Electronic Supplementary Information

Room temperature phosphorescence *vs* thermally activated delayed fluorescence in carbazole – pyrimidine cored compounds

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Table S1 Peak positions of absorption, fluorescence and phosphorescence spectra of the compounds **1a-d** in 1 w.t.% Zeonex and PMMA thin films.

	λ_{ABS}^{Zeonex} (nm)[a]	λ_{ABS}^{PMMA} (nm)[b]	λ_{FL}^{Zeonex} (nm)[c]	λ_{FL}^{PMMA} (nm) [d]	λ_{PH}^{Zeonex} (nm) [e]	λ_{PH}^{PMMA} (nm) [f]
1a	352	342	384	404	460	461
1b	355	342	388	404	463	463
1c	362	362	394	420	475	460
1d	358	344	435	475	477	488

[a], [c], [e] Absorption, fluorescence and phosphorescence spectrum maximum, respectively, in 1 w.t. % Zeonex film.
[b], [d], [f] Absorption, fluorescence and phosphorescence spectrum maximum, respectively, in 1 w.t. %PMMA film.

Table S2 Orbital composition of $S_0 \rightarrow T_1$ and $S_0 \rightarrow T_2$ transitions with fractional contribution values for carbazole-pyrimidine compounds **1a-1d**. The main transitions are indicated in bold.

	$S_0 \rightarrow T_1$		$S_0 \rightarrow T_2$	
	Transition	Contribution (%)	Transition	Contribution (%)
1a	HOMO-5→LUMO	0.13	HOMO-1→LUMO+1	0.02
	HOMO-1→LUMO	0.02	HOMO-3→LUMO	0.10
	HOMO-3→LUMO+1	0.07	HOMO-1→LUMO	0.04
	HOMO-1→LUMO	**0.61**	HOMO-1→LUMO+1	0.08
	HOMO→LUMO	0.04	**HOMO→LUMO**	**0.75**
	HOMO-1→LUMO+1	0.12		
1b	HOMO-11→LUMO	0.11	HOMO-10→LUMO	0.08
	HOMO-10→LUMO+1	0.03	HOMO-5→LUMO	0.05
	LUMO-10→LUMO+4	0.03	HOMO-1→LUMO+1	0.07
	HOMO-5→LUMO+1	0.19	HOMO-1→LUMO+4	0.04
	HOMO-1→LUMO	**0.46**	**HOMO→LUMO**	**0.76**
	HOMO→LUMO+1	0.13		
	HOMO→LUMO+5	0.03		
1c	HOMO-8→LUMO	0.08	HOMO-7→LUMO	0.05
	HOMO-7→LUMO	0.04	HOMO-5→LUMO	0.06
	HOMO-5→LUMO+1	0.03	HOMO-1→LUMO	0.04
	HOMO-1→LUMO	**0.69**	HOMO-1→LUMO+1	0.05
	HOMO-1→LUMO+1	0.03	**HOMO→LUMO**	**0.77**
	HOMO→LUMO	0.03	HOMO→LUMO+1	0.03
	HOMO→LUMO+1	0.09		
1d	HOMO-10→LUMO	0.02	HOMO-7→LUMO	0.03
	HOMO-7→LUMO+1	0.04	HOMO-1→LUMO	0.03
	HOMO-2→LUMO	0.05	**HOMO→LUMO**	**0.95**
	HOMO→LUMO+1	**0.77**		
	HOMO→LUMO+5	0.08		
	HOMO→LUMO+7	0.03		

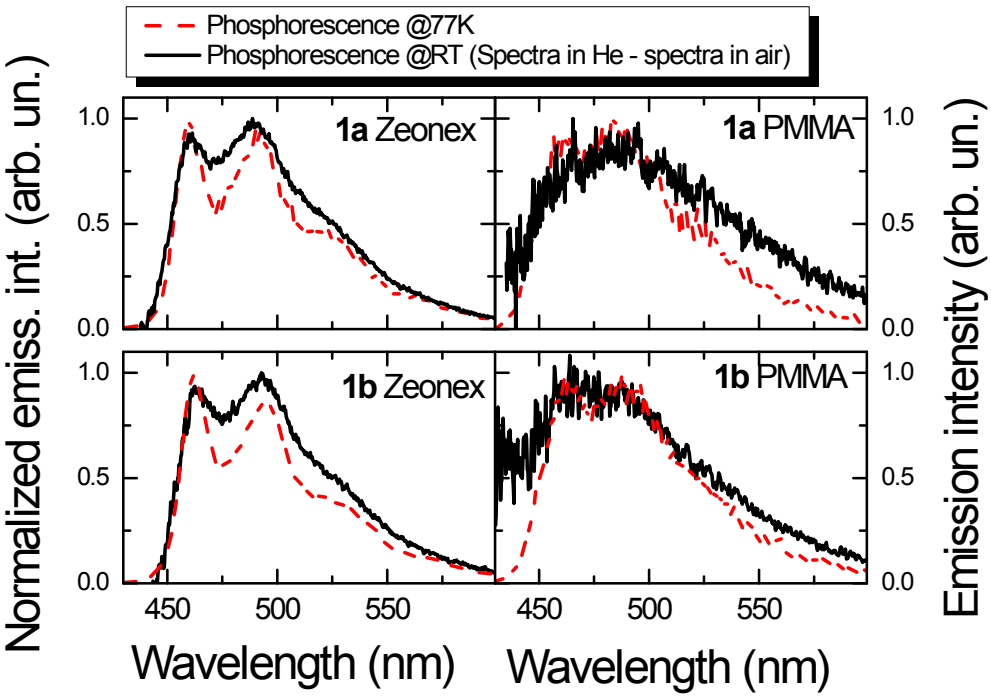

Fig. S1 Phosphorescence spectra of compounds **1a** and **1b** in 1w.t. % in Zeonex and PMMA films at 77K (red lines) and room temperature (black lines). Room temperature PH spectra were obtained by subtracting the Fl spectra obtained in oxygen-saturated ambient from those obtained in oxygen-deficient ambient.

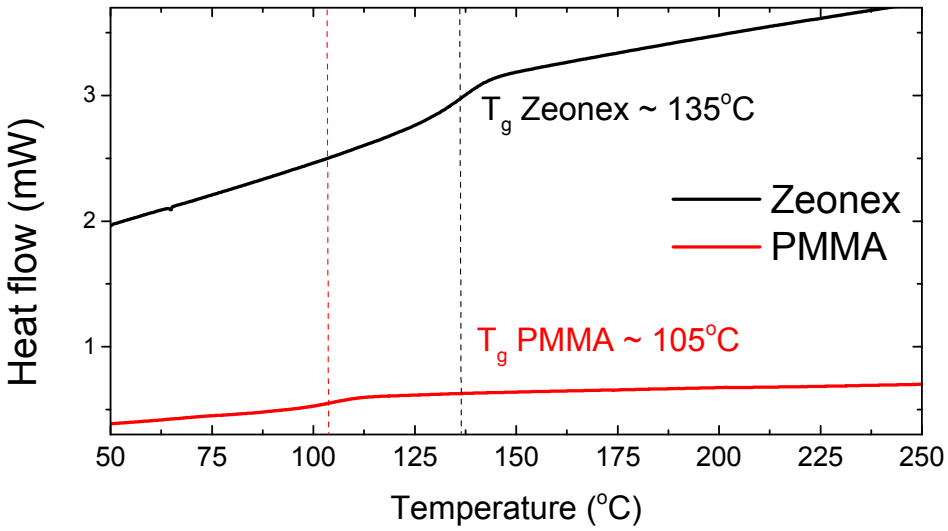

Fig. S2 Differential scanning calorimetry curves of Zeonex and PMMA.

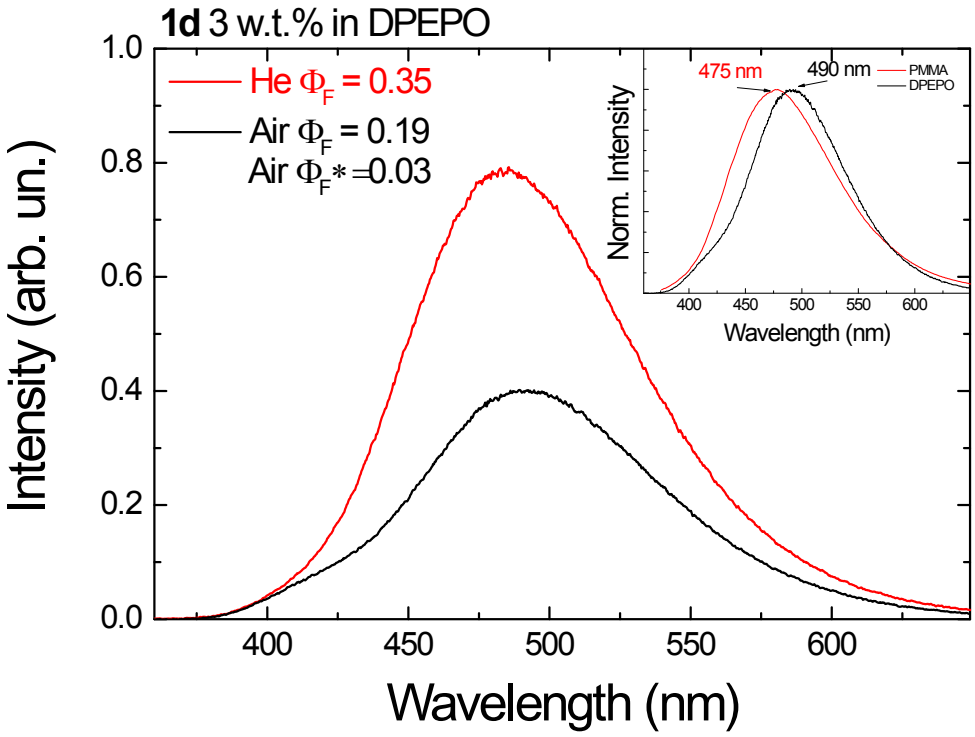

Fig. S3 Fluorescence spectra of 3 w.t.% DPEPO film of compound **1d** in oxygen-saturated (black line) and oxygen-deficient (red line) ambient. Φ_F is a fluorescence quantum yield, Φ_F* - fluorescence quantum yield excluding the TADF part (true Φ_F for the prompt fluorescence). Inset shows fluorescence spectra of 3 w.t.% DPEPO (black line) and 1 w.t.% PMMA (red line) films of compound **1d**.

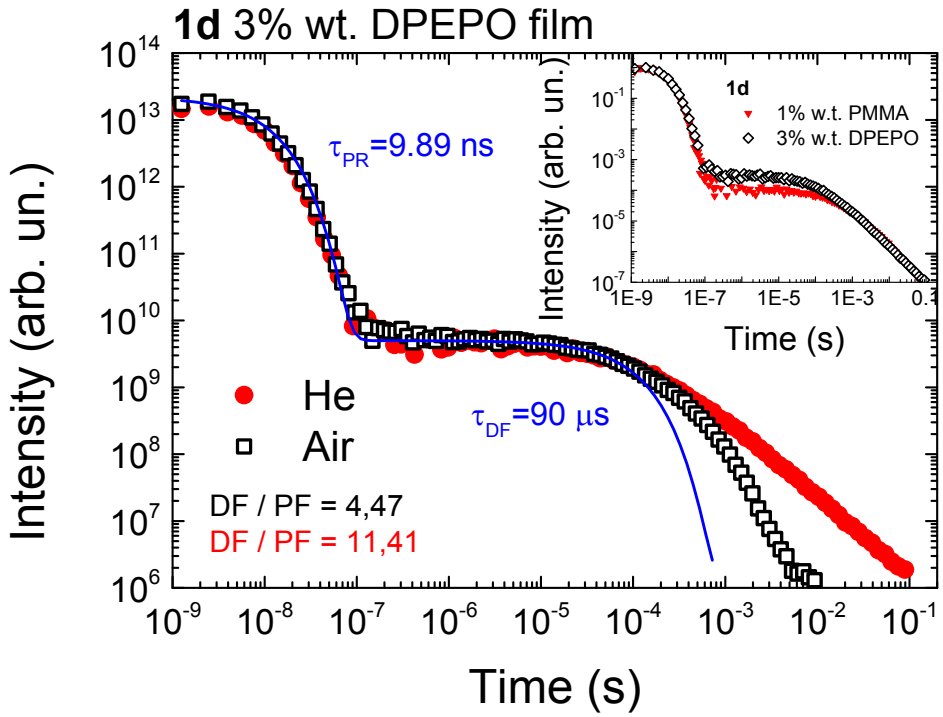

Fig. S4 Log – log scale photoluminescence decays of 3 w.t.% DPEPO film of compoud **1d** in oxygen-saturated and oxygen-deficient ambients. The inset shows the comparison of log – log scale photoluminescence decays of **1d** in 1w.t.% PMMA film (red triangles) and 3 w.t.% DPEPO film (open squares). Blue line is the bi-exponential fit.

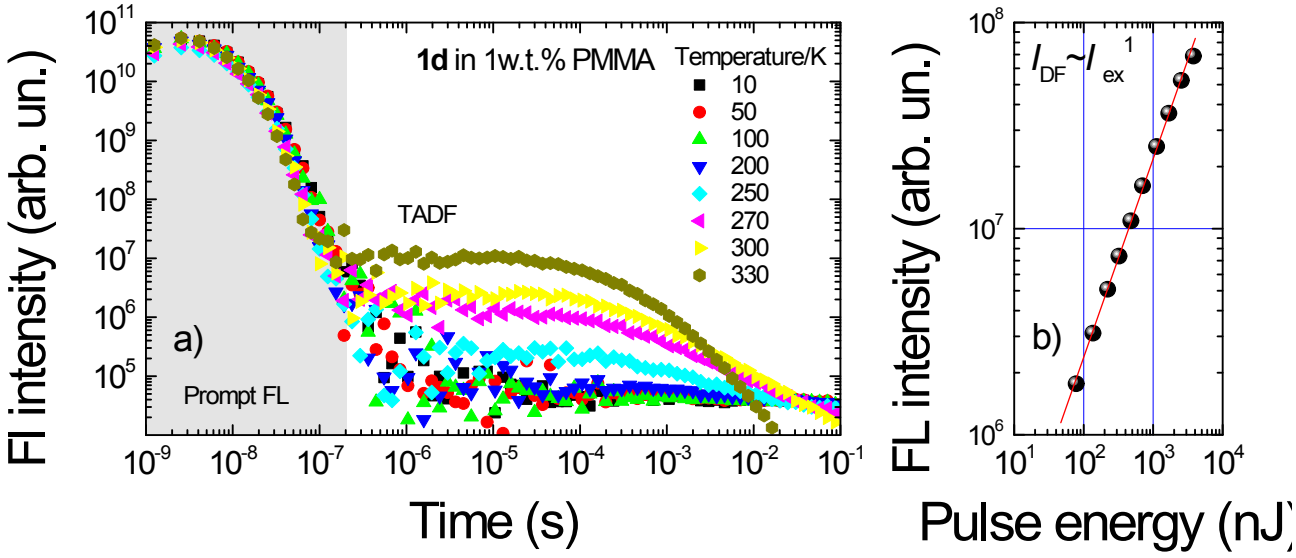

Fig. S5 a) Log – log scale photoluminescence decays of compound **1d** in 1% w.t. PMMA at various temperatures. The emergency of TADF is clearly seen at the temperatures above ~200K. b) Delayed fluorescence intensity dependence on the laser fluence of compound **1d** in 1% w.t. PMMA. Red line shows linear fit.

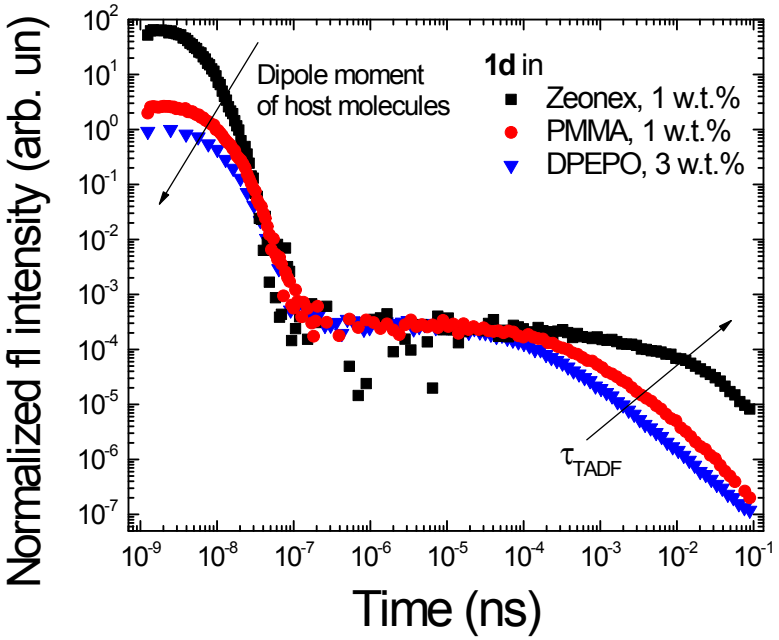

Fig. S6 Fluorescence decay transients of compound **1d** in diluted Zeonex (black figures), PMMA (red figures) and DPEPO (blue figures) films. Transients were normalized to initial intensity of delayed fluorescence. Clear trend of decrease of delayed fluorescence lifetime (τ_{TADF}) upon the increase of dipole moment of host molecules is observed.

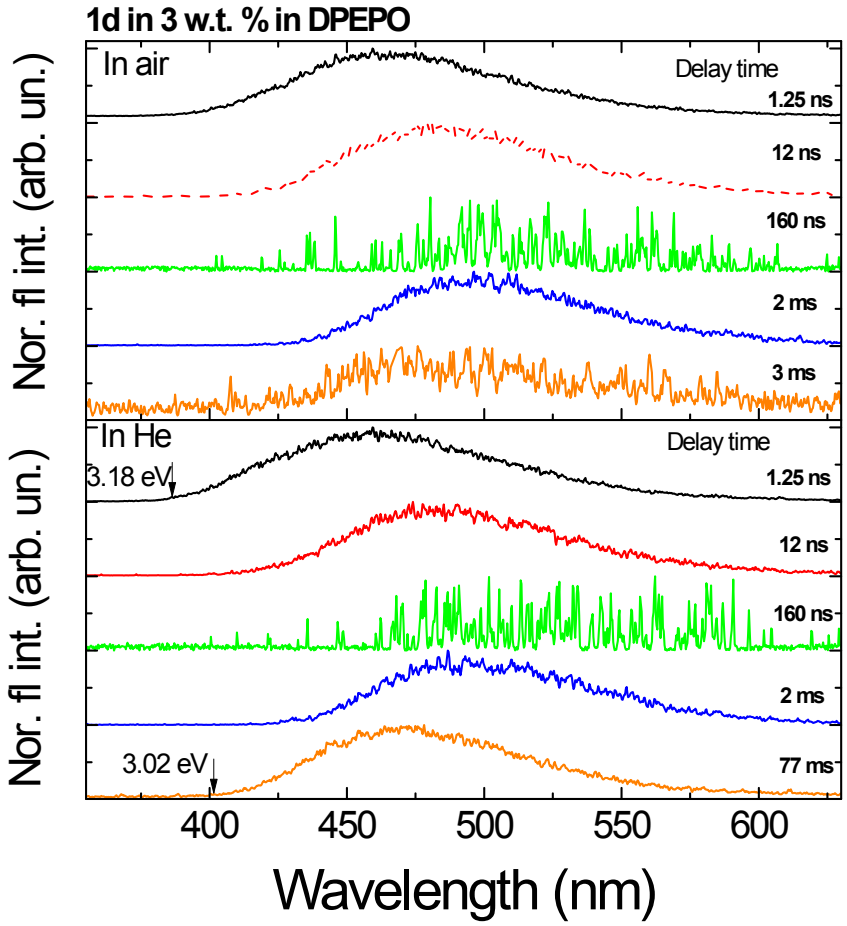

Fig. S7 Normalized time resolved fluorescence spectra of 3 w.t.% **1d**:DPEPO film in oxygen-saturated (upper picture) and oxygen-deficient (lower picture) ambients. Numbers denotes the delay time. Numbers near the arrows denotes the on-set energies of fluorescence spectra. All spectra were shifted vertically for clarity.

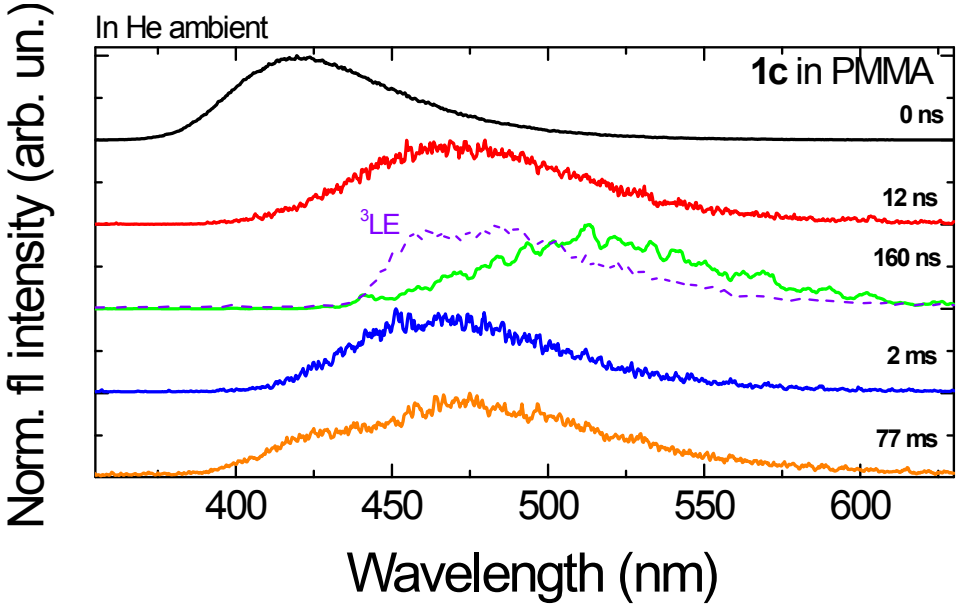

Fig. S8 Normalized time resolved fluorescence spectra of 1 w.t.% **1c** PMMA film in oxygen-deficient ambient. Numbers denote the delay time. Dotted spectrum is phosphorescence spectra obtained at 77K temperature. All spectra were shifted vertically for clarity.

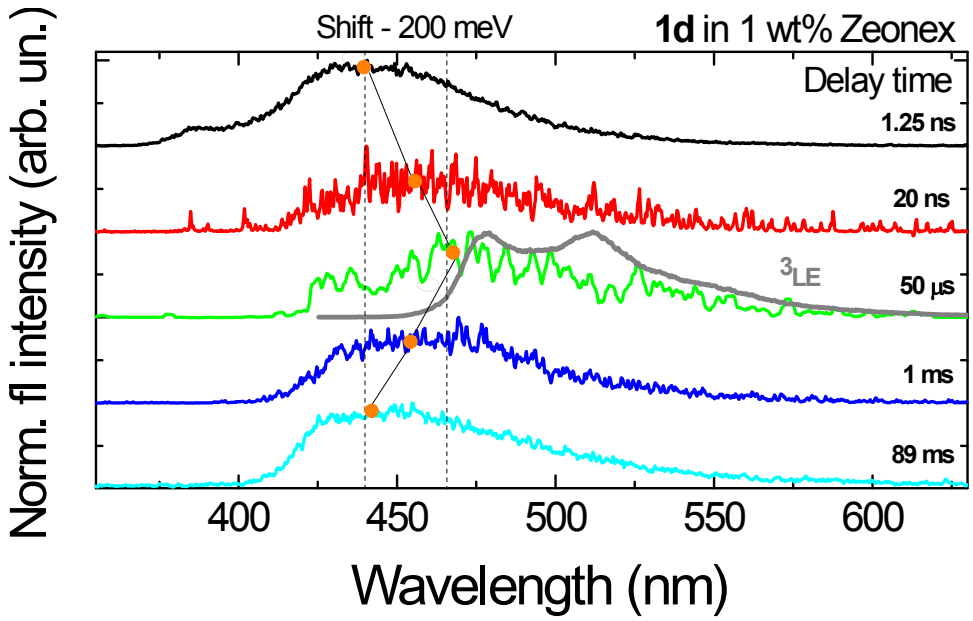

Fig. S9 Normalized time resolved fluorescence spectra of 1 w.t.% **1d** Zeonex film in oxygen-deficient ambient. Numbers denotes the delay time. Dark grey spectrum is phosphorescence spectra obtained at 77K temperature. All spectra were shifted vertically for clarity.