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## ELECTRONIC SUPPLEMENTAL INFORMATION

### Functional Polymer Particles via Thiol-Ene and Thiol-Yne Suspension

#### “Click” Polymerization

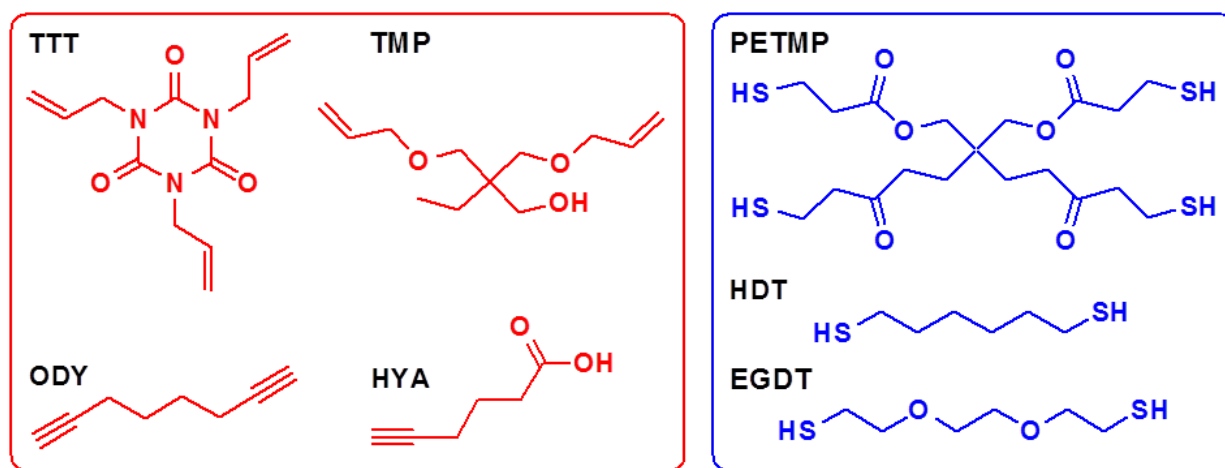
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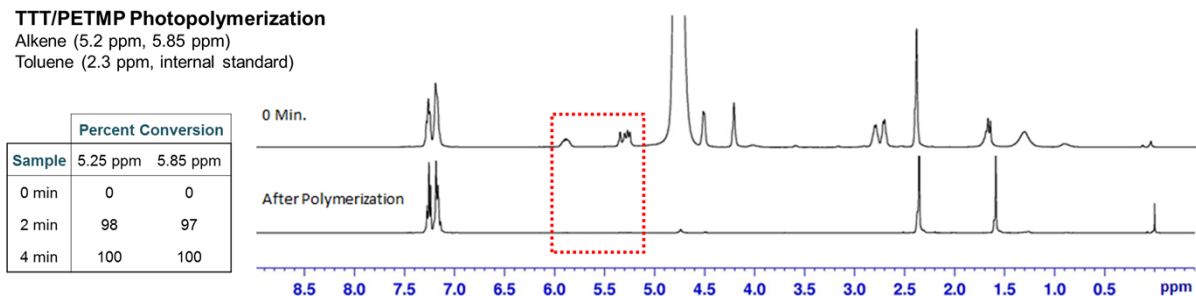
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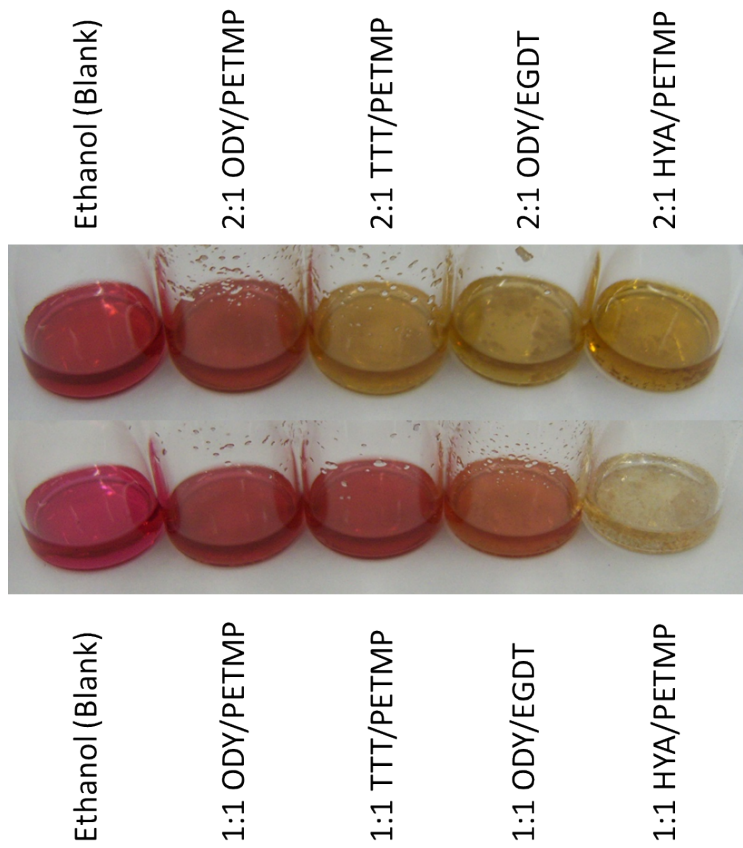
**Figure SI-1.** Chemical structures of alkyne, alkyne, and thiol monomers utilized in the syntheses of polymer networks.



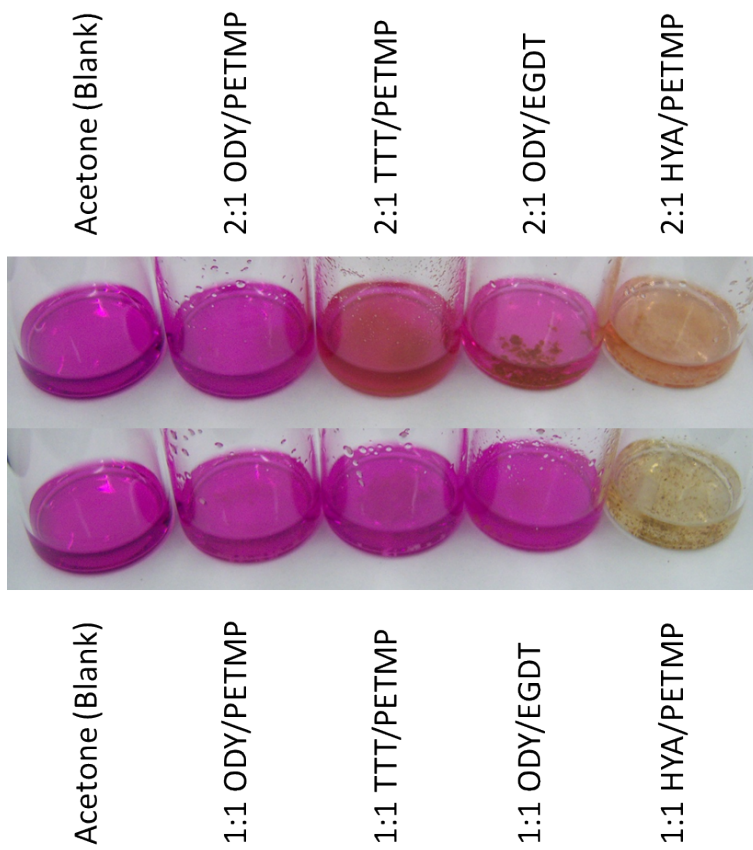
**Figure SI-2.**  $^1\text{H}$  NMR spectra of a TTT/PETMP photopolymerization reaction before and after photopolymerization. Kinetics data is also provided showing that the reaction reaches nearly 100% conversion by 4 minutes of curing under UV light in this water-borne system for the development of polymer particles.

#### *Confirmation of Residual Functionality in Polymer Particles*

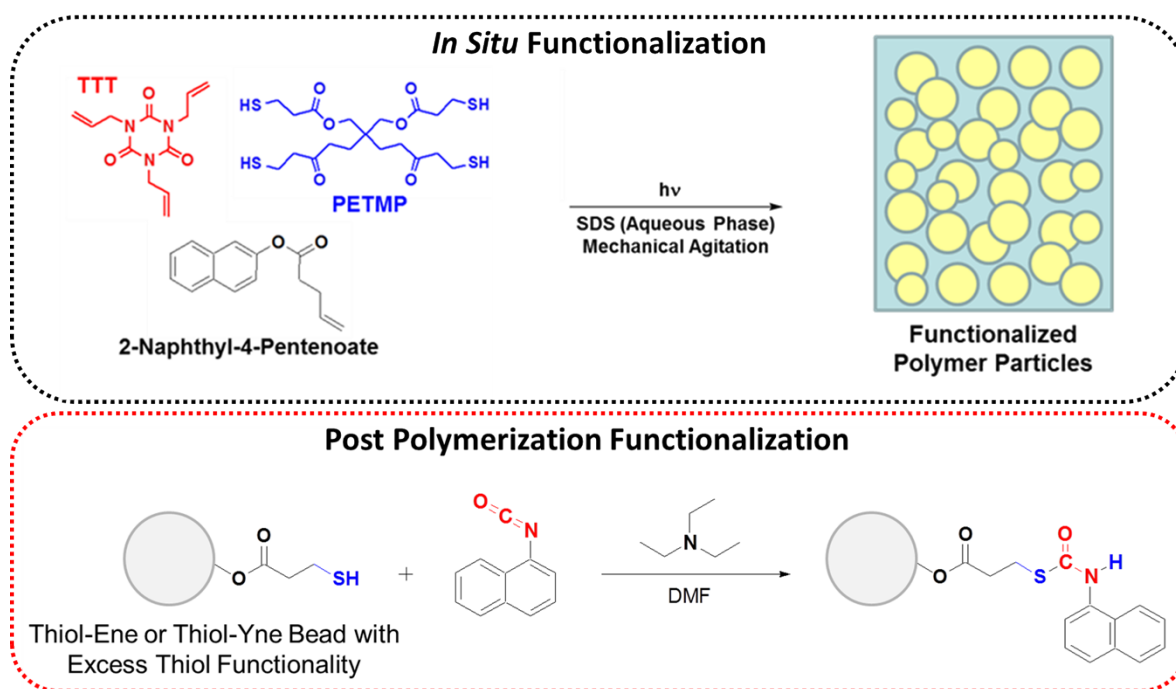
Thiol-ene and thiol-yne particles made using an excess of thiols or enes/yne as presented were examined with colorimetric analyses to demonstrate the availability of desired functionality. Baeyer's reagent was used to test for alkene and alkyne unsaturation. A positive test was the development of a brown solution (Figures SI-3, SI-4). Quantification of excess thiol functionality was examined using the titration of silver nitrate ( $\text{AgNO}_3$ ) and pyridine with sodium hydroxide ( $\text{NaOH}$ ) in the presence of free thiols. Both methods demonstrate the presence of excess functionality within the synthesized polymer particles.



**Figure SI-3.** Results from Baeyer's reagent test for unsaturation of thiol-ene and thiol-yne particles using ethanol as a blank.



**Figure SI-4.** Results from Baeyer's reagent test for unsaturation of thiol-ene and thiol-yne particles using acetone as a blank.



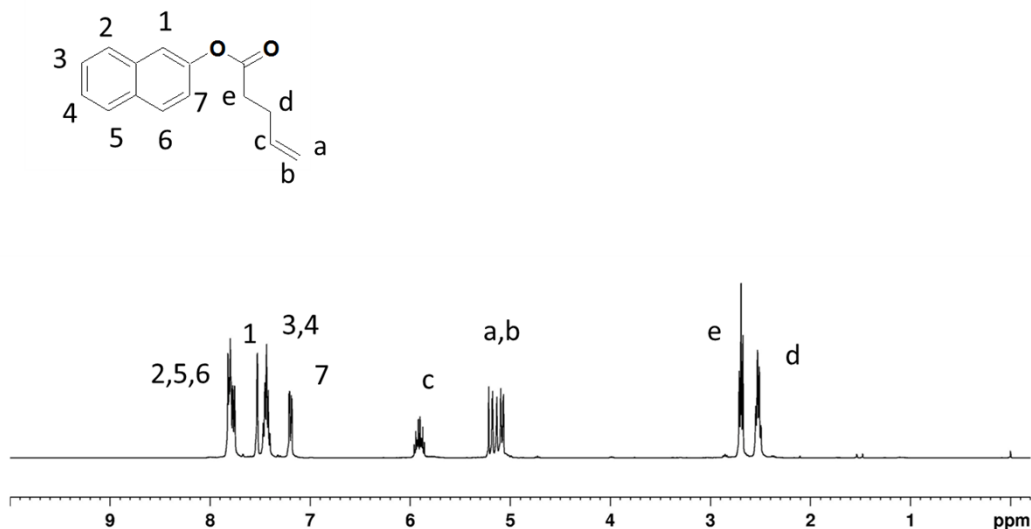
**Figure SI-5.** Comparison of *in situ* and post-polymerization functionalization pathways utilized for the development of functionalized thiol-ene and thiol-yne polymer particles.

#### *Synthesis of 2-Naphthyl-4-Pentenoate*

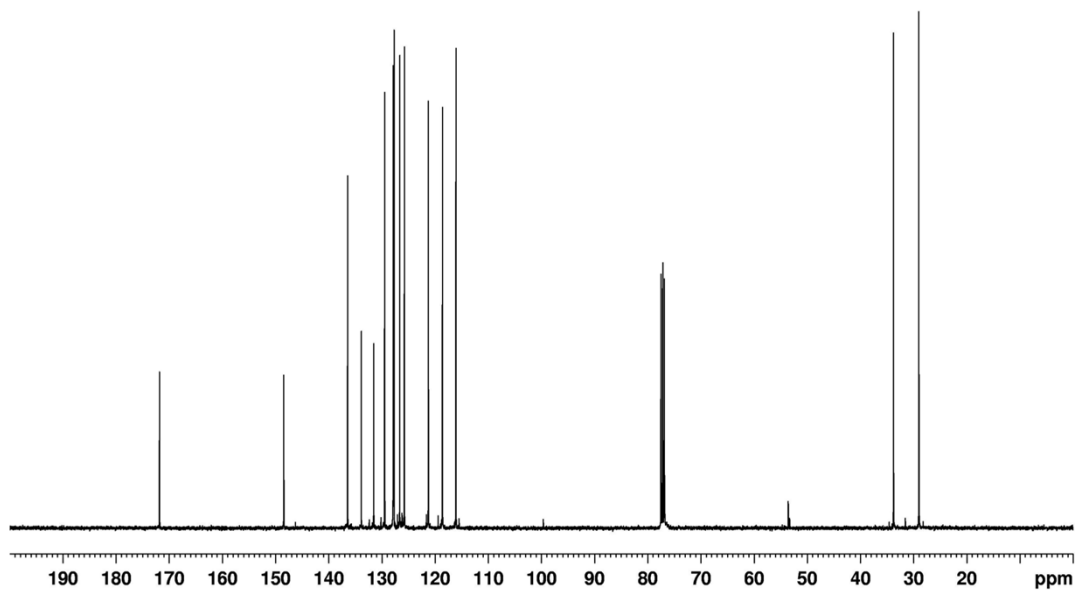
All glassware was dried in an oven overnight. In a 100 ml three neck round bottom flask, 5 g (0.03468 moles) of 2-naphthol was added with a stir bar; the side necks were secured with rubber septa and a 50 ml addition funnel was assembled and sealed with a rubber septum. The assembly was purged with  $N_2$  for 30 minutes, followed by the drop-wise addition of ~30 mL of anhydrous DCM. The reaction solution was sonicated for 30 minutes to facilitate dissolution and then placed in an ice bath, when 5.3 mL (0.03803 moles) of triethyl amine was added. After the triethyl amine was added, the 2-naphthol completely dissolved and the solution turned a dark brown. After stirring for 30 minutes under  $N_2$ , 3.8 mL (0.03442 moles) 4-pentenoyl chloride was added to the addition funnel which also contained ~5 mL of DCM. The 4-pentenoyl chloride was added drop-wise to the stirring solution over the ice bath whereupon an orange precipitate

formed. The reaction was allowed to stir overnight at room temperature. The following day, the solution was vacuum filtered to remove the triethylammonium chloride salt. The filtrate was then transferred to a separatory funnel and washed three times with ~15 mL aliquots of saturated sodium bicarbonate solution followed by three washes with ~15mL aliquots of distilled water. The organic layer was dried over magnesium sulfate for 15 minutes. The product was concentrated by rotary evaporation and became an amber-red oily residue. The reaction product was further dried under vacuum, and became a honey beige solid when placed in a freezer. The product was characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR and UV-visible spectroscopies.

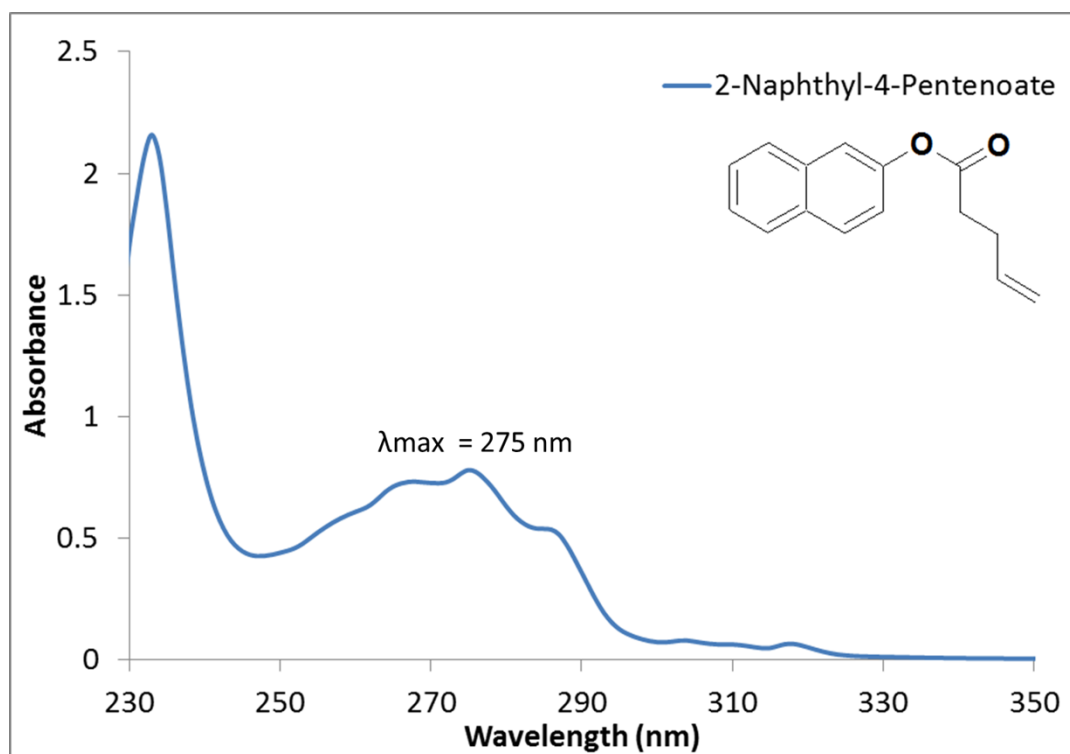
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 7.80 (m, 3H, *Ar* (2, 5, 6)); 7.5 (s, 1H, *Ar* (1)); 7.44 (m, 2H, *Ar* (3, 4)); 7.21 7.19 (m, 1H, *Ar* (7)); 5.90 (m, 1H,  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{COO}-\text{Ar}$ ); 5.14 (m, 2H,  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{COO}-\text{Ar}$ ); 2.71 (t, 2H,  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{COO}-\text{Ar}$ ); 2.53 (q, 2H,  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{COO}-\text{Ar}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) 171.82 ( $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}-\text{OO}-\text{Ar}$ ); 148.51 (*Ar* (1)); 136.49 ( $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{COO}-\text{Ar}$ ); 133.90 (*Ar* (3)); 131.59 (*Ar* (9)); 129.53 (*Ar* (8)); 127.91 (*Ar* (7)); 127.77 (*Ar* (5)); 126.69 (*Ar* (4)); 125.82 (*Ar* (6)); 121.31 (*Ar* (10)); 118.65 (*Ar* (2)); 116.13 ( $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{COO}-\text{Ar}$ ); 33.82 ( $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{COO}-\text{Ar}$ ); 29.05 ( $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{COO}-\text{Ar}$ ). FT-IR ( $\text{cm}^{-1}$ ): 1756  $\text{cm}^{-1}$  (Ester), 1639  $\text{cm}^{-1}$  (Alkene), 1602  $\text{cm}^{-1}$  (Alkene), 1512  $\text{cm}^{-1}$  (Aromatic).



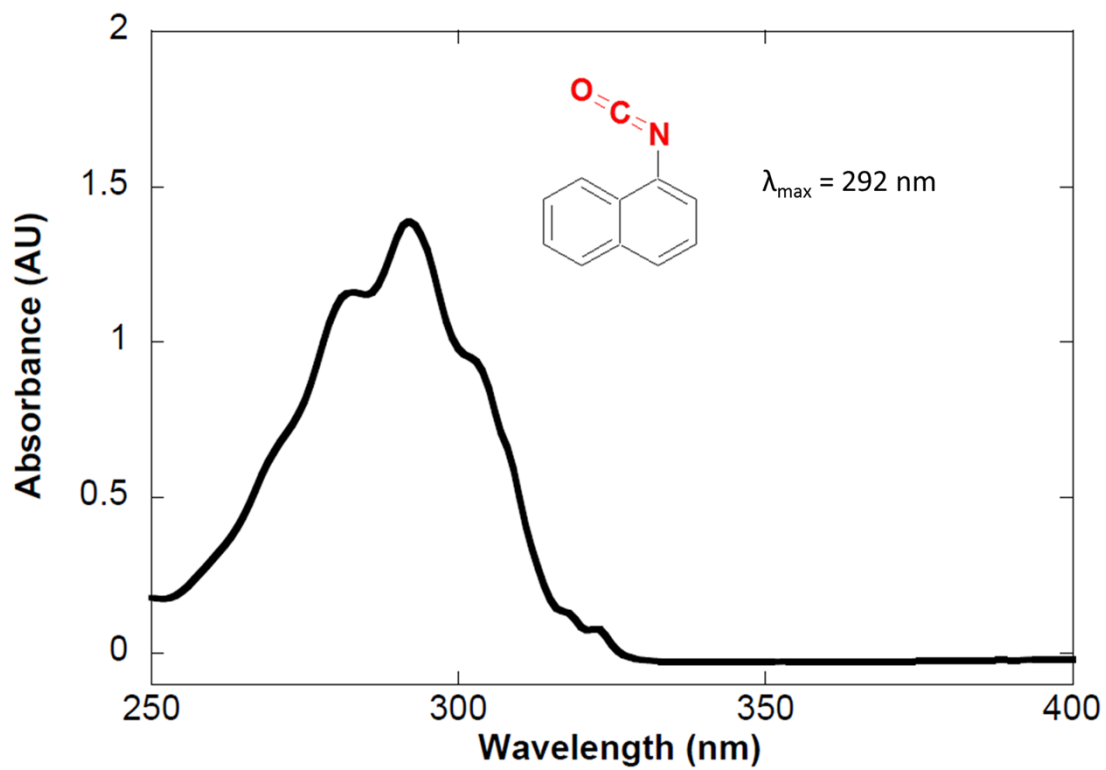
**Figure SI-6.**  $^1\text{H}$  NMR spectra of synthesized 2-naphthyl-4-pentenoate.



**Figure SI-7.**  $^{13}\text{C}$  NMR spectra of synthesized 2-naphthyl-4-pentenoate.



**Figure SI-8.** UV-Vis spectra of 2-naphthyl-4-pentenoate in DCM. The concentration was  $3.508 \times 10^{-5}$  M and the molar absorptivity was calculated as  $19150 \text{ L/mol}\cdot\text{cm}$ .



**Figure SI-9.** UV-Vis spectra of 1-naphthyl isocyanate in dichloromethane. The concentration analyzed was  $8.714 \times 10^{-5} \text{ M}$  and the molar absorptivity was calculated as  $15927.8 \text{ L/mol}\cdot\text{cm}$ .