Supplementary Material (ESI) for J. Mater. Chem.

Supporting information

Imidazolide monolayers for reactive microcontact printing†

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Characterization of SAMs

Table 1 *Advancing θ_a (°) and receding θ_r (°) water contact angles, atomic ratios of C and N from XPS of SAMs shown in Figure 1.*

SAMs	θ_a (°)	θ_r (°)	C:N (XPS)	C:N (calcd)
NH_2 SAM	68 ± 2	55 ± 2	2.7 ± 0.2	2.5
IM SAM	52 ± 2	27 ± 1	2.5 ± 0.2	2.3

The XPS measurements show a small carbon contamination of the amino (**NH_2 SAM**) and imidazolide SAMs (**IM SAM**). The change in C/N ratio between **NH_2 SAM** and **IM SAMs** is too small to provide a definite conclusion about the success of formation of the imidazolide SAM. Stronger evidence for the formation of imidazolide groups on the **IM SAM** stems from the XPS narrow scans of the carbon 1s region. The new peaks at 287.8 and 288.9 eV in the C_{1s} spectrum of the **IM SAM** are consistent with and characteristic for the N-***C***(O)-N carbon and N-***C***-N of the imidazolide intermediate.

Reaction rate of ADF and Atto520

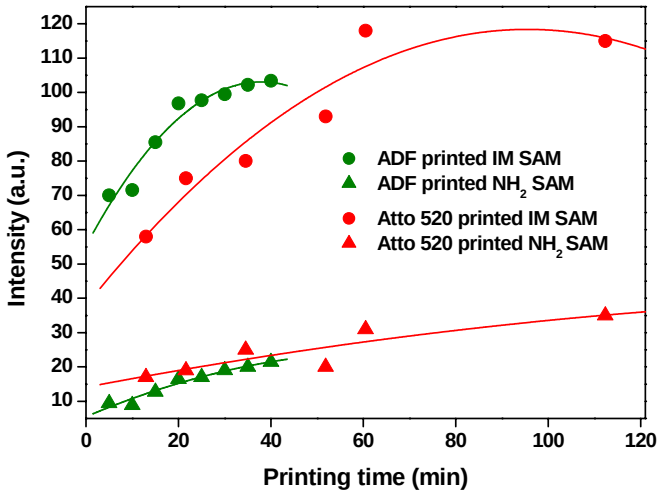

Fig. 1 Reaction rate of ADF and Atto520 printed onto **IM SAM** and **NH_2 SAM**

Kinetic printing of Atto520

Different printing times were applied ranging from 5 min to 2 h and the substrates were vigorously rinsed and sonicated with acetate buffer for 10 min directly after printing. The intensity of the patterns printing with **IM SAMs** increased in time and leveled off after 1h. Instead, the intensity profiles of the **NH_2 SAMs** showed consistent relatively weak pattern, which might come from the physisorption of Atto520.

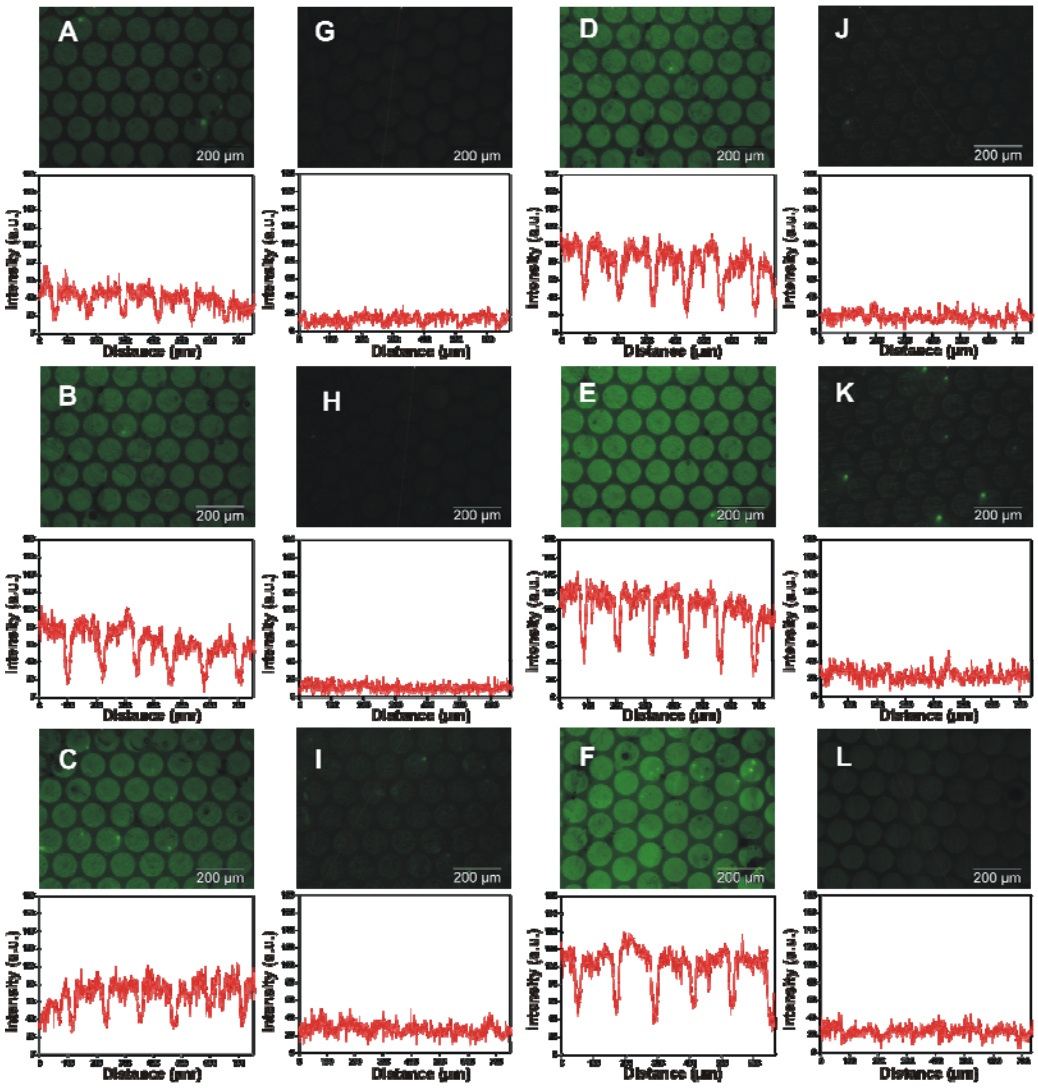

Fig. 2 Fluorescence microscopy images (884 µm x 666 µm) of 100 µm Atto520 printed dots onto **IM** (A,B,C,D,E,F) and **NH_2 SAMs** (G,H,I,J,K,L) for 5 min, 15 min, 30 min, 50 min, 1h and 2h.

Alkyl-chain vs. Fluoroalkyl-chain molecules for reverse microcontact printing

Octadecylamine was used as non-fluorescent ink to compare with the printing result of heptadecafluoroundecylamine. The ink was prepared in acetonitrile (1M) and follows the same procedure for heptadecafluoroundecylamine. A stamp was inked with the solution for 30 s, dried under nitrogen flow, and brought into conformal contact with imidazolide-terminated glass slides for 1h. After 1 h, the stamp was removed and the substrate rinsed with a copious volume of dichloromethane and blown dry with nitrogen. The remaining area was incubated with 0.1 mM Atto520 prepared in MilliQ water overnight. The reverse pattern was not clearly observed compared with heptadecafluoroundecylamine.

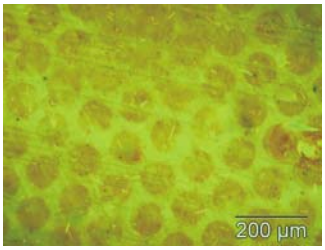

Fig. 3 Fluorescence microscopy image (884 µm x 666 µm) of Octadecylamine (1 M in acetonitrile) printed 100 µm diameter dots onto **IM SAM** for 1h. The remaining area was filled by exposing samples to Atto520 in solution overnight (0.1mM in MilliQ water).

boc-protected ADF printing on IM-SAM

The reference molecule boc-ADF was synthesized (see next page) to demonstrate covalent binding between the introducing molecules and **IM SAM** is required for immobilization of the microcontact printed molecules. A 1mM of the boc-protected molecules (boc-ADF) was prepared in acetonitrile and printed onto **IM SAM** for 20 min. As shown in the **Figure 4**, the pattern is completely removed after rinsing and sonicating with THF. These data corroborate covalent binding is occurring in the printing of the non-protected ADF on **IM SAM**.

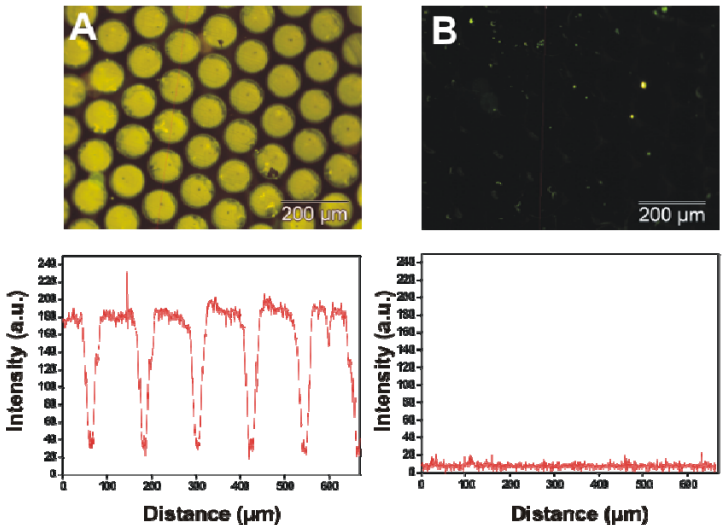

Fig. 4 Fluorescence microscopy image (884 μm x 666 μm) of boc-ADF (1 mM in acetonitrile) printed 100 μm diameter dots onto **IM SAM** for 20 min before (**A**) and after (**B**) THF rinsing.

Synthesis of boc-ADF

4-(2-aminoethylamino)-7-(N,N-dimethylsulfamoyl)benzofurazan (25mg, 0.0876mmol) was dissolved in 25 ml of water/chloroform (50:50 v/v) in the presence of sodium hydroxide (5.25mg, 0.0131mmol). After stirring for 15 min, di-*tert*-butyl dicarbonate (Boc_2O) (19.12mg, 0.0876mmol) was added at 0 ºC, and the reaction mixture was allowed to stand overnight at room temperature. The reaction was extracted with 4 x 50ml of chloroform. The organic layer was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, diclomethane/methanol = 98:2) to give the desired product in 63 % yield as a yellow powder (15.75mg).1H NMR (300 MHz, $CDCl_3$, 20ºC,TMS) δ: 7.83 (d, J=7.8 Hz, 1H), 6.06(d, J=7.8 Hz, 1H), 3.43 (m, 2H, CH_2), 3.12 (m, 2H, CH_2), 2.79 (s, 6H, CH_3), 1.39 (s, 9H, CH_3) ppm.

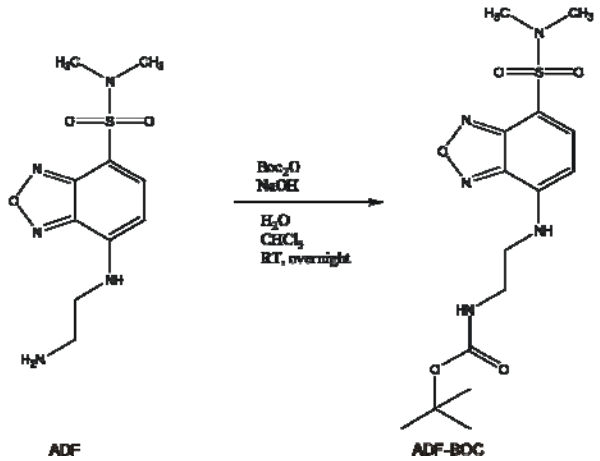

Fig. 5 Molecular structure of ADF and its reaction with di-*tert*-butyl dicarbonate (Boc_2O) for the preparation of boc-ADF.