

## Electronic Supporting Information

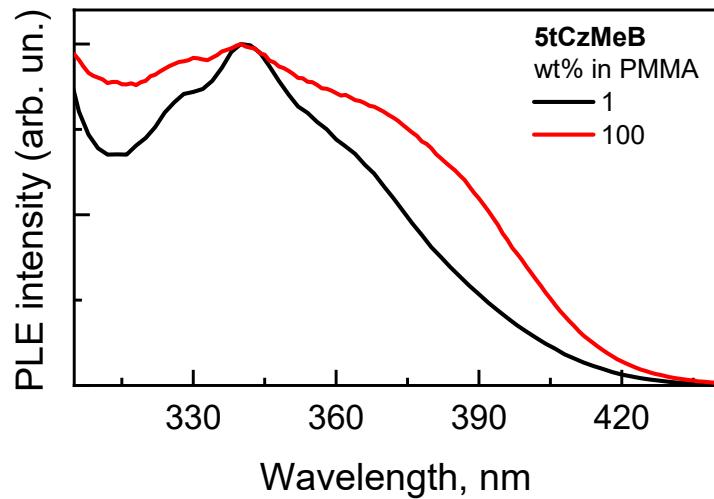
### Conformational disorder enabled emission phenomena in heavily doped TADF films

Tomas Serevičius<sup>a\*</sup>, Rokas Skaisgiris<sup>a</sup>, Dalius Gudeika<sup>b</sup>, Karolis Kazlauskas<sup>a</sup>, Saulius Juršėnas<sup>a</sup>

<sup>a</sup>Institute of Photonics and Nanotechnology, Vilnius University, Sauletekio 3, LT-10257 Vilnius, Lithuania.

<sup>b</sup>Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu 19, LT-50254 Kaunas, Lithuania

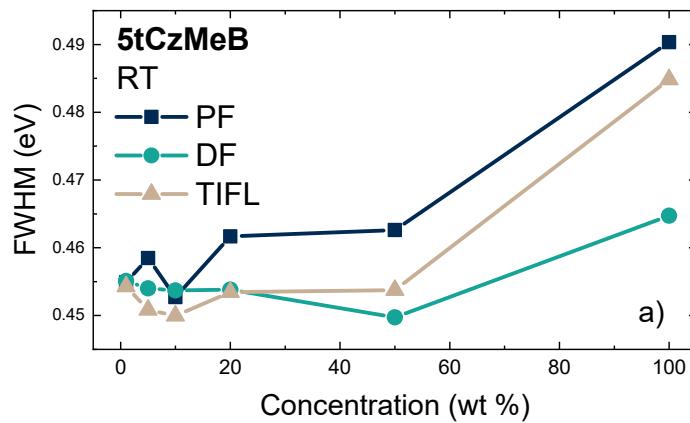
\*tomas.serevicius@tmi.vu.lt



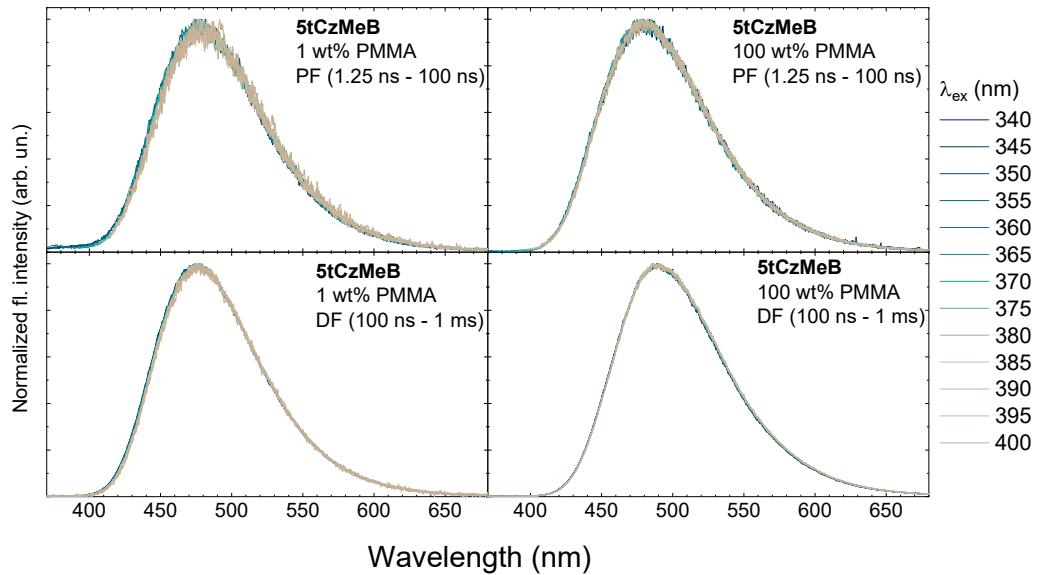
**Fig.S1** Photoluminescence excitation spectra of **5tCzMeB** in 1 wt% and 100 wt% PMMA films. Excitation wavelength range was 300-450 nm, emission intensity was collected at 490 nm.

**Table S1** On-set energy values of fluorescence and phosphorescence spectra as well as singlet-triplet energy gaps for **5tCzMeB** at different doping concentration in PMMA at 10 K.  ${}^3\text{LE}$  energy value was taken from ref.<sup>1</sup>

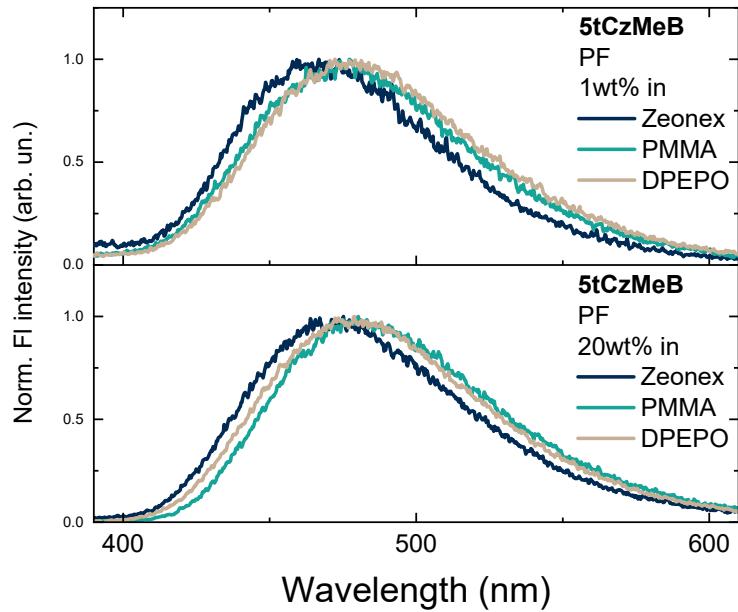
Concentration	$S_1({}^1\text{CT})$ (eV)	$T_1({}^3\text{LE})$ (eV)	$T_1({}^3\text{CT})$ (eV)	$\Delta E_{\text{ST}}({}^1\text{CT}-{}^3\text{CT})$ (meV)
1 wt%	2.93	2.99	2.88	50
5 wt%	2.94	2.99	2.87	70
10 wt%	2.94	2.99	2.85	90
20 wt%	2.95	2.99	2.85	100
50 wt%	2.96	2.99	2.84	120
100 wt%	2.96	2.99	2.82	140



**Fig. S2** FWHM values of PF, DF and TIFL spectra of **5tCzMeB** in PMMA at different doping concentration at room temperature.



**Fig. S3** Normalized fluorescence spectra of 1 wt% and 100 wt% PMMA films of **5tCzMeB** at different excitation wavelength ( $\lambda_{ex}$ ).



**Fig. S4** PF spectra of 1wt% (a) and 20 wt% (b) films of **5tCzMeB** in Zeonex, PMMA and DPEPO films at room temperature.

**Table S2** Fluorescence quantum yields and decay rates of **5tCzMeB** at different doping concentration in PMMA. Its noteworthy that solution-processed **5tCzMeB** films showed lower fluorescence quantum yields than vacuum-processed analogous films in ref.<sup>2</sup>

wt %	$\Phi_{FL}^a$	$\Phi_{PF}^b$	$\Phi_{DF}^c$	$k_{FL}$ ( $\times 10^8$ ) <sup>d</sup>	$k_R$ ( $\times 10^6$ ) <sup>e</sup>	$\tau_{DF}$ (μs) <sup>f</sup>	$k_{ISC}$ ( $\times 10^8$ ) <sup>g</sup>	$k_{rISC}$ ( $\times 10^6$ ) <sup>h</sup>	$k_{nr}^T$ ( $\times 10^4$ ) <sup>i</sup>	$k_{CQ}^T$ ( $\times 10^4$ ) <sup>j</sup>
1	0.50	0.018	0.48	2.7	5.0	14.3	2.7	1.9	3.6	-
5	0.55	0.018	0.53	2.8	5.0	13.2	2.8	2.3	3.5	-
10	0.57	0.018	0.55	3.1	5.7	9.9	3.1	3.1	4.4	0.9
20	0.51	0.019	0.49	3.4	6.3	8.0	3.4	3.4	6.3	2.7
50	0.44	0.017	0.42	3.9	6.4	6.2	3.8	4.1	9.2	5.7
100	0.29	0.013	0.28	4.1	5.8	4.6	4.0	4.8	16.0	12.2

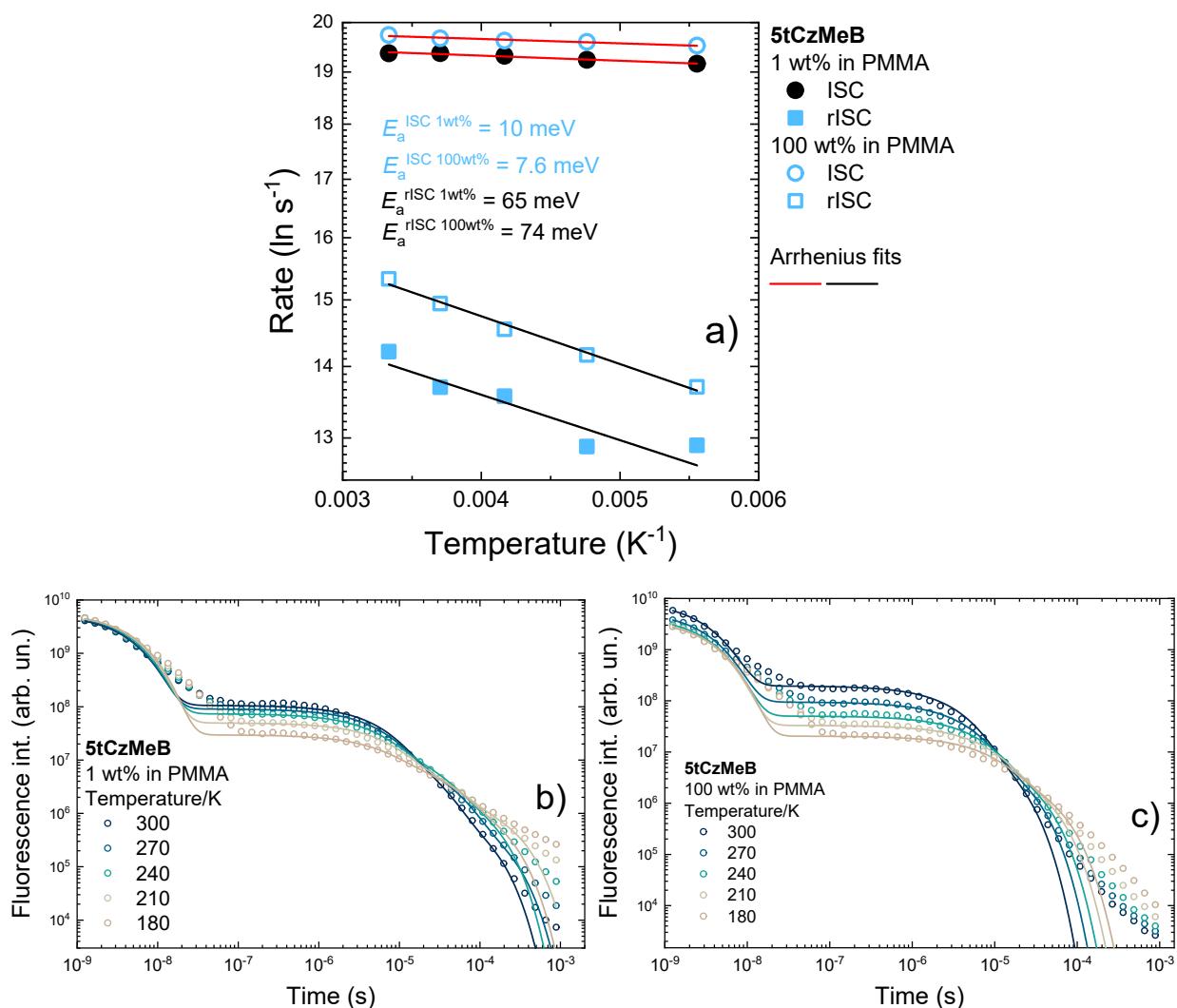
<sup>a, b, c</sup> Fluorescence quantum yield and yields of PF and DF, respectively.

<sup>d</sup> Fluorescence decay rate.

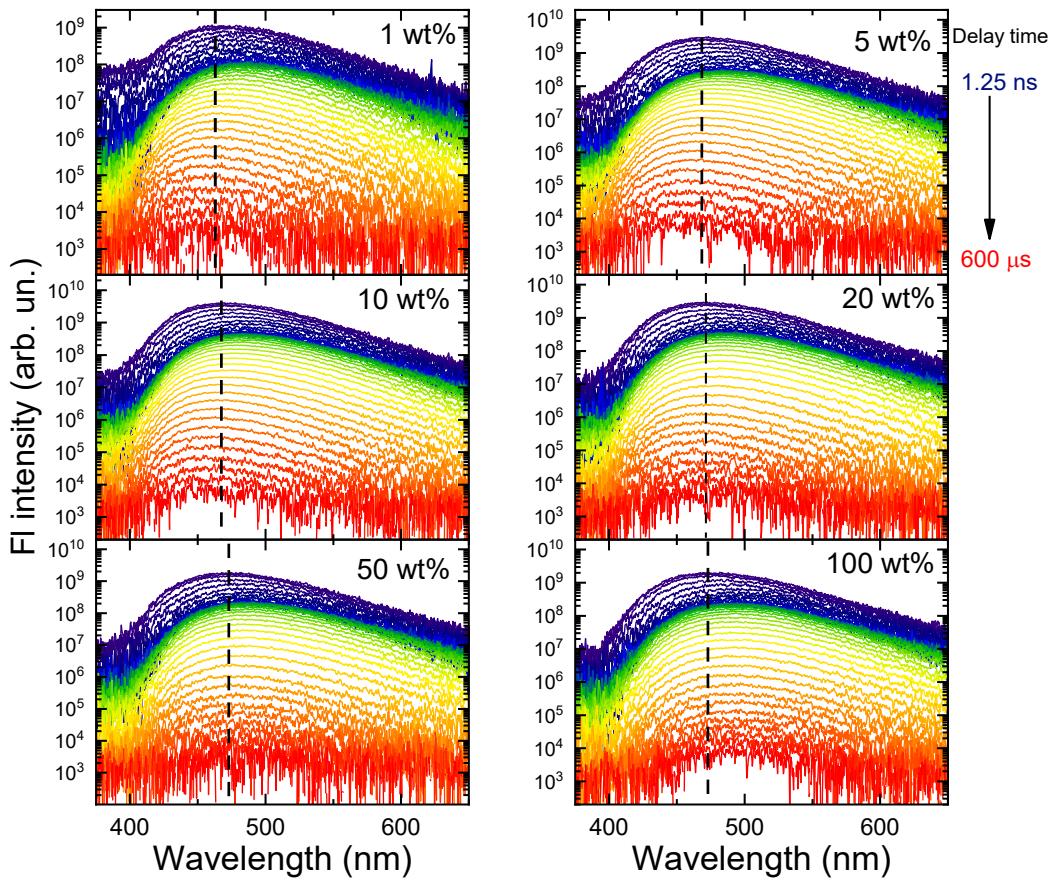
<sup>e</sup> Radiative decay rate.

<sup>f</sup> TADF decay time.

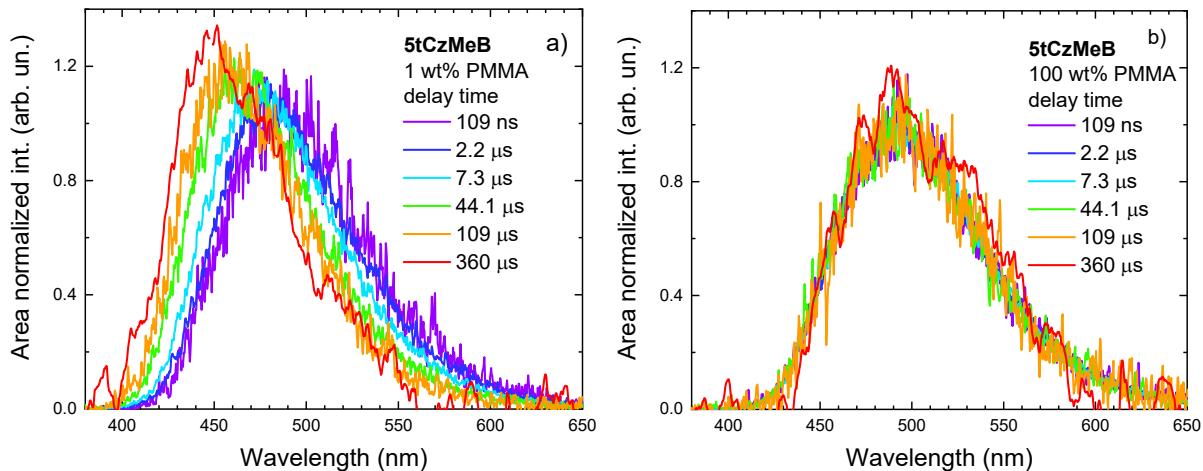
<sup>g, h, i, j</sup> ISC, rISC, nonradiative triplet decay and triplet concentration quenching rates, respectively.



**Fig. S5** Arrhenius plots for ISC and rISC rates for **5tCzMeB** doped at 1wt% and 100wt% in PMMA (a). Fluorescence decay transients of 1wt% and 100wt% PMMA films of **5tCzMeB** at 300-180K temperature (b, c, respectively).



**Fig. S6** TRPL spectra of **5tCzMeB** in PMMA at different doping loads in oxygen-free surrounding at room temperature. Lines are guides for eyes.



**Fig. S7** Area-normalized time-resolved fluorescence spectra of 1 wt% (a) and 100 wt% (b) PMMA films of **5tCzMeB** at room temperature.

## References

- 1 T. Hosokai, H. Matsuzaki, H. Nakanotani, K. Tokumaru, T. Tsutsui, A. Furube, K. Nasu, H. Nomura, M. Yahiro and C. Adachi, *Sci. Adv.*, 2017, **3**, e1603282.
- 2 G. Kreiza, D. Banovičius, J. Jovaišaitė, K. Maleckaitė, D. Gudeika, D. Volyniuk, J. V. Gražulevičius, S. Juršėnas and K. Kazlauskas, *J. Mater. Chem. C*, 2019, **7**, 11522–11531.