Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Thermally Activated Delayed Fluorescence with Narrow Emission Spectrum and Organic Room Temperature Phosphorescence by Controlling Spin-Orbit Coupling and Phosphorescence Lifetime of Organic Molecules

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S1 - Synthesis

2,7-di(carbazol-9-yl)-N-hexylacridin-9-one (**1**) and 3,7-di(carbazol-9-yl)-N-butylphenothiazine (**2**) were synthesized according to the previously established procedure.[1]

3,5-di(9H-carbazol-9-yl)pyridine (**BCbmPy**) was prepared according to the literature.[2]

S2 – Supplementary photophysical data and experimental details

Photophysics. Solutions (10^{-5} M) were degassed with 5 freeze-thaw cycles. Absorption and fluorescence spectra were collected using a UV-3600 double beam spectrophotometer (Shimadzu), and a Fluorolog fluorescence spectrometer (Jobin Yvon). Temperature-dependent and room temperature measurements were acquired using a continuous flow liquid nitrogen cryostat coupled with a vacuum pump. Phosphorescence (PH), prompt fluorescence (PF), and delayed fluorescence (DF) spectra and decays were recorded using nanosecond gated luminescence and lifetime measurements (from 400 ps to 1 s) with a high energy pulsed Nd:YAG laser emitting at 355 nm (EKSPLA) or N2 laser emitting at 337 nm (Lasertechnik Berlin). Emission was focused onto a spectrograph and detected on a sensitive gated iCCD camera (Stanford Computer Optics) having a sub-nanosecond resolution. PF/DF time-resolved measurements were performed by exponentially increasing gate and delay times. Photoluminescence quantum yields in solid state were determined using already described methods.[3,4] Photoluminescence quantum yield in solution was recorded against 9,10-diphenylanthracene as a standard, with $\Phi_{PL} = 0.90$.[5]

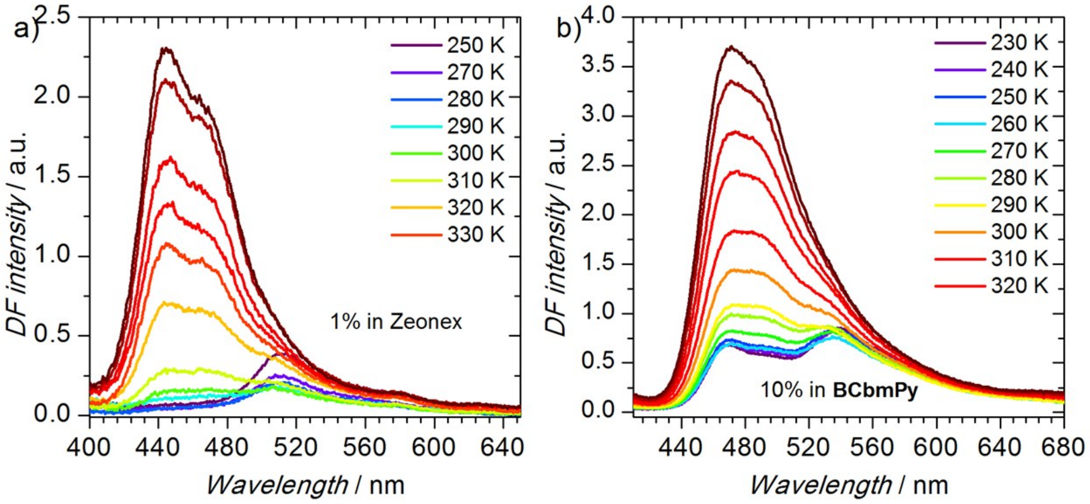

Figure S1. Integrated spectra of **1** doped films at 10 ms delay at various temperatures. a) 1% in zeonex; b) 10% in **BCbmPy**.

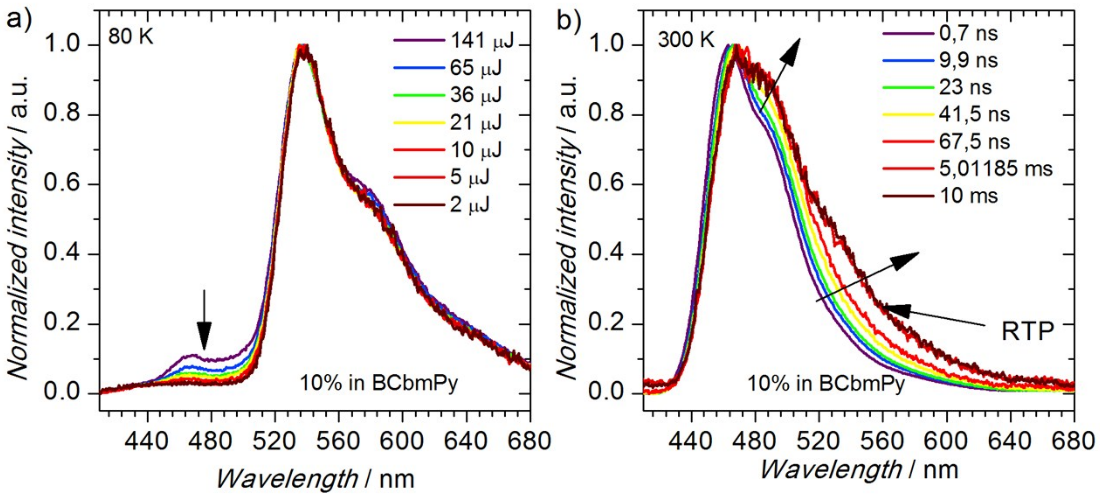

Figure S2. a) Phosphorescence spectra of **1** (delay 10 ms) at 80 K recorded using various laser pulse energy. The delayed fluorescence shows supralinear laser pulse dependence which indicates triplet-triplet annihilation; b) Time-resolved spectra of **1** recorded at 295 K. The emission spectrum gradually loses the vibronic structure with time delay. RTP – room temperature phosphorescence.

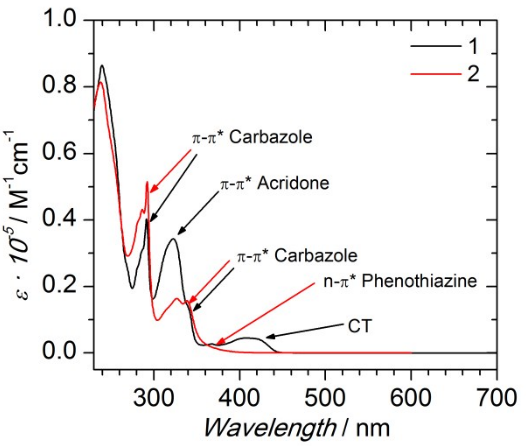

Figure S3. Absorption spectra of **1** and **2** in methylcyclohexane (MCH).

Table S1. Absorption maxima and absorption coefficients for **1** and **2** in methylcyclohexane (MCH).

Compound	**λ_{max}, nm ($\varepsilon \cdot 10^{-5}$, M^{-1} cm^{-1})**
1	239 (0.87), 291 (0.40), 322 (0.34), 407 (0.05)
2	238 (0.81), 292 (0.52), 327 (0.16), 338 (0.16)

Table S2. Prompt, delayed fluorescence and phosphorescence lifetime in various solvents and matrices.

Molecule	**Environment**	**τ_{PF}, ns[a]**	**τ_{DF}, ms[b]**	**τ_{PH}, ms[c]**
1	Toluene	14 ± 2	-	-
	Ethanol	18 ± 2	-	-
	Zeonex, 1%	9.1 ± 0.6	26.8 ± 0.7	500 ± 200 (80 K)
	BCbmPy, 10%	9.3 ± 0.4	10.2 ± 0.5	-
2	Toluene	1.81 ± 0.02	-	-
	Zeonex, 1%	1.96 ± 0.02	-	23 ± 1 (295 K) 38 ± 2 (80 K)
	BCbmPy, 10%	-	-	2.2 ± 0.2 (58 %) 19 ± 2 (42 %) (295 K) 32 ± 2 (80 K)

[a] prompt fluorescence lifetime at room temperature; [b] delayed fluorescence lifetime at room temperature; [c] phosphorescence lifetime.

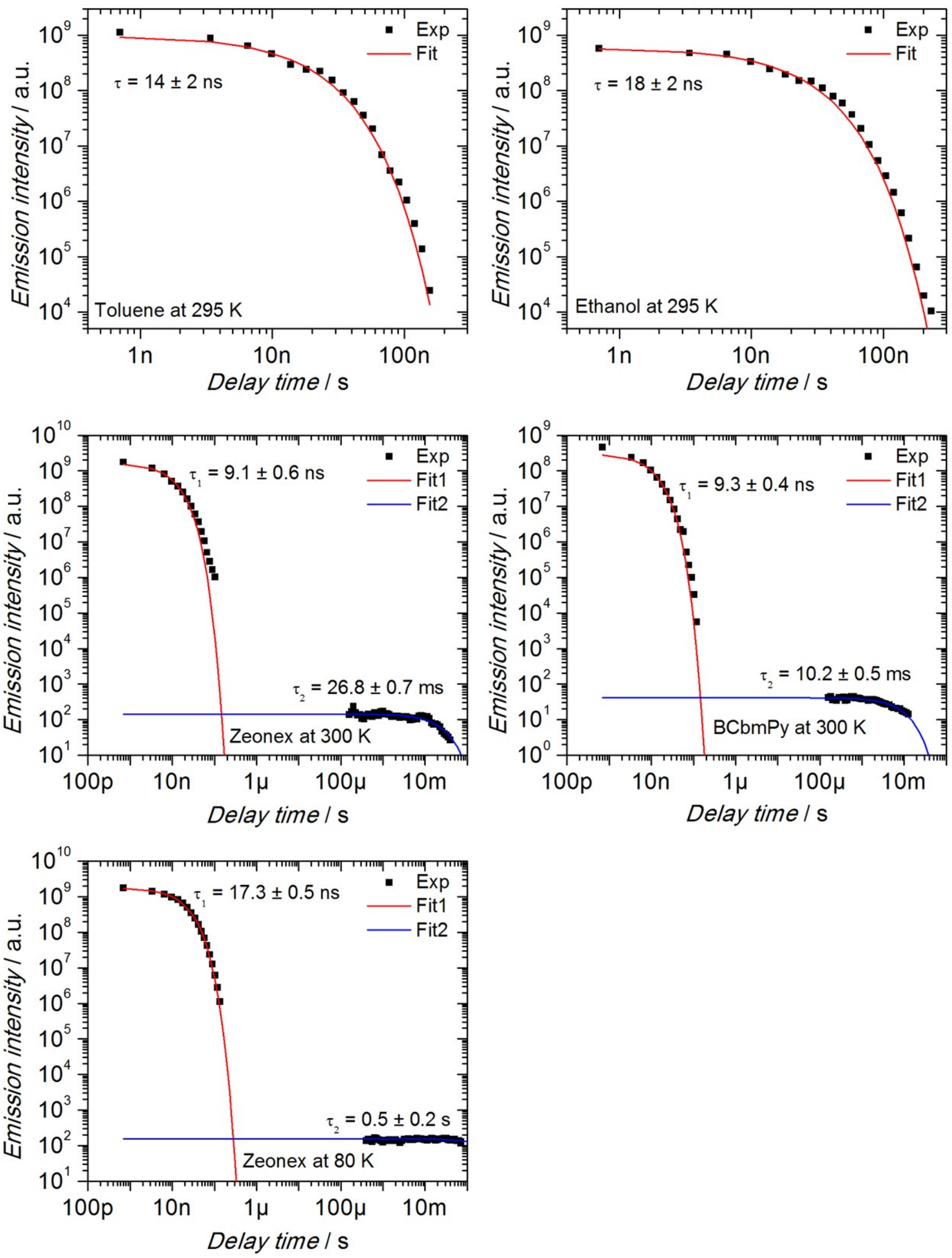

Figure S4. Prompt, delayed fluorescence and phosphorescence decay fits of **1** in various solvents and matrices.

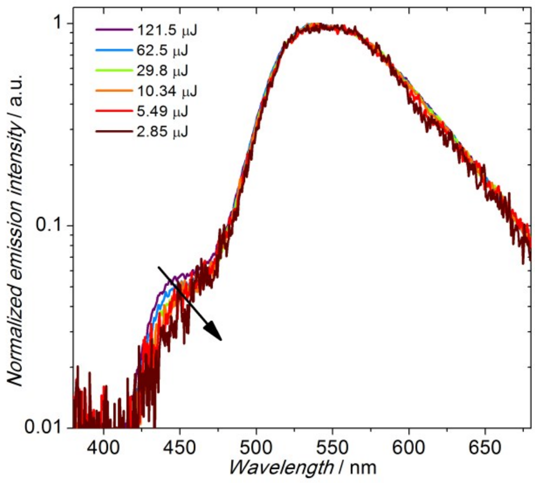

Figure S5. Phosphorescence spectra of **2** 10% in **BCbmPy** recorded at various laser pulse energy. A tail at *ca.* 450 nm decreases at small powers indicating supralinear power dependence, which suggests triplet-triplet annihilation.

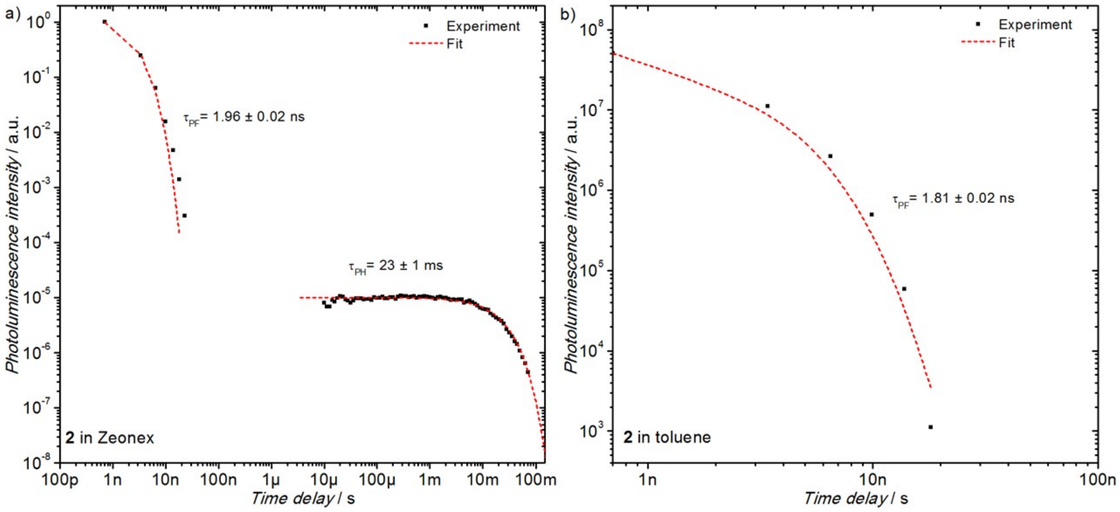

Figure S6. Room temperature decay of **2** in zeonex (a) and toluene (b) with fitting curves.

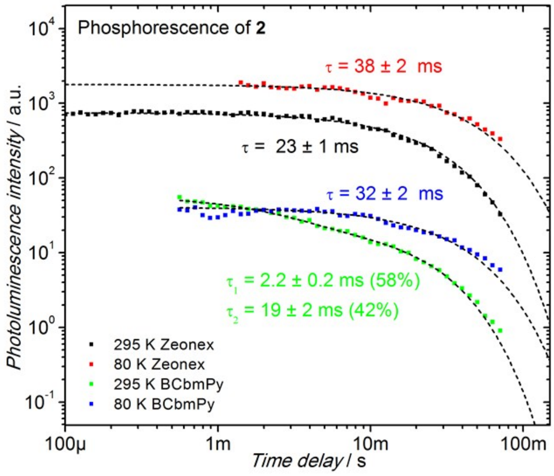

Figure S7. Room and low-temperature phosphorescence decay of **2** in zeonex and **BCbmPy** with fitting curves.

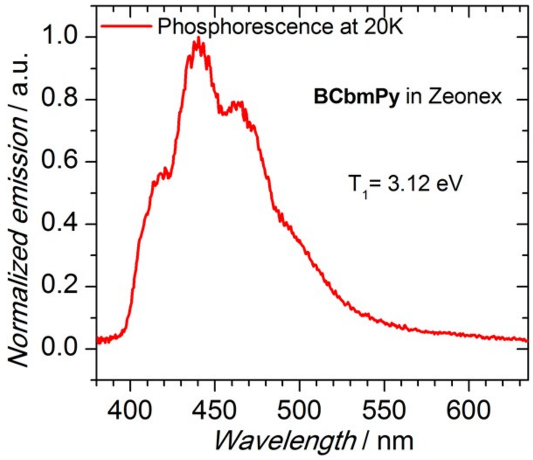

Figure S8. Fluorescence and phosphorescence spectra of **BCbmPy** 1% doped zeonex film (delay 10 ms).

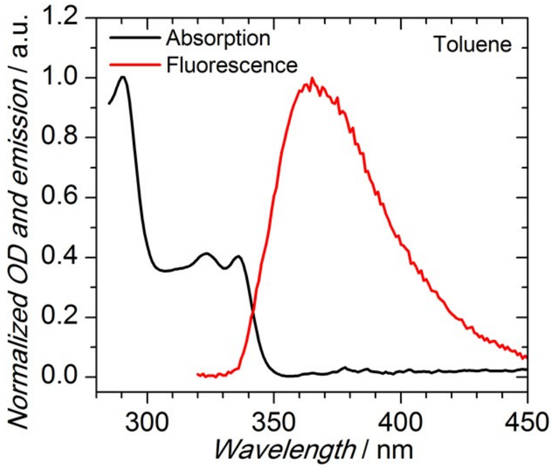

Figure S9. Absorption and emission spectra of **BCbmPy** in toluene.

S3 – Device fabrication experimental details

All organic evaporated compounds were purified by Creaphys organic sublimation system, TAPC - 4,4′-Cyclohexylidenebis[*N*,*N*-bis(4-methylphenyl)benzenamine] (97%, Sigma Aldrich), NPB - *N,N′*-Di-1-naphthyl-*N,N′*-diphenylbenzidine (TCI-Europe), TPBi - 2,2',2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (Molekula), LiF (99.995%, Sigma Aldrich), Aluminium wire (99.9995%, Alfa Aesar). OLED devices were fabricated using pre-cleaned indium-tin-oxide (ITO) coated glass substrates with a sheet resistance of 20 Ω/cm^2 and ITO thickness of 100 nm. The formed OLED devices had a pixel size of 4 mm by 2 mm. All organic and cathode layers were thermally evaporated using Kurt J. Lesker Spectros II deposition at 10^{-6} mbar. All organic materials and aluminium were deposited at a rate of 1 Å s^{-1} and between 0.1 – 2 Å s^{-1} for coevaporated layers. The LiF layer was deposited at 0.2 Å s^{-1}. Characterization of OLED devices was conducted in the 10-inch integrating sphere (Labsphere) connected to a Source Measure Unit.

S4 – References

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(2) Z. Liu, M. F. Qayyum, C. Wu, M. T. Whited, P. I. Djurovich, K. O. Hodgson, B. Hedman, E. I. Solomon, M. E. Thompson, *J. Am. Chem. Soc.* **2011**, *133* (11), 3700-3703.

(3) Williams, A. T. R.; Winfield, S. A.; Miller, J. N.: Analyst **1983**, *108*, 1067.

(4) J.C. de Mello, H.F. Wittmann, R.H. Friend, Adv Mater, **1997**, *9*(3), 230.

(5) S. Hamai, F. Hirayama, J. Phys. Chem., **1983**, *87*, 83.