

# Solvent Effects on the Architecture and Performance of Polymer White-Light-Emitting Diodes with Conjugated Oligoelectrolyte Electron-Transport Layers

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Multilayered structures improve the function of organic optoelectronic devices. For example, operational voltages can be substantially decreased, and the light output to current ratio increased, upon insertion of electron-injection/transport layers (ETLs) or hole-injection/transport layers at the cathode and anode interfaces, respectively.<sup>[1–8]</sup> These layers can reduce the barriers to charge injection from the electrodes into the organic semiconductor, and improve efficiencies via mechanisms that have been summarized in the literature.<sup>[8–12]</sup> One practical challenge concerns methods for fabricating multilayered systems via procedures that are efficient and that provide for control of active-layer thicknesses and organic/organic interfaces widths. The fabrication of small-molecule-based devices benefits from the ability of vacuum deposition methods to sequentially deposit materials, with excellent precision over the individual layer thickness and without large disruptions of underlying organic coatings.<sup>[13,14]</sup>

The situation with conjugated polymer-based devices, such as polymer light-emitting diodes (PLEDs), is different. PLEDs offer the possibility of solution-based fabrication options and of tailoring blends that incorporate multiple components in a single layer.<sup>[15–18]</sup> However, multilayer fabrication is challenging if one wishes to deposit layers atop of each other when the materials have similar solubility characteristics.<sup>[19]</sup> Under these circumstances, one observes poorly defined interfaces and a disruption of the underlying polymer layers.

It is in the context of PLED preparation that conjugated polyelectrolytes can offer new options to build well-defined multilayered structures.<sup>[20–25]</sup> These materials are described as presenting a backbone with an electronically delocalized structure, that is, the semiconducting component, and pendant groups bearing ionic functionalities. Such structural attributes lead to higher solubility

in polar solvents than their neutral counterparts, and enable multilayer formation by alternatively depositing layers from solvents with orthogonal polarities.<sup>[26–28]</sup> It is possible in these devices to use high-work-function metals, such as Al or Au, and to obtain turn-on voltages and efficiencies similar to those observed with low-work-function metals, such as Ba. Recent mechanistic work has demonstrated the importance of ion migration and charge-carrier accumulation at the emissive layer/conjugated polyelectrolyte interface in modulating barriers to injection.<sup>[29]</sup> Despite this improved understanding of function, the full scope of how the choice of solvent for fabrication influences the device performance has yet to emerge.<sup>[30,31]</sup>

Conjugated oligoelectrolytes may offer some advantages over their polymeric analogs, in that their molecular structures are precisely defined and their synthesis yields no batch-to-batch variations. One example is the hexacationic fluorene trimer with (*N,N,N*-trimethylammonium)hexyl substituents and tetrakis(1-imidazolyl)borate counterions (**FFF-BIm<sub>4</sub>**), shown in Figure 1. This structure is representative of three consecutive repeat units in the corresponding cationic poly(fluorene) species. It was shown recently that PLEDs that utilize a conjugated oligoelectrolyte as the ETL can show efficiencies similar to those that incorporate conjugated polyelectrolytes.<sup>[32]</sup>

In this contribution, we use **FFF-BIm<sub>4</sub>** to investigate how solvent mixtures used for the ETL deposition can influence the performance of polymer white-light-emitting diodes (PWLEDs). We show that solvent mixtures need to be carefully adjusted in order to avoid selective extraction of components from active layers containing multiple molecular species. Proper management of the conjugated-oligoelectrolyte deposition can indeed lead to PWLEDs with Al electrodes, which display low turn-on voltages and high efficiencies. Our studies used a blend containing poly(*N*-vinylcarbazole) (PVK), 1,3-bis[2-(4-*tert*-butylphenyl)-1,3,4-oxadiazole-5-yl]benzene (OXD-7), bis(2-(4,6-difluorophenyl)-pyridinato-*N,C'*) picolinate Iridium (FIr-pic), and bis(1-phenylisoquinoline)(acetylacetonate) iridium ((pic)<sub>2</sub>Ir(acac))<sup>[33a]</sup> as the emissive layer (EML, see Fig. 1 for molecular structures). This combination of materials was chosen to serve as a model system, because of its multicomponent nature and the previous work demonstrating white emission with efficiencies on the order of 16 cd A<sup>−1</sup>.<sup>[33b]</sup>

PLEDs were fabricated with the structure indium tin oxide (ITO)/PEDOT:PSS/EML/cathode, where PEDOT:PSS is poly(ethylenedioxythiophene):poly(styrenesulfonate) (see the Experimental

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DOI: 10.1002/adma.200802548

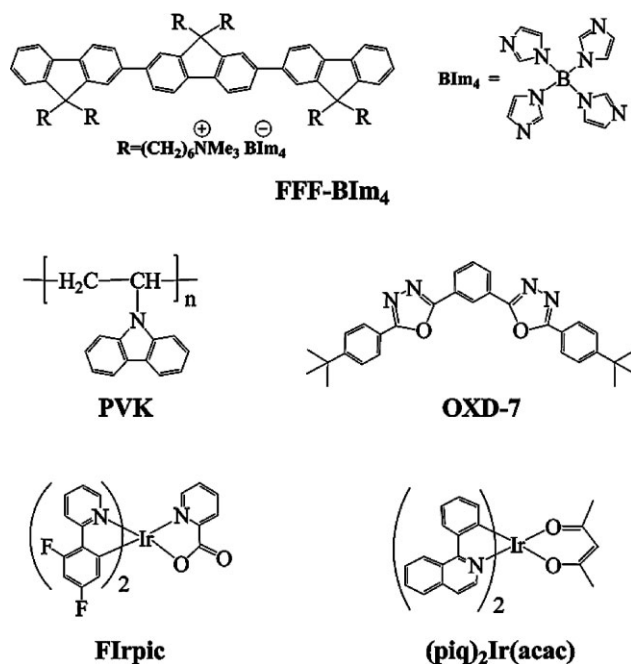


Figure 1. Molecular structures of the materials used in this study.

Section for the exact ratio of the component in the EML blend). Cathodes used included Al, Ba/Al, and Al deposited above a thin layer of **FFF-BIm<sub>4</sub>**. **FFF-BIm<sub>4</sub>** was spun-cast from methanol or methanol/water mixtures atop the EML. The current density ( $J$ )–voltage ( $V$ ) and efficiency ( $E$ ) and luminance ( $L$ ) versus  $J$  characteristics of devices with different cathodes are shown in Figure 2. Figure 2a and b provide the data obtained from ITO/PEDOT:PSS/EML/Al and ITO/PEDOT:PSS/EML/Ba/Al, which serve as “baseline” measurements for this study. The well-established improvement obtained with the low-work-function electrode is observed.<sup>[34]</sup>

Figure 2c and d correspond to the characteristics of ITO/PEDOT:PSS/EML/**FFF-BIm<sub>4</sub>**/Al devices, in which the **FFF-BIm<sub>4</sub>** was deposited from MeOH or mixtures of MeOH and H<sub>2</sub>O with compositions 7:1, 3:1, 1:1, and 1:2 (MeOH:H<sub>2</sub>O, v/v). Comparison of the data for ITO/PEDOT:PSS/EML/Al and ITO/PEDOT:PSS/EML/**FFF-BIm<sub>4</sub>** (MeOH)/Al (**FFF-BIm<sub>4</sub>** (MeOH) indicates a **FFF-BIm<sub>4</sub>** layer deposited from methanol) shows that introducing **FFF-BIm<sub>4</sub>** from MeOH results in higher  $J$  at the same bias, but without an improvement in the  $E$  and  $L$ , unlike the situation for PLEDs where poly(2-methoxy-5-(2'-ethylhexyloxy)-1, 4-phenylenevinylene) (MEH-PPV) was used as the emissive layer. Figure 2c and d also show that the device performance improves remarkably when **FFF-BIm<sub>4</sub>** was deposited from a solvent containing MeOH/H<sub>2</sub>O mixtures. The best performance was obtained when a ratio MeOH:H<sub>2</sub>O = 3:1 was used. The  $E$  and  $L$  of this device (15.1 cd A<sup>-1</sup> and 11890 cd m<sup>-2</sup>, respectively) were higher than those observed with a Ba/Al cathode (13.2 cd A<sup>-1</sup> and 10030 cd m<sup>-2</sup>), and were almost an order of magnitude higher than those with Al (2.4 cd A<sup>-1</sup> and 263 cd m<sup>-2</sup>) or when pure MeOH was used to deposit **FFF-BIm<sub>4</sub>** (1.8 cd A<sup>-1</sup> and 483 cd m<sup>-2</sup>). The turn-on voltage was also significantly reduced

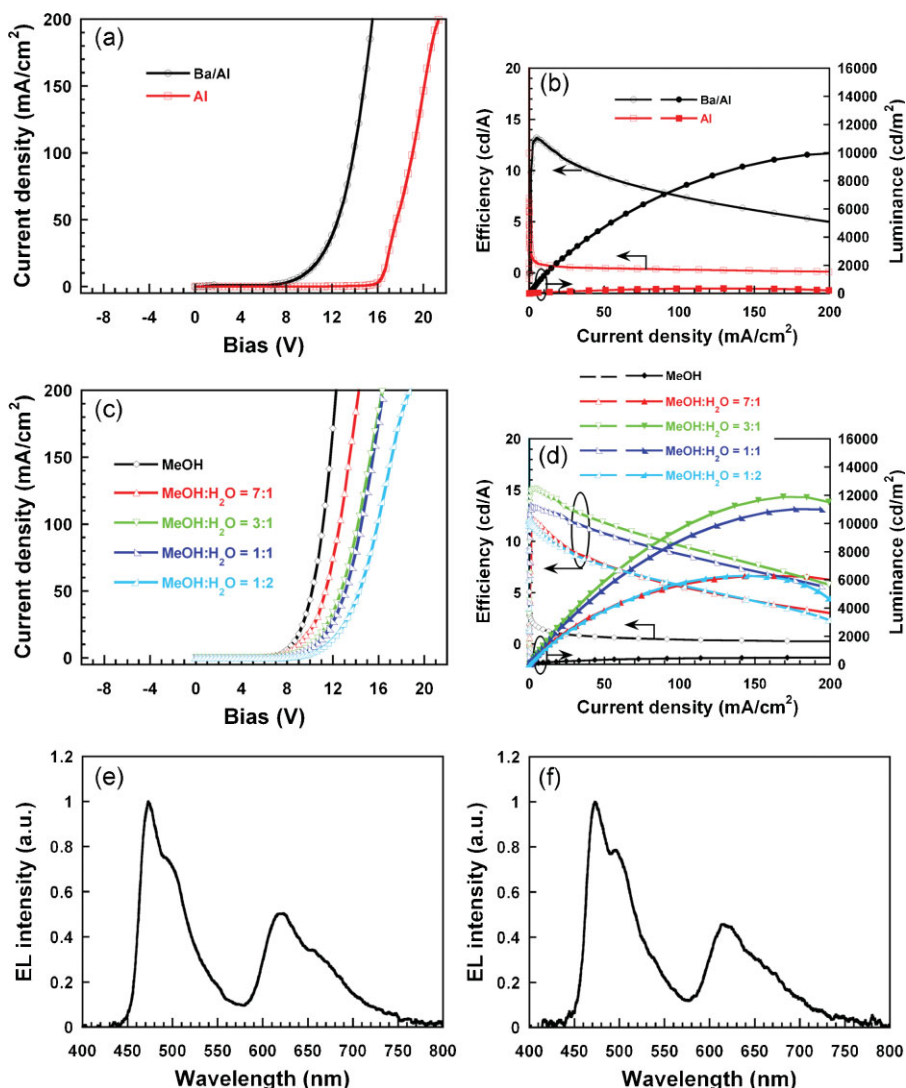
(5.6 V) compared to devices with Al cathodes (9.3 V), suggesting that an enhancement in electron-injection occurred. The reason why water has such a strong impact on device performance became the central question addressed in subsequent experiments, as described below.

The electroluminescence (EL) spectra in Figure 2e and f for ITO/PEDOT:PSS/EML/Ba/Al and ITO/PEDOT:PSS/EML/**FFF-BIm<sub>4</sub>** (MeOH:H<sub>2</sub>O = 3:1)/Al are similar. The emitting species are thus not influenced by previous contact with water. The *Commission Internationale d'Eclairage* (CIE) coordinates obtained at 100 mA cm<sup>-2</sup> were (0.31,0.34) and (0.31,0.35) for the Ba/Al and **FFF-BIm<sub>4</sub>** (MeOH:H<sub>2</sub>O = 3:1)/Al devices, respectively, very near the desired pure-white point, (0.3333,0.3333). When the  $J$  was increased from 10 mA cm<sup>-2</sup> to 200 mA cm<sup>-2</sup>, the CIE coordinates changed from (0.30,0.35) to (0.32,0.35), for ITO/PEDOT:PSS/EML/**FFF-BIm<sub>4</sub>** (MeOH:H<sub>2</sub>O = 3:1)/Al.

Atomic force microscopy (AFM) was used to image the surface topography after **FFF-BIm<sub>4</sub>** deposition atop the EML from either MeOH or 3:1 MeOH/H<sub>2</sub>O. Results are shown in Figure 3. Rough surfaces were observed for both films, possibly due to low molecular weight of **FFF-BIm<sub>4</sub>**. However, the quality of the film is much poorer when formed from the mixed solvent (Fig. 3b), and suggests poor contact during spin-coating, as a result of the mismatch between the hydrophobic EML surface and the increased solvent polarity when water is present. Despite the poor film-forming ability of **FFF-BIm<sub>4</sub>** (MeOH:H<sub>2</sub>O = 3:1), we recall the improved charge injection of ITO/PEDOT:PSS/EML/**FFF-BIm<sub>4</sub>** (MeOH:H<sub>2</sub>O = 3:1)/Al compared to ITO/PEDOT:PSS/EML/Al, as demonstrated in Figure 2.

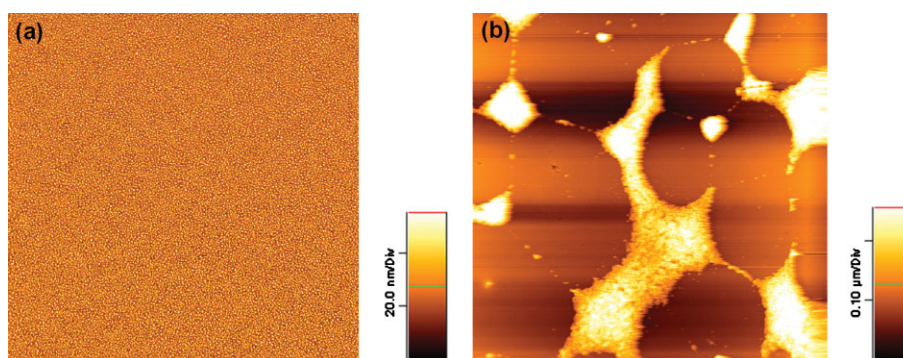
Possible perturbations on the EML composition were probed by absorption spectroscopy. In these studies, the EML was first deposited on quartz. A set volume (100 μL) of MeOH or 3:1 MeOH/H<sub>2</sub>O was subsequently deposited on the surface, and the substrate was spun-dried under conditions similar to those used for PLED fabrication. Films were then annealed by heating to 120 °C for 10 min. Figure 4a shows the absorbance spectra of the EML film with and without exposure to the solvent. Notably, the absorption is decreased after MeOH treatment, but not when MeOH/H<sub>2</sub>O is used. Furthermore, the difference in the absorption profile for the EML film before and after MeOH treatment is very similar to the absorption measured for OXD-7 (Fig. 4b). It can be concluded from this comparison that pure MeOH preferentially extracts OXD-7 from the EML layer. Such a compositional variation in the active layer is likely responsible for the poor performance of the ITO/PEDOT:PSS/EML/**FFF-BIm<sub>4</sub>** (MeOH)/Al devices.

Changes in layer thickness are consistent with OXD-7 extraction. The thicknesses were characterized by AFM, as shown in Figure 5. The as-cast EML thickness of ~80 nm (Fig. 5a) is reduced to ~45 nm after MeOH treatment (Fig. 5b). For samples treated by MeOH:H<sub>2</sub>O (3:1), a thickness of ~80 nm was measured, thus no obvious thickness change was observed. We next consider the EML composition as PVK:OXD-7:FIrpic:(piq)<sub>2</sub>Ir(acac) = 46.9:46.9:6:0.2% (by weight). Assuming equal densities for all components, OXD-7 constitutes ~47% of the EML volume. Thus, the loss in volume, which is proportional to the decrease in height (43%), is consistent with a large fraction of the OXD-7 being removed by MeOH from the EML.



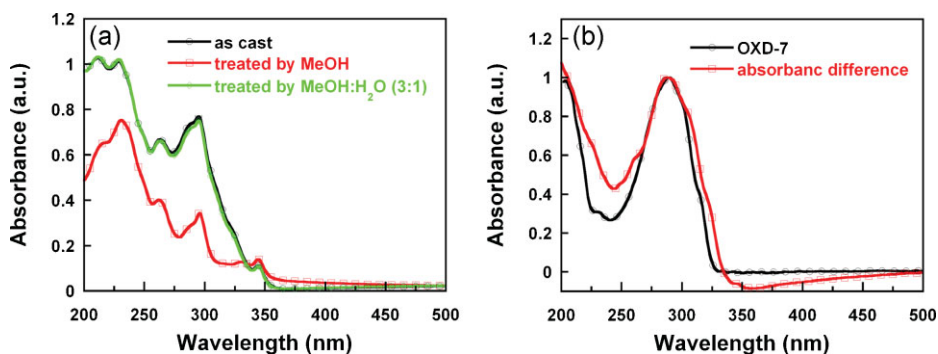
**Figure 2.** a)  $J$ - $V$  and b)  $E$ - $J$ - $L$  characteristics of devices with Ba and Al cathodes at  $100 \text{ mA cm}^{-2}$ . c)  $J$ - $V$  and d)  $E$ - $J$ - $L$  characteristics of devices with FFF-Bim<sub>4</sub> (deposited from different solutions)/Al cathodes. e, f) EL spectra of devices with Ba/Al and FFF-Bim<sub>4</sub> (MeOH:H<sub>2</sub>O = 3:1)/Al cathodes.

In summary, we have shown that PWLEDs can be fabricated where conjugated oligoelectrolytes are effective for lowering electron-injection barriers at the metal/organic interface. This feature allows use of stable metals, such as aluminum, as the cathode, and is relevant for the problem of charge injection into wide-band-gap host materials. We have also shown that the choice of solvent bears a strong influence on the internal composition of the device. Pure methanol proved capable of extracting a critical component of the EML blend. Examination of surface features does not provide sufficient insight for this determination; rather, the internal composition needs to be established by, for example, absorption spectroscopy. Addition of water to methanol decreases the interaction with the hydrophobic EML surface, thereby avoiding extraction of OXD-7. Note that this poor solvent/surface interaction also leads to poor wetting and to the formation of large fractional areas of the EML surface that appear not to be covered by the conjugated oligoelectrolyte. The extent to which ion motion versus dipole effects influence charge injection is still not clear. Despite these apparently detrimental features and mechanistic uncertainties, the PLED performance is excellent ( $15 \text{ cd A}^{-1}$  and  $11890 \text{ cd m}^{-2}$ ), and the color coordinates are appropriate for white-light illumination. Present studies are aimed at probing how the ETL may change characteristics and coverage during the

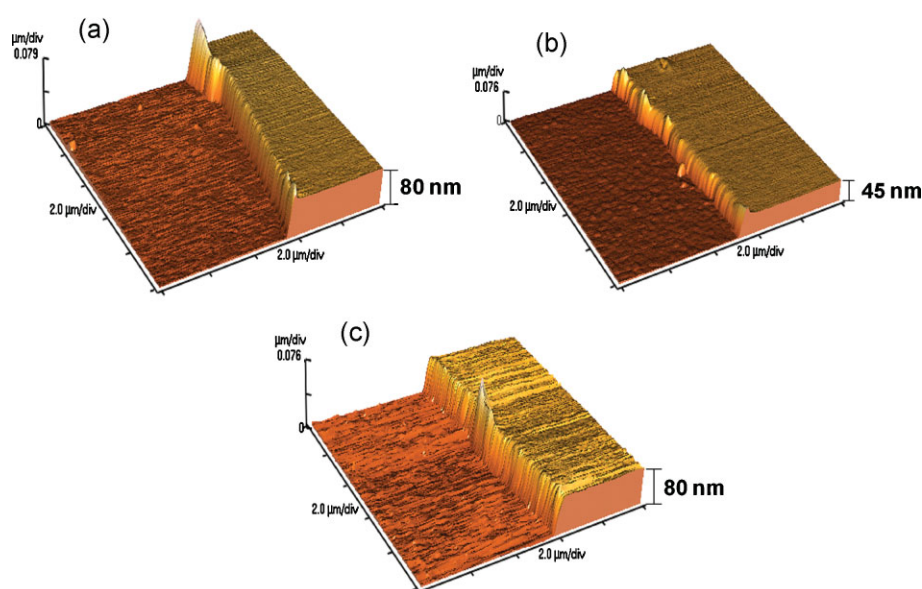


**Figure 3.** AFM surface-morphology images of films of FFF-Bim<sub>4</sub> deposited atop the EML from a) (MeOH) and b) (MeOH:H<sub>2</sub>O = 3:1). The size of the image is  $50 \mu\text{m} \times 50 \mu\text{m}$ .





**Figure 4.** a) Absorbance spectra of samples as cast and treated with MeOH and MeOH:H<sub>2</sub>O (3:1). b) Absorbance spectrum of OXD-7 and absorption-difference spectra between absorbance of films as cast and treated with MeOH.



**Figure 5.** AFM thickness images of films a) as cast and treated with b) MeOH and c) MeOH:H<sub>2</sub>O (3:1).

metal-deposition step. It is likely that morphological changes induced by the required experimental conditions may lead to better EML coverage by **FFF-BIm<sub>4</sub>**.<sup>[32]</sup>

## Experimental

**Materials:** **FFF-BIm<sub>4</sub>** was synthesized using a method previously described [32]. Poly(styrenesulfonate) (PEDOT: PSS, Baytron P VP CH 8000) was obtained from H. C. Stark. PVK was purchased from Aldrich. Flrpic and (piq)<sub>2</sub>Ir(acac) were purchased from American Dye Source. OXD-7 was purchased from Sensient. All materials were used as received.

**Device Fabrication:** The devices were fabricated with the base structure of ITO/PEDOT: PSS/EML/Ba or **FFF-BIm<sub>4</sub>**/Al. Prior to PEDOT:PSS deposition, patterned ITO substrates underwent wet-cleaning in an ultrasonic bath and UV-ozone treating for 30 min. A thin layer of anode buffer of PEDOT: PSS was spun-cast on top of the ITO. After annealing for 10 min at 200 °C, an EML film 80 nm thick was spun-cast from chlorobenzene (PVK:

OXD-7:Flrpic:(piq)<sub>2</sub>Ir(acac) = 9.96:9.96:1.28:0.043 mg mL<sup>-1</sup>). The active layer consisted of a blend host of PVK:OXD-7 (1: 1 by weight) and two phosphorescent iridium emitters of 6 wt% blue-green Flrpic and 0.2 wt% red (piq)<sub>2</sub>Ir(acac). Following annealing for 30 min at 120 °C, the **FFF-BIm<sub>4</sub>** layer was cast from MeOH or MeOH:H<sub>2</sub>O (3:1) solutions. Finally, after annealing at 120 °C for 10 min, the cathode consisting of either 100 nm Al or 4 nm Ba covered with a 100 nm Al was thermally evaporated at a pressure of  $1.33 \times 10^{-4}$  Pa.

**Sample Preparation for AFM and Absorbance Measurements:** Samples for AFM studies were fabricated by spin-coating the EML on quartz substrates. Following annealing at 120 °C for 30 min, the treatment was carried out by dropping MeOH or MeOH:H<sub>2</sub>O (3:1) on top of the EML and spinning to dry them. To maximize the removal of residual solvent, samples were heated at 120 °C for 10 min. EMLs for absorbance studies were prepared by spin-casting the same solutions used in device fabrication on top of quartz substrates, which were subsequently heated at 120 °C for 30 min.

**Device Characterization:** The J–V–L characteristics were measured using a Keithley 2602 system source meter unit and a calibrated silicon photodiode. The EL spectra were recorded using an Ocean Optics spectrometer. AFM images were obtained using a Digital Instruments CP-II

scanning probe microscope (Veeco). PL and absorption spectra were performed using a Quantum Master fluorometer (PTI) and UV-2401 PC diode array spectrometer (Shimadzu), respectively.

## Acknowledgements

This work is supported by the National Science Foundation (DMR 0606414) and the Department of Energy (DE-FC26-04NT42277). Y.H.X. is grateful to Xiong Gong for fruitful discussion, and acknowledges the support from the Doctorate Foundation of South China University of Technology.

Received: August 29, 2008

Revised: October 8, 2008

Published online: November 25, 2008

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