

Supporting Information

Luminescent Graphene Quantum Dots (GQDs) for Organic Photovoltaic Devices

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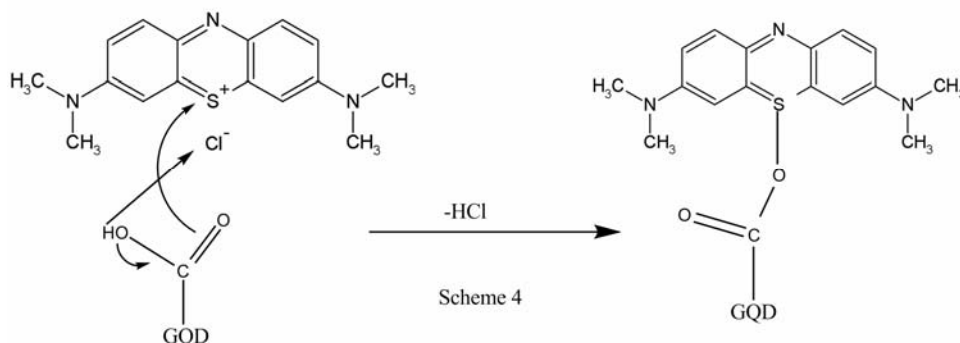
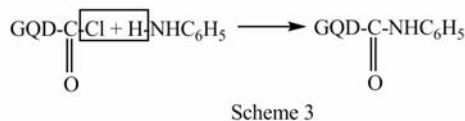
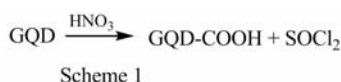
For carboxylation, Acylation and Amidation of GQDs, standard procedures were followed as given below.

(1) Carboxylation (scheme 1): In a typical experiment, GQDs were taken in a round-bottom flask fitted with a reflux condenser and to this 100 ml of 10 M nitric acid was added. The mixture was refluxed for 2h at 70°C. The mixture was then filtered and washed several times with distilled water till washings were neutral to pH paper and dried under reduced pressure and weighed. The yield of of carboxylated GQDs was 54%.

(2) Acylation (scheme 2): The carboxylated GQDs were stirred in 20:1 mixture of thionyl chloride and DMF (N,N-dimethyl formamide), at 70°C for 24h. After the acyl chlorination, the GQDs were filtered, washed with anhydrous THF (tetrahydrofuran) and dried under vacuum at room temperature for ~ 30 min. and chlorinated GQDs were obtained.

(3) Amidation (scheme 3): The chlorinated GQDs were reacted with aniline by the well known acylation reaction in which aniline reacts more readily with acyl chlorides and $C_6H_5-NH-CO-GQD$ (anilide) is synthesized. The chlorinated GQDs were refluxed with aniline in the 3:1 wt. ratio at 110°C for five days. The excess aniline was washed first with DMF, followed by anhydrous THF until the sharp photoluminescence peak of aniline at 326 nm disappeared completely (**Fig. S4**).

(4) Synthesis of MB-GQD (scheme 4): To attach MB to GQDs, the prepared COOH-GQD was reacted with MB also by acylation reaction discussed above and MB-GQD is obtained.



References: http://en.wikipedia.org/wiki/Acyl_chloride and <http://en.wikipedia.org/wiki/Aniline>

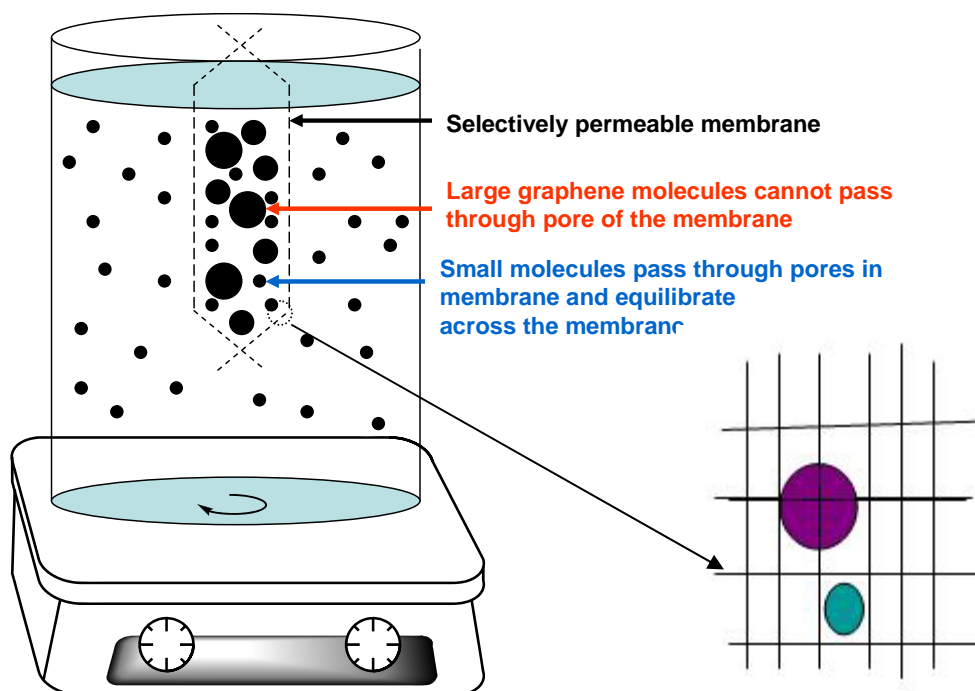


Figure S1. Schematic diagram of the graphene dialysis process.

Dialysis is a process used to separate colloidal particles. The colloidal solution is placed in the semi-permeable membrane (a semi-permeable membrane is a membrane that lets some molecules pass through while not letting other). When a colloidal mixture is placed in a semipermeable membrane, which is then placed in an aqueous solution or pure water, dissolved ions and small molecules are allowed to pass through this membrane. This causes colloidal particles to stay in the membrane, because these particles are unable to pass through the small pores of the membrane (inset of Figure S1). Dialysis is possible because of the *unequal rates of diffusion* through a semipermeable. This function is similar to kidney's dialysis unit for blood.)

References: http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Solutions/Dialysis_by_Katrina_Lau and

<http://www.chemistry.wustl.edu/~courses/genchem/LabTutorials/Dialysis/Kidneys.html>

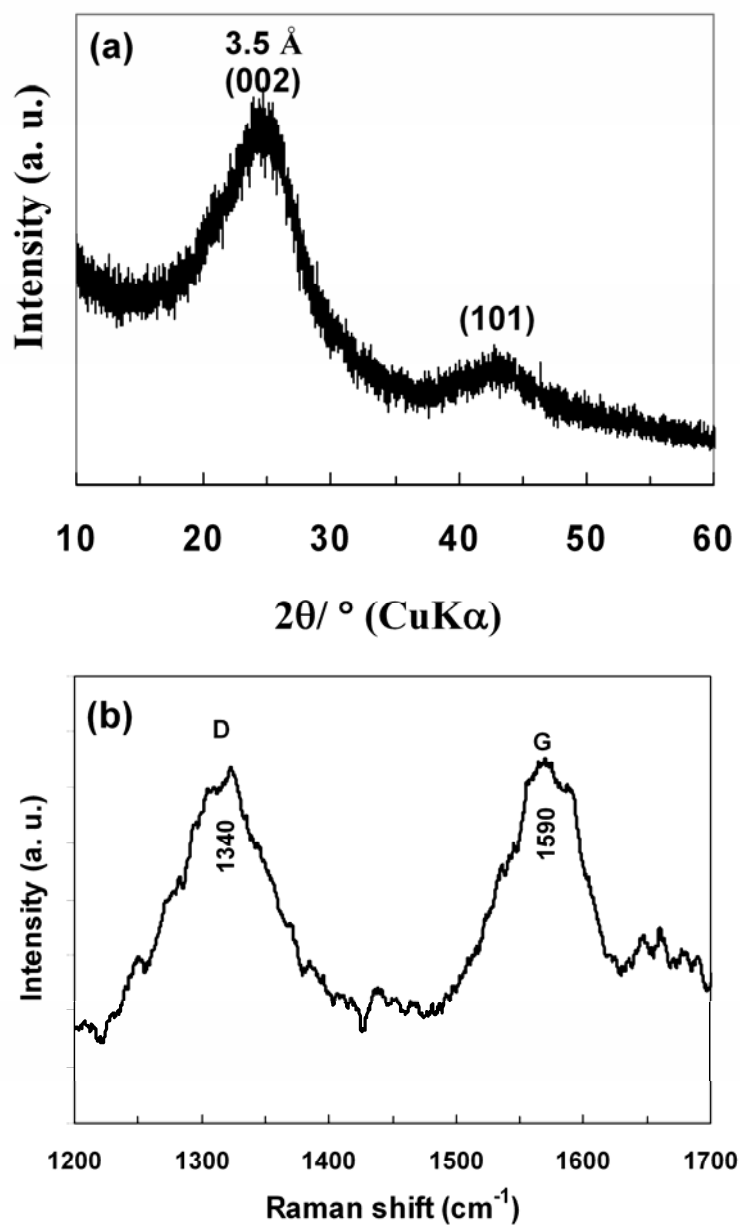


Figure S2. (a) X-ray diffraction and (b) Raman spectrum of GQD

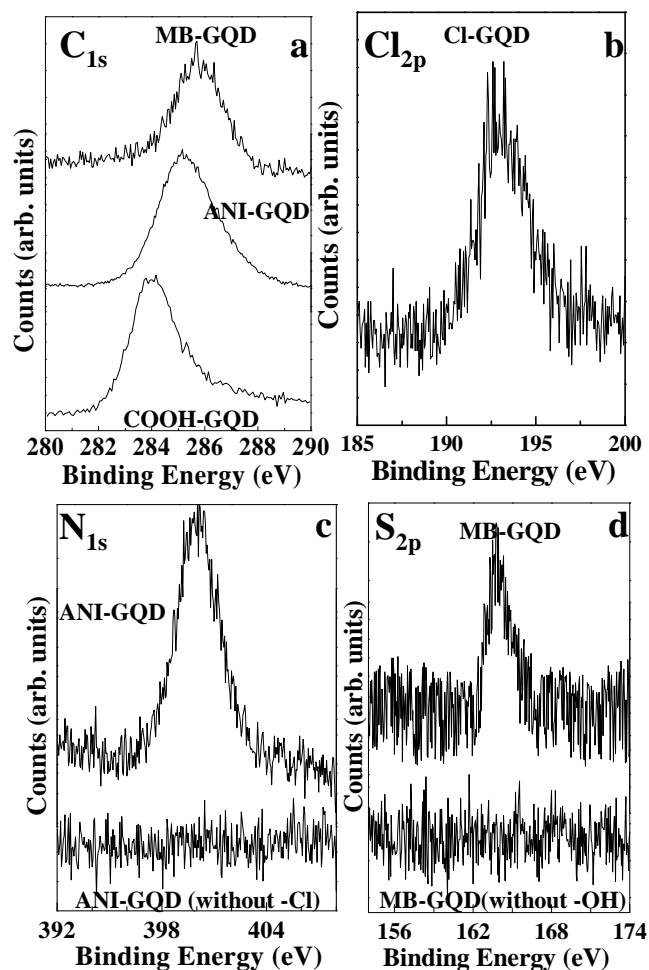


Figure S3. XPS core level spectra; (a) C_{1s} of Carboxylated GQDs, ANI-GQD, MB-GQD, (b) Cl_{2p} of chlorinated GQD, (c) N_{1s} of ANI-GQD shown at the top was prepared after acylation step and below was prepared without acylation directly after carboxylation step. In the former case amidation of GQD has successfully occurred and in the later case no amidation has occurred. It confirms the synthesis of COCl-GQD as without this aniline would not bind to GQD. (d) similarly S_{2p} core level shown at the top was prepared after carboxylation step and below was prepared without carboxylation. In the former case, MB-GQD binding has successfully occurred. However, without carboxylation MB would not bind to GQD and hence no peak was obtained in the later case

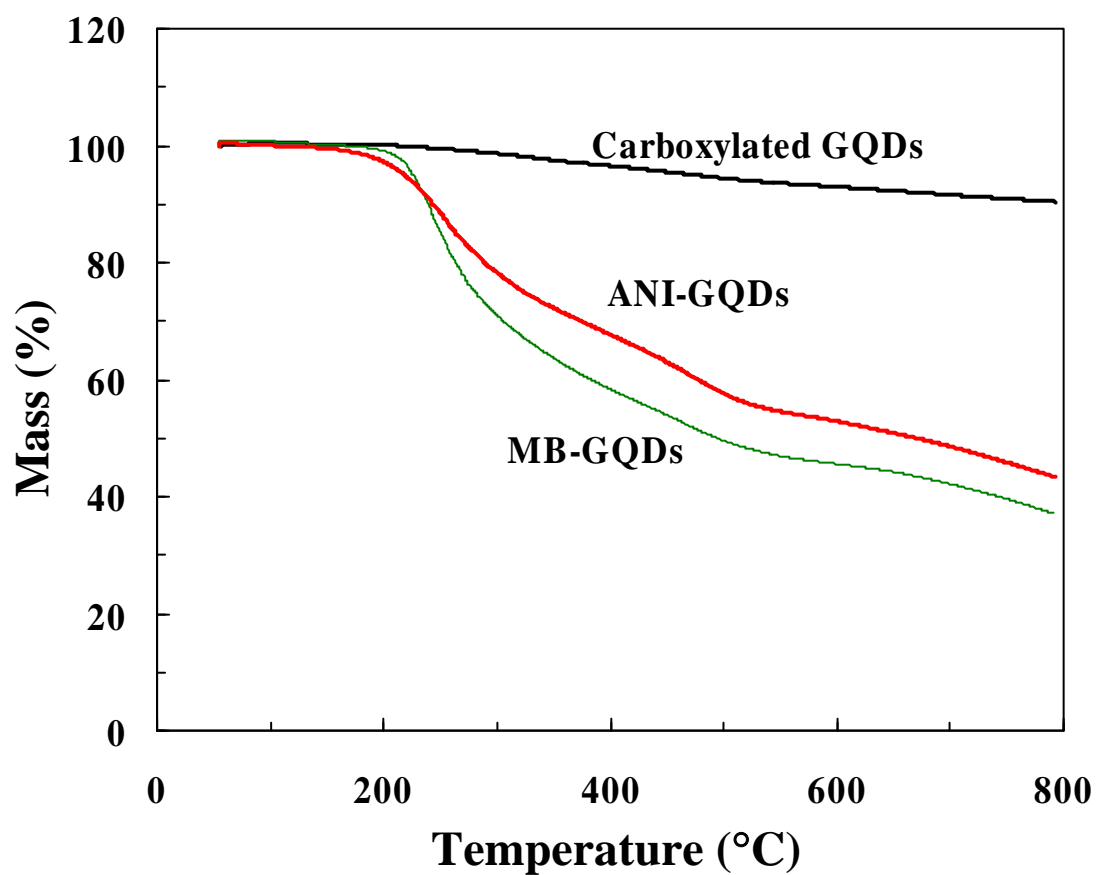


Figure S4 TGA curves of the carboxylated GQDs, ANI-GQDs and MB-GQDs in the range of 50 to 800°C at the heating rate of 5°C min⁻¹ in nitrogen flow.

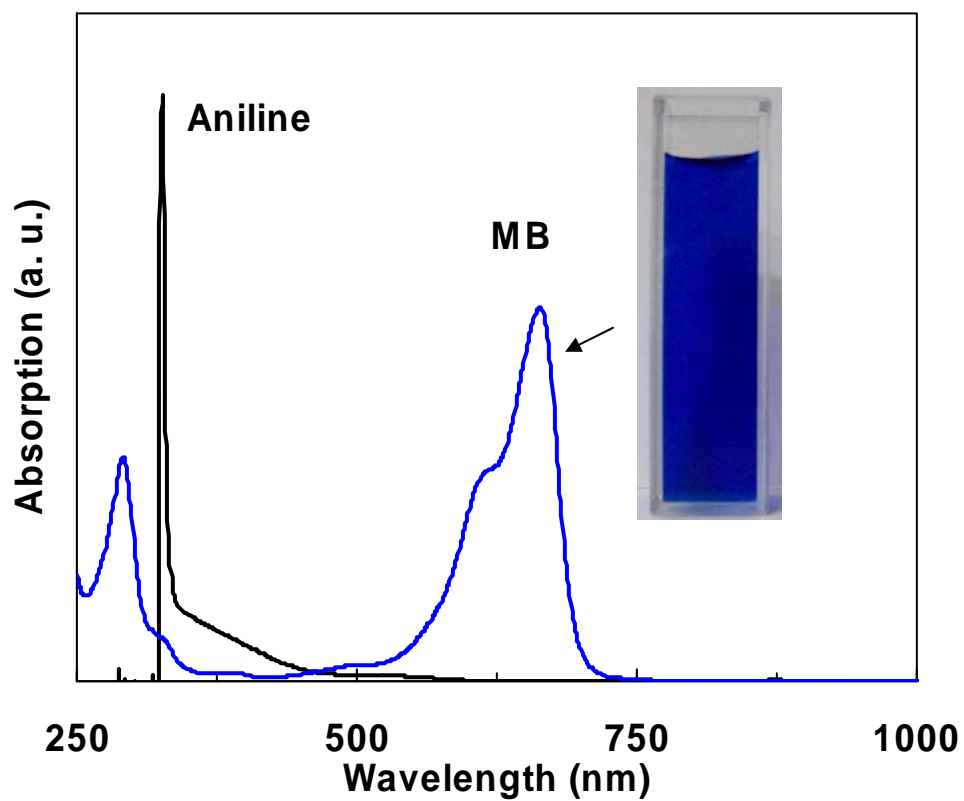


Figure S5 UV-vis absorption spectra of aniline and MB dispersed in ethanol.

Solar cell device fabrication

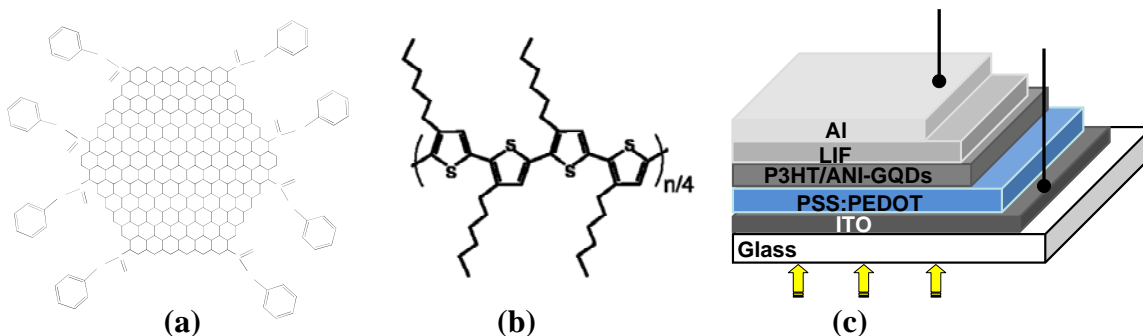


Figure S6 (a, b) The idealized chemical structure of ANI-GQD and P3HT and (c) Schematic of the device with P3HT/ANI-GQD thin film as the active layer and the structure ITO (ca. $9 \Omega \text{ sq}^{-1}$)/PEDOT:PSS (100 nm)/P3HT/ANI-GQD (100 nm)/LiF (1 nm)/Al (70 nm)

Description: Solar cells were fabricated in the standard configuration (Fig.1). Subsequent layers were deposited on Indium Tin Oxide (ITO) glasses. ITO glass substrates were carefully cleaned with detergent followed by treatment in ultrasonic bath using two different solvents (in chlorobenzene and subsequently in isopropanol). Poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS) conductive polymer was deposited by spin-coating at 2500 rpm using an aqueous solution (film thickness 120nm). The films were thermally annealed for 30 min in an oven at 100°C . On the top of the film subsequently a layer of P3HT/ANI-GQD was spin coated at 2000 rpm from a chlorobenzene solution. The concentration of P3HT was 10mg/ml. The films were also annealed at 160°C for 20 min. The quantity of ANI was varied from 0 to 5%. LiF (1 nm) and Al (120 nm) were then vacuum-deposited as the top contact (Figure S6(c)). The active area of the cells was $5 \times 5 \text{ mm}^2$. The same process was followed for ANI-GS and GQD.

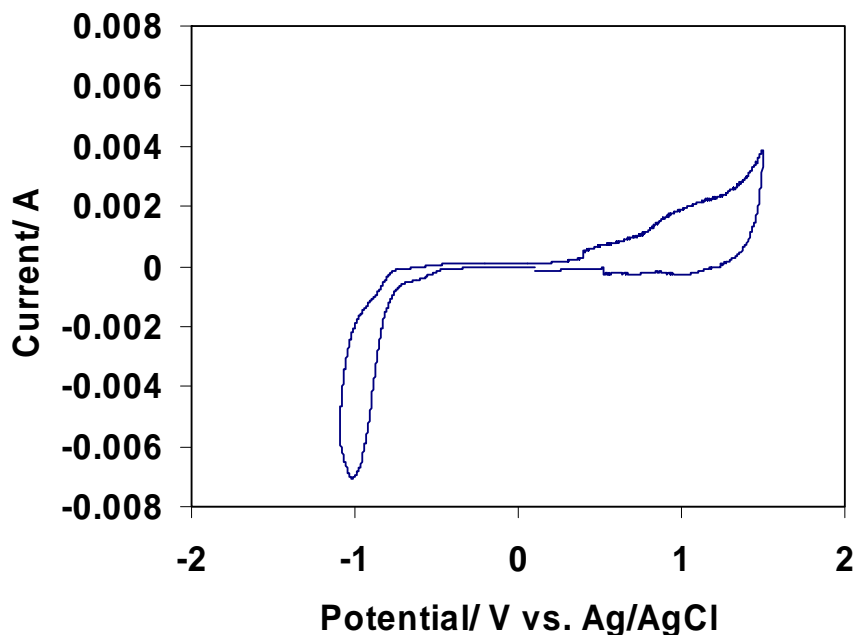


Figure S7 CV curve of GQD on platinum electrode

To estimate their HOMO and LUMO energy levels, cyclic voltammetry (CV) was carried out by using a standard three-electrode system, which consists of platinum sheet coated with GQDs as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. The electrode was prepared by drop-casting of GQDs/DCB solution onto the platinum electrode. CV was recorded in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆, Aldrich) as the supporting electrolyte. The HOMO and LUMO energy levels in eV as well as the electrochemical energy gap (E_g in eV) of the samples were calculated according to the following equations [1]:

$$E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.4) \quad (1)$$

$$E_{\text{LUMO}} = -e(E_{\text{red}} + 4.4) \quad (2)$$

where E_{ox} and E_{red} are the onset of oxidation and reduction potential, respectively.

The E_{red} and E_{ox} were determined to be 0.85 and 0.98 V, respectively.

The corresponding LUMO and HOMO levels were -3.55 and -5.38, respectively.

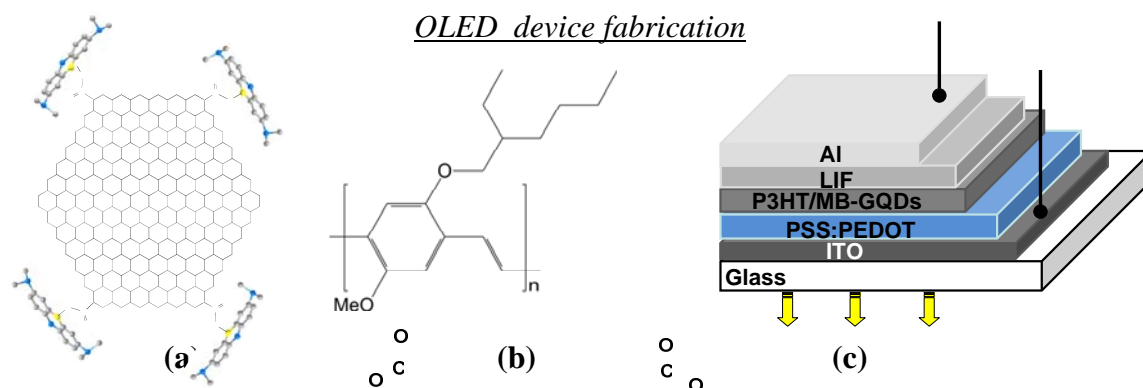


Figure S8 (a, b) The idealized chemical structure of MB-GQD and MEHPPV and (c) Schematic of the device with MEHPPV/MB-GQD thin film as the active layer and the structure ITO (ca. $9 \Omega \text{ sq}^{-1}$)/PEDOT:PSS (100 nm)/ MEHPPV: MB-GQD (120 nm)/LiF (1 nm)/Al (70 nm)

Description: OLEDs were fabricated in the standard configuration (Fig.1). Subsequent layers were deposited on Indium Tin Oxide (ITO) on glasses. ITO glass substrates were carefully cleaned with detergent followed by treatment in ultrasonic bath using two different solvents (in chlorobenzene and subsequently in isopropanol). Poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS) conductive polymer was deposited by spin-coating at 2500 rpm using an aqueous solution (film thickness 120nm). The films were thermally annealed for 30min in an oven at 100°C . On the top of the film subsequently a layer of MEH-PPV was spin coated at 2000 rpm from a chlorobenzene solution. The concentration of MEH_PPV was 10mg/ml.. Alternatively, layers of QDs/MEH-PPV hetero structures were deposited at the same speed. The films were also annealed at 150°C for 2hr. The MEH_PPV:QD structure was prepared by mixing 0.5ml of MEH-PPV (10mg/ml) with QD in chlorobenzene under vigorous stirring. The quantity of QD was varied from 0 to 3%. LiF (1 nm) and Al (100 nm) were then vacuum-deposited as the top contact (Figure S6(c)). The active area of the cells was $5 \times 5 \text{ mm}^2$.