## Supporting Information

## An Aromatic Micelle with Bended Pentacene-based Panels: Encapsulation of Perylene Bisimide Dyes and Graphene Nanosheets

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#### Materials and methods

NMR: Bruker AVANCE III 400 (400 MHz) and HD 500 (500 MHz), MALDI-TOF MS: Bruker UltrafleXtreme, ESI-TOF MS: Bruker micrOTOF II, FT-IR: SHIMADU IRsprit-T, UV-vis: JASCO V-670DS, Fluorescence: Hitachi F-7000, Absolute PL quantum yield: Hamamatsu C9920-02G with an integration sphere, DLS: Wyatt Technology DynaPro NanoStar, Raman: HORIBA Ltd LabRAM HR Evolution.

DFT calculation: Spartan'10 (Wavefunction, Inc.) and Gaussian 16 Rev A.03 (Gaussian, Inc.), Molecular mechanics calculation (geometry optimization): Forcite module, Materials Studio, version 5.5.3 (Dassault Systèmes Co.).

Solvents and reagents: TCI Co., Ltd., FUJIFILM Wako Chemical Co., Kanto Chemical Co., Inc., Sigma-Aldrich Co., and Cambridge Isotope Laboratories, Inc. Compound **AA** was synthesized according to ref. S2. **GNS** and **SG** were purchased from TCI Co., Ltd. (G0499 Graphene Nanoplatelets 2-10 nm (thick), 5  $\mu$ m (wide)) and Chuetsu Graphite Works Co., Ltd. (Synthetic Graphite G-6S, 10  $\mu$ m (average size)).

#### References

- [S1] a) J. Bouffard, R. F. Eaton, P. Müller, T. M. Swager, J. Org. Chem. 2007, 72, 10166–10180; b) S. E. Wheeler, A. J. McNeil, P. Müller, T. M. Swager, K. N. Houk, J. Am. Chem. Soc. 2010, 132, 3304–3311.
- [S2] K. Kondo, M. Akita, T. Nakagawa, Y. Matsuo, M. Yoshizawa, *Chem. Eur. J.* 2015, 21, 12741–12746.
- [S3] L. G. Cançado, K. Takai, T. Enoki, M. Endo, Y. A. Kim, H. Mizusaki, A. Jorio,
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Synthesis of 1<sub>CH3</sub>

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Pentacene (505 mg, 1.81 mmol) and dimethyl acetylenedicarboxylate (2.0 mL) were added to a 100 mL glass flask filled with N<sub>2</sub> and the mixture was stirred at 180 °C for 3 h. The crude product was purified by silica-gel column chromatography (ethyl acetate:hexane = 1:6) and then by gel permeation chromatography (CHCl<sub>3</sub>) to give  $\mathbf{1}_{CH3}$  as a white solid (468 mg, 1.11 mmol, 62% yield).<sup>[S1]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, r.t.): δ 7.84 (s, 4H), 7.73 (m, 4H), 7.41 (m, 4H), 5.67 (s, 2H) 3.81 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, r.t.): δ 166.0 (CO), 145.6 (C<sub>q</sub>), 139.5 (C<sub>q</sub>), 132.0 (C<sub>q</sub>), 127.8 (CH), 126.3 (CH), 122.6 (CH), 52.6 (CH), 51.6 (CH<sub>3</sub>). FT-IR (KBr, cm<sup>-1</sup>): 3055, 3004, 2951, 1717, 1634, 1435, 1325, 1268, 1217, 1062, 750. HR MS (ESI, CH<sub>3</sub>OH): m/z Calcd. for C<sub>28</sub>H<sub>20</sub>O<sub>4</sub>Na 443.1254 [M + Na]<sup>+</sup>, Found 443.1235.



Figure S1. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, r.t.) of  $\mathbf{1}_{CH3}$ .







Figure S3. HR MS spectrum (ESI, CH<sub>3</sub>OH) of 1<sub>CH3</sub>.



Compound  $\mathbf{1}_{CH3}$  (200 mg, 476 µmol), 1 M NaOH aqueous solution (2 mL), and CH<sub>3</sub>OH (4 mL) were added to a 20 mL Schlenk flask. The mixture was stirred at 90 °C for 2 h. The reaction solution was neutralized with concentrated HCl at 0 °C and then the product was extracted with ethyl acetate. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and evaporated to give  $\mathbf{1}_{H}$  as a pale yellow solid (159 mg, 404 µmol, 85% yield).

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, r.t.):  $\delta$  7.87 (s, 4H), 7.77 (br, 4H), 7.41 (br, 4H), 5.90 (s, 2H). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD, r.t.):  $\delta$  168.9 (CO), 148.3 (C<sub>q</sub>), 141.3 (C<sub>q</sub>), 133.4 (C<sub>q</sub>), 128.7 (CH), 127.0 (CH), 123.2 (CH), 53.3 (CH). FT-IR (KBr, cm<sup>-1</sup>): 3437, 3057, 1577, 1507, 1270, 1298, 1080, 1022, 895, 832, 780, 746. HR MS (ESI, CH<sub>3</sub>OH): *m/z* Calcd. for C<sub>26</sub>H<sub>15</sub>O<sub>4</sub> 391.0965 [M – H]<sup>-</sup>, Found 391.0954.



Figure S4. <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>3</sub>OD, r.t.) of  $\mathbf{1}_{H}$ .



Figure S5. <sup>13</sup>C NMR spectrum (125 MHz, CD<sub>3</sub>OD, r.t.) of  $\mathbf{1}_{H}$ .



Figure S6. HR MS spectrum (ESI,  $CH_3OH$ ) of  $1_H$ .



Compound  $\mathbf{1}_{H}$  (150 mg, 382 µmol), dry DMF (one drop), and dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) were added to a 2-necked 50 mL glass flask filled with N<sub>2</sub>. Oxalyl chloride (260 µL, 3.03 mmol) was added dropwise to the flask at 0 °C and then the mixture was stirred at r.t. for 30 min. The reaction mixture was evaporated under vacuum and the resultant yellow solid was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) under N<sub>2</sub>. Dry 2-dimethylamino ethanol (150 µL, 1.53 mmol) was added dropwise to the flask and the mixture was stirred at r.t. for 1 h. The resultant solution was washed with saturated NaHCO<sub>3</sub> aq., dried over MgSO<sub>4</sub>, filtrated, and evaporated under vacuum. The same procedure was repeated to the product. The obtained solid was washed with small portions of CH<sub>3</sub>OH to give **2** (89 mg, 167 µmol, 44% yield) as a yellow solid.

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, r.t.):  $\delta$  7.82 (s, 4H), 7.73 (m, 4H), 7.41 (m, 4H), 5.67 (s, 2H), 4.32 (t, *J* = 6.0 Hz, 4H), 2.62 (t, *J* = 6.0 Hz, 4H), 2.29 (s, 12H). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD, r.t.):  $\delta$  165.4 (CO), 145.4 (C<sub>q</sub>), 139.6 (C<sub>q</sub>), 132.0 (C<sub>q</sub>), 127.8 (CH), 126.2 (CH), 122.5 (CH), 63.6 (CH<sub>2</sub>), 57.5 (CH<sub>2</sub>), 51.6 (CH), 46.0 (CH<sub>2</sub>). FT-IR (KBr, cm<sup>-1</sup>): 3422, 3053, 2947, 2859, 2822, 2772, 1711, 1634, 1458, 1318, 1268, 1212, 1049, 953, 889, 749. HR MS (ESI, CH<sub>3</sub>OH): *m*/*z* Calcd. for C<sub>34</sub>H<sub>35</sub>N<sub>2</sub>O<sub>4</sub> 535.2591 [M + H]<sup>+</sup>, Found 535.2582.



Figure S8. <sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>, r.t.) of 2.



Figure S9. HR MS spectrum (ESI, CH<sub>3</sub>OH) of 2.



Compound 2 (80.0 mg, 150  $\mu$ mol) and CH<sub>3</sub>CN (4 mL) were added to a screw-top test tube. CH<sub>3</sub>I (93  $\mu$ L, 1.5 mmol) was added dropwise to the test tube and the resultant mixture was stirred at r.t. for 12 h. After evaporation of the solvent, the obtained solid was washed with hexane to give **3** (105 mg, 146  $\mu$ mol, 97% yield) as a yellow solid. Compound **3** (100 mg, 138  $\mu$ mol), AgCl (102 mg, 712  $\mu$ mol), and H<sub>2</sub>O (5 mL) were added to a screw-top test tube. The resultant mixture was stirred at 80 °C for 12 h. After removal of the solvent, the crude product was dissolved in CH<sub>3</sub>OH (10 mL). The resultant solution was filtrated through a filter paper to remove AgI. The solvent was removed under vacuum and the obtained solid was washed with acetone (2 mL) and acetonitrile (4 mL) to give **PA** (70 mg, 110  $\mu$ mol, 80% yield) as a white solid.

Compound **3**: <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, r.t.):  $\delta$  7.94 (s, 4H), 7.79 (m, 4H), 7.44 (m, 4H), 5.92 (s, 2H), 4.78 (br, 4H), 3.87 (t, *J* = 4.6 Hz, 4H), 3.26 (s, 18H). HR MS (ESI,

CH<sub>3</sub>OH): m/z Calcd. for C<sub>36</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub> 282.1489 [M – 2•I]<sup>2+</sup>, Found 282.1476.

Compound **PA**: <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, r.t.):  $\delta$  7.91 (s, 4H), 7.79 (m, 4H), 7.45 (m, 4H), 5.88 (s, 2H), 4.77 (br, 4H), 3.84 (t, *J* = 4.4 Hz, 4H), 3.25 (s, 18H). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD, r.t.):  $\delta$  165.7 (CO), 147.9 (C<sub>q</sub>), 140.5 (C<sub>q</sub>), 133.4 (C<sub>q</sub>), 128.8 (CH), 127.4 (CH), 123.5 (CH), 65.8 (CH<sub>2</sub>), 60.3 (CH<sub>2</sub>), 54.5 (CH<sub>3</sub>), 52.4 (CH). FT-IR (KBr, cm<sup>-1</sup>): 3432, 3017, 2962, 1719, 1631, 1478, 1318, 1251, 1208, 951, 888, 757. ESI-TOF MS: *m*/*z* Calcd. for C<sub>36</sub>H<sub>40</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub> 599.27 [M – Cl]<sup>+</sup>, Found 599.27.



**Figure S10.** <sup>1</sup>H NMR spectrum (400 MHz,  $CD_3OD$ , r.t.) of **3**.









**Figure S12.** <sup>1</sup>H NMR spectrum (400 MHz,  $CD_3OD$ , r.t.) of **PA**.







# Formation of aromatic micelle (PA)<sub>n</sub> KI154, 181 $\begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & &$

Amphiphile **PA** (6.4 mg, 10 µmol) and D<sub>2</sub>O (0.5 mL) were added to a glass test tube. When the mixture was stirred at r.t. for 1 min, the formation of aromatic micelle (**PA**)<sub>n</sub> was confirmed by NMR, DLS, UV-visible, and fluorescence analyses. The final optimized structures were obtained starting from the assemblies of (**PA**)<sub>n</sub> (n = 4, 5, and 6) with various orientation, by performing the geometry optimizations implemented in the Forcite program (Materials Studio, version 5.5.3).

<sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O, 20 mM based on **PA**, r.t., TMS as an external standard):  $\delta$  7.67 (m, 4H), 7.46 (m, 4H), 7.42 (s, 4H), 5.45 (s, 2H), 4.62 (m, 4H), 3.65 (m, 4H), 3.03 (s, 18H). <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O, 20 mM based on **PA**, r.t.):  $\delta$  165.0 (CO), 146.5 (C<sub>q</sub>), 138.2 (C<sub>q</sub>), 131.3 (C<sub>q</sub>), 127.7 (CH), 126.5 (CH), 122.3 (CH), 64.2 (CH<sub>2</sub>), 59.4 (CH<sub>2</sub>), 53.6 (CH<sub>3</sub>), 50.4 (CH). DOSY NMR (500 MHz, D<sub>2</sub>O, 20 mM based on **PA**, 25 °C):  $D = 2.51 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ .



Figure S15. <sup>1</sup>H NMR spectrum (500 MHz, D<sub>2</sub>O, r.t., 20 mM based on PA) of (PA)<sub>n</sub>.



 $_{200}$  190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm **Figure S16.**  $^{13}$ C NMR spectrum (500 MHz, D<sub>2</sub>O, r.t., 20 mM based on PA) of (PA)<sub>n</sub>.



Figure S17. DOSY NMR spectrum (500 MHz, D<sub>2</sub>O, 20 mM based on PA, 25 °C) of (PA)<sub>n</sub>.



**Figure S18.** Concentration-dependent <sup>1</sup>H NMR spectra (400 MHz,  $D_2O$ , r.t., TMS as an external standard) of  $(\mathbf{PA})_n$ .



**Figure S19.** a) UV-visible spectra (r.t.) of **PA** in CH<sub>3</sub>OH and H<sub>2</sub>O (1.0 mM based on **PA**). b) Fluorescent spectra (r.t.,  $\lambda_{ex} = 240$  nm) and fluorescent quantum yields of **PA** (CH<sub>3</sub>OH, 1.0 mM) and (**PA**)<sub>n</sub> (H<sub>2</sub>O, 1.0 and 20 mM based on **PA**).



**Figure S20.** DLS charts ( $H_2O$ , r.t.) and average diameters (Z-average) of (PA)<sub>n</sub>: a) 10 mM, b) 20 mM, and c) 50 mM based on PA.



**Figure S21.** Optimized structures and average diameters of  $(\mathbf{PA})_4$ ,  $(\mathbf{PA})_5$ , and  $(\mathbf{PA})_6$ . The geometry optimizations of  $(\mathbf{PA})_4$ ,  $(\mathbf{PA})_5$ , and  $(\mathbf{PA})_6$  were performed with the Forcite module of Materials Studio (version 5.5.3).



A mixture of **PA** (1.3 mg, 2.0 µmol) and pigment red 149 (**PBI-1**; 0.3 mg, 1.0 µmol) was ground for 5 min by using an agate mortar and pestle. After the addition of  $H_2O$  (2.0 mL), the suspended solution was centrifuged (16,000 g) for 10 min and then filtered by a membrane filter (pore size: 200 nm) to give a red solution of  $(\mathbf{PA})_n \cdot (\mathbf{PBI-1})_m$ . Host-guest complex  $(\mathbf{PA})_n \cdot (\mathbf{NR})_m$  was also prepared from **PA** (1.3 mg, 2.0 µmol) and Nile red (**NR**; 0.3 mg, 1.0 µmol). By the same protocol, a red solution of  $(\mathbf{AA})_n \cdot (\mathbf{PBI-1})_m$  and a red-purple solution of  $(\mathbf{AA})_n \cdot (\mathbf{NR})_m$  were obtained by the treatment of **AA** with **PBI-1** and **NR**, respectively. The formation of  $(\mathbf{PA})_n \cdot (\mathbf{PBI-1})_m$ ,  $(\mathbf{PA})_n \cdot (\mathbf{NR})_m$ ,  $(\mathbf{AA})_n \cdot (\mathbf{PBI-1})_m$ , and  $(\mathbf{AA})_n \cdot (\mathbf{NR})_m$  was confirmed by UV-vis analysis.



Figure S22. UV-visible spectra (H<sub>2</sub>O, 1.0 mM based on PA or AA, r.t.) and photographs of a) (PA)<sub>n</sub>•(PBI-1)<sub>m</sub> and (AA)<sub>n</sub>•(PBI-1)<sub>m</sub>, and b) (PA)<sub>n</sub>•(NR)<sub>m</sub> and (AA)<sub>n</sub>•(NR)<sub>m</sub>.



**Figure S23.** UV-visible spectra (H<sub>2</sub>O, 1.0 mM based on PA or AA, r.t.) of  $(PA)_n \cdot (PBI-1)_m$  and  $(AA)_n \cdot (PBI-1)_m$  before (solid line) and after four months (dash line).



A mixture of **PA** (1.3 mg, 2.0 µmol) and perylene orange (**PBI-2**; 0.7 mg, 1.0 µmol) was ground for 5 min by using an agate mortar and pestle. After the addition of H<sub>2</sub>O (2.0 mL), the suspended solution was centrifuged (16,000 g) for 10 min and then filtered by a membrane filter (pore size: 200 nm) to give a red solution of  $(\mathbf{PA})_n \cdot (\mathbf{PBI-2})_m$ . By the same protocol, a purple solution of  $(\mathbf{AA})_n \cdot (\mathbf{PBI-2})_m$  was obtained from **AA** and **PBI-2**. The formations and structures of  $(\mathbf{PA})_n \cdot (\mathbf{PBI-2})_m$  and  $(\mathbf{AA})_n \cdot (\mathbf{PBI-2})_m$  were confirmed by UV-vis, DLS, and <sup>1</sup>H NMR analyses. The host-guest ratios were determined as  $(\mathbf{PA})_6 \cdot (\mathbf{PBI-2})_2$  and  $(\mathbf{AA})_4 \cdot (\mathbf{PBI-2})_2$  by the <sup>1</sup>H NMR analysis of the products in DMSO- $d_6$ . The final optimized structure was obtained starting from the assembly of  $(\mathbf{PA})_6 \cdot (\mathbf{PBI-2})_2$  with various orientation, by performing the geometry optimizations implemented in the Forcite program.



**Figure S24.** a) UV-visible (H<sub>2</sub>O, r.t., 1.0 mM based on **PA** or **AA**) and photographs, and b) fluorescent spectra ( $\lambda_{ex} = 498$  nm) of (**PA**)<sub>n</sub>•(**PBI-2**)<sub>m</sub> and (**AA**)<sub>n</sub>•(**PBI-2**)<sub>m</sub>.



Figure S25. DLS charts (H<sub>2</sub>O, r.t., 0.1 mM based on PA or AA) and average diameters (Z-average) of a)  $(PA)_n \cdot (PBI-2)_m$  and b)  $(AA)_n \cdot (PBI-2)_m$ .



**Figure S26.** <sup>1</sup>H NMR spectra (500 MHz, r.t.) of isolated  $(\mathbf{PA})_n \bullet (\mathbf{PBI-2})_m$  and  $(\mathbf{AA})_n \bullet (\mathbf{PBI-2})_m$  in DMSO-*d*<sub>6</sub>.



**Figure S27.** Optimized structures and core diameter of  $(\mathbf{PA})_6 \bullet (\mathbf{PBI-2})_2$  with a) parallel and b) cross stacking conformations of  $(\mathbf{PBI-2})_2$ . The geometry optimization of  $(\mathbf{PA})_6 \bullet (\mathbf{PBI-2})_2$  was performed with the Forcite module of Materials Studio (version 5.5.3).





A mixture of compound **PA** (0.6 mg, 1.0 µmol) and fullerene  $C_{60}$  ( $C_{60}$ ; 0.4 mg, 0.5 µmol) was ground for 5 min by using an agate mortar and pestle. After the addition of  $H_2O$  (1.0 mL), the suspended solution was sonicated for 10 min, centrifuged (16,000 g) for 10 min, and then filtered by a membrane filter (pore size: 200 nm) to give a clear brown solution of  $(PA)_n \cdot (C_{60})_m$ .<sup>[82]</sup> In the same way, a clear brown solution of  $(AA)_n \cdot C_{60}$  was obtained from AA and  $C_{60}$ .<sup>[S1]</sup> The formation and structure of  $(PA)_n \cdot (C_{60})_m$  were confirmed by UV-vis and DLS analyses. The host-guest ratio of the product (i.e., n = 6 and m = 1) was confirmed by the UV-vis analysis of the extracted guest in toluene. Host-guest complexes  $(PA)_n \cdot CNT$  and  $(AA)_n \cdot CNT$  were also prepared from PA or AA (1.0 µmol) and single-walled carbon nanotubes (CNT; 0.3 mg; 0.7-0.9 nm in diameter). The final optimized structures were obtained starting from the assemblies of  $(PA)_6 \cdot C_{60}$ , PA · C<sub>60</sub>, and AA · C<sub>60</sub> with various orientation, by performing the geometry optimizations implemented in the Forcite program.



Figure S28. a) UV-visible spectra (H<sub>2</sub>O, r.t., 1.0 mM based on PA or AA) and photographs of  $(PA)_n \circ (C_{60})_m$  and  $(AA)_n \circ (C_{60})_m$ . b) DLS chart and average diameter (Z-average) (H<sub>2</sub>O, 1.0 mM based on PA, r.t.) of  $(PA)_n \circ (C_{60})_m$ .



**Figure S29.** Optimized structure and core diameter of  $(PA)_6 \cdot C_{60}$ . The geometry optimization of  $(PA)_6 \cdot C_{60}$  was performed with the Forcite module of Materials Studio (version 5.5.3).



Figure S30. UV-visible-NIR spectra and photographs (H<sub>2</sub>O, r.t., 1.0 mM based on PA or AA) of  $(PA)_n \bullet CNT$  and  $(AA)_n \bullet CNT$ .

#### **Encapsulation of GNS by PA**

KI205, 226, 246, 248, 250



A mixture of compound PA (0.6 mg, 1.0 µmol) and graphene nanosheets (GNS; 0.3 mg; graphene nanoplatelets (TCI; 2-10 nm in thickness, 5 µm in width)) was ground for 5 min by using an agate mortar and pestle. After the addition of  $H_2O$  (1.0 mL), the suspended solution was sonicated for 10 min, centrifuged (16,000 g) for 30 min, and then filtered by a membrane filter (pore size: 200 nm) to give a clear black solution of  $(PA)_n \bullet GNS$ .<sup>[S2]</sup> In the same way, a black solution of  $(PA)_n \bullet SG$  was obtained from PA and synthetic graphite (SG; 0.3 mg; 10 µm in average size). The formation and structure of (PA), •GNS and (PA), •SG were confirmed by UV-vis-NIR, DLS, and Raman analyses. The amount of GNS in the black aqueous solution of  $(PA)_n \cdot GNS$  was estimated to be 0.18 mg/mL on the basis of the absorption band of (AA), •GNS. Compounds AA and SDS were employed for the control experiments under the same conditions. The amount of GNS in the black solution of (AA), GNS was estimated to be 0.13 mg/mL by vacuum freeze drying and washing with methanol.<sup>[S2]</sup> The final optimized structures were obtained starting from the assemblies of (PA)<sub>66</sub>•GNS, PA•GNS, and AA•GNS with various orientation, by performing the geometry optimizations implemented in the Forcite program.



Figure S31. UV-visible-NIR spectra (H<sub>2</sub>O, 1.0 mM based on the amphiphiles, r.t.) and photographs of a)  $(PA)_n \circ GNS$ ,  $(AA)_n \circ GNS$ , and  $(SDS)_n \circ GNS$ , and b)  $(PA)_n \circ SG$ ,  $(AA)_n \circ SG$ , and  $(SDS)_n \circ SG$ .



**Figure S32.** UV-visible-NIR spectra (H<sub>2</sub>O, 1.0 mM based on PA, r.t.) of  $(PA)_n \cdot GNS$  and  $(AA)_n \cdot GNS$  before (solid line) and after three weeks (dash line).



Figure S33. DLS charts (H<sub>2</sub>O, r.t., 0.1 mM based on PA or AA) of a) (PA)<sub>n</sub>•GNS, b)  $(AA)_n•GNS, c) (PA)_n•SG$ , and d)  $(AA)_n•SG$ .



**Figure S34.** Optimized structure and core diameters of  $(PA)_{66}$ •GNS (including a three-layer graphene sheet). The geometry optimization of  $(PA)_{66}$ •GNS was performed with the Forcite module of Materials Studio (version 5.5.3).



**Figure S35.** Optimized, partial structures of a) **PA•GNS** and b) **AA•GNS**. The geometry optimizations of **PA•GNS** and **AA•GNS** were performed with the Forcite module of Materials Studio (version 5.5.3).



**Figure S36.** Optimized structures of a)  $PA \cdot C_{60}$  and b)  $AA \cdot C_{60}$ . The geometry optimizations of  $PA \cdot C_{60}$  and  $AA \cdot C_{60}$  were performed with the Forcite module of Materials Studio (version 5.5.3).

#### Raman analysis KI249

All normal Raman measurements were performed using a LabRAM HR Evolution confocal Raman microscope (Horiba Jobin Yvon). A long-working distance objective lens (50 times magnification: LMPLFLN from Olympus) was used with a numerical aperture of 0.5 in order to focus a diode-pumped solid state (DPSS) laser (excitation wavelength of 532 nm at typical laser power around 0.2 mW) 150 µm below the solution surface. The Raman signal was collected in a back-scattering geometry.



**Figure S37.** Normal Raman spectra (r.t., DPSS laser,  $\lambda = 532$  nm, solid) of a) pristine **GNS** and b) pristine **SG**.



Figure S38. Normal Raman spectra (H<sub>2</sub>O, r.t., DPSS laser,  $\lambda = 532$  nm, 1.0 mM based on PA or AA) of a) (PA)<sub>n</sub>•GNS, b) (AA)<sub>n</sub>•GNS, c) (PA)<sub>n</sub>•SG, and d) (AA)<sub>n</sub>•SG.



**Figure S39.** Normal Raman spectra (H<sub>2</sub>O, DPSS laser,  $\lambda = 532$  nm, r.t.) of a) (**PA**)<sub>n</sub>•GNS, b) ground GNS, c) ground and sonicated GNS, and d) GNS (solid).



Figure S40. Deconvoluted D, G, and D' bands of a) (PA)<sub>n</sub>•GNS and b) pristine GNS (solid).

	(PA) <sub>n</sub> ∙GNS	GNS	Grind.	Sonic.	(AA) <sub>n</sub> ∙GNS	( <b>PA</b> ) <sub>n</sub> •SG	( <b>AA</b> ) <sub>n</sub> •SG
<i>D</i> (cm <sup>-1</sup> )	1348	1350	1348	1348	1347	1348	1348
I <sub>D</sub>	33009	7638	8929	9084	29461	17280	17164
<i>G</i> (cm <sup>-1</sup> )	1584	1582	1581	1580	1584	1585	1584
I <sub>G</sub>	12622	18848	14153	12454	10609	5453	6324
<i>D</i> '(cm <sup>-1</sup> )	1623	1621	1620	1619	1622	1622	1622
<i>I</i> <sub>D</sub> ,	2860	827	1052	983	2864	2134	2114
I <sub>D</sub> / I <sub>G</sub>	2.62	0.41	0.63	0.73	2.78	3.17	2.71
L <sub>a</sub> (nm) <sup>a</sup>	7.4	46.9	30.5	26.3	6.9	6.1	7.1

**Table S1.** The  $I_D$ ,  $I_G$ ,  $I_D$ ,  $I_D/I_G$ , and  $L_a$  values of  $(\mathbf{PA})_n \cdot \mathbf{GNS}$ , pristine **GNS**, ground **GNS**, ground and sonicated **GNS**,  $(\mathbf{AA})_n \cdot \mathbf{GNS}$ ,  $(\mathbf{PA})_n \cdot \mathbf{SG}$ , and  $(\mathbf{AA})_n \cdot \mathbf{SG}$  obtained by Raman analysis.

 $^{a}$   $L_{a}$  = (  $2.4\times10^{-10}$  )  $\lambda$  (  $I_{D}/I_{G}$  )^{-1 [S3]},  $\lambda$  = 532 nm



Figure S41. FT-IR spectra (KBr, r.t.) of a) pristine GNS, b) (PA)<sup>,</sup>•GNS, and c) PA.