Supporting Information

Model System Study of Environmentally Persistent Free Radicals Formation in a Semiconducting Polymer Modified Copper Clay System at Ambient Temperature

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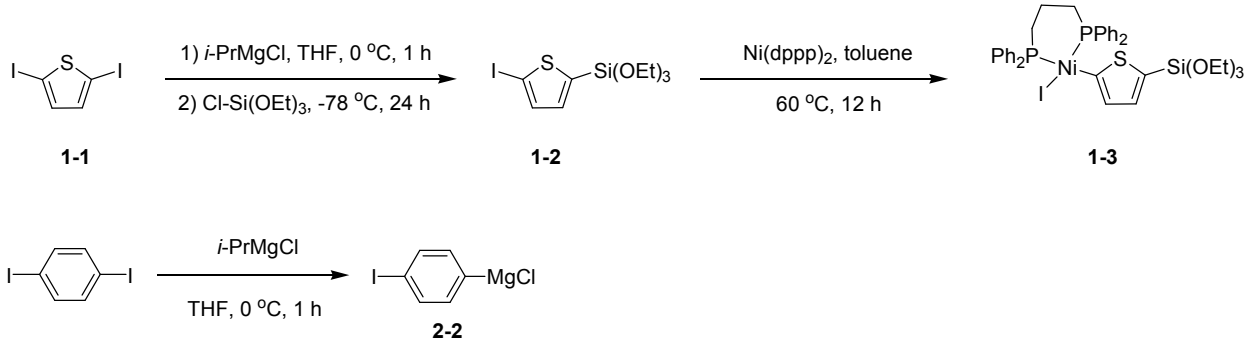
Clay Modification

Preparation of substrate (Clay): A 200 mg sample of clay was dried in the vacuum oven at 70 °C overnight, and subsequently transferred to the glove box for further air-free reactions.

Scheme SS1-2. Preparation of reagents for surface-confined Kumada catalyst-transfer polymerization.



Preparation of catalytic initiator 1-3. The catalytic initiator **1-3** for surface-confined polymerization was prepared following the procedures described in ref. 1.

Preparation of surface-immobilized initiators on the substrate (clay). Dried clay (200 mg) was immersed into 7 mL of 2.5 mM solution of the polymerization catalytic initiator **1-3** in toluene and kept at 60 °C for 3 days with stirring. In order to remove non-chemically attached initiator, the clay samples were centrifuged at 3,000 rpm for 1 min to precipitate clay, followed by gentle rinsing with anhydrous THF. Due to air sensitive nature of compounds involved, all manipulations were carried out under a nitrogen gas flow or inside a glove box.

Grignard monomer for polymerization (compound 2-1). A solution of 0.066 g of 1,4-diiodobenzene (0.2 mmol) in 20 mL of anhydrous THF was stirred at 0 °C under a nitrogen atmosphere. A solution of isopropylmagnesium chloride (0.25 mL of 2.0 M solution, 0.205 mmol) was then added dropwise and the solution was stirred for 1 h.

Surface-confined polymerization of Grignard monomer. The clay modified with surface-attached catalytic initiator **1-3** was immersed into the Grignard monomer **2-2** solution prepared as described above with gentle stirring at room temperature for 12 h. The reaction mixture was then quenched with methanol, and washed successively with chloroform, acetone, methanol, and water following drying the sample in vacuum oven at 70 °C for 12 h.

EPR Spectra for DMPO-OH

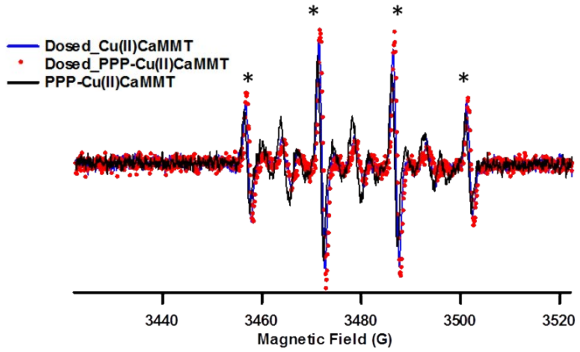


Fig. S1. EPR spectra for DMPO-OH (Asterisks) after 8h incubation for Dosed_Cu(II)CaMMT (blue), phenol exposed Cu-loaded clay, Dosed _PPP-Cu(II)CaMMT (Red) and PPP-Cu(II)CaMMT(black). Spectra recorded at 100 G width.

Reference

1. C. A. Chavez, J. Choi and E. E. Nesterov, *Macromolecules*, 2014, **47**, 506-516.