Self-assembly of polychlorotriphenylmethyl organic radicals on surfaces

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**INTRODUCTION**

Polychlorotriphenylmethyl (PTMs) radicals.

- Highly persistent
- Easily functionalized
- Open-shell structures (magnetism)

- Electroactive

- Fluorescence
  600nm (red)
Motivation

A switch or memory device mechanism → **Bistable systems**

A molecule having two stable and fully reversible states exhibiting different optical, magnetic or electrical properties
UV/Vis Spectra of the PTM Radical and Anion in a Chronoamperometric Experiment.
**INTRODUCTION**

**Redox-Switching of the UV/Vis-Response between the PTM-Radical and the PTM-Anion**

- **PTM - Radical**
  - $\varepsilon = 35400 \text{ mol}^{-1}\text{cm}^{-1}$
  - (sd: +/- 3.3%)

- **PTM - Anion**
  - $\varepsilon = 28100 \text{ mol}^{-1}\text{cm}^{-1}$
  - (sd: +/- 4.3%)
PTM RADICALS ARE GOOD BUILDING BLOCKS FOR PREPARING MULTIFUNCTIONAL MOLECULAR SWITCHES

PTM - Radical

ON STATE

OFF STATE

PTM - Anion

Functionalise surfaces with PTM radicals for memory devices/switches
Functionalization of different surfaces

Key role for the functionalization

SiO$_2$/quartz

Gold

Graphite
PREPARATION OF PTM SELF ASSEMBLED MONOLAYERS (SAMs) ON SILICON OXIDE AND QUARTZ SURFACES

Two-steps

Adsorption

Organization

PTM SAM based on Covalent Bonding

Contact angle, Ellipsometry, X-Ray photoelectron spectroscopy (XPS)

<table>
<thead>
<tr>
<th>SAM</th>
<th>$\theta_{\text{adv.}} , (^\circ)$</th>
<th>$\theta_{\text{rec.}} , (^\circ)$</th>
<th>Ell.thick.(nm)</th>
<th>Cl/N (XPS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$</td>
<td>57.3±1.2</td>
<td>22.7±3.7</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>PTM</td>
<td>84.0±0.2</td>
<td>44.0±2.0</td>
<td>1.3</td>
<td>1.6 1 PTM / 4.4 NH$_2$</td>
</tr>
</tbody>
</table>
Optical Characterisation and EPR of the SAM (on quartz and glass)

**UV-vis spectra:**

**Fluorescence emission spectra:**

**Electron paramagnetic resonance (EPR)**

- $g = 2.0024$
- $\Delta H_{pp} \approx 5.2G$
PTM radical generated in situ on the surface

Possible to carry out chemical reactions on the PTM SAMs
Chemical Switch with Optical and Magnetic Response

ON STATE ↔ OFF STATE

PTM radical “ON state”

PTM anion “OFF state”

Chemical Switch with Optical and Magnetic Response

Angew. Chem. Int. Ed. 2007, 46, 2215
**Patterning of the surface:** Fluorescent, magnetic and redox active patterned glass surface.

**MICROCONTACT PRINTING:**

1) Functionalization of a glass slide with the amino-terminated monolayer.
2) The stamp is dipped in the ink solution (PTM solution).
3) The stamp is brought in contact with the amino monolayer and kept for some minutes before careful removal.
Both strategies (covalent and non-covalent) are good to obtain a patterned surface.
Functionalization of different surfaces

SiO₂/quartz  Gold  Graphite
PREPARATION OF PTM SAMs ON GOLD

Electrochemical *in situ* characterization

![Image of molecular structures and electrochemical curves with potentials -0.14V and +1.68V.](image-url)
Preparation of PTM SAMs on Gold: Direct Anchoring

**Synthesis:**

1. **MeSNa, HMPA**
   - MeS-\(\text{CHO}\) + 1. MeSNa, HMPA → AcS-\(\text{CHO}\) + 1

2. **AcCl**
   - AcS-\(\text{CHO}\) + 2. AcCl → \(\text{CHO}\)

3. **1BuOK, THF**
   - \(\text{CHO}\) + 1BuOK, THF + 2.1, THF → SAc

4. **(nBu)\(_4\)NOH, AgNO\(_3\)**
   - SAc + 1) (nBu)\(_4\)NOH + 2) AgNO\(_3\) → \(\text{S-S}\)

**EPR**

![EPR spectrum](image)

*JACS, in press.*
PREPARATION OF PTM SAMs ON GOLD. Direct anchoring

\[ \Delta E = 68 \text{ mV (at 100mV/s)} \]

Crivillers et al. JACS, in press.
Functionalization of different surfaces

\[ \text{SiO}_2/\text{quartz} \quad \text{Gold} \quad \text{Graphite} \]
CONCLUSIONS

Multifunctional surfaces

MAGNETIC

ELECTRO-ACTIVE

OPTICAL PROPERTIES

Chemical switch

Electrochemical switch
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