Electronic Supplementary Information

Photocatalyzed dimethylacrylamide polymerization in aqueous solution using 4-nitrophenylacetylene-modified Cu_2O crystals

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Synthesis of Cu_2O crystals

To synthesize cubes and octahedra, 35.68 and 23.60 mL of deionized water were respectively introduced into two sample vials containing 0.348 g of sodium dodecyl sulfate (SDS) surfactant. The surfactant solutions were kept in a 31 ºC water bath with vigorous stirring. Next, 2.0 and 0.8 mL of 0.1 M $CuCl_2$ solution was added into the vials respectively for cubes and octahedra and stirred for 10 min. Next, 0.72 mL and 0.8 mL of 1.0 M NaOH solution were added to the vials for cubes and octahedra, respectively. The color of the solution would change from colorless to light blue with the formation $Cu(OH)_2$. After stirring for 4 sec, 1.6 mL of 0.1 M $NH_2OH{\cdot}HCl$ and 5.2 mL of 0.1 M $NH_2OH{\cdot}HCl$ solutions were injected into the vials respectively and stirred for 10 sec. Then the solutions were aged for 50 and 25 min, respectively.

To synthesize rhombic dodecahedral cuprous oxide, 27.68 mL of deionized water was introduced into the sample vial containing 0.348 g of SDS surfactant. The solution was kept in a 31 ºC water bath with vigorous stirring. Then 2 mL of 0.1 M $CuCl_2$ solution was added into the vial. Next, 0.72 mL of 1.0 M NaOH solution was added. After stirring for 4 sec, 9.6 mL of 0.1 M $NH_2OH{\cdot}HCl$ solution was introduced and stirred for 20 sec. Finally, the solution was aged for 50 min.

When the reaction time is over, the solutions were centrifuged at 9000 rpm for 10 min using a Universal 320R centrifuge, and washed with 1:1 volume ratio of water and ethanol for 3 times to remove unreacted chemicals and the SDS surfactant, and finally washed with absolute ethanol. After washing, the particles were stored in absolute ethanol.

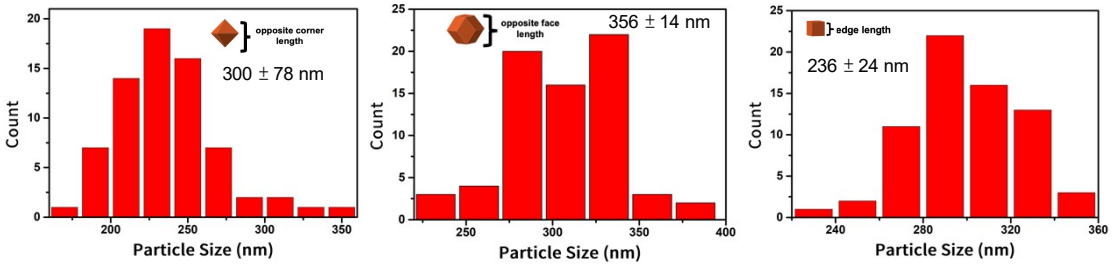


Fig. S1 Size distribution histograms of the synthesized Cu_2O crystals.

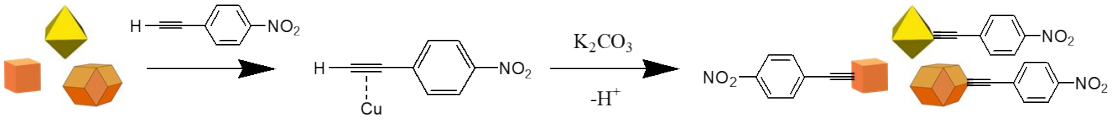


Fig. S2 Illustration of 4-NA modification on Cu_2O crystals.

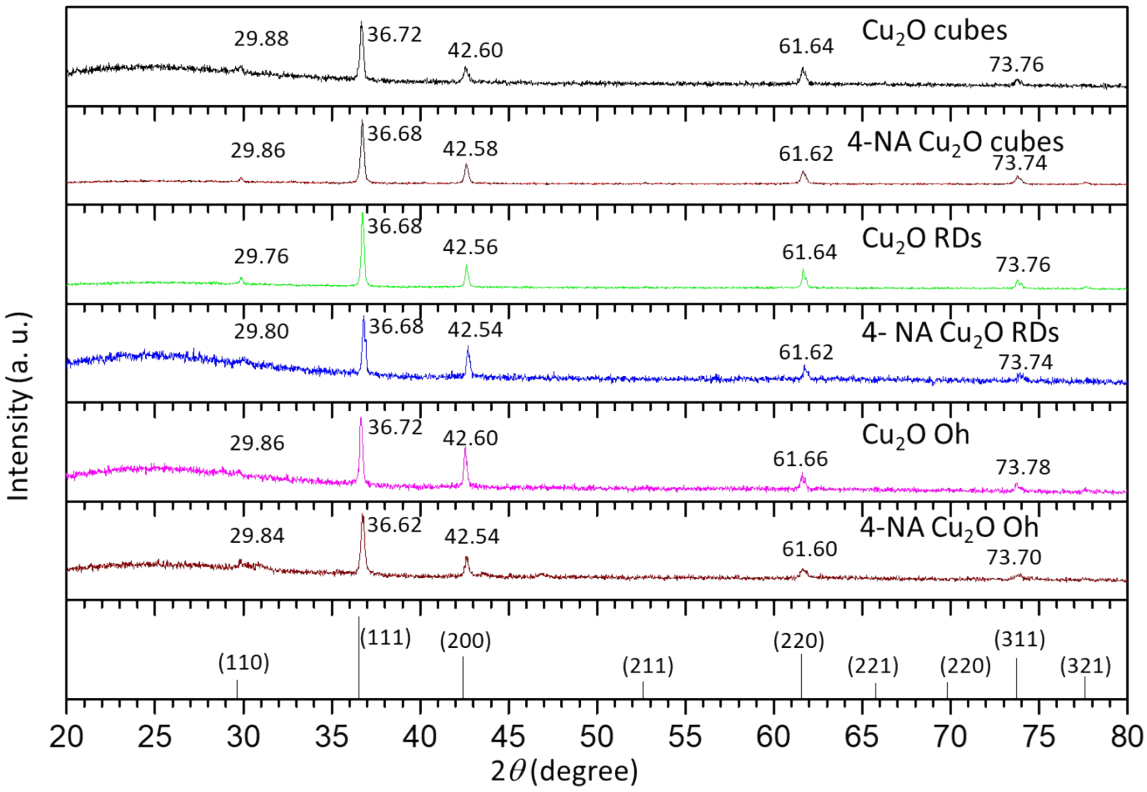


Fig. S3 XRD patterns of the pristine Cu_2O and 4-NA-modified Cu_2O crystals. A standard pattern of Cu_2O is included.

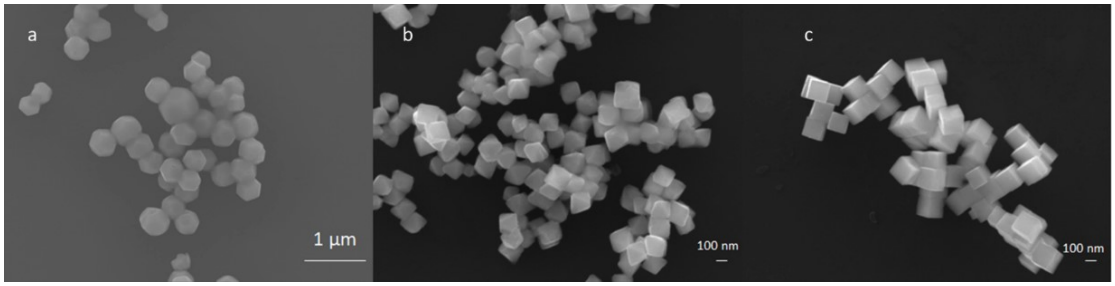


Fig. S4 SEM images of the 4-NA-functionalized Cu_2O (a) rhombic dodecahedra, (b) octahedra, and (c) cubes.

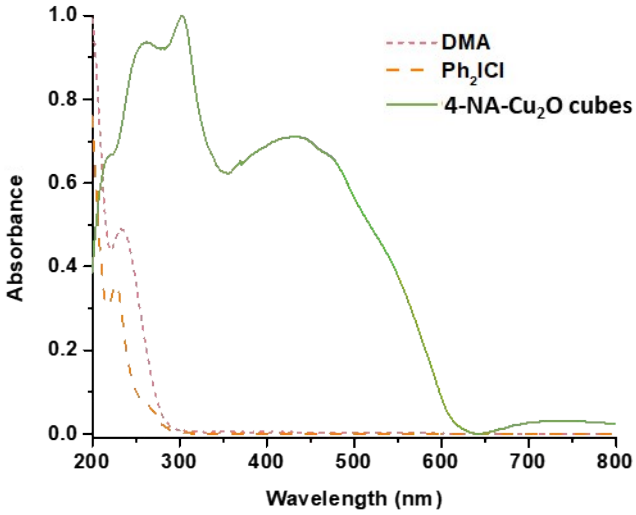


Fig. S5 UV–vis absorption spectra of DMA, Ph_2ICl, and 4-NA-modified Cu_2O cubes.

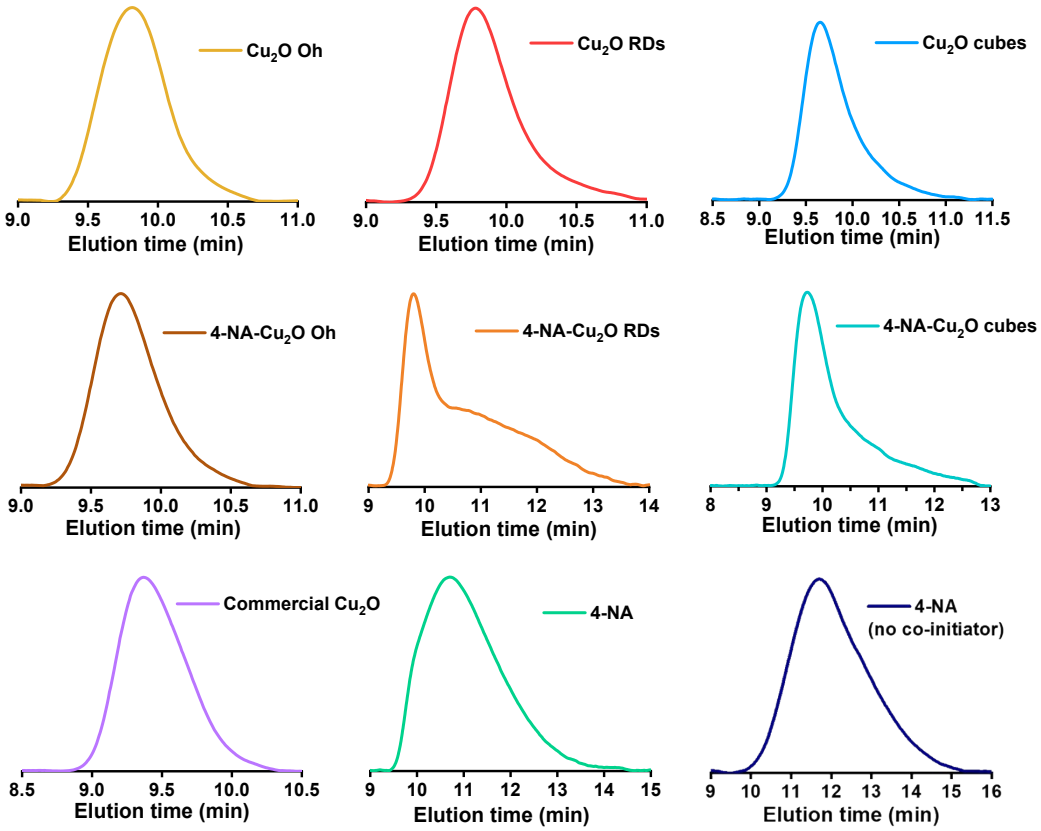


Fig. S6 GPC chromatograms of the produced PDMA using different Cu_2O photocatalysts.

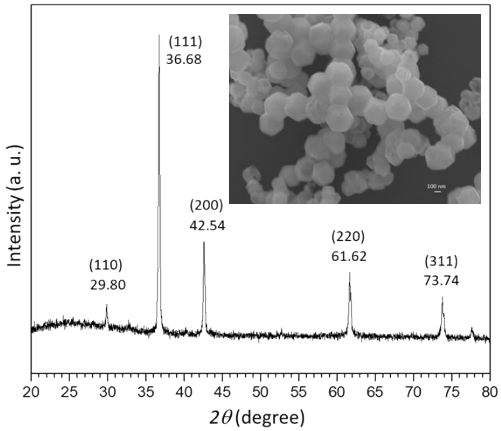


Fig. S7 XRD pattern and SEM image of 4-NA-modified Cu_2O rhombic dodecahedra after the polymerization reaction.

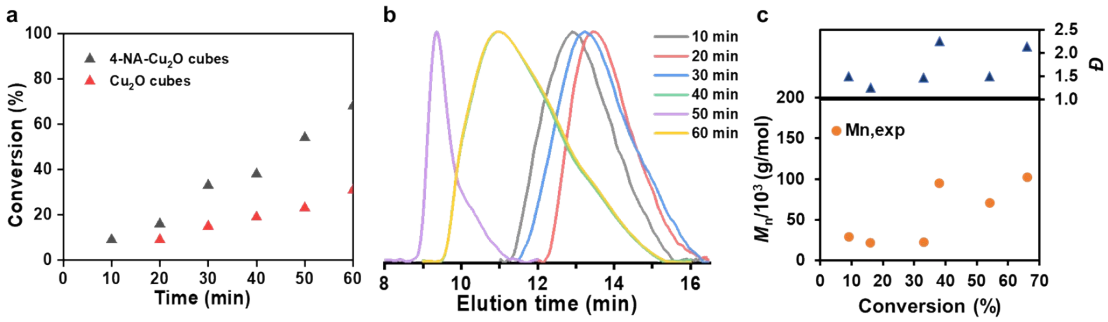


Fig. S8 (a) Extent of DMA conversion versus the reaction time using pristine and 4-NA-modified Cu_2O cubes as the photocatalysts with light irradiation from 420 nm mercury lamps. (b) GPC chromatograms of the produced PDMA using 4-NA-modified Cu_2O cubes. (c) Evolution of M_n and $Đ$ versus monomer conversion using 4-NA-modified Cu_2O cubes from the reaction in (a).

Table S1 Conditions used for the scavenger experiment

Catalyst	DI water	Monomer	Co-initiator	Scavenger	Time	Conversion
4-NA-Cu_2O cubes 5.3 mg	1 mL	DMA 1 g	Ph_2ICl 15 mg	benzoquinone (e^-) 30 mg	1 h	no reaction
4-NA-Cu_2O cubes 4.8 mg	1 mL	DMA 1 g	Ph_2ICl 15 mg	$Na_2C_2O_4$ (h^+) 30 mg	1 h	55%

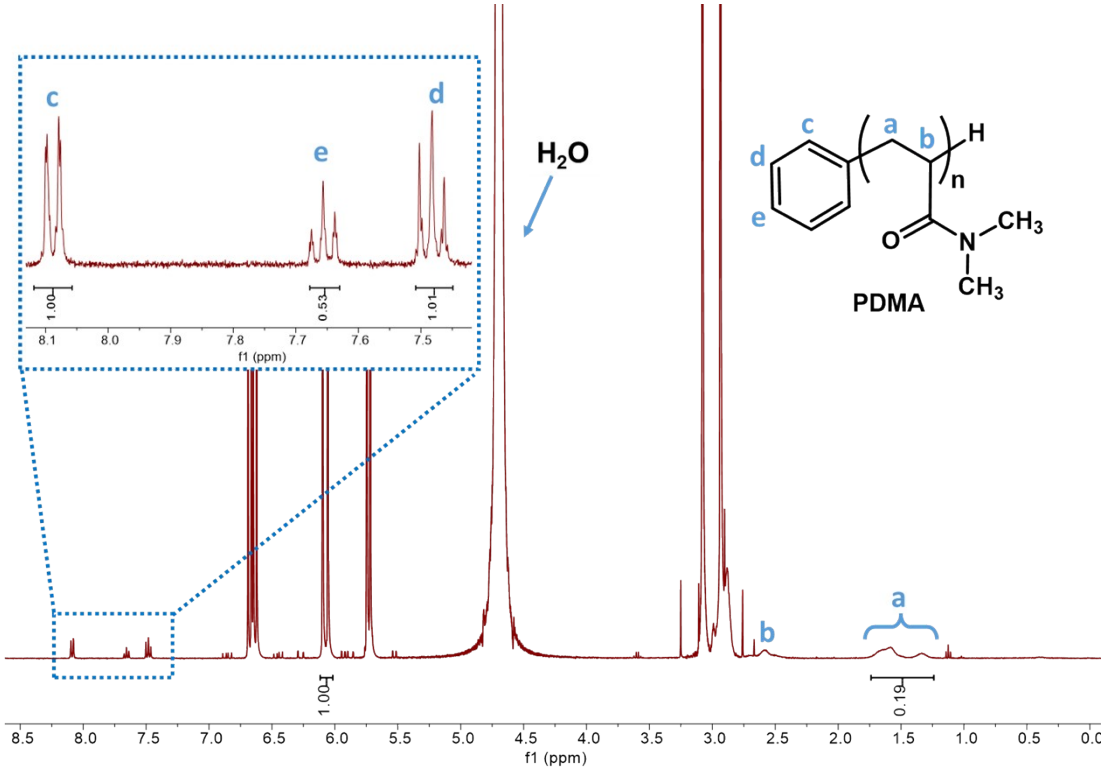


Fig. S9 ^{1}H-NMR spectrum of the sample for MALDI-TOF mass spectrometry analysis.

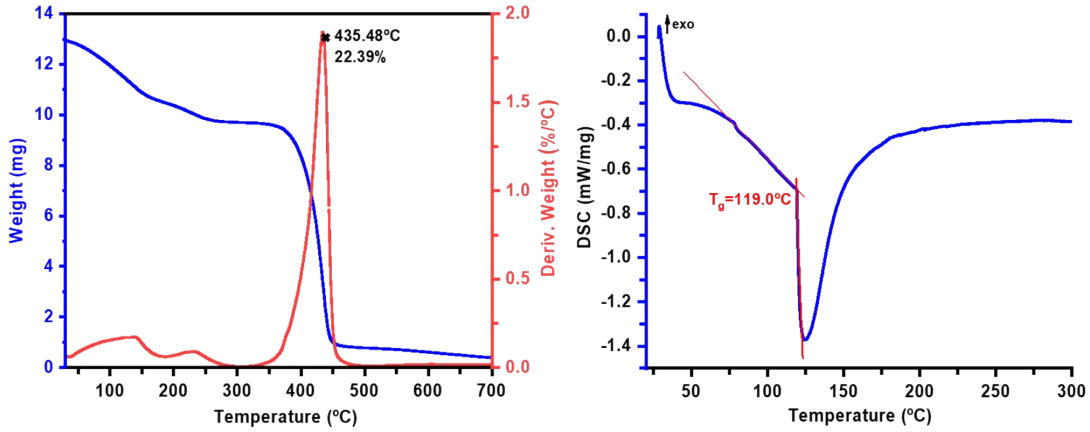


Fig. S10 Thermogravimetric analysis and differential scanning calorimetry of the synthesized PDMA.

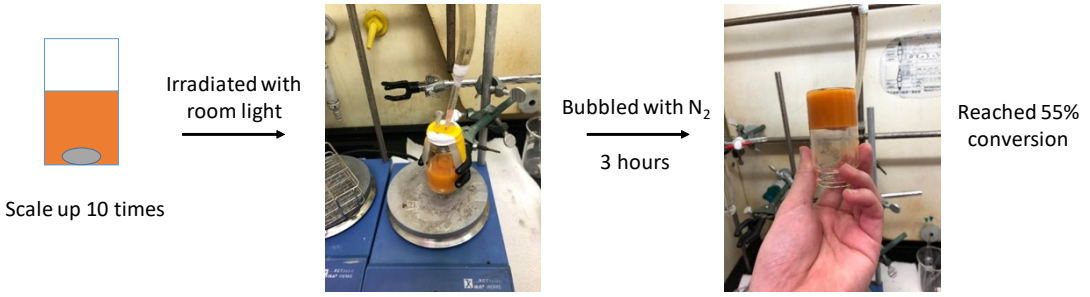


Fig. S11 Scaled up photopolymerization process using 4-NA-modified Cu_2O cubes as the catalyst.

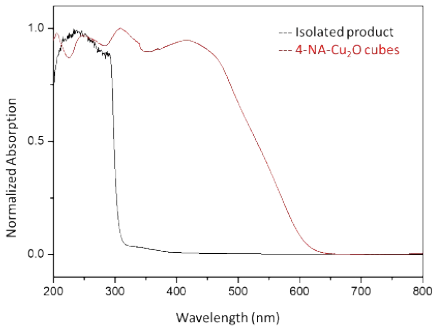
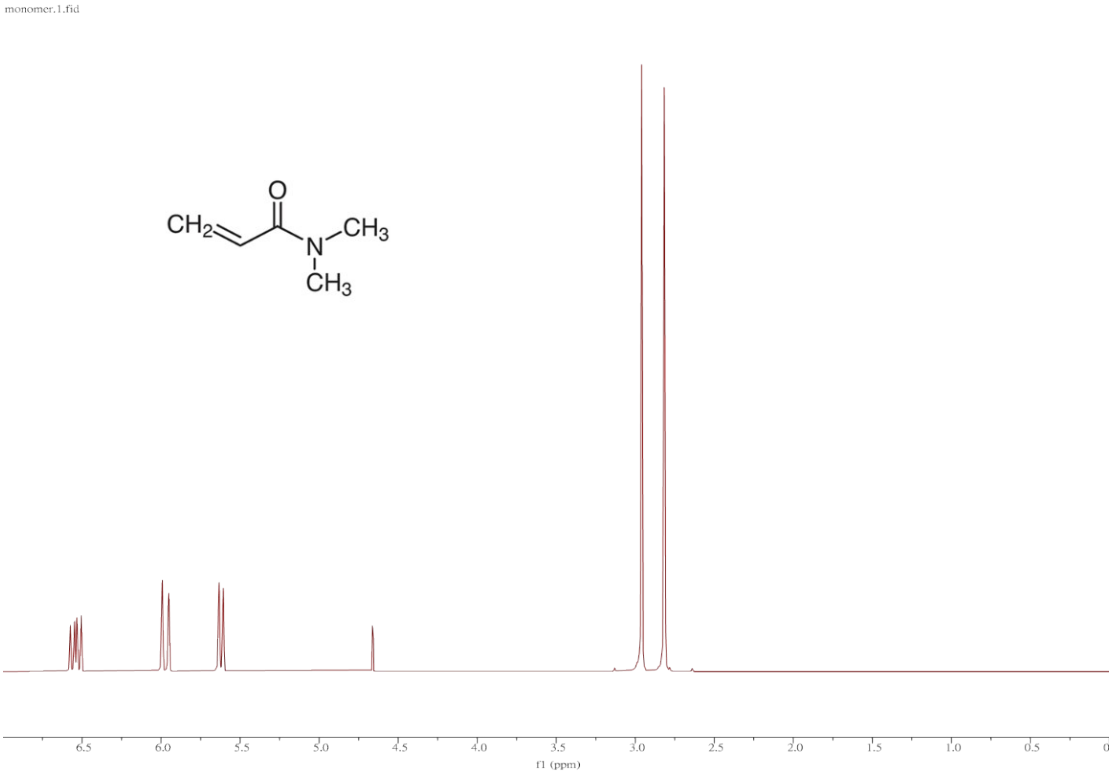
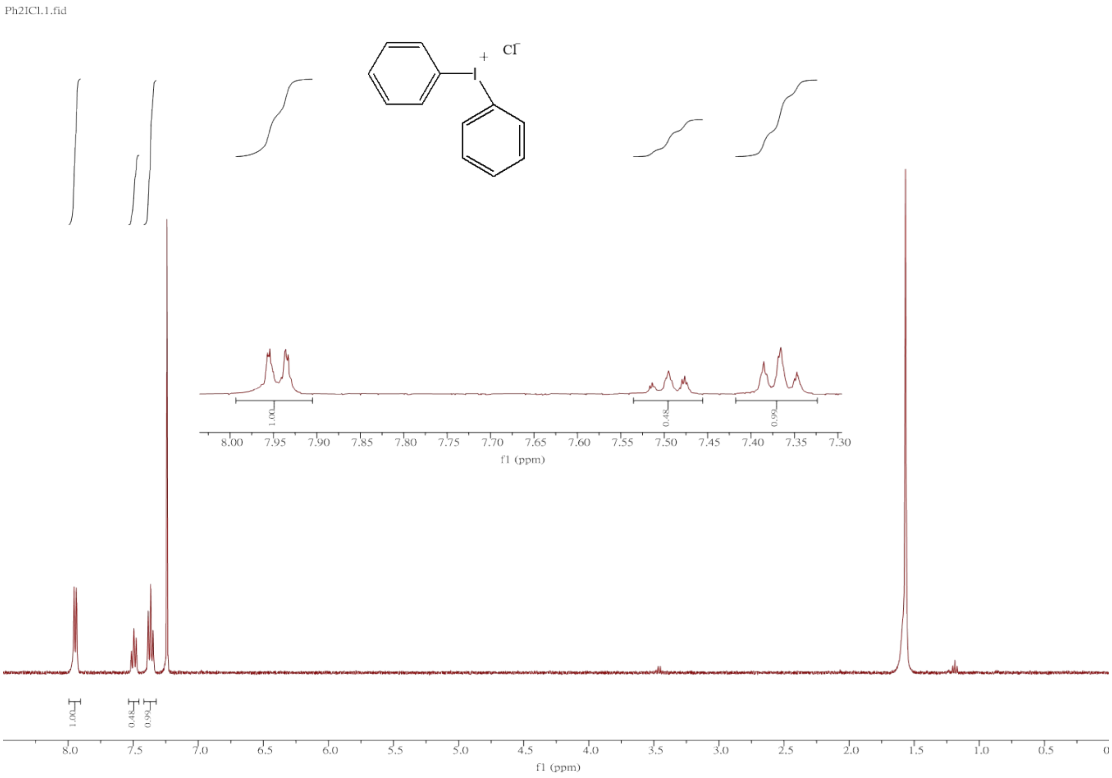


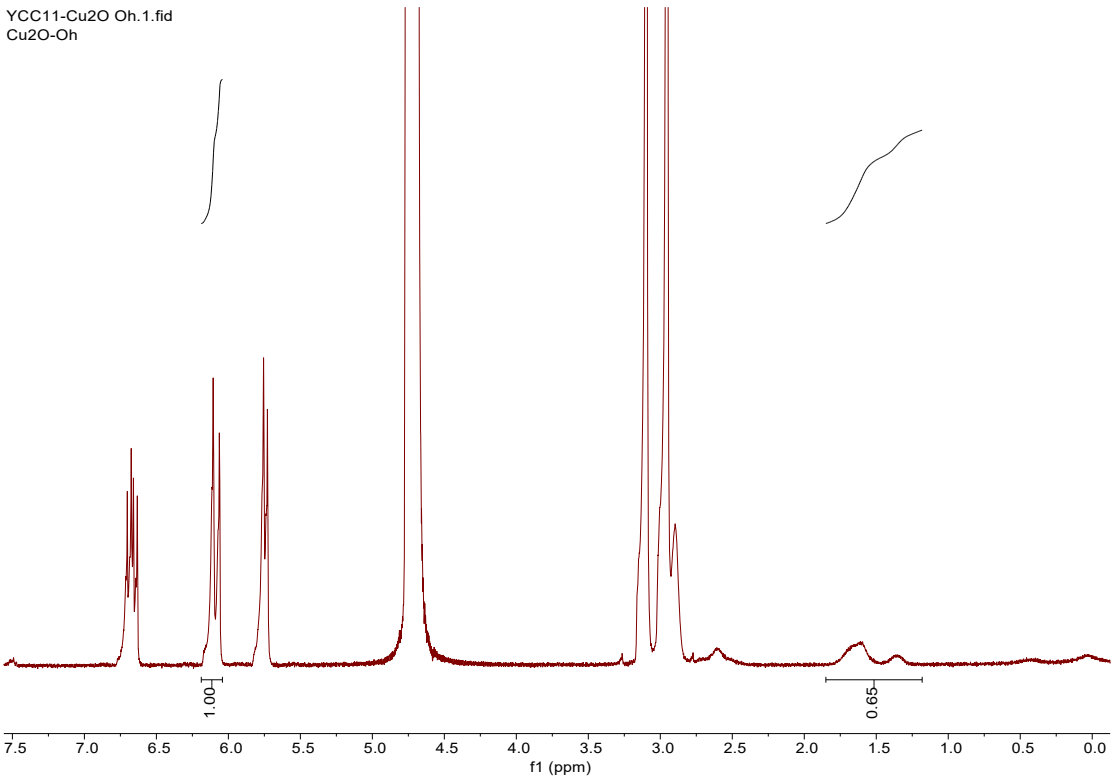
Fig. S12 UV–vis absorption spectra of the isolated polymer and 4-NA-modified Cu_2O cubes. The polymer is clearly separated from the orange-colored Cu_2O crystals.



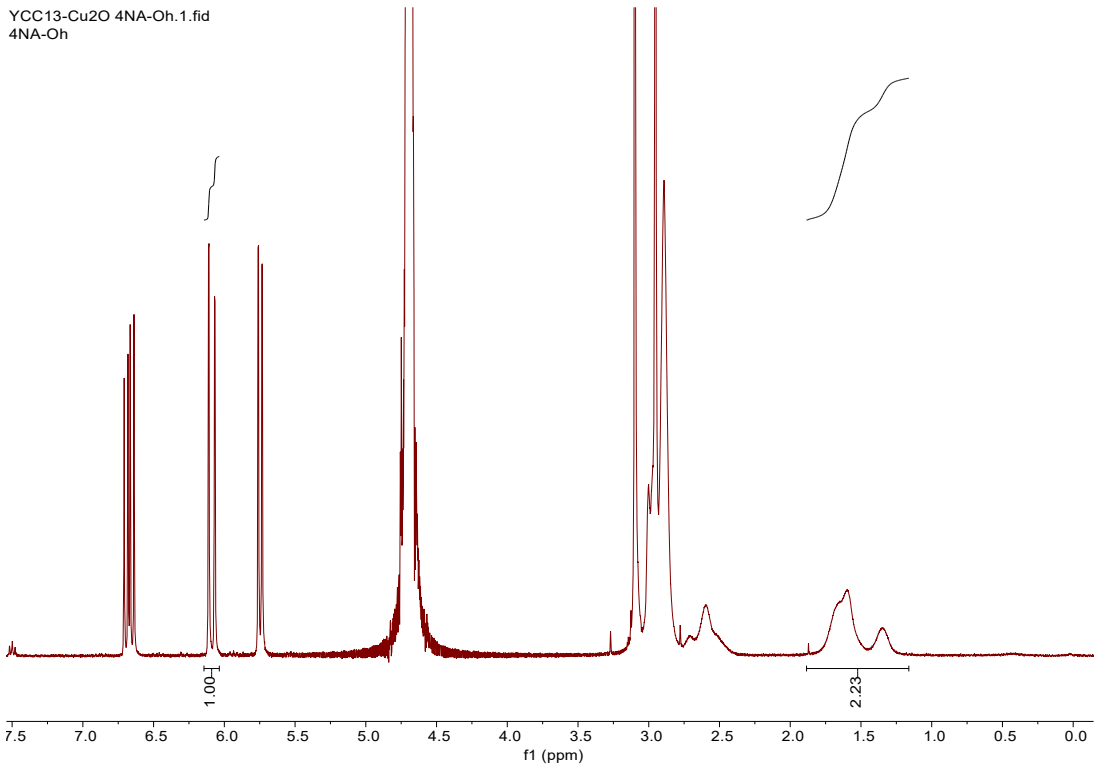
Spectrum S1 ^{1}H-NMR spectrum of the DMA monomer.



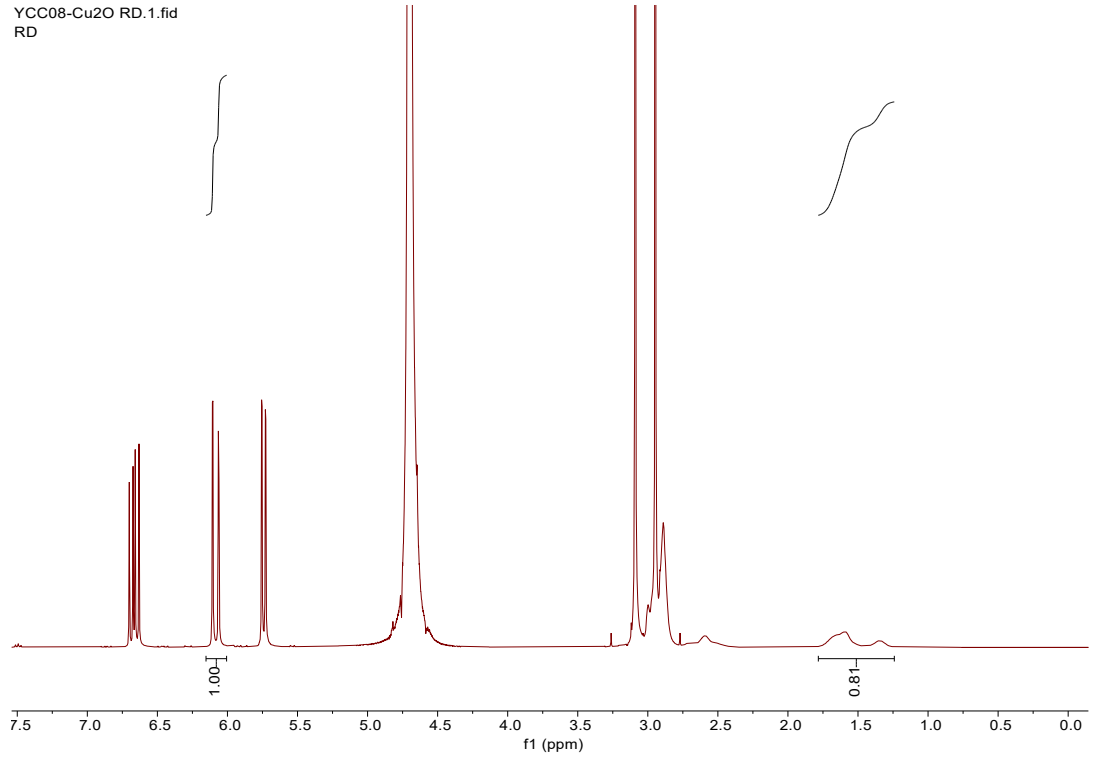
Spectrum S2 ^{1}H-NMR spectrum of the Ph_2ICl co-initiator.



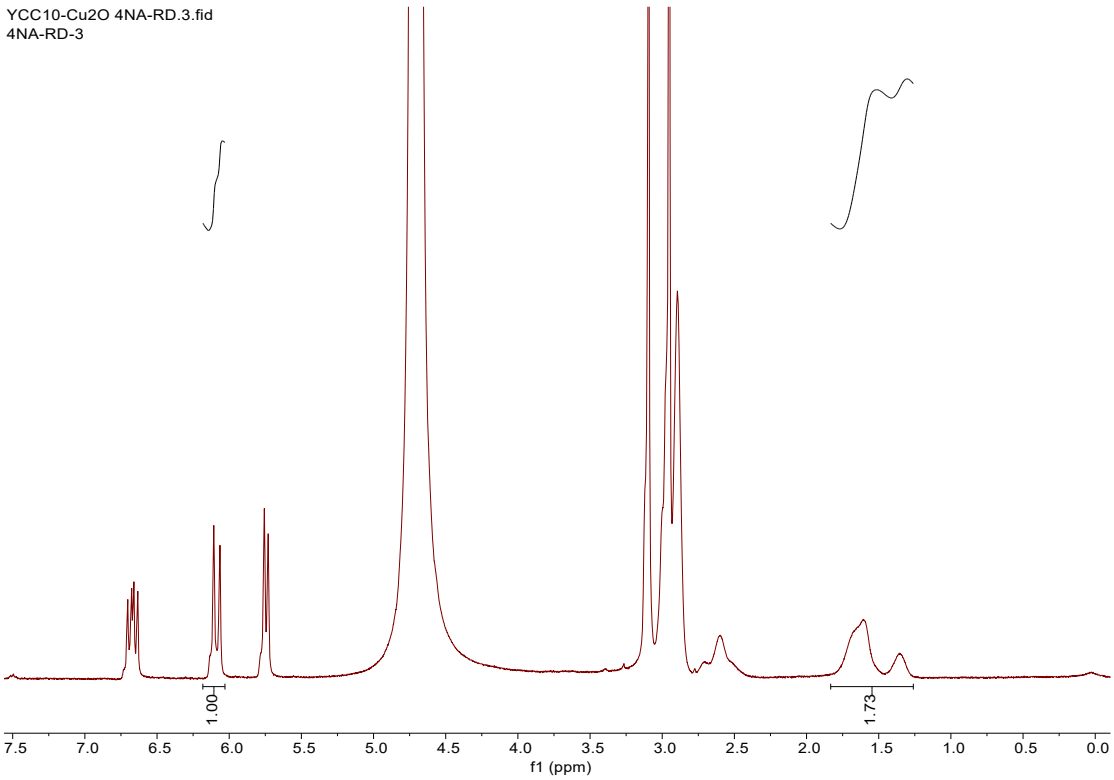
Spectrum S3 ^{1}H-NMR spectrum of DMA polymerization using Cu_2O octahedra as the photocatalyst.



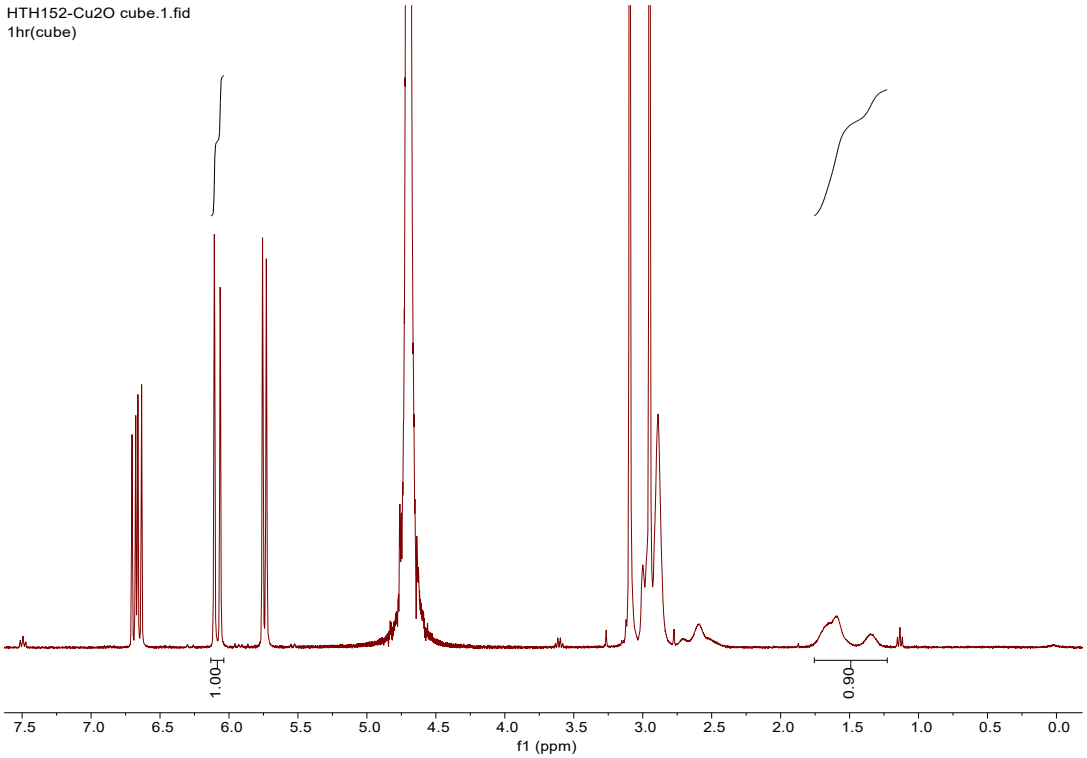
Spectrum S4 ^{1}H-NMR spectrum of DMA polymerization using 4-NA-modified Cu_2O octahedra as the photocatalyst.



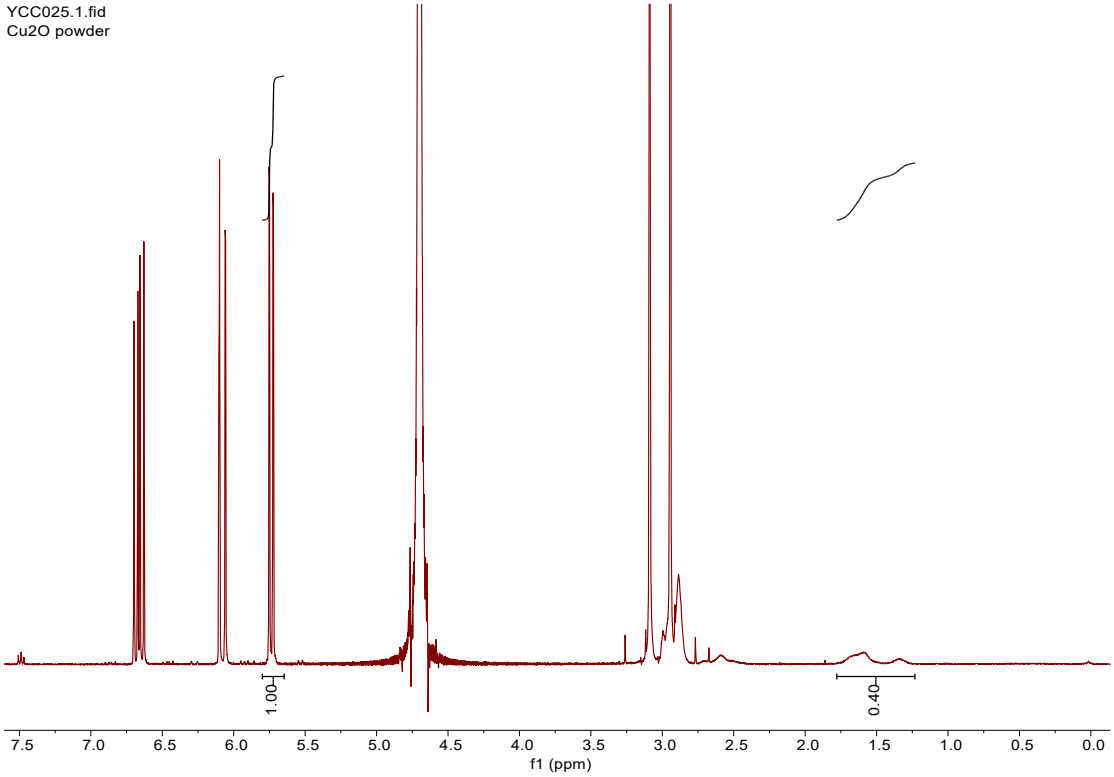
Spectrum S5 ^{1}H-NMR spectrum of DMA polymerization using Cu_2O rhombic dodecahedra as the photocatalyst.



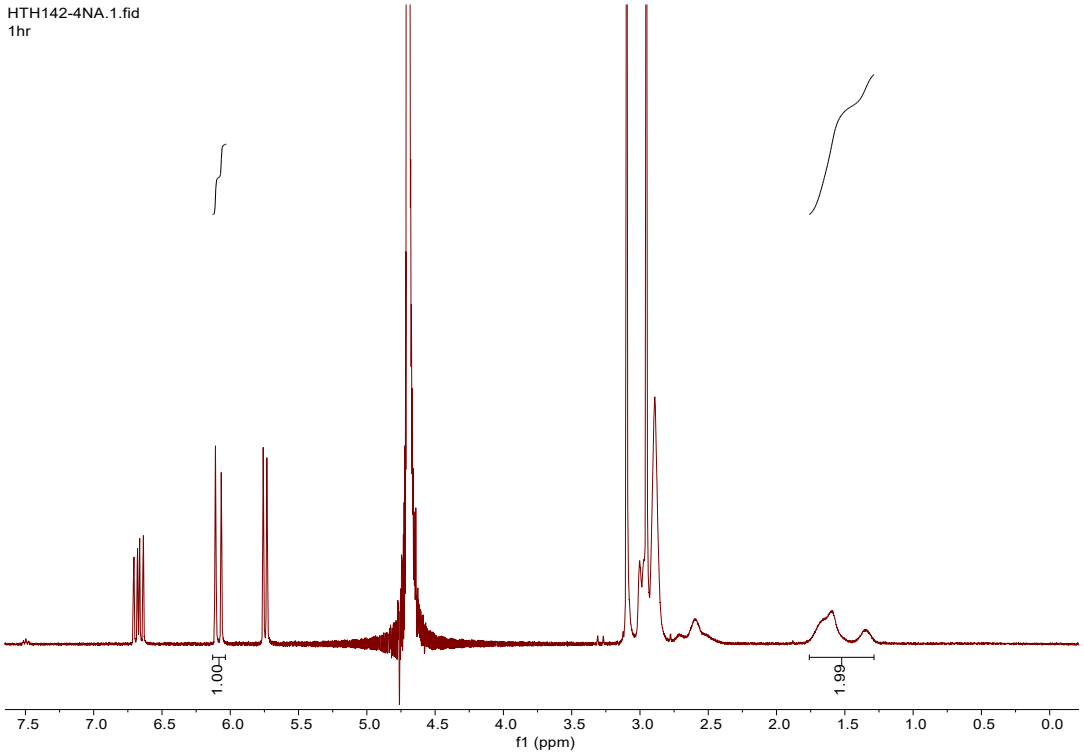
Spectrum S6 ^{1}H-NMR spectrum of DMA polymerization using 4-NA-modified Cu_2O rhombic dodecahedra as the photocatalyst.



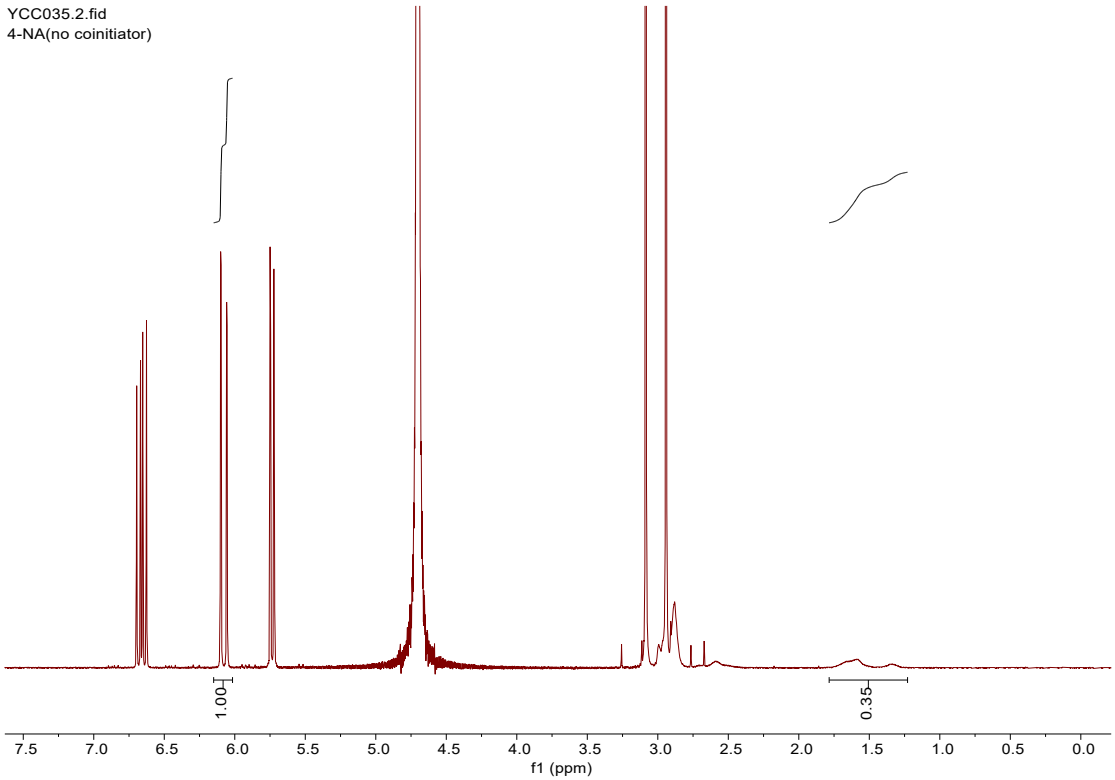
Spectrum S7 ^{1}H-NMR spectrum of DMA polymerization using Cu_2O cubes as the photocatalyst.



Spectrum S8 ^{1}H-NMR spectrum of DMA polymerization using commercial Cu_2O powder as the photocatalyst.



Spectrum S9 ^{1}H-NMR spectrum of DMA polymerization in the presence of free 4-nitrophenylacetylene.



Spectrum S10 ^{1}H-NMR spectrum of DMA polymerization in the presence of 4-NA only without Ph_2ICl.