Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

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Ethylenediamine Functionalized Fullerene Nanoparticles as Independent Electron Transport Layer for High-Efficiency Inverted PolymerSolar Cells

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Materials and Characterization

Metallofullerene Gd@C_{82} was purchased from Xiamen Funano New Material Technology Company. The Gd@C_{82} was characterized to be 99% purity by high performance liquid chromatography (HPLC) and matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) in Fig. S1. Other reagents and organic solvents were all commercially available and used as received. Water was purified with Millipore Milli-Q Synthesis purifier (18.0 MΩ cm, Barnstead). MALDI-TOF-MS spectrum was achieved by SHIMAZU & BIOTECH AXIMA Assurance. X-ray photoelectron spectroscopy (XPS) analysis was performed on ESCALab220i-XL (VG Instruments). Zeta potential were carried out on a Malvern Instruments Zetasizer Nano ZSI at a 173° scattering angles. Infrared (IR) spectra were recorded in the range from 500 to 4000 cm^{-1} with Nicolet iN10 MX IR microscopy (Thermo Fisher Scientific).

Preparation of Fullerene-EDA Nanoparticles: fullerene-EDA nanoparticles (NPs) were prepared by a facile solid-liquid reaction. Solid fullerenes (50 mg) were added into 100 mL EDA, and the mixtures were stirred at room temperature until the solid fullerenes were totally dissolved in EDA. Then, EDA was totally removed by a rotary evaporator, and the residual solid was dissolved in aqueous solution of HCl (2 mM). Excessive HCl was neutralized by aqueous solution of NaOH (4 mM), and the solution was dialysed with a cellulose dialysis bag (MWCO = 3500) against ultrapure water for a 2-day dialysis (water changed every 24 h). The solution of fullerene-EDA hydrochloride was obtained as chlorine was detected by electron probe micro-analysis (EPMA) in Fig. S2a and b. In order to obtain pristine fullerene-EDA NPs without protonated amino, the solution was processed through anion exchange with ion exchange resin (Ambersep/r 900). Then, the obtained solution was packed in a cellulose dialysis bag (MWCO = 3500) for a 2-day dialysis (water changed every 24 h). In Fig. S2c and d, non-chlorine was detected by EPMA after anion exchange, indicating protonated amino were turned back to raw amino. Solid powders of Gd@C_{82}-EDA NPs and C_{60}-EDA NPs were obtained by freeze drying.

Considering the relative contents of carbon and nitrogen from the elemental analysis (EA) in Table S1, their average chemical compositions were estimated to C_{60}-$(EDA)_9$ and Gd@C_{82}-$(EDA)_8$, respectively. Moreover, the zeta potentials were measured three times per sample in water at pH 7.0. The EDAs on surface made them exhibit positive zeta potentials, and the relatively large value suggested they were stable enough in water.

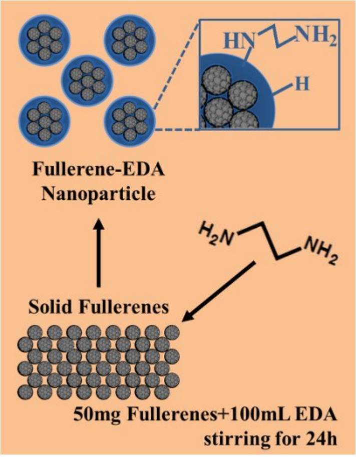
Device Fabrication: the inverted polymer solar cells (i-PSCs) based on PTB7-Th:$PC_{71}BM$ were fabricated according to the reported method,[1] and the basic structure was ITO/ETL/active layer/MoO_3/Ag. The devices were prepared on glass substrates with tin-doped indium oxide (ITO, 15Ω sq^{-1}) patterned on the surface. The ITO glass were cleaned by ultrasonic treatment with deionized water, acetone and isopropanol, and then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 20 min. ZnO films (40 nm) were obtained by spin-coating ZnO precursor, following annealing at 200°C for 10 min and then continuously annealing in air at 200°C for 1 h. The C_{60}-EDA or Gd@C_{82}-EDA layer was spin coated at 2000 r.p.m from the corresponding EDA solution (1 mg/mL). The active layer was spun from a mixture solvent of chlorobenzene and DIO (97:3 vol%) at 2000 r.p.m. for 1 min. The total concentration of the solution was 20 mg/mL and the weight ratio of PTB7-Th to $PC_{71}BM$ was 1:1.5. Then MoO_3 (5 nm) was thermally evaporated as a hole transport layer, followed by the thermal evaporation of Ag (80 nm). The device area was 0.04 cm^2. The samples for UPS and AFM measurements were spun on 1cm×1cm glasses fully covered by ITO. Moreover, the devices based on PBDTTT-C-T:$PC_{71}BM$ were analogously fabricated to investigate the universality of the fullerene-EDA ETL in different active layer systems.

Device Characterizations: The J-V curves were measured under ambient situation with a Keithley 2420 source-measure unit. Photocurrent was measured under AM 1.5 G illumination at 100mW/cm^2 using a Newport Thermal Oriel 91159A solar simulator. Light intensity was calibrated with a Newport oriel PN91150V Si-based solar cell. The EQE measurements of the devices were carried out in the air with an Oriel Newport system (Model 66920).

Electrical Conductivity Measurements: The electronic conductivities of the ZnO ETL and the fullerene-EDA ETL were conducted with bias voltage of 0.5 V on a NTEGRA Spectra AFM (NT-MDT).[2] An AFM tip coated with 10 nm Au on both sides (NSG03, NT-MDT) was contacted with the surface of ZnO and fullerene-EDA thin films coated onto ITO glass. Meanwhile, the surface topography AFM images of ZnO and fullerene-EDA were observed simultaneously.

Work Function Measurements: the work functions of the ITO, ITO/ZnO and ITO/fullerene-EDA layers were investigated by UPS, respectively. UPS spectra were measured via a He discharged lamp (He I 21.22 eV).

Optical Interference Measurements: We measure the reflectance spectra of the device: ITO/ETL/PTB7-Th:$PC_{71}BM$ (1:1.5 w/w, 90 nm)/MoO_3/Ag with ZnO, C_{60}-EDA and Gd@C_{82}-EDA as ETL, respectively, and the device without ETL as the reference (ITO/PTB7-Th:$PC_{71}BM$)/MoO_3/Ag). Since all the devices are identical except the material for ETL, comparisons of the reflectance yield information on the additional absorption A in PTB7-Th:$PC_{71}BM$ composite film as result of the spatial redistribution of the light intensity by the ETL. Here A is defined by $A \approx -(1/2d)\ln(I_{out}^*/I_{out})$, where I_{out}^* is the intensity of the reflected light from the device with ETL and I_{out} is that from the reference device. Optical interference effects were measured under the procedure corresponding to the published procedure.[3] The results in Fig. 5 demonstrate a clear increase in absorption of the active layer over the whole photocurrent response region.



Scheme S1 solid-liquid reaction to prepare fullerene-EDA.

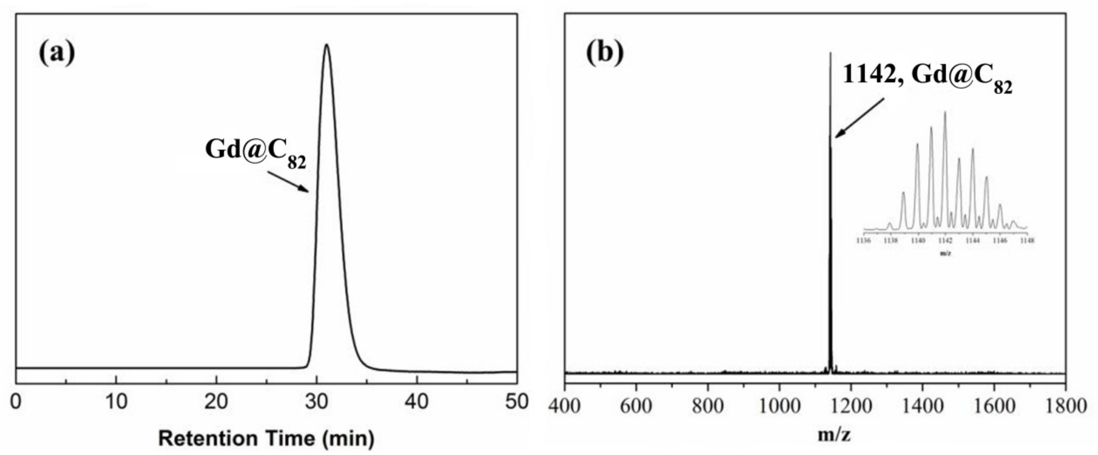
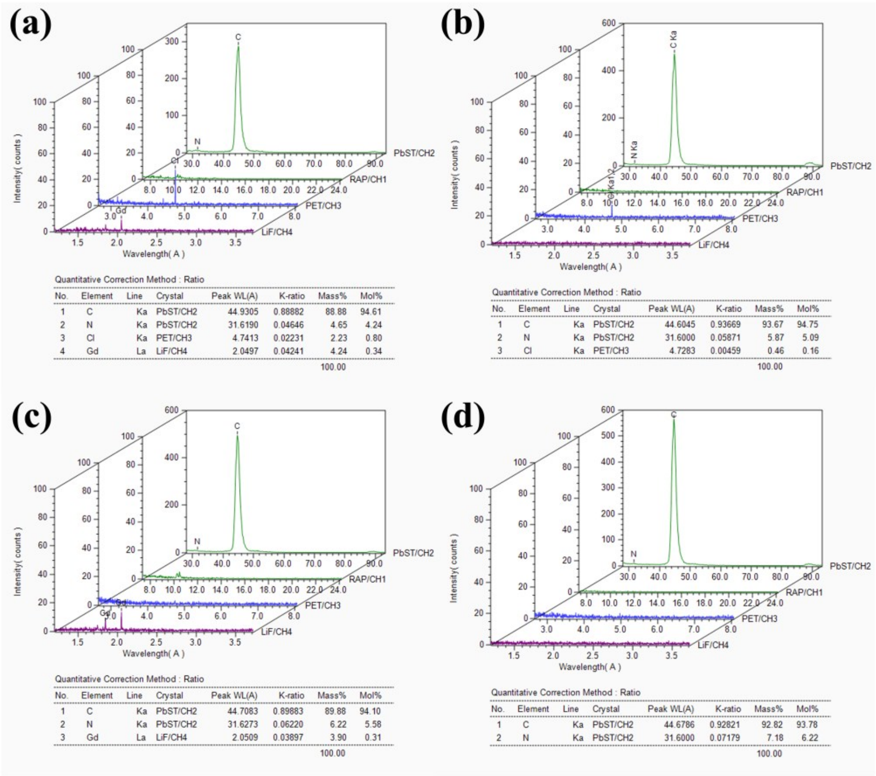


Fig. S1 (a) Chromatogram of the purchasedGd@C_{82} on a Buckyprep-M column (Chromatographic column 20 × 250 mm; flow rate 12 mL/min; toluene as eluent; Wavelength 310 nm). (b) MALDI-TOF-MS spectrum of the purchasedGd@C_{82}.



(a)

Quantitative Correction Method : Ratio

No.	Element	Line	Crystal	Peak WL(A)	K-ratio	Mass%	Mol%
1	C	Ka	PbST/CH2	44.9305	0.88882	88.88	94.61
2	N	Ka	PbST/CH2	31.6190	0.04646	4.65	4.24
3	Cl	Ka	PET/CH3	4.7413	0.02231	2.23	0.80
4	Gd	La	LiF/CH4	2.0497	0.04241	4.24	0.34
						100.00	

(b)

Quantitative Correction Method : Ratio

No.	Element	Line	Crystal	Peak WL(A)	K-ratio	Mass%	Mol%
1	C	Ka	PbST/CH2	44.6045	0.93669	93.67	94.75
2	N	Ka	PbST/CH2	31.6000	0.05871	5.87	5.09
3	Cl	Ka	PET/CH3	4.7283	0.00459	0.46	0.16
						100.00	

(c)

Quantitative Correction Method : Ratio

No.	Element	Line	Crystal	Peak WL(A)	K-ratio	Mass%	Mol%
1	C	Ka	PbST/CH2	44.7083	0.89883	89.88	94.10
2	N	Ka	PbST/CH2	31.6273	0.06220	6.22	5.58
3	Gd	La	LiF/CH4	2.0509	0.03897	3.90	0.31
						100.00	

(d)

Quantitative Correction Method : Ratio

No.	Element	Line	Crystal	Peak WL(A)	K-ratio	Mass%	Mol%
1	C	Ka	PbST/CH2	44.6786	0.92821	92.82	93.78
2	N	Ka	PbST/CH2	31.6000	0.07179	7.18	6.22
						100.00	

Fig. S2 EPMA for (a) Gd@C_{82}-EDA hydrochloride, (b) C_{60}-EDA hydrochloride, (c) pristine Gd@C_{82}-EDA and pristine C_{60}-EDA after anion exchange, respectively.

Table S1. EA of solid C_{60}-EDA and Gd@C_{82}-EDA, respectively.

	C_{60}-EDA	Gd@C_{82}-EDA
C	57.60	62.15
H	4.59	3.89
N	15.38	11.38

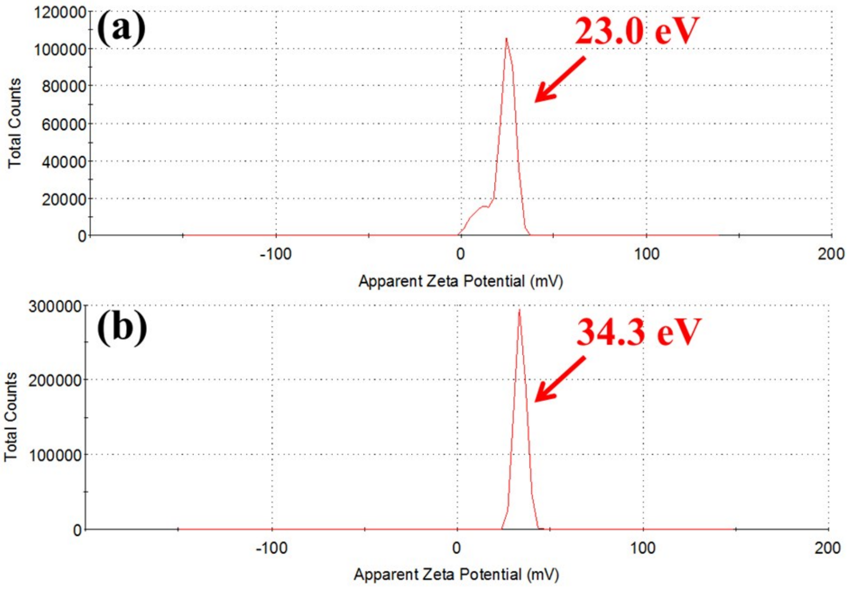


Fig. S3 Zeta potential of (a) C_{60}-EDAand (b) Gd@C_{82}-EDA are 34.3eV and 23.0eV, respectively.

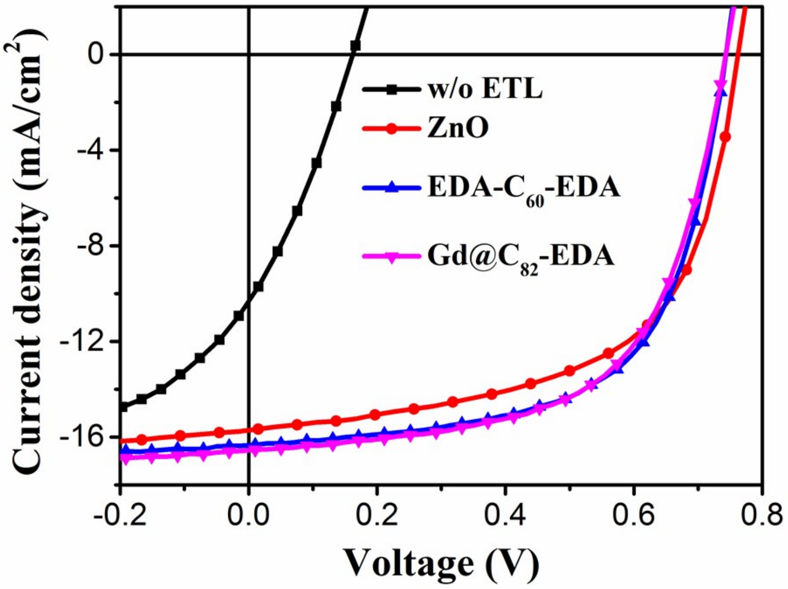


Fig. S4 Current density-Voltage (*J-V*) characteristicsof the inverted PSCs based on PBDTTT-C-T:PC_{71}BM with orwithout the ETL.

Table S2 Best photovoltaic performance of polymer solar cells based on PBDTTT-C-T:$PC_{71}BM$ under the illumination of AM 1.5G, 100 mW cm^{-2}. ()^b is the average value of 5 solar cells.

ETL	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
W/O	0.162	10.33	30.13	0.50 (0.374)^b
ZnO	0.762	15.69	59.35	7.10 (6.78)
C_{60}-EDA	0.743	16.35	62.13	7.55 (7.50)
Gd@C_{82}-EDA	0.743	16.54	60.55	7.44 (7.41)

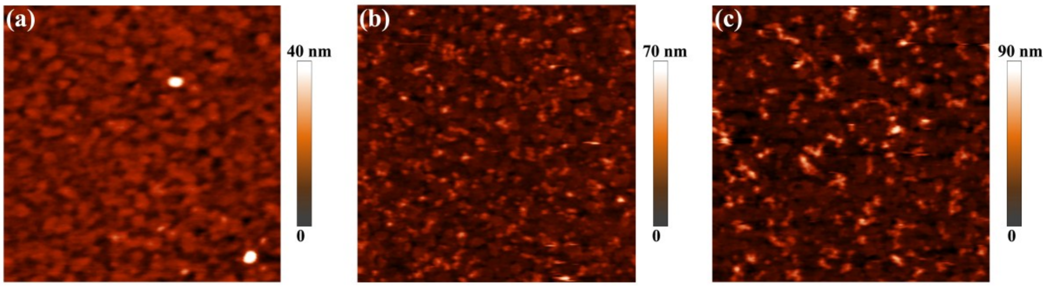


Fig. S5 The topography AFM images of (a) ZnO, (b) C_{60}-EDA and (c) Gd@C_{82}-EDA. The scan size is 3 µm×3 µm.

Reference

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