Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Cu(II) Metal-Organic Framework as Recyclable Catalyst for ARGET ATRP

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Experimental Section

Materials. All the reagents, catalyst and solvents were used as received unless otherwise noted. Benzyl methacrylate (BzMA, Alfar Aesar, 98%), styrene (St, Acros, 99%), 4-vinylpyridine (4VP, Sigma Aldrich, ≥95 %) and isoprene (Sigma Aldrich, >99 %) were filtered through a basic aluminum oxide (Brockman type I, Acros, 50-200 μm, 60 Å) column to remove the inhibitor. Copper(II) acetate monohydrate (Roth, ≥98%), $CuBr_2$ (Alfa Aesar, 99%), diazabicyclo[2.2.2]octane (DABCO, Alfa Aesar, 97%), *N*,*N*-dimethylformamide (DMF, VWR, ACS), 1,4-Dioxane (Acros, 99.5%, extra dry over molecular sieve), ethyl α-bromoisobutyrate (EBIB, Sigma Aldrich, 98%), 1,1,4,7,7-Pentamethyldiethylentriamin (PMDETA, Acros, >98%), 1,4-terephthalic acid (H_2bdc, Alfa Aesar, >98%) and tetrahydrofuran (THF, VWR, HPLC grade).

Fabrication of $Cu_2(bdc)_2(dabco)$ (Cu(II) MOF). $Cu_2(bdc)_2(dabco)$ was employed as the Cu(II) MOF to catalyze the polymerization process demonstrated in this study. The Cu(II) MOF were prepared under solvothermal condition, and after removing of the included guest molecules, the as synthesized MOF was characterized with PXRD (Figure S1a), nitrogen adsorption and desorption measurements (Figure S1b) and FESEM (Figure S2). The obtained PXRD pattern shows good accordance with the literature, indicating the accurate microstructure formed by the applied metallic ion and organic ligands with in specific ratio. The specific surface area and the pore volume were calculated as 2280 m^2/g and 0.91 cc/g, respectively *via* the BET method. The property of the ultrahigh specific surface area reveals the advantage of the given Cu(II) MOF as a catalyst for polymerization. Following, the crystal structure with uniform particle size around hundred nm can be observed in the FESEM image.

Cu(II) MOF-Mediated ARGET ATRP. The typical polymerization of BzMA was as follows:[1] $[BzMA]_0/[I]_0/[RA]_0$ = 180:1:2, 50 °C for 6 hr; $[St]_0/[I]_0/[RA]_0$ = 110:1:5, 110 °C for 12 hr; $[Isoprene]_0/[I]_0/[RA]_0$ = 805:1:5, 120 °C for 72 hr; $[4VP]_0/[I]_0/[RA]_0$ = 370:1:5, 60 °C for 9 hr. In a glass vial Cu(II) MOF (0.8 g) was added to the bulk solution of BzMA (13 g). Ethyl α-bromoisobutyrate (EBIB) (0.078 g) and DABCO (0.09 g) were added under stirring. The polymerization was performed at

50 ºC for 12 hours under Argon. The reaction was terminated by THF, the solution was centrifuged, the solution was precipitated in methanol and the solid product dried under vacuum. The PS was synthesized by the same procedure with the condition:[2] 110 ºC for 12 hr; $[St]_0/[EBIB]_0/[DABCO]_0$ = *110:1:5*. Regarding to the polymerization of isoprene[3] and 4-vinylpyridine,[4] the condition was adjusted based on reference and the applied parameter is shown below: $[isoprene]_0/[EBIB]_0/[DABCO]_0$ = *805:1:12* (120 °C, 72 hr) and $[4VP]_0/[EBIB]_0/[DABCO]_0$ = *370:1:5* (60 °C, 9 hr). For the kinetic analysis, after the reaction was terminated by THF at specific time, the solution was centrifuged and the clear suspension was filtered for GC-MS to evaluate the monomer conversion.

Chain Extension with Isobornyl Methacrylate (IBMA). The homopolymers obtained from Cu(II) MOF-mediated ARGET ATRP were utilized as macroinitiators for the block copolymer comprised with IBMA. $[PBzMA\text{-}Br/\ PS\text{-}Br]_0/[IBMA]_0/[K]_0/[L]_0/[RA]_0$ = 1:400:0.4:1:2.4, 50 °C for 24 hr; $[PI\text{-}Br]_0/[IBMA]_0/[K]_0/[L]_0/[RA]_0$ = 1:1100:1.1:2.75:6.6, in 50 vol% dioxane at 50 °C for 24 hr; $[P4VP\text{-}Br]_0/[IBMA]_0/[K]_0/[L]_0/[RA]_0$ = 1:450:0.45:1.13:2.7, in 50 vol% dioxane at 50 °C for 24 hr.

Reference ARGET ATRP Polymerization. The typical polymerization of BzMA and styrene (St) was as follows. In a glass vial $CuBr_2$ (1.83 mg) and PMDETA (2.9 mg) was added to the bulk solution of BzMA (3.0 g) under stirring. Subsequently, ethyl α-bromoisobutyrate (EBIB) (0.04 g) and DABCO (0.43 mg) was introduced in the solution. The polymerization was performed at 50 ºC for 12 hours under Argon. The reaction was terminated by THF, passed through a neutral aluminum oxide column, precipitated in methanol and the product dried under vacuum. The PS was synthesized by the same procedure with the condition: 110 °C for 12 hr; $[St]_0/[EBIB]_0/[CuBr_2]_0/[PMDETA]_0/[DABCO]_0$ = 245:1:1:2:0.45.

Recycling of Cu(II) MOF in Cascade ARGET ATRP of Benzyl Methacrylate and Styrene. The given amount of Cu(II) MOF (0.1 g) was utilized to polymerize BzMA and styrene alternatively referring to the reaction condition in Cu(II) mediated-ARGET ATRP, and the polymerization was three times repeated for each monomer. The conversion of the given cycle was determined by GC-MS, and yield was measured by the weight of polymer product. After every polymerization, the Cu(II) MOF was washed *via* THF once a day for 3 days, dried under vacuum , and then the weight increment was recorded before the next reaction.

Characterization. The microstructure of the Cu(II) MOF was characterized by a Bruker D8 powder X-ray diffractometer (PXRD) using Cu-Kα radiation (λ = 0.154 nm) and a scintillation counter (KeveX Detector). Nitrogen adsorption and desorption experiments were performed using Quantachrome Quadrasorb at the temperature of liquid nitrogen, and the results were analyzed on the basis of the Brunauer, Emmett and Teller (BET) method. All the samples were degassed at 110 °C for 20 hours before measurements and analyzed with the QuadraWin software (version 5.05). The observations of field-emission scanning electron microscopy (FESEM) were performed on a LEO 1550 Gemini instrument. Samples were located on carbon coated aluminum holder and measured without any additional coating. The UV-vis spectra were recorded on UV-2501PC/2550 (Shimadzu Corporation, Japan) at room temperature. The remnant of copper in polymer products were determined by inductively coupled plasma optical emission spectrophotometer (ICP-OES), and the measurement was performed on a Perkin Elmer Optima 8000, calibrating with standard solutions. Gas chromatography-mass spectrometry (GC-MS) analysis was performed using an Agilent Technologies 5975 gas chromatograph equipped with a MS detector and a capillary column (HP-5MS, 30 m, 0.25 mm, 0.25 micron) for conversion determination. All ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy were recorded on a Bruker Ascend 400 NMR spectrometer in chloroform-*d* at a concentration of 1 wt% for proton, and 10 wt% for carbon analysis. Size exclusion chromatography (SEC) for P4VP was conducted in NMP (Fluka, GC grade) with 0.05 mol L^{-1} LiBr and BSME as internal standard at 70 °C using a column system by PSS GRAM 100/1000 column (8 x 300 mm, 7 μm particle size) with a PSS GRAM precolumn (8 x 50 mm) and a Shodex RI-71 detector and a PS calibration with standards from PSS. SEC for PBzMA, PS, PI and PIBMA copolymers was conducted in THF with toluene as internal standard at 25 °C using a column system by PSS SDV 1000/10000/1000000 column (8 x 300 mm, 5 µm particle size) with a PSS SDV precolumn (8 x 50 mm), a SECcurity RI detector and a SECcurity UV/VIS detector and a calibration with PS standards from PSS. The polydispersity defined as $Đ = M_w/M_n$. The theoretical number averaged molecular mass $M_{n,\text{theo}}$ was calculated according to the equation: ([monomer]$_0$/[I]$_0$) x conversion.

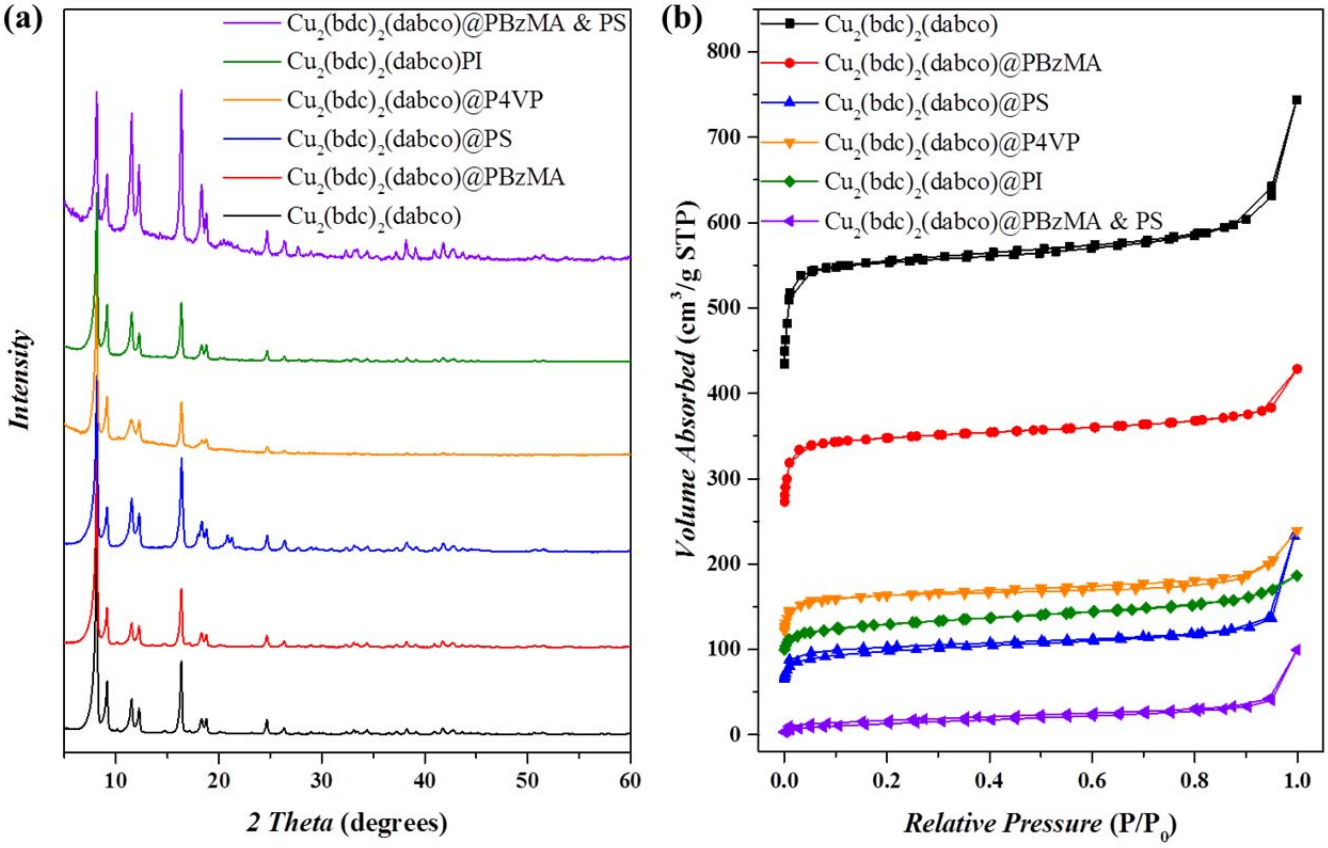

Figure S1. Corresponding (a) PXRD profiles and (b) N_2 adsorption-desorption isotherm of $Cu_2(bdc)_2(dabco)$ before and after polymerization of various monomers. The calculated specific surface area and pore volume is 2280 m^2/g and 0.91 cc/g for $Cu_2(bdc)_2(dabco)$, 1400 m^2/g and 0.55 cc/g after polymerization with PBzMA, 370 m^2/g and 0.20 cc/g after polymerization with PS, 640 m^2/g and 0.28 cc/g after polymerization with P4VP, 490 m^2/g and 0.24 cc/g after polymerization with PI, and 40 m^2/g and 0.15 cc/g for PBzMA and PS cascade polymerization after 6 cycles.

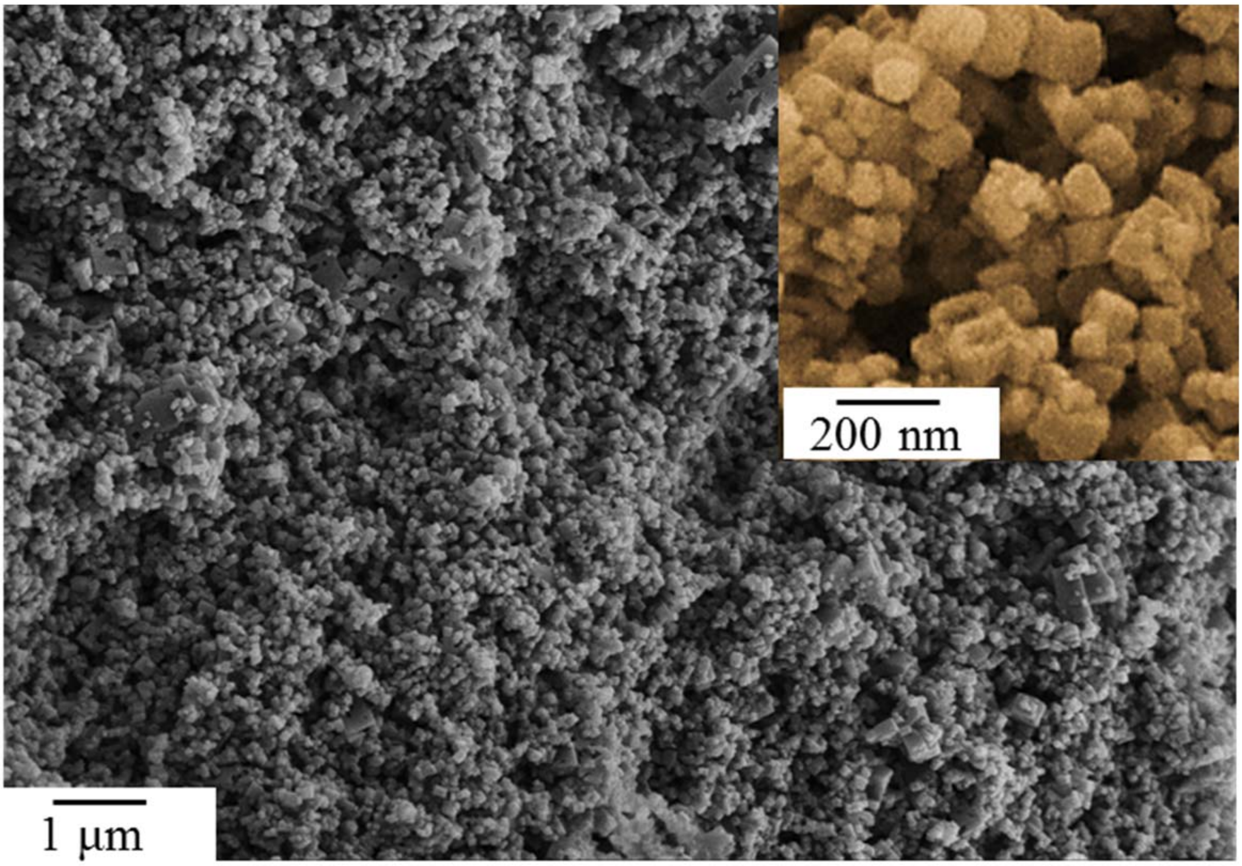

Figure S2. FESEM micrograph of the as fabricated $Cu_2(bdc)_2(dabco)$.

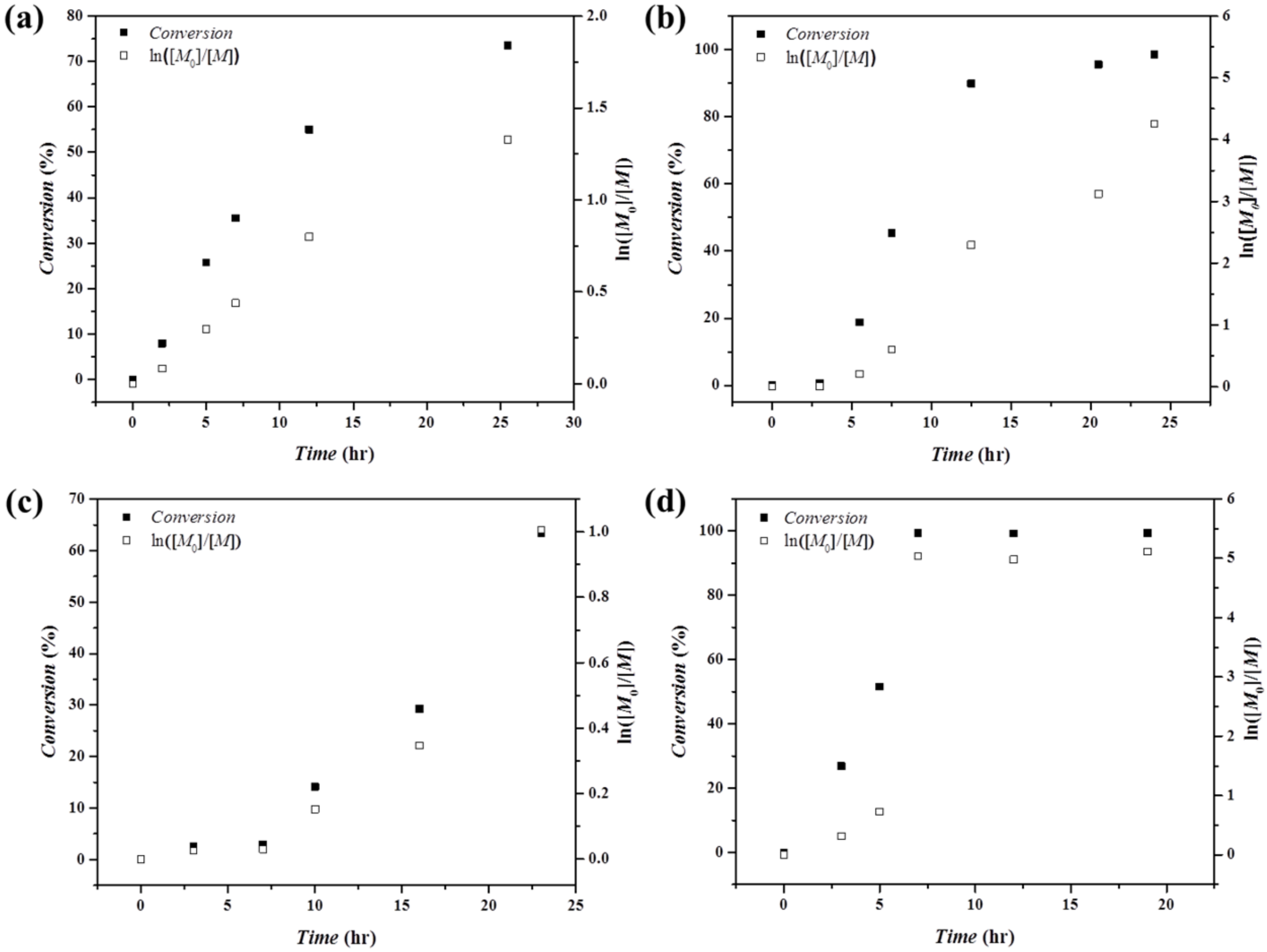

Figure S3. Kinetic evolution of monomer conversion with the utilization of $Cu_2(bdc)_2(dabco)$: (a) PBzMA and (b) PS, comparing to the polymerization conducted by conventional CuBr: (c) PBzMA and (d) PS.

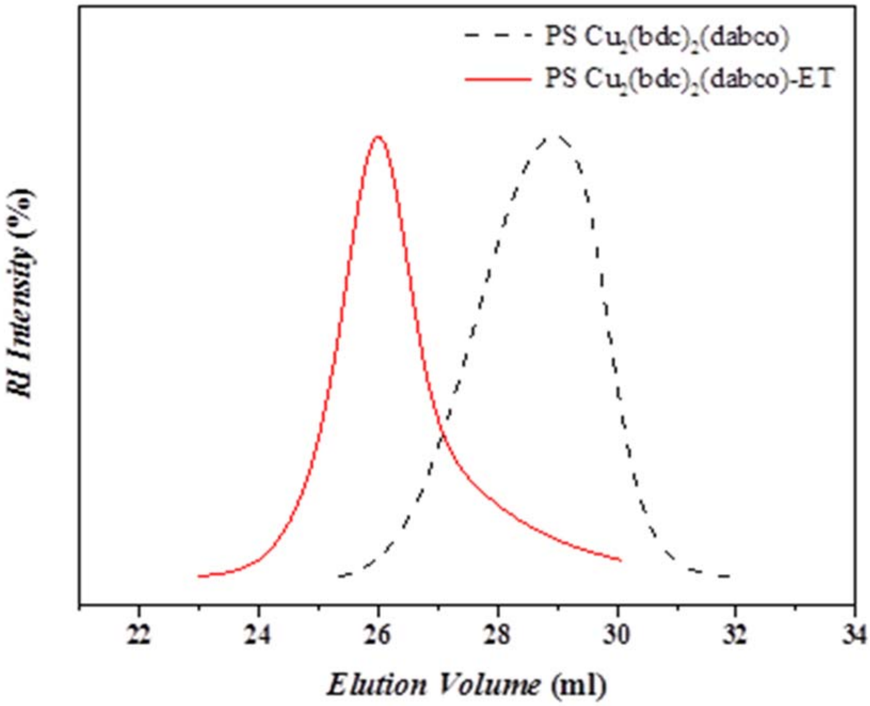

Figure S4. The SEC chromatogram of the Cu(II) MOF-mediated PS after chain extension with PS (M_n: 32200 g/mol; $Đ$:1.4).

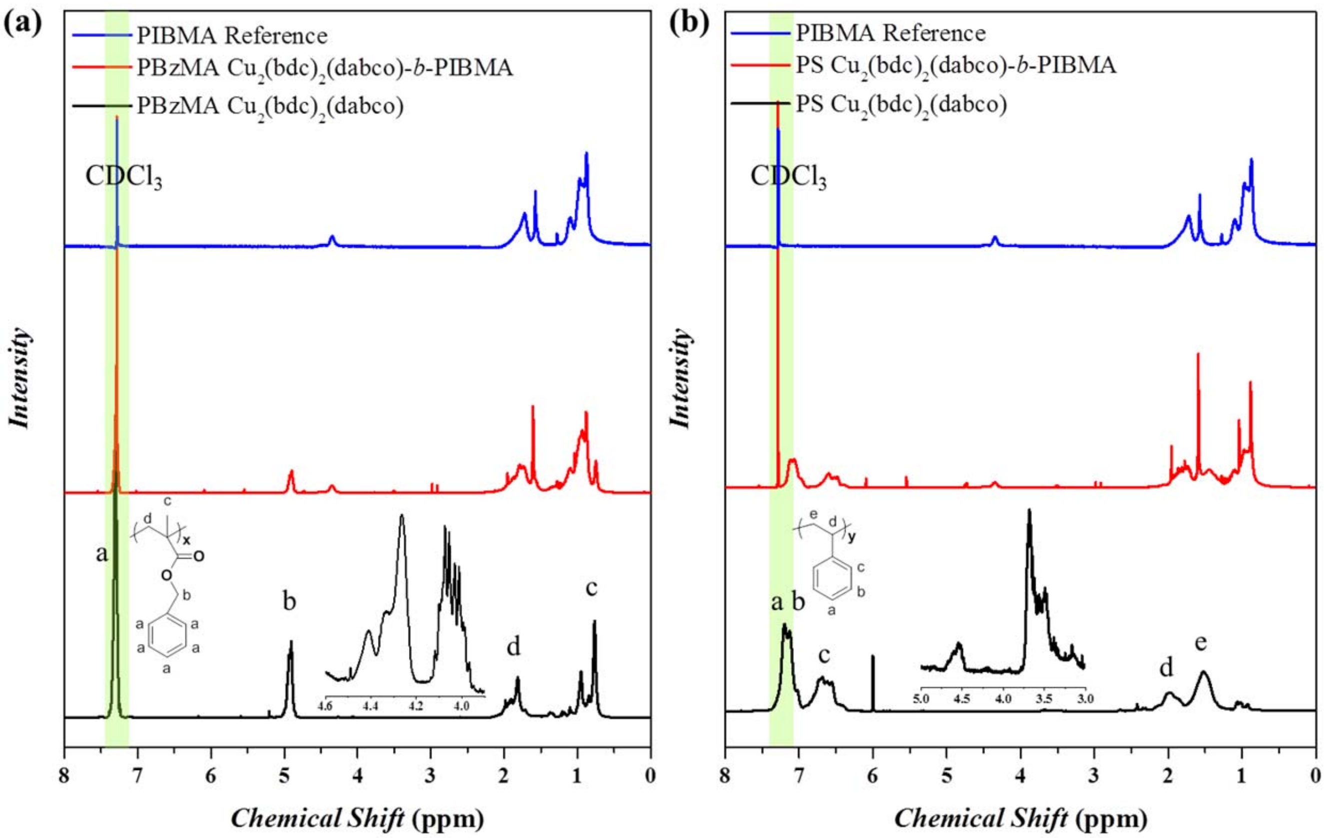

Figure S5. The corresponding ^{1}H NMR of Cu(II)-mediated ARGET in chloroform-*d*: (a) PBzMA (17200 g/mol) and (b) PS (11200 g/mol) homopolymer and block copolymer after chain extension with IBMA (PBzMA-*b*-PIBMA, 28600 g/mol; PS-*b*-PIBMA, 20200 g/mol). The inset indicates the ethyl end group given by the ARGET ATRP initiator (PBzMA: ester end group CH$_2$ 4.0-4.1 ppm) or the proton next to the bromide chain end (PS: CHBr 4.5 ppm, ester end group CH$_2$ 3.5 ppm).

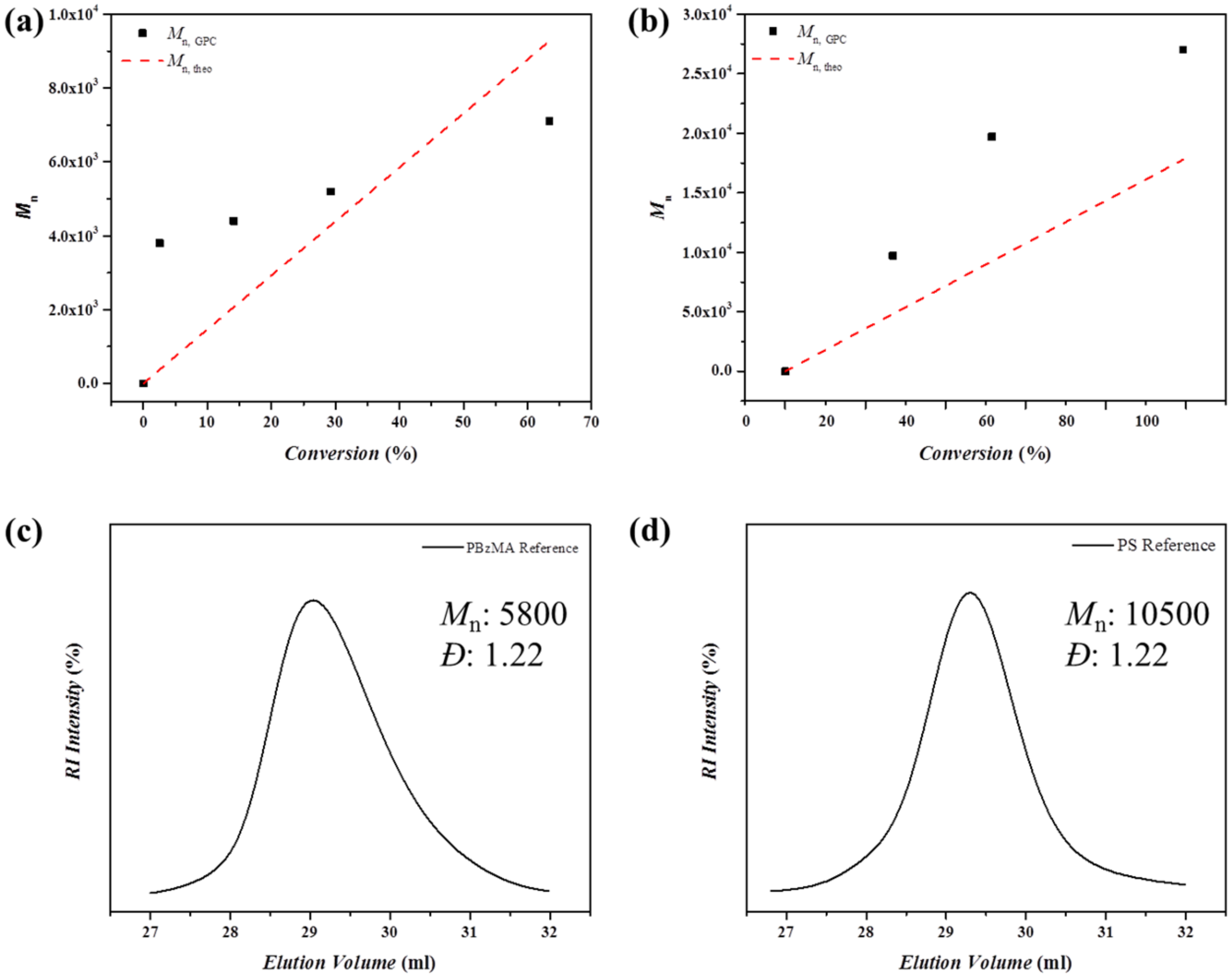

Figure S6. The evolution of M_n with conversion for $CuBr_2$-catalyzed (a) PBzMA and (b) PS polymerization. SEC chromatograms of the as synthesized (c) PBzMA and (d) PS.

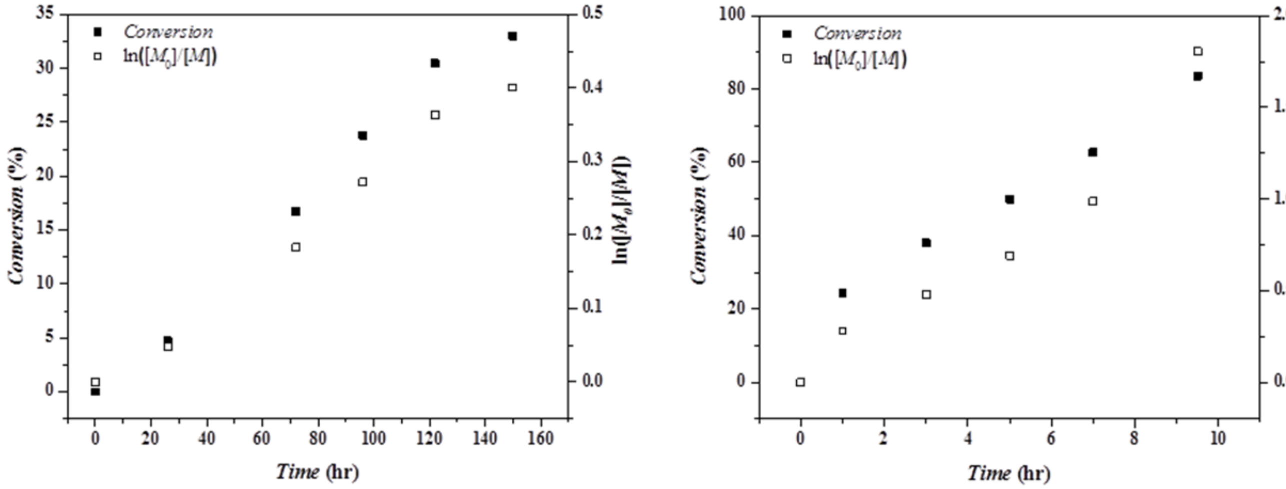

Figure S7. Kinetic evolution of monomer conversion in polymerization of (a) isoprene and (b) 4VP with the utilization of $Cu_2(bdc)_2(dabco)$.

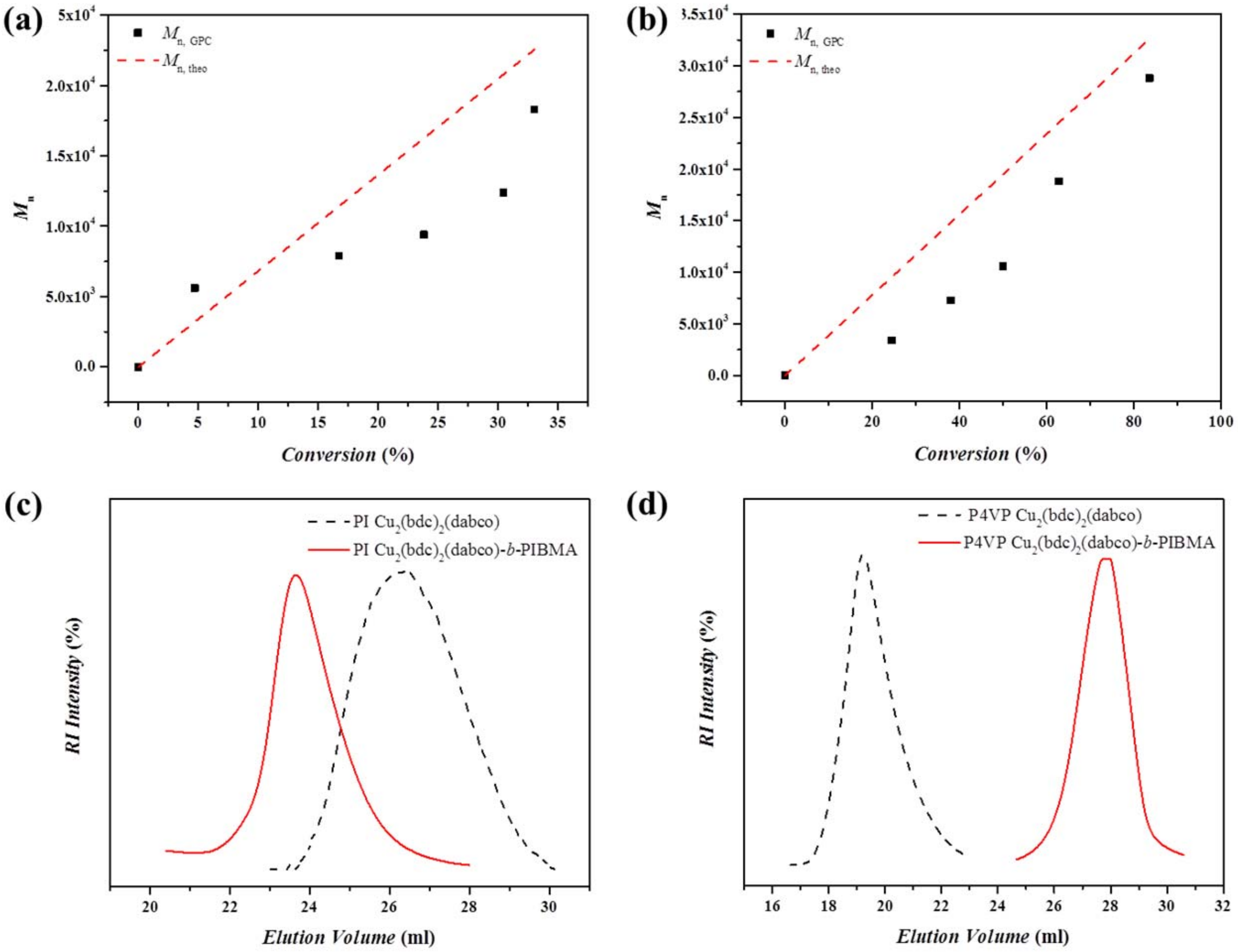

Figure S8. The evolution of M_n with conversion for (a) isoprene and (b) 4VP polymerization. SEC chromatograms of the as synthesized (a) PI and (b) P4VP before and after chain extension with IBMA. Note, owing to the low solubility, the P4VP homopolymer was analyzed in NMP with PS as standard. It is speculated that the slightly lower molecular weight of the as synthesized polymers comparing to the theoretical value is attributed to the leakage of the isoprene monomer at high temperature (120 °C), and the association of 4VP monomer on the surface of Cu(II) MOF.

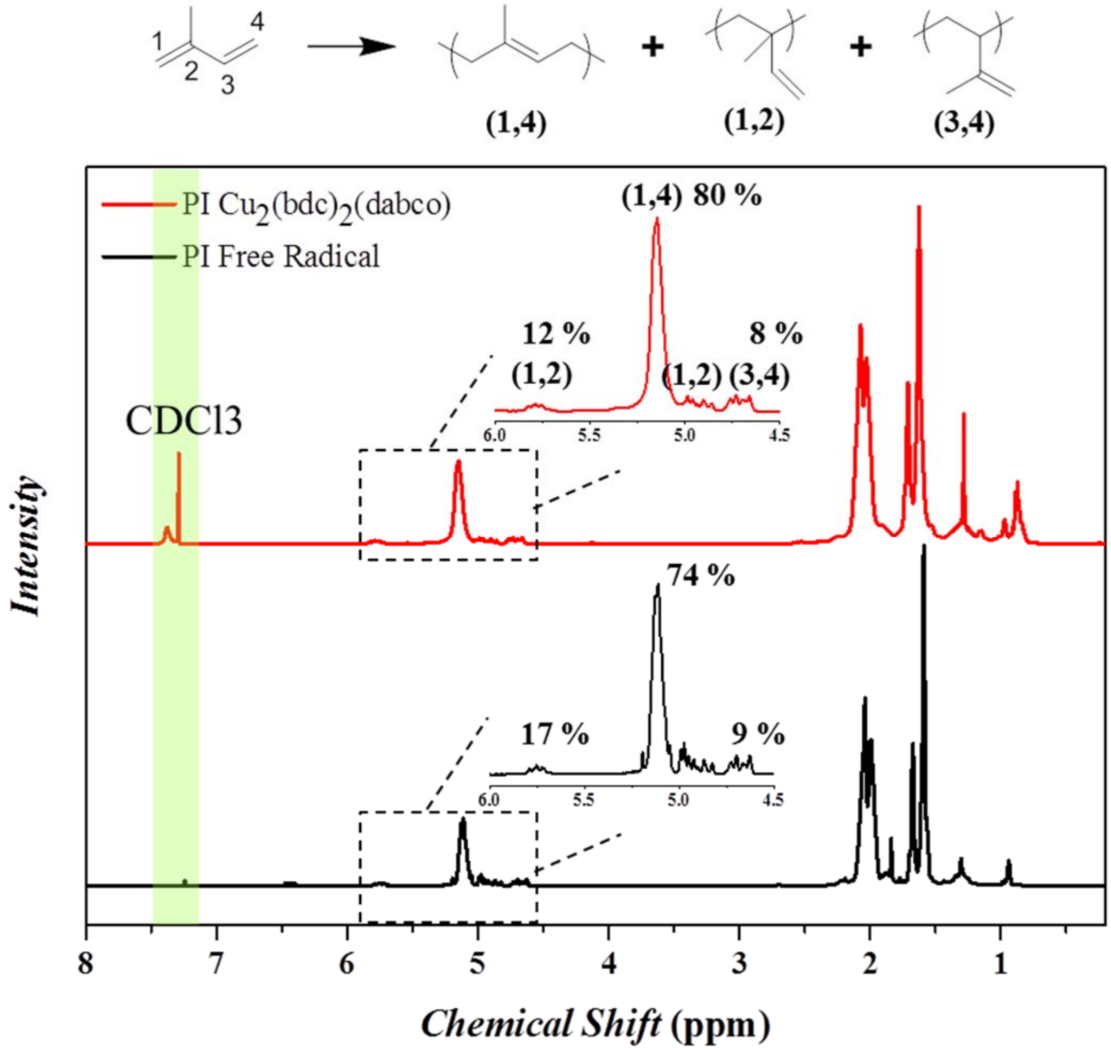

Figure S9. The comparison of ^{1}H NMR spectra of PI synthesized by free radical polymerization and Cu(II) MOF-mediated ARGET ATRP which with the calculated ratio of (1,4) addition for 80%, (1,2) for 12% and 8% for (3,4) in chloroform-*d*, with respect to free radical polymerization with the ratio of 74%, 17% and 9%.

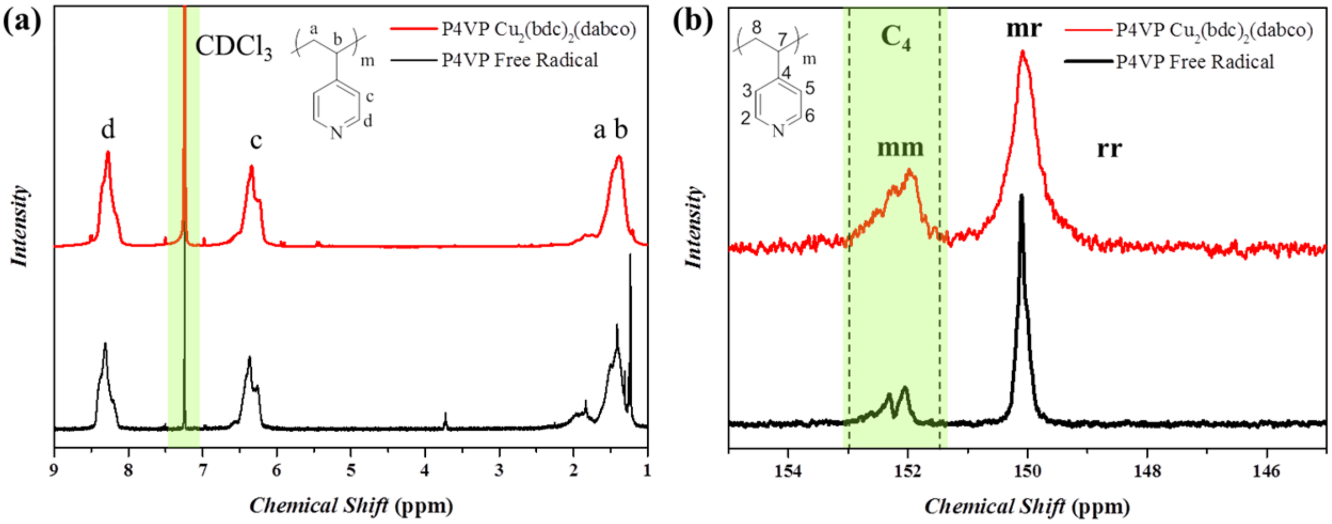

Figure S10. The comparison of (a) ^{1}H and (b) ^{13}C NMR spectra of P4VP synthesized by free radical polymerization and Cu(II) MOF-mediated ARGET ATRP in chloroform-*d*.

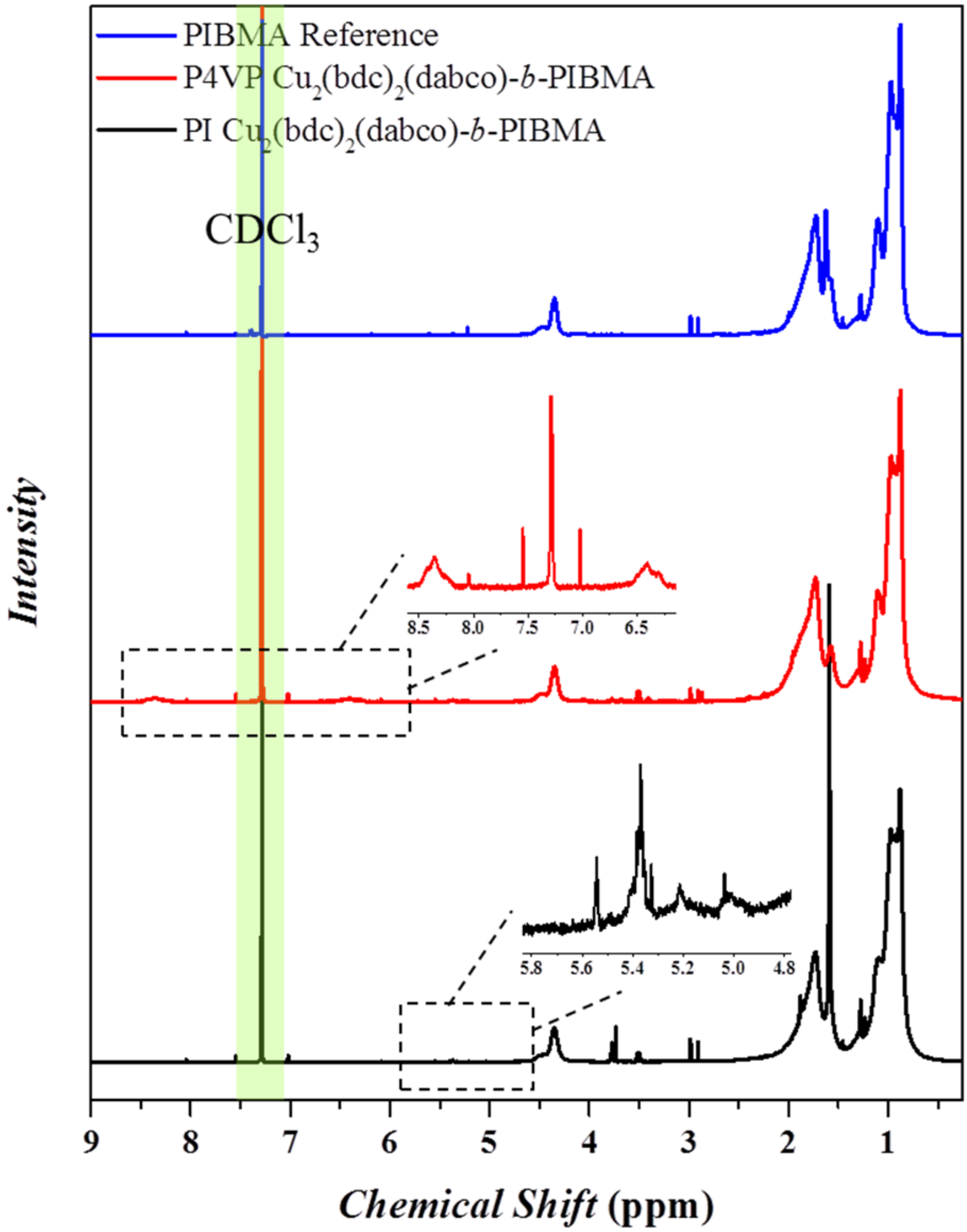

Figure S11. The corresponding ^{1}H NMR of Cu(II) MOF-mediated ARGET PI and P4VP after chain extension with IBMA (PI-*b*-PIBMA, 104900 g/mol; P4VP-*b*-PIBMA, 16000 g/mol).

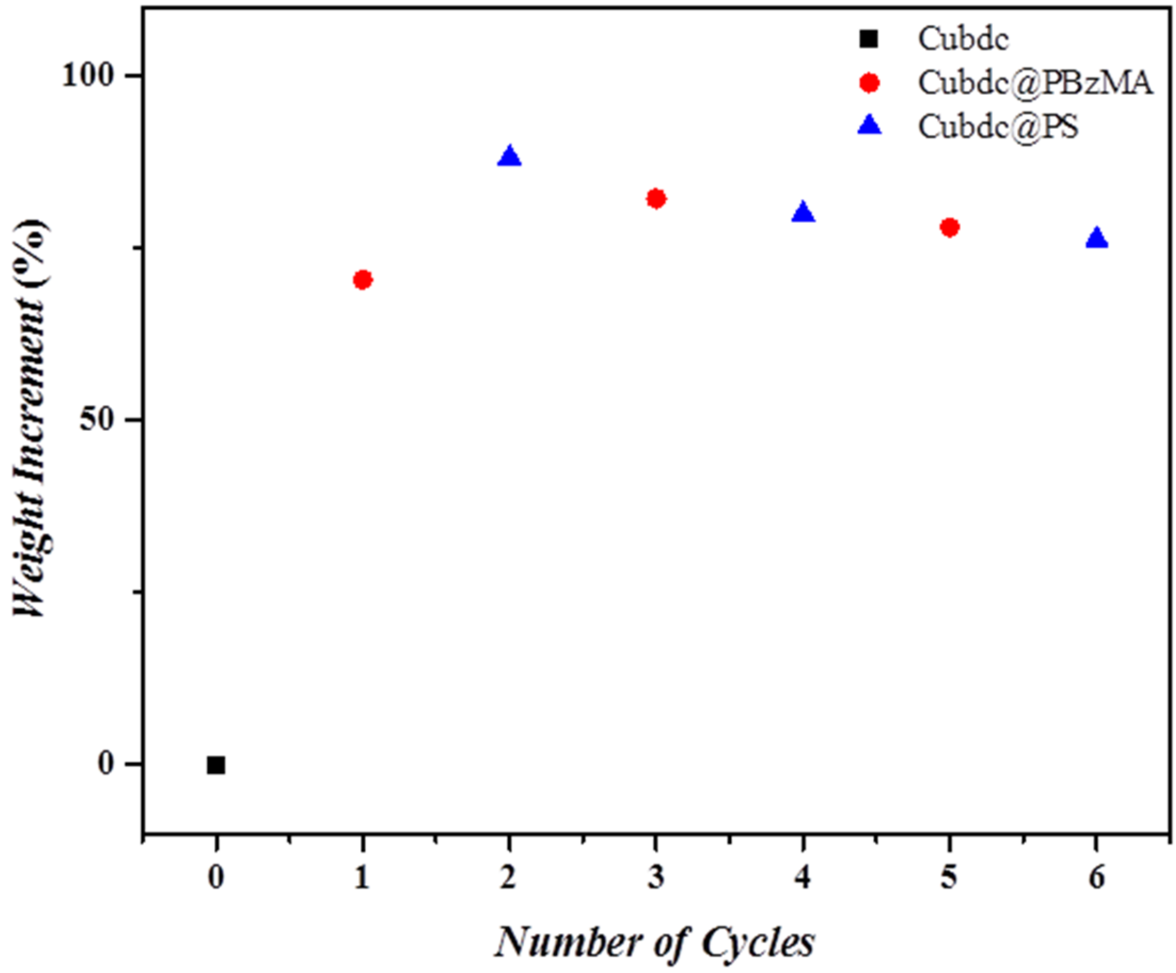

Figure S12. Evolutionary weight increment of the $Cu_2(bdc)_2(dabco)$ after different cycles of the PBzMA and PS cascade polymerization.

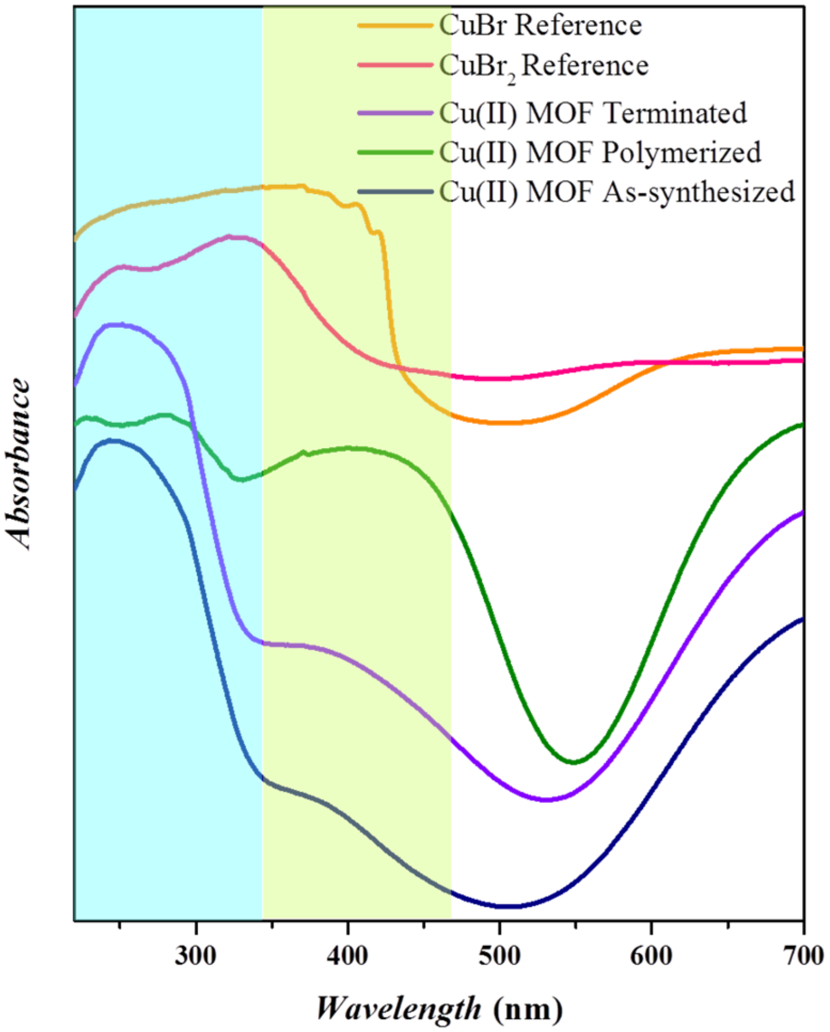

Figure S13. Solid-state UV-Vis spectra of Cu catalysts, Cu(II) MOF and CuBr in different oxidation state.

Table S1. The remaining Cu concentration (mg/g) in the polymer products formed *via* $CuBr_2$ and $Cu_2(bdc)_2(dabco)$ catalysis. [a]

	$CuBr_2$		$Cu_2(bdc)_2(dabco)$	
	Bulk Solution [b]	Precipitation [c]	Bulk Solution [b]	Precipitation [c]
PBzMA	0.6 mg/g	0.1 mg/g	0.09 mg/g	0.07 mg/g
PS	2.1 mg/g	0.6 mg/g	0.19 mg/g	0.01 mg/g

[a] Determined *via* ICP-OES. [b] The as-synthesized polymer was extracted by THF, the solvent removed and the dry residue was analyzed by ICP. [c] The as-synthesized polymer was precipitated in methanol from THF with the volume ratio 1:4, the precipitate was isolated *via* centrifugation, vacuum dried and the residue was analyzed by ICP-OES.

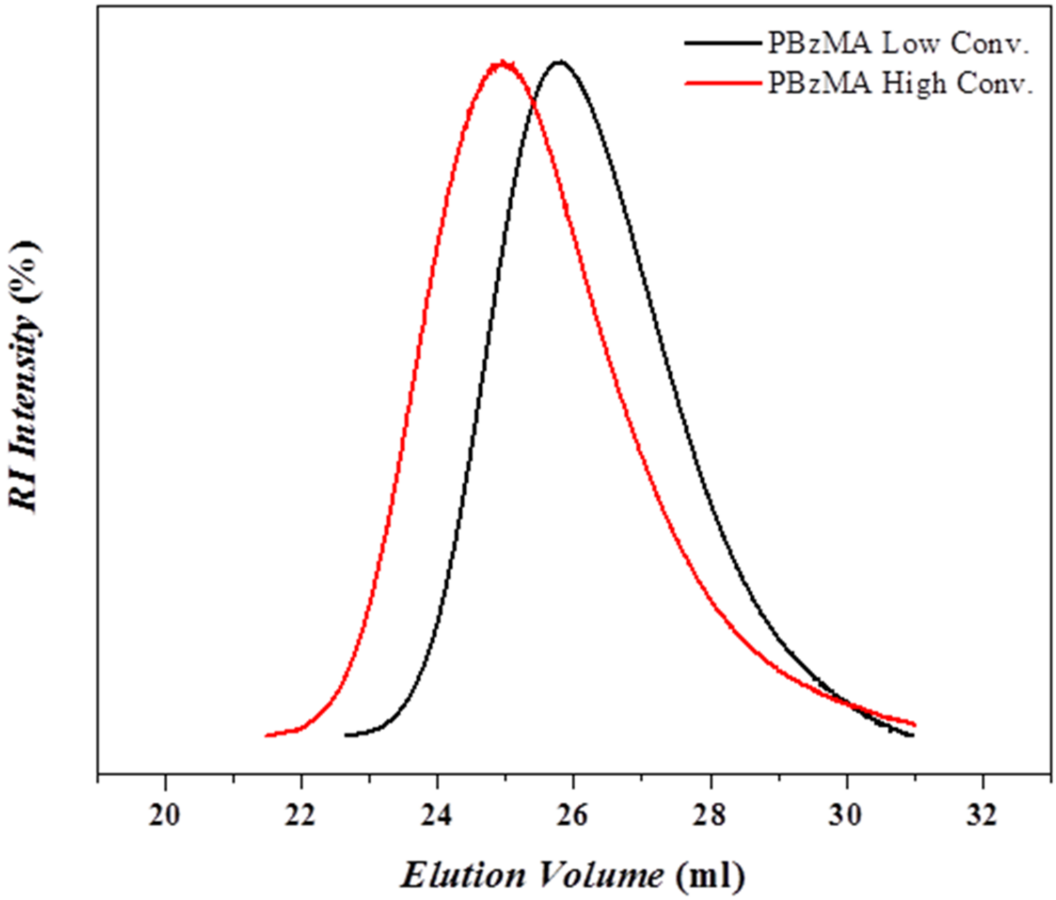

Figure S14. SEC chromatograms of the PBzMA synthesized by $Cu_2(bdc)_2(dabco)$ with the concentration of 500 ppm (approximately 112 ppm Cu(II) ion) with different conversions.

Table S2. Polymerization of PBzMA *via* $Cu_2(bdc)_2(dabco)^a$ with the concentration of 500 ppm Cu(II) MOF (approximately 112 ppm Cu(II) ions).

Homopolymer	Time (hr)	Conv. (%)	$M_{n,theo}$	$M_{n,SEC}$	*Đ*
PBzMA	40	33	12800	31400	1.52
	65	60	23500	40500	1.81

[a] Polymerization condition: $[BzMA]_0/[I]_0/[DABCO]_0 = 220:1:2$, 50 ºC.

Reference

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