Supporting Information

Investigation for the enhanced performance and lifetime of organic solar cells using solution-processed carbon dots as the electron transport layer

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Additional Experimental Results

The UV-vis spectrum shows absorption peaks at ca. 343nm and ca. 241 nm attributed

to the n-p* and p-p* transitions for CDs (Fig. S1).¹



Fig. S1 UV/Vis absorption spectra of CDs in aqueous solution (0.01 mg mL⁻¹).

As shown in FT-IR spectra (Fig. S2), broad and intense peaks around 3425 cm⁻¹ correspond to the O–H stretching vibration. The peaks at 1646 cm⁻¹ and 1390 cm⁻¹ are attributed to C=O and C–H bonds vibration, respectively. The peaks at 1567 cm⁻¹ and

1126cm⁻¹ are consistent with asymmetric stretching vibrations of C-NH-C and bending vibrations of N-H, respectively.



Fig. S2 FT-IR spectra of the CDs.

Fig. S3 shows the fluorescence spectra of the CDs, which exhibits an excitationdependent emission phenomenon. With the increase of excitation wavelength, the CDs emits at longer wavelength. The reasons for this phenomenon may be attributed to the distribution of different emissive sites influenced by the degree of surface oxidation on each C-dots and different particle sizes of the C-dots connected with quantum confinement effects.^{2, 3}



Fig. S3 Photoluminescent spectra of CDs at different excitation wavelengths in aqueous solution (0.5 mg mL⁻¹)

The surface groups are investigated by XPS analysis. The XPS full scan spectrum and the content of each element are displayed in Fig. S4a and the three peaks at about 285.6 eV, 400.0 eV, and 531.7 eV corresponded to C 1s, N 1s, and O 1s, respectively. In detail, the C 1s spectrum (Fig. S4b) shows four peaks at 284.5 eV, 285.1 eV, 286.1 eV, and 287.8 eV, which are attributed to C–C, C–N, C–O, and C=O, respectively.



Fig. S4 (a) XPS and (b) C1 s spectra of CDs;

The TEM image (Fig. S5) shows that well distributed uniform circular CDs are formed with diameters within 1-2 nm.



Fig. S5 TEM and diameter distributions images of CDs. Scale bar is 50 nm.

The XRD patterns of the CDs (Fig. S6) shows a broad peak about at 25° (0.34 nm), which is consistent with highly disordered carbon atoms.⁴ Elemental analysis revealed that the composition are C 50.63 wt.%, H 6.14 wt.%, N 15.55 wt.%, and O (calculated)27.68 wt.%.



Fig. S6 XRD spectra of CDs.

Atomic force microscopy (AFM) measurements are performed to investigate the CDs interlayers spun cast on the DR3TBDTT:PC₇₁BM active material, which is shown in Figure S7. The values of a root mean square (RMS) roughness are 1.05, 24.9, 15.7, 10.3, 5.4, and 1.0 nm for the control without ETL, and CDs of the various concentrations with 1.0, 0.5, 0.1, 0.05, 0.01 mg/ml treatment, respectively. As these observe, the CDs do not completely cover the active layer surface. The CDs with higher concentrations are easily aggregated and the pretty lower concentration plays a role the same as methanol. Especially, the CDs with optimal concentration (0.1 mg/ml) is well uniformly distributed and the appropriate thickness ($30 \sim 45$ nm) is obtained.



Fig. S7 Tapping-mode AFM images of the devices with (a)the control without ETL, and the CDs of (b)1.0, (c)0.5, (d)0.1, (e)0.05, (f)0.01mg/ml spun cast on the DR3TBDTT:PC₇₁BM active material.

Table S1 The thickness and RMS roughness for the devices without ETL, with pure methanol treatment, and with CDs of various concentrations spun cast on the DR3TBDTT:PC₇₁BM active material.

	thickness	RMS roughness
None	1 ~ 3 nm	1.05 nm
1.0 mg/ml	$70 \sim 100 \text{ nm}$	24.9 nm
0.5 mg/ml	45 ~ 65 nm	15.7 nm
0.1 mg/ml	$30 \sim 45 \text{ nm}$	10.3 nm
0.05 mg/ml	$10 \sim 25 \text{ nm}$	5.4 nm
0.01 mg/ml	$5 \sim 10 \text{ nm}$	1.0 nm



Fig. S8 J = V characteristics of the devices without ETL, LiF as the ETL, and the CDs of optimized concentration (0.1 mg/ml) in the dark.



Fig. S9 J_{Dark} versus $(V - V_{\text{bi}})$ plots for the electron-only diode fabricated from Al/DR3TBDTT:PC71BM/ETL/Al. The solid line is fits of the data points. (a) – (f) corresponding to the devices with the control without ETL, and CDs of the various concentration with 1.0, 0.5, 0.1, 0.05, 0.01 mg/ml.



Fig. S10 Photocurrent density versus effective voltage $(J_{\rm ph} - V_{\rm eff})$ characteristics without the log graph for the devices without ETL (squares), with LiF as the ETL (circles), and with CDs of the optimal concentration as the ETL (up-triangles, 0.1 mg/ml).All the devices under constant incident light intensity simulated 100 mW cm⁻² AM 1.5G illumination.

The Ultraviolet Photoelectron Spectroscopy (UPS) measurements (Thermo ESCALAB 250) are carried out using the He I (hv=21.2 eV) source.

 $W_{f} = hv - E_{sec} \qquad (1)$

 W_f is the work function of CDs/Al, *hv* is the energy of He I source (21.2 eV), E_{sec} is the energy of second cutoff.

 $E_{HOMO} = E_{onset} + W_f$ (2)

 E_{HOMO} is the HOMO of the CDs, E_{onset} is the energy of the onset, W_f is the work function of CDs/Al.



Fig. S11 UPS spectra of CDs/Al film. a) Onset, b) Low energy cutoff regions for CDs/Al film. CDs/Al film is made by CDs of optimal concentration (0.1 mg/ml) spun cast on Al film.

	Second cutoff	W_{f}	Oneset	НОМО
Al ^[a]	-16.92	-4.3	-	-
CDs/Al	-17.66	-3.56	-2.75	-6.31

Table S2 The work function of Al and CDs/Al film.

[a] The work function of Al from Ref 5



Fig. S12 Absorption spectra of the blends (squares) and CDs of the optimal concentration (up-triangles, 0.1 mg/ml) spin-coated onto the active layer.

The detailed degradation data of PCE, J_{sc} , V_{oc} and FF vs time presented in Fig S13 – R16.



Fig. S13 Stability curves of (a) short circuit current (J_{sc}), (b) open circuit voltage (V_{oc}), (c) fill factor (FF) and photoconversion efficiency (PCE) of the unencapsulated devices stored in glove box.



Fig. S14 Stability curves of (a) short circuit current (J_{sc}), (b) open circuit voltage (V_{oc}), (c) fill factor (FF) and photoconversion efficiency (PCE) of the unencapsulated devices stored in air.



Fig. S15 Stability curves of (a) short circuit current (J_{sc}) , (b) open circuit voltage (V_{oc}) , (c) fill factor (FF) and photoconversion efficiency (PCE) of the encapsulated devices stored in glove box.



Fig. S16 Stability curves of (a) short circuit current (J_{sc}) , (b) open circuit voltage (V_{oc}) , (c) fill factor (FF) and photoconversion efficiency (PCE) of the encapsulated devices stored in air.

The calculation method of standard deviations:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \mu)^2}{n}}$$

In calculation standard deviations, we selected 15 high performance devices for the standard deviation calculation. σ is the standard deviations, n is the population of the devices (this is, n is 15), xi is each date of the 15 devices, and μ is the average of those 15 value.

Table S3 Standard deviations (σ) of photovoltaic parameters (V_{oc} , J_{sc} , FF, and PCE) of SMSCs without ETL, with LiF as the ETL, and with CDs of the different concentration as the ETL.

ETL	σ_{Voc}	$\sigma_{J_{ m SC}}$	σ_{FF}	σ_{PCE}
None	0.0109	0.2617	0.0334	0.1332
LiF	0.0051	0.0864	0.0009	0.1240
1.0 mg/ml	0.0082	0.2814	0.0115	0.3307
0.5 mg/ml	0.0063	0.1126	0.0115	0.1164
0.1 mg/ml	0.0004	0.1400	0.0096	0.0778
0.05 mg/ml	0.0065	0.1416	0.0125	0.1687
0.01 mg/ml	0.0021	0.2149	0.0128	0.1892



Fig. S17 J - V curves of the devices ITO/PEDOT:PSS/P3HT:PC₆₁BM with or without

ETLs/Al under simulated 100 mW cm⁻² AM1.5G illumination.

Reference

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