

Supporting Information

Facile and purification-free synthesis of nitrogenated amphiphilic graphitic carbon dots

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1. Experimental Section

Preparation of N-GCDs

The N-GCDs were prepared by thermal treatment of fumaronitrile powder (FN) purchased from Tokyo Chemical Industry Co., Ltd. In a typical procedure, 0.3g FN dispersed in 10 mL DI water was injected into a 50 mL round bottle flask, and then heated to 225°C for 10 min using a hot plate while continually stirring to obtain stable and uniformed products. In consequence, the color of the liquid was changed from colorless to pale yellow, indicating that N-GCDs are successfully formed. After removing excess DI-water using vacuum evaporator, the final product (N-GCDs) was collected after drying process.

Instrumentation

Atomic force microscopy (AFM) imaging was performed in air using an NX-10 (Park systems). High resolution transmission electron microscopy (HRTEM) image of N-GCDs were obtained with a Tecnai G2 F20 operating at 200kV. UV-*vis* absorption and photo-luminescence (PL) were characterized by Jasco V-670 spectrophotometer and Horiba NanoLog-C, respectively. The Fourier transform infrared (FT-IR) spectrum was obtained on a FT-IR spectrophotometer (Jasco FT/IR-6600). The Raman spectra were obtained using a Horiba Jobin Yvon-Labram HR UV-Visible-NIR Raman microscope spectrometer. X-ray photoelectron spectroscopy was carried out using monochromated Al K α X-ray photons ($h\nu = 1486.6$ eV). To measure the electron lifetime of N-GCDs, time resolved photoluminescence (TRPL) was performed. The second harmonic (SHG = 360 nm) of a tunable Ti:sapphire laser

(MaiTai, Spectra Physics) with an approximate ~ 100 fs pulse width and 80 MHz repetition rate was used as the excitation source.

Device Fabrication and Measurement

Solar cell devices were fabricated on 1 x 1 cm pre-patterned ITO coated glass substrates. The ITO-coated glass substrates were cleaned with ethanol, acetone and 2-propanol. The ITO-coated glass was treated with O₂ plasma for 40 sec. PEIE solution was spin-coated with 7 nm thickness and the PEIE film was baked at 110 °C for 15 min under ambient conditions. After cooling, the substrates were then transferred into a nitrogen-filled glove box. The blend of PTB7:PC₇₁BM (1:1.5 (by weight)) with 2 wt% N-GCDs ternary blend solution was spin-coated onto the PEIE layer to form a 110 nm thick active layer. Finally, MoO₃ (10nm) and Ag (80nm) were sequentially deposited on the active layer by thermal evaporation in a vacuum of 6×10^{-7} Torr, which defines the active area of 0.0464 cm². The un-encapsulated solar cells were tested under ambient conditions using a Keithley 2400 SMU and an Oriel xenon lamp (450 W) with an AM 1.5 G filter. A mask was used to define the device illumination area of 0.0464 cm² to minimize photocurrent generation from the edge of the electrodes. The solar cells (with no protective encapsulation) were then tested in air under an AM 1.5 G illumination of 100 mW cm⁻² (Oriel 1 kW solar simulator), which was calibrated with the International System of Units (SI) (SRC-1000-TC-KG5-N, VLSI Standards, Inc) for accurate measurement. The external quantum efficiency (EQE) was measured using a Oriel IQE-200 (NewPort), a calibrated Si UV detector, and an SR8570 low noise current amplifier.

2. Visual dispersibility test for N-GCDs

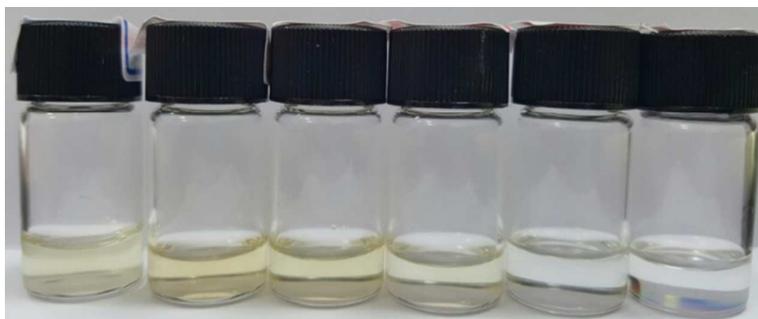


Fig. S1 The visual dispersibility test for N-GCDs (from left: DI-water, ethanol, DMF, THF, chloroform and chlorobenzene). Each sample (conc.: 0.1 mg/mL) was sonicated for 5 sec and allowed to settle for 120 hr.

3. Typical XPS survey spectrum of N-GCDs

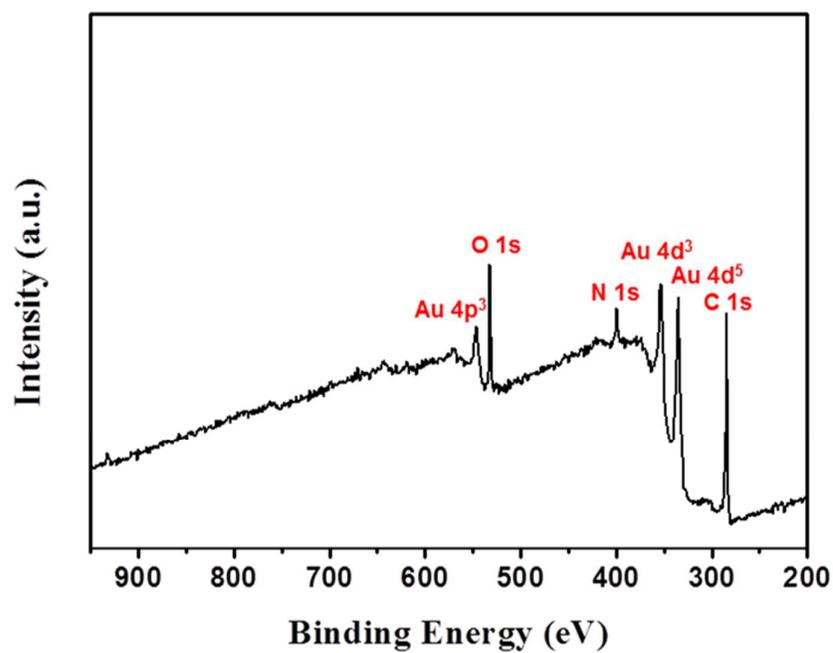


Fig. S2 Typical XPS survey spectrum of N-GCDs on Si/SiO₂/Cr/Au substrate.

4. High resolution NEXAFS spectrum of N-GCDs

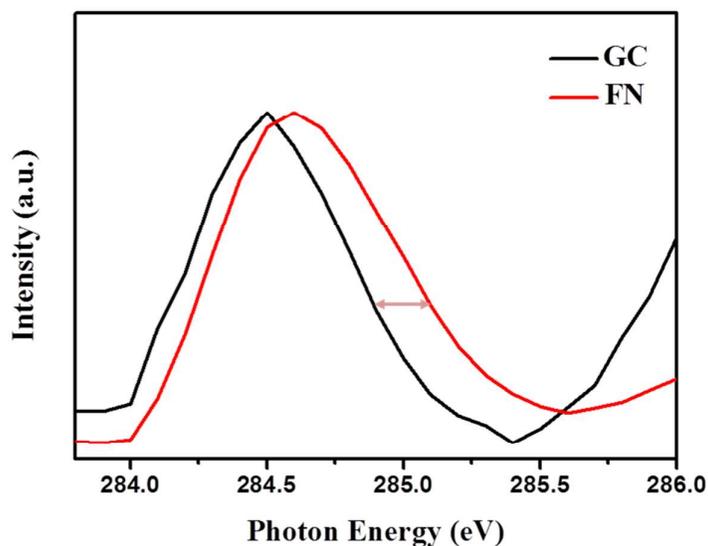


Fig. S3 C K-edge NEXAFS spectra of two different kinds of carbon based QDs. Each spectrum was obtained at 54.7° incidence of the X-ray beam.

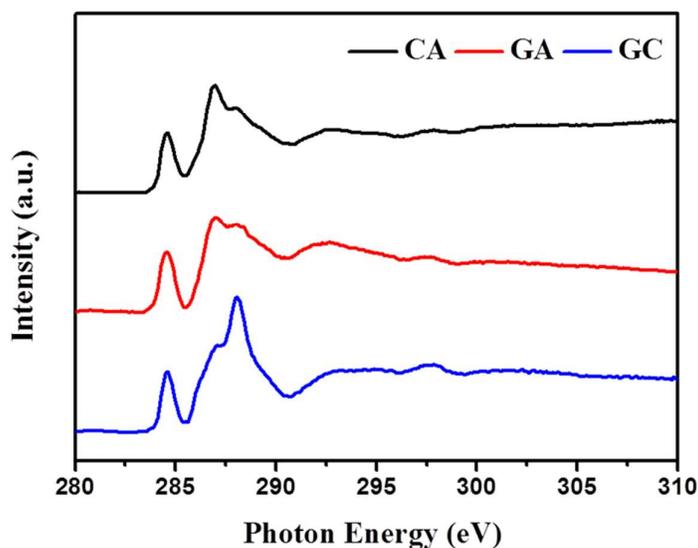


Fig. S4 Overlay plot of the normalized NEXAFS spectra taken at the C K-edge for various carbon based QDs prepared from different organic precursors. Each spectrum was secured at 54.7° incidence of the X-ray beam.

5. PL mechanism of N-GCDs

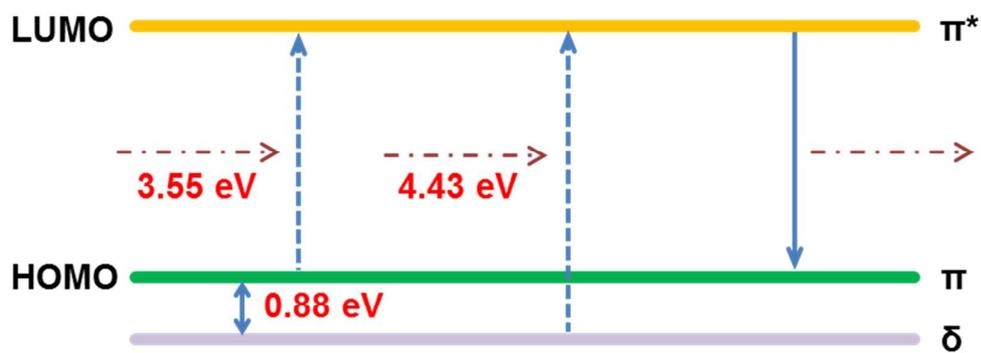


Fig. S5 Typical electronic transitions of triple carbenes at zigzag sites observed in the optical spectra.

6. Measurement of fluorescence quantum yield of N-GCDs

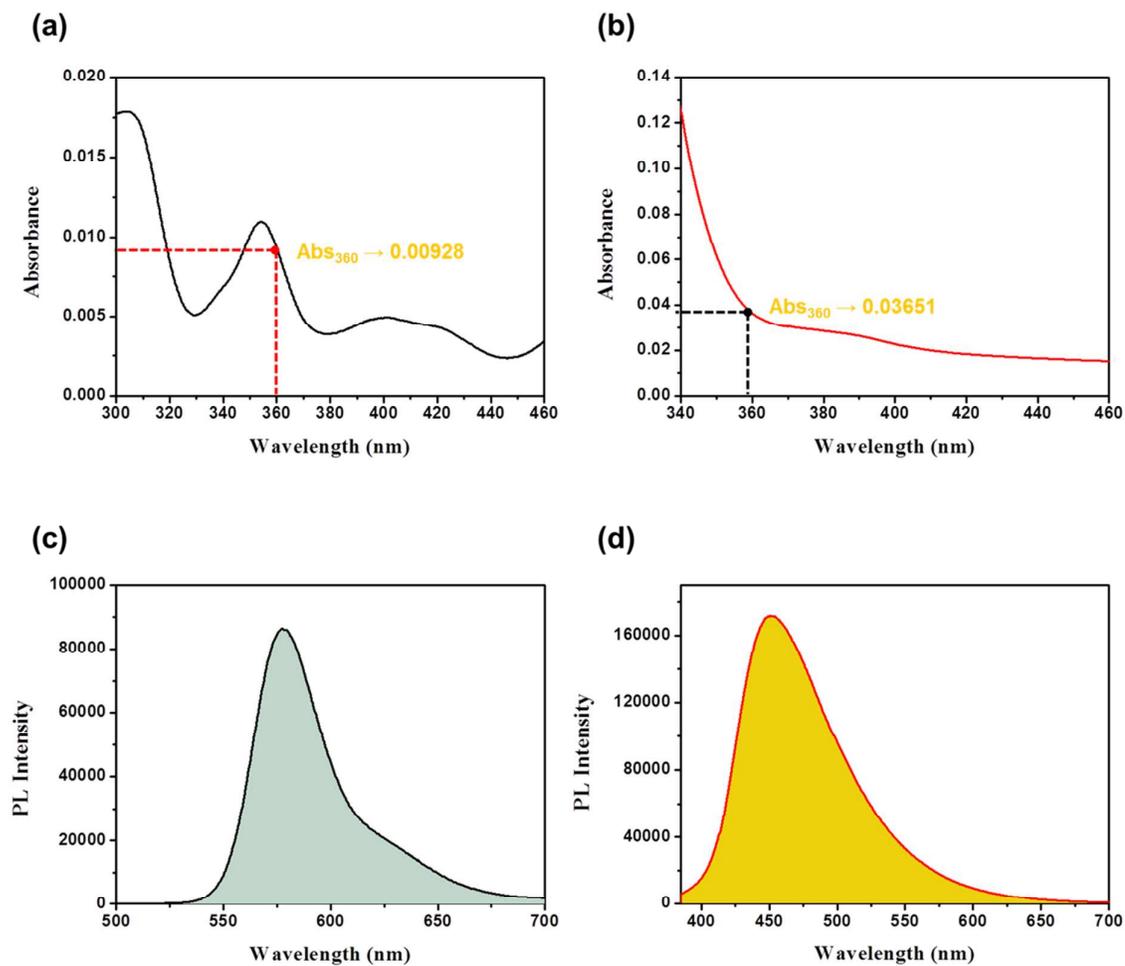


Fig. S6 UV-vis absorption spectra of the Rhodamine B (a) and N-GCDs (b). PL spectra of the Rhodamine B (c) and N-GCDs (d).

7. Stability test of N-GCDs solution using PL measurement system.

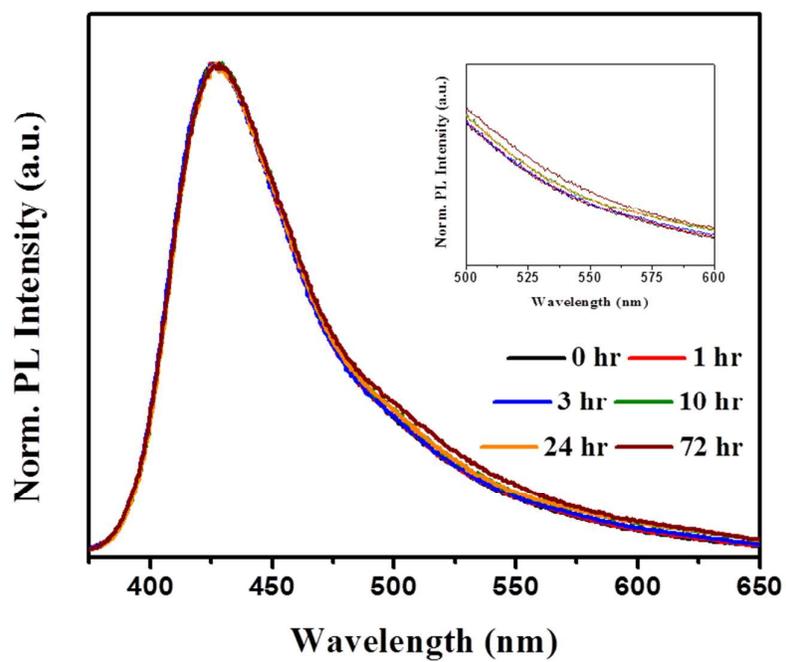


Fig. S7 PL spectra of N-GCDs dissolved in THF. The PL spectra were obtained for excitation at 350 nm during 3 days.

8. Schematic illustration of an inverted type polymer-fullerene BHJ solar cell

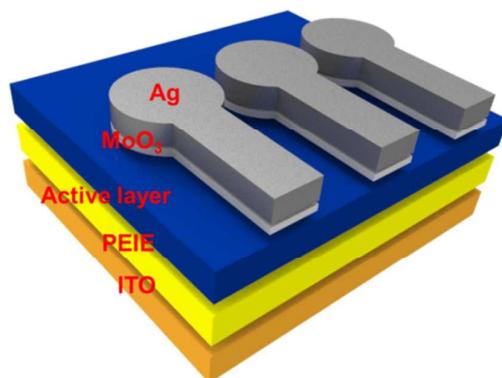


Fig. S8 Schematic illustration of the iPSC structure with the configuration of ITO/PEIE/Active layer (PTB7:PC₇₁BM)/MoO₃/Ag.

9. Absorbance of the ITO/PEIE/PTB7:PC₇₁BM and ITO/PEIE/PTB7:PC₇₁BM + 2 wt% N-GCDs films

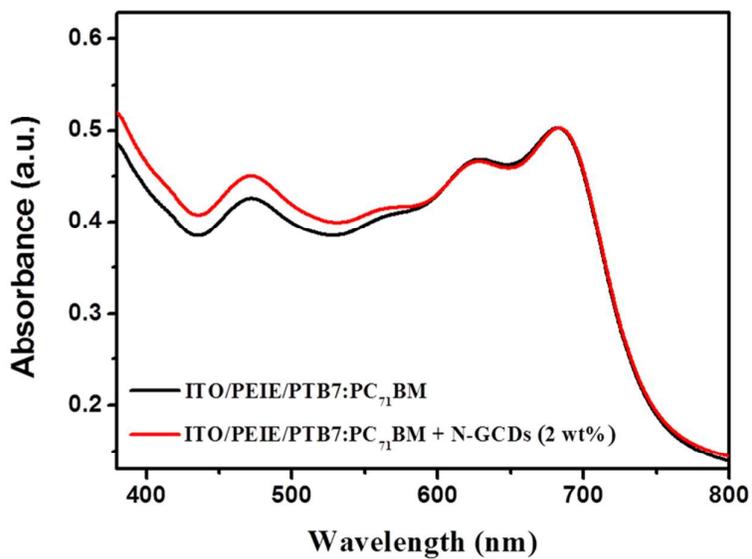


Fig. S9 UV-Vis absorption spectra of the PEIE/PTB7:PC₇₁BM and PEIE/PTB7:PC₇₁BM + N-GCDs (2 wt%) films on ITO substrates.

10. Ultraviolet photoelectron spectra (UPS) of the N-GCDs sample.

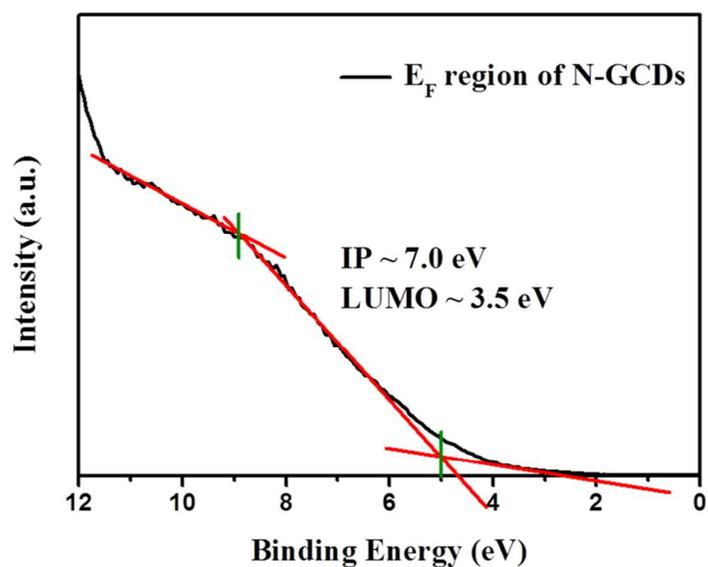


Fig. S10 UPS spectra of the N-GCDs sample.

11. Absorbance of the photo-active materials and PL emission of N-GCDs

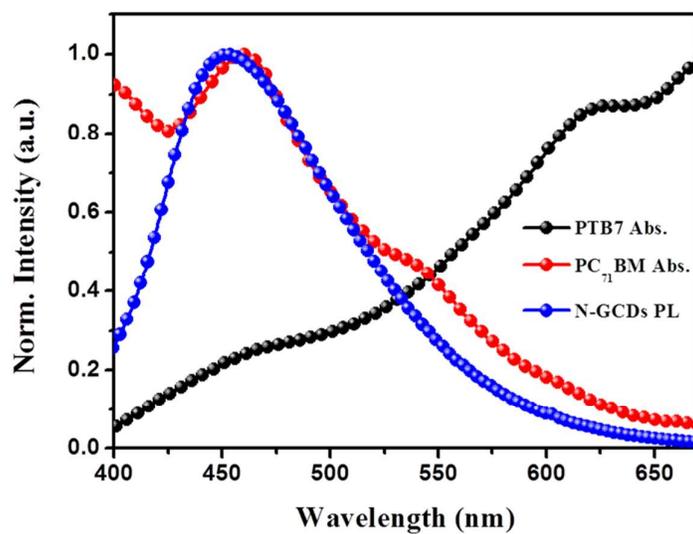


Fig. S11 Normalized absorption spectra of PTB7 and PC₇₁BM samples and photoluminescence spectra of N-GCDs sample.

12. Time-resolved PL of N-GCDs.

Table S1. PL lifetimes of the N-GCDs with 360 nm excitation wavelength.

Sample ^{a)}	A_1	τ_1	A_2	τ_2	A_3	τ_3	τ_{avr}	χ^2
N-GQDs	0.104	1.789	0.085	5.244	0.026	14.107	7.86 ns	1.012

a) Monitored wavelength was 460 nm. The PL decay curves were fitted by a tri-exponential function to calculate the lifetimes of the samples. The intensity weighted average exciton lifetime (τ_{avr}) was $((A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)/(A_1\tau_1 + A_2\tau_2 + A_3\tau_3))$. χ^2 is the reduced chi-squared value.

13. Device performance of inverted polymer solar cells with/without N-GCDs.

Table S2. Optimized photovoltaic response data for PTB7: PC₇₁BM inverted solar cells with/without N-GCDs.

Sample	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (Avg.) (%)
Control (PTB7:PC ₇₁ BM)	15.3 (± 0.11)	0.73 (± 0.002)	0.65 (± 0.02)	7.3 (7.1)
with 2 wt% N-GCDs	16.6 (± 0.14)	0.74 (± 0.003)	0.71 (± 0.03)	8.6 (8.4)

14. Stability tests of polymer solar cells with/without N-GCDs in PTB7:PC₇₁BM blend system under ambient conditions.

We examined the stability of the iPSCs with/without N-GCDs in PTB7:PC₇₁BM blend system over 100 hours, which were not encapsulated and were stored in air under ambient conditions. As shown in Fig. S12, there is not much difference in air stability between control (without N-GCDs) and modified devices (with 2 wt% N-GCDs).

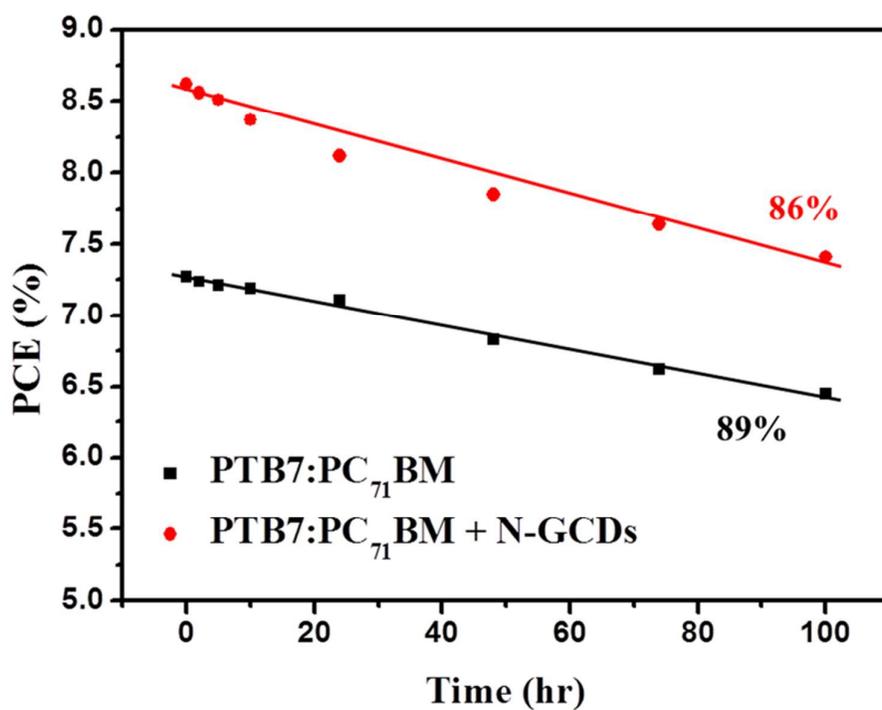


Fig. S12 PCEs as a function of storage time for unencapsulated PTB7:PC₇₁BM inverted solar cells fabricated with/without N-GCDs in air under ambient conditions.