Black Phase-changing Cathodes for High-contrast Organic Light-Emitting Diodes

Jia-Xiu Man,[†,‡] Shou-Jie He,[†,‡] Tao Zhang,[†,‡] Deng-Ke Wang,[†,‡] Nan Jiang,[†,‡] and Zheng-Hong Lu*[,†,‡,§]

[†]Department of Physics, and [‡]Yunnan Key Laboratory for Micro/Nano Materials and Technology, Yunnan University, Kunming, Yunnan 650091, China

[§]Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario M5S 3E4, Canada

Supporting Information

All of the calculations in this paper are based on transfer matrix method.[1-4] Typically, an OLED comprises a stack of thin-film multilayers, which are assumed to be isotropic and homogenous with plane parallel interfaces. Consider a plane wave incident into the stratified structure between two semi-infinite layers (j=0, j=m+1) as Figure S1 shown. Each layer has a thickness of d_j and its optical properties are described by its complex refractive index of $\tilde{n}_j = n_j + i\kappa_j$ which is a function of wavelength of incident light. The optical electric field at any point in the system can be resolved into two components, one propagating in the positive direction and another one propagating in the negative direction, represented by E_j^+ and E_j^- respectively.

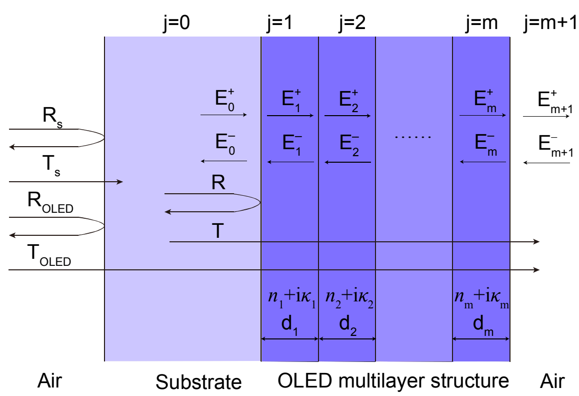

Figure S1. Light propagation in the stacked OLED structure.

Assume that the multilayer is illuminated from the substrate along the surface normal. An interface matrix I_{jk} is describing the optical field at layer j and layer k interface

$$I_{jk} = \frac{1}{t_{jk}} \begin{bmatrix} 1 & r_{jk} \\ r_{jk} & 1 \end{bmatrix} \tag{S1}$$

where r_{jk} and t_{jk} are the Fresnel complex reflection and transmission coefficients at layer jk interface, respectively:

$$r_{jk} = \frac{\tilde{n}_j - \tilde{n}_k}{\tilde{n}_j + \tilde{n}_k}, \qquad t_{jk} = \frac{2\tilde{n}_j}{\tilde{n}_j + \tilde{n}_k} \tag{S2}$$

Layer matrix L_j describes the propagation through a layer j, which can caused absorption and phase shift:

$$L_j = \begin{bmatrix} e^{-i\xi_j d_j} & 0 \\ 0 & e^{i\xi_j d_j} \end{bmatrix} \tag{S3}$$

where $\xi_j = (2\pi/\lambda)\,\tilde{n}_j$. The electric field in the two outermost layer j=0 and j=m+1 are related via transfer matrix S:

$$\begin{bmatrix} E_0^+ \\ E_0^- \end{bmatrix} = S \begin{bmatrix} E_{m+1}^+ \\ E_{m+1}^- \end{bmatrix} \quad \text{(S4)}$$

where

$$S = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} = \left(\prod_{j=1}^{m} I_{(j-1)j} L_j\right) \cdot I_{m(m+1)} \quad \text{(S5)}$$

When incident light is from the substrate side in the positive direction, there is no wave propagating in the negative direction in layer j=m+1, which means that E_{m+1}^-=0. The reflection and transmission coefficients of the coherent stack layers can be expressed by using the matrix elements of S in Equation S5, respectively as:

$$\mathrm{r} = \frac{E_0^-}{E_0^+} = \frac{S_{21}}{S_{11}}, \qquad t = \frac{E_{m+1}^+}{E_0^+} = \frac{1}{S_{11}} \quad \text{(S6)}$$

The reflectance and transmittance of the coherent OLED stack layers is given by:

$$\mathrm{R} = |r|^2, \qquad T = \frac{\tilde{n}_{m+1}}{\tilde{n}_0}|t|^2 \quad \text{(S7)}$$

As the electric field in substrate is incoherent with OLED multilayer, the reflectance and transmittance can be expressed as:

$$\mathrm{R}_s = \left|\frac{1-\tilde{n}_0}{1+\tilde{n}_0}\right|^2, \qquad T_s = \left|\frac{2}{1+\tilde{n}_0}\right|^2 \quad \text{(S8)}$$

where $\tilde{n}_0$ is the refractive index of substrate. The reflectance and transmittance of OLED device with substrate can be described by:

$$\mathrm{R}_{OLED} = \frac{\mathrm{R}_S + R}{1+\mathrm{R}_S R}, \qquad T_{OLED} = \frac{\mathrm{T}_S T}{1+\mathrm{R}_S R} \quad \text{(S9)}$$

Generally speaking, in OLED device, the last layer is a thick metal electrode that the incident visible light cannot penetrate through. There is a phase change at the interface between the metal layer and the adjacent organic layer, the phase shift is given by:[5]

$$\varphi_e = \arctan\left(\frac{2n_o\kappa_e}{n_o^2 - n_e^2 - \kappa_e^2}\right) \quad \text{(S10)}$$

where n_e and κ_e are real and imaginary parts of the metal electrode refractive index; and n_o is the refractive index of the adjacent organic material.

Based on transfer matrix method, we optically design the black PC-cathode structure by optimizing the complex refractive index and thickness of PC layer. We vary the complex refractive index n+iκ (n=0~5, κ=0~5) of the organic material to find the ideal optical constants which render the HC-OLED device lowest reflectance. Figure S2 gives the situation of a 30nm thick PC layer at 550nm incident light. We can find an asymmetric zone of absorption resonance cavity appears where the reflectance of the OLED device drops to zero at $\tilde{n} = 2.76 + 0.43\mathrm{i}$. Moreover, the dark blue area has optical constant value corresponding to the reflectance less than 10% in the large range of n=2.38~3.11 and κ=0.11~1.12.

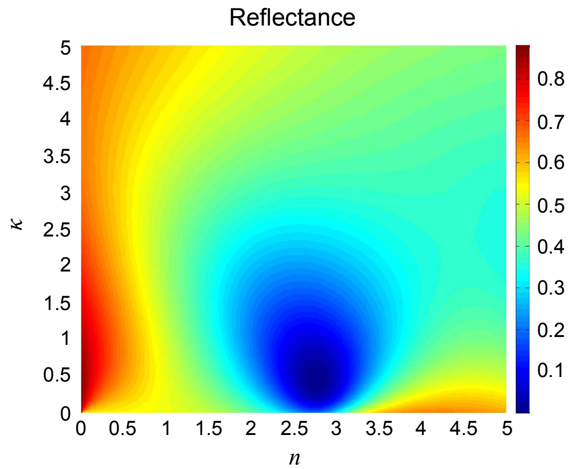

Figure S2. Reflectance (in color scale) of HC-OLED with a black PC-cathode. The PC layer having complex refractive index $\tilde{n}=n+i\kappa$ are computed for a constant 30 nm organic layer and for an incident wavelength λ = 550 nm.

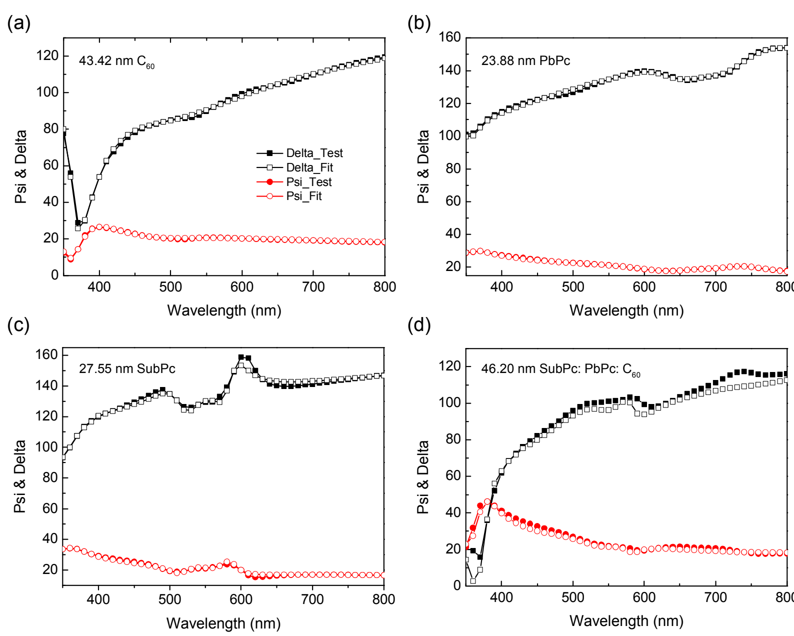

Figure S3. The fit for Psi and delta of C_{60}, SubPc, PbPc, and SubPc: PbPc: C_{60} ternary mixture (the weight ratio is 1:1:1) on Si substrate at the incident angle of 65° measured by a spectroscopic ellipsometer (ELLIP-SR-I)

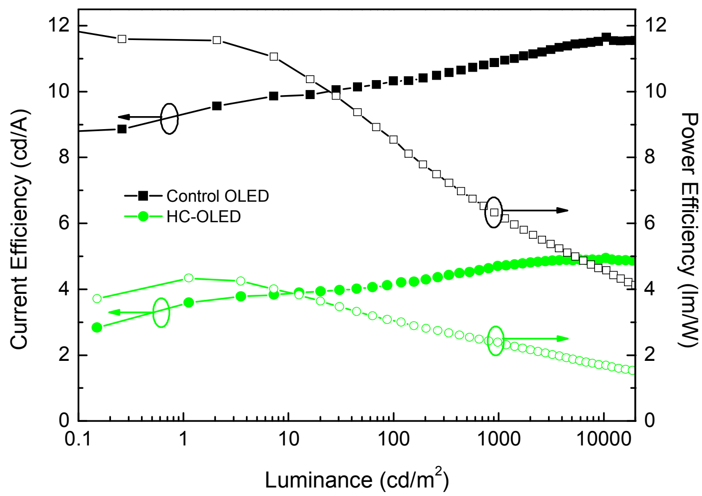

Figure S4 Current efficiency and power efficiency of the Control OLED and the HC-OLED

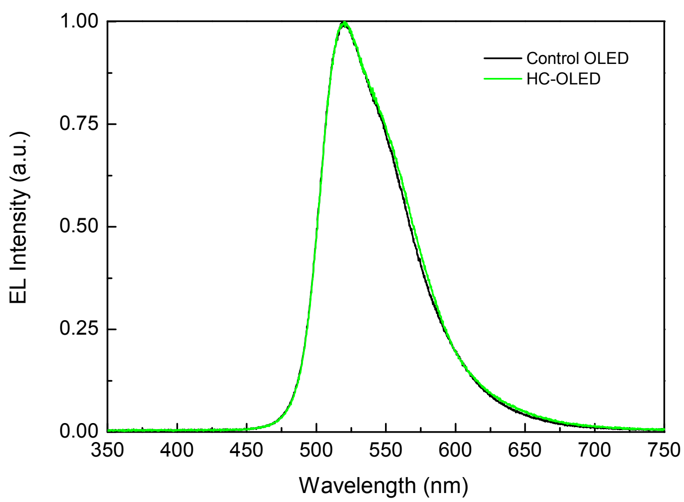

Figure S5 Electroluminescence spectra of the Control OLED and the HC-OLED

Figure S6a-b shows a schematic test device structure for testing resistance of the PC-cathode. Figure S6c shows measured J-V curve. Because the thin semi-transparent metal layer (5 nm Al) has extremely high lateral resistance, we used 100 nm Al to study the electrical property of the PC-cathode. From Figure S6c, we observe that the electrical conductivity over the PC-cathode is extremely high, reaches 500 mA/cm^2 at 1.4 eV, which is below the turn-on voltage of OLED.

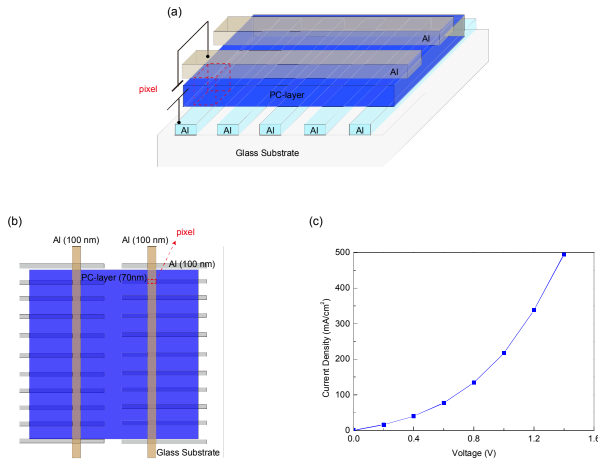

Figure S6 Schematic test device structure configuration of (a) space pattern, (b) top view pattern, and (c) the corresponding I-V curves of the PC-cathode.

References:

(1) Kang, K., Lee; Y., Kim, J.; Lee, H.; Yang, B. A Generalized Fabry–Pérot Formulation for Optical Modeling of Organic Light-Emitting Diodes Considering the Dipole Orientation and Light Polarization. *IEEE Photonics Journal* **2016**, *8*, 1-19.

(2) Pettersson, L. A. A.; Roman, L. S.; Inganäs, O. Modeling photocurrent action spectra of photovoltaic devices based on organic thin films. *J. Appl. Phys.* **1999**, *86*, 487-496.

(3) Peumans, P.; Yakimov, A.; Forrest, S. R. Small molecular weight organic thin-film photodetectors and solar cells. *J. Appl. Phys.* **2003**, *93*, 3693-3723.

(4) Wang, Z. B.; Helander, M. G.; Xu, X. F.; Puzzo, D. P.; Qiu, J.; Greiner, M. T.; Lu, Z. H. Optical design of organic light emitting diodes. *J. Appl. Phys.* **2011**, *109*, 053107.

(5) Dodabalapur, A.; Rothberg, L. J.; Jordan, R. H.; Miller, T. M.; Slusher, R. E.; Phillips, J. M. Physics and applications of organic microcavity light emitting diodes. *J. Appl. Phys.* **1996**, *80*, 6954-6964.