calculated. $V = V_{3CT\text{-}1CT}$

θ ° deviation	p_{T1}	$\Delta E_{3CT\rightarrow 1CT}$ [eV]	$\Delta E_{3CT\rightarrow 1CT}*p_{T1}$	λ_{in} [eV]	λ_{sum} [eV]	k_{rISC} [s^{-1}]	$k_{rISC}*p_{T1}$	V [cm^{-1}]	$V*p_{T1}$
±30	1.95×10^{-9}	0.096	1.9×10^{-10}	0.004	0.096	2.27×10^{-5}	4.41×10^{-4}	0.11	2.1×10^{-10}
±25	2.41×10^{-6}	0.074	1.8×10^{-7}	0.003	0.074	4.95×10^{-5}	1.19	0.10	2.4×10^{-7}
±20	2.87×10^{-4}	0.053	1.5×10^{-5}	0.002	0.053	1.09×10^{-6}	3.13×10^{-2}	0.09	2.6×10^{-5}
±15	7.40×10^{-3}	0.033	2.5×10^{-4}	0.001	0.033	1.76×10^{-6}	1.30×10^{-4}	0.07	5.2×10^{-4}
±10	6.1×10^{-2}	0.018	1.1×10^{-3}	0.001	0.018	2.26×10^{-6}	1.38×10^{-5}	0.05	3.1×10^{-3}
±8	0.11	0.013	1.4×10^{-3}	0.000	0.013	2.04×10^{-6}	2.23×10^{-5}	0.04	4.4×10^{-3}
±6	0.17	0.009	1.6×10^{-3}	0.000	0.009	1.58×10^{-6}	2.68×10^{-5}	0.03	5.1×10^{-3}
±4	0.23	0.006	1.5×10^{-3}	0.000	0.006	9.30×10^{-5}	2.16×10^{-5}	0.02	4.6×10^{-3}
±2	0.27	0.005	1.3×10^{-3}	0.000	0.005	2.87×10^{-5}	7.87×10^{-4}	0.01	2.7×10^{-3}
0	0.15	0.004	6.5×10^{-4}	0.000	0.004	0	0	0	0
SUM	**1.000**		**0.0078**				**9.37×10^{-5}**		**0.020**

Medium: Tol/Hex. Each $\Delta E_{3CT\rightarrow 1CT}$ (θ) is divided by constant b = 0.502 to attain $\mathbf{\Delta} E_{(3CT\rightarrow 1CT)w}$ = 15.6 meV. $V = V_{3CT\text{-}1CT}$

θ ° deviation	p_{T1}	$\Delta E_{3CT\rightarrow 1CT}$ [eV]	$\Delta E_{3CT\rightarrow 1CT}*p_{T1}$	λ_{in} [eV]	λ_{sum} [eV]	k_{rISC} [s^{-1}]	$k_{rISC}*p_{T1}$	V [cm^{-1}]	$V*p_{T1}$
±30	1.95×10^{-9}	0.191	3.7×10^{-10}	0.004	0.191	3.98×10^{-3}	7.74×10^{-6}	0.11	2.1×10^{-10}
±25	2.41×10^{-6}	0.148	3.6×10^{-7}	0.003	0.148	2.00×10^{-4}	4.83×10^{-2}	0.10	2.4×10^{-7}
±20	2.87×10^{-4}	0.105	3.0×10^{-5}	0.002	0.105	1.01×10^{-5}	0.3	0.09	2.6×10^{-5}
±15	7.40×10^{-3}	0.067	4.9×10^{-4}	0.001	0.067	3.44×10^{-5}	2.54×10^{-3}	0.07	5.2×10^{-4}
±10	6.1×10^{-2}	0.035	2.2×10^{-3}	0.001	0.035	8.05×10^{-5}	4.93×10^{-4}	0.05	3.1×10^{-3}
±8	0.11	0.026	2.8×10^{-3}	0.000	0.026	8.72×10^{-5}	9.54×10^{-4}	0.04	4.4×10^{-3}
±6	0.17	0.018	3.1×10^{-3}	0.000	0.018	7.82×10^{-5}	1.33×10^{-5}	0.03	5.1×10^{-3}
±4	0.23	0.013	3.0×10^{-3}	0.000	0.013	5.13×10^{-5}	1.19×10^{-5}	0.02	4.6×10^{-3}
±2	0.27	0.010	2.6×10^{-3}	0.000	0.010	1.69×10^{-5}	4.63×10^{-4}	0.01	2.7×10^{-3}
0	0.15	0.009	1.3×10^{-3}	0.000	0.009	0	0	0.00	0
SUM	**1.000**		**0.0156**				**4.46×10^{-5}**		**0.0205**

Medium: DMSO. Each $\Delta E_{3CT\rightarrow 1CT}$ (θ) is divided by constant b = 1.58 to attain $\mathbf{\Delta} E_{(3CT\rightarrow 1CT)w}$ = 5.0 meV. $V = V_{3CT\text{-}1CT}$

θ ° deviation	p_{T1}	$\Delta E_{3CT\rightarrow 1CT}$ [eV]	$\Delta E_{3CT\rightarrow 1CT}*p_{T1}$	λ_{in} [eV]	λ_{sum} [eV]	k_{rISC} [s^{-1}]	$k_{rISC}*p_{T1}$	V [cm^{-1}]	$V*p_{T1}$
±30	1.95×10^{-9}	0.061	1.2×10^{-10}	0.004	0.061	1.12×10^{-6}	2.18×10^{-3}	0.11	2.1×10^{-10}
±25	2.41×10^{-6}	0.047	1.1×10^{-7}	0.003	0.047	1.79×10^{-6}	4.33	0.10	2.4×10^{-7}
±20	2.87×10^{-4}	0.033	9.6×10^{-6}	0.002	0.033	2.92×10^{-6}	8.36×10^{-2}	0.09	2.6×10^{-5}
±15	7.40×10^{-3}	0.021	1.6×10^{-4}	0.001	0.021	3.57×10^{-6}	2.64×10^{-4}	0.07	5.2×10^{-4}
±10	6.1×10^{-2}	0.011	6.9×10^{-4}	0.001	0.011	3.66×10^{-6}	2.24×10^{-5}	0.05	3.1×10^{-3}
±8	0.11	0.008	9.0×10^{-4}	0.000	0.008	3.08×10^{-6}	3.37×10^{-5}	0.04	4.4×10^{-3}
±6	0.17	0.006	1.0×10^{-3}	0.000	0.006	2.26×10^{-6}	3.85×10^{-5}	0.03	5.1×10^{-3}
±4	0.23	0.004	9.5×10^{-4}	0.000	0.004	1.28×10^{-6}	2.97×10^{-5}	0.02	4.6×10^{-3}
±2	0.27	0.003	8.4×10^{-4}	0.000	0.003	3.87×10^{-5}	1.06×10^{-5}	0.01	2.7×10^{-3}
0	0.15	0.003	4.1×10^{-4}	0.000	0.003	0	0	0.00	0
SUM	**1.000**		**0.0050**				**1.38×10^{-6}**		**0.0205**

Approach 2. V_{w} is constant and higher than $V_{\mathrm{3CT\to1CT}}$; V_{w} = 0.044 cm^{-1}(selected examples)

Medium: DCE. $\Delta E_{\mathrm{3CT\to1CT}}$ (θ) as calculated. To each $V_{\mathrm{3CT\text{-}1CT}}(\theta)$ a constant value c = 0.021 is added to attain V_{w} = 0.044 cm^{-1}

θ ° deviation	p_{T1}	$\Delta E_{\mathrm{3CT\to1CT}}$ [eV]	$\Delta E_{\mathrm{3CT\to1CT}}{*}p_{\mathrm{T1}}$	λ_{in} [eV]	λ_{sum} [eV]	k_{rISC} [s^{-1}]	$k_{\mathrm{rISC}}{*}p_{\mathrm{T1}}$	V [cm^{-1}]	$V{*}p_{\mathrm{T1}}$
±30	1.95×10^{-9}	0.096	1.9×10^{-10}	0.004	0.096	3.22×10^{-5}	6.26×10^{-4}	0.13	2.5×10^{-10}
±25	2.41×10^{-6}	0.074	1.8×10^{-7}	0.003	0.074	7.24×10^{-5}	1.75	0.12	2.9×10^{-7}
±20	2.87×10^{-4}	0.053	1.5×10^{-5}	0.002	0.053	1.66×10^{-6}	4.76×10^{-2}	0.11	3.2×10^{-5}
±15	7.40×10^{-3}	0.033	2.5×10^{-4}	0.001	0.033	2.98×10^{-6}	2.20×10^{-4}	0.09	6.7×10^{-4}
±10	6.1×10^{-2}	0.018	1.1×10^{-3}	0.001	0.018	4.56×10^{-6}	2.79×10^{-5}	0.07	4.3×10^{-3}
±8	0.11	0.013	1.4×10^{-3}	0.000	0.013	4.74×10^{-6}	5.18×10^{-5}	0.06	6.7×10^{-3}
±6	0.17	0.009	1.6×10^{-3}	0.000	0.009	4.56×10^{-6}	7.76×10^{-5}	0.05	8.7×10^{-3}
±4	0.23	0.006	1.5×10^{-3}	0.000	0.006	3.91×10^{-6}	9.06×10^{-5}	0.04	9.5×10^{-3}
±2	0.27	0.005	1.3×10^{-3}	0.000	0.005	2.76×10^{-6}	7.56×10^{-5}	0.03	8.5×10^{-3}
0	0.15	0.004	6.5×10^{-4}	0.000	0.004	1.34×10^{-6}	1.94×10^{-5}	0.02	5.8×10^{-3}
SUM	**1.000**		**0.0078**				**3.45×10^{-6}**		**0.044**

Medium: Tol/Hex. Each $\Delta E_{\mathrm{3CT\to1CT}}$ (θ) divided by constant b = 0.502 to attain $\mathbf{\Delta E_{(3CT\to1CT)w}}$ = 15.6 meV. To each $V_{\mathrm{3CT\text{-}1CT}}(\theta)$ a constant value c = 0.021 is added to attain V_{w} = 0.044 cm^{-1}

θ ° deviation	p_{T1}	$\Delta E_{\mathrm{3CT\to1CT}}$ [eV]	$\Delta E_{\mathrm{3CT\to1CT}}{*}p_{\mathrm{T1}}$	λ_{in} [eV]	λ_{sum} [eV]	k_{rISC} [s^{-1}]	$k_{\mathrm{rISC}}{*}p_{\mathrm{T1}}$	V [cm^{-1}]	$V{*}p_{\mathrm{T1}}$
±30	1.95×10^{-9}	0.191	3.7×10^{-10}	0.004	0.191	5.64×10^{-3}	1.10×10^{-5}	0.13	2.5×10^{-10}
±25	2.41×10^{-6}	0.148	3.6×10^{-7}	0.003	0.148	2.93×10^{-4}	7.07×10^{-2}	0.12	2.9×10^{-7}
±20	2.87×10^{-4}	0.105	3.0×10^{-5}	0.002	0.105	1.54×10^{-5}	4.41×10^{-1}	0.11	3.2×10^{-5}
±15	7.40×10^{-3}	0.067	4.9×10^{-4}	0.001	0.067	5.81×10^{-5}	4.30×10^{-3}	0.09	6.7×10^{-4}
±10	6.1×10^{-2}	0.035	2.2×10^{-3}	0.001	0.035	1.62×10^{-6}	9.94×10^{-4}	0.07	4.3×10^{-3}
±8	0.11	0.026	2.8×10^{-3}	0.000	0.026	2.03×10^{-6}	2.22×10^{-5}	0.06	6.7×10^{-3}
±6	0.17	0.018	3.1×10^{-3}	0.000	0.018	2.26×10^{-6}	3.85×10^{-5}	0.05	8.7×10^{-3}
±4	0.23	0.013	3.0×10^{-3}	0.000	0.013	2.15×10^{-6}	5.00×10^{-5}	0.04	9.5×10^{-3}
±2	0.27	0.010	2.6×10^{-3}	0.000	0.010	1.62×10^{-6}	4.45×10^{-5}	0.03	8.5×10^{-3}
0	0.15	0.009	1.3×10^{-3}	0.000	0.009	7.97×10^{-5}	1.16×10^{-5}	0.02	5.8×10^{-3}
SUM	**1.000**		**0.0156**				**1.77×10^{-6}**		**0.044**

Medium: DMSO. Each $\Delta E_{\mathrm{3CT\to1CT}}$ (θ) is divided by constant b = 1.58 to attain $\mathbf{\Delta E_{(3CT\to1CT)w}}$ = 5.0 meV. To each $V_{\mathrm{3CT\text{-}1CT}}(\theta)$ a constant value c = 0.021 is added to attain V_{w} = 0.044 cm^{-1}

θ ° deviation	p_{T1}	$\Delta E_{\mathrm{3CT\to1CT}}$ [eV]	$\Delta E_{\mathrm{3CT\to1CT}}{*}p_{\mathrm{T1}}$	λ_{in} [eV]	λ_{sum} [eV]	k_{rISC} [s^{-1}]	$k_{\mathrm{rISC}}{*}p_{\mathrm{T1}}$	V [cm-^{1}]	$V{*}p_{\mathrm{T1}}$
±30	1.95×10^{-9}	0.061	1.2×10^{-10}	0.004	0.061	1.59×10^{-6}	3.09×10^{-3}	0.13	2.5×10^{-10}
±25	2.41×10^{-6}	0.047	1.1×10^{-7}	0.003	0.047	2.63×10^{-6}	6.33	0.12	2.9×10^{-7}
±20	2.87×10^{-4}	0.033	9.6×10^{-6}	0.002	0.033	4.44×10^{-6}	1.27×10^{-3}	0.11	3.2×10^{-5}
±15	7.40×10^{-3}	0.021	1.6×10^{-4}	0.001	0.021	6.03×10^{-6}	4.46×10^{-4}	0.09	6.7×10^{-4}
±10	6.1×10^{-2}	0.011	6.9×10^{-4}	0.001	0.011	7.39×10^{-6}	4.52×10^{-5}	0.07	4.3×10^{-3}
±8	0.11	0.008	9.0×10^{-4}	0.000	0.008	7.17×10^{-6}	7.84×10^{-5}	0.06	6.7×10^{-3}
±6	0.17	0.006	1.0×10^{-3}	0.000	0.006	6.54×10^{-6}	1.11×10^{-6}	0.05	8.7×10^{-3}
±4	0.23	0.004	9.5×10^{-4}	0.000	0.004	5.39×10^{-6}	1.25×10^{-6}	0.04	9.5×10^{-3}
±2	0.27	0.003	8.4×10^{-4}	0.000	0.003	3.72×10^{-6}	1.02×10^{-6}	0.03	8.5×10^{-3}
0	0.15	0.003	4.1×10^{-4}	0.000	0.003	1.79×10^{-6}	2.60×10^{-5}	0.02	5.8×10^{-3}
SUM	**1.000**		**0.0050**				**4.92×10^{-6}**		**0.044**

Approach 3. V_w is dependent on the medium. variable. (selected examples)

Medium: DCE. $\Delta E_{3CT\to1CT}$ (θ) as calculated. To each $V_{3CT-1CT}(\theta)$ a constant value $c = 0.0213$ is added to attain $V_w = 0.045$ cm^{-1}

θ ° deviation	p_{T1}	$\Delta E_{3CT\to1CT}$ [eV]	$\Delta E_{3CT\to1CT}*p_{T1}$	λ_{in} [eV]	λ_{sum} [eV]	k_{rISC} [s^{-1}]	$k_{rISC}*p_{T1}$	V [cm^{-1}]	$V*p_{T1}$
±30	1.95×10^{-9}	0.096	1.9×10^{-10}	0.004	0.096	3.23×10^{-5}	6.29×10^{-4}	0.13	2.6×10^{-10}
±25	2.41×10^{-6}	0.074	1.8×10^{-7}	0.003	0.074	7.28×10^{-5}	1.76	0.12	2.9×10^{-7}
±20	2.87×10^{-4}	0.053	1.5×10^{-5}	0.002	0.053	1.67×10^{-6}	4.79×10^{-2}	0.11	3.2×10^{-5}
±15	7.40×10^{-3}	0.033	2.5×10^{-4}	0.001	0.033	3.00×10^{-6}	2.22×10^{-4}	0.09	6.8×10^{-4}
±10	6.1×10^{-2}	0.018	1.1×10^{-3}	0.001	0.018	4.60×10^{-6}	2.81×10^{-5}	0.07	4.4×10^{-3}
±8	0.11	0.013	1.4×10^{-3}	0.000	0.013	4.78×10^{-6}	5.23×10^{-5}	0.06	6.7×10^{-3}
±6	0.17	0.009	1.6×10^{-3}	0.000	0.009	4.61×10^{-6}	7.85×10^{-5}	0.05	8.7×10^{-3}
±4	0.23	0.006	1.5×10^{-3}	0.000	0.006	3.96×10^{-6}	9.19×10^{-5}	0.04	9.6×10^{-3}
±2	0.27	0.005	1.3×10^{-3}	0.000	0.005	2.81×10^{-6}	7.71×10^{-5}	0.03	8.6×10^{-3}
0	0.15	0.004	6.5×10^{-4}	0.000	0.004	1.37×10^{-6}	2.00×10^{-5}	0.02	5.8×10^{-3}
SUM	**1.000**		**0.0078**				**3.50×10^{-6}**		**0.045**

Medium: Tol/Hex. Each $\Delta E_{3CT\to1CT}$ (θ) divided by constant $b = 0.502$ to attain $\mathbf{\Delta E_{(3CT\to1CT)w}}$ = 15.6 meV. To each $V_{3CT-1CT}(\theta)$ a constant value $c = 0.027$ is added to attain $V_w = 0.051$ cm^{-1}

θ ° deviation	p_{T1}	$\Delta E_{3CT\to1CT}$ [eV]	$\Delta E_{3CT\to1CT}*p_{T1}$	λ_{in} [eV]	λ_{sum} [eV]	k_{rISC} [s^{-1}]	$k_{rISC}*p_{T1}$	V [cm^{-1}]	$V*p_{T1}$
±30	1.95×10^{-9}	0.191	3.7×10^{-10}	0.004	0.191	6.17×10^{-3}	1.20×10^{-5}	0.14	2.7×10^{-10}
±25	2.41×10^{-6}	0.148	3.6×10^{-7}	0.003	0.148	3.23×10^{-4}	7.79×10^{-2}	0.13	3.1×10^{-7}
±20	2.87×10^{-4}	0.105	3.0×10^{-5}	0.002	0.105	1.71×10^{-5}	4.90×10^{-1}	0.12	3.4×10^{-5}
±15	7.40×10^{-3}	0.067	4.9×10^{-4}	0.001	0.067	6.60×10^{-5}	4.88×10^{-3}	0.10	7.2×10^{-4}
±10	6.1×10^{-2}	0.035	2.2×10^{-3}	0.001	0.035	1.91×10^{-6}	1.17×10^{-5}	0.08	4.7×10^{-3}
±8	0.11	0.026	2.8×10^{-3}	0.000	0.026	2.45×10^{-6}	2.68×10^{-5}	0.07	7.3×10^{-3}
±6	0.17	0.018	3.1×10^{-3}	0.000	0.018	2.82×10^{-6}	4.81×10^{-5}	0.06	9.7×10^{-3}
±4	0.23	0.013	3.0×10^{-3}	0.000	0.013	2.83×10^{-6}	6.57×10^{-5}	0.05	1.1×10^{-2}
±2	0.27	0.010	2.6×10^{-3}	0.000	0.010	2.31×10^{-6}	6.33×10^{-5}	0.04	1.0×10^{-2}
0	0.15	0.009	1.3×10^{-3}	0.000	0.009	1.32×10^{-6}	1.92×10^{-5}	0.03	7.4×10^{-3}
SUM	**1.000**		**0.0156**				**2.35×10^{-6}**		**0.051**

Medium: DMSO. Each $\Delta E_{3CT\to1CT}$ (θ) is divided by constant $b = 1.58$ to attain $\mathbf{\Delta E_{(3CT\to1CT)w}}$ = 5.0 meV. To each $V_{3CT-1CT}(\theta)$ a constant value $c = 0.0154$ is added to attain $V_w = 0.038$ cm^{-1}

θ ° deviation	p_{T1}	$\Delta E_{3CT\to1CT}$ [eV]	$\Delta E_{3CT\to1CT}*p_{T1}$	λ_{in} [eV]	λ_{sum} [eV]	k_{rISC} [s^{-1}]	$k_{rISC}*p_{T1}$	V [cm^{-1}]	$V*p_{T1}$
±30	1.95×10^{-9}	0.061	1.2×10^{-10}	0.004	0.061	1.46×10^{-6}	2.83×10^{-3}	0.13	2.4×10^{-10}
±25	2.41×10^{-6}	0.047	1.1×10^{-7}	0.003	0.047	2.39×10^{-6}	5.76	0.12	2.8×10^{-7}
±20	2.87×10^{-4}	0.033	9.6×10^{-6}	0.002	0.033	4.00×10^{-6}	1.15×10^{-3}	0.11	3.0×10^{-5}
±15	7.40×10^{-3}	0.021	1.6×10^{-4}	0.001	0.021	5.31×10^{-6}	3.93×10^{-4}	0.09	6.3×10^{-4}
±10	6.1×10^{-2}	0.011	6.9×10^{-4}	0.001	0.011	6.27×10^{-6}	3.84×10^{-5}	0.07	4.0×10^{-3}
±8	0.11	0.008	9.0×10^{-4}	0.000	0.008	5.91×10^{-6}	6.47×10^{-5}	0.06	6.1×10^{-3}
±6	0.17	0.006	1.0×10^{-3}	0.000	0.006	5.18×10^{-6}	8.82×10^{-5}	0.05	7.7×10^{-3}
±4	0.23	0.004	9.5×10^{-4}	0.000	0.004	4.02×10^{-6}	9.32×10^{-5}	0.04	8.2×10^{-3}
±2	0.27	0.003	8.4×10^{-4}	0.000	0.003	2.50×10^{-6}	6.84×10^{-5}	0.03	7.0×10^{-3}
0	0.15	0.003	4.1×10^{-4}	0.000	0.003	9.63×10^{-5}	1.40×10^{-5}	0.02	4.2×10^{-3}
SUM	**1.000**		**0.0050**				**3.71×10^{-6}**		**0.038**

Table S9. Linear regression parameters for the fitted dependencies Figure 6 main text.

Parameter	**Plot Exp.**	**Plot** $V = \mathrm{V}_{3CT\rightarrow 1CT}$	**Plot** $V = 0.44\ \mathrm{cm}^{-1}$	**Plot** V **variable**
Slope	-1.14 ± 0.09	-2.58 ± 0.27	-2.39 ± 0.25	-1.09 ± 0.09
Intercept	18.28 ± 0.26	21.14 ± 0.81	21.92 ± 0.75	18.15 ± 0.28
R^2	0.98	0.97	0.97	0.98

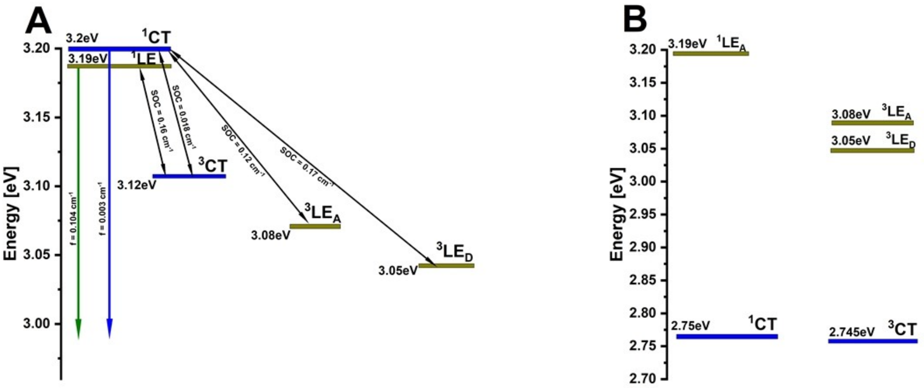

Figure S12. Energy diagram for TMCz-BO in (A) Benzene in 77K, (B) in DMSO in RT .

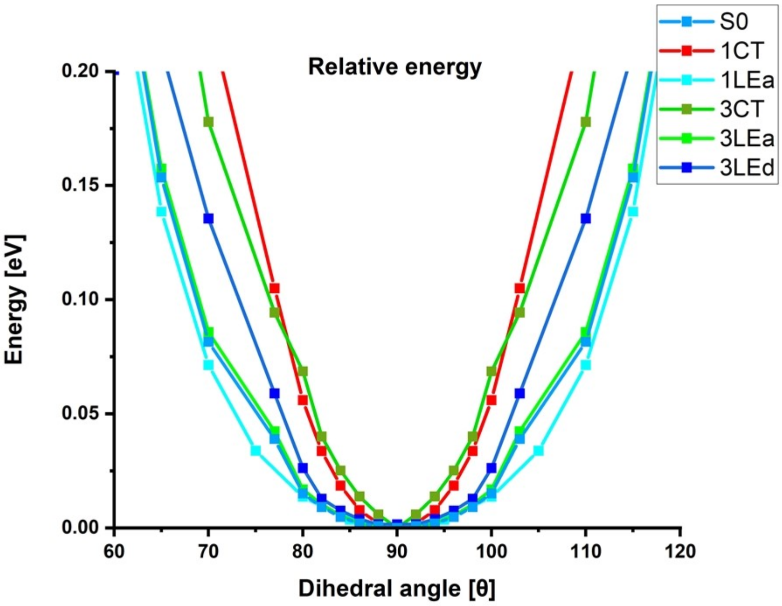

Figure S13. The dependence of relative energy of electronic state on dihedral angle θ

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