DIRECT SURFACE PATTERNING THROUGH PHOTOCHEMISTRY

By: Brittney Moncrieffe Fors Lab
Insight behind Surface Patterning

- Methods for developing surface functionality
- Simple patterns like binary patterns follow on/off scheme
- Complex grayscale patterns show various degrees of functionality

Binary Pattern

01001000 01101001

Grayscale Pattern

Real-World Applications

**Biological Assays**


**Antibiofouling Surfaces**

Specialized Antifouling Surface
Inhibits Bacterial Growth on Surface

*J. Mater. Chem.*, 2008, 18, 3405-3413
Patterning Techniques

Micro-contact printing
- Marks a Specific Area of a Surface with Functionality.
- Similar to a Stamp

Physical Vapor Deposition
- Process Used to Deposit Thin Layers of Material
Limitations of Conventional Patterning Methods

1. Fail to Create High Resolution Grayscale Patterns
   - Large Length-Scales (cm scale)

2. Multistep Process
   - Costly
   - Time Consuming
PHOTO-MEDIATED REACTIONS

Goal: A New Surface Patterning Method

- A Direct Surface Patterning Method
  - Single Step to Functionalization

- Create New Patterning Agents
  - Vary Hydrophobicity of Groups
    - (eg. Perflouranated agents, carbon chains, etc)

- Characterize Using Water/Surface Contact Angle
Proposed Synthesis of Patterning Agents
Patterned Agent Synthesis: Acid Catalyzed Acetal Synthesis

ROH + MeCHO → Me

CaCl₂

0.1 eq p-TsOH

ROOR

3 eq 1 eq

R = C_{12}H_{25}, \% yield = 74 \%

R = \text{triethyl}, \% yield = 73\%
Patterning Agent Synthesis: Chlorination/Nucleophilic Substitution

\[
\text{RO} \quad \text{OR} \quad + \quad \text{BCl}_3 \quad \xrightarrow{\text{DCM}, -78^\circ\text{C} \text{ to } \text{RT}} \quad \text{RO} \quad \text{Cl} \quad \text{Me}
\]

1.5 eq 1 eq

\[
\text{R} = \text{C}_{12}\text{H}_{25}
\]
Patterning Agent Synthesis: Chlorination/Nucleophilic Substitution

\[ \text{ROOR} + \text{BCl}_3 \xrightarrow{\text{DCM} -78^\circ \text{C} \text{ to RT}} \text{ROCl} \]

\[ \text{R = C}_{12}\text{H}_{25} \]

\[ \text{S} \xrightarrow{\text{NaS} \xrightarrow{\text{NEt}_2}} \]

\[ \text{DCM} \]
Proposed Synthesis of Patterning Agents: Round 2
Proposed Synthesis of Patterning Agents: Round 2
Patterned Agent Synthesis: Transetherification

\[ \text{ROH} + \overset{\text{1 eq}}{\text{2 eq}} \overset{1 \text{ mol}\% [\text{Ir(COD)Cl]}_2}{\overset{0.6 \text{ eq Na}_2\text{CO}_3}{\text{Toluene, 100 °C}}} \overset{\text{RO}}{\text{R}} \]

- \( \text{R} = \text{C}_{12}\text{H}_{25}; \text{ % yield} = 59\% \)
- \( \text{R} = \text{C}_{8}\text{H}_4\text{F}_{13}; \text{ % yield} = 45\% \)
Patterning Agent Synthesis: Chlorination/Nucleophilic Substitution

\[
\begin{align*}
\text{RO} & \xrightarrow{\text{HCl, Et}_2\text{O}} \text{ROCl} & \text{Me} & \xrightarrow{\text{NaSNEt}_2, \text{Et}_2\text{O, RT}} & \text{RO} & \text{S} & \text{S} & \text{NEt}_2 \\
\text{R} = \text{C}_{12}\text{H}_{25} & ; \text{yield} = 43\% & \text{R} = \text{C}_8\text{H}_4\text{F}_{13} & ; \text{yield} = 18\% 
\end{align*}
\]
Patterning Test Reaction:
Small Molecule Acetal Formation

\[
\text{R = C}_{12}\text{H}_{25}, \ 80\% \ \text{Conversion} \\
\text{R = C}_{8}\text{H}_{4}\text{F}_{13}, \ 52\% \ \text{Conversion}
\]
Patterning Test Reaction: Small Molecule Acetal Formation

`C_6F_{13}OCH(OEt)_2S(S)NEt_2 + OH OH OH OH \xrightarrow{[\text{Ir}(dF(CF_3)ppy)_2(dCF_3bpy)]PF_6} \frac{\text{MeCN}, 450 \text{ nm}, 30 \text{ min}}{\text{Si} \quad \text{Si}} \frac{\text{Me}}{\frac{\text{C}_6\text{F}_{13}}{\text{OR} \quad \text{OR} \quad \text{OR}}} \quad \text{Water/Surface Contact Angle:}  

CA = 15°

CA = 81°
Conclusion:

- Synthesized new Patterning Agents
- Expanded Scope of Patterning Reaction
- Mastered the art of running my own columns and evaluating TLC test
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