Hierarchical patterning of organic molecules for self-referenced vapor sensing†

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Unique square-in-ring patterns of organic molecules were fabricated by a facile hierarchical patterning strategy, which could find applications in fields such as multi-color display and self-referenced fluorescence sensing.

The schemes of positioning functional materials in predetermined microscopic areas are of great scientific and technological interest.1 Patterning functional organic molecules into highly ordered microarrays can be very important for many photonic and electronic applications, such as organic field-effect transistors (FETs),2 multiple color displays3 and array-based sensors.4 Particularly, a sensing array based on functional organic molecules has emerged as a powerful tool for the high throughput detection of chemically diverse analytes.4,5

During the last decade, there has been significant developments in the fabrication of ordered microarrays by either lithographic or non-lithographic techniques.6 However, despite the fast progress in the field, the fabrication of binary or multiple component microarrays by non-lithographic methods still poses a challenge. Only a few methods have been reported for producing multi-component patterns. For example, Chi et al. described a procedure for fabricating a hierarchical luminescence pattern based on multiscaled self-assembly.7 Naaman and Gotesman utilized pre-patterned substrates to assemble Au and CdSe nanoparticles into arrays.8 Wang and Zhang fabricated Au–Ag binary arrays via stepwise angle-resolved colloidal lithography.9 Yang et al. reported a two-step method to fabricate unique bull’s-eye-like microstructure arrays using polymers and nanoparticles.10 To date, there is still a lack of methods to pattern small organic molecules into binary or multi-component microarrays.11

In previous work,12 we have demonstrated a process to fabricate highly ordered two-dimensional ring array patterns.13 Herein, we propose a facile method to fabricate a unique square-in-ring structured binary microarray using small organic molecules. We then investigated the feasibility of using such binary organic microarray for self-referenced vapor sensing applications.

As important organic dyes, oligo(p-phenylene vinylene)s (OPVs) have been extensively studied, due to their good stability, high luminescent efficiency, and wide potentials in opto-electronics and molecular devices.14,15 We report herein the patterning of two OPV molecules, which are thiomethyl-terminated OPV (TOPV) and pyridine-terminated OPV (POPV) as shown in Fig. 1, while the patterning of other materials are shown in the ESI†. Our previous work has shown that the TOPV molecule exhibits excellent solid state fluorescence and two-photon absorption properties.15,16 The POPV molecule has a very similar structure to TOPV; except that it consists of two pyridine terminal groups. The details of the synthesis and spectroscopic characterization of POPV are available in the ESI†.

Both compounds are highly fluorescent in diluted solutions. Using the same excitation wavelength λex = 400 nm, the emission maxima of TOPV and POPV exhibit prominent fluorescence peaks at 460 and 475 nm, respectively. The TOPV shows stable fluorescence, whose absorption and emission peaks do not shift upon the addition of acid (Fig. 1a, Fig. S1a†). In contrast, the POPV molecule exhibits a highly pH-dependent emission (Fig. 1b, Fig. S1b†). Upon addition of diluted HCl, the band at 475 nm quickly vanished and a new broad band appeared at around 580 nm. Such an acid-induced change is clearly visible as the emission of the POPV solutions changed from blue to orange (Fig. 1b inset). The fluorescence change is highly reversible, as the blue emission can be fully recovered upon the addition of ammonia. The pH-dependent emission change can be readily attributed to the protonation–deprotonation process of the terminal pyridine groups, which allows the reversible interconversion between the cationic and neutral forms of POPV. The fluorescence

**Fig. 1** Molecular structures of TOPV and POPV, and the fluorescence spectrum of TOPV in tetrahydrofuran (THF) (a), the fluorescence spectra of POPV at different pH (ethanol : H2O = 2 : 1) (b), λex = 400 nm.
change of POPV occurs in the visible range, making it a suitable visual sensing material.

A two-step surface patterning procedure was developed to fabricate the POPV–TOPV binary microarray patterns, which consists of two sequential surface-directed patterning processes as described in Scheme 1. Firstly, the Au substrate was patterned by 1-octadecanethiol–11-mercaptoundecanoic acid (ODT–MUA) self-assembled monolayers (SAMs) via conventional microcontact printing (μCP), which generated a hydrophobic–hydrophilic alternating microarray (Scheme 1b). After immersing the heterogeneous patterned substrate in a POPV solution in tetrahydrofuran (THF), it was withdrawn and the solution wetted and was retained exclusively on the hydrophilic area, producing a POPV microarray replicating the underlying hydrophilic regions (Scheme 1c). Other polar solvents, such as dichloromethane (DCM), chloroform and toluene, have also been tested and could give similar square patterns. However, under our experimental conditions, THF appeared to give the most uniform and reproducible result for the POPV molecule. Secondly, the POPV square array was cooled below the dew-point to allow water droplets to condense on the pattern. The water droplets formed preferentially on the POPV domains and gave a uniform water droplet array (Scheme 1d). It is believed that the POPV domains favor the nucleation of water droplets for two reasons. Firstly, the POPV region is more hydrophilic than the ODT region. Secondly, the POPV forms microcrystals on the surface, which offers nucleation sites for the water droplets. The freshly formed water droplet array was then dipped into a DCM solution of TOPV and withdrawn. During the evaporation of the DCM above the water droplets, TOPV rings were formed at the edges of the water droplets. After the subsequent evaporation of water, a uniform binary array with each unit consisting of a “square-in-ring” type structure was produced. Finally, the obtained binary array can be exploited for different applications, such as multi-color chemical sensing (Scheme 1e, f).

The fabrication process for the binary patterns was monitored by optical and fluorescence microscopy. Fig. 2a shows the fluorescence image of the deposited POPV layer on the patterned substrate. The uniform array of the square-shaped pattern reflects the lateral pattern of varying the wettability on the surface. It is noticeable that the fluorescent molecules were deposited preferably in the hydrophilic squares, and cannot be observed on the ODT background. These results can be understood as the nonpolar ODT surface repels the polar solvent, while the highly polar MUA surface has a much stronger interaction with the solvent. Small micro-scale bright spots are observed inside the POPV squares, indicating that the POPV molecules form microcrystalline structures on the surface. The fluorescence images illustrate strong fluorescence from the POPV covered area, which is consistent with our previous report that this series of OPV molecules exhibit strong solid state fluorescence. When the POPV patterned array was exposed to a humid atmosphere, water droplets started to form and grow on the hydrophilic area with condensation time until an evaporation-condensation equilibrium was reached. In this process, we intentionally used relatively long condensation times to ensure that the water droplet was slightly larger than the hydrophilic domain. Fig. 2b gives a fluorescence image of the ordered 2D array of the TOPV rings, in which the rings are larger than the underlying hydrophilic squares.

Previous research has suggested that many nanoparticles and macromolecules exhibit surfactant-like behavior, which is beneficial for the formation of regular ring patterns. However, a small molecule like TOPV is not expected to self-assemble at the liquid–liquid interface. The ring formation in this work is attributed to the difference in the solvent evaporation rate. The organic solvent was the slowest to evaporate in the area close to the water droplet due to capillary forces and the high heat capacity of the water. As a consequence, the TOPV molecules accumulated at the edges of the water droplets after the evaporation of the organic solvent. In this process, water droplets served as not only templates for the formation of the TOPV rings, but also as “shields” for the POPV molecules. It is essential to have the ring larger than the square so that possible “cross-talking” between the two fluorescent molecules can be avoided. Fig. 2c shows the fluorescence image of an array of such square-in-ring microstructures, which illustrates that they are highly ordered with uniform sizes over a large area. As our OPV molecules have a large two photon absorption cross section, the patterns can also be
A representative SEM image of the TOPV ring (a) and POPV–TOPV binary array (b).

The fluorescence image of the binary array exposed to HCl vapor (a) and NH$_4$H$_2$O vapor (b), insets are magnifications of the same sample.

strategy method is that the materials which are to form the rings can be dissolved in an organic solvent that is immiscible with water. We have successfully fabricated similar square-in-ring binary structures using a variety of organic molecules, organometallic complexes and quantum dots (QDs) (Fig. S2, S3†). The capability of patterning multiple components onto the same substrate in high densities opens new avenues to a lot of potential applications, such as array-based sensors, multi-color displays and high resolution two-photon fluorescence imaging.

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Notes and references