Hierarchical Patterning of Organic Molecules for Self-referenced Vapor Sensing

Meng-Jie Chang, Yong Ai, Li Zhang, Fei Gao, Hao-Li Zhang*

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, China

*Email: haoli.zhang@lzu.edu.cn
Materials

Gold substrates were prepared by sputtering onto silicon wafers whose surfaces had been primed with thin layers of chromium. 1-octadecanethiol (ODT) and 11-mercaptopoundecanoic acid (MUA) were purchased from Aldrich. Microcontact printing (µCP) of chemical patterns on the gold substrates were performed using poly(dimethylsiloxane) (PDMS) stamps. The PDMS stamps were fabricated using Dow Coring Sylgard 184 elastomer kits (Midland, MI). The OPV with different terminal substitute (pyridine-terminated POPV, and thiomethyl-terminated TOPV molecules) were synthesized as reported previously. Trioctlyphosphate oxide (TOPO) capped CdSe QDs was synthesized using a one-pot synthesis as reported previously. All chemicals and solvents were obtained from commercial suppliers and used without further purification unless otherwise noted.

Synthesis of POPV

![Scheme S1](image)

**Scheme S1** Synthesis route of pyridine-terminated POPV.

To the 2,5-bismethoxy-1,4-xylene-bis(diethyl phosphonate) (200mg, 0.457mmol) and 4-pyridinecarboxaldehyde (98mg, 0.914mmol) mixture in 10ml THF cooled in an ice bath was added 2 eq NaH in small portions during a 1h period. The reaction mixture was stirred at 0°C for 12h and then poured into water. After being extracted with CH₂Cl₂, the pooled organic phases were washed with water, dried over anhydrous Na₂SO₄, filtered, and evaporated. The crude product was purified by flash chromatography on silica gel by means of CH₂Cl₂/petroleum ether (1:10).

1H NMR (400 MHz, CDCl₃) δ 8.57 (d, J = 6Hz, 4H), 7.68 (d, J = 16.4Hz, 2H), 7.40 (d, J = 6.4Hz, 4H), 7.14 (s, 2H), 7.06 (d, J = 16.4Hz, 2H), 3.95 (s, 6H);
\(^1\)C (100 MHz, CDCl\(_3\)) \(\delta\) 151.8, 150.2, 145.0, 127.6, 126.8, 126.4, 120.9, 109.4, 56.4; m.p. = 276 °C; MS (EI): 166 [M\(^+\)].

**Instruments**

The fluorescence spectra were recorded on an Edinburgh FLS920 spectrometer, fluorescence images were acquired using a Nikon eclipse 80i fluorescence microscope. Field emission scanning electron microscopy (FESEM) images were obtained using Hitachi S4800 SEM. UV-Vis absorption spectra were recorded using a T6 UV-Vis spectrometer (Purkinje General, China). NMR (\(^1\)H, \(^13\)C) spectra were recorded on a Bruker ADVANCE III 400MHz spectrometer at room temperature. The \(^1\)H and \(^13\)C chemical shifts (\(\delta\)) are reported in parts per million and the tetramethylsilane(TMS) was used as an internal standard. Electrospray ionization (ESI) mass spectra were measured on a Bruker Esquire 6000 instrument. Two-photon excited fluorescence micrographs were acquired using Olympus FluoView 1000 Confocal laser scanning microscope.

**Experimental details for the fabrication of square-in-ring microarray**

Scheme 1 summarizes the procedure for fabricating ordered binary POPV/TOPV array. Detailed experimental condition is given below. Firstly, PDMS stamp with topographic features containing 26 µm squares was inked by octadecanethiol (ODT, 1 mM in ethanol) to print the patterned hydrophobic self-assembled monolayers (SAMs) onto Au substrate. Next, the patterned substrates were submerged into an ethanol solution of mercaptoundecanoic acid (MUA, 1 mM in ethanol) for 30 mins to give hydrophobic/hydrophilic alternating pattern. Subsequently, the patterned substrates were rinsed with a copious amount of deionized water, dried with a stream of flowing N\(_2\). And then the patterned substrates were placed into a solution of 10^-3 mg/mL POPV in tetrahydrofuran (THF), followed by exposing it to an atmosphere with controlled humidity to nucleate water droplets. Growth and freeze of water droplets took place selectively on the POPV covered areas. Finally, the water droplet-covered substrates were dipped into a dichloromethane (DCM) solution of 10^-3 mg/mL TOPV and
withdrawn. After a complete solvent evaporation, ordered square-in-ring microarrays were obtained.

**Absorption and TOPV, POPV upon addition of HCl**

![Absorbance vs Wavelength graph](image)

**Figure S1.** (a) Absorption spectra of TOPV in THF upon addition different amount of HCl, (b) Uv-Vis absorption spectra of POPV (in ethanol: H₂O=2:1) under different pH values.

**Patterns of various materials**

![Fluorescent micrograph](image)

**Figure S2.** Fluorescent micrograph of TOPV/CdSe square-in-ring binary array.
Figure S3. Optical images of the ferrocene/9,10-diphenylanthracene (DPA) square-in-ring binary array

Reference