

# Improving the performance of organic semiconductor nanoparticles for hydrogen evolution via chemical modification

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## Introduction

### Green hydrogen

Hydrogen is hailed as the eco-friendly fuel of the future, essential for achieving a carbon-neutral society. Its versatility as an energy carrier, particularly in fuel cells that generate electricity with only water as a byproduct, positions hydrogen as a promising alternative to fossil fuels, pivotal for shaping a low-carbon energy future. Nevertheless, the predominant method of hydrogen production through natural gas reforming presents a substantial challenge. Addressing this issue using environmentally friendly methods is of paramount importance.

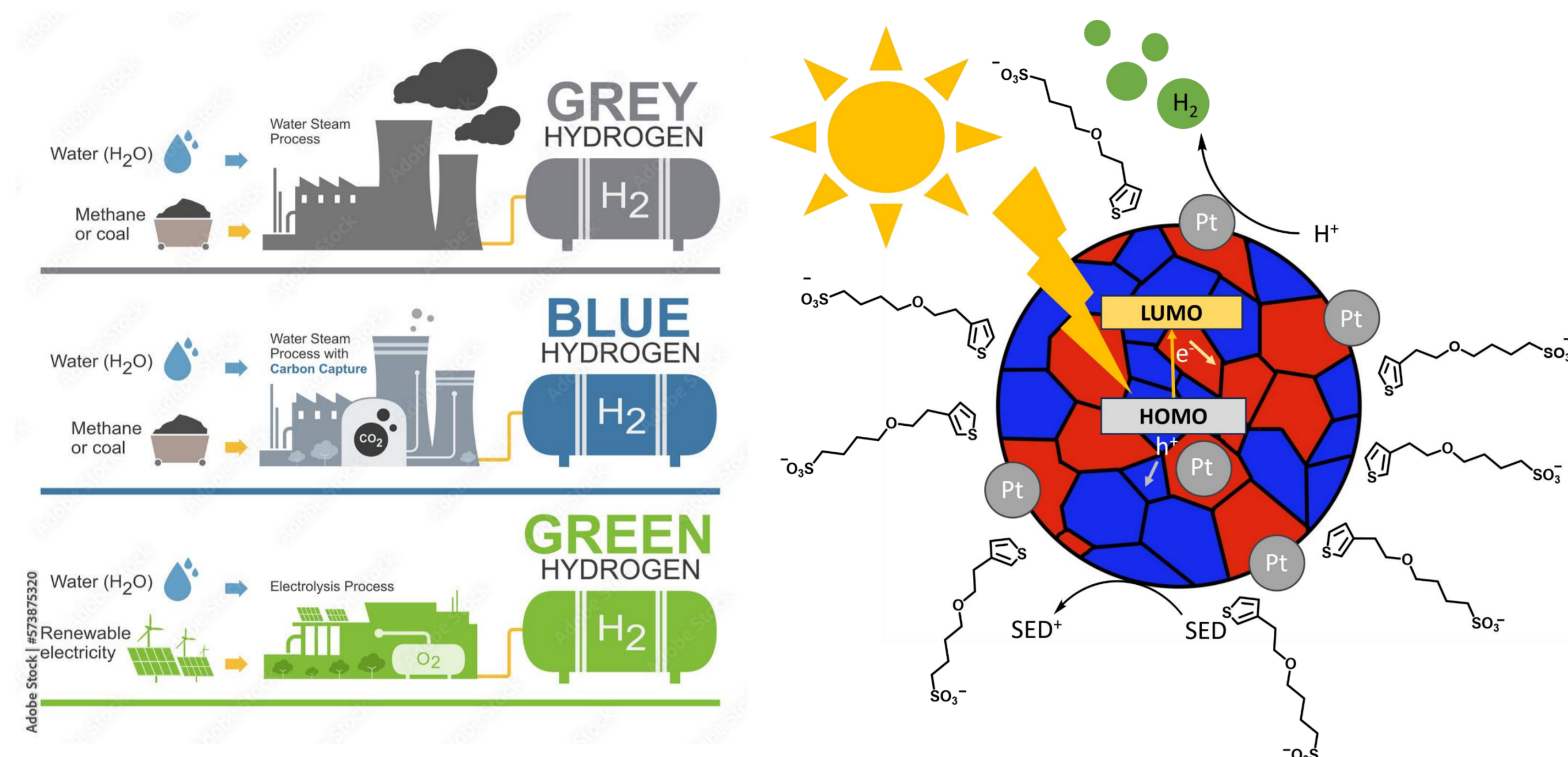


Figure 1. different types of hydrogen / bulk heterojunction nanoparticle for photocatalytic HER

### Photocatalyst for green hydrogen production

Photocatalysis is a catalytic process to produce hydrogen driven by the absorption of light by a semiconductor material, typically titanium dioxide or other suitable compounds. When these materials are exposed to light energy, the electrons within the semiconductor are excited, creating electron-hole pairs. These charged carriers then participate in chemical reactions, like water splitting, by transferring their energy to reactant molecules. This mechanism enables the conversion of solar energy into a clean and sustainable green hydrogen production.

### Organic semiconductors

Organic semiconducting polymers in combination with small molecule acceptors are widely investigated for use in solar cells [1].

The benefits of using these materials over traditional semiconductors such as silicon are their low cost, abundance, ease of processing, flexibility and tunability of the bandgap. However, some issues remain in terms of stability and the diffusion of the acceptor molecules through the active layer, thus yielding aggregation. One very successful pairing is PM6 as donor polymer and the non-fullerene small molecule acceptor Y6, which could achieve a power conversion efficiency of > 17% in organic solar cells. [2]

### Bulk heterojunction polymer nanoparticles for HER

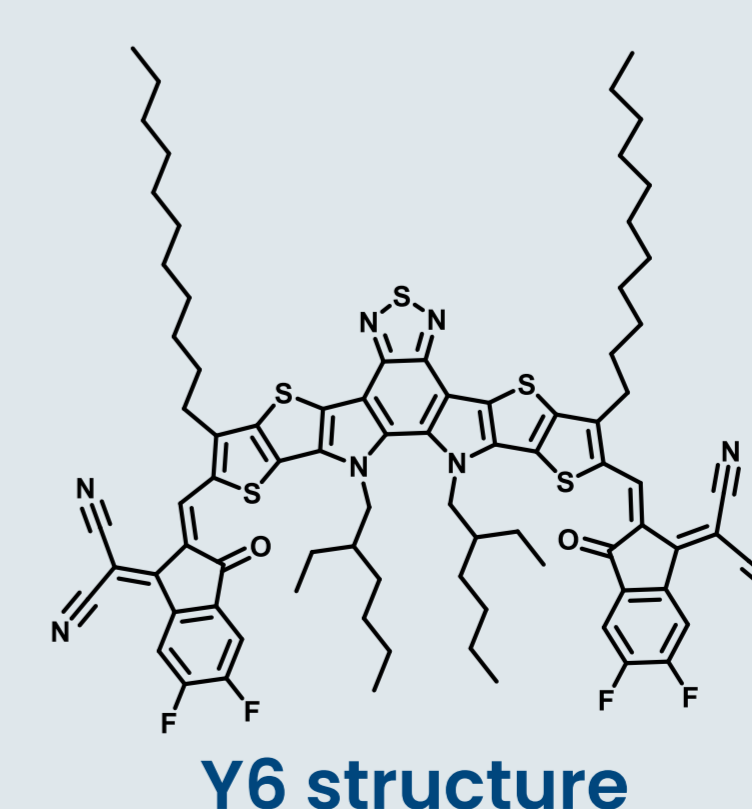
Recently, the same materials have also been investigated as photocatalysts for the hydrogen evolution reaction (HER). [3] Here two setups exist, (1) use of the active layer as a film, and (2) nanoparticles formed of the bulk heterojunction suspended in water, often in combination with a noble metal cocatalyst and stabilized by surfactants (Figure 1).

In this very recent research field several aspects require optimization such as the

- morphology of the nanoparticles - both donor and acceptor need to be present in nanodomains on the surface of the particle
- stability under the reaction conditions
- wettability
- accessibility of the surface

### Next steps

- Determination of band gaps of synthesised polymers
- Performance and stability check of solar cells with cross-linked polymers and Y6
- Analysis of hydrophilicity of the novel materials by water contact angles
- Performance and stability assessment in nanoparticles for HER

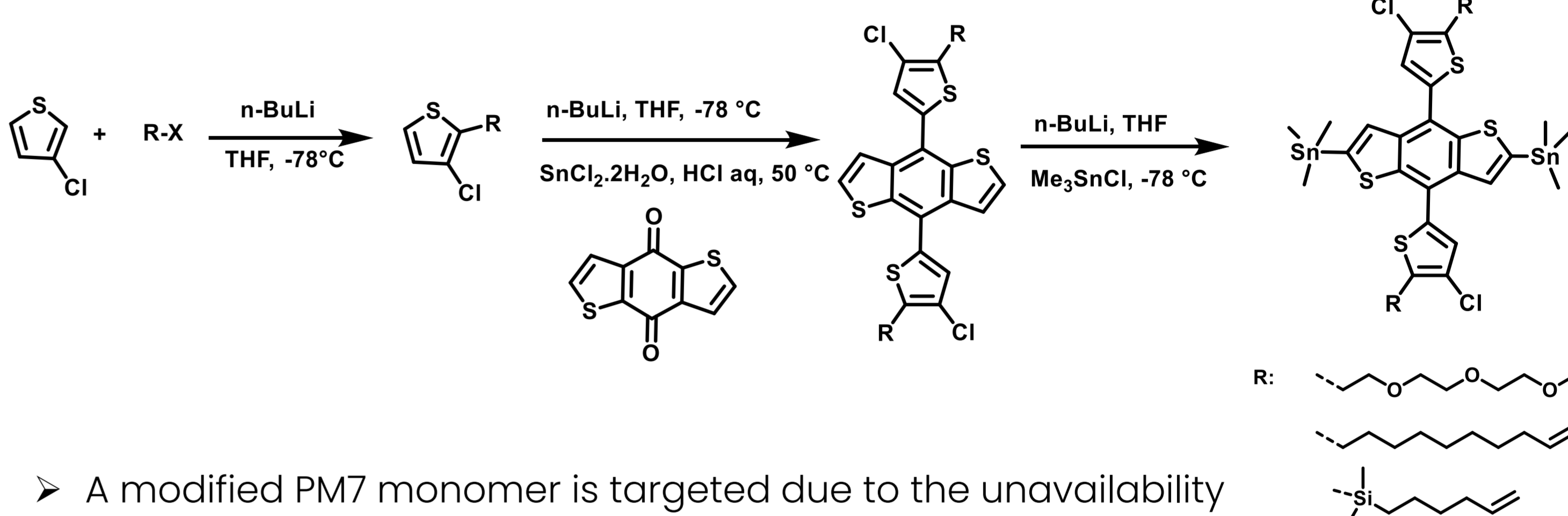


### Research approach

Based on the successful PM6/Y6 pair, the aim of this project is to address these issues via side chain modification of one of the monomers of PM6.

## Monomer synthesis

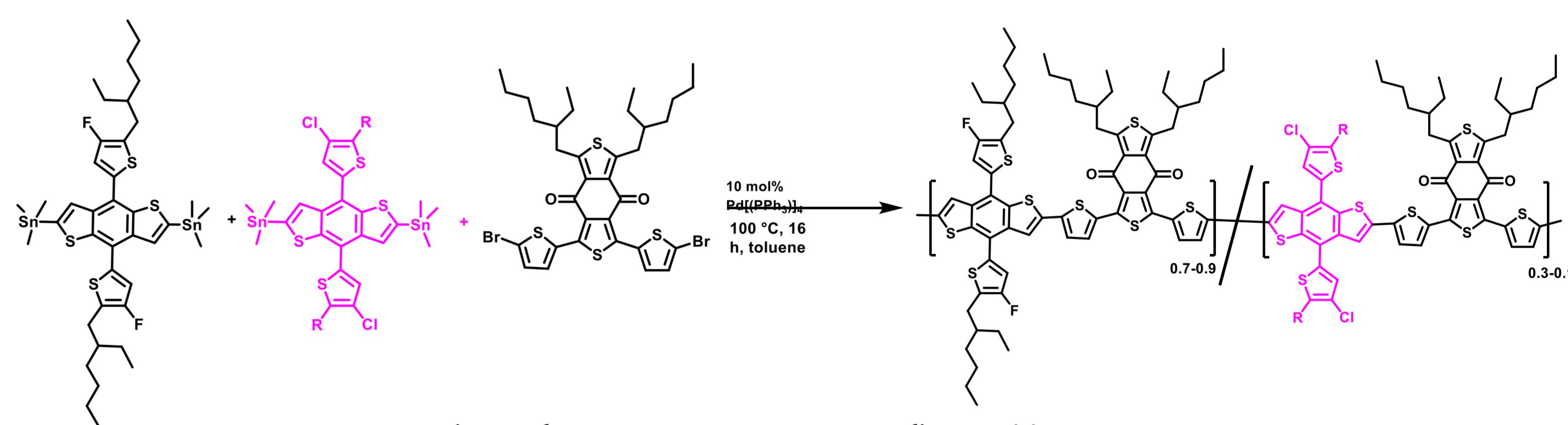
### Introduction of functionalities into the side chains of PM7 monomer



- A modified PM7 monomer is targeted due to the unavailability of fluorothiophene
- Initially  $\text{Bu}_3\text{Sn}$  derivatives were synthesised to reduce toxicity, but were difficult to purify and polymerisation did not proceed well
- Alkenes can be cross-linked thermally during annealing in solar cells or via linkers
- Other polar groups will be introduced in the future

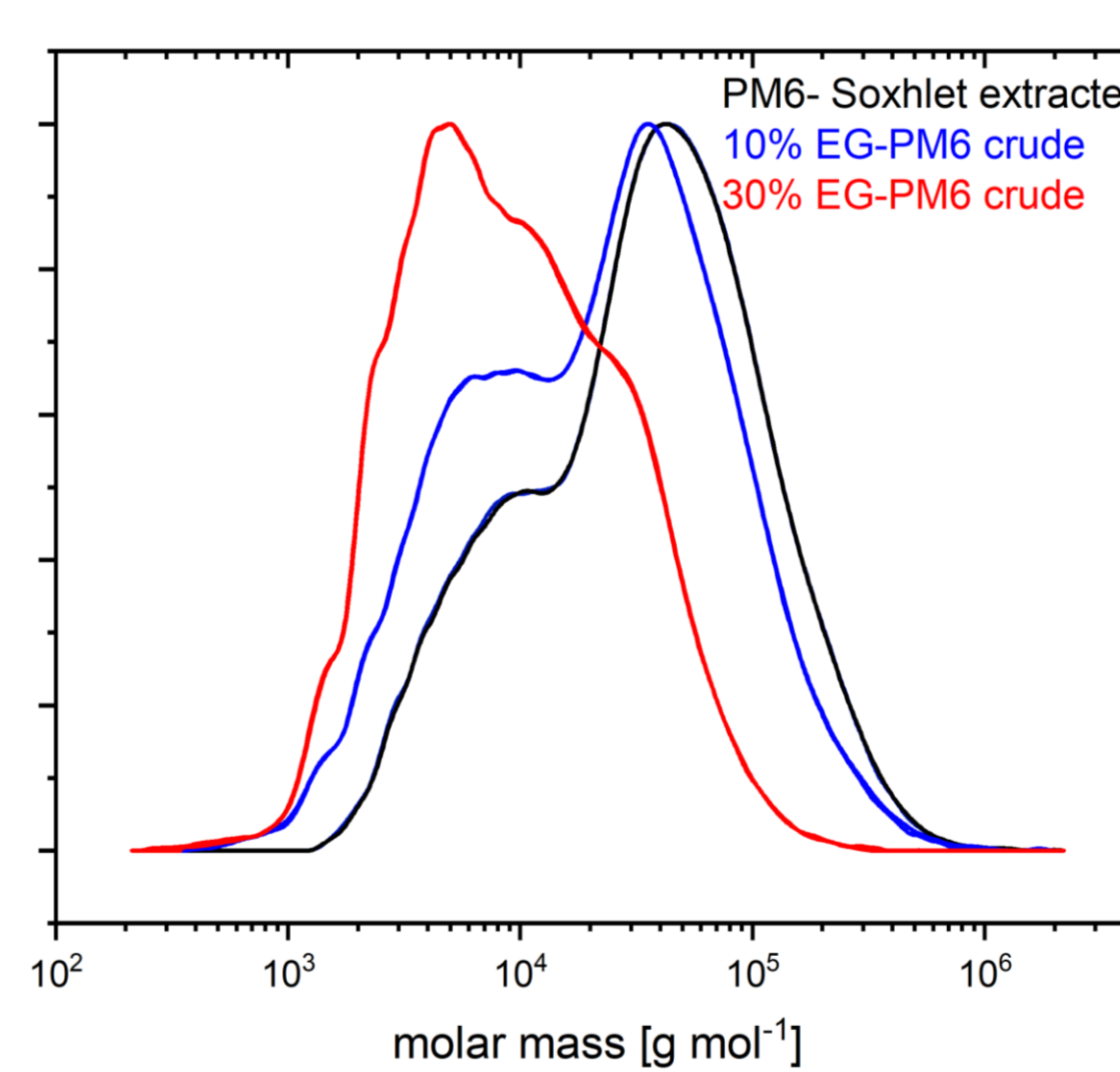
## Polymerisation

The modified monomers are incorporated into PM6 in varying amounts by copolymerisation via Stille coupling.



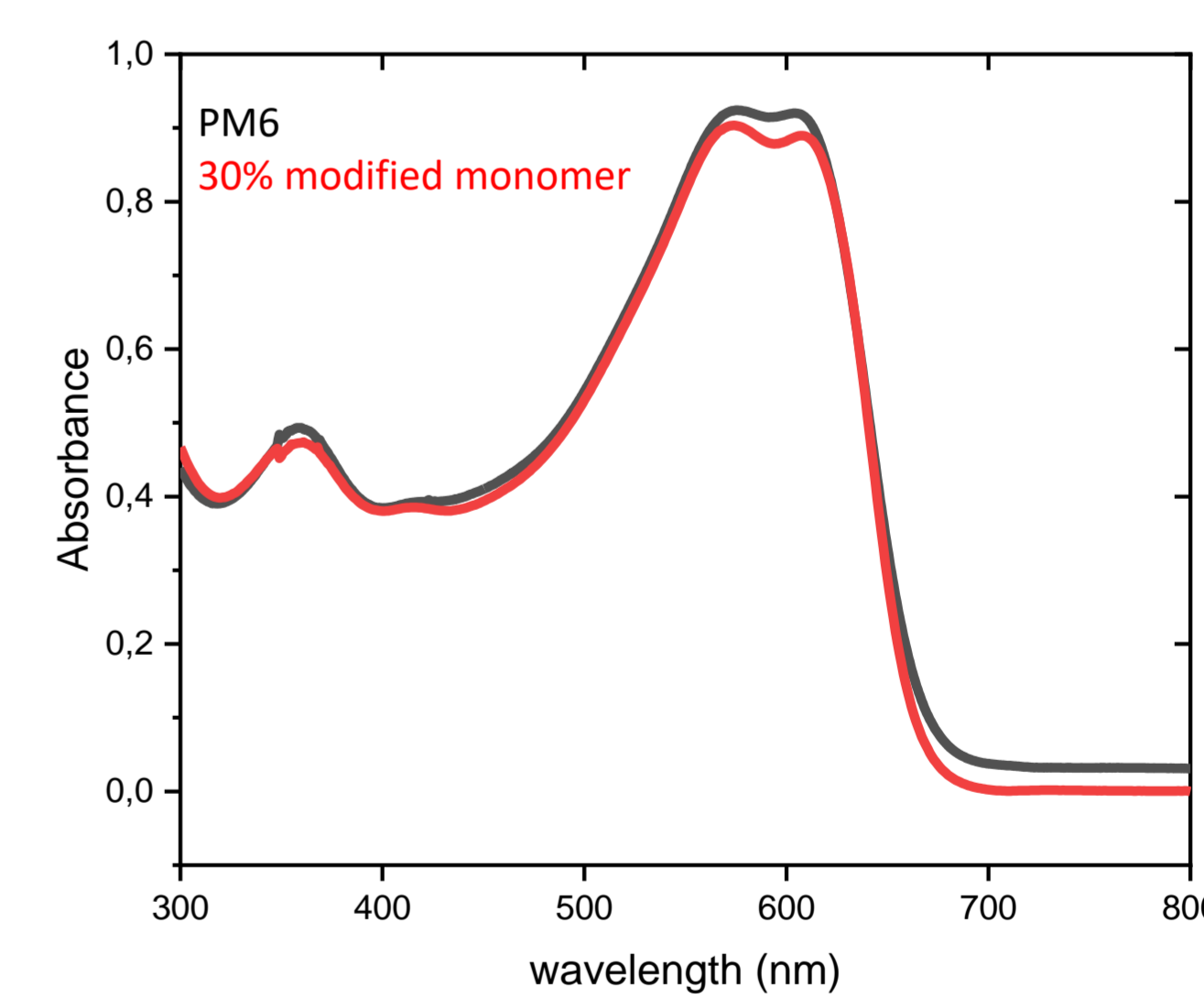
- Incorporation of new monomers confirmed by NMR

### GPC analysis



- When adding glycol side chain monomer ( $\text{Bu}_3\text{Sn}$  based), the molar mass was lower than pure PM6
- Shorter chains of different masses indicate low incorporation of new monomer

### UV-Vis spectra



- UV-Vis absorption is not affected by incorporation of monomers with modified side chains