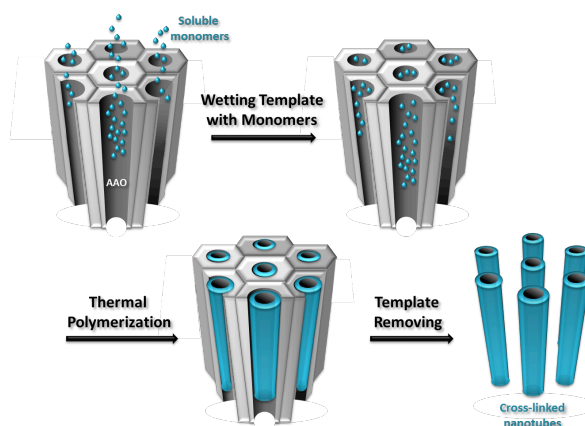


## Template-assisted *in situ* polymerization for forming blue organic light-emitting nanotubes

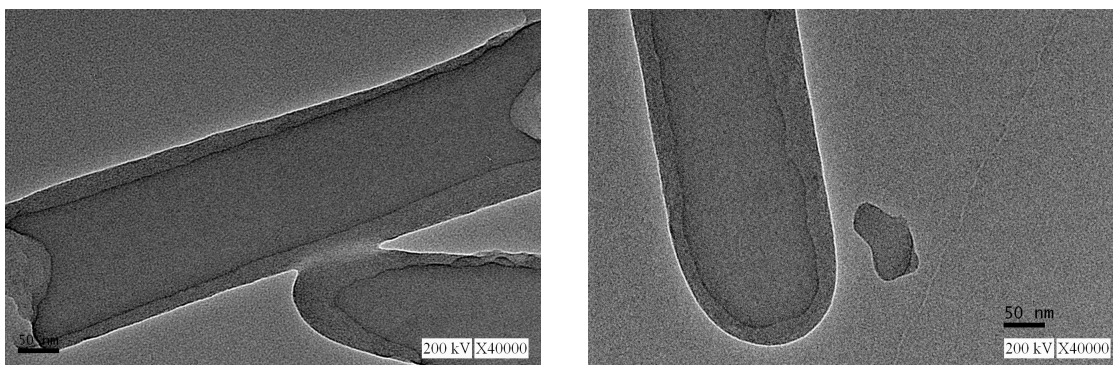
Li-Chi Lee<sup>a</sup>, Han-Han<sup>a</sup>, Yu-Tang Tsai<sup>b</sup>, Gang-Lun Fan<sup>a</sup>, Hsiang-Fang Liu<sup>a</sup>, Chung-Chih Wu<sup>\*b</sup>, Jing-Jong Shyue<sup>c</sup>, Shih-Sheng Sun<sup>d</sup>, Chien-Liang Liu<sup>a</sup>, Pi-Tai Chou<sup>a</sup> and Ken-Tsung Wong<sup>\*a</sup>

### Supporting Information

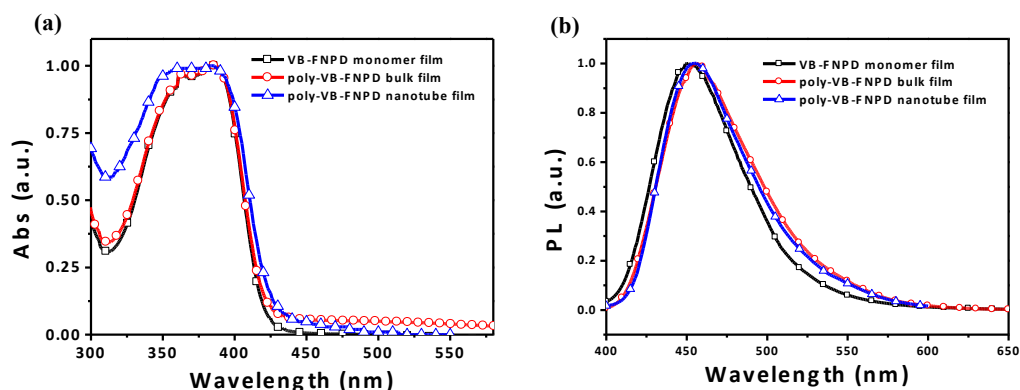
Preparation of organic nanotubes: A concentrated solution of **VB-FNPD** (2 mg in 60  $\mu\text{L}$  THF) was drop-casted on an AAO membrane (Whatman, diameter of 47 mm, thickness of 60  $\mu\text{m}$ , pore size of 0.2  $\mu\text{m}$ ), which was then immediately clamped with glass slides and pressed with two-kilogram weight overnight to facilitate the infiltration and to reduce the evaporation of solvent. Afterward, the **VB-FNPD**-filled AAO membrane was annealed at 120  $^{\circ}\text{C}$  for 30 min. under nitrogen with the protection of glass slides. The glass slide-sandwiched sample further proceeded with the thermal *in situ* polymerization at 165  $^{\circ}\text{C}$  for 10 min. and then 175  $^{\circ}\text{C}$  for 40 min. After cooling to the ambient temperature, the nanotubes-implanted AAO membrane was treated with potassium hydroxide aqueous solution (1.0 M, 20 mL) with ultrasonication for 2 h to remove the template and release the nanotubes. The aqueous suspension was centrifuged (8000 rpm, 2 min), decanted and added with fresh deionized water (20 mL) for three cycles, giving purified poly-**VB-FNPD** nanotubes, which were then dispersed in ethanol for further characterization.



**Scheme S1** Preparation of poly-**VB-FNPD** nanotubes uses AAO-templated *in situ* polymerization.



**Fig. S1** Selected TEM images of poly-**VB-FNPD** nanotubes showing the meniscus (left) and close ends (right). The images also indicate the inhomogeneous tube thickness (25~50 nm).



**Fig. S2** Absorption (a) and emission (b) spectra of **VB-FNPD**.

#### **Photoluminescence (PL) quantum yield measurements:**

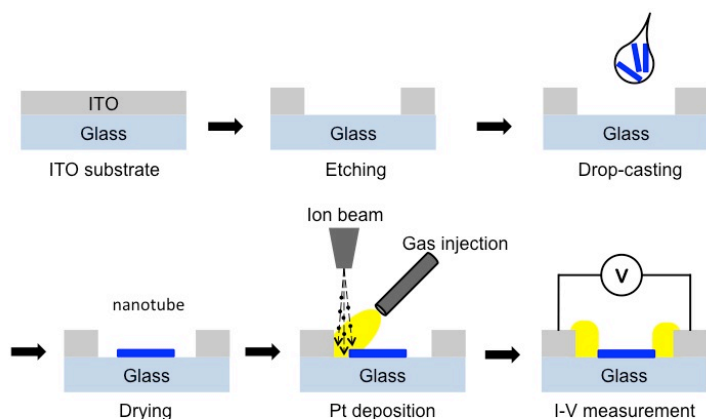
The PL quantum yields were then measured using an integration sphere (Hamamatsu C10027).  
**Solution:** The monomer **VB-FNBD** (1 mg) was dissolved in THF (1 mL) and then mixed with 99.5% EtOH (1 mL). Then, diluted this mixed solution (1 mL) with 99.5% EtOH (9 mL). The poly-**VB-FNPD** nanotubes obtained from the standard protocol as mentioned in Schem 1 was dispersed in 99.5% EtOH.

**Films:** The monomer **VB-FNBD** (10 mg) dissolved in chlorobenzene (1 mL) was spin-coated (3000 rpm, 40 second) on an ITO glass. The sample was heated under nitrogen at 110 °C for 30 mins for removing the solvent. The nanotube film was formed by drop-casting of a 30  $\mu$ L of poly-**VB-FNPD** nanotubes suspension in EtOH on an ITO glass.

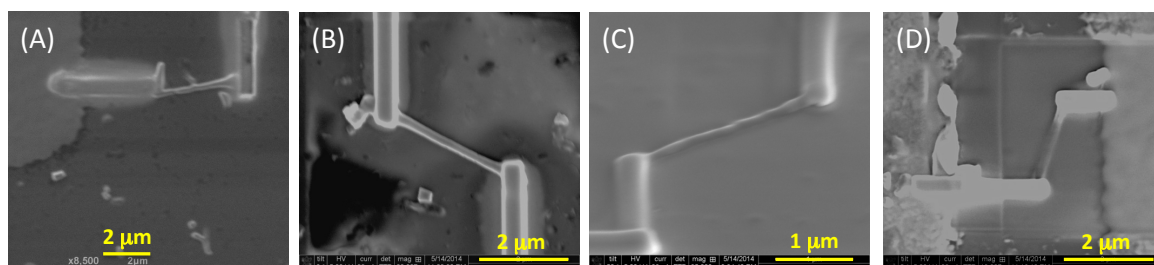
#### **Fabrication of the nano device with focused ion beam:**

For the laboratory-scale fabrication of nano-devices, the use of a focused ion beam (FIB) is a rapid and flexible method for making stable, low-resistance ohmic contacts at nanoscale.

Nanotube sample (in Ethanol solvent) was drop-casted onto a glass substrate with photo-lithography patterned ITO electrodes. Then, the FIB micromanipulator (FEI Nova 600i) was used for the platinum (Pt) electrode deposition, which was accomplished by using a focused beam of gallium ions ( $\text{Ga}^+$ ) to sputter trimethylcyclopentadienylplatinum ( $(\text{CH}_3)_3\text{Pt}(\text{C}_p\text{CH}_3)$ ) to selectively deposit Pt atoms for connecting the ITO electrodes to the nanotube. In order to avoid damaging to the organic sample, the  $\text{Ga}^+$  ions were accelerated to 30 kV at 28 pA, and the thickness of FIB-written Pt metal on the electrode is 100 nm. The DC electrical property of the FIB-written nanotube device was measured using an HP-4156 parameter analyzer. The fabrication of the nano device for conductivity measurement is illustrated in Scheme S2.



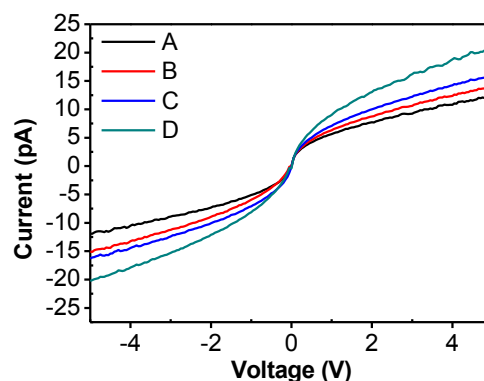
**Scheme S2** FIB-assisted fabrication of nanodevice for conductivity measurement.



$$\rho = \pi R[D^2 - (D-2W)^2]/4L$$

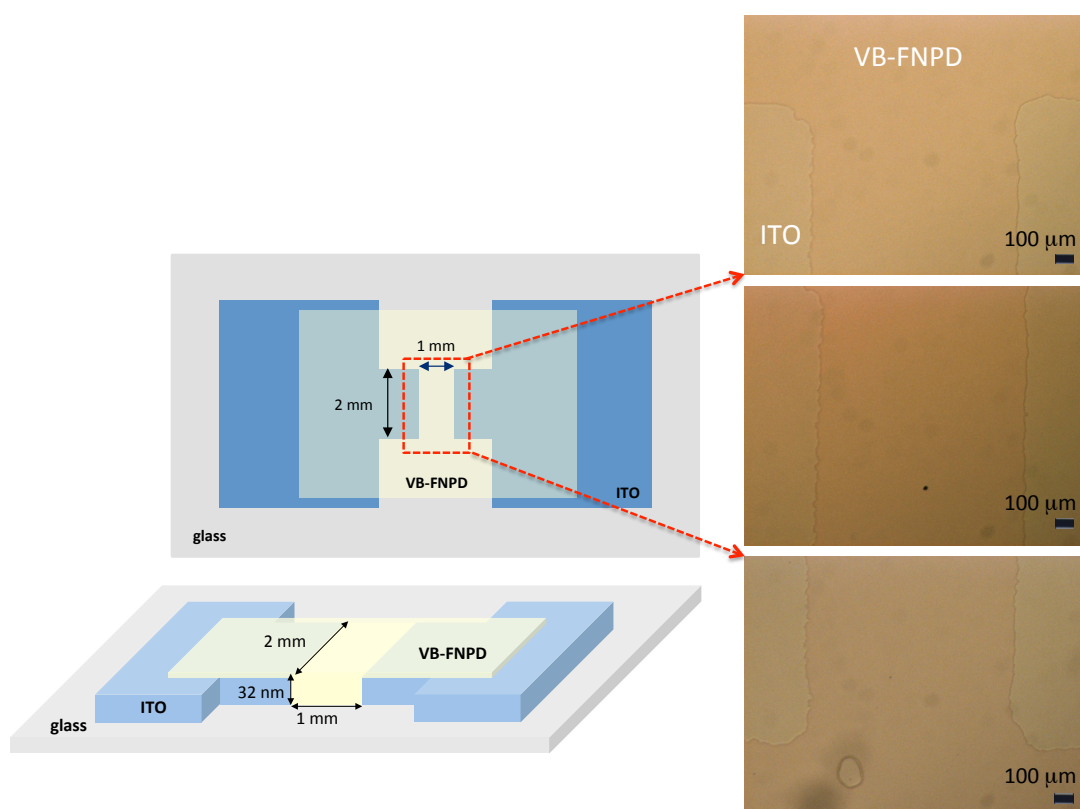
| Tube | L (μm) | R (x 10 <sup>11</sup> )<br>Ω | ρ (x 10 <sup>5</sup> )<br>Ω·cm | σ (x 10 <sup>-6</sup> )<br>S cm <sup>-1</sup> |
|------|--------|------------------------------|--------------------------------|---|
| A    | 2.7    | 6.4                          | 1.87~3.27                      | 3.06~5.35                                     |
| B    | 2.6    | 5.6                          | 1.69~2.96                      | 3.38~5.91                                     |
| C    | 2.2    | 5.0                          | 1.77~3.10                      | 3.22~5.64                                     |
| D    | 1.7    | 3.8                          | 1.76~3.09                      | 3.24~5.67                                     |

diameter (D): ~ 200 nm,  
wall thickness (W): 25~ 50 nm



**Fig. S3** The SEM images of four nanodevices (A~D) obtained by FIB-assisted fabrication for the conductivity measurements, the corresponding data, and the I-V profiles.

**The conductivity measurement of a spin-casted VB-FNPD film:** The monomer VB-FNBD (10 mg) dissolved in chlorobenzene (1 mL) was spin-coated (3000 rpm, 40 second) on an pre-etched ITO electrode (thickness 100 nm, sheet resistance  $\sim 45$  (ohm/sq) as shown in Scheme S4, The sample was heated under nitrogen at 110 °C for 30 mins for removing the solvent. The thickness was determined with AFM (NT-MDT) to be 32 nm. The device was measured with a semiconductor device analyser (Agilent Technologies B1500A) to give the I-V profile as shown in Fig. S4.



**Scheme S3.** Device structure used for the conductivity measurement of a spin-casted VB-FNPD film and the photos (Nikon) taken from the designated regions.

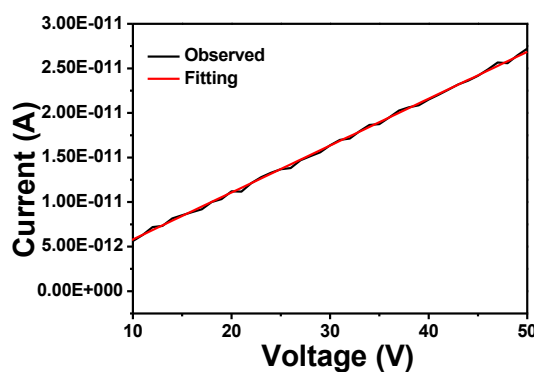
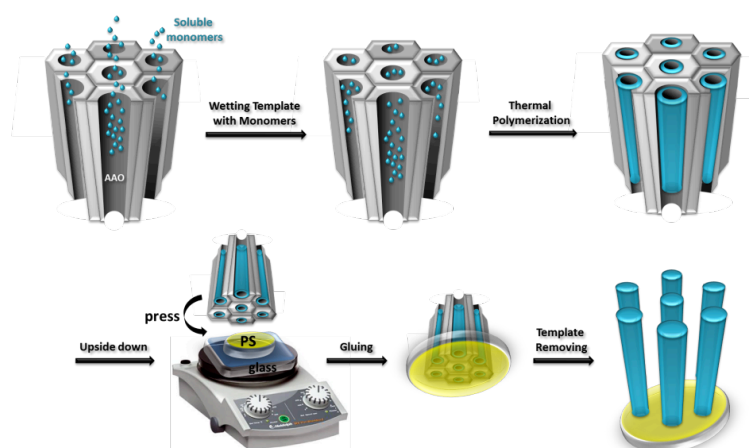


Fig. S4. Fitting slope:  $5.26187 \times 10^{-13}$ , device resistance (R):  $1.9 \times 10^{12}$  (ohm). With active layer with spacing (L): 1 mm, area (A) = 32 (nm) x 2 (mm), the calculated film bulk resistance (r) ( $R = rL/A$ ):  $1.216 \times 10^5$  (ohm-m) and the conductivity (s):  $8.22 \times 10^{-6}$  (S/m) or  $8.22 \times 10^{-8}$  (S/cm).

Before being subjected to de-template in aqueous KOH, the nanotube-implanted AAO membrane was pressed on a pre-heated (230 °C) melt polystyrene (PS) ( $M_w = 250,000$  g/mol) (Scheme S4).



**Scheme S4** The processes for the preparation of poly-VB-FNPD nanotube arrays.

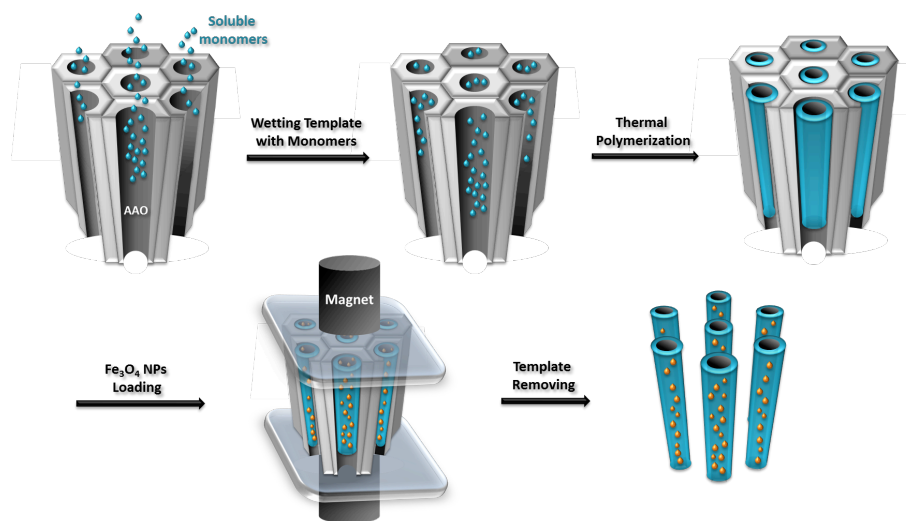
Since we used commercially available AAO, which contains some channels are even not open on both sides. The nanotube-implanted AAO membrane was covered with the  $\text{Fe}_3\text{O}_4\text{NP}$  solution without removing (vacuum) the air inside the channels. The inside air and hydrophobic surface of poly-VB-FNPD nanotubes will impede the movement of hydrophilic  $\text{Fe}_3\text{O}_4\text{NP}$  solution inside the nanotubes. Therefore, it is necessary to have an external force to facilitate the impregnation of  $\text{Fe}_3\text{O}_4\text{NP}$ . It is worthy to note that the impregnation of the magnetic particles without the assistance of an external magnetic field was unsuccessful. We only observed limited  $\text{Fe}_3\text{O}_4\text{NP}$  insertion close to the nanotube tip.

Before being subjected to de-template in aqueous KOH, the nanotube-implanted AAO membrane was drop-casted with an ethanol solution (60  $\mu\text{L}$ ) of magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles ( $\text{Fe}_3\text{O}_4\text{NP}$ ) ( $12 \pm 1$  nm) capped with oleylamine/oleic acid as prepared according to our previous method.<sup>1</sup> Then, the AAO membrane was immediately clamped with glass slides. The sandwiched sample was fixed with two small magnets overnight to facilitate the

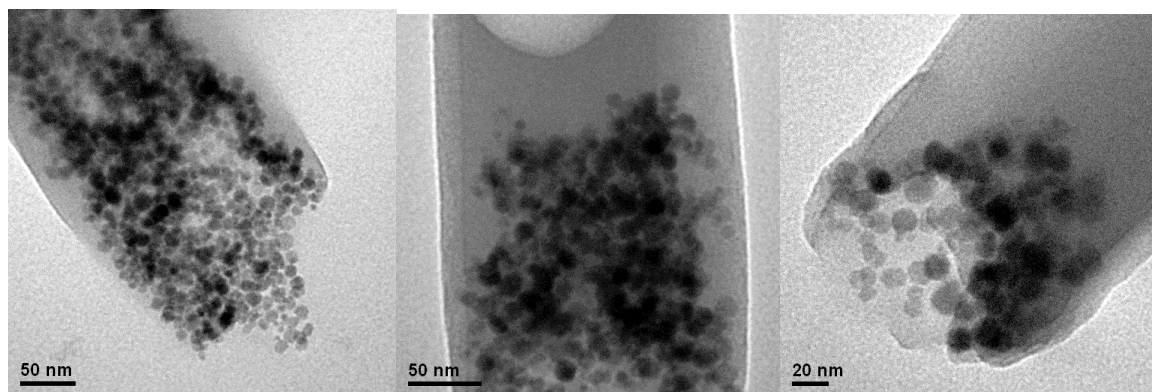
<sup>1</sup> C.-W. Lai, Y.-H. Wang, C.-H. Lai, M.-J. Yang, C.-Y. Chen, P.-T. Chou, C.-S. Chan, Y. Chi, Y.-C. Chen and J.-K. Hsiao *Small*, 2008, **4**, 218.



introduction of  $\text{Fe}_3\text{O}_4$  NPs into the poly-VB-FNPD tubes. After then, the AAO template was removed and the  $\text{Fe}_3\text{O}_4\text{NP/OLET}$  nanocomposites were isolated follow the protocols described in Scheme S1.



**Scheme S5** The processes for the preparation of  $\text{Fe}_3\text{O}_4$  nanoparticles ( $\text{Fe}_3\text{O}_4$  NP) and poly-VB-FNPD magnetic nanocomposites.



**Fig. S5** Representative TEM images of poly-VB-FNPD nanotubes loaded with  $\text{Fe}_3\text{O}_4\text{NP}$ . It is clear to see that the degrees of the NPs loading into the poly-VB-FNPD nanotubes are randomly distributed depending on the different locations. The precise determination of the  $\text{Fe}_3\text{O}_4\text{NP}$  loading efficiency is rather difficult. However, an average loading percentage (w/w %) may be obtainable by conducting a TGA analysis of the loaded nanotubes.