

Supporting Information

All Solution-Processed Red Organic Light-Emitting Diodes Based on New Thermally Cross-Linked Heteroleptic Ir(III) Complex

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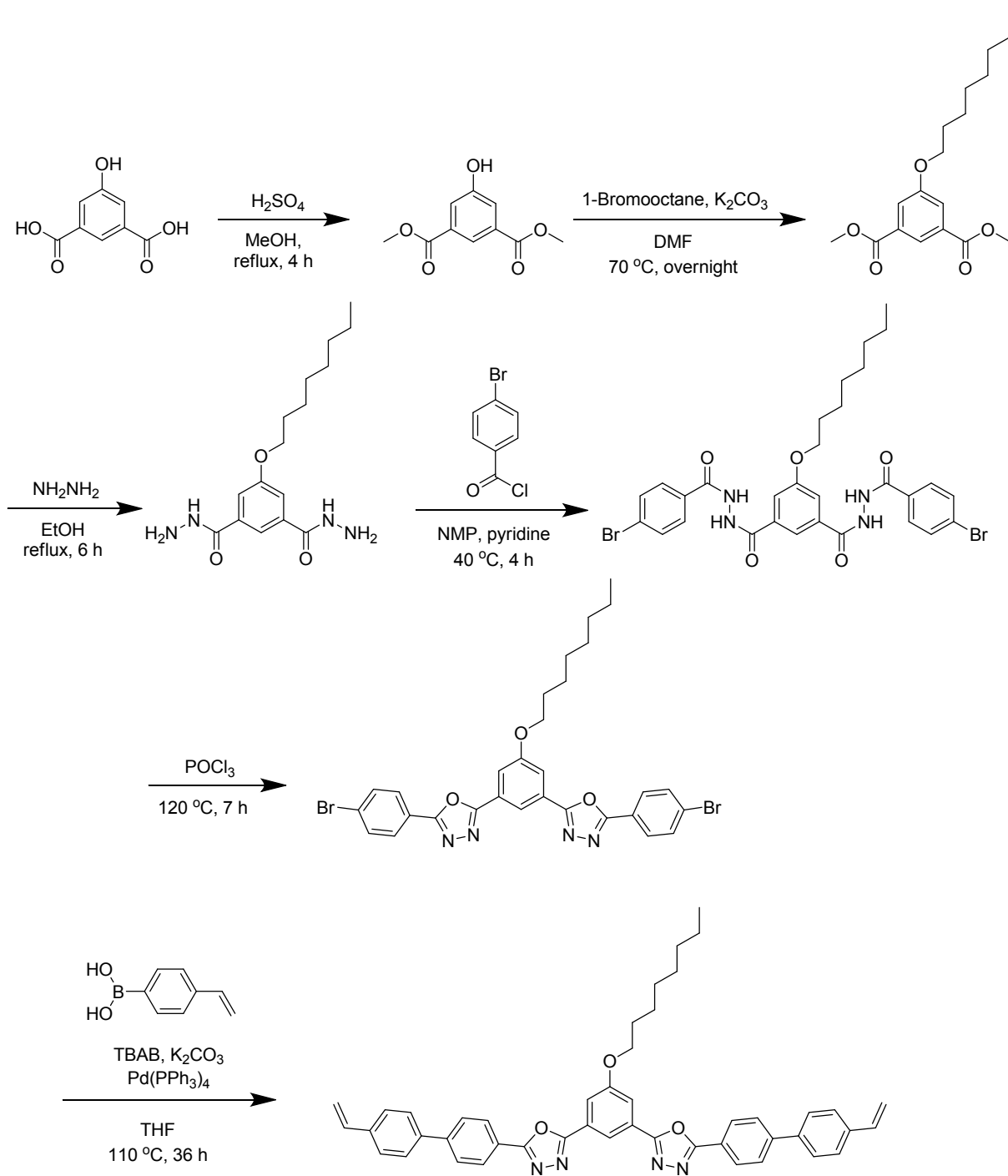
Device fabrication

Patterned indium tin oxide (ITO) glass substrate with a sheet resistance of 10Ω per square was pre-cleaned with a cleaning detergent (Sigma-Aldrich, Micro-90 concentrated cleaning solution) followed by deionized water, acetone, and isopropyl alcohol in ultrasonic bath at 50°C . After this cleaning cycle, the ITO glass was treated in UV-ozone chamber for 20 min before device fabrication. Firstly, the HTL was VNPB (Lumtec, 95%+), which is a 0.5 wt% solution in chlorobenzene (CB), was spin-coated onto the PEDOT:PSS (Clevios P VP AI4083). The HTL was then annealed at 150°C for 30 min in glove box for thermal cross-linking. The EML, which is a mixed solution of VNPB:DV-OXD (weight ratio, 1:1) doped with 10 wt% of the Ir(III) complex, were spin-coated onto the cross-linked HTL (X-HTL) coated substrate. The configuration of ITO/PEDOT:PSS (40 nm)/X-HTL (30 nm)/EML (40 nm)/TmPyPB (50 nm)/LiF (1 nm)/Al (100 nm). The EML was then annealed at 185°C for 30 min in glove box. ETL and cathode evaporated in vacuum chamber.

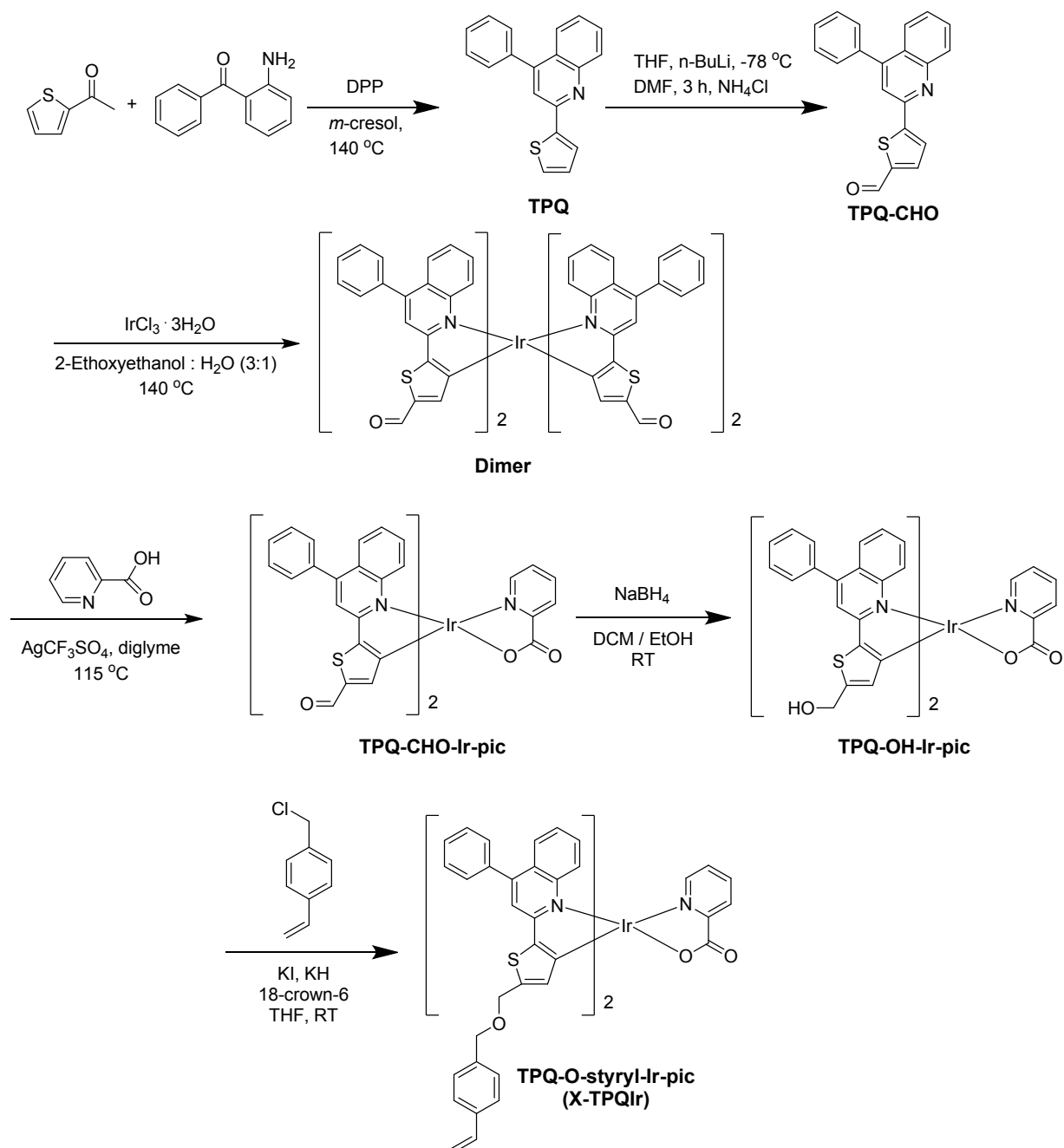
Compared the devices of ETL fabrication through vacuum deposition and solution-processing. The HIL, HTL and EML were followed cross-linking red PHOLEDs method. The ETL was TPBi, which was soluble in organic solvents, to compare the different method of ETL fabrication. Firstly, vacuum deposition was evaporated in vacuum at pressure 5×10^{-6} Torr. The deposition rate of ETL was 1 \AA/s . Secondly, solution-processing was a 1 wt% in CB. Which was spin-coated onto the cross-linked EML coated substrate. The ETL was then annealed at 100°C for 30 min in glove box to remove residual solvent. Finally, both devices, LiF and Al were evaporated under 5×10^{-6} Torr in a vacuum chamber at deposition rates of 0.1 \AA/s and 5 \AA/s , respectively. The emitting area of PHOLED device was 9 mm^2 for all the samples.

All measurements were carried out under ambient condition at RT. The thickness of each layer was measured by an Alpha-step IQ surface profiler (KLA Tencor, San Jose, CA). The

current density and voltage were controlled with a measurement unit (Keithley, model 236) power source. The luminance, current efficiency, external quantum efficiency, Commission International de L'Eclairage (CIE) coordinates (x,y), current density characteristics, and electroluminescence spectra were measured by a spectra scan CS-2000 photometer (Minolta).



Scheme S1 Synthetic route of DV-OXD.



Scheme S2 Synthetic route of X-TPQIr.

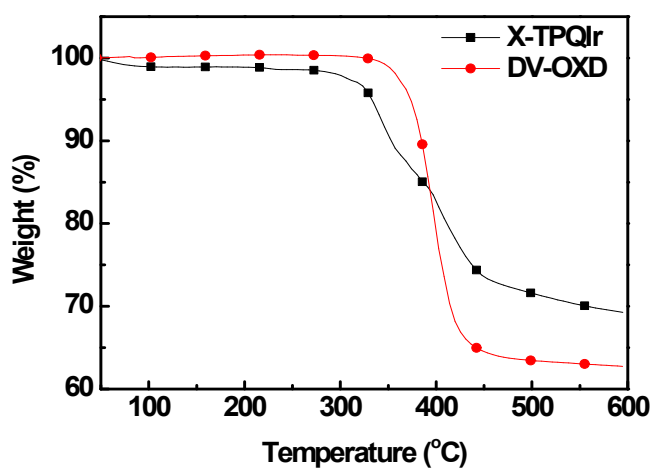


Fig. S1 TGA thermogram of X-TPQIr and DV-OXD.

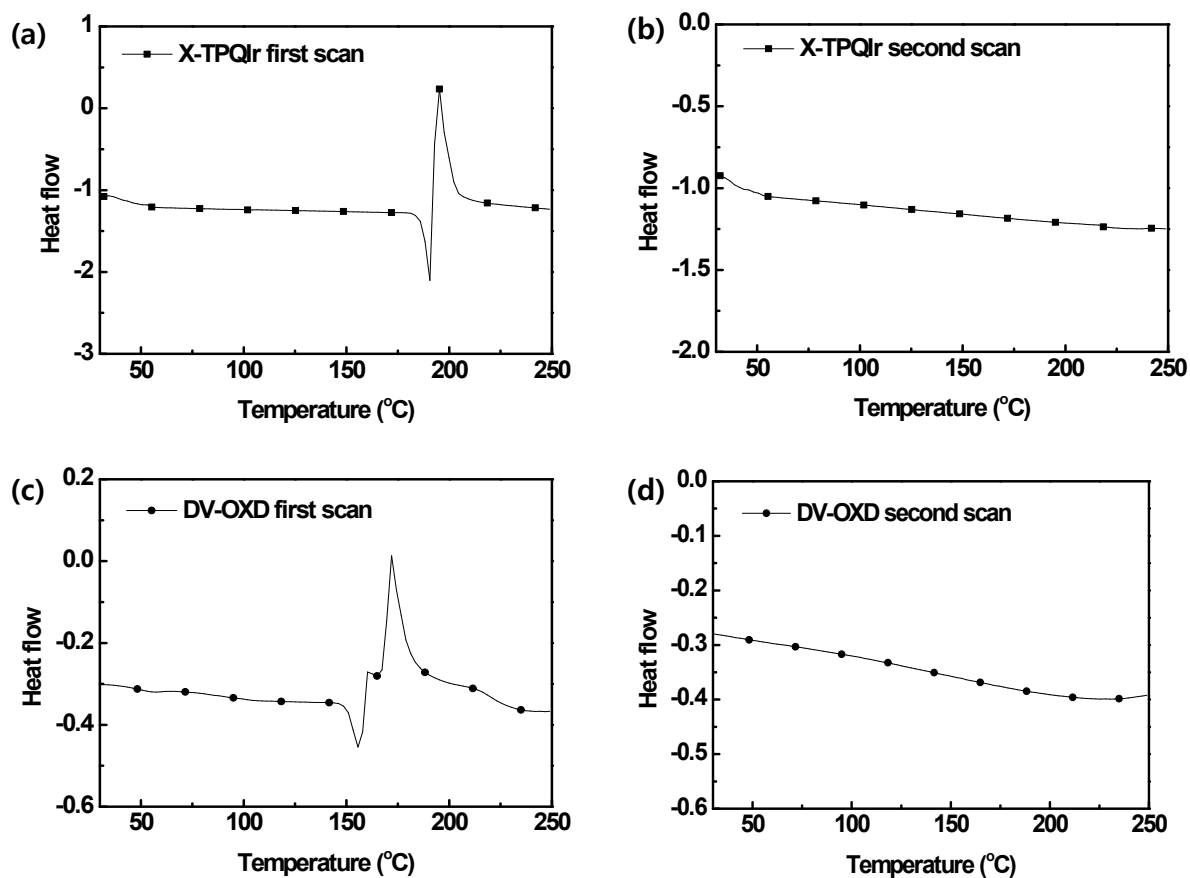


Fig. S2 DSC curves (first scan and second scan) of (a), (b) X-TPQIr and (c), (d) DV-OXD measured at a scan rate of 10 °C/min under a N₂ atmosphere.

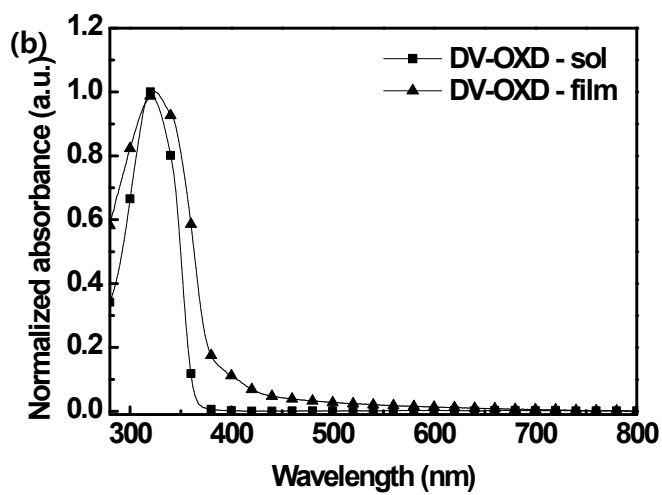
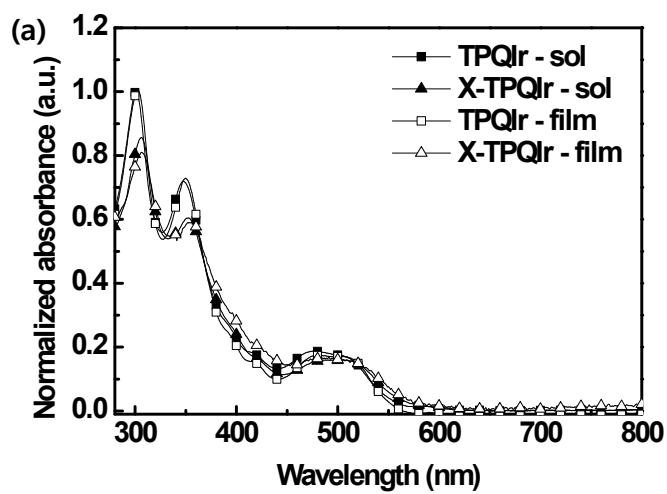


Fig. S3 UV-vis absorption of (a) X-TPQIr and (b) DV-OXD.

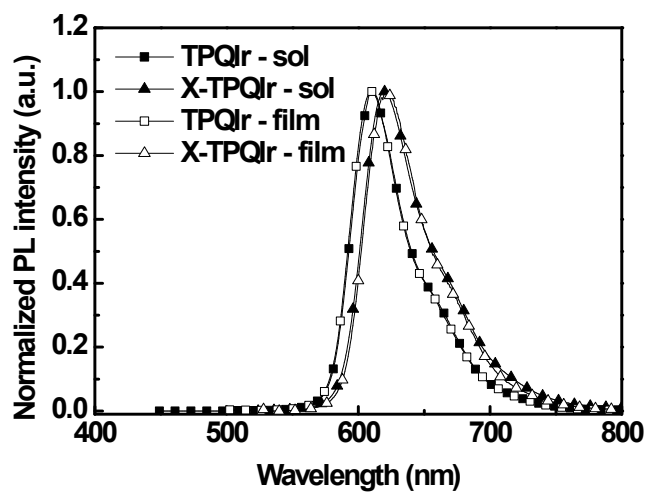


Fig. S4 PL spectra of X-TPQIr.

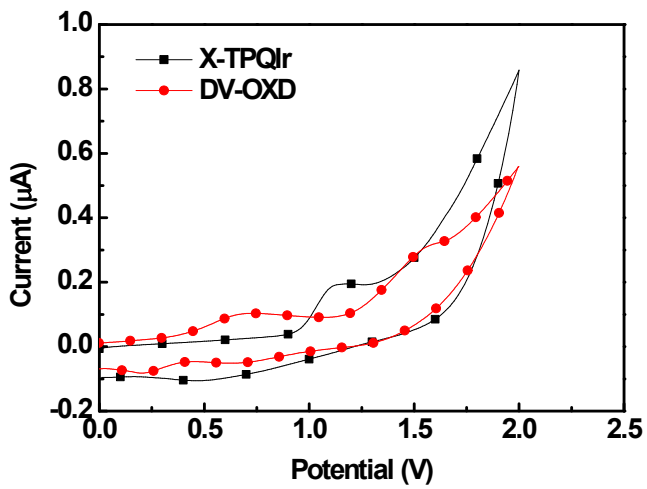


Fig. S5 CV of X-TPQIr and DV-OXD measured in MC at a scan rate of 100 mV/S.

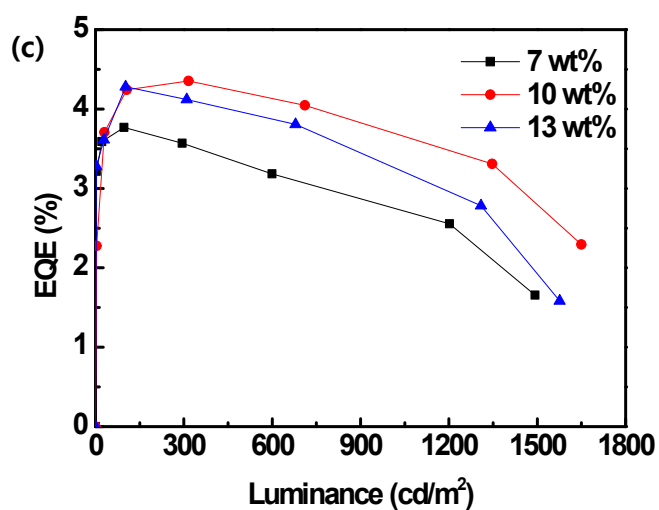
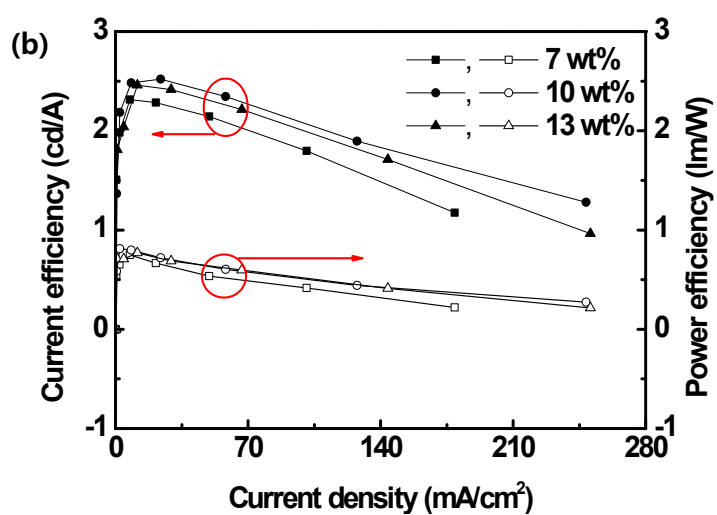
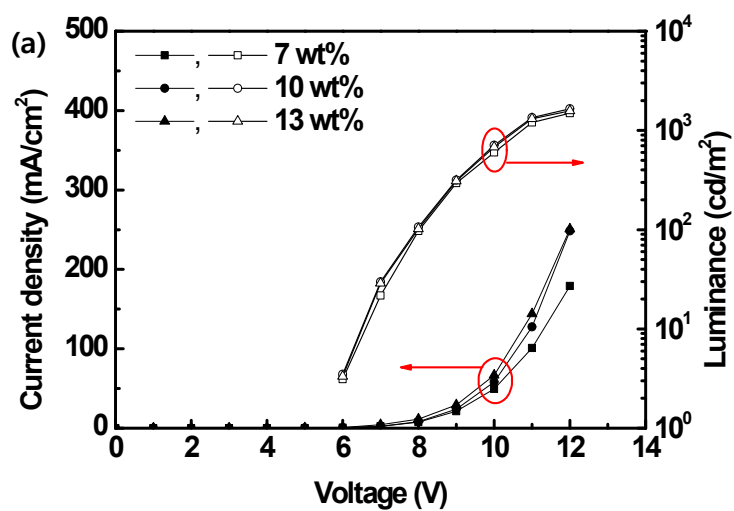


Fig. S6 (a) J-V-L characteristic, (b) CE-J-PE and (c) EQE of deep-red PHOLEDs with different doping ratio of cross-linked EML.

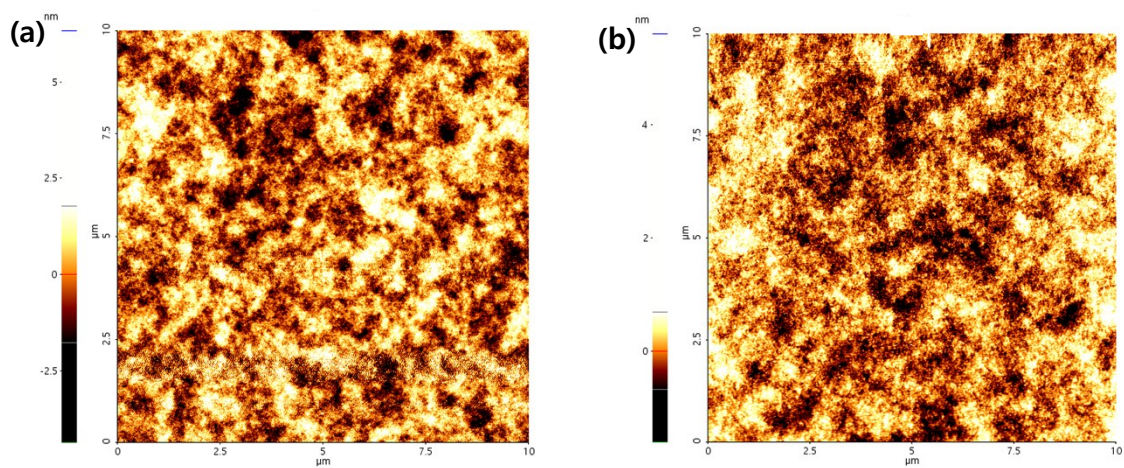


Fig. S7 AFM topographic image of (a) cross-linking and (b) after rinsing.

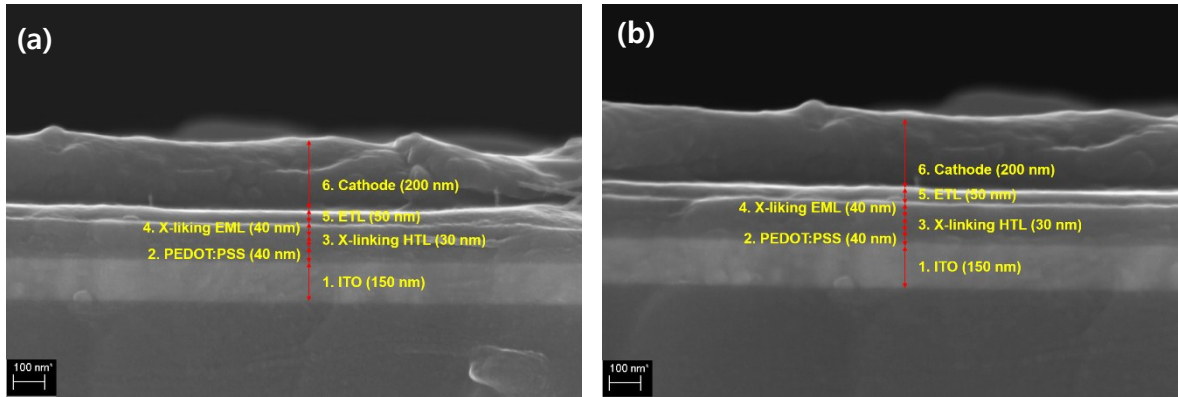


Fig. S8 SEM image of cross section of (a) cross-linking and (b) after rinsing.

Table S1 Thermal, photophysical and electrochemical data of new complexes.

	T_d^a	λ_{abs}^b	λ_{abs}^c	λ_{em}^d	λ_{em}^e	Φ_{PL}^f	Φ_{PL}^g	E_g^h	HOMO/LUMO ⁱ
	(°C)	(nm)	(nm)	(nm)	(nm)			(eV)	(eV)
DV-OXD	378	320	325	-	-	-	-	3.4	-5.63/-2.22
Ir(III) complex	330	306,352,479	306,357,487	620	621	0.20	0.26	2.1	-5.29/-3.16

^aTemperature with 5% mass loss measure by TGA with a heating rate of 5 °C/min under N₂. ^bMeasured in CHCl₃ solution at 1x10⁻⁵ M concentration. ^cMeasured in a film state. ^dMaximum emission wavelength, measured in CHCl₃ solution at 1x10⁻⁵ M concentration. ^eMaximum emission wavelength measured in a film state. ^fMeasured in 1x10⁻⁵ M CHCl₃ solution relative to Ir(piq)₂(acac) (Φ_{PL} = 0.2). ^gMeasured in a film state relative to Ir(piq)₂(acac) (Φ_{PL} = 0.2). ^hEstimated from the onset of the absorption in CHCl₃ solution. ($E_g^{opt} = 1240/\lambda_{onset}$). ⁱDetermined from the onset of CV oxidation and UV-visible absorption edge.

Table S2 Device performances of cross-linking red PHOLEDs with Ir(III) complex.

Doping concentration	Annealing temperature	Turn-on ^a	EQE ^b	CE ^b	PE ^b	Luminance ^b	CIE at 30 cd/m ²
(%)	(°C)	(V)	(%)	(cd/A)	(lm/W)	(cd/m ²)	(x, y)
7	180	5.11	3.76	2.31	0.74	1492	(0.67, 0.31)
10	180	5.32	4.35	2.52	0.81	1649	(0.68, 0.31)
13	180	5.23	4.28	2.46	0.77	1575	(0.68, 0.31)

^a@ 1 cd/m². ^bMaximum efficiency.

Table S3 Comparative performance of OLEDs containing a cross-linked EML.

Year	Previous literature	CIE coordinates (x, y)	CE ^a , Luminance ^a	EQE
2007	Ref. [1]	(0.67, 0.32)	2.1 cd/A, 700 cd/m ²	-
2008	Ref. [2]	(0.55, 0.44)	18.4 cd/A, 100 cd/m ²	-
2009	Ref. [3]	-	- , 350 cd/m ²	2.1%
2010	Ref. [4]	-	0.28 cd/A, 40 cd/m ²	-
2013	Ref. [5]	(0.38, 0.60)	34.4 cd/A, 110 cd/m ²	-
2016	Ref. [6]	(0.54, 0.45)	0.37 cd/A, 120 cd/m ²	0.3%
		(0.61, 0.38)	0.40 cd/A, 150 cd/m ²	0.37%
2018	Our work	(0.68, 0.31)	2.52 cd/A, 1499 cd/m ²	4.59%

^a Maximum efficiency.

References

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