# Nanoscale

(DOI: 10.1039/c4nr02308k)

Electronic Supplementary Information (ESI) for

# Graphene controlled H- and J-stacking of perylene dye into highly stable supramolecular nanostructures for enhanced photocurrent generation

Shiyu Gan<sup>1, 2</sup>, Lijie Zhong<sup>1,†</sup>, Christian Engelbrekt<sup>2</sup>, Jingdong Zhang<sup>2</sup>, Dongxue Han<sup>1</sup>, Jens Ulstrup<sup>2</sup>, Qijin Chi<sup>2\*</sup> and Li Niu<sup>1\*</sup>

<sup>1</sup> State Key Laboratory of Electroanalytical Chemistry, c/o Engineering Laboratory for Modern Analytical Techniques, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, and University of Chinese Academy of Sciences, Beijing, 100049, P. R. China.

<sup>2</sup> Department of Chemistry, Technical University of Denmark, Kemitorvet Building 207, DK-2800 Kongens Lyngby, Denmark.

<sup>+</sup> Present address: Department of Energy Conversion and Storage, Technical University of Denmark, Kemitorvet Building 207, DK-2800 Kongens Lyngby, Denmark.

\*Correspondence and requests for materials should be addressed to Q. C. (email: cq@kemi.dtu.dk) or to L. N. (email: lniu@ciac.ac.cn).

# **Table of the Contents**

I. Materials and Methods3						
II. Supplementary Figures and Tables5						
1.	AFM and UV-vis characterization of GO and RGO nanosheets (Figure					
	1)5					
2.	UV-vis spectra of perylene, heated perylene and GO-perylene (Figures S2 to S4)6					
3.	Comparison of Raman spectroscopic analysis (Table S1)9					
4.	Evaluation of long-term stability of GO-Py and RGO-Py nanostructures in aqueous					
	solution (Figure S5)10					
5.	TEM and AFM characterizations of GO-Py integrated manostructures (Figures S6 and					
	S7)					
6.	TEM and AFM Characterizations of RGO-Py self-assembled nanostructures (Figures					
	S8 and S9)					
7.	FFT and SAED of GO-Py and RGO-Py (Figure 10)15					
8.	XPS analysis of GO and RGO structures (Figure S11)16					
9.	Performances of prototype optoelectronic devices (Figure S12) 17					
10	Photoelectrochemistry performances of pure Py (Figure S13)					
III. S	Supplementary Discussions18					
1.	Structural features of GO-Py and RGO-Py nanostructures					
2. Possible formation mechanisms of Py supramolecular nanostructures						
IV. Supplementary References21						

#### I. Materials and Methods

**Materials and chemicals.** Graphite flakes (<20 μm) from Sigma-Aldrich was used as starting material for preparation of graphene oxide (GO). Other reagents including Perylene-3, 4, 9, 10-tetracarboxylic dianhydride (PTCDA, 97%, Aldrich), I<sub>2</sub> (> 99.8%, Alfa), LiI (99.9%, Sigma-Aldrich), acetonitrile (> 99.9%, Sigma-Aldrich), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) stock solution (30%, Fluka), hydrazine hydrate solution (5%, N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, Sigma-Aldrich), H<sub>2</sub>SO<sub>4</sub> (95%-97%, Sigma-Aldrich), HCI (25%, Sigma-Aldrich), NaOH (≥ 97%, Sigma-Aldrich), tetrabutylammonium hexafluorophosphate (>99.0%, Alfa, TBAPF<sub>6</sub>), CH<sub>3</sub>CN, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, P<sub>2</sub>O<sub>5</sub> and KMnO<sub>4</sub> (Merck, Germany) were at least of analytical grade and used as received. Milli-Q water (18.2 MΩ cm) was used throughout.

Synthesis of GO-Py and RGO-Py nanomaterials. GO was synthesized according to our previously reported procedures based on the modified Hummer method.<sup>S1, S2</sup> In a typical preparation, GO-Py was synthesized by heating the mixture of GO aqueous solution (1.22 ml, 2 mg ml<sup>-1</sup>), water (39 ml) and Py aqueous solution (60 ml, 56  $\mu$ g ml<sup>-1</sup>) at 95 °C for 35-45 min. After cooling to room temperature, the mixture was subjected to dialysis against pure water using dialysis tubes with a cutoff molecular weight of ca. 14,000 to remove free Py monomers. The dialysis lasted for at least 3 days, during which exchanging water was renewed regularly (at least totally 8 times during 3 days). RGO-Py was prepared by heating the mixture of GO aqueous solution (1.22 ml, 2 mg ml<sup>-1</sup>), water (19 ml), NH<sub>3</sub>·H<sub>2</sub>O (40  $\mu$ L, 25%), N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (25  $\mu$ L, 5%) and Py aqueous solution (80 ml, 56  $\mu$ g ml<sup>-1</sup>) at 95 °C for 35-45 min, followed by a similar dialysis purification process to remove excess and free Py molecules. GO-Py and RGO-Py with different Py loadings were prepared by controlling the initial mass ratio of GO to Py. The as-synthesized sample solutions were kept at 4 °C in a refrigerator.

**Microscopic and spectroscopic characterizations.** TEM measurements were performed by a Tecnai G2 T20 system (FEI Company) operating at 200 kV. To prepare TEM samples, a 60  $\mu$ l sample solution (20  $\mu$ g ml<sup>-1</sup>) was drop-cast on carbon-supported copper grids and the sample was left for drying overnight. Sample solutions were drop-cast on freshly cleaved mica substrates for atomic force microscopy (AFM) measurments. All AFM images were recorded in the tapping mode using a 5500 AFM system (Agilent Technologies, Chandler,

USA). UV-vis spectra were acquired using a 8453 spectrophotometer from Agilent Technologies (Santa Clara, CA) or/and a U-3900 spectrophotometer (Hitachi, Japan). Raman spectroscopic measurements were carried out at a JY-T64000 (Horiba-JobinYvon, France) Raman system at room temperature (the laser power at the sample position was 400  $\mu$ W with an average spot size of 1  $\mu$ m in diameter). The laser excitation wavelength applied was 514.5 nm. Raman samples were prepared by spin-coating of sample solutions on glass substrates. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB MKII X-ray photoelectron spectrometer using monochromated Al K $\alpha$  X-ray.

**Fabrication and tests of optoelectronic devices.** Prototype optoelectronic devices were prepared in-house. Glass or quartz substrates were first cleaned by boiling in H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (v/v, 3:1) solution and washed with Milli-Q water. (*Caution*: this hot H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> solution is a strong oxidizing agent and very dangerous. It should be handled carefully with protective equipment). Two metal layers, i.e. 5 nm Cr and 25 nm Au, were deposited on the clean glass plates by a sputter coater (BAL-TEC, SCD 050, Germany) under high-vacuum conditions. The deposited Au films were used as the drain (D) and source (S) electrodes. Sample solutions of GO-Py (0.236 mg containing 0.126 mg Py), RGO-Py (0.228 mg containing 0.126 mg Py), pure Py (0.126 mg), RGO (0.102 mg) and GO (0.11 mg) were deposited on the device surface by drop-casting to form uniform ultrathin films, followed by drying devices at 100 °C for 4 h. The GO-Py based devices were put in a hydrazine-containing desiccator for about 2 h in order to achieve vapor reduction of GO to RGO. A 500 W xenon arc lamp equipped with a UV cut filter ( $\lambda > 400$  nm) (CHF-XM35-500W, Beijing Trusttech, China) was used to provide a simulated solar light for optoelectronic response experiments. The photocurrent was recorded using an electrochemical workstation (CHI 920C, USA).

**Photoelectrochemical measurements.** Photoelectrochemistry were performed in a two-armed electrode cell composed of materials modified ITO ( $1 \times 1.5 \text{ cm}^2$ ) as a working electrode and Pt plate as a counter electrode. Sample solutions of GO (0.138 mg), RGO (0.127 mg), Py (0.158 mg), GO-Py (0.296 mg containing 0.158 mg Py) and RGO-Py (0.285 mg containing 0.158 mg Py ) were drop-cast on the cleaned ITO electrodes, and the materials-loaded electrodes were then dried at  $60^{\circ}$ C in an oven. 0.5 M Lil and 0.01 M I<sub>2</sub> in acetonitrile solution were used as a redox couple and electrolytes with N<sub>2</sub> saturated prior to

measurements. The light source was used with the same optoelectronic device measurements. Electrochemical measurements were performed at electrochemical workstation (CHI 920C, USA).

### **II. Supplementary Figures and Tables**

1. AFM and UV-vis spectroscopic characterization of GO and RGO nanosheets (Figures S1)



**Figure S1.** Comparison of AFM analyses and UV-vis spectra for GO and RGO nanosheets. (a, b) AFM images (top) and cross-sectional height profiles (bottom) of GO (a) and RGO (b) nanosheets deposited on mica surfaces; the scale bar is 500 nm in (a) and (b). (c) UV-vis spectra of GO and RGO solutions.

2. UV-vis spectra of perylene, heated perylene and GO-perylene (Figures S2 to S4)



**Figure S2.** (a) UV-vis absorption spectra of Py with different concentrations (15 to136  $\mu$ M).(b)Enlarged spectra in the wavelength range of 350 nm to 550 nm showing no peak shift by increasing Py concentration.



**Figure S3. (a)**Digital photos of a Py aqueous solution before and after heated at 95°C for 35 min, showing no colour change occurred in solution. **(b)** Comparison of UV-vis spectra of Py aqueous solution before and after heated at 95 °C for 35 min.



Figure S4. High-resolution UV-vis absorption spectrum of GO-Py nanostructures in aqueous solution (black curve). The spectrum is analyzed with three key absorption bands assigned to  $A^{0 \rightarrow 2}$  (456 nm, red curve),  $A^{0 \rightarrow 1}$  (492 nm, blue curve),  $A^{0 \rightarrow 0}$  (550 nm, green curve), respectively. The intensity ratio of  $A^{0 \rightarrow 0}$  to  $A^{0 \rightarrow 1}$  is estimated as 0.57.

## 3. Comparison of Raman spectroscopic analysis (Table S1)

Symmetry mode <sup>a</sup>	GO	RGO	Ру	GO-Py	RGO-Py
A <sub>g</sub> (ν <sub>C-C</sub> , δ <sub>C-H</sub> )			1284.3		
Α <sub>g</sub> (δ <sub>C-H</sub> )			1304.1	1298.4	1299.8
D-band	1357.0	1347.5		1340.1	1343.1
B <sub>3g</sub> (δ <sub>C-C</sub> )			1347.4		
A <sub>g</sub> (δ <sub>C-H</sub> , ν <sub>C-C</sub> )				1379.5	1380.1
$A_g\left(\delta_{C\text{-}C\text{-}H},\nu_{C\text{-}C}\right)$				1451.6	1572.1
A <sub>g</sub> (ν <sub>C-C</sub> , δ <sub>C-H</sub> )			1564.3	1570.3	1572.1
A <sub>g</sub> (ν <sub>C-C</sub> , δ <sub>C-H</sub> ,)				1588.9	1592.5
G-band	1605.1	1607.6		1617.2	1616.3

<sup>a</sup>The symmetry modes of Py precursor (PTCDA) were used as a reference (Ref. S3) to evaluate those of Py and Py supramolecular nanostructures on GO and RGO.

4. Evaluation of long-term stability of GO-Py and RGO-Py nanostructures in aqueous solution (Figure S5)



**Figure S5. UV-vis absorption spectra of GO-Py (a) and RGO-Py (b) solutions.** The solutions were stored at 4°C in refrigerator, and the UV-vis spectra were recorded regularly. The insets show the optical images of GO-Py and RGO-Py solutions after one-year storage, no aggregation or precipitation detectable.

5. TEM and AFM characterizations of GO-Py integrated nanostructures (Figures S6 and S7)



**Figure S6. (a-c)** TEM images of GO-Py samples with different magnifications. **(d)** A split nanotube structure. **(e)** A high-resolution image obtained in the area marked in **(d)** with the inset showing the thickness of nanotube walls to be 1.2 nm. **(f)** A cross-sectional profile through the line marked by the red arrows in the inset of **(e)**. **(g)**An extended nanotube structure. **(h)** A high-resolution image obtained in the area marked in the area marked in **(d)** with the inset solution image obtained in the area marked in **(g)** with the inset showing the thickness of nanotube walls to be 1.4 nm. **(i)** A cross-sectional profile through the line marked by the red arrows in the inset of **(h)**.



**Figure S7.** (**a-d**) AFM images of GO-Py nanostructures deposited on mica surfaces. (**e**) A cross-sectional profile obtained along the blue line marked in (the area without perylene nanotubes) (**c**), showing the thickness of GO nanosheets (ca. 1.0 nm). (**f**) A cross-sectional profile obtained along the blue line marked in (**d**), and the diameter of individual perylene nanotubes is estimated as 6-8 nm.

6. TEM and AFM Characterizations of RGO-Py self-assembled nanostructures

(Figures S8 and S9)



**Figure S8.** TEM images of RGO-Py integrated nanostructures. **(a, b)** TEM images with a large area. **(c-e)** TEM images focused on a single RGO-Py nanosheet with different magnifications. **(f)** A cross-sectional profile obtained along the line marked in **(e)**.



**Figure S9. (a-d)** AFM images of pure RGO nanosheets(**a**) and Py integrated RGO nanosheets (**b-d**). (**e-g**) Cross-sectional profiles obtained along the lines marked in (a), (b) and (c), respectively, with the thickness estimated for pure RGO sheets, the no visible Py regions on RGO-Py sheets, and Py supramolecular nanostructure on RGO-Py sheets as 0.6-0.7, 1.3-1.4 and 5.0-6.0 nm. Note that pure RGO aqueous solution (0.02 mg ml<sup>-1</sup>) was prepared by the same procedure but in the absence of Py.

### 7. FFT and SAED of GO-Py and RGO-Py (Figure S10)



**Figure S10.** FFT and SAED for GO-Py and RGO-Py. (**a**, **b**) HRTEM image (**a**) and corresponding FFT (**b**) for GO-Py. (**c**, **d**) TEM image (c) and corresponding SAED (d) for GO-Py. (**e**-**f**) FFT and SAED results for RGO-Py.

#### 8. XPS analysis of GO and RGO structures (Figure S11)



**Figure S11.** The C1s XPS spectra of GO (**a**) and RGO (**b**). The binding energies for each bond are C-C (284.6 eV), C-OH (285.6 eV), O-C-O (286.7 eV), COOH (288.5 eV). (**c**) Comparison of the XPS survey spectra of GO and RGO. (**d**) The estimated atom oxygen content and C/O atom ratio obtained from the survey spectra. \*GO and \*RGO are the reported data in Ref. S4 (Stankovich, S. et al. *J. Mater. Chem.* **16**, 155-158 (2006)).

#### 9. Performances of prototype optoelectronic devices (Figure S12)



**Figure S12. (a)** Comparison of *I-V* curves of casted thin film based devices composed of pure Py (black line), hydrazine-annealed GO-Py (blue line) and RGO-Py (red line) under light-off conditions. The voltage scan rate is 100 mV s<sup>-1</sup>. The insets are the optical images of GO-Py (top) and RGO-Py (bottom) devices. **(b)** Transient photocurrent curves of hydrazine-annealed GO-Py based devices in response to ON-OFF switching of light illumination, in which the currents are normalized to the off-state current to show the on-off ratio.

#### 10. Photoelectrochemistry performances of pure Py (Figure S13)



Figure S13. The photocurrent response of pure Py/ITO electrode at open circuit potential.

#### **III. Supplementary Discussions**

#### 1. Structural features of GO-Py and RGO-Py nanostructures

The density of nanotubes on GO or/and nanobuds on RGO is associated with the initial mass ratio of GO to Py. The density of nanostructures is at the sub-monolayer or monolayer level at low Py concentrations. We used AFM to analyze these regions of GO or RGO nanosheets, on which no visible nanostructures are found by TEM or AFM. In the regions of GO without Py nanotubes, the height was measured as  $\approx$  1.1 nm (Figure S7c and S7e), which is the same as that for bare GO nanosheets (Figure S1a). This suggests that there are no Py molecules in these regions. In contrast, in the case of RGO the regions uncovered apparently with nanobuds (Figure S9b) have an AFM height of  $\approx$ 1.3 nm (Figure S9f), which is about twice that of bare RGO nanosheets (about 0.7 nm, Figure S1b or Figure S9e). This suggests that Py molecules are in fact absorbed on these so-called uncovered regions but have not grown into nanobuds. The difference implies that distinct molecular self-assembly strategies are adapted by Py, determined by the difference in the intrinsic structures of GO and RGO. These analyses offer crucial clues to identify the possible formation mechanisms.

The FFT and selected area electron diffraction (SAED) results for GO-Py and RGO-Py are shown in Fig. S10. Two HRTEM images are chosen for FFT analysis (Figure S10a and S10e). The FFT image for GO-Py displays no specific pattern (Figure S10b), while a weak hexagonal arrangement is observed for RGO-Py indicating a relatively hierarchical organization. To obtain more structural information, we further performed SAED experiments. Both GO-Py and RGO-Py exhibit typical six-fold symmetrical electron diffraction spots of graphene (Figure S10d and S10h). Corresponding d-spacings for GO-Py and RGO-Py were determined as 2.12 Å/2.13 Å (inner circle) and 1.26 Å/1.23 Å (external circle), which are consistent with the {100} and {110} planes of graphene<sup>S5</sup>, respectively. These results indicate that GO and RGO maintain its intrinsic carbon plane structures after the non-covalent functionalization by Py molecules.

#### 2. Possible Py supramolecular nanostructure formation mechanisms

GO and RGO support directed supramolecular self-assembly of Py into two distinct types of nanostructures. Although the exact formation mechanisms are not fully understood at present, directed supramolecular self-assembly is associated closely with the intrinsic structures of GO and RGO which in turn determine interactions between graphene nanosheets and Py molecules. GO is known to contain oxygen-rich groups both on the planes and at the edges<sup>S6</sup> (Figure 1a). The GO samples used in the present work contain oxygen up to 37% or a C/O atom ratio around 2:1 (Figure S11). This suggests that GO planes contain a number of hydrophilic and polar oxygen-rich groups (e.g., in the forms of hydroxyl groups and epoxy). In contrast, RGO is a product of chemical reduction of GO. Upon hydrazine reduction, most oxygen-containing groups on the planes are removed and the sp<sup>2</sup> structure is largely restored in RGO, although some carboxylic groups were supposed to be retained at the edges (Figure 1b). Our RGO samples have a relatively high C/O ratio around 10:1, i.e., the oxygen content was reduced to 9% compared to that for GO (Figure S11).

Known from supramolecular chemistry of PBIs, Py and its derivatives favor two types of molecular self-assembly into different supramolecular structures<sup>57-59</sup>. J-stacking and H-stacking aggregations are notably different in terms of molecular interaction modes. J-stacking is a slipped molecular coupling process, leading to formation of "hollow" nanostructures including nanotubes, nanocages and nanorings<sup>S7,S10</sup>. In contrast, H-stacking of PBI molecules represents "face-to-face" molecular connections via the molecular core  $\pi$ - $\pi$  stacking interactions. H-type molecular self-assembly normally results in the formation of "solid" nanostructures such as nanorods<sup>S10</sup> and nanofibers<sup>S11</sup>. It is not overstated that in supramolecular chemistry of PBI molecules, effective control of stacking modes is of critical importance in order to assemble specific supramolecular structures with desired optical and electronic properties. However, the control of these two types of molecular interactions still is a challenging issue.

On the basis of our experimental observations and Py supramolecular chemistry, we propose the possible mechanisms for the formation of Py supramolecular nanostructures on GO and RGO (Figure 4). In the case of GO, J-type stacking molecular self-assembly is responsible for the formation of nanotubular structures (Figure 4a). Supramolecular self-assembly is initiated by hydrogen-bonding interactions between Py molecules and oxygen-containing hydrophilic domains on the GO plane. This results indicated that Py molecules were most likely adsorbed on GO with hydrogen-bond interaction in the first step and further serves as a structural scaffold facilitating J-type intermolecular interactions of Py molecules coming from the solution. Once the formation of a nanotube is completed, J-stacking aggregation is terminated. This proposed process accords well with the experimental observations: (1) the thickness of the Py nanotube walls is around 1.2-1.4 nm, corresponding to a single-layer lateral dimension of Py molecules. (2) Py nanotubes can be formed even at low concentrations of Py monomers, as expected for J-stacking self-assembly. (3) In terms of the density of nanotubes, a monolayer (or sub-monolayer) rather than multilayers on GO was consistently observed even at relatively high concentrations of Py monomers.

In the case of RGO, H-type stacking molecular self-assembly leads to the formation of solid and tree-like structures consisting of Py nanobuds. Perylene is structurally like a molecule-size RGO nanosheet (Figure 1b and 1c), which would facilitate chemically compatible  $\pi$ - $\pi$  stacking interactions between Py and RGO. As illustrated in Figure 4b, Py molecules are *first* absorbed on the RGO plane via  $\pi$ - $\pi$  stacking interactions to form a (sub)monolayer. *Then*, small nanobuds are formed by local H-stacking. *Finally*, these small nanobuds grow along both the horizontal and vertical directions into a tree-like networked nanostructure by expanding H-stacking aggregation. The main experimental evidences supporting the proposed mechanism include: (1) the formation of nanobuds requires a threshold concentration (Figure 3f-3j). (2) The blue shifts in UV-vis spectra are clearly observed and become more profound with increasing Py concentration (Figure 3l), which is consistent with the effects of PBI concentration on H-type self-assembly<sup>S7</sup>. (3) The 10-20 nm width and 5-6 nm height of nanobuds reflect 10-20 molecules self-assembled in horizontal and vertical directions, respectively (Figure 2e-2h and Figures S8-S9).

## **IV. Supplementary References**

- S1. S. Y. Gan, L. J. Zhong, T. S. Wu, D. X. Han, J. D. Zhang, J. Ulstrup, Q. J. Chi and L. Niu, *Adv. Mater.*, 2012, 24, 3958-3964.
- S2. N. Zhu, S. Han, S. Gan, J. Ulstrup and Q. Chi, Adv. Funct. Mater., 2013, 23, 5297-5306.
- S3. A. Y. Kobitski, R. Scholz and D. R. T. Zahn, J. Mol. Struct. (Theochem) 2003, 625, 39-46.
- S4. S. Stankovich, R. D. Piner, X. Q. Chen, N. Q. Wu, S. T. Nguyen and R. S. Ruoff, J. *Mater. Chem.*, 2006, 16, 155-158.
- S5. X. Huang, S. Li, Y. Huang, S. Wu, X. Zhou, S. Li, C. L. Gan, F. Boey, C. A. Mirkin and H. Zhang, *Nat. Commun.*, 2011, 2, 292 doi:10.1038/ncomms1291
- S6. D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228-240.
- S7. S. Ghosh, X. Q. Li, V. Stepanenko and F. Würthner, *Chem. Eur. J.*, 2008, **14**, 11343-11357.
- S8. F. Würthner, T. E. Kaiser and C. R. Saha-Moller, Angew. Chem. Int. Ed., 2011, 50, 3376-3410.
- S9. D. Görl, X. Zhang and F. Würthner, Angew. Chem. Int. Ed., 2012, 51, 6328-6348.
- S10.S. Yagai, Y. Goto, X. Lin, T. Karatsu, A. Kitamura, D. Kuzuhara, H. Yamada, Y. Kikkawa, A. Saeki and S. Seki, *Angew. Chem. Int. Ed.*, 2012, **51**, 6643-6647.
- S11. L. Xue, H. X. Wu, Y. Shi, H. Y. Liu, Y. L. Chen and X. Y. Li, Soft Matter 2011, 7, 6213-6221.