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Water-soluble pillar[5]arene induced the morphology transformation of self-assembled nanostructures and further application in paraquat detection⁺

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1. Materials and methods

All reagents were commercially available and used as supplied without further purication. Water soluble pillar[5]arene **WP5** was prepared according to the literature procedure.^{S1} ¹H or ¹³C NMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Scanning electron microscopy investigation was carried out on a JEOL 6390LV instrument. The fluorescence spectra were recorded on a Perkin Elmer LS55 fluorescence spectrophotometer. Lowresolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with IonSpec 4.7 Tesla FTMS. The TEM images were obtained using a JEM-1200EX instrument with an accelerating voltage of 80 kV. UV–Vis spectroscopy was measured on a Shimadzu UV-2501 PC UV–Vis spectrometer. Confocal images were acquired using an Olympus FLUOVIEW FV1000 confocal laser scanning unit mounted on an IX81 fixed stage upright microscope.

2. Syntheses of hexamethylendiamine functionalized tetrachloroperylene bisimides (compound A)



Scheme S1. Synthetic route to compound A

1,6,7,12-Tetrachloroperylene 3,4,9,10-tetracarboxylic acid dianhydride (0.5 g, 0.94 mmol) and hexane-1,6-diamine (2.32 g, 2.00 mmol) were mixed with 50 mL of NMP and 0.5 mL of acetic acid. The reaction mixture was stirred at 75 °C for 24 h. After cooling to room temperature, HCl was added to the mixture to adjust the pH value. Dark purple precipitate was filtrated and washed successively with water and then dried in vacuum (Dark purple powder, 0.31 g). The product was further purified by column chromatography on a silica gel (eluent CH₃OH:CH₂Cl₂ = 1:9). ¹H NMR (400 MHz, DMSO-*d*₆, 298K): 8.44 (s, 4H), 3.14 (m, 4H), 2.69 (m, 4H), 1.72–1.26 (m, 12H). ¹³C NMR (100 MHz, DMSO-*d*₆, 298K): 162.1, 134.5, 132.9, 132.3, 128.8, 121.8, 41.3, 40.1, 37.9, 32.5, 28.9, 27.7, 27.6 ppm. LRESIMS is shown in Figure S3: *m/z* 417.2 [**M** + DMSO 2NH₄]²⁺.



Figure S1. ¹H NMR spectrum (400 Hz, DMSO-*d*₆, 298K) of Hex-4CIPBI.



Figure S1. ¹³C NMR spectrum (100 Hz, DMSO- d_6 , 298K) of Hex-4CIPBI.



Figure S3. Electrospray ionization mass spectrum of Hex-4ClPBI. Assignment of the main peak: m/z 417.2 [M + DMSO + 2NH₄]²⁺.

2. characterization of the self-assembly process



Figure S4. Calculated minimize energy sturcture of compound A by ChemBio 3D 12.0.



Figure S5. Small-angle X-ray diffraction study of nanoribbon formed by compound A.



Figure S6. Calculated minimize energy sturcture of compound B by ChemBio 3D 12.0.



Figure S7. Fluorescence spectra of compound B before (black line) and after (red line) addition of WP5.



Figure S8. DLS data of compound B before (a) and after (b) addition of WP5.



Figure S9. Fluorescent photographs of compound **B** & **WP5-based** solid-state thin films before (left) and after addition of methyl paraquat 1 (right).

4. References:

S1. (a) T. Ogoshi, M. Hashizume, T.-a. Yamagishi, and Y. Nakamoto, *Chem. Commun.*, 2010, 46, 3708. (b) Y.
Yao, K. Jie, Y. Zhou, and M. Xue, *Chem. Commun.*, 2014, 50, 5072.