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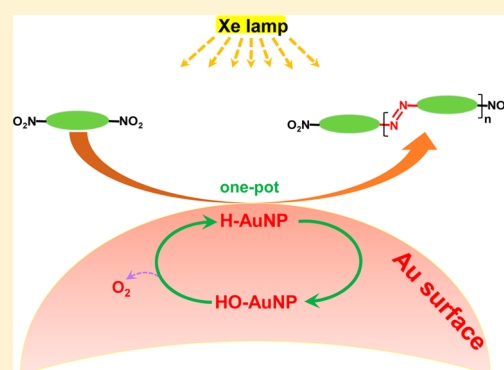
A Straightforward Protocol for the Highly Efficient Preparation of Main-Chain Azo Polymers Directly from Bisnitroaromatic Compounds by the Photocatalytic Process

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S Supporting Information

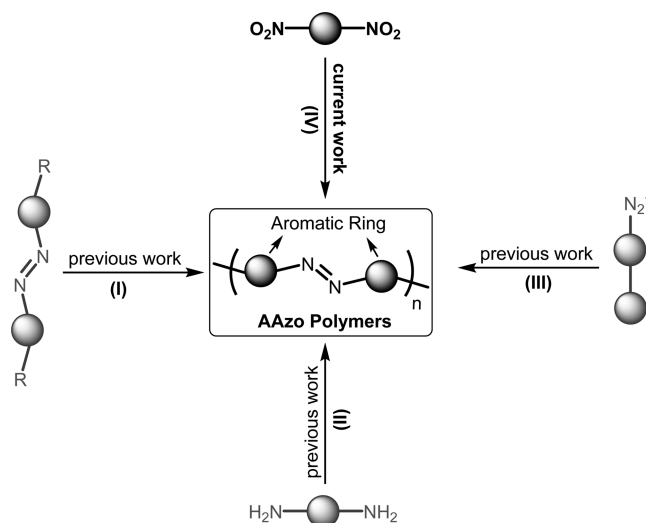
ABSTRACT: A novel strategy for the synthesis of main-chain Azo polymers directly from bisnitroaromatic compounds by the photocatalytic process has been achieved under mild conditions. This approach avoids the tedious synthesis of Azo monomers and proceeds with a high monomer conversion ($\sim 100\%$) and excellent selectivity ($\sim 100\%$) but without generating a significant amount of inorganic wastes and impurities (Cu^{2+} or azoxy groups) existing in main-chain Azo polymers compared to previous methods. The polymerization was monitored by UV-vis, FT-IR, and MALDI-TOF-MS, indicating that the reaction process proceeded with formation of the azoxy repeating units from the corresponding bisnitroaromatic monomers and the reduction of corresponding azoxy repeating units to the azo repeating units. Furthermore, the recyclable heterogeneous photocatalysts represent an attractive green process for production of main-chain Azo polymers.



INTRODUCTION

Over the past few decades, polymers containing aromatic Azo and its derivatives (Azo polymers) have drawn considerable attention owing to their outstanding mechanical, unique physicochemical properties, and the well-known reversible *trans*–*cis* photoisomerization of the Azo group.^{1,2} As compared with side-chain Azo polymers, the main-chain Azo polymers show much more attractive thermal stability and optoelectronic properties, such as good conductivities (up to $10^{-4} \Omega^{-1} \text{cm}^{-1}$), liquid crystallinity, and nonlinear optical properties.^{3,4} However, relatively few studies have been done in this area, partly due to the lack of a straightforward method to prepare main-chain Azo polymers under mild conditions.⁵ Usually, the main-chain Azo polymers can be prepared by several methods, including polycondensation of Azo monomers, coupling polymerization of primary aromatic diamines, and Azo coupling reaction of monomers with diazonium salts and electron-rich aromatic units as depicted in Scheme 1. The first method, including amidation,⁶ esterification,⁷ Suzuki–Miyaura coupling,⁸ click chemistry,⁹ and other coupling reactions,¹⁰ has been reported to prepare main-chain Azo polymers, however, needing sophisticated design and elaborate synthesis of Azo monomers prior to polymerization. The second method, the oxidative coupling polymerization of aromatic diamines, first independently reported by Kotlyarevskii et al. and Bach, commonly employs a copper–amine complex as catalyst.^{11,12} The obtained main-chain Azo polymers from this strategy

Scheme 1. Different Strategies for the Synthesis of Azo Polymers



contain a substantial amount of copper (Cu^{2+}) (about to one copper atom per 3.5 repeating units), which results from the

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co-occurrence of a symmetric aromatic hydroxylation side reaction. Furthermore, azoxy groups are also found as the other impurity existed in the final polymers. The third method, Azo coupling reaction, was first employed to functionalize vinyl polymers in acetic acid medium by Katz and co-workers.¹³ Subsequently Wang et al. effectively expanded this method to prepare linear, hyperbranched, and block Azo polymers in organic solvent.¹⁴ Nevertheless, this method is confined to electron-rich aromatic compounds and/or stoichiometric amounts of bisdiazonium salts and polyphenols and generates a significant amount of inorganic wastes. Moreover, most of nitrogen sources in bisdiazonium salts, Azo monomers, and aromatic diamines are from aromatic nitro compounds, which are much stabler than bisdiazonium salts and aromatic diamines. Therefore, developing an efficient method for the preparation of main-chain Azo polymers directly from bisnitroaromatic monomers will be of scientific and practical interest.

Basically, developing an efficient approach for synthesis of functional small Azo compounds, prior to preparing the corresponding Azo polymers, is of prime importance. Compared to other methods, such as Azo coupling reaction,¹⁵ Mills reaction,¹⁶ oxidation of anilines, and so on,^{17,18} reductive coupling of aromatic nitro derivatives showed many advantages for synthesizing Azo compounds, including wider availability, enhanced stability of substrates, higher tolerance of various functionalities, one-pot procedure, and so on.^{15,1} As matters stand, a myriad of reducing agents are innovated and developed for producing Azo compounds directly from nitroarenes, which included LiAlH_4 ,¹⁹ NaBH_4 ,²⁰ $\text{Mg}/\text{HCO}_2\text{HNEt}_3$,²¹ $\text{In}(\text{OTf})_3/\text{Et}_3\text{SiH}$,²² Pd/KOH ,²³ etc. The major limitations of these procedures, however, are excessive use of reducing agent, lack of selectivity, and forming environmentally unfriendly by-products.¹⁵ Moreover, some methods suffer from difficulty avoiding the existence of the azoxybenzene, which becomes the major obstacle in preparing main-chain Azo polymers with high purity.²⁴ Thus, developing the efficient approach along with high selectivity and effective conversion for preparing Azo monomers/polymers is urgently needed. Recently, supported gold nanoparticles (AuNPs) were reported by facilitating target specific synthesis of Azo compounds with high yields and good selectivity directly from nitroarenes.²⁵ Up to now, AuNPs with different supports, such as TiO_2 , CeO_2 , ZrO_2 , and $\text{Mg}_4\text{Al-HT}$, have been successfully reported as heterogeneous catalysis to prepare Azo compounds from nitroarenes.²⁶ More recently, Zhu and co-workers prepared ZrO_2 -supported AuNPs by a photocatalytic process to synthesize Azo compounds directly from nitroarenes in one step.²⁷ This unique methodology prevents the formation of harmful byproducts from reducing agents, meanwhile avoiding unstable intermediates and use of higher temperature and pressure. If direct reduction of bisnitroaromatic compounds can be successfully conducted by above strategy, the first preparation of main-chain Azo polymers would be achieved in a much more controlled, simplified, and greener way (Scheme 1).

In this work, we developed a novel approach for preparing the main-chain Azo polymers directly from bisnitroaromatic compounds photocatalyzed by ZrO_2 -supported AuNPs under mild conditions. With high monomer conversion, this novel strategy produces relatively high molecular weight (M_n up to 29 800 g/mol) Azo polymers with good selectivity. Moreover, the recovered photocatalysts still exhibited highly catalytic efficiency after twice reutilization. The retention of the activity

and selectivity of recovered catalysts, combined with the utilization of solar energy under mild conditions, will pave a novel avenue for the preparation of main-chain Azo polymer materials.

■ EXPERIMENTAL SECTION

Materials. Bromohexane (98%, J&K Chemical), 1-bromododecane (98%, J&K Chemical), 1,12-dibromododecane (98%, J&K Chemical), ethyl formate (98%, J&K Chemical), dodecylmagnesium bromide (1.0 M solution in diethyl ether, J&K Chemical), chloroauric acid ($\geq 98\%$, Aldrich), carbazole (90%, Aldrich), zirconium dioxide (99.9%, Beijing Dk Nano Technology Co., Ltd.), 9H-fluorene (98%, Acros), and 2,7-dinitro-9,9-dioctyl-9H-fluorene (monomer A) (Longrepharm Laboratories (China), Ltd.) were used as received without further purification. All solvents were dried with 4 Å molecular sieves before use. Other chemicals were purchased from Shanghai Chemical Reagent Co. Ltd., Shanghai, China, and used without further purification except mentioned specifically. The synthesis and characterization of nitroaromatic compounds and bisnitroaromatic monomers are described in the Supporting Information.

Characterization. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker nuclear magnetic resonance instrument (300 MHz) using deuterated chloroform (CDCl_3) as the solvent and tetramethylsilane (TMS) as the internal standard at room temperature. The number-average molecular weight (M_n) and polydispersity ($\text{PDI} = M_w/M_n$) of polymers were determined by a HLC-8320 size exclusion chromatograph (SEC, TOSOH) equipped with a refractive index detector, using two TSKgel Super Multipore HZ-N columns (4.6×150 mm, $3 \mu\text{m}$ particle size) in series with molecular weights ranging from 7×10^2 to 2×10^5 g/mol. THF was used as the eluent at a flow rate of 0.35 mL/min and 40°C . These samples were calibrated with PS standards purchased from TOSOH. Ultraviolet–visible (UV–vis) absorption spectra of the samples were recorded on a Shimadzu UV-2600 spectrophotometer at room temperature. FT-IR spectra were recorded on a Bruker TENSOR-27 FT-IR spectrometer using KBr pellets. Atomic absorption spectrometry was detected by a Varian Spectra 220FS atomic absorption spectrometer. Elemental analysis of C, H, and N was measured with an EA1110 CHNO-S instrument. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurement was performed using a Bruker UltrafleXtreme (MALDI-TOF/TOF) mass spectrometer equipped with a 355 nm Nd:YAG laser. Both matrix (2-[(2E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB)) (at a concentration of ca. 20 mg/mL) and all samples were dissolved in chloroform (at a concentration of ca. 10 mg/mL). The cationizing agent sodium trifluoroacetate was dissolved in ethanol (at a concentration of ca. 10 mg/mL). The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). This mixture solution (0.5 μL) was placed on a metal sample plate. The sample was air-dried at ambient temperature. Transmission electron microscopy (TEM) was recorded on HITACHI HT7700 employing an accelerating voltage of 120 kV. The purity of the products was determined on a high-performance liquid chromatograph (HPLC, mode 515, Waters) using acetonitrile as the eluent at 30°C . The light intensity was measured by UV radiometer fabricated by a photoelectric instrument factory of Beijing Normal University.

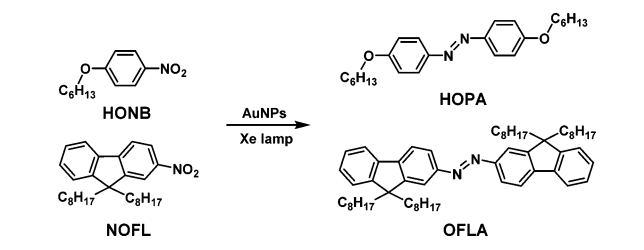
Preparation of Main-Chain Azo Polymers. To a mixture of monomer A (80 mg), potassium hydroxide (5.6 mg), 3 mL of toluene, and 3 mL of isopropyl alcohol was added catalyst (33 mg) under room temperature. The solution was bubbled with argon for 10 min, and then the ampule was flame-sealed and magnetically stirred under the illumination of a Xe lamp ($3.1 \text{ mW}/\text{cm}^2$) at 45°C for 12 h. The ampule was opened, and the resulting mixture was precipitated into 250 mL of methanol. The polymer (PA) was obtained by filtration and dried under vacuum at 40°C to constant weight with a yield of 96%. The M_n and M_w/M_n values were determined to be 28 000 g/mol and 2.63, respectively. PBs and PCs were prepared with the similar procedures.

RESULTS AND DISCUSSION

The photocatalysts, ZrO₂-supported AuNPs developed by Zhu et al., presented a high conversion and high selectivity for the reduction of nitrobenzene to azobenzene under irradiation with above 400 nm light.^{21b} The above excellent performance of ZrO₂-supported AuNPs motivated us to test the possibility of preparing main-chain Azo polymers, directly from the reduction of bisnitroaromatic compounds. The ZrO₂-supported AuNPs, with 3.0 wt % gold loading on the ZrO₂ powder (particle size less than 100 nm), were prepared as described by Zhu's group,^{27b} which was confirmed by atomic absorption spectra and transmission electron microscopy (TEM) images (Figure S1). Similarly, the ZrO₂-supported AuNPs show obvious absorption around 450–650 nm, and the size of gold nanoparticles is about 6–8 nm. As reported, the gold content existing in photocatalysts determined the catalytic activity of the catalyst; too low or high gold content (1.5 or 5 wt %) presented poor performance (lower monomer conversion and selectivity).^{27b} Therefore, the ZrO₂-supported AuNPs with suitable 3 wt % gold content were designed and employed to conduct the preparation of main-chain Azo polymers via the photocatalyzed reduction of bisnitroaromatic compounds (xenon-lamp light irradiation with about 3.1 mW/cm² measured by UV radiometer, UV-420).

Two nitroaromatic compounds, 2-nitro-9,9-dioctyl-9H-fluorene (NOFL) and 1-(hexyloxy)-4-nitrobenzene (HONB), were designed (Schemes S2 and S1, Figures S2–S4) and employed as the model compounds to confirm the catalytic activity of AuNPs (Scheme 2). Mixed solvents (toluene/isopropyl alcohol

Scheme 2. Photocatalytic Reduction of Model Nitroaromatic Compounds



(IPA)) were used to ensure the complete dissolution of polymers in the following procedure. Multiple conditions and diverse solvents mixed with IPA were investigated, and the results are shown in Table 1 and Table S1. As expected, the AuNPs photocatalysts efficiently photocatalyzed the reduction of NOFL and HONB with $\geq 96\%$ conversion and $\geq 96\%$ selectivity (Table 1, entries 2, 3, and 6–8) in optimized conditions. In addition, the conversion and selectivity of NOFL and HONB increased along with the reaction time as shown in Table 1. The photocatalyzed reduction of NOFL and HONB was almost completed within 8 h. Meanwhile the AuNPs exhibited excellent catalytic capability in IPA/toluene (3/3, v/v) mixed solvents, compared to that in IPA/(tetrahydrofuran, dichloromethane, chlorobenzene, anisole, acetone, or chloroform) (3/3, v/v) (entries 2–8 in Table S1). The color change before and after reaction also partially supported the results above (Figure S5). High volume ratio of toluene in the mixed solvent would decrease the catalytic capability and, thus, led to the incomplete transformation of azoxybenzene to azobenzene unit. Furthermore, a high volume ratio of IPA in the mixed

Table 1. Photocatalyzed Reduction of Nitroaromatic Compounds in Different Experimental Conditions^a

entry	IPA/toluene (mL/mL)	t (h)	conv (%)	yield ^b (%)
1	3/3	2	100	10
2	3/3	8	100	>98
3 ^c	3/3	8	100	>98
4 ^d	3/3	2	48	1
5 ^d	3/3	4	65	38
6 ^d	3/3	6	96	>96
7 ^d	3/3	8	100	>99
8 ^e	3/3	8	100	>97

^aReaction conditions: isopropyl alcohol (3 mL), NOFL (80 mg), catalyst (33 mg), KOH (5.6 mg), 8 h. The photocatalyzed reactions were conducted in an argon atmosphere at 45 °C. ^bYields measured by HPLC analysis. ^cNOFL (150 mg). ^dHONB (80 mg). ^eHONB (110 mg).

solvent would result in the precipitation of target polymers due to their poor solubilities in IPA.

The investigation highlighted herein demonstrated an enormous potential to prepare main-chain Azo polymers by the directly photocatalyzed reduction of bisnitroaromatic monomers. The conjugated monomer **A** (2,7-dinitro-9,9-dioctyl-9H-fluorene), **B** (3,6-dinitro-9-(pentacosan-13-yl)-9H-carbazole) (Scheme S2, Figures S6a and S7a), and unconjugated monomers **C** (1,12-bis(2-(dodecyloxy)-4-nitrophenoxy)dodecane) (Scheme S3, Figures S6b and S7b) were designed and employed to synthesize main-chain Azo polymers (Figure 1). Further efforts to explore the photo-

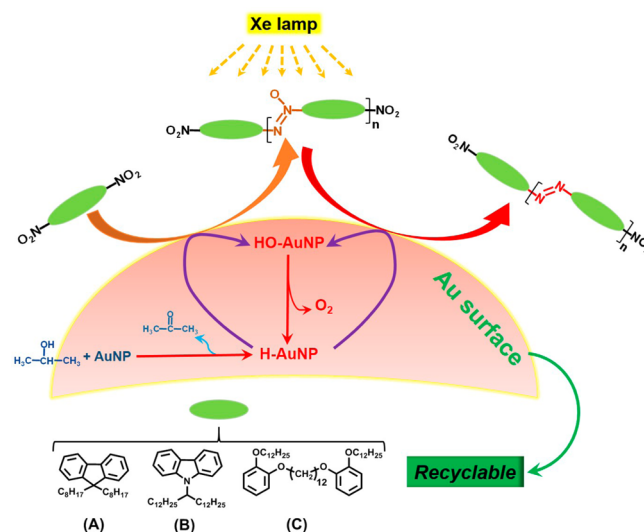


Figure 1. Plausible mechanism for the photocatalyzed polymerization of bisnitroaromatic monomers.

catalyzed polymerization behavior of bisnitroaromatic monomers were implemented with compound **A** as the model monomer as presented in Table 2. The conjugated Azo polymers were successfully obtained with high monomer conversions and molecular weight of **PA** increased with reaction time and up to 29 800 g/mol.

This strategy was also expanded to the other bisnitroaromatic monomers (**B**, **C**). Owing to the excellent solubility of monomer **A** in the mixed solvents, the molecular weight of **PA** is much higher than that of **PB** and **PC** (Table 2, Table S2, Figure S8) in the same polymerization conditions. The other

Table 2. Photocatalyzed Polymerization of Bisnitroaromatic Monomers at Different Experimental Conditions^a

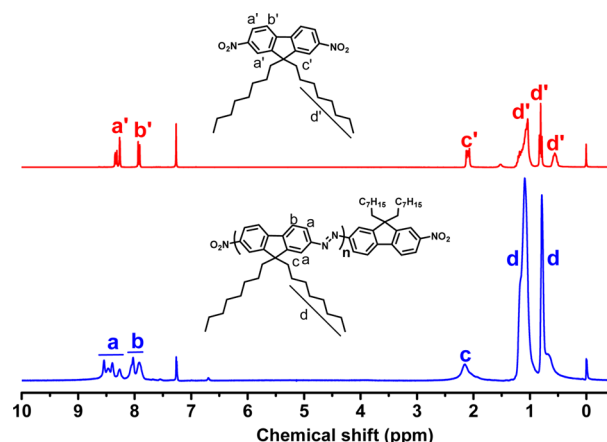
entry	PA-2h	PA-4h	PA-8h	PA-12h	PB-24h	PC-24h
<i>t</i> (h)	2	4	8	12	24	24
conv (%)	77	96	95	96	95	92
<i>M</i> _{n,GPC} (g/mol)	2300	21600	29800	28000	4100	4600
<i>M</i> _w / <i>M</i> _n	1.13	2.49	4.11	2.63	1.16	1.50

^aThe reaction was carried out with 80 mg of bisnitroaromatic monomers (A, B, and C) in argon atmosphere at 45 °C, and the polymers were precipitated in methanol. Isopropyl alcohol (3 mL), toluene (3 mL), catalyst (33 mg), KOH (5.6 mg).

polymerization results of monomers B and C at various conditions are given in Table S2. In addition, the dosage of monomer C has no obvious effect on the monomer conversion, however, which slightly affected the molecular weights of the obtained polymers (Table S2, entries 5–7). The reason may be attributed to the low catalytic efficiency resulted from aggregation of catalysts in high content of catalyst and less catalytic points in low content of monomer.

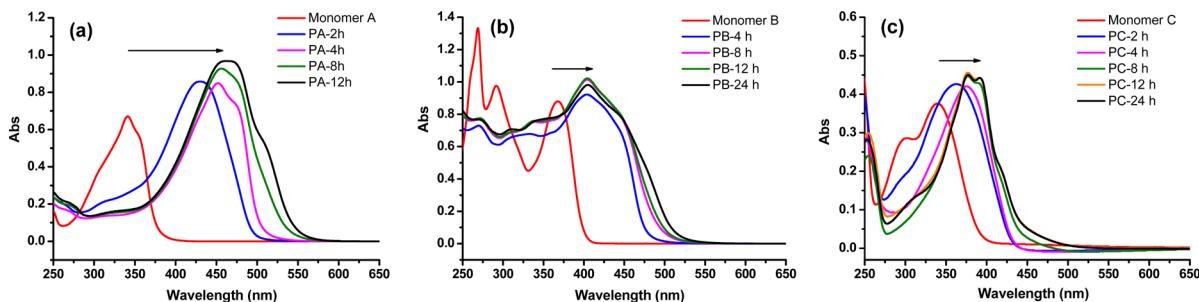
The polymerization processes of monomers A, B, and C were monitored by UV–vis (Figure 2a–c) and FT-IR (Figure S9). As presented in Figure 2a–c, the UV–vis spectra of the monomers (A, B, and C) and the corresponding polymers (PAs, PBs, and PCs) with different reaction time showed significantly stepwise red-shifts (125 nm from 340 to 465 nm for monomer A and PA, 38 nm from 368 to 406 nm for monomer B and PB, and 35 nm from 340 to 375 nm for monomer C and PC) with the elongation of conjugated systems and suggested the polymerization processes.²⁸ A further evidence for successful formation of PA, PB, and PC was provided by FT-IR spectra. As presented in Figure S9, the absorption peaks around 1602, 1594, and 1585 cm^{−1} attributed to the stretching vibration of Azo group in PA, PB, and PC chains^{12a} became obvious stronger along with the reaction time, respectively. Simultaneously, the nitro absorption around 1342, 1334, and 1350 cm^{−1} became weaker along with the reaction time,²⁹ which leveled off after 8 h. The weaker nitro absorption peaks are ascribed to the stretching vibration of nitro groups in PA, PB, and PC chain ends.

The chemical structures of PA, PB, and PC were characterized by ¹H NMR (Figure 3 and Figure S10). The characteristic chemical shifts from 7.75 to 8.73 ppm, 7.30 to 9.50 ppm, and 6.90 to 7.55 ppm were attributed to the protons of the aromatic rings in the main-chain Azo polymers PA, PB, and PC, respectively. The characteristic peaks of methylene group close to the 9-position of fluorene in PA at 2.20 ppm

**Figure 3.** ¹H NMR spectra of monomer A and PA-12h in CDCl₃.

were clearly observed. The characteristic peaks of methyne group close to N atoms of the carbazole unit in PB at 4.62 ppm and the methoxy group in PC at 4.06 ppm were also confirmed by ¹H NMR spectra.

Furthermore, a thorough study of the obtained polymer structure was carried out by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS).³⁰ The MALDI-TOF-MS spectra of PAs with different reaction time (PA-2h, PA-12h) are presented in Figure 4. As expected, a representative peak of *m/z* at 2665.0 corresponding to 5-mer of PA-2h is in good agreement with the calculated mass ([*M*' + Na]⁺, calcd: 2664.9), and a regular interval 432.3 Da was observed in PA-2h, agreeing well with the molar mass of the corresponding azoxy repeating unit. A representative peak of *m/z* at 2563.4 corresponding to 5-mer of PA-12h with a proton is in good agreement with the calculated mass ([*M* + H]⁺, calcd: 2562.9), and a regular interval 416.4 Da was observed in PA-12h, which is attributed to the molar mass of the corresponding Azo repeating unit in PA chain. Meanwhile, similar experimental data were obtained in MALDI-TOF-MS spectra of PBs and PCs with different reaction time as given in Figure S11. These data agree well with UV–vis, FT-IR, and ¹H NMR studies as discussed above. In order to study the polymerization mechanism, the reaction time was reduced to 0.5 h for the photocatalyzed reduction reaction of NOFL and monomer A. Indeed only the azoxy products with single N–O bond are generated evidenced by ¹H NMR, MALDI-TOF-MS, and FT-IR, rather than two N–O bonds. These data are very similar to those of products obtained in 2 h and not shown here. It turns out that the overall polymerization reaction process involved two main steps as depicted in Figure 1, which

**Figure 2.** UV–vis absorption spectra of (a) bisnitroaromatic monomers A and corresponding polymers PAs, (b) B and PBs, and (c) C and PCs with different reaction time in THF (*C*_{n,A}, *C*_{n,C}, *C*_{n,PA}, *C*_{n,PC} = 0.02 g/L; *C*_{n,B}, *C*_{n,PB} = 0.05 g/L).

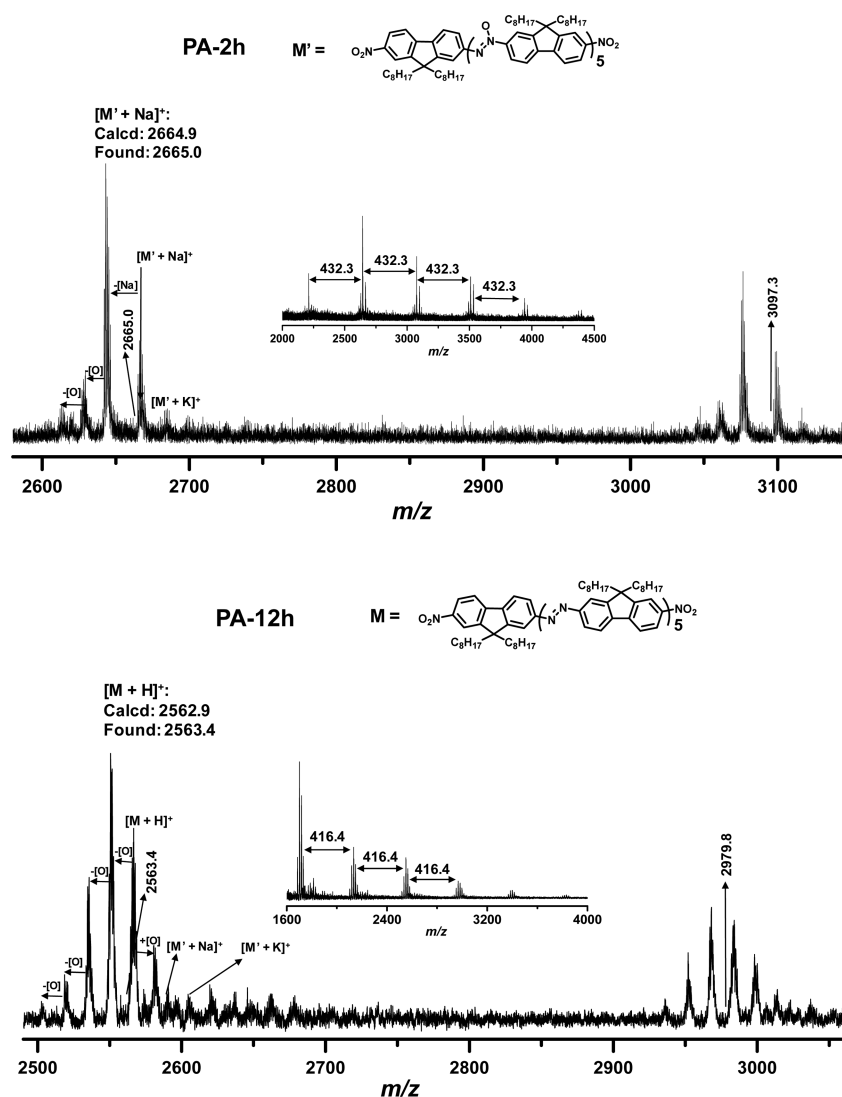


Figure 4. MALDI-TOF-MS spectra of PA-2h (top) and PA-12h (bottom).

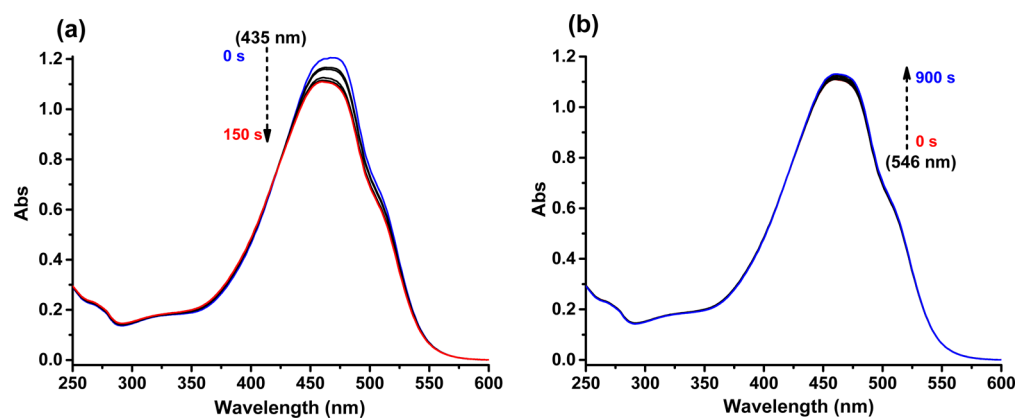


Figure 5. Absorption spectra of PA-4 solution during continuous 435 nm (a) and 546 nm (b) light irradiation in THF. The concentration of PA-4 ($M_{n, GPC} = 28\,000$ g/mol, $M_w/M_n = 2.63$) is 0.02 g/L.

is slightly different as proposed by Zhu's group.^{27b} In the first step, the azoxy repeating units were formed from the corresponding bisnitroaromatic monomers. In the second step, the Azo repeating units were formed via the reduction of corresponding azoxy repeating units.

Considering the intrinsic ability of *trans*–*cis* photoisomerization of Azo chromophore, the *trans*–*cis* photoisomerizations of PA, PB, and PC were investigated by UV–vis spectra. As evidenced in Figure 5 and Figures S12 and S13, the absorption bands centered at 465/410/375 nm contributing to the π – π^* electronic transition of the *trans*-Azo in PA/PB/PC backbone

were observed. Unusually, the solution of PA/PB showed a slight decrease in the π – π^* electronic transition of the *trans*-Azo absorption around 465/410 nm upon the 435/404 nm light irradiation (Figure 5 and Figure S12). It is likely due to the rigid conjugated backbone structures of polymers.^{3b} Expectedly, the obvious *trans*–*cis* photoisomerization of Azo chromophore in PC chain was observed upon time-dependent irradiation with 365 nm UV light (2.6 mW/cm²), which is evidenced by a sharp decrease of the absorbance at 375 nm along with a concomitant slight increase at 475 nm (Figure S13a). Subsequently, the *cis*–*trans* photoisomerization was completed upon the 180 s visible-light (435 nm, 0.9 mW/cm²) irradiation (Figure S13b).

To further confirm the effectiveness of the current photocatalyst system, the catalyst (ZrO₂-supported AuNPs) was recycled and reused to catalyze the reduction of the nitroaromatic (NOFL) and bisnitroaromatic (monomer A) compounds. As shown in Figure 6, the recycled photocatalyst

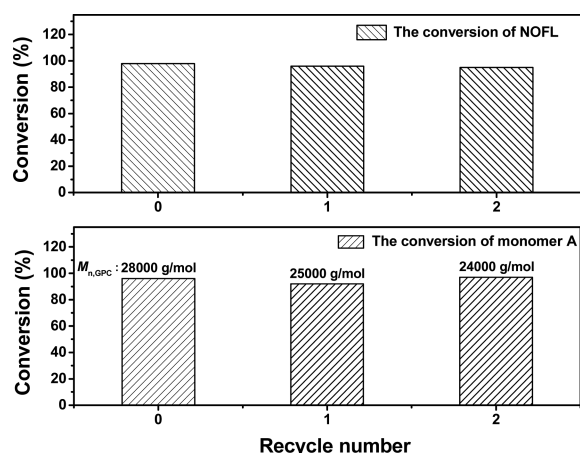


Figure 6. Catalyst efficiency of the recycled AuNPs for the reduction of nitroaromatic compound NOFL and monomer A.

can be reused at least two times without obvious loss of activity on this scale. The UV–vis spectra, TEM images, and atomic absorption spectroscopy (Figures S14 and S15) all confirmed almost no change in the size and dispersion of the gold nanoparticles supported on ZrO₂ before and after reuse, demonstrating the excellent retention of the effectiveness of the recycled catalyst.

CONCLUSIONS

In summary, we have developed a novel approach to prepare the main-chain Azo polymers directly from bisnitroaromatic compounds photocatalyzed by ZrO₂-supported AuNPs under mild conditions. The most outstanding feature of this photocatalyst is its excellent activity and selectivity in the reduction of bisnitroaromatic compounds, which prevents the formation of the azoxy units in the final polymer chains. The other advantage of current system is the preparation of Azo polymers from the direct reduction of bisnitroaromatic compounds, without additional procedures for tedious design and synthesis of aromatic dianilines or Azo monomers as reported. The retention of activity and selectivity of recovered catalysts and relatively lower reaction temperature and pressure, combined with the potential to utilize solar energy, reveal an attractive green process for preparation of main-chain Azo polymers and will open a novel window for preparing Azo polymer materials. Studies are ongoing in our group to prepare

Azo polymers with other topological structures and investigate the application of conjugated Azo polymers synthesized via the current approach.

ASSOCIATED CONTENT

Supporting Information

Synthesis, ¹H NMR spectra, ¹³C NMR spectra, TEM images, GPC traces, FT-IR spectra, UV–vis spectra, and MALDI-TOF-MS spectra of compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) (a) Tamai, N.; Miyasaka, H. *Chem. Rev.* **2000**, *100*, 1875–1890. (b) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817–1845. (c) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847–1873. (d) Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139–4175. (e) Sourisseau, C. *Chem. Rev.* **2004**, *104*, 3851–3891. (f) Merino, E. *Chem. Soc. Rev.* **2011**, *40*, 3835–3853. (g) Bandara, H. M. D.; Burdette, S. C. *Chem. Soc. Rev.* **2012**, *41*, 1809–1825. (h) Griffiths, J. *Chem. Soc. Rev.* **1972**, *1*, 481–493. (i) Nuyken, O.; Scherer, C.; Baidl, A.; Brenner, A. R.; Dahn, U.; Gärtner, R.; Kaiser-Röhrich, S.; Kollefath, R.; Matusche, P.; Voit, B. *Prog. Polym. Sci.* **1997**, *22*, 93–183. (j) Yesodha, S. K.; Pillai, C. K. S.; Tsutsumi, N. *Prog. Polym. Sci.* **2004**, *29*, 45–74. (k) Wang, D. R.; Wang, X. G. *Prog. Polym. Sci.* **2013**, *38*, 271–301. (l) Kamiya, Y.; Asanuma, H. *Acc. Chem. Res.* **2014**, *47*, 1663–1672. (m) Bisoyi, H. K.; Li, Q. *Acc. Chem. Res.* **2014**, *47*, 3184–3195.
- (2) (a) Yu, Y. L.; Nakano, M.; Ikeda, T. *Nature* **2003**, *425*, 145–145. (b) Wang, D. R.; Ye, G.; Wang, X. L.; Wang, X. G. *Adv. Mater.* **2011**, *23*, 1122–1125. (c) Yamada, M.; Kondo, M.; Mamiya, J. I.; Yu, Y. L.; Kinoshita, M.; Barrett, C. J.; Ikeda, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 4986–4988. (d) Li, C.; Zhang, Y. Y.; Ju, J.; Cheng, F. T.; Liu, M. J.; Jiang, L.; Yu, Y. L. *Adv. Funct. Mater.* **2012**, *22*, 760–763. (e) Zhang, W.; Yoshida, K.; Fujiki, M.; Zhu, X. L. *Macromolecules* **2011**, *44*, 5105–5111. (f) Schmidt, B. V. K. J.; Hetzer, M.; Ritter, H.; Barner-Kowollik, C. *Macromolecules* **2013**, *46*, 1054–1065. (g) Blasco, E.; Schmidt, B. V. K. J.; Barner-Kowollik, C.; Piñol, M.; Oriol, L. *Macromolecules* **2013**, *47*, 3693–3700. (h) Bobrovsky, A.; Shibaev, V.; Bubnov, A.; Hamplová, V.; Kašpar, M. *Macromolecules* **2013**, *46*, 4276–4284. (i) Li, J. Z.; Zhou, Z.; Ma, L.; Chen, G. X.; Li, Q. F. *Macromolecules* **2014**, *47*, 5739–5748. (j) Sano, M.; Nakamura, S.; Hara, M.; Nagano, S.; Shinohara, Y.; Amemiya, Y.; Seki, T. *Macromolecules* **2014**, *47*, 7178–7186. (k) Wang, W.; Sun, X. M.; Wu, W.; Peng, H. S.; Yu, Y. L. *Angew. Chem., Int. Ed.* **2012**, *51*, 4644–4647.
- (3) (a) Xue, X. Q.; Zhu, J.; Zhang, Z. B.; Zhou, N. C.; Tu, Y. F.; Zhu, X. L. *Macromolecules* **2010**, *43*, 2704–2712. (b) Lee, K. M.; Wang, D. H.; Koerner, H.; Vaia, R. A.; Tan, L. S.; White, T. J. *Angew. Chem., Int. Ed.* **2012**, *124*, 4193–4197. (c) Wang, D. H.; Wie, J. J.; Lee, K. M.; White, T. J.; Tan, L. S. *Macromolecules* **2014**, *47*, 659–667.

- (4) (a) Kuo, T.; Hall, H. K., Jr. *Synth. Met.* **1987**, *22*, 115–120. (b) Angeloni, A. S.; Caretti, D.; Carlini, C.; Chiellini, E.; Galli, G.; Altomare, A.; Solaro, R.; Laus, M. *Liq. Cryst.* **1989**, *4*, 513–527. (c) Komura, M.; Komiyama, H.; Nagai, K.; Iyoda, T. *Macromolecules* **2013**, *46*, 9013–9020. (d) Komiyama, H.; Sakai, R.; Hadano, S.; Asaoka, S.; Kamata, K.; Iyoda, T.; Komura, M.; Yamada, T.; Yoshida, H. *Macromolecules* **2014**, *47*, 1777–1782. (e) Li, Z. A.; Wu, W. B.; Yu, G.; Liu, Y. Q.; Ye, C.; Qin, J. G.; Li, Z. *ACS Appl. Mater. Interfaces* **2009**, *1*, 856–863.
- (5) (a) Zhao, Y.; He, J. *Soft Matter* **2009**, *5*, 2686–2693. (b) Ueki, T.; Nakamura, Y.; Yamaguchi, A.; Niitsuma, K.; Lodge, T. P.; Watanabe, M. *Macromolecules* **2011**, *44*, 6908–6914. (c) Zhang, Y. Y.; Cheng, Z. P.; Chen, X. R.; Zhang, W.; Wu, J. H.; Zhu, J.; Zhu, X. L. *Macromolecules* **2007**, *40*, 4809–4817.
- (6) (a) Acerno, D.; Amendola, E.; Bugatti, V.; Concilio, S.; Giorgini, L.; Iannelli, P.; Piotta, S. P. *Macromolecules* **2004**, *37*, 6418–6423. (b) Agata, Y.; Kobayashi, M.; Kimura, H.; Takeishi, M. *Polym. Int.* **2005**, *54*, 260–266. (c) Bahulayan, D.; Sreekumar, K. *J. Mater. Chem.* **1999**, *9*, 1425–1429. (d) Boissiere, O.; Han, D. H.; Tremblay, L.; Zhao, Y. *Soft Matter* **2011**, *7*, 9410–9415. (e) Everlofa, G. J.; Jaycox, G. D. *Polymer* **2000**, *41*, 6527–6536. (f) Faghihi, K.; Hagibeygi, M. *Eur. Polym. J.* **2003**, *39*, 2307–2314. (g) Howe, L. A.; Jaycox, G. D. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2827–2837. (h) Jaycox, G. D. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 566–577. (i) Irie, M.; Hirano, Y.; Hashimoto, S.; Hayashi, K. *Macromolecules* **1981**, *14*, 262–267. (j) Keum, C. D.; Ikawa, T.; Tsuchimori, M.; Watanabe, O. *Macromolecules* **2003**, *36*, 4916–4923. (k) Sapich, B.; Vix, A. B. E.; Rabe, J. P.; Stumpe, J. *Macromolecules* **2005**, *38*, 10480–10486. (l) Xu, Z. S.; Drnoyan, V.; Natansohn, A.; Rochon, P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2245–2253.
- (7) (a) Wu, Y. L.; Natansohn, A.; Rochon, P. *Macromolecules* **2001**, *34*, 7822–7828. (b) Aruna, P.; Rao, B. S. *React. Funct. Polym.* **2009**, *69*, 20–26. (c) Huang, D. Y.; Zhang, C.; Dalton, L. R.; Weber, W. P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 546–559. (d) Palanisamy, A.; Sundar, S.; Radhakrishnan, G. *J. Appl. Polym. Sci.* **2004**, *93*, 444–454. (e) Sandhya, K. Y.; Pillai, C. K. S. *J. Appl. Polym. Sci.* **2004**, *91*, 1976–1982. (f) Smitha, P.; Asha, S. K.; Pillai, C. K. S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4455–4468.
- (8) (a) Izumi, A.; Teraguchi, M.; Nomura, R.; Masuda, T. *Macromolecules* **2000**, *33*, 5347–5352.
- (9) (a) Shen, X. Q.; Liu, H. W.; Li, Y. S.; Liu, S. Y. *Macromolecules* **2008**, *41*, 2421–2425. (b) Xu, X.; Zhou, N. C.; Zhu, J.; Tu, Y. F.; Zhang, Z. B.; Cheng, Z. P.; Zhu, X. L. *Macromol. Rapid Commun.* **2010**, *31*, 1791–1797. (c) Xue, X. Q.; Zhu, J.; Zhang, W.; Zhang, Z. B.; Zhu, X. L. *Polymer* **2009**, *50*, 4512–4519.
- (10) (a) Izumi, A.; Teraguchi, M.; Nomura, R.; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1057–1063. (b) Izumi, A.; Nomura, R.; Masuda, T. *Macromolecules* **2001**, *34*, 4342–4347. (c) Ding, L.; Zhang, L. Y.; Han, H. J.; Huang, W.; Song, C. M.; Xie, M. R.; Zhang, Y. Q. *Macromolecules* **2009**, *42*, 5036–5042. (d) Heo, J.; Kim, Y. J.; Seo, M.; Shin, S.; Kim, S. Y. *Chem. Commun.* **2012**, *48*, 3351–3353. (e) Ouchi, Y.; Morisaki, Y.; Ogoshi, T.; Chujo, Y. *Chem.—Asian J.* **2007**, *2*, 397–402. (f) Yu, X. W.; Luo, Y. H.; Deng, Y.; Yan, Q.; Zou, G.; Zhang, Q. *J. Eur. Polym. J.* **2008**, *44*, 881–888.
- (11) (a) Kotlyarevskii, I. L.; Terpugova, M. P.; Andrievskaya, É. K. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1964**, *10*, 1854–1860. (b) Bach, H. C. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1967**, *8*, 610.
- (12) (a) Nguyen, H. T.; Coulembier, O.; Gheysen, K.; Martins, J. C.; Dubois, P. *Macromolecules* **2012**, *45*, 9547–9550. (b) Arab, P.; Rabbani, M. G.; Sekizkardes, A. K.; İslamoğlu, T.; El-Kaderi, H. M. *Chem. Mater.* **2014**, *26*, 1385–1392.
- (13) Schilling, M. L.; Katz, H. E.; Cox, D. I. *J. Org. Chem.* **1988**, *53*, 5538–5540.
- (14) (a) Wang, X. G.; Chen, J. I.; Marturunkakul, S.; Li, L.; Kumar, J.; Tripathy, S. K. *Chem. Mater.* **1997**, *9*, 45–50. (b) Wang, X. G.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1997**, *30*, 219–225. (c) Che, P. C.; He, Y. N.; Wang, X. G. *Macromolecules* **2005**, *38*, 8657–8663. (d) He, Y. N.; He, W.; Wei, R. B.; Chen, Z.; Wang, X. G. *Chem. Commun.* **2012**, *48*, 1036–1038. (e) He, Y. N.; He, W.; Liu, D.; Gu, T. H.; Wei, R. B.; Wang, X. G. *Polym. Chem.* **2013**, *4*, 402–406.
- (15) (a) Svele, I.; Zollinger, H. *Top. Curr. Chem.* **1983**, *112*, 1–66. (b) Haghighi, K.; Tan, E. W. *J. Org. Chem.* **1998**, *63*, 4503–4505.
- (16) (a) Ueno, K.; Akiyoshi, S. *J. Am. Chem. Soc.* **1954**, *76*, 3667–3670. (b) Davey, H. H.; Lee, R. D.; Marks, T. J. *J. Org. Chem.* **1999**, *64*, 4976–4979. (c) Tie, C.; Gallucci, J. C.; Parquette, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 1162–1171.
- (17) (a) Zhang, C.; Jiao, N. *Angew. Chem., Int. Ed.* **2010**, *49*, 6174–6177. (b) Zhu, Y. G.; Shi, Y. A. *Org. Lett.* **2013**, *15*, 1942–1945. (c) Reddy, C. B. R.; Reddy, S. R.; Naidu, S. *Catal. Commun.* **2014**, *56*, 50–54.
- (18) (a) Tanner, D. D.; Gidley, G. C.; Das, N.; Rowe, J. E.; Potter, A. *J. Am. Chem. Soc.* **1984**, *106*, 5261–5267. (b) Takeda, Y.; Okumura, S.; Minakata, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 7804–7808. (c) Okumura, S.; Lin, C. H.; Takeda, Y.; Minakata, S. *J. Org. Chem.* **2013**, *78*, 12090–12105.
- (19) Nystrom, R. F.; Brown, W. G. *J. Am. Chem. Soc.* **1948**, *70*, 3738–3740.
- (20) Hutchins, R. O.; Lamson, D. W.; Rua, L.; Milewski, C.; Maryanoff, B. *J. Org. Chem.* **1971**, *36*, 803–806.
- (21) Srinivasa, G. R.; Abiraj, K.; Gowda, D. C. *Aust. J. Chem.* **2004**, *57*, 609–610.
- (22) Sakai, N.; Fujii, K.; Nabeshima, S.; Ikeda, R.; Konakahara, T. *Chem. Commun.* **2010**, *46*, 3173–3175.
- (23) Hu, L.; Cao, X. Q.; Shi, L. Y.; Qi, F. Q.; Guo, Z. Q.; Lu, J. M.; Gu, H. W. *Org. Lett.* **2011**, *13*, 5640–5643.
- (24) (a) Ke, X. B.; Zhang, X. G.; Zhao, J.; Sarina, S.; Barry, J.; Zhu, H. Y. *Green Chem.* **2013**, *15*, 236–244. (b) Guo, X. N.; Hao, C. H.; Jin, G. Q.; Zhu, H. Y.; Guo, X. Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 1973–1977.
- (25) Stratakis, M.; García, H. *Chem. Rev.* **2012**, *112*, 4469–4506.
- (26) (a) Blaser, H. U. *Science* **2006**, *313*, 312–313. (b) Grirrane, A.; Corma, A.; García, H. *Science* **2008**, *332*, 1661–1664. (c) Liu, X.; Li, H. Q.; Ye, S.; Liu, Y. M.; He, H. Y.; Cao, Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 7624–7628.
- (27) (a) Zhu, H. Y.; Chen, X.; Zheng, Z. F.; Ke, X. B.; Jaatinen, E.; Zhao, J. C.; Guo, C.; Xie, T. F.; Wang, D. J. *Chem. Commun.* **2009**, 7524–7526. (b) Zhu, H. Y.; Ke, X. B.; Yang, X. Z.; Sarina, S.; Liu, H. W. *Angew. Chem., Int. Ed.* **2010**, *49*, 9657–9661.
- (28) Lu, B. Y.; Zhen, S. J.; Zhang, S. M.; Xu, J. K.; Zhao, G. Q. *Polym. Chem.* **2014**, *5*, 4896–4908.
- (29) (a) Haap, W. J.; Walk, T. B.; Jung, G. *Angew. Chem., Int. Ed.* **1998**, *37*, 3311–3314. (b) Simões, P. N.; Reva, I.; Pedroso, L. M.; Fausto, R.; Portugal, A. A. *J. Phys. Chem. A* **2008**, *112*, 3432–3443.
- (30) (a) Luftmann, H.; Rabani, G.; Kraft, A. *Macromolecules* **2003**, *36*, 6316–6324. (b) Ulmer, L.; Mattay, J.; Torres-Garcia, H. G.; Luftmann, H. *Eur. J. Mass Spectrom.* **2000**, *6*, 49–52. (c) Sarver, A.; Scheffler, N. K.; Shetlar, M. D.; Gibson, B. W. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 439–448.