

Supplementary Material

Supplementary Table 1. Summary of device performance parameters for state-of-the-art OLEDs using interfacial exciplex as host, including both thermal-evaporated OLEDs (e-OLEDs) and solution-processed OLEDs (s-OLEDs), respectively.

Type	EML	$V_{on/1000}$ [V]	$L_{max.}$ [cd/m ²]	$EQE_{max./1000}$ [%]	$PE_{max./1000}$ [lm/W]	CIE [x,y]	Ref.
e-FOLED	TAPC:1%DBP/TmPyTz	2.18/-	520.3	10.1/-	17.8/-	0.62,0.38 [a]	[1]
	TAPC:1%DBP/TAPC(3nm)/TmPyTz [b]	2.18/-	457.1	14.5/-	42.9/-	0.53,0.46 [a]	[1]
	TAPC:1%DBP/mCP(3nm)/TmPyTz [c]	2.18/-	2956.8	14.8/-	38.8/-	0.54,0.45 [a]	[1]
	TCTA/rubrene(0.2nm)/TPBi	3.1/-	18310	-/-	12.7/-	[d]	[2]
e-PhOLED	CBP:6 mol.% Ir(ppy) ₃ /B3PYMPM	-/-	-	20.1/-	-/-	[e]	[3]
	TAPC/BTPC:11 wt.% Flrpic	2.5/3.4	-	-/17.2	-/33.8	[f]	[4]
	TCTA/CzTrz: 3% PO-01[i]	-/-	-	27.0/25.6[g]	73.1/52.1[g]	[h]	[5]
	TAPC:o-DTPPC: 6 wt.% Ir(mphmq) ₂ tmd	4.35	>15000	21.0/18.8[g]	18.0/12.6[g]	[j]	[6]
	TAPC/Ir(ppy) ₂ (acac) (0.8nm)/TmPyPB [k]	5.76[l]/-	~ 40000	36.9/-	60.0/-	0.35,0.61	[7]

	TCTA/(tbt) ₂ Ir(acac) (0.3 nm) /B3PYMPM	3.2/-	17400	19.5/12.0	53.1/-	[m]	[8]
e-TADF OLED	CBP: 5 wt.% 4CzIPN/B4PyPPM	2.33/	-	25.7/24.8	106.9/79.4	[n]	[9]
	CBP: 20 wt.% DACT-II/B4PyMPM	2.30	>10000	27.6/21.7	124.5/76.5	[o]	[10]
s-OLED , in which s-FOLED , s-PhOLED and s-TADF OLED were classified by their used dopant, i.e. fluorescent, phosphorescent or TADF emitter, respectively.							
s-FOLED	-	-	-	-	-	-	-
	m-MTDATA: 1 wt.% Ir(Flpy-CF ₃) ₃ /TmPyPB	2.36/3.0 3	43085	25.2/23.7	97.2/72.5	0.52,0.47	[11]
	m-MTDATA: 10 wt.% G0/TmPyPB	2.36/3.0 3	41539	18.1/17.8	81.1/62.5	0.35,0.59	[11]
s-PhOLED	m-MTDATA: 5 wt.% Ir(TPAPQ) ₂ (acac)/TmPyPB	2.36/3.4 2	17902	16.3/14.9	29.0/18.8	0.64,0.36	[11]
	m-MTDATA: 3 wt.% Ir(DPA-Flpy-CF ₃) ₂ acac/TmPyPB	2.3/2.8 [p]	~ 10000	19.3/19.0[p]	44.5/36.2[p]	0.64,0.36	[12]
	m-MTDATA: 3 wt.% Ir(Flpy-CF ₃) ₂ acac/TmPyPB	2.2/2.6 [p]	23005	23.7/-	80.4/-	0.56,0.43	[13]
	CBP: 5 wt.% 4CzIPN/B4PyMPM	2.5/4.7	-	16[p]/13	55/27	[n]	[14]
s-TADF OLED	TAPC:20 wt.% PAPTC/TmPyPB	2.50/-	26321	14.9/14.3	50.1/-	0.34,0.56	[15]
	DCzDCN:SimCP2(2:1):10 wt.% TXO-TPA/CDBP(3.5 nm)/B4PYPPM	-	-	10.02/-	20.71/-	0.32,0.34 [q]	[16]

Note:

[a]: at 1mA cm⁻². Because of incomplete energy transfer from TAPC/TmPzTz interfacial exciplex host to DBP, EL spectra of e-OLEDs were varied as increasing the driving voltage(or current density or luminance);

[b]: exciton formation region was dominantly formed at the TAPC/TmPyTz interface, followed by Förster energy transfer to DBP emitter throughout pure TAPC(3nm) layer;

[c]: actual exciplex host was long-range charge-transfer couple of TAPC and TmPyTz, in which mCP functioned as spacer;

[d]: EL spectra of OLEDs displayed the whole emission from rubrene emitter, in which λ_{EL} located at 561 nm;

[e]: purely from the green Ir(ppy)₃ emitter;

[f]: purely from the blue FIrpic emitter;

[g]: at the luminance of 5000 cd/m²;

[h]: purely from the orange PO-01 emitter;

[i]: in this work, device lifetime, efficiency and roll-off behaviors of PhOLEDs using interfacial or bulk exciplex host were systematically compared in parallel, confirming the superiorities of interfacial exciplex host in optimizing all of these critical device parameters;

[j]: purely from the red Ir(mphmq)₂tmd emitter;

[k]: interfacial exciplex couple was TAPC/TmPyPB, and the device was two-unit tandem PhOLED;

[l]: at 0.2 mA/cm²;

[m]: purely from the orange (tbt)₂Ir(acac) emitter;

[n]: purely from the green 4CzIPN TADF emitter;

[o]: purely from the green DACT- II TADF emitter;

[p]: at a luminance of 100 cd/m².

[q]: at a luminance of 500 cd/m². The EL spectra consisted of blue-orange complementary two colors for white emission, in which blue and orange component came from interfacial exciplex of CDBP/B4PYPPM (λ_{EL} : 445nm and TXO-TPA emitter (via partial Förster Energy transfer from the interfacial exciplex, i.e. λ_{EL} : 568 nm), respectively.

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