

## Supporting Information

### Organocatalyzed Atom Transfer Radical Polymerization (ATRP) using Triarylsulfonium Hexafluorophosphate Salt (THS) as a Photocatalyst

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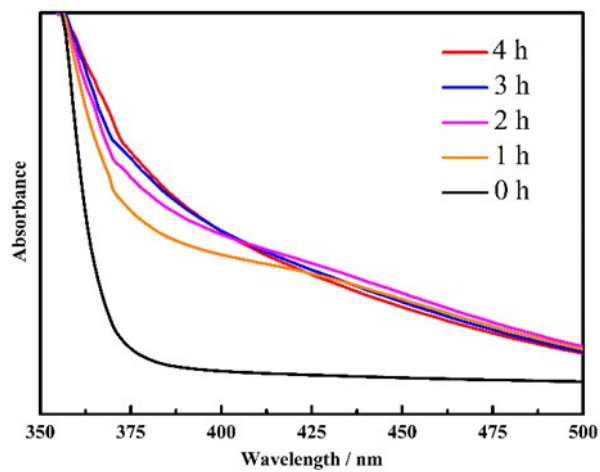
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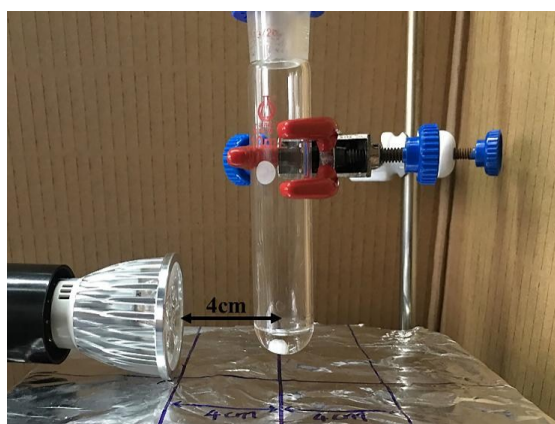
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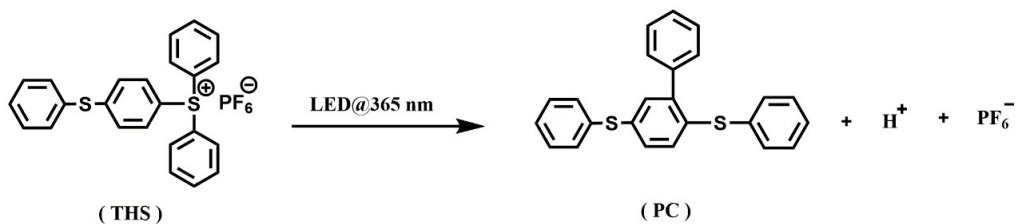
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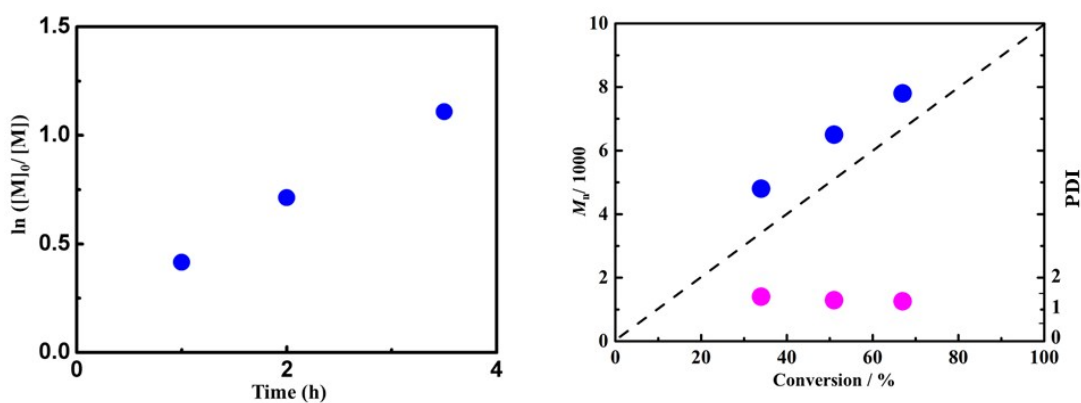
**Figure S1.** UV-vis absorption spectra of THS irradiated with LED@365 nm at different times.



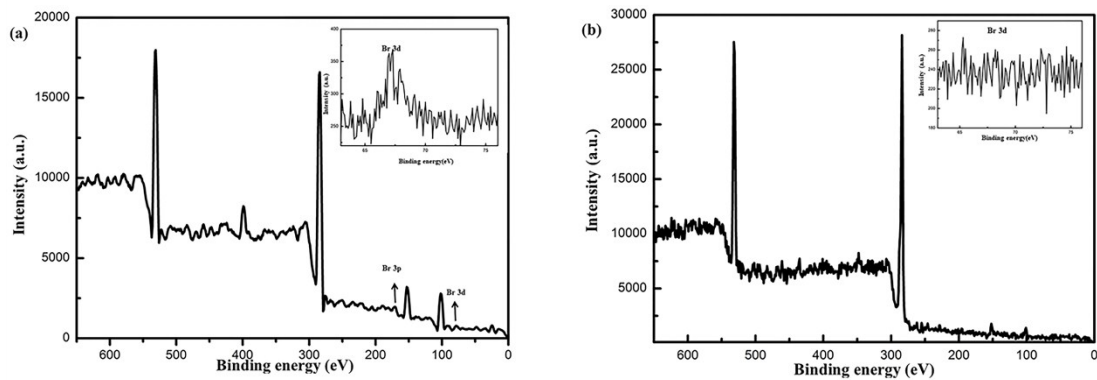
**Figure S2.** The picture of LED-light (365 nm, 5 x 1 w bulb, 480 mW/cm<sup>2</sup>).



**Figure S3.** Under LED@365nm irradiation, molecular rearrangement of the triarylsulfonium moiety resulted in the generation of free  $\text{H}^+$ .<sup>1</sup>



**Figure S4.** Plot of  $\ln ([M]_0 / [M])$  vs time. (b) The number-average molecular weight ( $M_{n, \text{GPC}}$ ) and polydispersity indices (PDI) versus monomer conversion. Polymerization conditions:  $[\text{MMA}] : [\text{EBiB}] : [\text{THS}] = 100 : 1 : 1$ , containing 0.25 g methyl methacrylate and 0.75 g solvent ( $V_{\text{DMAc}} : V_{\text{THF}} = 3 : 1$ ).



**Figure S5.** XPS analysis of Si-Br (a) and Si-PMMA-Br (b).

### References

1. A. Douvas, P. Argitis, K. Misiakos, D. Dimotikali, P. S. Petrou and S. E. Kakabakos, *Biosens. Bioelectron.*, 2002, **17**, 269-278.