Flexible white top-emitting organic light-emitting diode with a MoO_x roughness improvement layer*

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(Received 24 April 2013; revised manuscript received 8 June 2013)

In this paper, an MoO_x film is deposited on a polyethylene terephthalate (PET) substrate as a buffer layer to improve the surface roughness of the flexible PET substrate. With an optimized MoO_x thickness of 100 nm, the surface roughness of the PET substrate can be reduced to a very small value of 0.273 nm (much less than 0.585 nm of the pure PET). Flexible white top-emitting organic light-emitting diodes (TEOLEDs) with red and blue dual phosphorescent emitting layers are constructed based on a low-reflectivity Sm/Ag semi-transparent cathode. The flexible white emission exhibits the best luminance and current injection characteristics with the 100-nm-thick MoO_x buffer layer and this result indicates that a smooth substrate is beneficial to the enhancement of device electrical and electroluminescence performances. However, the white TEOLED with a 50-nm-thick MoO_x buffer layer exhibits a maximum current efficiency of 4.64 cd/A and a power efficiency of 1.9 lm/W, slightly higher than those with a 100-nm MoO_x buffer layer, which is mainly due to an obvious intensity enhancement but limited current increases in 50-nm MoO_x-based white TEOLED. The change amplitudes of the Commission International de l'Eclairage (CIE) chromaticity coordinates are less than (0.016, 0.005) for all devices in a wide luminance range over 100 cd/m^2, indicating an excellent color stability in our white flexible TEOLEDs. Additionally, the flexible white TEOLED with an MoO_x buffer layer shows excellent flexibility to withstand more than 500 bending times under a curvature radius of approximately 9 mm. Research demonstrates that it is mainly attributed to the high surface energy of the MoO_x buffer layer, which is conducible to the improvement of the surface adhesion to the PET substrate and the Ag anode.

Keywords: flexible white TEOLED, MoO_x buffer layer, color stability, flexibility

PACS: 85.60.Jb, 78.60.Fi, 81.05.Fb **DOI:** 10.1088/1674-1056/22/12/128506

1. Introduction

The top-emitting organic light-emitting diodes (TEOLEDs) have received significant attention in recent years because of their potential application in full-color flat-panel displays.[1–4] The advantages of display technologies using TEOLEDs are self-luminescence, wide viewing angle ($> 170^\circ$), prompt response time (~ 1 μs), low operating voltage (3 V–10 V), high luminance efficiency, high aperture ratio, and high resolution. A novel TEOLED based on a flexible substrate not only possesses the advantages of the TEOLEDs but also can be bent or rolled into any desired shape, so more attention has been paid to the flexible flat panel displays recently.[5] Over the past few years, stainless-steel foil, ultrathin glass sheet, and a variety of plastic films have been considered as possible substrate options for flexible OLED displays.

In 2003, Xie *et al.*[6] utilized a stainless-steel foil as a substrate to fabricate flexible TEOLED, which has very good barrier properties. In 2002, Krasnov[7] fabricated the flexible TEOLEDs based on ultrathin glass sheets for flexible display with preformed, curved, or conformed shapes, but each of them has a very limited flexibility. Currently, most flexible OLEDs are fabricated on flexible plastic substrates such as polyethylene terephthalate (PET),[8–15] polyethylene naphthalate (PEN),[16] and polyethersulfone (PES),[17] etc. However, these flexible TEOLEDs have short lifetimes and low performances because plastics bring some problems such as surface roughness and low resistance to moisture and oxygen. It is necessary to find an effective method to smooth the plastic substrate surface before the industrialization of flexible TEOLEDs becomes reality.

In 2003, Innocenzo *et al.*[18] reported on their research work with flexible OLEDs on PEN on DuPont display and their result indicated that the introduction of a smooth acrylic layer has efficiently improved the roughness values (≤ 0.02 μm) of the PEN substrates. In 2006, Hsu *et al.*[12] fabricated a novel flexible OLED on PET by using a dot-nickel embedded ITO anode and improved the surface roughness values (from 2.60 nm to 0.36 nm) of the ITO anode. Embedding Ni in the surface of the ITO anode can reduce the turn-

*Project supported by the National Key Basic Research and Development Program of China (Grant No. 2009CB930600), the National Natural Science Foundation of China (Grant Nos. 61274065, 60907047, 51173081, and 61136003), the "333" and "Qing Lan" Program of Jiangsu Province, and the "Qing Lan" and "Pandeng" Project of Nanjing University of Posts and Telecommunications (Grant Nos. NY210040, NY211069, and NY 210015).

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on voltage by 2.3 V. In 2008, Legnani *et al.*[19] used Bacterial Cellulose (BC) membranes as flexible substrates to fabricate an OLED. An SiO_2 thin film interlayer between the BC membrane and the anode reduced the roughness of the BC membrane from 120 nm to 45 nm, and the maximum luminance value was increased from 600 cd/m^2 to 1200 cd/m^2. To date, much effort has been focused on the improvement of the surface smoothness between substrate and anode. The common surface-smooth buffer layers in flexible TEOLEDs include metal, polymer, or silicide.

In this paper, an MoO_x film is deposited on the PET substrate as a buffer layer to fabricate a PET-based flexible TEOLED. It is noted that as a broad bandgap semiconductor with a work function of 5.3 eV, MoO_x can be used not only as a hole injection layer (HIL) to improve the hole injection ability and to reduce the operating voltage, but also as a planarization layer to smooth the PET substrate surface. Compared with other metals and silicide, MoO_x can be easily obtained and thermally deposited on the PET substrate surface through a simple process without high evaporation temperature. This method of dealing with PET substrate surfaces has a very good repeatability. We fabricate flexible white TEOLEDs and analyzed the influence of the MoO_x buffer layer on the optoelectrical performances in the present paper. It is worth pointing out that only one white TEOLED based on a flexible substrate has been reported by Ji *et al.*[15] up to now. Our device structure combines red and blue phosphorescent dual emitting layers (EMLs) to synthesize the white emission together with the strategy of inserting a spacer layer to effectively prevent Dexter energy transferring from the blue triplet state to the red triplet state in a flexible white TEOLED. Not only a relatively high efficiency and an excellent color stability, but also an excellent flexibility have been observed in the white TEOLED.

2. Experiment

Prior to the device deposition, the flexible PET substrates were cleaned with acetone and ethanol by using an ultrasonic bath, rinsed with deionized water, and then dried in an oven at 80 °C for ten minutes. Different thickness values of the MoO_x films were deposited in vacuum onto the PET substrates to improve the surface roughness of PET, and the atomic force microscope (AFM) was used for surface morphology analysis to observe the influence of the deposition of the MoO_x film on the surface roughness of PET. The white TEOLEDs? configurations are as follows: PET/MoO_x (x nm)/Ag (70 nm)/MoO_x (3 nm)/*m*-MTDATA:1.8 wt% F_4-TCNQ (25 nm)/NPB (10 nm)/CBP: 0.5 wt% Ir(MDQ)$_2$(acac) (5 nm)/CBP (3 nm)/CBP: 10 wt% FIrpic (25 nm)/Bphen (40 nm) /Sm (8 nm)/Ag (16 nm) (Fig. 1), where the devices modified with the MoO_x thickness values of 0, 50, 100, and 200 nm are denoted as devices A, B, C, and D, respectively. Here, Alq_3, *m*-MTDATA, F_4-TCNQ, NPB, Bphen, CBP, Ir(MDQ)$_2$(acac), and FIrpic are the abbreviations of tris-(8-hydroxyquinoline)aluminum, 4, 4′, 4″-tris(3-methylphenylphenylamino) triphenylamine, tetrafluoro-tetracyanoqino dimethane, N, N′-bis(naphthalen-1-yl)- N, N′-bi(phenyl)-benzidine, 4,7-diphenyl-1,10-phenanthroline, (4, 4′-N, N′-dicarbazole) biphenyl, iridium-(III)bis(2-methyldibenzo-[f,h]quinoxaline)(acetylacetonate), and iridium(III)bis[4,6-(di-fluorophenyl)-pyridinato-N,C^2], respectively. *m*-MTDATA:F_4-TCNQ, NPB, Ir(MDQ)$_2$ (acac) doped CBP, CBP, FIrpic doped CBP, and Bphen were utilized as an HIL, a hole transporting layer (HTL), a red EML, an interlayer, a blue EML, and an electron transporting layer (ETL). The Ag anode film, a 3-nm-thick MoO_x HIL film, all organic layers, and the Sm/Ag cathodes were deposited sequentially without breaking vacuum. The Sm/Ag bilayer was utilized as an effective cathode due to Ag environmental stability and Sm low work function of $\sim$ 2.7 eV and relatively high transparence in the visible range.[20,21] All depositions were finished in a high vacuum of about 10^{-4} Pa with a rate of 0.1 nm/s–0.3 nm/s. The electroluminescent (EL) characteristics of all the devices were measured with a Keithley 2400 source measurement unit and a Photo-Research PR-655 Spectra Scan Colorimeter in a glove box.

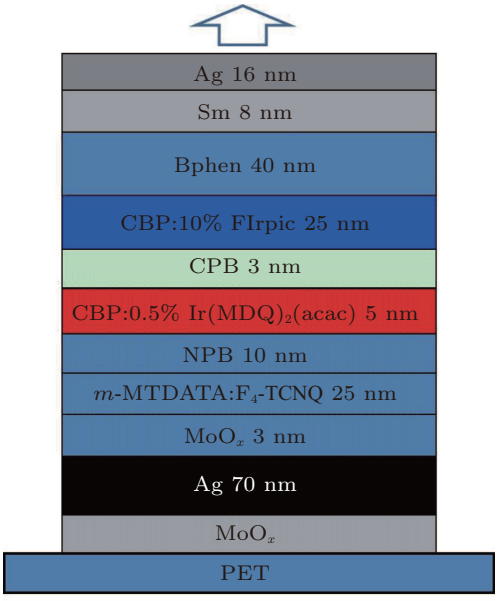


Fig. 1. (color online) Schematic diagram of flexible white TEOLEDs. Devices A, B, C, and D each own an identical device structure but different MoO_x modification thickness values of 0, 50, 100, and 200 nm.

3. Results and discussion

The AFM images in Fig. 2 show the PET surface morphologies with different MoO_x thickness values, from which one observes that the PET surface with the 100-nm-thick MoO_x film exhibits the smallest surface roughness (R_{ms}) of only 0.273 nm, far less than 0.585, 0.726, and 0.787 nm for 0-, 50-, 200-nm thick MoO_x films.

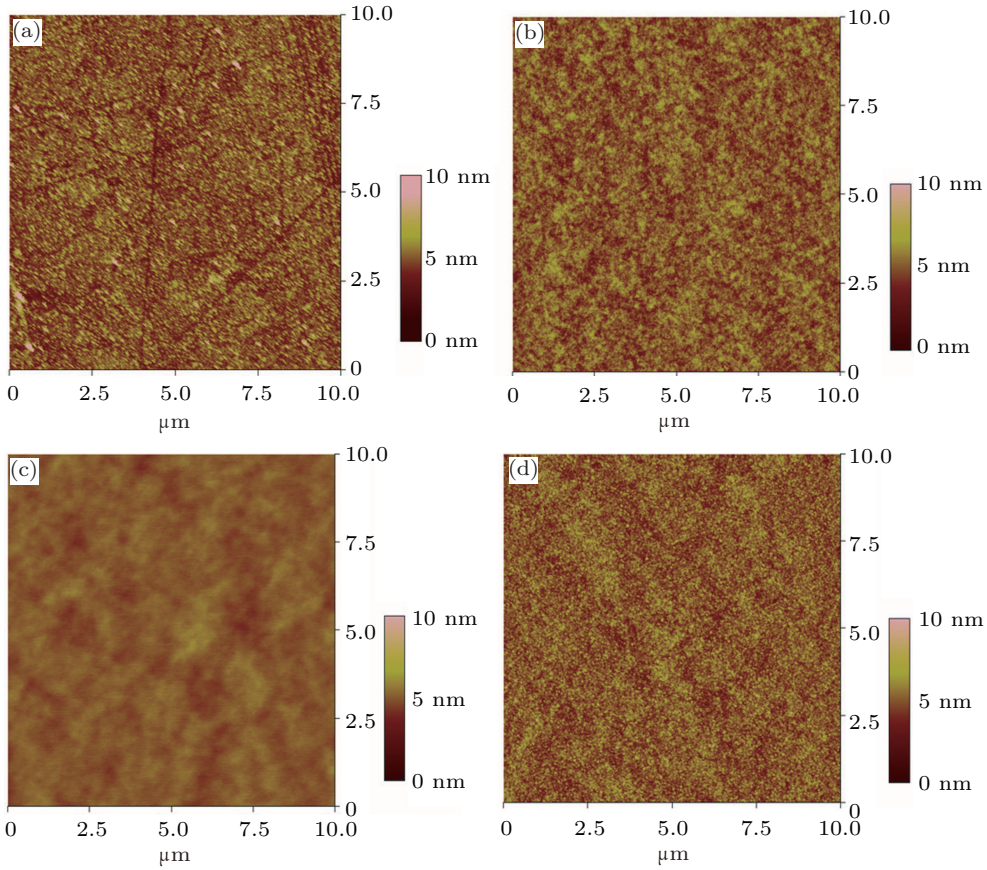


Fig. 2. (color online) The AFM surface morphology images with (a) 0- ($R_{ms} = 0.585$ nm), (b) 50- ($R_{ms} = 0.726$ nm), (c) 100- ($R_{ms} = 0.273$ nm), and (d) 200- ($R_{ms} = 0.787$ nm) nm-thick MoO_x modified PET substrates.

To make sure of the influence of R_{ms} on the electrical characteristics of the device, we compared the luminance–voltage (L–V), current density–voltage (J–V), current and power efficiency characteristics of devices A–D, as shown in Fig. 3, from which one observes that the flexible device with an MoO_x modification layer shows better electrical injection and EL performances than without a modification layer. Among all the devices, device C with a 100-nm-thick MoO_x buffer layer exhibits the best luminance and the highest injection current, indicating a smooth substrate is helpful to enhance both electrical injection ability and improve EL performances. The maximum luminances of devices B (50-nm MoO_x), C (100-nm MoO_x), and D (200-nm MoO_x) reach 3389, 4313, and 2803 cd/m^2 at 11 V, while that of device A (no MoO_x) is 2594 cd/m^2. The maximum current efficiencies for devices A, B, C, and D are 3.47 cd/A (11 V), 4.64 cd/A (8 V), 4 cd/A (11 V), and 4.24 cd/A (8 V), and the power efficiencies correspond to 1.2 lm/W (9 V), 1.9 lm/W (7 V), 1.4 lm/W (7 V), and 1.7 lm/W (7 V), respectively. The above results demonstrate that although device C demonstrates the largest brightness together with the highest injection current in all devices, its efficiency shows a little decrease due to obviously enhanced current density.

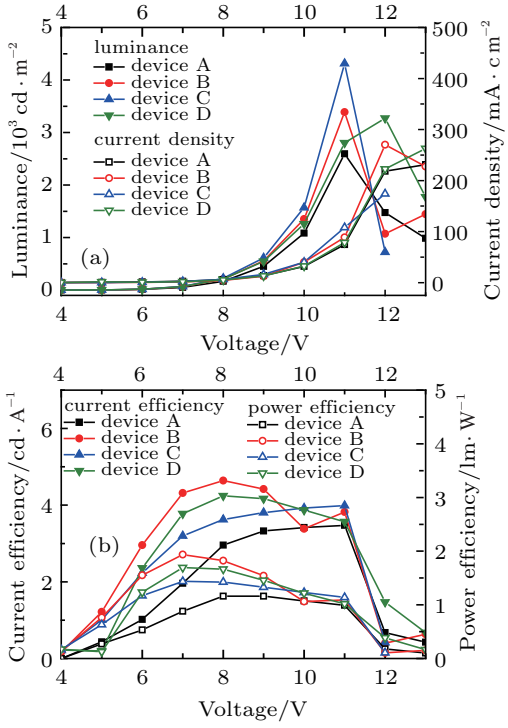


Fig. 3. (color online) (a) L–V and J–V, (b) current efficiency and power efficiency characteristics of devices A–D.

Figure 4 shows the normalized EL spectra of devices A–D under different driving voltages of 5 V–11 V. Obviously, a relatively large chromaticity shift, e.g., (0.1, 0.02), occurs

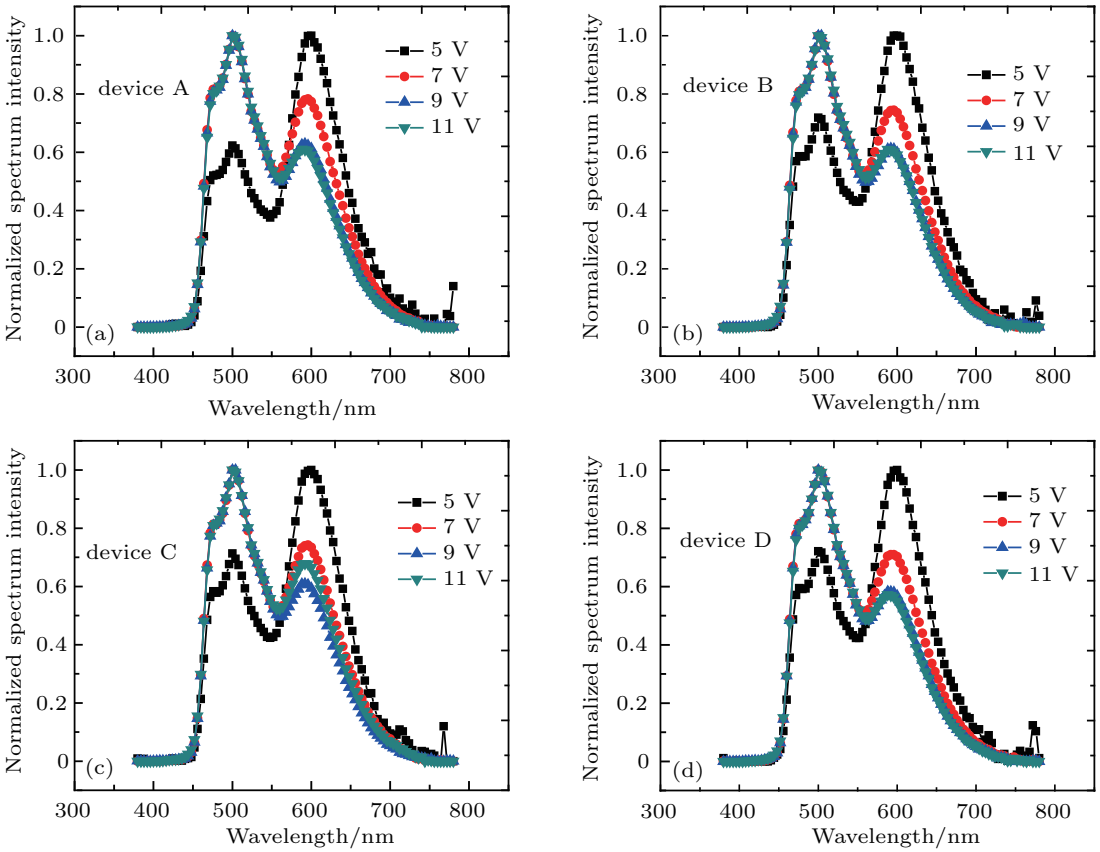


Fig. 4. (color online) Variations of EL spectrum with voltage for devices A–D.

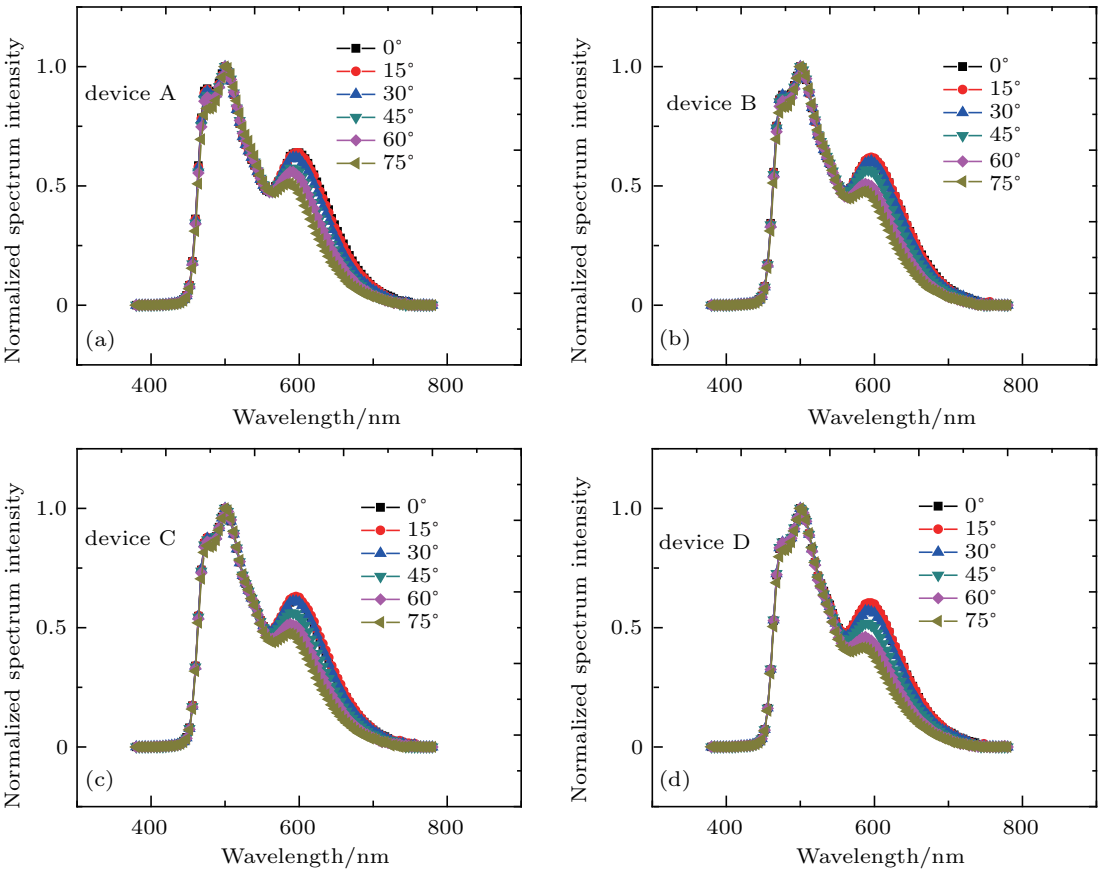


Fig. 5. (color online) Angular dependences of EL spectrum of devices A–D.

in all devices in a large change range of luminance from a turn-on luminance (1 cd/m^2) to the highest emission intensity. Fortunately, the EL spectra seem to be more stable with an EL intensity of over 100 cd/m^2, with a change amplitude of less than (0.016, 0.005) for all devices, indicating an excellent color stability in our white flexible TEOLEDs. A 3-nm-thin CBP film, as a bipolar transport material, inserted into the red and the blue EMLs can effectively confine the Dexter energy transfer of excitons and further enhance device EL performances and color stability.[22] In addition, the thin CBP film that also acts as the host of both red and blue EMLs is useful to obtain a high EL efficiency due to no introduction of additive energy barriers. Figure 5 shows the normalized EL spectra of devices A–D under different viewing angles from 0° to 75° at 10 V. The corresponding CIE$_{x,y}$ coordinate changes are (0.033, 0.024), (0.035, 0.017), (0.036, 0.012), and (0.046, 0.01) for devices A, B, C, and D, respectively. The weak angular dependence in the EL spectrum indicates that there exists a weak microcavity effect in our white device, mainly owing to the very low reflectivity of the combined Sm/Ag cathode.

The mechanical bending tests of all the above flexible white TEOLEDs have been conducted with a 9-mm radius of curvature at an initial intensity of 1000 cd/m^2 ($\sim$ 10 V). From the variation curves of the emission intensity with bending times shown in Fig. 6, one observes that an MoO_x buffer layer on the PET substrate helps to improve the surface adhesion of the PET substrate due to the surface energy of oxide ($>$ 500 mJ/m^2) higher than 44.6 mJ/m^2 for a baked PET. So the flexible white light with an MoO_x buffer layer can give obvious light-emission without break even if the bending times are as high as 500 times, while that without an MoO_x buffer layer gives no emission within 200 times. It must be noted that all devices decrease to half the initial luminance within 30 times, indicating the introduction of MoO_x cannot reduce the decrease of the conductivity values of electrodes, which is caused by repeated bending although Ag has very good malleability and ductility.

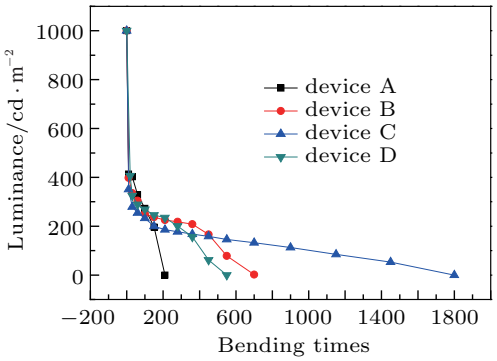


Fig. 6. (color online) Mechanical bending measurements for devices A–D with an initial EL intensity of 1000 cd/m^2.

4. Conclusions

We developed novel flexible white TEOLEDs with MoO_x as a planarization layer, which is directly deposited onto the PET substrate. With an optimized MoO_x thickness of 100 nm, the PET surface roughness can be reduced to 0.273 nm. The flexible white TEOLEDs are constructed with red and blue phosphorescent dual EMLs to synthesize the white emission together with a low reflectivity of an Sm/Ag bilayer cathode. The maximum luminance and the current efficiency of the flexible white emission are 4313 cd/m^2 at 11 V and 4.64 cd/A at 8 V, with an enhancement factor of 1.7/1.2, respectively. In addition, it should be pointed out that the flexible white TEOLED can withstand more than 500 bending times at a bending curvature radius of approximately 9 mm and has an excellent color stability with a large variation of luminance of over 100 cd/m^2.

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