A Facile Method for Preparing One-molecule-thick Free-standing Organic Nanosheets with a Regular Square Shape
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Materials:
Cucurbit[8]uril CB[8] was purchased from NewSouth Innovation Pty Ltd, Sydney. Carbazole, naphthalene 1,2,3,4-tetrahydronaphthalene were purchased from Alfa Aesar Company. Quinoline, styrene, ethanol and other chemicals were purchased from Beijing Chemicals Company. Deionized water was further purified with RF ultrapure water system.

Synthesis and elemental analysis of CB[8]-quinoline nanosheets:
In a typical synthesis, 50 μL of a 2 mM aqueous quinoline solution (or 2 mM naphthalene/styrene/carbazole/1,2,3,4-tetrahydronaphthalene solution in ethanol) was added into 1 mL of 10^-4 M aqueous CB[8] solution. Ultrasonic was then employed for around 1 min to help disperse the solutes. After standing for about 3 h a translucent colloid of nanosheets was obtained. 2 mM quinoline aqueous solution was prepared as follows: 12 μL quinoline was added into 2 mL ethanol, into which deionized water was added to 50 mL. The resultant nanosheets were collected by centrifugation. After washing and drying, the obtained sample was used for powder XRD measurement, elemental analysis and calculation of yield. A yield of about 30% was obtained for the square nanosheets. Since only relatively large nanosheets could be collected by centrifugation, the yield virtually is much larger than 30%. Elemental analysis for m(CB8·2quinoline·25H2O):
Calculated: C=38.89%, H=5.5%, N=23.40%; Found: C=37.97%, H=4.47%, N=25.15%.

Characterization of the CB[8]-quinoline nanosheet:
TEM experiments were performed with JEOL 2010 microscope operating at 150kv. TEM samples were prepared by dripping 10 μL of as prepared CB[8]-quinoline colloid on copper grid and dried in air. STM experiments were carried out in air with a NanoScope IIIa scanning probe microscope (Digital Instruments). HOPG substrate was rinsed in the CB[8]-quinoline mixture for 30 min, taken out and rinsed with deionized water. UV-vis spectrum was obtained using a Perkin Elmer Lambda 35 spectrometer. FL spectra were collected with Perkin Elmer LS55 spectrometer, with excitation at 313 nm, and the samples were dried on quartz glass. FTIR spectra were obtained with Nicolet 360 FT-IR spectrometer. FT-IRRAS spectra were collected with an IFS-66v/S FTIR spectrometer (Bruker) in vacuum at around 1 to 2 mbar of pressure, with p-polarized light incidence at 80° relative to the surface normal using a Bruker accessory; the sample for FT-IRRAS were prepared by dripping 20 μL of as prepared CB[8]-quinoline colloid on gold substrate. AFM images were obtained with a Multimode Nanoscope III system (Santa Barbara, CA), on Si substrate. XPS data were collected with a PHI5300 ESCA instrument using an Al Kα X-ray source at a power of 250 W. Computer simulation was conducted with CHEM 3D software.
Analysis of the thickness of the fabricated nanosheets:

Dropping the as-prepared colloids solution on Si substrate leads to multi-layered nanosheets stacking together, and it’s not possible to read a height for a piece of nanosheet in AFM images. So we dipped the Si substrate in the colloid solution for 10 min., picked it out with tweezers, and rinsed it carefully with deionized water before it dried for 3 times. Thus, most deposited nanosheets were washed away and we have a chance to get the height of a single layer.

Typical AFM images were displayed in Figure S1. The measured thicknesses of 54 pieces of nanosheets were listed in Table S1. 66.1% of the values fall in the range 1.65 ~ 2.10 nm with an average of 1.84 nm. 17.9% nanosheets have a thickness of 3.50 ~ 4.10 nm with an average 3.77 nm, and other 16% outside these two ranges. So 1.84 nm is considered as the thickness of a single layer of the nanosheet, and 3.77 corresponds to double-layers. Number 48-52 in the “others” column in Table 1 approach these two values (1.84 nm or 3.77 nm) and may be caused by some random errors in the testing process, number 53-54 may correspond to three or four layers.

Figure S1. Typical AFM images and section analysis of the nanosheets at different spots.
Figure S2 TEM image of CB[8]-quinoline nanosheet assembled from more concentrated solutions. The concentration of CB[8] and quinoline is $2.0 \times 10^{-4}$ M, and multi-layer nanosheets of larger lateral size were obtained.
**Figure S3** FTIR spectra of quinoline (top), CB[8] powder (middle) and CB[8]-quinoline nanosheets powder (below): the characteristic peaks of CB[8] dominate the spectra of the sheets, which indicate that quinoline locate inside the cavity of CB[8], and is not detectable in FTIR due to space-confinement effect.

**Figure S4** Top-side view (a) and top view (b) of minimized structure of CB[8]-quinoline complex network by computer simulation.
**Figure S5** TEM images of CB[8]-quinoline mixture obtained (a) in neutral environment to form square sheet and (b) under pH=1.0: parallelogrammic sheets form.

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