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## Anthracene-based indium metal–organic framework as a promising photosensitizer for visible-light-induced atom transfer radical polymerization†

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Metal-organic frameworks (MOFs) provide an attractive platform for designing and synthesizing photoactive hybrid materials for photochemical reactions. We report here the utilization of a new visible-light responsive indium MOF for inducing the atom transfer radical polymerization (ATRP) of methacrylate monomers, where well-designed polymers with controlled molecular weights, narrow molecular weight distribution and high retention of chain-end groups have been prepared. The kinetics study reveals that the MOF-mediated ATRP shows characteristics of controlled radical polymerization (CRP). Besides, the polymerization can be easily regulated by light. Furthermore, the heterogeneous MOF can be easily recovered from the reaction and recycled for the photopolymerization. This study has involved photoactive MOFs materials into a new photochemical reaction of polymer synthesis.

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## Introduction

Metal-organic frameworks (MOFs) are a class of crystalline organic-inorganic hybrid materials constructed by the coordination interaction between metal ions and organic linkers, showing rich structures and multiple functionalities.<sup>1-11</sup> Until now, MOFs have shown versatile applications in gas storage, separation, luminescence, chemical sensing, drug delivery, heterogeneous catalysis, and so on.<sup>12-19</sup> Very recently, visible light responsive MOFs for artificial photocatalysis and photosynthesis have attracted much attention due to the increasing global energy demand and environmental issues.<sup>20-24</sup> MOFs provide an interesting platform for designing and synthesizing visible light photocatalysts due to the easy incorporation of the photoactive chromophores into their structures. Studies of visible light responsive MOFs based on either metalorganic or organic chromophores have been reported, where these photoactive MOFs have made notable progress such as degradation of organic pollutants,<sup>25,26</sup> water splitting,<sup>27-29</sup> and CO<sub>2</sub> reduction.<sup>30,31</sup> However, it is still a great challenge to synthesize novel visible-light photoactive MOFs. Meanwhile,

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far fewer catalytic systems have been investigated for MOF photocatalysts, such as the photopolymerization.

Atom transfer radical polymerization (ATRP) mediated by transition metal catalysts has emerged as one of the most successful polymerization techniques for the easy access to useful polymer materials.<sup>32-40</sup> It provides the ability to produce polymers with controlled molecular weight, narrow molecular weight distribution, and high degrees of chain-end functionalities. The mechanism of ATRP can be simplified to a reversible redox system, where the transition metal catalyst undergoes a reversible one electron oxidation and reduction process. The application of photochemical redox reactions to synthetic polymer chemistry brought significant advantages compared to traditional techniques. Very recently, the photoinduced ATRP has been rapidly developed owing to its easy temporal and spatial control of the chain extension process.<sup>41-44</sup> Typically, the photoinduced ATRP relies on the in situ reduction of the deactivator of a Cu(II) complex to the activator of the Cu(1) complex for the polymerization. In view of their photoinduced charge generation, MOFs are potential heterogeneous photosensitizers that activate the copper complex, inducing the ATRP.

In the present work, we explore the possibility of utilizing visible light photoactive MOFs material as a photoreducing agent for the generation of a Cu(i) complex to induce the ATRP. By the incorporation of the chromophore of an anthracene group into a carboxylic ligand, a new three-dimensional indium MOF showing broad-band absorption in the visible

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light region has been prepared. It has been demonstrated that the as-prepared indium MOF is an effective photosensitizer for inducing the photopolymerization of methacrylates, showing characteristics of controlled radical polymerization.

### **Experimental section**

#### Materials and physical studies

Methacrylate monomers of *i*-butyl methacrylate (*i*-BMA) (98%, TCI), n-butyl methacrylate (n-BMA) (98%, TCI), methyl methacrylate (MMA) (99.8%, TCI) and styrene (St) (99%, TCI) were purified by passing through a basic alumina column to remove the inhibitor. N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) (99%, TCI), ethyl α-bromoisobutyrate (EBiB) (98%, Accela), copper(II) bromide (CuBr<sub>2</sub>) (99%, Acros), acetonitrile (CH<sub>3</sub>CN) (99.9%, Acros), tetrahydrofuran (THF) (99.99%, Acros) and other reagents were used as received without further purification. The Fourier transform infrared spectra (FTIR) were collected using a Bruker Vertex 70 in ATR mode. Thermogravimetric analyses (TGA) were performed with a heating rate of 10 °C min<sup>-1</sup> using the Perkin-Elmer TGA-7 thermogravimetric analyzer from room temperature to 800 °C under atmosphere. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D-MAX 2550 automated powder diffractometer, using Cu-K $\alpha$  radiation ( $\lambda$  = 0.15417 nm) at room temperature with  $2\theta$  ranging from 3° to 40°. The UVvis spectra for solid state samples were taken on a HITACHI U-4100 spectrophotometer while the spectra for liquid samples were taken on a SHIMADZU UV-2550 spectrophotometer. The EPR spectra were recorded on a JES-FA 200 EPR spectrometer at 25 °C with a microwave power of 0.998 mW. The sample was irradiated with a microwave frequency of 9.45 GHz and the measurement with a sweep width of 40 mT was centred at 340 mT. The in situ experiments were carried out using a 500 W xenon arc lamp where a 420 nm optical filter was used to cut off the ultraviolet part of light. The stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) was used as a standard for the calculation of g values. Gel permeation chromatography (GPC) measurements were conducted using an Agilent Technologies PL-GPC-50 Integrated GPC system. THF was used as an eluent at a flow rate of 1.0 mL min<sup>-1</sup> at 30 °C. The molecular weights were calibrated with PMMA standards having a narrow molecular weight distribution.

#### Synthesis of ligand

The anthracene derived ligand  $H_4L$  [5,5'-(anthracene-9,10diylbis(ethyne-2,1-diyl))diisophthalic acid] was synthesized from 9,10-dibromoanthracene and diethyl 5-ethynylisophthalate *via* the Sonogashira coupling reaction. Typically, diethyl 5-ethynylisophthalate (0.5 g, 2 mmol), 9,10-dibromoanthracene (0.3 g, 0.92 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and CuI were added into the solution of DMF. The mixture was refluxed under an N<sub>2</sub> atmosphere. The reaction was quenched with water, extracted with CHCl<sub>3</sub>, washed with brine and dried over MgSO<sub>4</sub>. Recrystallization from CHCl<sub>3</sub> gave the product as a red solid. To this product (2.5 g, 3.75 mmol), KOH was added (1.68 g, 30 mmol) and the resulting solution was stirred under reflux. The mixture was acidified with HCl, and then the precipitate 5,5'-(anthracene-9,10-diylbis(ethyne-2,1-diyl))diisophthalic acid (H<sub>4</sub>L) was filtered and dried. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.715 (*d*, 4H), 8.533 (*s*, 4H), 8.515 (*s*, 2H), 7.842 (*d*, 4H). IR (KBr): v = 2922, 1694, 1593, 1437, 1202 cm<sup>-1</sup>. The analytical data are in accordance with that reported in the literature.<sup>45</sup>

#### Synthesis of NNU-32

A mixture of the organic ligand  $H_4L$  (10 mg, 0.018 mmol) and  $In(NO_3)_3 \cdot 4H_2O$  (6.7 mg, 0.018 mmol) was dissolved in a mixed solvent of DMF/H<sub>2</sub>O (1.6 mL, 8:1, v/v). Thereafter, 4 M HCl (35  $\mu$ L, aq.) was added, and the vial (20 mL) was capped and placed in an oven at 65 °C for 5 days. The resulting yellow octahedron shaped crystals were collected and washed with DMF several times. Yield: *ca.* 50% based on the ligand.

#### Single crystal X-ray diffraction

The single-crystal X-ray diffraction structure of NNU-32 was collected on a Bruker Smart ApexIICCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) under room temperature. Raw data of the structure was processed using SAINT and absorption corrections data were corrected using the multiscan program SADABS. The crystal structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  with anisotropic displacement using SHELXTL (Table S1, ESI†).<sup>46</sup> CCDC 1410541 contains the supplementary crystallographic data for this paper.

#### Photoinduced ATRP

*i*-BMA (2 mL, 12.5 mmol), PMDETA (11.6  $\mu$ L, 0.0558 mmol), CuBr<sub>2</sub> (4.2 mg, 0.0186 mmol), EBiB (14  $\mu$ L, 0.093 mmol), acetonitrile (0.5 mL, 9.57 mmol), and NNU-32 (20 mg) were placed into a Schlenk tube, and the reaction mixture was degassed by three freeze-pump-thaw cycles and left under vacuum. The mixture was irradiated by the 300 W xenon arc lamp equipped with a 520 nm band-pass optical mirror and filter under magnetic stirring. The light intensity was 25 mW cm<sup>-2</sup> measured by using a power meter. After the reaction, NNU-32 was first separated by centrifugation. The resulted polymers were precipitated in methanol for several times and then dried under vacuum. Monomer conversions were measured gravimetrically. The polymerization conditions for *n*-BMA (2 mL) MMA (1.35 mL) and St (1.44 mL) are the same as those for *i*-BMA.

Chain extension was performed using a macroinitiator instead of EBiB under the following conditions:  $[i\text{-BMA}]_0/$ [Macroinitiator]\_0/[CuBr\_2]\_0/[PMDETA]\_0 = 135/0.1/0.2/0.6. The macroinitiator PBMA-Br ( $M_{n,GPC}$  = 15160,  $M_w/M_n$  = 1.10) was prepared by photoinduced ATRP for 8 h. PBMA-Br (141 mg, 9.3 × 10<sup>-3</sup> mmol), *i*-BMA (2 mL, 12.5 mmol), CuBr<sub>2</sub> (4.2 mg, 0.0186 mmol), PMDETA (11.6 µL, 0.0558 mmol), and NNU-32 (20 mg) were put into a Schlenk tube, and the reaction mixture was degassed by three freeze-pump-thaw cycles and left under vacuum. The mixture was irradiated under the same experimental conditions and the reaction was ceased after 6 h. Finally, methanol was added to precipitate the polymers, and the obtained polymer was dried under vacuum.

## Results and discussion

Single crystal X-ray diffraction analysis reveals that the indium MOF with a formula of (Me2NH2)[InL]·3(H2O)·0.5DMF (denoted as NNU-32) crystallizes in the tetragonal space group  $P4_2/mmc$ . In the structure, the mononuclear  $In^{3+}$  ion in an 8-coordinated geometry is bonded to four chelating carboxylate groups, forming a tetrahedral 4-connected node. The anthracene-derived carboxylate ligand binds to four In<sup>3+</sup> ions in a square-planar fashion (Fig. 1). A view along the crystallographic c-axis shows the primary square-shaped channels running through the structure (Fig. 1). The approximate diameter of the channel is 9.9 Å defined by the geometry of the In-carboxylates units and the span of the tetratopic linker. These channels are interconnected by square windows composed of four indium centers and four ligands, which can be viewed along the crystallographic a- or b-axes. Since each In<sup>3+</sup> ion is bonded to four carboxylate groups, the framework is negatively charged. The FTIR spectrum (Fig. S1, ESI<sup>+</sup>) shows an intense peak at 1660 cm<sup>-1</sup> ( $\nu_{C=O}$ ), confirming the presence of DMF molecules. The peak due to the carboxylate groups in the ligand ( $v_{sym(COO)}$ ) is around 1382 cm<sup>-1</sup>. The peak at 2484 cm<sup>-1</sup> is attributed to the vibration of the ammonium group N-H<sup>+</sup> belonging to protonated dimethylamine,<sup>47</sup> where it is well known that DMF is easily decomposed, leading to the formation of dimethylamine.48,49 Several weak absorptions at 3068, 2926, 2855, 2809 cm<sup>-1</sup> correspond to the vibrations of the C-H bonds associated to the DMF molecules and protonated dimethylamine. These vibrations around 3000 cm<sup>-1</sup> are characteristic of the stretching  $v_{st}$  and combination vibrations  $v_{\rm comb}$  of the ammonium group.<sup>48,50</sup> This broad band vibration reveals also the complex intermolecular hydrogen bonding between water, DMF molecules and protonated dimethylamine.50 The thermogravimetric curve of NNU-32 (Fig. S2, ESI<sup>+</sup>) shows a continuous weight loss (6.5%) from room temperature up to 120 °C assigned to



Fig. 1 (a) The structure of NNU-32 viewed along the *c*-axis. (b) A view of the structure of NNU-32 showing the 4,4-net coordination between the anthracene-based ligands and indium ions. The hydrogen atoms and guest molecules are omitted for clarity.

water molecules (calc. 6.7%). The weight loss (10.1%) from 120 to 420 °C is attributed to the gradual removal of DMF and protonated dimethylamine (calc. 10.2%). The following weight loss (66.6%) is attributed to the decomposition of the organic ligand (calc. 65.8%). The remaining plateau (16.8%) is assigned to the indium oxide  $In_2O_3$  (calc. 17.3%). The phase purity of the as-prepared sample was confirmed by powder X-ray diffraction (PXRD), where the experimental and simulated patterns matched well (Fig. S3, ESI†). NNU-32 shows no gas absorption after activation by the solvent exchange process, due to the loss of its structure during the activating process.<sup>51</sup>

The light absorption of NNU-32 was studied by UV-vis spectrum in solid state at room temperature, where it displays a broad absorption band in the visible light region from 400 nm to 650 nm (Fig. 2a). The broad-band adsorption of NNU-32 is attributed to the inhomogeneous broadening resulting from the energy transfer and/or charge transfer processes from ligand to metal ions (LMCT).<sup>52,53</sup> The LMCT process is also verified by the significantly lower energy absorption of NNU-32 as compared to the ligand (Fig. 2a). The visible-light-induced charge generation was further studied by electron paramagnetic resonance (EPR) spectroscopy. As shown in Fig. 2b, the freshly prepared crystalline sample of NNU-32 showed no EPR signal; whereas a characteristic EPR signal attributed to free radical at g = 2.003 was detected when NNU-32 was irradiated by visible light, suggesting the ligand-based free radicals formation in the structure.<sup>54</sup> The ability of photoinduced radical formation from anthracenederived ligands was further verified by the observation of the same EPR signal at g = 2.003 when the ligand in the solid state was exposed to visible light. To further study the photoinduced radical formation in NNU-32, as shown in Fig. 2c, time evolution in situ EPR experiments were performed under visible light irradiation. For NNU-32, the intensity of the EPR signal at g = 2.003 increased rapidly under continuous visible light illumination and saturated after 3 min. Thereafter, this signal was sustained over ten minutes in the dark. The EPR studies indicate the long-lived photoinduced charge generation of NNU-32, which resulted from the radical formation of the ligand. It is notable that MOFs showing photoinduced radical generation are rare.55-57

The above optical studies suggest that NNU-32 could be a potential photoreducing agent for the *in situ* generation of the Cu(1) activator in the ATRP reaction. Hence, the photocatalytic system of NNU-32/initiator/copper(1) complex/monomer was investigated, where NNU-32 is the photosensitizer for the reduction of copper catalyst *via* the visible-light-induced electron-transfer process. The reaction was carried out using CuBr<sub>2</sub>/PMDETA as the catalyst and EBiB as the initiator in acetonitrile. The photopolymerization of the *i*-BMA monomer was first investigated with a molar ratio of [*i*-BMA]<sub>0</sub>/[EBiB]<sub>0</sub>/[CuBr<sub>2</sub>]<sub>0</sub>/[PMDETA]<sub>0</sub> = 135/1/0.2/0.6. To eliminate the absorption interference from the Cu(1)/PMDETA complex, the UV-vis spectroscopy of the reaction system in the absence of NNU-32 was first studied where it showed



Fig. 2 (a) The UV-vis spectra of NNU-32 and the ligand in DMF. (b) Photoinduced EPR spectra of NNU-32 and the ligand. (c) Time-evolution variation of EPR intensities of NNU-32.

almost no absorption at 520 nm (Fig. S4, ESI<sup>†</sup>). And the control experiment showed that it was not reactive under this wavelength (Table 1, entry 1), which is consistent with the reported studies.<sup>58,59</sup> Thereafter, the NNU-32 mediated ATRP reaction was performed under the irradiation of 520 nm monochromatic light.

Upon the addition of NNU-32, the photopolymerization with ca. 71% monomer conversion was observed after 10 h irradiation (entry 2). Gel permeation chromatography (GPC) measurement showed that the molecular weight distribution  $(M_w/M_n)$  of the resulting polymer was well controlled  $(M_w/M_n)$ = 1.11), indicating the feasibility of the NNU-32 mediated ATRP reaction. A range of control experiments were carried out to clarify the role of each component in the reaction. As shown in Table 1 (entry 3), there was no product of polymer when the polymerization was conducted in the absence of EBiB, which states that the EBiB initiator is essential for the reaction. When the photopolymerization was performed without CuBr<sub>2</sub> (entry 4), the reaction was out of control ( $M_{n GPC}$  = 31 3150 and  $M_w/M_n = 1.73$ ) as evidenced by GPC. This phenomenon can be reasoned by direct polymerization when the EBiB initiator was activated by the radical cation of the ligand via classical halogen abstraction.<sup>60</sup> It is necessary to investigate the influence of the catalysts for this photocatalytic system. As shown in Table 1, the yield of polymerization was slightly varied (66-74%) when the dosage of photosensitizer NNU-32 was changed from 10 mg to 30 mg (entry 5 and 6),

and the resulting polymers were both in narrow molecular weight distributions (1.09-1.12). When the amount of the Cu(II)/PMDETA catalyst was decreased (entry 7 and 8), the vields were relatively lower and the dispersibilities of the resulting polymers were wider. The versatility of NNU-32 mediated ATRP was investigated by the polymerization of other acrylate monomers such as n-BMA and MMA. For these monomers (entries 9 and 10), narrow molecular weight distributions were preserved with conversions of 31% (n-BMA) and 56% (MMA). Besides, the photopolymerization of styrene has also been investigated; however, no corresponding polymer has been obtained (entry 11). Because the photoactivity of NNU-32 relies on the anthracene-based ligand, hence it is necessary to investigate the photopolymerization by using the ligand instead of the In-MOF. However, the ligand with carboxylate groups coordinates strongly with the Cu<sup>2+</sup> ion, resulting in the destruction of the Cu/PMDETA catalyst. In this case, the 9,10-bis(phenylethynyl)anthracene (BPEA), a molecule with the same backbone of ligand lacking the carboxylate groups, is used to induce the photopolymerization. As shown in Table 1 (entry 12), no polymer was prepared under the same photocatalytic conditions. This result reveals that the as-prepared MOF is necessary and advanced compared to the ligand for the photoinduced polymerization.

The evolution of the molecular weights and polydispersities upon conversions was investigated based on the *i*-BMA monomer. As shown in Fig. 3a, an induction period of *ca.* 3 h

Entry <sup>a</sup>	[Monomer] <sub>0</sub> /[EBiB] <sub>0</sub> /[CuBr <sub>2</sub> ] <sub>0</sub> /[PMDETA] <sub>0</sub>	Sensitizer	Monomer	Conversion [%]	$M_{\mathrm{n,th}}^{b} [\mathrm{g \ mol}^{-1}]$	$M_{\mathrm{n,GPC}}^{c} [\mathrm{g \ mol}^{-1}]$	$M_{\rm w}/M_{\rm n}^{\ c}$
2	135/1/0.2/0.6	NNU-32	<i>i</i> -BMA	71	13 700	17 890	1.11
3	135/-/0.2/0.6	NNU-32	<i>i</i> -BMA	—	—	—	—
4	135/1/-/0.6	NNU-32	<i>i</i> -BMA	63	12 080	31 3150	1.73
$5^d$	135/1/0.2/0.6	NNU-32	<i>i</i> -BMA	66	12650	16 500	1.09
6 <sup>e</sup>	135/1/0.2/0.6	NNU-32	<i>i</i> -BMA	74	14 190	18 2 3 0	1.12
7	135/1/0.1/0.3	NNU-32	<i>i</i> -BMA	54	10350	21 430	1.19
8	135/1/0.02/0.06	NNU-32	<i>i</i> -BMA	40	7680	32 640	1.34
9	135/1/0.2/0.6	NNU-32	n-BMA	31	5 940	13 370	1.14
10	135/1/0.2/0.6	NNU-32	MMA	56	7 560	10 910	1.12
11	135/1/0.2/0.6	NNU-32	Styrene	_	_	_	_
12	135/1/0.2/0.6	BPEA	<i>i</i> -BMA	_	_	_	_

<sup>*a*</sup> Polymerization was performed under 520 nm visible light irradiation, time = 10 h, NNU-32 = 20 mg. <sup>*b*</sup>  $M_{n,th} = [i-BMA]_0/[EBiB]_0 \times M_{w,monomer} \times conversion. <sup>$ *c* $</sup> Number average molecular weight (<math>M_{n,GPC}$ ) and molecular weight distribution ( $M_w/M_n$ ) were determined by GPC. <sup>*d*</sup> NNU-32 = 10 mg. <sup>*e*</sup> NNU-32 = 30 mg. BPEA = 9,10-bis(phenylethynyl)anthracene.



**Fig. 3** NNU-32 mediated ATRP of *i*-BMA under 520 nm. (a) Kinetic plot. (b) Number average molecular weight  $(M_{n,GPC})$  and dispersity  $(M_w/M_n)$  vs. conversion. (c) GPC traces before (black) and after (blue) the chain extension process. Conditions for (a) and (b):  $[i-BMA]_0/[EBiB]_0/[CuBr_2]_0/[PMDETA]_0 = 135/1/0.2/0.6$  in 2 mL of acetonitrile, NNU-32 = 20 mg. Conditions for (c):  $[i-BMA]_0/[PBMA-Br]_0/[CuBr_2]_0/[PMDETA]_0 = 135/0.1/0.2/0.6$  in 2 mL of acetonitrile for 8 h, NNU-32 = 20 mg. All reactions were carried out at room temperature using 520 nm visible light.

was needed for the photoinduced polymerization, which is likely a result of the slow photoreduction of Cu(II)/PMDETA due to the heterogeneous nature of MOF photosensitizer. After this induction period, the reaction exhibited first-order kinetics, indicating the constant concentration of radicals from EBiB maintained through-out the reaction. Correspondingly, a linear increase in molecular weight upon monomer conversion was observed where all the polydispersity values at different conversions were relatively low  $(M_w/M_p = 1.09-1.12)$ (Fig. 3b). The GPC measurements for the resulting polymers revealed larger molecular weights compared to the calculated ones. This result is likely due to the slow initiation where EBiB was used as the initiator.<sup>61,62</sup> The kinetic analysis proves that the photopolymerization after the induction period was performed in a controllable way, exhibiting a living polymerization feature.

The "living" nature of the system was also certified by a chain extension experiment. A macroinitiator made by this method was used instead of EBiB. As shown in Fig. 3c, the chain-extended polymer shows a higher molecular weight  $(M_{n,GPC} = 114\ 130)$  compared to the macroinitiator  $(M_{n,GPC} = 15\ 160,\ M_w/M_n = 1.10)$  after 8 h of reaction, and the dispersity of the resulting polymer is very uniform  $(M_w/M_n = 1.07)$ . The results of the chain extension experiment illustrated a well-defined polymer with a halide group synthesized *via* the NNU-32 mediated photoinduced ATRP reaction.

As shown in Fig. 4, the NNU-32 mediated ATRP can be easily controlled by periodic light switching. When the reaction was kept in the dark for 4 h, no polymer was obtained. Then the reaction was exposed under 520 nm for 4 h, an 18% conversion of monomer was found. Afterward, the light was turned off for another 4 h. The conversion of reaction is nearly unchanged, indicating a negligible concentration of the active radical present under dark conditions. Then the light was turned on again, the polymerization was re-initiated and reached 48% conversion, where the kinetic character is almost the same as that observed in the first light-on process. The light-switching experiment was further cycled for the third time where a conversion of 80% was achieved.

The success of the NNU-32 mediated ATRP reaction implies the potential of MOFs as photosensitizers for the polymer synthesis, relying on the photoinduced electron transfer



Fig. 4 NNU-32 mediated photopolymerization at 520 nm. Conditions:  $[i-BMA]_0/[EBiB]_0/[CuBr_2]_0/[PMDETA]_0 = 135/1/0.2/0.6$  in 2 mL of acetonitrile, NNU-32 = 20 mg.

from MOFs to the copper complex. A proposed mechanism for this photocatalytic reaction is illustrated in Scheme 1. In the reaction, the Cu(II) complex is reduced by photosensitized NNU-32 *via* single electron transfer. The resulting Cu(I) complex reacts with the initiator of alkyl halide (R–X), forming radicals (R') to initiate the polymerization. Meanwhile, the resulting positive ligand cation in the MOF structure is reduced by the reductive amine of PMDETA to its pristine state, leaving intermediate amine<sup>+</sup>X<sup>-</sup> which supports the chainend halogen for the dormant species and returns to amine.<sup>63</sup> It is notable that there has been some research using



Scheme 1 Proposed mechanism of the photoinduced ATRP.

coordination polymers that control polymerization or oligomerization.64-68 These studies had revealed that the polymerization taking place in the nanochannel of coordination polymers supports unique advantage to control the structure and orientation of the as-prepared polymer. The NNU-32 mediated polymerization is different from these polymerizations as the reaction is driven by visible light and occurs outside the channel of the MOF. Moreover, the photopolymerization could be more precisely controlled, leading to a very narrow molecular weight distribution. The heterogeneous NNU-32 can be easily recovered from the reaction solution by centrifugation. As evidenced by the PXRD study, the structure of NNU-32 was maintained after the ATRP reaction, allowing its reuse in the subsequent reactions (Fig. S3, ESI<sup>+</sup>). The recycle experiments revealed that NNU-32 can be reused for at least three cycles without loss of activity (Fig. S5, ESI<sup>†</sup>).

## Conclusions

In summary, a new visible light responsive indium MOF, NNU-32, has been prepared based on an anthracene derivative. Remarkably, the long-lived charge generation in the MOF structure upon visible light irradiation is achieved by the radical formation of the ligand. We further demonstrated that NNU-32 could be utilized as a photosensitizer to conduct a visible-light-induced ATRP reaction for polymer synthesis. Results show that NNU-32 mediated ATRP for methacrylate monomers took place in a controllable way, leading to a narrow molecular weight distribution and high retention of the chain-end group. The kinetics study reveals that the reaction shows characteristics of controlled radical polymerization. Besides, it has been demonstrated that the MOF mediated ATRP reaction could be easily controlled by light switching. The success of MOF mediated photopolymerization exposes that the design and synthesis of MOF photocatalysts by the incorporation of chromophores is a feasible method. We further anticipate that photoactive MOFs would find more promising applications in polymer synthesis.

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