Supporting Information

Strongly Luminescent Binuclear Aluminum Chelate with Polymer-Like Molecular Packing and Solution-processibility

Juan Qiao, Li D. Wang, Jun F. Xie, Gang T. Lei, Guo S. Wu, and Yong Qiu*

Synthesis and Characterization.

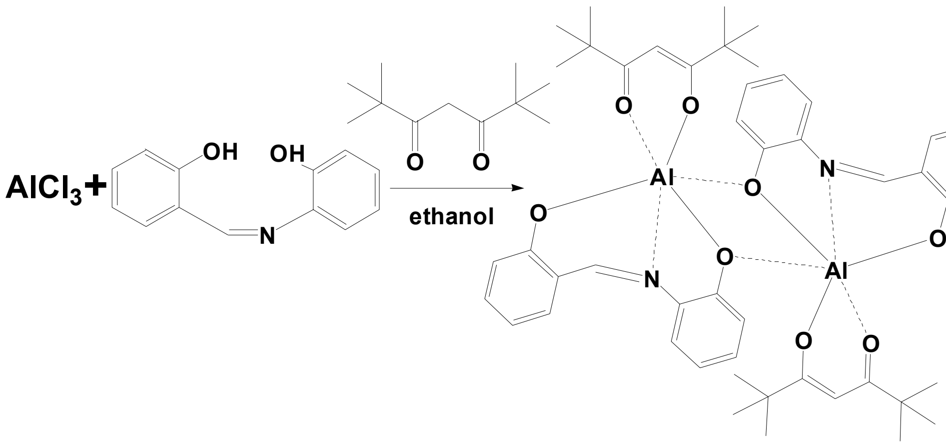
Equipments: ^{1}H NMR spectra were recorded on Bruker ARX400 NMR spectrometers with tetramethylsilane as the internal standard. Elemental analysis was determined on Elementar Vario EL (Germany) elemental analyzer. Infrared spectra were recorded on a Nicolet Magna-IR 750(USA) FT-IR microscope system. Surface morphology of the films was determined with the Atomic Force Microscopy (AFM, SPA-400). Absorption spectra were recorded with a UV-Vis spectrophotometer (HITACHI U3010), and PL spectra were obtained with a fluorospectrophotometer (HITACHI, F4500). Relative PL quantum efficiencies (ϕ_{PL}) were determined from DMF solutions by adjusting the concentration of the sample so that the optical densities at 390nm (excitation wavelength) were <0.05 absorption units. PL quantum yields were finally calculated relative to the known value for Alq_3 in DMF (ϕ_{PL}=0.116)[1] and are reported normalized to Alq_3. The equation

$$\Phi_s = \Phi_r \left(\frac{\eta_s{}^2 A_r I_s}{\eta_r{}^2 A_s I_r} \right)$$

was used to calculate quantum yields where Φ_s is the quantum yield of the sample, Φ_r is the quantum yield of the reference, η is the refractive index of the solvent, A_s and A_r are the absorbances of the sample and the reference at the wavelength of excitation, and I_s and I_r are the integrated areas of emission bands of the sample and the reference.[2]

Materials. All reagents and solvents were used as purified using standard procedures. DPM was purchased from Aldrich. The tridentate ligand of salicylidene-*o*-aminophenol (saph) was obtained by heating the mixture of salicylaldehyde and *o*-hydroxyaniline in a 1:1 molar ratio and the following recrystallization with ethanol. Yield 85%. m.p.:184-185°C.

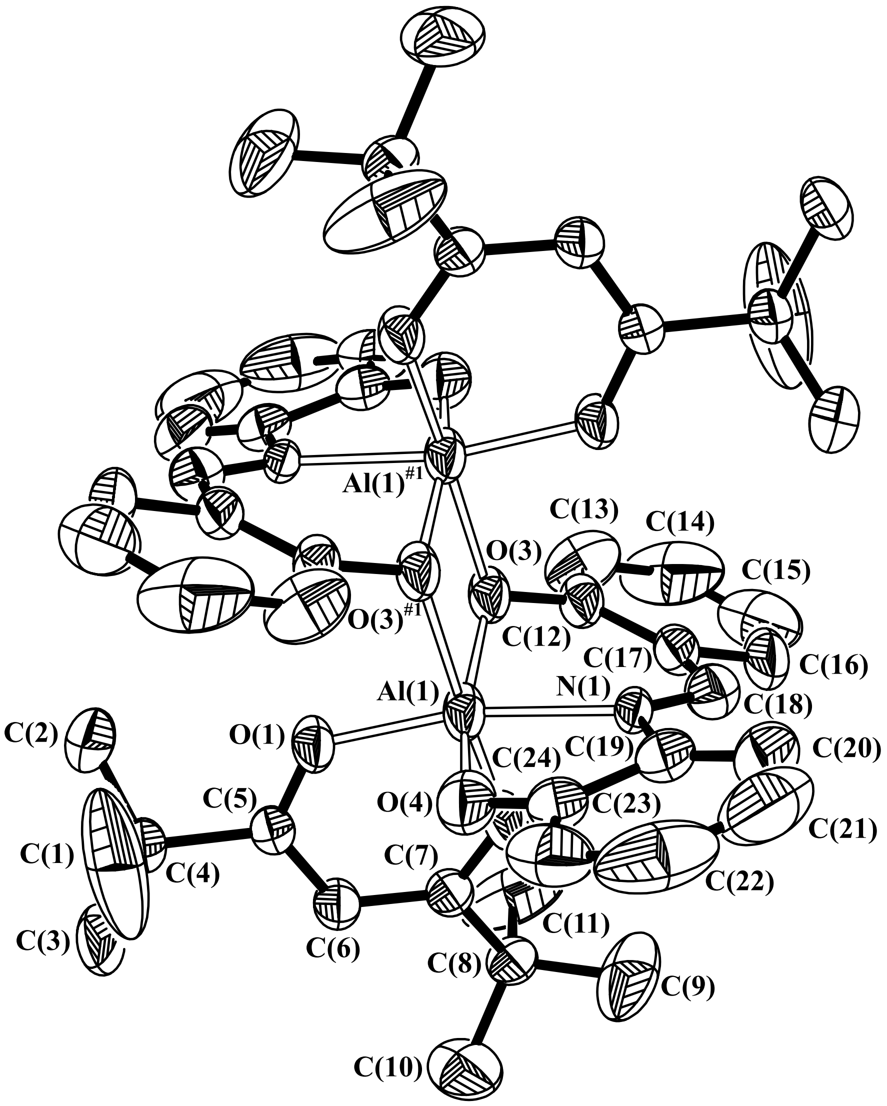
***Scheme S1.* Synthetic scheme for [Al(saph)DPM]$_2$**



Synthesis of [Al(saph)DPM]$_2$. [Al(saph)DPM]$_2$ was synthesized through a reaction in ethanol solution of dipivaloylmethane (DPM) and salicylidene- *o*-aminophenolate (saph) and $AlCl_3$ as *Scheme S1*. First, a solution of saph(1.065g, 5mmol) and piperidine(1ml, 10mmol) in ethanol(50ml) was added to a solution of $AlCl_3.6H_2O$(1.21g ,5mmol) in 10ml ethanol slowly. After the mixture was stirred for 10min, and then a solution of DPM (0.092g, 5mmol) and piperidine(0.5ml, 5mmol) in ethanol(10ml) was introduced, the mixture was stirred at room temperature till a green precipitate was produced. The crude product was collected by filtration and washed with ethanol, deionized water rapidly, and finally dried under an infrared lamp. The material was further purified by twice gradient-temperature sublimation before analysis and the device fabrication. The molecular structure was characterized by ^{1}H NMR spectroscopy, mass spectra, elemental analysis, and FT-IR spectroscopy. Yield: 85%. MS (EI) [*m/z*]: 842, 421, 407, 364, 238. ^{1}H NMR (DMSO-d_6, 400MHz): δ, ppm 8.84(s, 2H), 7.56(d, J=6.7HZ , 2H), 7.39(d, J=7.7 Hz, 2H), 7.18(t, J= 6.7HZ, 2H), 6.97(t, J=6.7 HZ, 2H),6.58-6.47(m,8H), 5.75(s,2H), 1.21(s, 18H), 0.74(s, 18H). FT-IR (cm^{-1}): 3070, 3014, 2958, 2930, 2904, 2868, 1630, 1579, 1545, 1512, 1473, 1457, 1401, 1361, 1306, 1253, 1229, 1179, 1156, 1121, 1028, 974, 924, 877, 835, 799, 753, 742. Anal. Found C 68.57, H 6.65 N, 3.37. Calcd. C 68.41, H 6.64, N 3.32.

X-ray crystallography: A single crystal suitable for X-ray crystallography was isolated by gradient temperature vacuum sublimation. Crystal data were collected on a Bruker SMART APEX CCD diffractometer equipped with graphite monochromatized Mo K_α radiation. The structural solutions and refinements were performed using the SHELXTL NT ver. 5.10 program package (Bruker, 1997)[3] on an IBM PC 586 computer. Raw intensities were corrected for Lorentz and polarization effects, and for absorption by empirical method. Direct phase determination yielded the positions of Al, O, N and the most C atoms, and the other C atoms were located in successive difference Fourier syntheses. Hydrogen atoms were generated theoretically and rode on their parent atoms in the final refinement. All non-hydrogen atoms were subjected to anisotropic refinement.

The following crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 197758. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.).



ORTEP drawing of [Al(saph)DPM]$_2$ with 35% probability ellipsoids, showing the atomic numbering scheme.

Table S1. Details of Data Collection, Processing and Structure Refinement

Sample code	**QJ-8**	
Molecular formula	$[Al(C_{13}H_9NO_2)(C_{11}H_{19}O_2)]_2$	
Molecular weight	842.90	
Color and habit	yellow granula	
Crystal size	0.2 × 0.1 × 0.1 mm	
Crystal system	monoclinic	
Space group	$P2_1/n$ (No. 14)	
Unit cell parameters	a = 13.4499(9) Å α = 90.00° b = 10.5525(7) Å β = 93.351(2)° c = 15.9848(11) Å γ = 90.00° V = 2264.8(3) Å^3 Z = 2 F(000) = 896	
Density (calcd)	1.236 g/cm^3	
Diffractometer	Bruker SMART APEX CCD	
Radiation	graphite-monochromatized Mo K_α, λ = 0.71073 Å	
Temperature	295±2K	
Scan type	ω-scan	
Data collection range	$-13 < h < 15$, $-12 < k < 12$, $-15 < l < 19$; $\theta_{max} = 25°$	
Reflections measured	Total: 12288 Unique (n): 3989	Observed [$I \geq 2\sigma(I)$]: 2719
Absorption coefficient	0.119 mm^{-1}	
Minimum and maximum transmission	0.848, 1.000	
No. of variables, p	274	
Weighting scheme	$w = \dfrac{1}{\sigma^2(F_o^2) + (0.001P)^2 + 3.5000P}$	$P = (F_o^2 + 2F_c^2)/3$
$R1 = \dfrac{\Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert}{\Sigma\lvert F_o\rvert}$ (for all reflections)	0.1023	0.0725 (for observed data)
$wR2 = \sqrt{\dfrac{\Sigma[w(F_o^2 - F_c^2)^2]}{\Sigma w(F_o^2)^2}}$ (for all reflections)	0.1391	0.1305 (for observed data)
Goof = S = $\sqrt{\dfrac{\Sigma[w(F_o^2 - F_c^2)^2]}{n - p}}$	1.047	
Largest and mean Δ/σ	0.065, 0.005	
Residual extrema in final difference map	-0.249 to 0.449 e Å^{-3}	

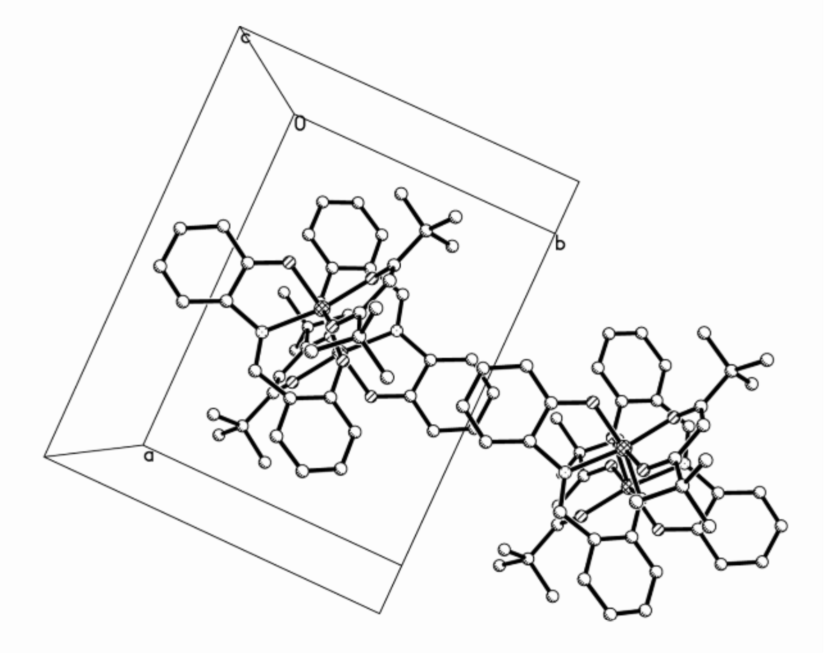
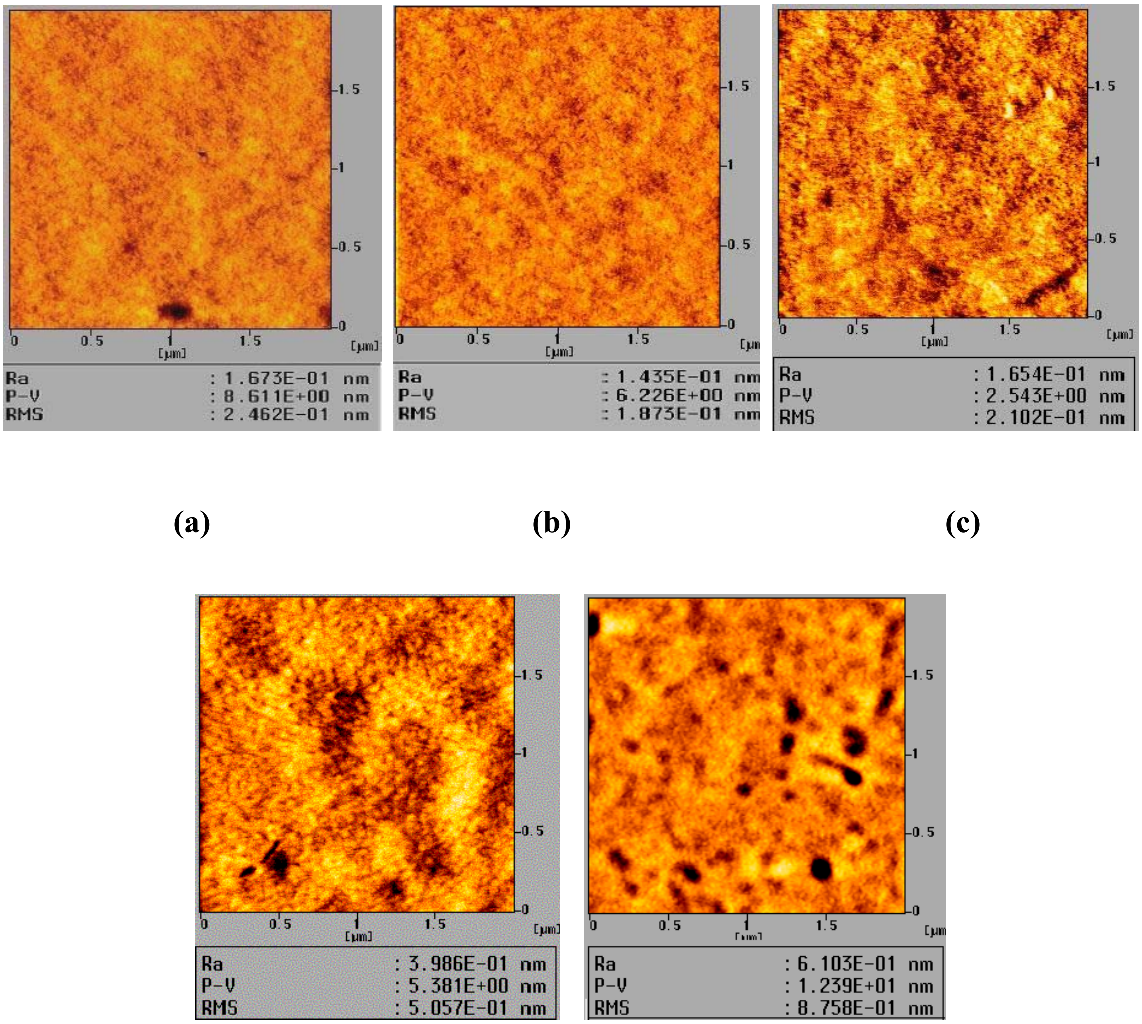


***Figure S1*. Crystal packing of [Al(saph)DPM]$_2$ [down (0,0,1)], showing the relative shifts of the π-π stacked phenyl rings. The disordering was omitted for clarity.**

Thin Films characterization:

[Al(saph)DPM]$_2$, was dissolved in THF or methanol(5mg/ml) and the solution was filtered through a Teflon mebrane filter(0.2μm). Thin films were spin-coated onto quartz or ITO glasses in a nitrogen-filled dry glove-box at a spin speed of 3000rpm for 30s. Residual solvent was removed by heating the films, to yield transparent films with a thickness of approximately 80nm, which was later measured using an Alpha-step 200 profilometer. Surface morphology was determined with the Atomic Force Microscopy.



(a) (b) (c)

(d) (e)

Figure S2. The AFM images of the thin films on quartz glasses under ambient atmosphere: (a) [Al(saph)DPM]$_2$ spin-coated from methanol solution. (b) [Al(saph)DPM]$_2$ spin-coated from THF solution. (c) PVK spin-coated from THF solution. (d) [Al(saph)DPM]$_2$ by evaporation. (e) Alq$_3$ by evaporation. RMS is root-mean-square of the roughness and P-V is the value of peak-to valley.

OLEDs Characterization.

For all the structures, the indium tin oxide (ITO) coated glass slices with a sheet resistance of 15Ω/□ were used as the substrate and anode. The substrates were ultrasonically cleaned in detergent solution for about 1 min, followed by thorough rinsing in de-ionized water. They were then rinsed in acetone followed by methanol, and dried in pure nitrogen gas between each step.

For the two-layer devices fabricated by spin-coating, a hole transfer layer (HTL) of N, N'-diphenyl-N,N'-bis(3-methylphenyl) 1,1'-biphenyl-4,4'-diamine(TPD) doped poly(N-vinylcarbazole) (PVK) (1:1 weight) was first spin-coated from chlorobenzene solution at 4000 rpm for 30s onto the cleaned ITO substrate. And then, [Al(saph)DPM]$_2$ solution in methanol (5mg/ml) was spin-coated on top of the PVK:TPD layer. For each of the above devices, a Mg/Ag (10:1 mass ratio) electrode was finally evaporated in a vacuum chamber at 1×10^{-4} Pa.

Electrical and optical measurements were made in air under ambient conditions without encapsulation. Devices were tested with ITO as the positive electrode in the forward bias configuration. The EL spectra were measured with a Photo Research PR650 spectrophotometer. Voltage-current-luminance measurements were performed with Keithley 4200 semiconductor characterization systems.

The device structures are following:
The undoped: ITO/PVK:TPD(50nm,1:1)/[Al(saph)DPM]$_2$(80nm) /Mg:Ag.
The doped: ITO/PVK:TPD(50nm,1:1)/[Al(saph)DPM]$_2$:rubrene(1wt%, 80nm) /Mg:Ag.

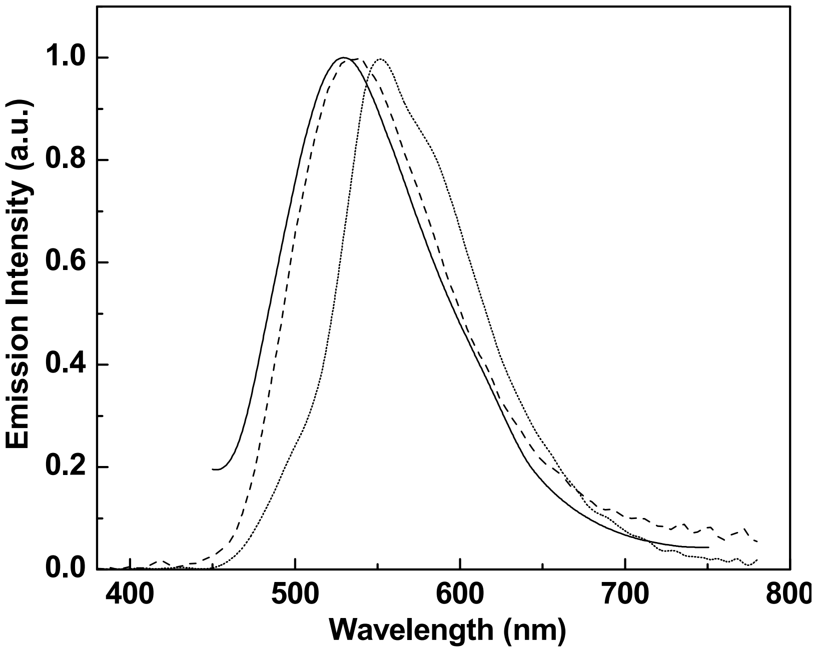


Figure S3. The normalized PL spectrum of the neat [Al(saph)DPM]$_2$ film(solid line) and EL spectra of the nondoped device (dashed line) and the doped device (dotted line).

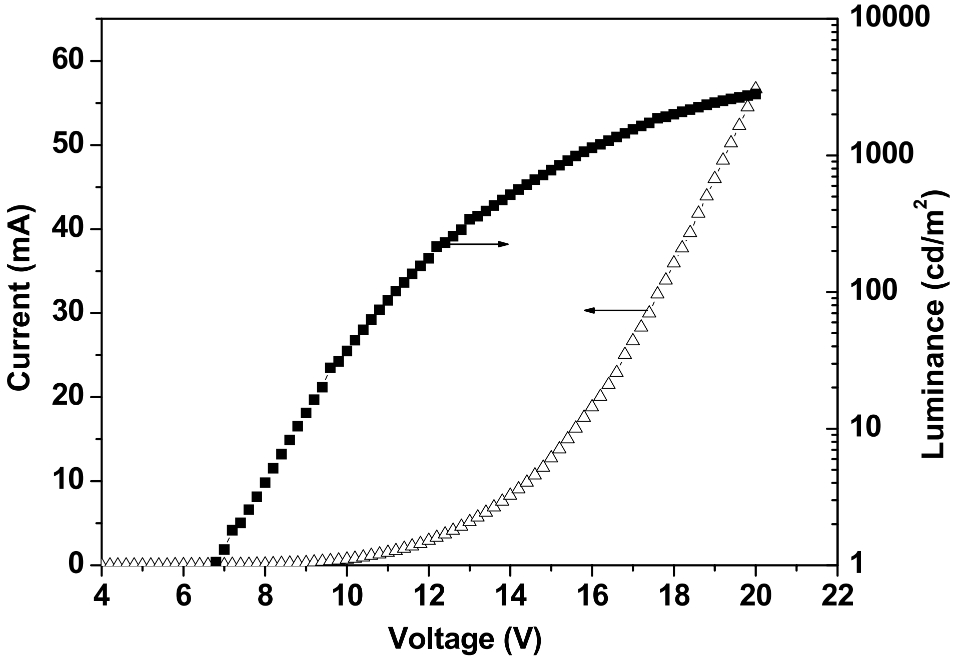


Figure S4. **Current-Voltage (triangle) and Luminance-Voltage (square) characteristics of device C with a configuration of ITO/PVK:TPD(1:1,50nm)/[Al(saph)DPM]$_2$(80nm)/Mg:Ag.**

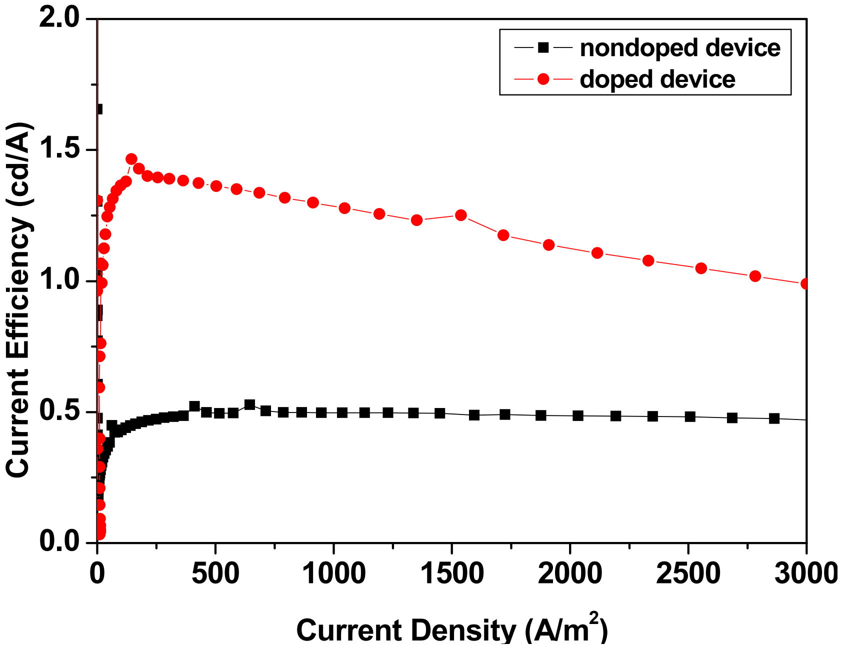


Figure S5. **Efficiency-Current characteristics of the two devices.**

References:

1 Lytle, F. E. Storey, D. R. and Juricich, M. E. *Spectrochimica Acta,* 1973, **29A**, 1357.

2 J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau, and M. E. Thompson, *Inorg. Chem*. 2002, **41**, 3055

3 G. M. Sheldrick, SHELXTL, version 5.1; Bruker Analytical X-ray System, Inc.: Madison, WI, 1997.