Supporting Information

for

Functionalized Graphene Quantum Dots as Novel Cathode Interlayer of Polymer Solar Cells

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Characterization: High-resolution transmission electron microscopy (HR-TEM) images were recorded on a Philips-FEI Tecnai F20 microscopy (Philips, The Netherlands) at an accelerating voltage of 200 kV. The samples for TEM measurements were made by depositing the GQD-TMA from an aqueous solution with a concentration of 0.1 mg/ml onto carbon-coated copper grids (300 meshes), followed by drying in vacuum for 7 h at 70 ^{o}C. AFM characterization was performed on a SPA300HV with a SPI3800N controller (Seiko Instruments, Inc., Japan) in tapping mode. A silicon micro cantilever (spring constant 40 N/m and resonance frequency ca. 300 kHz, Olympus Co., Japan) with an etched conical tip was used for the scan. The sample for AFM measurement was prepared by spin-coating the GQD-TMA aqueous solution (0.05 mg/mL) onto a mica substrate at 2000 rpm for 1 min. Thermal gravimetric analysis (TGA) was performed under a N_2 flow with a Perkin-Elmer-TGA 7 system. The temperature of degradation (T_d) corresponded to a 5% weight loss. UV-Visible absorption spectrum of GQD-TMA aqueous solution was carried out with a Shimadzu UV3600 spectrometer. The XPS and UPS measurements were performed on Thermo ESCALAB 250 using monochromatized Al Kα ($h\nu$ = 1486.8 eV for XPS) excitation and He-I (21.2 eV for UPS) discharge lamp. For UPS measurement, a sample bias of -12 V was used in order to separate the sample and the secondary edge for the analyzer.

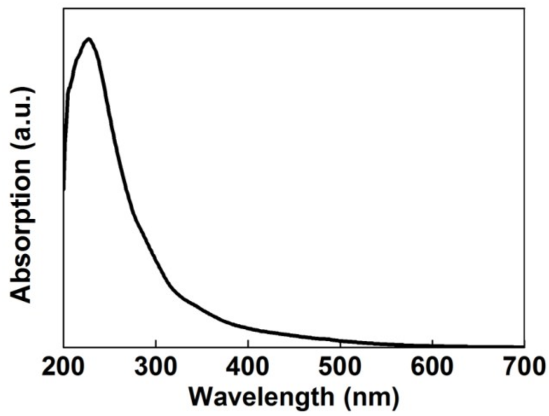

Fig. S1. UV-Vis absorption spectrum of GQD-TMA in aqueous solution.

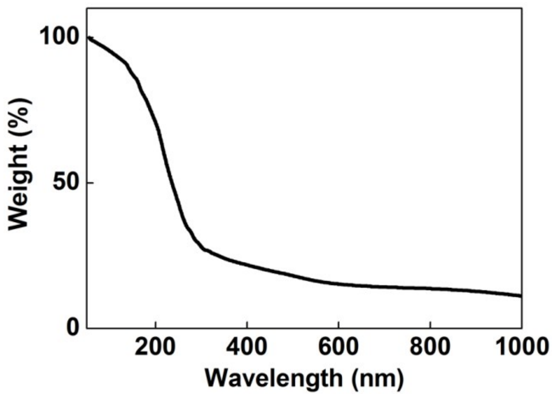

Fig. S2. TGA curve of GQD-TMA.

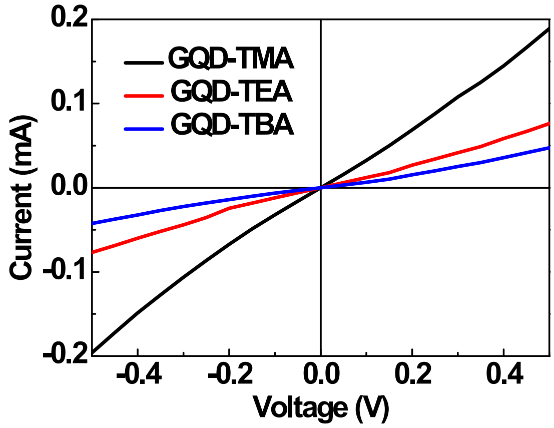

Fig. S3. *J-V* plots of the devices with the configuration of ITO/material/Al for conductivity measurement. According to the *J-V* plots, the conductivities of GQD-TMA, GQD-TEA and GQD-TBA are estimated to be 6×10^{-8} S cm^{-1}, 2×10^{-8} S cm^{-1} and 8×10^{-9} S cm^{-1}, respectively.

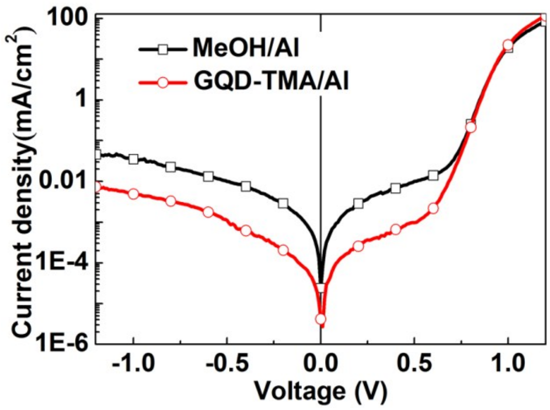

Fig. S4. The *J-V* plots in dark of the devices with/without GQD-TMA CIL based on PCDTBT:PC_{71}BM active layer.

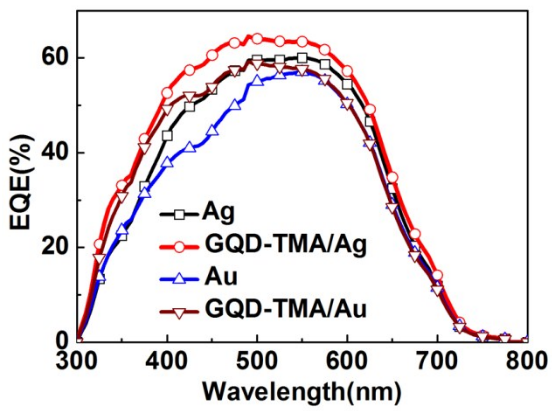

Fig. S5. EQE curves of the PSC devices with/without GQD-TMA as CIL and Ag or Au as cathode.

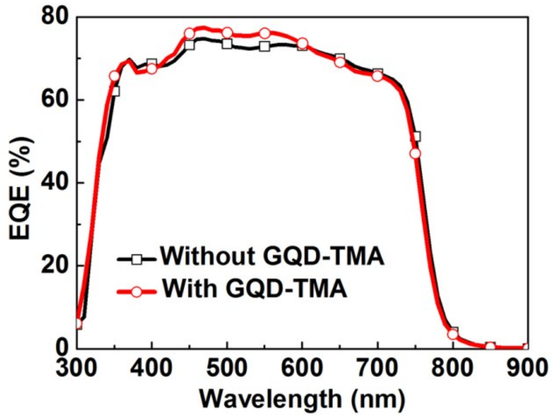

Fig. S6. EQE curves of the PSC devices based on PTB7-Th:$PC_{71}BM$ active layer with Al cathode with/without GQD-TMA as CIL.

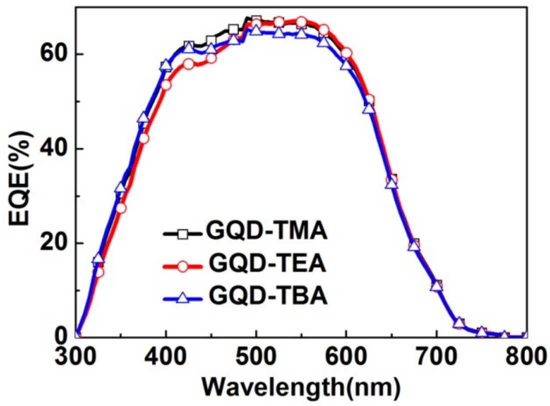

Fig. S7. EQE curves of the PSC devices based on PCDTBT:$PC_{71}BM$ active layer with Al as cathode and GQD-TMA, GQD-TEA or GQD-TBA as CIL.

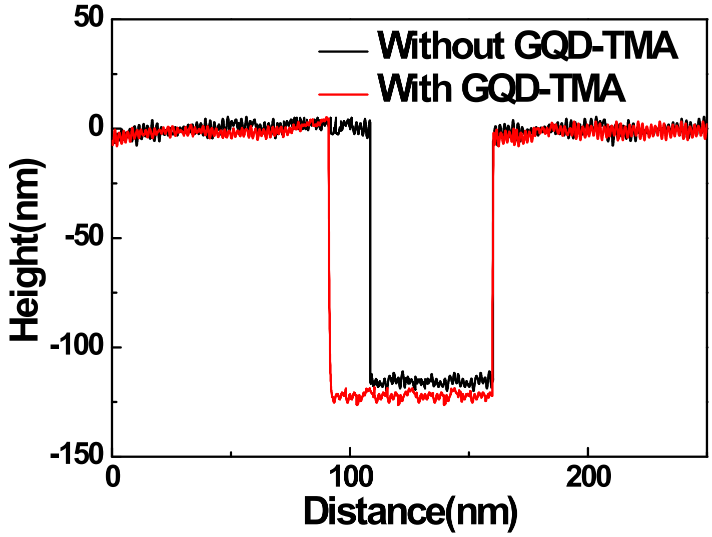

Fig. S8. The height profiles of the active layer film from PCDTBT:$PC_{71}BM$ on PEDOT:PSS with/without GQD-TMA (the thickness of the GQD-TMA is about 6 nm).

Table S1. Characteristics of the PSC devices with/without GQD-TMA as CIL and Al, Ag or Au as cathode. The R_S values are estimated from the *J-V* plots under AM1.5G illumination.

cathode	CIL	*Voc* (V)	*Jsc* (mA/cm^2)	FF (%)	PCE (%)	R_S (Ωcm^2)
Al	MeOH	0.88	10.10	65.40	5.81	7.07
	GQD-TMA	0.91	10.84	71.11	7.01	6.11
Ag	MeOH	0.87	9.68	61.45	5.18	12.55
	GQD-TMA	0.90	10.60	65.61	6.26	7.78
Au	MeOH	0.80	8.83	59.81	4.22	16.42
	GQD-TMA	0.89	9.42	64.52	5.41	9.41

Table S2. Characteristics of the PSC devices with Al as cathode and GQD-TMA, GQD-TEA, GQD-TBA as CIL. The R_S values are estimated from the *J-V* plots under AM1.5G illumination.

CIL	cathode	*Voc* (V)	*Jsc* (mA/cm^2)	FF (%)	PCE (%)	R_S (Ωcm^2)
GQD-TMA	Al	0.91	10.84	71.11	7.01	6.11
GQD-TEA	Al	0.90	10.69	70.92	6.82	6.95
GQD-TBA	Al	0.88	10.51	70.55	6.53	7.82