Communication
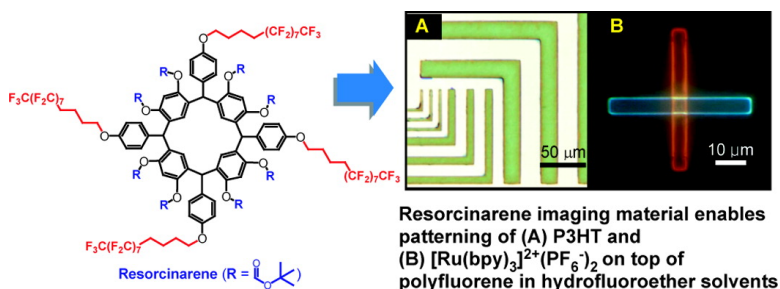
Acid-Sensitive Semiperfluoroalkyl Resorcinarene: An Imaging Material for Organic Electronics

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Resorcinarene imaging material enables patterning of (A) P3HT and (B) [Ru(bpy)$_3$]$^{2+}$(PF$_6^-$)$_2$ on top of polyfluorene in hydrofluoroether solvents

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Acid-Sensitive Semiperfluoroalkyl Resorcinarene: An Imaging Material for Organic Electronics

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Organic electronics is emerging as a promising technology to enable mechanically flexible devices through solution processing of organic materials.[1,2] As with traditional electronics, organic devices require active functional materials to be tailored into micropatterned and multilayered device components. While the former relies on photolithographic patterning techniques, the latter is restricted from adopting such robust, high-resolution, and high-throughput techniques because of the chemical compatibility issue between organic materials and patterning agents.[3] Namely, deterioration of materials' performance occurs during the photoresist deposition and removal stages due to aggressive organic solvents, as well as in the pattern development steps by aqueous base solutions. This challenge has stimulated the invention of alternative methods,[2,4,5] such as shadow mask evaporation,[4] ink-jet printing,[6] and microcontact printing.[7] Though some of these methods claim to enable manufacturing of organic devices for lower cost than traditional techniques used in silicon manufacturing, that goal remains elusive. Further, capital costs of any new technology are higher than that of an existing technology, particularly one as invested in as photolithography.[8] There have also been more practical approaches to enable the use of conventional lithography with sensitive organic materials. These efforts include the employment of protective coatings between the active material and photoresist films[9] and careful selection of less damaging processing solvents.[3,10] The latter approach, if there were to exist a suitable match of active material and processing solvent, can be an ideal strategy. In our search for universal, materials-friendly solvents, we have identified environmentally benign fluorous solvents combined with specifically tailored patterning materials as a possible solution to this complex problem.

Fluorous solvents are poor solvents for nonfluorinated organic materials.[11] Among the variety of fluorous solvents, segregated hydrofluoroethers (HFEs) attracted our attention because of their nonflammability, zero ozone-depletion potential and low toxicity for humans.[12] Recently, it has been reported that HFEs can be used for inorganic semiconductor processing,[13] but there has been no example of their use for the processing of organic electronic materials.[14]

In this communication, the synthesis and evaluation of a semiperfluoroalkyl resorcinarene which is processable in HFEs is described. This novel, high-performance imaging material is specifically designed to be orthogonal to the vast majority of organic semiconductors and hence enable their photolithographic patterning. Furthermore, this material paves the way for the multilevel patterning of organic semiconductors, as demonstrated by the

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Scheme 1. Synthesis and Acid-Catalyzed Deprotection of the Resorcinarene **6**[a]
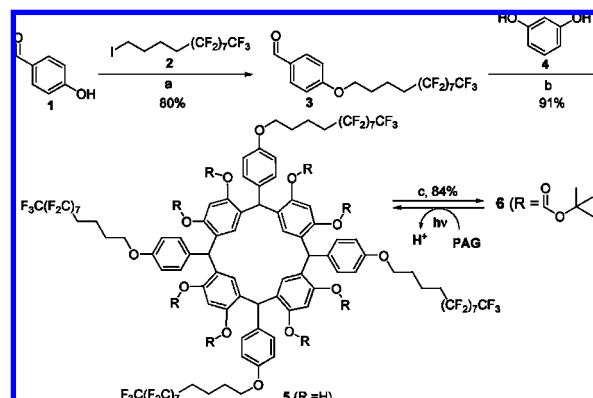
[a] Reagent and conditions: (a) K_2CO_3, DMF, 70 °C, 2 h; (b) *c*-HCl, EtOH, 75 °C, 2 h; (c) (*t*-Boc)$_2$O, DMAP, THF and benzotrifluoride, rt, overnight.

fabrication of overlaid patterns of a polyfluorene and a transition metal complex.

In general, materials with higher F content dissolve better in fluorous solvents. On the other hand, those materials are less adhesive on nonfluorinated surfaces. It is therefore desired to construct a material with a limited degree of fluorination while still exhibiting sufficient solubility and uniform dissolution behavior in HFEs. A design motif was hinted by molecular resists, which are amorphous small molecules with a monodisperse molecular weight distribution. Recently we have reported that a resorcinarene material shows excellent patterning properties under conventional lithographic conditions.[15] The same molecular framework was adopted, to which four semiperfluoroalkyl chains and eight acid-cleavable *tert*-butoxycarbonyl (*t*-Boc) groups were appended. The resulting resorcinarene **6** in Scheme 1 had 36% F content by weight. Resorcinarene **6** is able to form a negative tone image by transformation into an insoluble form upon an acid-catalyzed deprotection reaction, in which H⁺ is liberated from the photoacid generator (PAG) under UV exposure (Scheme 1).[16,17]

Synthesis of the resorcinarene **6** began with the alkylation of 4-hydroxybenzaldehyde **1** with the semiperfluoroalkyl iodide **2**.[18] The recrystallized product **3** was then reacted with an equimolar amount of resorcinol under acidic conditions.[19] The resorcinarene **5**, which is only sparingly soluble in THF, was recovered as a fine, pale-yellow powder in high yield. Size exclusion chromatography showed that the product **5** is composed mainly of two compounds, one with $M_n = 2500$ and the other with $M_n = 1700$ compared to the polystyrene standard (Supporting Information). It is believed that those two are stereoisomers which have different hydrodynamic
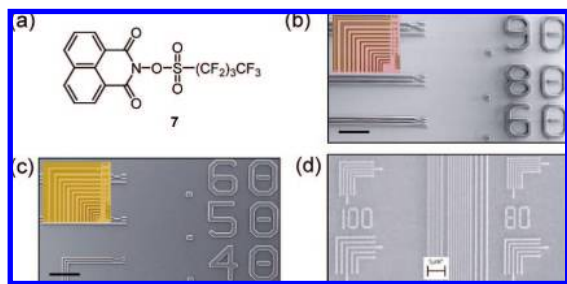
Figure 1. (a) Structure of a PAG used in the lithographic evaluations. SEM and optical microscope (insets) images of the developed resorcinarene **6** on (b) glass and (c) polyimide-coated wafer (scale bars are 10 μm). (d) SEM image of the developed resorcinarene **6** on Si wafer under e-beam exposure conditions (100 and 80 nm patterns).
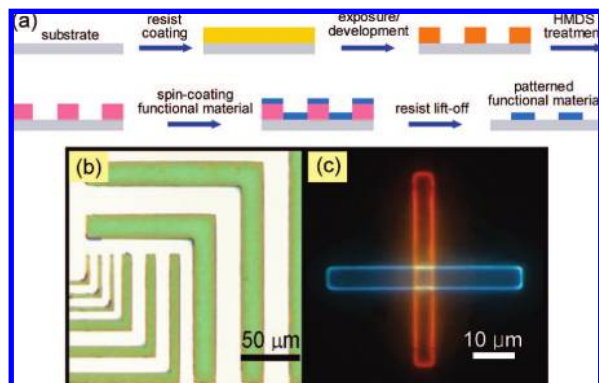
Figure 2. (a) General procedure for the lift-off patterning of functional materials. (b) Optical microscope image of patterned P3HT. (c) Fluorescent microscope image of overlaid patterns (feature width 5 μm) of poly(9,9-dioctylfluorene) (bottom) and $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ (top).

volumes.[19] The presence of stereoisomers stabilizes the amorphous state of the resorcinarene **6**, which would enable quality film formation (XRD data in Supporting Information). *t*-Boc protection of the eight hydroxyl groups in the resorcinarene **5** was completed in a mixed solvent of THF and benzotrifluoride. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) showed that resorcinarene **6** is stable up to 150 °C and undergoes glass transition at 82 °C. Solubility tests confirmed that resorcinarene **6** is moderately soluble in HFE-7200.

Lithographic evaluation began with spin-coating films of the resorcinarene **6** and PAG mixture on various substrates. The PAG **7** [Figure 1a] was employed because of its good sensitivity under UV ($\lambda = 365$ nm) exposure conditions.[20] Uniform films were cast on Si, glass, and polyimide-coated wafers from a solution in HFE-7500 (4 parts by vol.) mixed with a small amount of propylene glycol methyl ether acetate (1 part by vol.). Following UV exposure (84 mJ cm^{-2} with Si substrate), bake (at 70 °C), and development in HFE-7200, at least 600 nm features were generated on the aforementioned substrates [Figure 1b,c]. Under electron-beam exposure conditions, 80 nm patterns could be achieved without extensive optimization [Figure 1d], which demonstrates that lithography employing HFEs can be a useful tool to realize sub-100 nm features.

The new imaging material and lithographic processing in HFEs were then applied to making micron-sized patterns of organic electronic materials. Figure 2a illustrates a procedure of the lift-off patterning. A developed resorcinarene image becomes soluble again in HFEs through hexamethyldisilazane (HMDS) treatment, which reprotects the phenolic hydroxyl residue with a trimethylsilyl (TMS) group.[21] Deposition of an organic material and the following lift-off of the resorcinarene film in hot HFE-7100 generate an organic material pattern. It has been demonstrated that poly(3-hexylthiophene) (P3HT) [Figure 2b], poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), and Au could be patterned down to a 5 μm size. As a step further, an overlaid materials pattern was fabricated to demonstrate, for the first time, the multilevel patterning of solution processable organic layers. The electroluminescent polymer poly(9,9-dioctylfluorene) was patterned first according to the scheme in Figure 2, and then the same procedure was repeated with fluorescent material tris(2,2′-bipyridine)ruthenium(II) bis(hexafluorophosphate) $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ on top of the patterned poly(9,9-dioctylfluorene) film. Overlaid features down to a 5 μm size were made successfully [Figure 2c, profilometer and AFM image in Supporting Information]. The results show that the new imaging material described here brings unique capabilities to the world of organic electronics.

In summary, an acid-sensitive semiperfluoroalkyl resorcinarene, soluble in HFEs, was developed for applications in organic electronics. Features as small as 600 nm were produced on Si, glass, and polyimide-coated substrates. Its orthogonality to common organic electronic materials enabled multilevel patterning as demonstrated by the fabrication of overlaid patterns.

Supporting Information Available: Synthetic procedure, spectroscopic and thermal analysis data, and photolithographic patterning conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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