

## Fluorescent Bilayer Nanocoils from an Asymmetric Perylene Diimide with Ultrasensitivity for Amine Vapors

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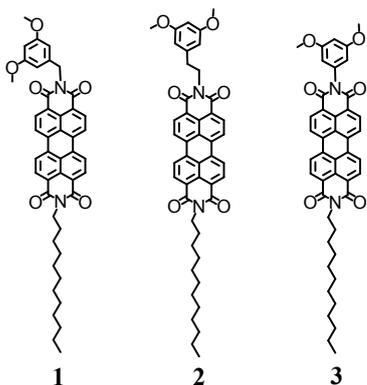
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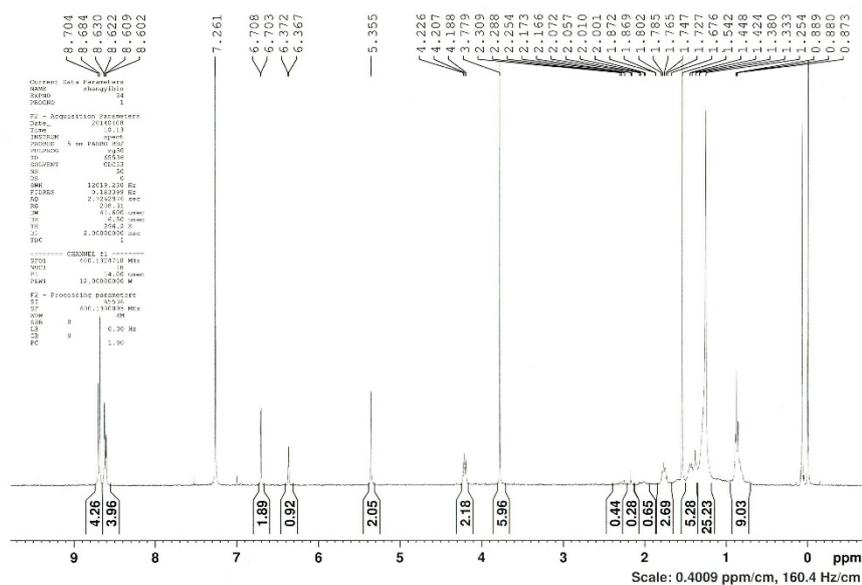
## Synthesis of molecule 1



N-dodecylperylene-3,4,9,10-tetracarboxyl-3,4-anhydride-9,10-imide was synthesized following previously reported procedure.<sup>1</sup> Typically, 300 mg of perylene tetracarboxylic dianhydride and 1 g of dodecyl amine were mixed in 50 mL of methanol and refluxed for 5 h. The reaction mixture was cooled to room temperature and acidified by 20 mL of concentrated HCl. After stirring overnight, the resulting red solid was collected by vacuum filtration through a 0.45  $\mu\text{m}$  membrane filter. The solid was washed thoroughly with methanol and distilled water until the pH of the washings turned neutral. The collected solid was then dried under vacuum at 60  $^{\circ}\text{C}$ . This raw product was not further purified before using for the next step of synthesis.

To the mixture of xylene (5 mL) and propanoic acid (2 mL) were added N-dodecylperylene-3,4,9,10-tetracarboxyl-3,4-anhydride-9,10-imide (50 mg) and 3,5-Dimethoxybenzylamine (75 mg), and the resulting mixture was then heated and stirred at 145  $^{\circ}\text{C}$  for 30 min. When the resultant mixture was cooled to room temperature, the red solid was collected by vacuum filtration through a 0.45  $\mu\text{m}$  membrane filter, followed by washing with ethanol and distilled water. The pure compound **1** was obtained through running column chromatography on a silica gel column (eluent: chloroform : acetone = 100 : 1). The pure target compound was confirmed by MALDI-MS and  $^1\text{H}$ NMR as below.

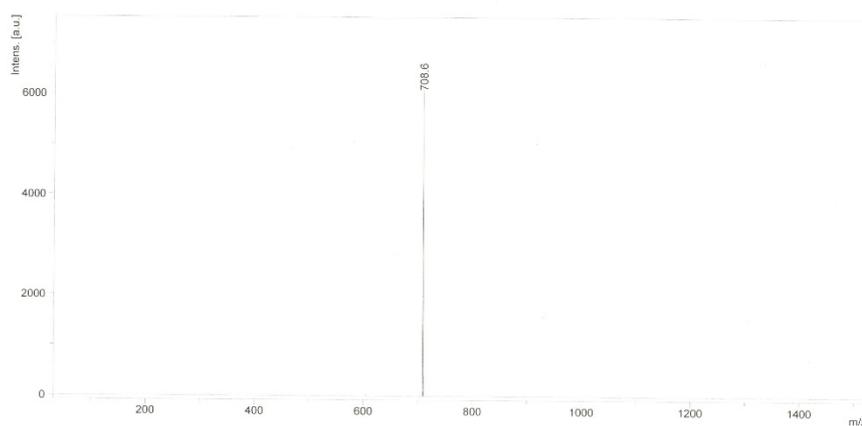
Molecule **1**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.87-0.89 (m, 3H,  $\text{CH}_3$ ), 1.25-1.38 (m, 18H, 9 $\text{CH}_2$ ), 1.74-1.80 (m, 2H,  $\text{CH}_2$ ), 3.78 (s, 6H, 2 $\text{OCH}_3$ ), 4.20 (t,  $J=7.6$  Hz,  $\text{CH}_2$ ), 5.36 (s, 2H,  $\text{CH}_2$ ), 6.36 (s, 1H, phenyl), 6.70 (s, 2H, phenyl), 8.60-8.63 (m, 4H, perylene), 8.68-8.70 (m, 4H, perylene); MALDI-MS: (m/z) 708.6. The spectra are shown below.



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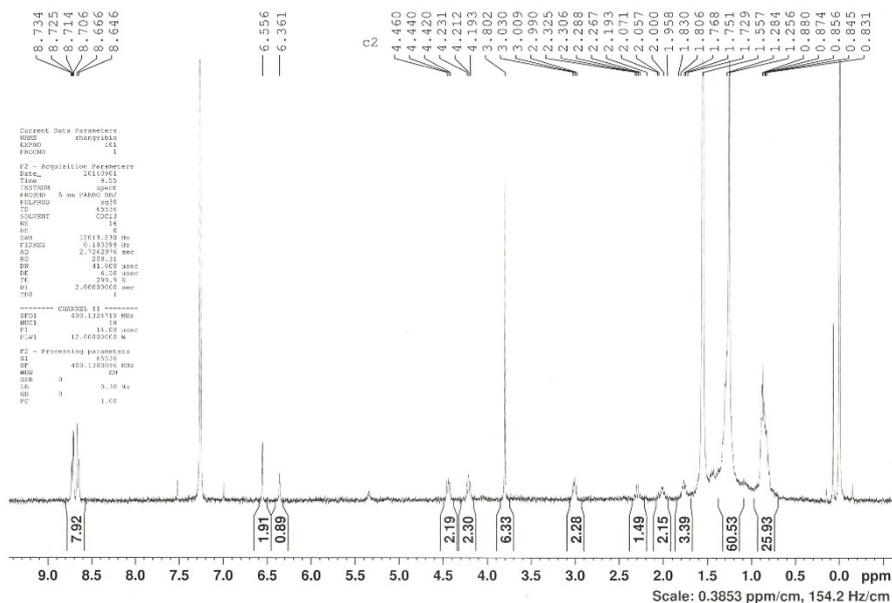
### MALDI-TOF, CCA, 3, 20140328



## Synthesis of molecules 2 and 3

Molecules **2** and **3** were synthesized following the literature method.<sup>1</sup> The pure compounds of **2**, **3** were obtained through running column chromatography on a silica gel column (eluent: chloroform : acetone = 100 : 1). The pure target compounds as obtained were confirmed by MALDI-MS and <sup>1</sup>H NMR as below.

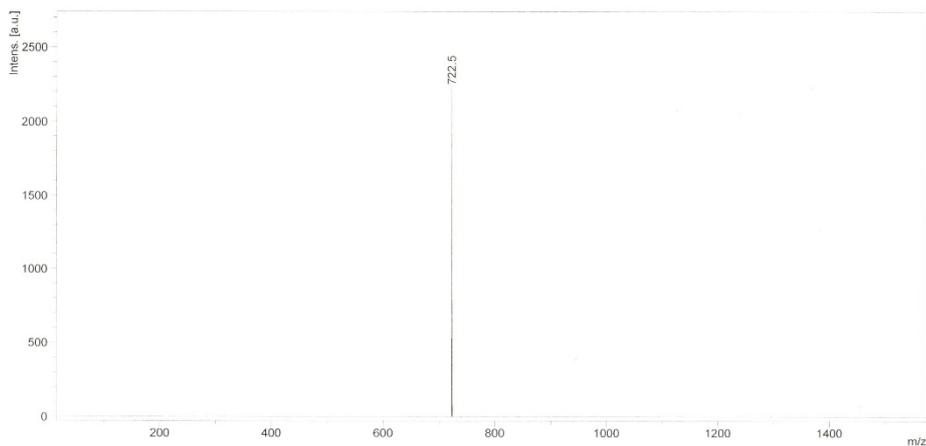
Molecule **2** : <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.85-0.88 (m, 3H, CH<sub>3</sub>), 1.25-1.38 (m, 18H, 9CH<sub>2</sub>), 1.72-1.76 (m, 2H, CH<sub>2</sub>), 3.01 (t, *J*=8.0Hz, 2H, CH<sub>2</sub>), 3.80 (s, 6H, 2OCH<sub>3</sub>), 4.21 (t, *J*=7.6Hz, 2H, CH<sub>2</sub>), 4.44 (t, *J*=8.0Hz, 2H, CH<sub>2</sub>), 6.36 (s, 1H, phenyl), 6.56 (s, 2H, phenyl), 8.64-8.67 (m, 4H, perylene), 8.71-8.73 (m, 4H, perylene); MALDI-MS: (m/z) 722.5. The spectra are shown below.



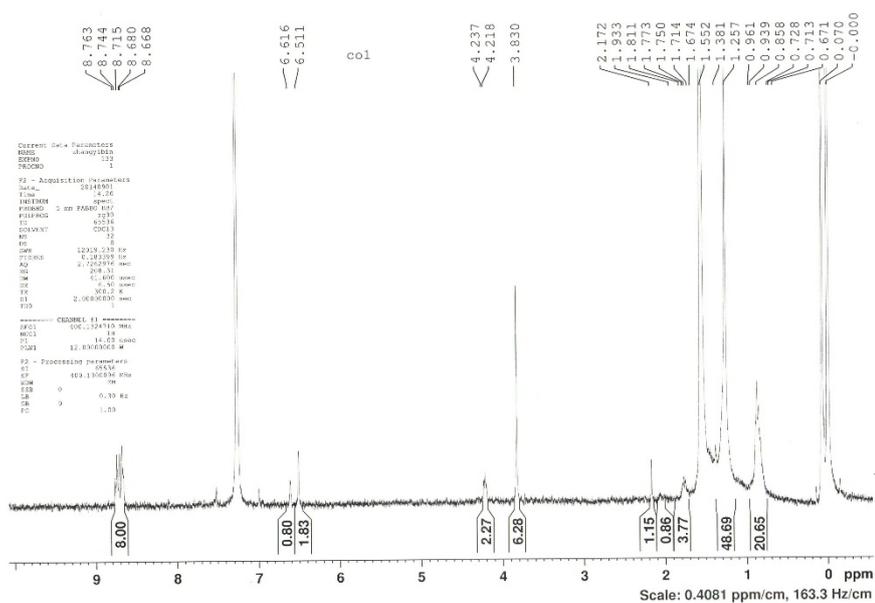
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### MALDI-TOF, CCA, 2, 20140512



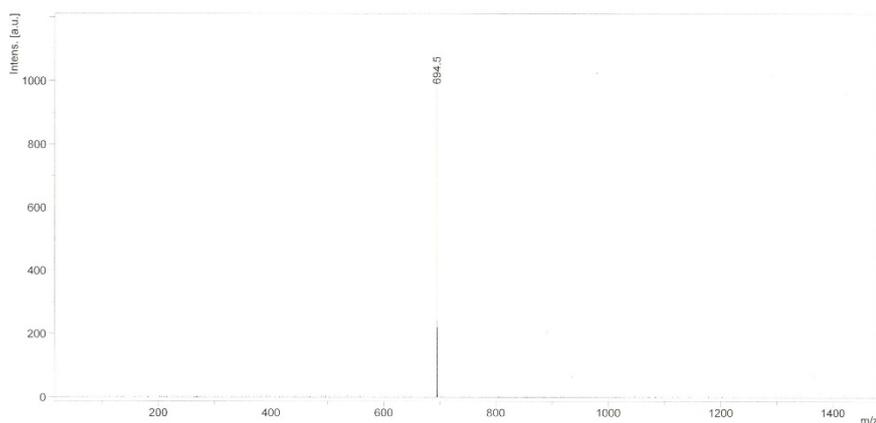
Molecule **3** :  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.67-0.72 (m, 3H,  $\text{CH}_3$ ), 1.25-1.38 (m, 18H,  $9\text{CH}_2$ ), 1.71-1.77 (m, 2H,  $\text{CH}_2$ ), 3.83 (s, 6H,  $2\text{OCH}_3$ ), 4.22 (t,  $J=7.6\text{H}$ ,  $\text{CH}_2$ ), 6.55 (s, 2H, phenyl), 6.62(s, 1H, phenyl), 8.6-8.76 (m, 8H, perylene); MALDI-MS: ( $m/z$ ) 694.5. The spectra are shown below.



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### MALDI-TOF, CCA, 1, 20140512



### Fabrication of bilayer nanostructures from 1-3

The bilayer nanocoils from **1** and nanoribbons from **2** or **3** were self-assembled by injecting of a chloroform (0.3 mL) solution of the corresponding compound (0.14 mM) into ethanol (5 mL) in a test tube followed by 3 days of aging. The nanocoils suspending in ethanol are stable at room temperature. After 4 months, the nanocoiled morphology (checked by TEM), the absorption and fluorescence spectra of the nanocoils, and the fluorescence quantum yield of the nanocoil film remain unchanged. The nanostructured materials thus formed can be transferred and cast onto a substrate (e.g., silica, glass slice, Polytetrafluoroethene (PTFE) film) by pipetting. We fabricated the nanocoil film by dropping-casting 300  $\mu$ L 10  $\mu$ g/mL solution of nanocoils suspending in ethanol onto about 1 cm<sup>2</sup> PTFE film or silica. We used AFM to estimate

the thickness of the nanocoil film on the silica and found the film thickness is not uniform, ranging from 200 to 500 nm.

### **Morphology and property characterizations**

UV-vis absorption spectra of the nanocoils and nanoribbons suspending in ethanol were obtained on a PerkinElmer Lambda 35 spectrophotometer. The fluorescence spectra of the nanocoils and nanoribbons deposited on a PTFE film were obtained on an Ocean Optics USB4000 fluorometer using a 455 nm LED lamp as the light source. The fluorescence quantum yields of the nanocoils and nanoribbons were determined by the integrating sphere method performed on Hamamatsu Absolute PL Quantum Yield spectrometer C11247. TEM measurements were performed with FEI TecnaiG<sup>2</sup> T20 (120 KV). X-ray diffraction measurements were carried out with a Philips X' PertPro XRD instrument (40 kV, 40 mA).

### **Fluorescence sensing measurements**

The fluorescence quenching by amines vapor was monitored following the similar method as previously developed.<sup>3</sup> Briefly, a series of sealed-jars (50 mL) containing small amount of different amines were on standby as sources of amine vapor. Before use some cotton was placed above the amines for helping maintain a constant vapor pressure. The jars were sealed for overnight to achieve saturated vapor inside. The diluted vapor pressures of amines was obtained by injecting a small volume of the saturated vapor of a specific amine into a sealed cuvette (5 mL volume). For example, injection of 5  $\mu$ L of saturated aniline vapor (880 ppm) into the 5 mL cuvette will produce a vapor pressure  $10^3$  times diluted, e.g., 880 ppb.

The fluorescence spectra changes and time-dependent fluorescence quenching profile were obtained with an Ocean Optics USB4000 fluorometer using a 455 nm LED lamp as the light source. The fluorescence quenching was carried out by blowing 5 mL of amine vapors at certain concentration onto the nanocoil film with a syringe at the speed of 2 mL/s, while the emission was continuously recorded by the fluorometer.

## Other supporting figures

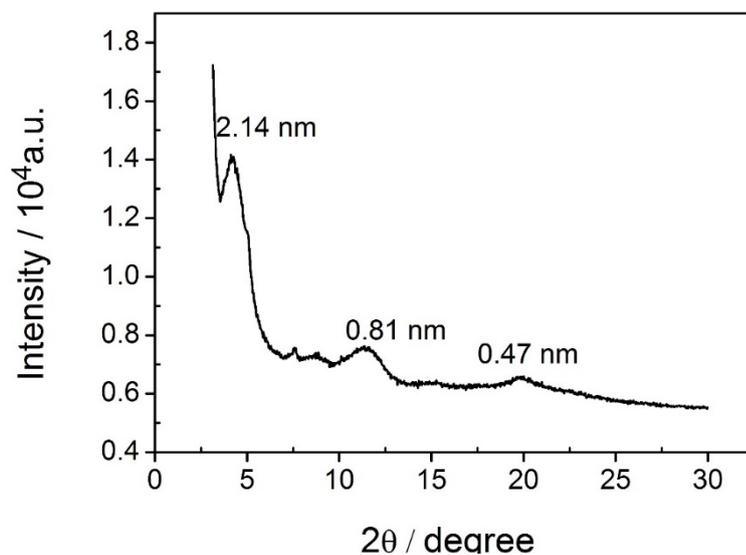


Figure S1. X-ray diffraction patterns of the nanocoils from molecule **1**.

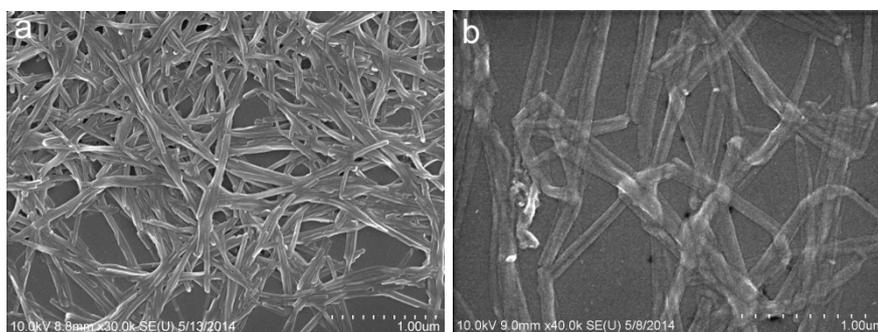


Figure S2. (a) SEM image of the nanoribbons from **2** deposited on a silica substrate; (b) SEM image of the nanoribbons from **3** deposited on a silica substrate.

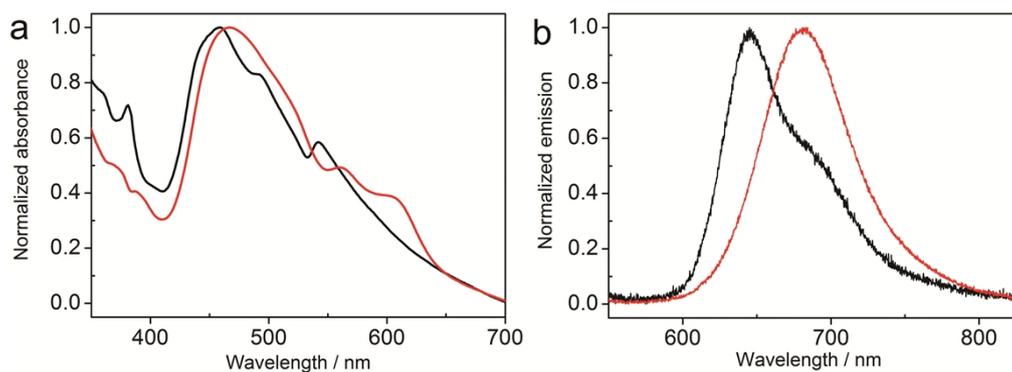


Figure S3. (a) The absorption spectra of the nanoribbons from **2** (black) and nanoribbons from **3** (red); (b) The fluorescence spectra of the nanoribbons from **2** (red) and nanoribbons from **3** (black).

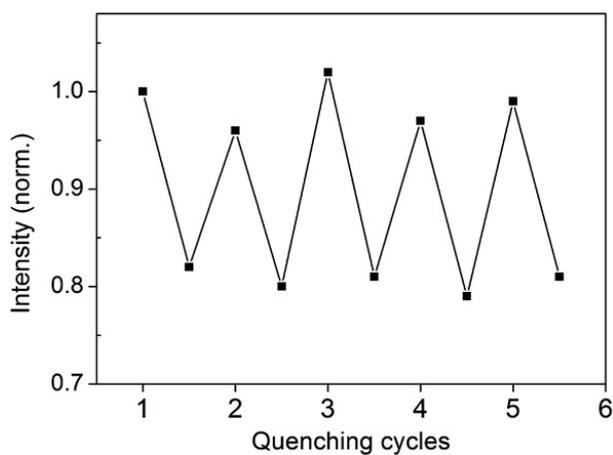


Figure S4. Five continuous cycles of quenching-recovery test of the nanocoils. The quenching was performed by blowing of phenethylamine vapor (0.3 ppm) over the nanocoils. After each cycle of quenching, the fluorescence of the nanocoils was recovered by heating at 60 °C for 10 minutes.

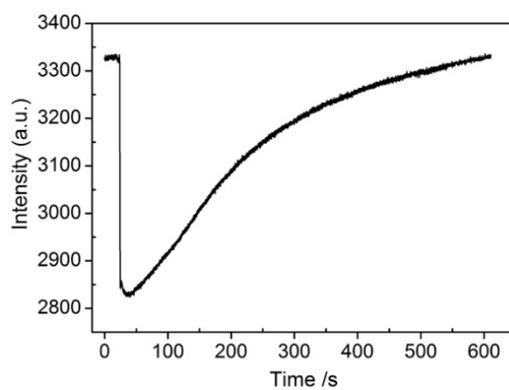


Figure S5. Time-course of fluorescence quenching of the nanocoils upon blowing of HCl vapor (25 ppm).

#### Reference

- 1 Y. Che, X. Yang, G. Liu, C. Yu, H. Ji, J. Zuo, J. Zhao and Zang, L, *J. Am. Chem. Soc.*, 2010, **132**, 5743.