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Supplementary Information

$Sc_3N@C_{80}$ and $La@C_{82}$ Doped Graphene for a New Class of Optoelectronic Devices

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Electrophoretic Deposition of END_1

Dispersions of END_1 (~ 0.01 mg, ~ 0.5 mg, and ~ 1 mg) exhibited optical absorption spectra in ~ 1 mL of o-DCB shown in Figure S1(a). Since endohedral fullerenes have low solubility in toluene, o-DCB was used for the dissolution of END_1.[1] END_1 suspensions shows a relatively high absorbance for λ ~ 450-680 nm, consistent with previous reports.[2] As the concentration of END_1 in o-DCB was increased, the absorption of END_1 also increased, consistent with the Lambert-Beer Law. Electrophoretic deposition was used to adhere END_1 on the substrate, similar to the technique reported for depositing C_{60} films,[3] where the current I as a function of the electrophoretic deposition time t is shown in Figure S1(b). A drop of the suspension was injected at voltage V ~ 0 V and a step potential was applied from ~ 0.05 V to ~ 0.3 V in ~ 0.05 V increments between the electrodes. The electrophoretic deposition I increased gradually as the step-potential increased with time for END_1. Upon saturation for a particular step V, I starts to decrease due to Joule heating as the resistance increases. After t ~ 12 min of deposition, a film of END_1 adhered on top of the Au/Ti electrodes. Eventually, the device was vacuum annealed for ~ 24 hours at ~ 180°C to drive off the residual solvents (i.e. at the approximate

boiling temperature of o-DCB). Prior to the fabrication of the END_1-graphene hybrid devices, reference measurements were conducted for END_1 in ~1 mL of o-DCB to gauge the optimal concentration needed of the END_1 in the construction of the graphene hybrid devices.

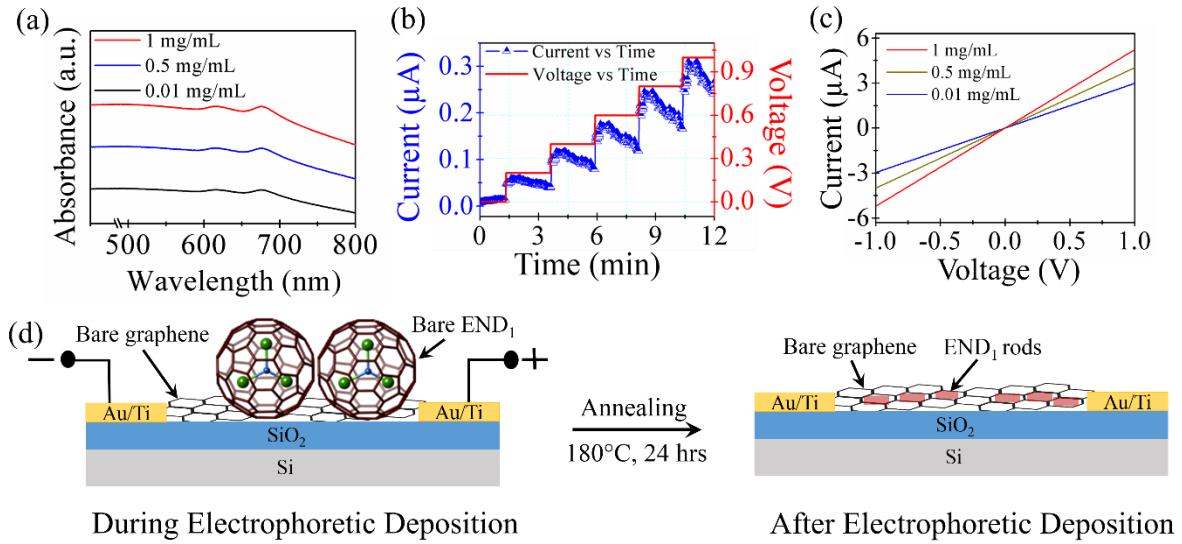

Figure S1: (a) Optical absorbance at various concentrations of END_1 as a function of λ. (b) Current measurements as a function of electrophoretic deposition time. (c) *I-V* of END_1 at various concentrations in o-DCB. (d) Schematic illustration for the electrophoretic deposition of END_1 on the graphene membrane. The graphene was mechanically exfoliated and Au/Ti electrical contacts were deposited followed by a lift-off process using SiO_2/Si substrate (schematic not to scale). For electrophoretic deposition, a ~ 1 mg suspension solution of END_1 in ~ 1 mL of o-DCB was used. During electrophoretic deposition, individual atoms of END_1 aggregated on top of the graphene membrane, but after annealing the hybrid for ~ 24 hrs at ~ 180 °C, END_1 aligns itself in the form of a rod-shaped crystal as shown schematically in the right image of (d).

The *I-V* Characteristic of bare END_1 films deposited on SiO_2/Si substrates for concentrations ~ 0.01 mg/mL, ~ 0.5 mg/mL and ~ 1 mg/mL under vacuum conditions are shown in Figure S1(c) from ~ -1 V to ~ 1 V. Since the ~ 1 mg/mL concentration of END_1 yielded the highest *I* values in o-DCB, this concentration was used to electrophoretically deposit the END_1 on top of the graphene membrane. Figure S1(d) shows a schematic depiction of the hybrid structure of END_1 aggregated on top of the graphene membrane, where the

aggregated film consists of individual END_1 molecules. However, after annealing the hybrid devices, END_1 aligns itself in the form of a rod-shaped crystal, as shown in Figure S1(d)-right. The END_1 molecules nucleate rapidly and then the crystal seeds start to grow via π-π stacking to form small particles where the growth of END_1 occurs along the long-axis and the crystals adopt a rod-shaped morphology,[2] as confirmed using SEM.

SEM and AFM Imaging Analysis END_1

SEM measurements were conducted to see the agglomeration of END_1 on top of graphene membrane. Figures S2(a)-(d) show typical SEM images of END_1 ((a) and (c)) and END_1-graphene ((b) and (d)), where the top-left inset of Figure S2(b) shows the bare graphene device only. The average length of END_1 rod-shaped ensembles after electrophoretic deposition was found to be ~ 4 μm as shown in Figure S2(c) and (d). More insights into the structural morphology was obtained using AFM conducted at a scan speed of 1 Hz. The height profile measurements were performed over an area of ~ 15 μm× 15 μm, as shown in Figure S2(e)-(i). The height profile from Figure S2(e)-(i) (red dotted lines) is reproduced in Figure S2(e)-(ii) which reveals the relatively smooth surface of the bare graphene membrane, where the inset shows the height profile of bare graphene with 24 nm thickness. Similar AFM measurements were performed for bare END_1 and END_1-graphene hybrid structures, as shown in Figures S2(f) and (g), respectively. Figures S2(f)(i)-(ii) illustrate the clusters of bare END_1 in the form of islands exhibiting a peak height of ~ 3.6 nm and diameter ~ 50 nm; Figures S2(g)(i)-(ii) on the other hand, show clustering of END_1 on the graphene surface with a peak height of ~ 9-20 nm and cluster diameter ~ 200-350 nm.

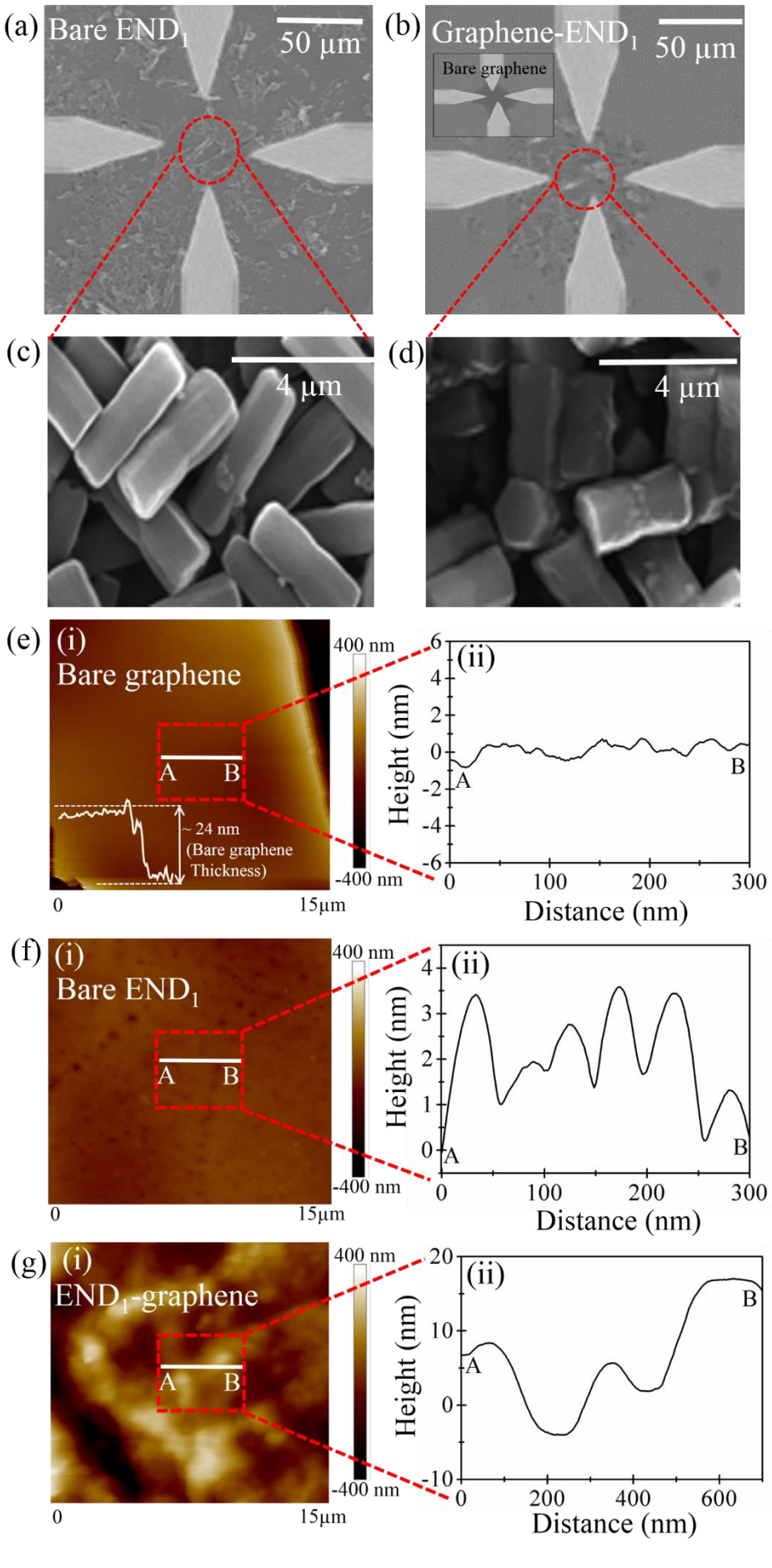
(a) Bare END1
50 μm
(b) Graphene-END1
Bare graphene
50 μm
(c)
4 μm
(d)
4 μm
(e)
(i)
Bare graphene
A
B
~ 24 nm
(Bare graphene
Thickness)
400 nm
-400 nm
0
15μm
(ii)
Height (nm)
Distance (nm)
(f)
(i)
Bare END1
(ii)
(g)
(i)
END1-graphene
(ii)

Figure S2: Low-magnification SEM images of electrophoretic deposition of (a) bare END_1, (b) END_1-graphene hybrid (inset shows the SEM of bare graphene). High-magnification SEM images showing (c) the micron-sized hexagonal END_1 rods with an average length of ~ 4 μm, and (d) the aggregation of END_1 on top of the graphene membrane after electrophoretic deposition. (e)-(g): (i) Large-area AFM scan (~ 15 μm× 15 μm), and (ii) shows the height profile of the A-to-B scan direction. The image in (e)-(i) reveals a uniform, smooth graphene surface, where the bottom left inset shows the bare graphene thickness to be ~ 24 nm thickness. (f)-(i)-(ii) illustrate the clusters of bare END_1 in the form of islands with a peak height of ~ 3.6 nm and diameter of ~ 50 nm; (g)-(i)-(ii) reveal the clustering of END_1 on the graphene surface in the form of islands with peak height of ~ 9-20 nm and diameter of ~ 200-350 nm.

Electrophoretic Deposition of END_2

Before the preparation of the END_2-graphene hybrid devices, initial measurements were conducted on the bare END_2 to measure the intrinsic conductance of these endohedrals, where ~ 0.1, ~ 0.2, and ~ 0.3 mg of END_2 was dissolved in ~ 1 mL of o-DCB. Electrophoretic deposition was used to adhere END_2 on the substrate, similar to the technique reported for depositing C_{60} films,[3] where the current I as a function of the electrophoretic deposition time t is shown in Figure S3(a). A drop of the suspension was injected at voltage V ~ 0 V and a step potential was applied from ~ 0.05 V to ~ 0.3 V in ~ 0.05 V increments between the electrodes.

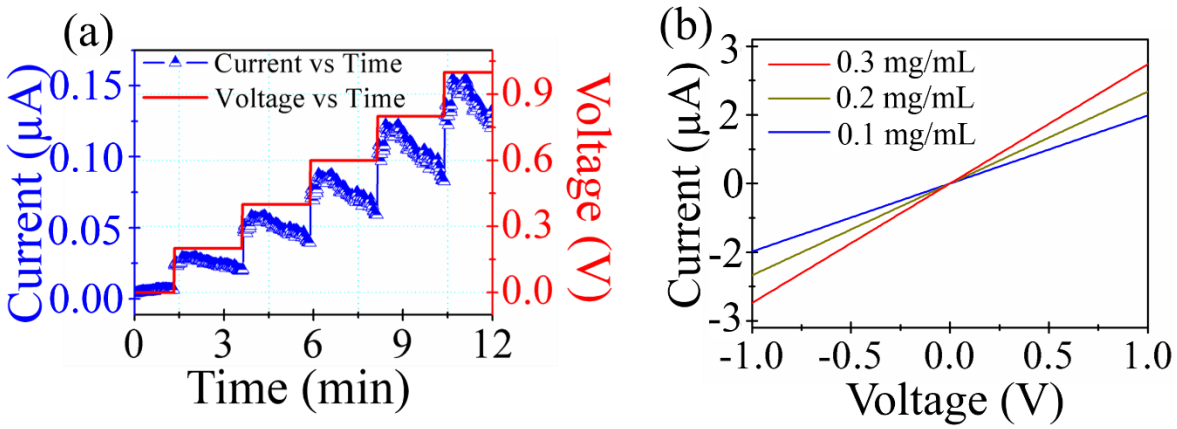

Figure S3: (a) Current measurements as a function of electrophoretic deposition time for END_2. (b) *I-V* Characteristic of END_2 at various concentrations in o-DCB.

The electrophoretic deposition *I* increased gradually as the step-potential increased with time for END_2. Upon saturation for a particular step *V*, *I* starts to decrease due to Joule heating as the resistance increases. After *t* ~ 12 min of deposition, a film of END_1 adhered on top of the Au/Ti electrodes. Eventually, the device was vacuum annealed for ~ 24 hours at ~ 180°C to drive off the residual solvents (i.e. at the approximate boiling temperature of o-DCB). The *I-V* Characteristic of bare END_2 films deposited on SiO_2/Si substrates for concentrations ~ 0.1 mg/mL, ~ 0.2 mg/mL and ~ 0.3 mg/mL under vacuum conditions are shown in Figure S3(b) from ~ -1 V to ~ 1 V. Since the ~ 0.3 mg/mL concentration of END_2 yielded the highest *I* values in o-DCB, this concentration was used to electrophoretically deposit the END_2 on top of the graphene membrane.

AFM Imaging of END_2

Figures S4(a) and (b) show the representative AFM images of the bare END_2 and END_2-graphene hybrid at a scan speed of ~ 1 Hz. The height profile of the region with the END_2 clusters was performed using AFM analysis, where the ~ 15 μm× 15 μm scan area is shown in Figure S4(a)-(i), over the A to B scan direction as illustrated in Figure S4(a)-(ii), where the bare graphene AFM scan profile height was ~ 12.8 nm. Figure S4(a)(i)-(ii) illustrate the clusters of bare END_2 in the form of islands exhibiting a height of ~ 35-40 nm and diameter ~ 170-250 nm; the cluster arrangement for END_2 on graphene is seen in Figure S4(b)(i)-(ii), which reveals a height ~ 45-55 nm and diameter ~ 184-240 nm for the clusters.

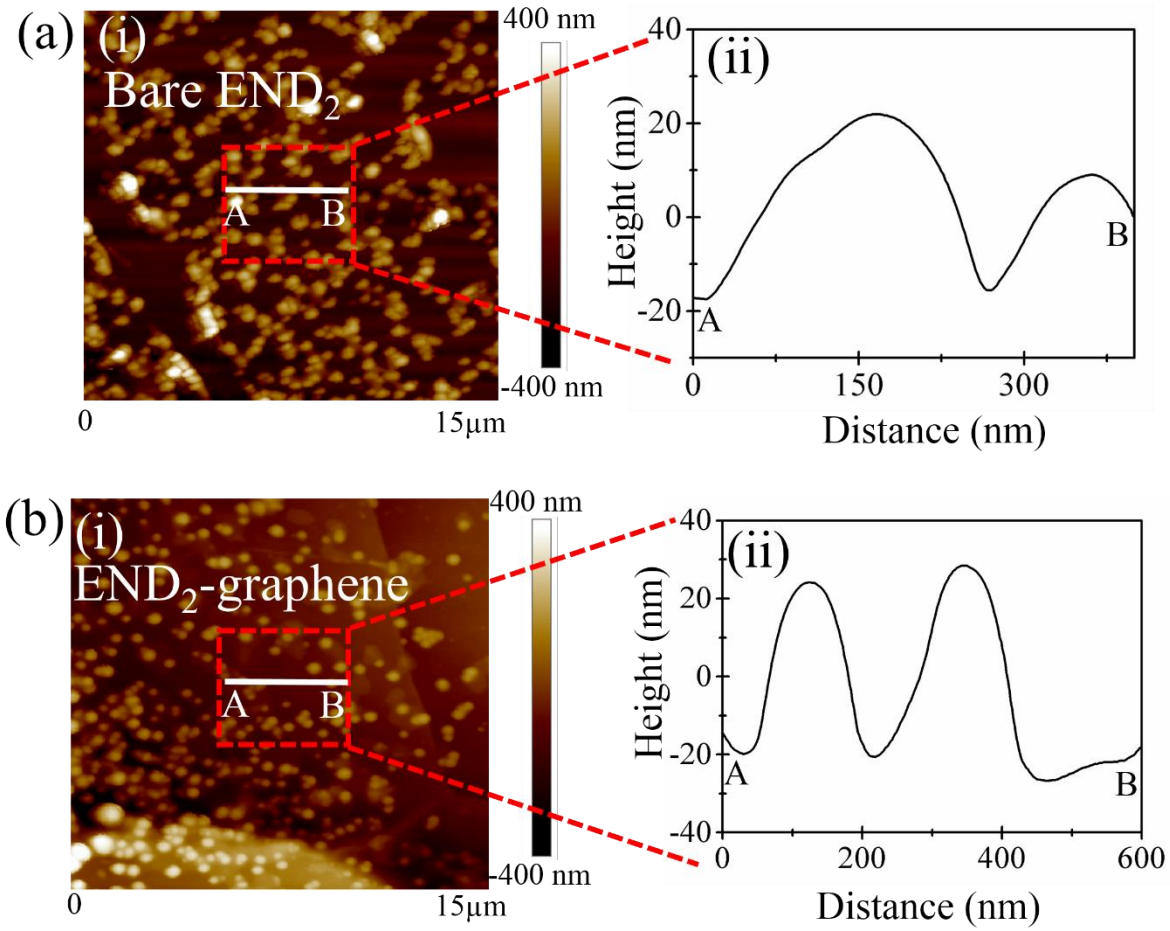

Figure S4: (a) and (b): (i) Large-area (~ 15 µm× 15 µm) AFM scan and (ii) illustrates the clusters of bare END_2 in the form of islands with a height of~ 35-40 nm and diameter ~ 170-250 nm in the A-to-B scan direction; (b)(i)-(ii) reveals the clustering of END_2 on the graphene surface in the form of islands ~ 45-55 nm and diameter ~ 184-240 nm in diameter. The height of the bare graphene was measured to be ~ 12.8 nm using AFM.

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