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A Cu(II) metal–organic framework as a recyclable catalyst for ARGET ATRP†

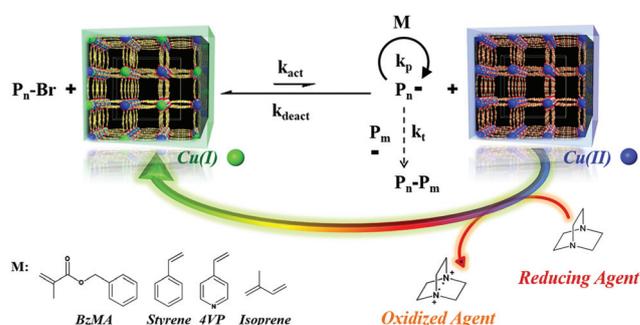
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A Cu(II) MOF can serve as an efficient catalyst for activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP), e.g. for the synthesis of poly(benzyl methacrylate) (PBzMA) and polystyrene (PS). Furthermore, poly(isoprene) (PI) and poly(4-vinylpyridine) (P4VP) can be formed in a controlled fashion as well, which used to be challenging to achieve by traditional strategies. Taking advantage of the heterogeneous nature of the catalyst, recycling *via* centrifugation and repeated utilization for at least six cycles are demonstrated.

Reversible deactivation radical polymerization (RDRP) has attracted significant attention in polymer as well as materials sciences, and without any doubt, atom transfer radical polymerization (ATRP) is one of the most significant synthetic techniques owing to its applicability and capability to synthesize well-defined polymers with a predetermined molecular weight, designed microstructure and tailored-made functionalities.^{1–4} Based on the principle of ATRP, activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP) with the advantages of high oxygen tolerance and low metal catalyst requirement were developed to further advance the synthetic field.^{5–8} However, the necessity for catalysts and associated ligands, inevitable interaction resulting from the monomer, catalyst (*i.e.* 4-vinylpyridine (4VP) and CuBr)^{9,10} and ligand (*i.e.* isoprene and PMDETA),^{11–13} and the hard to remove, non-reusable catalyst limit the ubiquity of this methodology.^{14–19} Although plenty of strategies have been launched and attempted to refine the current struggles, such as photocatalytic,²⁰ electrochemical-mediated polymerization²¹ or functionalization with supporting materials,^{22–24} heterogeneous catalysts feature more convenient handling for applications. Furthermore, metal–organic frameworks (MOFs) comprising of metal ions and linking ligands are attractive porous

materials due to their designable material features, ultrahigh specific surface area contributed by individual composition, morphology and functionality, imparting diverse potential to applications, such as gas storage, molecular separation, catalysis,^{25–30} as polymerization catalysts^{31–33} or as a polymerization environment.^{34,35}

Herein, a novel approach towards ARGET polymerizations is presented. The utilization of a Cu(II)-based MOF, namely Cu₂(bdc)₂(dabco) (bdc: terephthalic acid; dabco: 1,4-diazabicyclo[2.2.2]octane), as a heterogeneous polymerization catalyst is probed making use of the robust physical framework formed by ionic bonds. Scheme 1 illustrates the general concept of Cu(II) MOF-mediated ARGET ATRP universal to various monomers, such as benzyl methacrylate (BzMA), styrene, 4VP and isoprene. Compared to the conventional copper ion coordinated with a halide anion, the copper MOF can act as a catalyst and a ligand complex at the same time. Thus, a sometimes tedious synthetic procedure is significantly simplified, and side reactions within the mixture of monomer, metallic catalyst and the corresponding ligand are limited. Moreover, considering the particle size of a few hundred nanometers, the MOF catalyst can be easily collected by centrifugation and reused for other polymerizations.



Scheme 1 Schematic illustration for the proposed mechanism of Cu(II) MOF-mediated ARGET ATRP for various of monomers.

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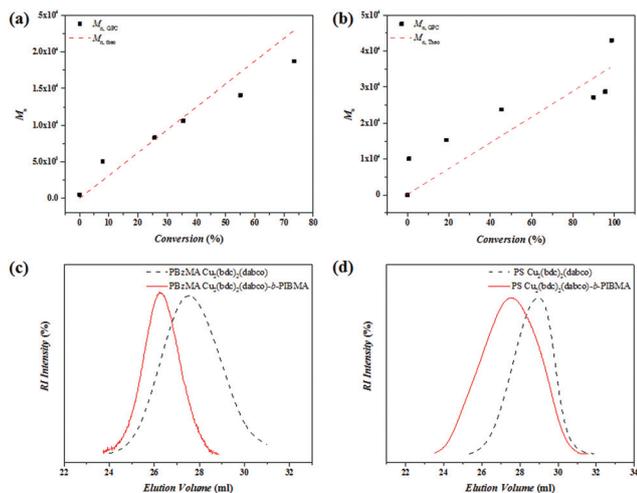


Fig. 1 The evolution of M_n with conversion for (a) BzMA and (b) styrene polymerization. SEC chromatograms of the as synthesized (c) PBzMA and (d) PS before (dashed line) and after chain extension with IBMA (solid line) measured in THF.

Since amine molecules possess the ability to reduce copper complexes from a high-valent to a low valent state as reducing agents in ARGET ATRP,^{36,37} additional DABCO was added to trigger the reduction of Cu(II) to active Cu(I).

After the Cu(II) MOF was synthesized and characterized according to the literature (Fig. S1/S2†),^{38,39} ARGET ATRP of various monomers was performed with the Cu(II) MOF compared to conventional copper-halogen coordinated catalysts. At the beginning, polymerizations of common monomers, BzMA and styrene, were conducted. The time-dependent progressions of monomer conversions (Fig. S3a/b†) reveal the constant concentration of the active propagating species in both PBzMA and PS systems, and 50% monomer conversion can be achieved within 10 hours at operational temperatures of 50 °C and 110 °C, respectively. Fig. 1a and b show the dependency of the molecular weight on conversion of BzMA and styrene revealed in Cu(II) MOF mediated ARGET ATRP, showing the gradual growth of polymer chains as well as the feature of the pre-determinable degree of polymerization, which is a prerequisite to be regarded as a RDRP process (Table 1). The slight deviation from the theoretical values can be attributed to slow

initiation originating from the heterogeneous nature of the catalyst. Furthermore, functionality of PBzMA and PS synthesized with the Cu(II) MOF in terms of initiator end-functionalization was investigated *via* chain extension with isobornyl methacrylate (IBMA) for the subsequent ARGET ATRP block copolymer formation and ¹H NMR (Fig. S4†). The SEC elugrams of the formed block copolymers (Fig. 1c and d) show an obvious shift to lower retention times, which corresponds to an increased chain length from 15 500 (PBzMA) to 28 600 g mol⁻¹ (PBzMA-*b*-PIBMA), and 16 800 (PS) to 20 200 g mol⁻¹ (PS-*b*-PIBMA). For PS-*b*-PIBMA a broadening of the molecular weight distribution is observed due to unfavourable chain extension with methacrylate. Thus, chain extensions with styrene were probed that show no significant broadening (Fig. S5†).

Therefore, the preservation of the halogen end group *via* the ability to initiate the second polymerization can be stated. The Cu(II) MOF derived polymers can be regarded as dormant chains and the preparation process can be filed as a RDRP process. The formation of block copolymers with the utilization of these macroinitiators can be again evidenced by the ¹H NMR spectra, indicating the composition of two polymer segments (Fig. S4†). As a reference, PBzMA and PS were also synthesized through traditional ARGET ATRP with the utilization of CuBr/PMDETA. The kinetic behavior (Fig. S3c/d†), time-dependent M_n evolution, and SEC distribution (Fig. S6†) show great resemblance between these two pathways in both polymer systems, indicating the Cu(II) MOF as a comparable, yet heterogeneous catalyst for ARGET ATRP.

In addition, the ARGET polymerization of isoprene and 4VP catalyzed *via* the Cu(II) MOF was investigated (Table 1), since these monomers have been proven to be rather challenging to polymerize *via* ATRP without the utilization of specified methods, such as enhanced ligands.^{9,10} The polymerization kinetics for PI and P4VP exhibit distinct linear semilogarithmic plots (Fig. S7†), and a linear increase of molecular weights in accordance with conversion (Fig. S8a/b†) can be observed in both cases. The superior polymerization results compared to non-MOF systems are probably due to the vexed coordination between the monomers and free catalysts and/or ligands. The Cu(II) MOF stabilized by the ionic bonding between the Cu(II) ions and ligands in the framework is obviously able to effectively avoid side reactions, which at the end results in polymerizations with a higher efficiency. Considering the living nature of the fabricated PI and P4VP,

Table 1 Polymerization of monomers *via* Cu₂(bdc)₂(dabco)² and the corresponding block copolymers resulting from chain extension with IBMA^b

Homo polymer	$M_{n,theo}$ (kg mol ⁻¹)	$M_{n,SEC}$ (kg mol ⁻¹)	D	Copolymer	$M_{n,theo}$ (kg mol ⁻¹)	$M_{n,SEC}$ (kg mol ⁻¹)	D
PBzMA	17.2	15.5	1.4	PBzMA- <i>b</i> -PIBMA	30.6	28.6	1.2
PS	11.2	16.8	1.3	PS- <i>b</i> -PIBMA	21.1	20.2	1.5
PI	21.8	23.0	1.4	PI- <i>b</i> -PIBMA	135.8	104.9	1.6
P4VP	11.6	9.2	1.5	P4VP- <i>b</i> -PIBMA	28.9	16.0	1.2

^a Polymerization conditions: [BzMA]:[I]:[DABCO] = 180:1:2, 50 °C for 6 h; [St]:[I]:[DABCO] = 110:1:5, 110 °C for 12 h; [isoprene]:[I]:[DABCO] = 805:1:5, 120 °C for 72 h; [4VP]:[I]:[DABCO] = 370:1:5, 60 °C for 9 h. Polymerizations were performed with 5.7 wt% Cu(II) MOF. ^b ET conditions: [PBzMA-Br/PS-Br]:[IBMA]:[CuBr₂]:[ligand]:[DABCO] = 1:400:0.4:1:2.4, 50 °C for 24 h; [PI-Br]:[IBMA]:[CuBr₂]:[ligand]:[DABCO] = 1:1100:1.1:2.75:6.6, in 50 vol% dioxane at 50 °C for 24 h; [P4VP-Br]:[IBMA]:[CuBr₂]:[ligand]:[DABCO] = 1:450:0.45:1.13:2.7, in 50 vol% dioxane at 50 °C for 24 h.



chain extensions *via* block copolymer formation with IBMA were studied (Fig. S8c/d,† Table 1). A shift of the full molecular weight distribution in the SEC elugram to lower retention times can be observed, which is a clear indication of the desired chain extended block copolymer product formation.

In addition, PI synthesized by the Cu(II) MOF appears to feature high regioselectivity, with a 1,4-addition above 80% (Fig. S9†).¹³ Additionally, referring to P4VP, the Cu(II) MOF catalyzed polymerization not only leads to controlled molecular weights and end groups, but even an effect on the microstructure of polymer chains is observed, which has been rarely reported so far. As shown in the ¹³C NMR profiles (Fig. S10†), the assignment of mm and mr triad from C4 carbon was identified at 152 and 150 ppm,⁴⁰ and compared to free radical polymerization, the control over tacticity is improved in the Cu(II) MOF-mediated P4VP, as reflected by the increased ratio of isotactic triads (mm) from 13% to 25%. It is speculated that the increased tacticity is due to the alignment of 4VP monomers along the MOF, because the Cu(II) MOF could act as a Lewis acid through forming strong coordination between the comprised Cu ions and nitrogen atoms from 4VP monomer and/or polymer chains.⁴¹ The characteristic properties of these particular polymers can be successfully passed onto the as-fabricated block copolymers as evidenced in the ¹H NMR (Fig. S11†), indicating a promising avenue for the synthesis of more controlled functional materials.

PXRD (Fig. S1†) was utilized to study the integrity of the MOF structure in each polymerization, revealing the preservation of the MOF structure, and the changes in relative peak intensities are attributed to guest molecules occupying the host nanochannels.³⁵ Therefore, it can be concluded that the MOF-based catalyst Cu₂(bdc)₂(dabco) is stable under ARGET ATRP conditions. The decreased specific surface area after polymerization (Fig. S1†) can be attributed to the incorporation of the monomer in the porous texture, and the decrease in volume corresponds to the size of the applied monomers. The monomer incorporation effect can be confirmed *via* the measurement of weight increase after recycling the catalyst (Fig. S12†), which has to be considered when switching monomers between various runs of polymerization.

As shown in Fig. 2, due to the particle size of the Cu(II) MOF of approximately 100 nm, the MOF crystals serve as a heterogeneous catalyst, which can be separated from the polymer solution easily *via* centrifugation (Fig. 2d) and the

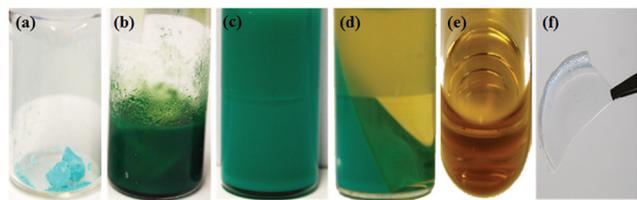


Fig. 2 Photographs of Cu₂(bdc)₂(dabco)-mediated ARGET ATRP at different stages: (a) Cu(II) MOF before polymerization; (b) Cu(II) MOF during polymerization; (c) termination with solvent; (d) removal of catalytic complex *via* centrifugation; (e) polymer solution and (f) polymer bulk after precipitation.

synthesized polymers can be obtained from the solution (Fig. 2e) after precipitation. At first, the Cu(II) MOF exhibits a characteristic light blue color because of the comprised Cu(II) ions, but once the ARGET ATRP proceeds, the suspension turns dark green owing to the reduction of Cu(II) into active Cu(I) with its intrinsic green color. The oxidation state of the MOF-derived Cu ions can be traced by solid-state UV-Vis spectroscopy (Fig. S13†). Resembling the CuBr₂ reference, the as-synthesized Cu(II) MOF exhibits a maximum absorption at around 250–350 nm, indicating the higher oxidation state. In contrast, during the polymerization process, an obvious red shift towards 300–550 nm can be identified, evidencing the oxidation of the Cu(II) framework to Cu(I). After termination of the polymerization, the absorption peak of the Cu MOF retreats to lower wavelengths with a blue shift, matching perfectly with the initial Cu(II) MOF. Thus, a reversible generation of the catalytic Cu(I) species can be stated.

Owing to the active-and-inactive properties, the MOF-based catalyst can be recycled at least six times by conducting the polymerization of PBzMA and PS alternatively. As elaborated in Fig. 3, the monomer to polymer conversions and product yields remain stable during the whole six runs, which indicates a promising applicability of utilizing this complex for various polymerizations. The discrepancy between the conversion of styrene and the yield of PS in the second cycle is probably due to the styrene monomer incorporation into the porous structure of Cu(II) MOF. The smaller molecular size of styrene with respect to BzMA leads to the mismatch of yield and conversion in the second cycle. However, yield and conversions are steady after the second cycle. The increase in weight of the operated catalyst shows a similar trend with the most obvious weight increase during the first two cycles due to polymer incorporation, and the weight remains constant with no significant loss afterwards (Fig. S11†). Accordingly, the specific surface area declines from 2280 to 40 m² g⁻¹ after 6 cycles, which supports the proposed explanation.

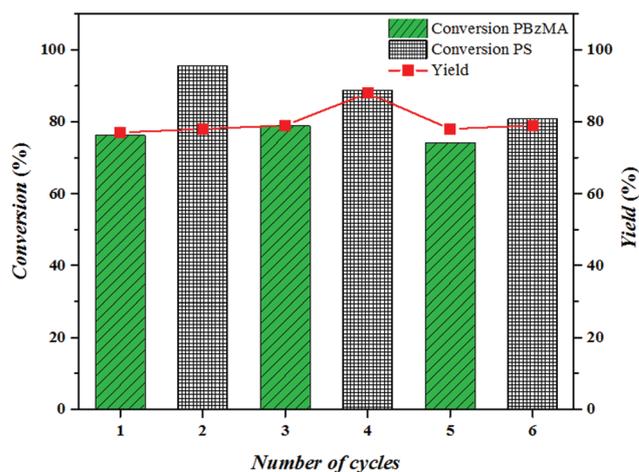


Fig. 3 Monomer conversion and polymer yield of Cu₂(bdc)₂(dabco)-mediated ARGET ATRP in catalyst recycling tests, executing the cascade polymerization of BzMA and styrene.



The possible leakage of Cu ions from the MOF template was investigated *via* inductively coupled plasma optical emission spectrometry (ICP-OES). After recycling 6-times, the contamination of the polymer product by Cu ions is insignificant in both PBzMA and PS synthesis (0.07–0.01 mg g⁻¹ after precipitation, Table S1†). Compared to the traditional CuBr₂ catalyzed reaction, the products from the crude bulk solutions of Cu(II) MOF mediated polymerization show almost 10 times lower Cu ion concentration compared to the conventional strategy. As a result, the contamination with the catalyst in polymer products can be efficiently avoided by the utilization of the Cu(II) MOF. Corresponding to the reversible UV-Vis profiles, the ICP results support the consistency of the Cu(II) MOF during the ARGET-ATRP polymerization reactions.

One remarkable property of ARGET ATRP is the requirement of low catalyst concentrations in polymerization. Therefore, the polymerization of PBzMA was exerted with the utilization of merely 500 ppm Cu(II) MOF (approximately 112 ppm Cu(II) ions). Under this condition, still conversions up to 60% can be reached after 65 hours at 50 °C, and decent polymers with a molecular weight of around 30 000 to 40 000 g mol⁻¹ and a PDI of 1.5 to 1.8 were obtained (Fig. S14 and Table S2†).

In conclusion, Cu(II) MOFs were utilized in the ARGET ATRP of various monomers. Styrene and BzMA were polymerized in a controlled fashion according to RDRP standards as proven *via* a linear increase of molecular weight with conversion and chain extension experiments. Furthermore, the challenging monomers 4VP and isoprene could be polymerized in a controlled way, as confinement of Cu(II) ions and ligands effectively suppresses the side reactions between reagents and monomers to successfully perform RDRP. As a heterogeneous catalyst, the copper catalyst can be separated simply from the polymer product by centrifugation, and be reused for further reactions. In summary, with the capability to simplify the polymerization procedure, to prevent side-effects in reactions and to solve the cumbersome catalyst removal, the Cu(II) MOF is demonstrated as a powerful catalyst complex for comprehensive polymerization offering well-controlled and living properties of the polymers so as to indeed expand the feasibility and applicability of ATRP in synthetic chemistry.

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