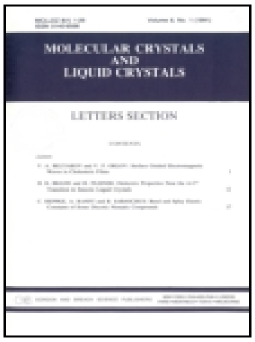

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Comparison Study of Phenylquinoline-based Iridium(III) Complexes for Solution Processable Phosphorescent Organic Light-Emitting Diodes by PEDOT:PSS and Graphene Oxide as a Hole Transport Layer

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Electroluminescent (EL) properties of Ir(III) complex, [(2,4-diphenylquinoline)]$_2$Iridium picolinic acid N-oxide [(DPQ)$_2$Ir(pic-N-O)] were investigated using PEDOT:PSS and reduced graphene oxide (rGO) as a hole transport layer for solution processable phosphorescent organic light-emitting diodes (PhOLEDs). High performance solution-processable PhOLED with PEDOT:PSS and (DPQ)$_2$Ir(pic-N-O) (8 wt%) doped CBP:TPD:PBD (8:56:12) host emission layer were fabricated to give a high luminance efficiency (LE) of 26.9 cd/A, equivelent to an external quantum efficiency (EQE) of 14.2%. The corresponding PhOLED with rGO as a hole transport layer exhibited the maximum brightness and LE of 13540 cd/m^2 and 16.8 cd/A, respectively. The utilization of the solution processable rGO thin films as the hole transport layer offered the great potential to the fabrication of solution processable PhOLEDs.

Keywords organic light-emitting diodes; iridium complex; phosphorescent; solution processable; graphene oxide; picolinic acid N-oxide

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Introduction

Organic light-emitting diodes (OLEDs) are being most extensively researched for many applications, including flat-panel displays and solid-state lightings [1]. As of now available light-emitting materials, phosphorescent iridium (Ir) complexes are particularly promising because they can emit the light from both singlet and triplet excitons, enabling the fabrication of phosphorescent organic light-emitting diodes (PhOLEDs) with close to 100% internal quantum efficiency [2]. Solution-processed PhOLEDs have several advantages, including its simplicity, manufacture ability on a large scaled area, and extremely low cost [3]. Thus, many research groups are still focused on the synthesis of suitable materials for the solution fabrication processes to improve the device performance [4].

The majority of PhOLEDs based on solution processed layers contain oligomers, conjugated polymers [5] and more recently dendrimers [6]. Through functionalization of the main ligands with electron-withdrawing and/or electron-donating substituents, several groups have demonstrated the tuning of the phosphorescence wavelength from blue to red [7].

Poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives have many interesting properties, including a good stability in oxidized state, a low-band gap, a high electrochromic contrast, and a rapidly switching time [8]. The insertion of PEDOT doped with poly(styrenesulfonate) (PEDOT:PSS) as a hole transport layer in multilayer optoelectronic devices can dramatically improve the device performance [9]. However, the poor solubility of PEDOT:PSS is a significant limitation in their practical use [10]. Another disadvantage of PEDOT:PSS is its acidic nature with pH values of 1.3-2.0, which often causes ITO etching to damage the emitting layer and device instability. Therefore, the search for alternative solution-processable hole transport layer with high transmittance in a sufficiently conducting state are one of hot current issues for the development of high performance organic electronics, such as PhOLEDs and organic photovoltaics (OPVs). Graphene, a new class of two-dimensional (2D) single atom thick carbon nanosheets consisting of hexagonally arranged carbon networks, has attracted extensive attention because of its unique electronic and optical properties [11]. Recently, many research groups reported the use of graphene, graphene oxide (GO), or reduced graphene oxide (rGO) to replace the PEDOT:PSS as a transparent electrode and/or hole transport layer in polymer light-emitting diodes and OPVs [12], [13].

In this paper, we carried out a strategic comparison study on the use of solution-processable PEDOT:PSS and rGO as a hole transport layer, respectively, in PhOLEDs. To the best of our knowledge, this is the first paper reporting the comparison work on the device performance using PEDOT:PSS and rGO as a hole transport layer in PhOLEDs.

Experimental

General Information

All chemicals and reagents were purchased from Aldrich Chemical Co. and used without further purification. The UV-visible and the fluorescence spectra were recorded on a JASCO V-570 and Hitachi F-4500 fluorescence spectrophotometers at room temperature. Cyclic voltammetry (CV) studies were carried out with a CHI 600C potentiostat (CH Instruments) at a scan rate of 100 mV/s in a 0.1 M solution of tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) in anhydrous acetonitrile/benzene (1:1.5 v/v). A platinum wire was used as the counter electrode and an $Ag/AgNO_3$ electrode was used as the reference electrode.

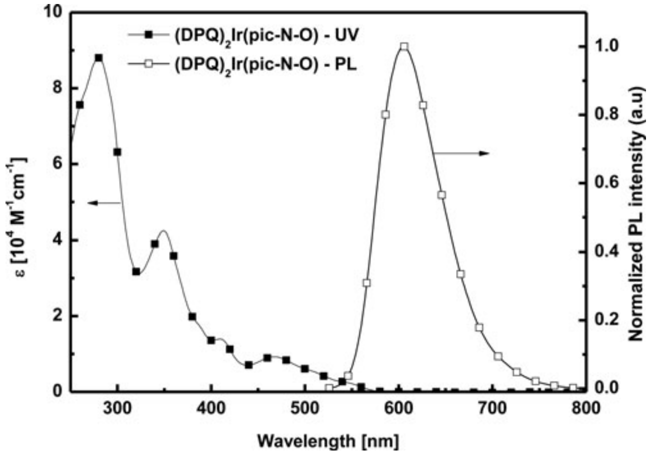


Figure 1. UV-visible absorption and emission spectra of the [(DPQ)$_2$Ir(pic-N-O)] in chloroform solution.

All of the electrochemical experimental studies were carried out in the open air at room temperature.

Device Fabrication and Measurements

The indium tin oxide (ITO) glass substrate with a sheet resistance of 20Ω/square was washed sequentially with a substrate cleaning detergent (Sigma-Aldrich, Micro-90®

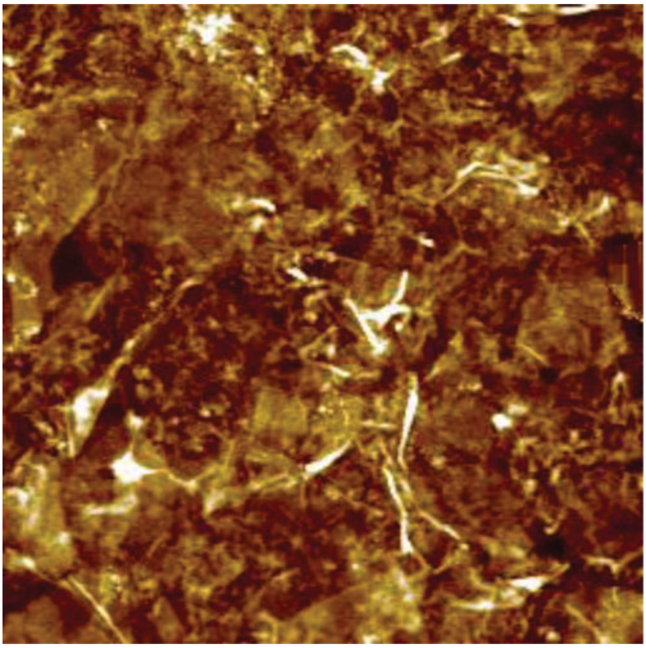


Figure 2. Representative AFM Image (2×2 μm^2) for spin casted graphene oxide on ITO glass substrate.

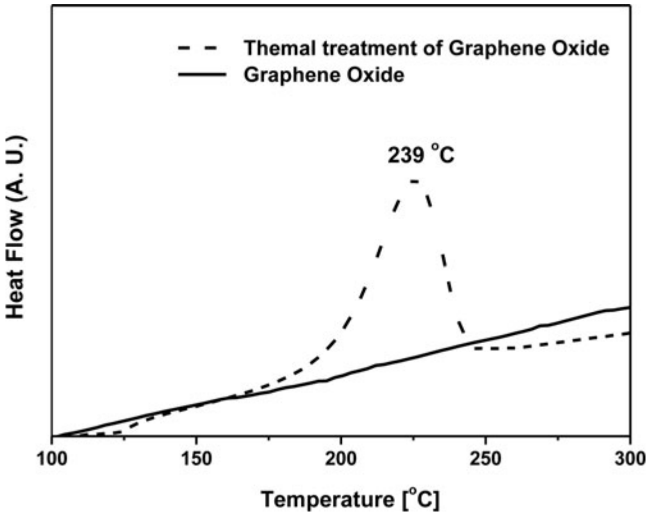


Figure 3. DSC curves of graphene oxide films : air-dried graphene oxide and thermally treated at 250°C.

concentrated cleaning solution), dionized water, aceton, and isopropyl alcohol in ultrasonic bath at 50°C. Prior to spin coating with the PEDOT:PSS layer, the ITO was precleaned and UV-ozone treated. Then a 40 nm-thick PEDOT:PSS (H.C.Starck, Clevios P VP AI 4083) layer was spin coated onto the ITO and baked in a nitrogen environment at 120°C for 20 min. Graphene oxide solution purchased from Graphene-Supermarket to characterize the effects of hole transport layer on the device performance. GO solution was dropped onto the UV-ozone treated ITO substrate, and then casted at 4000 rpm for 40 s. Thereafter, the spin-casted GO substrate was maintained at 250°C for 10 min in air. The EML is consisted of 2-(4-biphenyly)-5-(4-tert-butylphenyl)-1,3,4-oxadizole (PBD), N,N'-diphenyl-N,N'-bis(3-methyl-phenyl)-[1,1'biphenyl]-4,4;-diamine (TPD) and either of 4,4'-bis(9-cabazolyl)-biphenyl (CBP) as a mixed host and [(2,4-diphenylquinoline)]$_2$Iridium picolinic acid N-oxide [(DPQ)$_2$Ir(pic-N-O)] as a dopant. The blending ratio of CBP, TPD and PBD is 56:12:24 wt%, respectively, and doped with 8 wt% of [(DPQ)$_2$Ir(pic-N-O)] in chlorobenzene solution. The EML was obtained by spin coating onto the PEDOT:PSS or rGO layer and annealed at 70°C for 30 min in highly pure argon filled glove box in order to get thickness of 70 nm. Bphen (20 nm) as an electron transport layer as well as hole blocking layer, LiF (0.7 nm) and Al (100 nm) as typical cathode were evaporated under the vacuum less than 6×10^{-6} torr, which yielded a 9 mm^2 of emitting area for each pixel. Each layer of thickness was measured by an Alpha-step IQ surface profiler (KLA Tencor, San Jose, CA). The heating treatment of GO was monitored by XPS using Theta Probe AR-XPS (Thermo Fisher Scientific) system with a monochromated Al K$_\alpha$, hv = 1486.6 eV and Raman spectroscopy. The EL spectra and CIE coordinates were measured using a PR650 spectra colorimeter. To characterize the PhOLEDs, the current density-voltage-luminescence (J-V-L) changes were measured using a current/voltage source meter (Keithley 236) and an optical power meter (CS-1000, LS-100). All processes and measurements were carried out in the open air at room temperature.

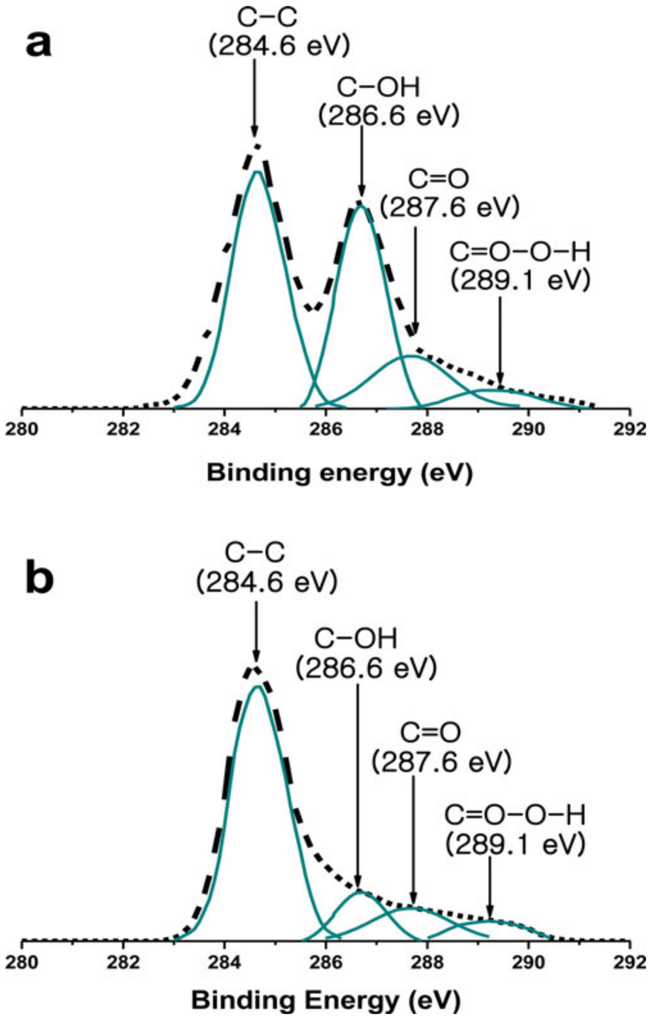
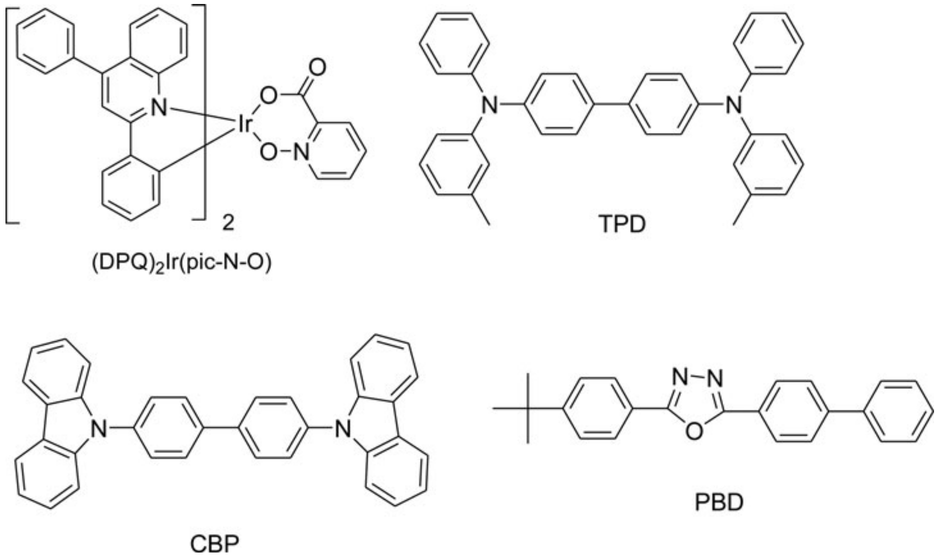


Figure 4. C1s region XPS spectra: graphene oxide films without thermal treatment (a) and with thermal treatment at 250°C (b).

Results and Discussion

Scheme 1 shows the molecular structures of the [(DPQ)$_2$Ir(pic-N-O)], PBD, TPD and CBP used in this study [14]. Fig. 1 presents the UV-visible absorption and emission spectra of the [(DPQ)$_2$Ir(pic-N-O)] in chloroform solution. As shown in Fig. 1, the absorption band is observed in the range of 280-550 nm. The intense peaks in the UV region below 400 nm were assigned to the allowed $^1\pi$-π^* transitions of the $C\hat{}N$ ligands. The weaker absorption tail that appeared above 400 nm were assigned to singlet and triplet transitions of MLCT. Under photoexcitation, [(DPQ)$_2$Ir(pic-N-O)] showed the orange-red emission color as shown in Fig. 1, which originated from the predominantly ligand-centered $^3\pi$-π excited state in the solution state. The maximum emission peak of (DPQ)$_2$Ir(pic-N-O) is shown at 586 nm. Another important requirement for PhOLED applications is that the Ir(III) complex should have high PL quantum efficiency (Φ_{pl}). The Φ_{pl} of [(DPQ)$_2$Ir(pic-N-O)] in chloroform solution were measured with $(piq)_2Ir(acac)$ as a standard ($\Phi_{pl} = 0.2$). The Φ_{pl} for $(DPQ)_2Ir$(pic-N-O) was found to be 0.83.



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

To investigate the charge carrier injection properties of the [$(DPQ)_2Ir$(pic-N-O)] and evaluate their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, we carried out redox measurements using CV. The HOMO energy levels of $(DPQ)_2Ir$(pic-N-O) with respect to the ferrocene/ferrocenium (4.8 eV) standard were estimated to be -5.5 eV. The optical band gaps (E_g) of [$(DPQ)_2Ir$(pic-N-O)] was determined from the UV-visible absorption edge and found to be 2.3 eV for $(DPQ)_2Ir$(pic-N-O). The LUMO energy level was calculated from the values of the E_g and HOMO energy to be -3.2 eV for $(DPQ)_2Ir$(pic-N-O).

To extend our ability to solution-processed method for the fabrication of PhOLEDs, we used rGO dispersed in water, instead of PEDOT:PSS, for spin-casting the hole transport layer for comparison. We fabricated the solution processable PhOLED with a configuration of ITO/ PEDOT:PSS or rGO (5 nm)/EML (70 nm)/Bphen (20 nm)/LiF (0.7 nm)/Al (100 nm). Here, EML layer was CBP:TPD:PBD:$(DPQ)_2Ir$(pic-N-O) (56:12:24:8), which was desolved in chlorobenzene and spin-casted on PEDOT:PSS or rGO layer to give a 70 nm thick film. To obtain an unifrom GO layer on the ITO glass substrate, GO solution (5 mg/mL) was casted at 4000 rpm for 40 sec to give an average thickness of about 5 nm (Fig. 2). After spin coating, the substrate was placed at 250°C for 10 min to remove residual water and achieve thermal reduction. DSC measurements (Fig. 3) provided proof of reduction of GO film after thermal treatment at 250°C. The reduction of GO film is accompanied by a highly exothermic peak centered at 239°C, which this peak is absent on the DSC thermogram of rGO film.

4,7-Diphenyl-1,10-phenanthrolin (Bphen) was thermally evaporated at a base pressure of 6×10^{-6} Torr on the spin-coated EML as an electron transport layer as well as hole blocking layer due to the high electron mobility (2.8×10^{-4} cm^2/ V·s) and high-lying HOMO [15].

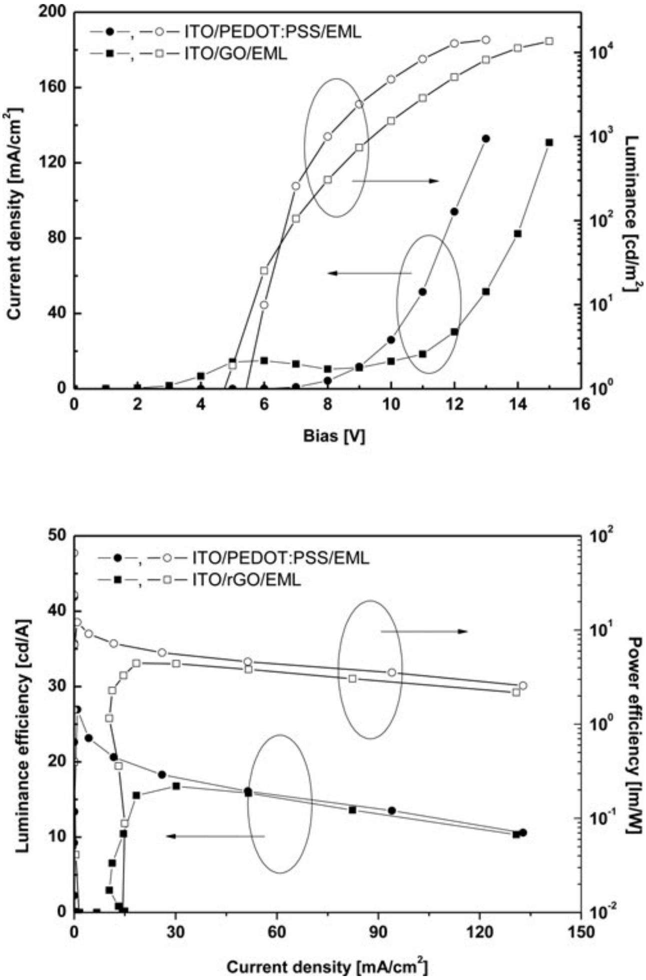


Figure 5. (a) Current density-voltage-luminance and (b) luminance efficiency-current density-power efficiency characteristics of $(DPQ)_2Ir$(pic-N-O) using PEDOT and rGO as the hole transport layer.

HOMO and LUMO energy levels of $(DPQ)_2Ir$(pic-N-O) lie above and below those of CBP host. Therefore, it is expected that $(DPQ)_2Ir$(pic-N-O) trap both electrons and holes within EML. Moreover, the hole block/electron transporting properties of PBD was introduced into the host components for effective electron injection/transport and charge carrier balance within the EML. The LUMO energy levels of PBD and Bphen were closely aligned to the LUMO levels of $(DPQ)_2Ir$(pic-N-O). This good alignment of energy levels is important for efficient electron injection into the both transport molecules and $(DPQ)_2Ir$(pic-N—O).

The GO film was investigated by X-ray photoelectron spectroscopy (XPS) before and after the thermal treatment. After Shirley background correction, the C1s region of the XPS spectra was curve fitted using Gaussian-Lorentzian peak (Fig. 4). Before the thermal treatment, four different functional groups: the C—C bond (284.6 eV), C—O bond (286.6 eV), C=O (287.6 eV), and O=C—OH bond (289.1 eV), were observed for the GO. Interestingly, the intensity of C—O, C=O, and O=C—OH bonds was significantly decreased

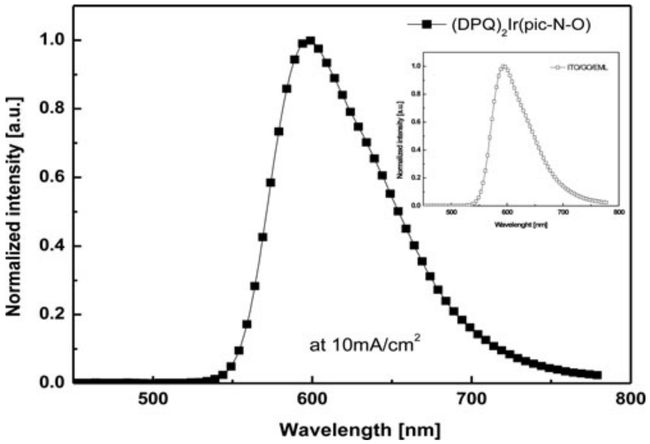


Figure 6. EL spectrum of (DPQ)$_2$Ir(pic-N-O) using PEDOT as the hole transport layer. Inset: EL spectrum of (DPQ)$_2$Ir(pic-N-O) using rGO as the hole transport layer.

after the thermal treatment at 250°C. Thus, oxygen functional groups in the solution processed GO film have been efficiently removed through the thermal treatment at 250°C. Fig. 5 presents J-V-L and current density-luminance efficiency and power efficiency (J-LE-PE) characteristics using rGO and PEDOT:PSS as a hole transport layer for comparison. The PEDOT:PSS-based PhOLED shows turn-on voltage of 5.1 V. With increasing current density, the LE and PE of (DPQ)$_2$Ir(pic-N-O) decreased slightly and showing a maximum EQE of 14.2%, LE of 26.9 cd/A, and PE of 12.1 lm/W, with a maximum brightness of 14070 cd/m^2. For PhOLED with rGO as a hole transport layer, the turn-on voltage and maximum brightness exhibited 4.8 V and 13540 cd/m^2, respectively. rGO has a work function value around 4.9 eV, which is very close to the work function of ITO and make it a very good hole transport material. The maximum EQE value of rGO-based PhOLED was 8.4% with LE and PE value of 16.8 cd/A and 4.4 lm/W. The shape of EL spectrum of PhOLED with rGO showed almost identical with that of PEDOT:PSS-based PhOLED as shown in inset of Fig. 6. The PhOLED using rGO as the hole transport layer delivered lower device performance than the PhOLED using PEDOT:PSS is because of the folding and wrinkling of spin-coated rGO films owing to their flexible nature. The ordered structure of rGO layer plays an effective role in hole injection and leading to better device performance of the PhOLED making it a good alternative hole transport material in PhOLEDs.

Conclusions

We have demonstrated the incorporation of solution processable rGO as the hole transport layer for PhOLED. The maximum EQE value of rGO-based PhOLED was 8.4% with LE and PE value of 16.8 cd/A and 4.4 lm/W. The overall result showed that although the device performance has not been fully optimized yet, the utilization of the solution processable rGO thin film as the hole transport layer offered the great potential for the fabrication of solution processable PhOLEDs.

Acknowledgments

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