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# Molecular Structural Design of Conjugated Microporous Poly(Benzooxadiazole) Networks for Enhanced Photocatalytic Activity with Visible Light

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Sunlight is a clean and inexhaustible source of renewable energy. Especially, the visible range of the solar spectrum accounts for 44% of the total energy as opposed to only 3% from the ultraviolet (UV) light. Inspired by nature's ability to convert solar energy to chemical potentials in photosynthesis, organic chemists have developed a variety of visible light photocatalysts to mimic the natural process.<sup>[1]</sup> As a result, many molecular inorganic, transition metal-based complexes or organic dye compounds that absorb significantly in the visible spectrum were intensely studied to harvest solar energy and catalyze organic photochemical reactions.<sup>[2,3]</sup> Nevertheless, there are some intrinsic drawbacks associated with these homogeneous systems, such as high cost, toxicity of these rare metals, as well as limited availability and postreaction purification steps for catalyst removal. The above-mentioned disadvantages have led material scientists to pursue the further development of stable, recyclable, reusable, and transition metal-free photocatalysts for organic synthesis.

In recent years, there have been few responses to the acute need of heterogeneous nonmetal photocatalytic systems.<sup>[4]</sup> Conjugated microporous polymers (CMPs), combining photoactive  $\pi$ -electron backbone and microporous properties, have recently emerged as an efficient and stable platform for heterogeneous visible light-promoted chemical transformations such as molecular oxygen activation,<sup>[5]</sup> selective oxidation of organic sulfides,<sup>[6]</sup> C–C bond formation,<sup>[7]</sup> reductive dehalogenation reaction,<sup>[8]</sup> oxidative hydroxylation of arylboronic acids,<sup>[9]</sup> visible light-initiated free radical and cationic polymerization,<sup>[10]</sup> and light-induced hydrogen evolution.<sup>[11]</sup>

For transition metal-based homogeneous organometallic complexes, the redox potential can be easily adjusted by modifying the metal center and surrounding ligands, in order to meet the specific activation energies of the organic reactions.<sup>[3]</sup> Similarly, the effective valence (VB) and conduction band (CB) positions of inorganic heterogeneous metal photocatalytic systems can also be modified by the formation of hybrid or heterostructures with selected metals to achieve enhanced photoactivity.<sup>[12]</sup>

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DOI: 10.1002/adma.201502735



Motivated by the band position tuning methods for transition metal-based and other inorganic systems, we herein present a simple structural design principle of conjugated microporous polymers as pure organic, heterogeneous photocatalytic systems to allow the fine alignment of the valence and conduction band levels for enhanced catalytic activity. As shown in Scheme 1, we show that by merely altering the substitution positions on the centered phenyl unit, which functions as the 3D center of the polymer network, the VB and CB positions can be aligned to optimally bracket the redox potentials of individual catalytic reactions, without changing the electron donor and acceptor moieties in the polymer network backbone. Under light irradiation, the photogenerated electrons and holes function as the reductive and oxidative sides of the organic polymerbased photocatalyst, respectively. The enhanced photocatalytic activity of the CMPs was demonstrated in the oxidative coupling of amines under irradiation of a 23 W household energy saving fluorescent light bulb.

The chemical structures of the synthesized CMPs are displayed in Scheme 1. Taking a phenyl unit as the 3D center, a well-known electron acceptor, benzoxadiazole (BO) unit was connected via a triple bond to the phenyl unit on its 1,3,5-, 1,2,4- and 1,2,4,5-positions, forming the microporous polymer networks B-BO-1,3,5 B-BO-1,2,4 and B-BO-1,2,4,5, respectively. The synthetic details and characterization data are described in the Experimental Section and Supporting Information. The resulting polymers are insoluble in all common organic solvents tested. Solid state <sup>13</sup>C/MAS NMR spectroscopy showed similar signals for all three CMPs between 80 and 160 ppm, which can be assigned to the aromatic carbons. The Brunauer-Emmett-Teller surface areas of B-BO-1,3,5, B-BO-1,2,4 and B-BO-1,2,4,5 were measured to be 474 m<sup>2</sup> g<sup>-1</sup>, 475 m<sup>2</sup> g<sup>-1</sup>, and  $378 \text{ m}^2 \text{ g}^{-1}$ , with pore volumes of 0.31 cm<sup>3</sup> g<sup>-1</sup>, 0.37 cm<sup>3</sup> g<sup>-1</sup>, and 0.20 cm<sup>3</sup> g<sup>-1</sup>, respectively. Similar pore diameters of round 1.5 nm were determined for all three polymers (Table S1 and Figures S1 and S2, Supporting Information). Thermal gravimetric analysis measurements showed a high thermal stability of B-BO-1,3,5 and B-BO-1,2,4 up to ≈350 °C, while B-BO-1,2,4,5 showed a lower thermal stability of up to  $\approx 200$  °C (Figure S3, Supporting Information). The Fourier transform infrared (FTIR) spectra of the polymers are displayed in Figure S7–S9 (Supporting Information). the signal at 1620 cm<sup>-1</sup> can be assigned to the C=N stretching mode of the BO unit of the polymer networks. Signals between 1370 and 1440 cm<sup>-1</sup> indicate the skeleton vibration of the aromatic rings in the polymers. A C=C stretching mode at1600 cm<sup>-1</sup> was observed. All



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## Structural Design Principle



Scheme 1. Geometry design principle of valence and conduction band position modification of conjugated microporous poly(benzooxadiazole) networks by altering the substitution position on the 3D center.

networks showed the typical C=C stretching mode at about 2200  $\rm cm^{-1}.$ 

The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the three CMPs illustrated different morphologies at submicron scale (**Figure 1**). In particular, B-BO-1,3,5 appeared as fiber-like structures with a diameter of less than 100 nm (Figure 1a,d), whereas a porous flake-like shape was observed for CMP B-BO-1,2,4 (Figure 1b,e) and B-BO-1,2,4,5 showed a fused irregular particle-like structure (Figure 1c,f). This formation mechanism could stem from the steric effect inside the polymer network due to different substitution positions of their 3D center.

In **Figure 2**a, the UV/Vis diffuse reflectance (DR) spectra of the CMPs are displayed. B-BO-1,3,5 show a broad absorption range until 800 nm, while B-BO-1,2,4 and B-BO-1,2,4,5 absorb significantly up to the near-infrared region, indicating a decreasing optical band gap within the CMP series. This also corresponds to the color change in the CMP series, from yellowish, brown to almost black for B-BO-1,3,5, B-BO-1,2,4 and B-BO-1,2,4,5, respectively (Figure S10, Supporting Information).

Cyclic voltammetry measurements revealed lowering potentials during the reductive and oxidative cycles within the polymer series (Figure 2b and Figures S14-S16, Supporting Information), implying different VB and CB positions of the polymer series. B-BO-1,3,5 exhibited VB and CB at +1.55 V and -1.19 V. In comparison, the VB and CB positions of B-BO-1,2,4 and B-BO-1,2,4,5 were determined to be at +1.45 V/-1.13 V and +1.14 V/-0.89 V, respectively. This is comparable to the redox potentials of established organometallic photocatalysts such as  $[Ru(bpy)_3]^{3+}$  (+1.29 V) and  $[Ru(bpy)_3]^{2+}$  (-0.81 V). The electron paramagnetic resonance (EPR) spectra showed a large increase in the intensity B-BO-1,3,5 under light irradiation, whereas B-BO-1,2,4 and B-BO-1,2,4,5 barely exhibited an enhanced signal (Figure S11-S13, Supporting Information). This probably indicates that longer living electron-hole pairs were generated in B-BO-1,3,5 under light irradiation compared to those of other CMPs.

It was previously shown that conjugated macromolecular systems could mediate the electron transfer from N, N, N', N'-tetramethyl-phenylenediamine (TMPD) ( $E_{\text{oxi}} = 0.12$  V vs saturated calomel electrode (SCE)) to molecular oxygen, resulting

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![](_page_2_Figure_3.jpeg)

**Figure 1.** SEM images of a) B-BO-1,3,5, b) B-BO-1,2,4, and c) B-BO-1,2,4,5, and TEM images of d) B-BO-1,3,5, e) B-BO-1,2,4, and f) B-BO-1,2,4,5.

in blue-colored cationic radical and the activated oxygen species superoxide ( $O_2^{\bullet-}$ ) ( $E_{red} = 0.86$  V vs SCE) under light irradiation, using the photogenerated hole inside the conjugated system as the oxidative side and the photoexcited electron as reductive

![](_page_2_Figure_6.jpeg)

Figure 2. a) UV/Vis DR spectra. b) Valence band (VB) and conduction band (VB) positions of the CMPs and redocx potentials of some substrates such as benzylamine (BA) and molecular oxygen into superoxide used in the photocatalytic reaction determined via cyclic voltammetry.

side.<sup>[13]</sup> As shown in **Figure 3**a, the intensity variations in UV/ Vis absorption spectra of the resulting blue-color species verified the superior photooxidative activity of B-BO-1,3,5 compared to B-BO-1,2,4 and B-BO-1,2,4,5, which results from the highest oxidation potential of 1.55 V and reduction potential of -1.19 V of B-BO-1,3,5 (Figure 2b). Previously, we reported that CMPs could generate singlet oxygen species (<sup>1</sup>O<sub>2</sub>) under light irradiation, using triplet electrons in the excited state.<sup>[14]</sup> Here, spin trap EPR experiments were conducted using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) as superoxide and singlet oxygen trapping agents, respectively. As shown in Figure 3c,d, both active oxygen species  $O_2^{\bullet-}$  and <sup>1</sup>O<sub>2</sub> could be determined, with B-BO-1,3,5 generating the most intense signals among the three polymers.

To further determine the feasibility of CMPs and confirm the superior catalytic activity of B-BO-1,3,5 in visible light-promoted photocatalytic chemical transformation reactions, the oxidative coupling reaction of benzvlamines was chosen as a model reaction. The three CMPs were employed under exactly the same reaction conditions to catalyze the photooxidative coupling of benzylamine and its derivatives bearing electrondonating (-OCH<sub>3</sub>) and electron-withdrawing (-F) moieties (Table 1, entries 1–3). As expected, the reactions catalyzed with B-BO-1,3,5 achieved significantly higher conversions (entry 1) than the other two CMPs in all three cases. This further demonstrates that 3D network structure with 1,3,5-substitution on the center phenyl unit delivers the highest reduction and oxidation potentials and therefore the most efficient photocatalyst. Terao et al. reported structurally defined conjugated polymers and demonstrated that significantly higher charge mobility can be attained by simply changing the configuration of poly(phenylene-ethynylene) from linear (para, via 1,4-positions) to zigzag (meta, via 1,3-positions) chain through the phenyl unit.<sup>[15]</sup> This could explain the superior photocatalytic performance of B-BO-1,3,5.

To further investigate the reaction mechanism and the specific roles of the photogenerated electron-hole pairs during oxidative coupling reaction of benzylamines, we extended the study by conducting control experiments and adding different hole and electron scavengers into the reaction mixture (Table 1). From entries 4–6, it could be concluded that all three components, B-BO-1,3,5 as photocatalyst, light, and oxygen, are indispensable for achieving high conversion. By adding KI, i.e., a hole scavenger, a reduced conversion of 14% was obtained (entry 7). By adding benzoquinone as superoxide scavenger, a conversion of only 5% was found (entry 8). Using sodium azide as a singlet oxygen scavenger led to a conversion of 24% (entry 9). All these results indicate that both activated oxygen species (e.g., superoxide and singlet oxygen) took part in the oxidative coupling reaction of benzylamine, with superoxide playing a more significant role. Based on our observations from the screening and control experiments, we propose a modified reaction mechanism similar to the literature.<sup>[16]</sup> As displayed in Figure 3b, under light irradiation, benzylamine loses an electron to the photogenerated hole of the CMP and then forms its cationic radical intermediate, which reacts with both photogenerated active oxygen species to form the intermediate hydroperoxy (phenyl)methanamine. During the monitoring experiment (Figure S18, Supporting Information), we did not

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Figure 3. a) UV/Vis spectra and photograph of the cationic radical of TMPD ( $100 \times 10^{-3}$  M in 3 mL CH<sub>3</sub>CN) after photoinduced oxidation by CMPs (2 mg mL<sup>-1</sup>) after 1 h under a blue LED in air. Inset: i) B-BO-1,3,5, ii) B-BO-1,2,4, iii) B-BO-1,2,4,5. b) Proposed reaction mechanism of the photocatalytic oxidative coupling of benzylamine. ISC: intersystem crossing. c) ESR spectra of DMPO-O2<sup>•</sup>, and d) TEMPO-<sup>1</sup>O2 adducts for deferent CMPs under light and dark conditions.

Table 1. Oxidative coupling of benzylamines using the CMPs as photocatalyst.

Entry <sup>a)</sup>	СМР	O <sub>2</sub>	Light	Additive	Conversion <sup>b)</sup> [%]		
					R=H	R=F	$R = OCH_3$
1	B-BO-1,3,5	+	+	_	48	28	15
2	B-BO-1,2,4	+	+	-	17	8	6
3	B-BO-1,2,4,5	+	+	-	13	5	4
4 <sup>c)</sup>	-	+	+	-	<5	n.d.	n.d.
5 <sup>d)</sup>	B-BO-1,3,5	+	_	-	<1	n.d.	n.d.
6 <sup>e)</sup>	B-BO-1,3,5	-	+	-	<1	n.d.	n.d.
7 <sup>f)</sup>	B-BO-1,3,5	+	+	Hole scavenger	14	n.d.	n.d.
8 <sup>g)</sup>	B-BO-1,3,5	+	+	Superoxide scavenger	5	n.d.	n.d.
9 <sup>h)</sup>	B-BO-1,3,5	+	+	Singlet oxygen scavenger	24	n.d.	n.d.
10 <sup>i)</sup>	B-BO-B	+	+	_	68	n.d.	n.d.

a)All experiments were conducted with 1 mmol of substrate, 6 mg of CMP in 3 mL CH<sub>3</sub>CN under the irradiation of blue LED (460 nm, 1.2 W cm<sup>-2</sup>) for 3 h (1 atm O<sub>2</sub>, room temperature).<sup>b)</sup>Conversion determined by <sup>1</sup>H NMR and GCMS, n.d. indicates not detected. <sup>c)</sup>Without B-BO-1,3,5, under light, 1 atm O<sub>2</sub>. <sup>d)</sup>With B-BO-1,3,5, no light, 1 atm  $O_2$ . <sup>e)</sup>With B-BO-1,3,5, under light, no  $O_2$ . <sup>f)</sup>KI as hole scavenger. <sup>g)</sup>Benzoquinone (BQ) as superoxide scavenger. <sup>h)</sup>NaN<sub>3</sub> as singlet oxygen scavenger. <sup>i)</sup>B-BO-B as homogeneous catalyst, concentration: 2 mg mL<sup>-1</sup> in CH<sub>3</sub>CN, blue LED, 3 h.

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![](_page_4_Picture_1.jpeg)

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observe any evidence of benzaldehyde as a possible intermediate after the elimination of water and ammonia from hydroperoxy (phenyl)methanamine, we thus propose that it could form directly the imine species after elimination of  $H_2O_2$ ,<sup>[17]</sup> which then reacts with an additional benzylamine molecule, forming N-benzyl-1-phenylmethanediamine as intermediate. Interestingly, after reaching the full conversion of the catalytic reaction, benzaldehyde was determined (Figure S18, Supporting Information). This indicates that benzaldehyde is probably not an active intermediate, but an overoxidized side product after the reaction. After elimination of ammonia from the intermediate N-benzyl-1-phenylmethanediamine, the final product is obtained. Both photogenerated electrons and holes actively participate in the photooxidative coupling of amines. The reductive (-1.19 V) and oxidative (1.55 V) potentials of B-BO-1,3,5 are sufficiently high to reduce molecular oxygen into its active species and oxidize benzylamine into its cationic radical form ( $E_{oxi} = +1.08$  V) (Figure 2b). In comparison, the lower reductive (-0.89 V) and oxidative (1.14 V) potentials of B-BO-1,2,4,5 are rather insufficient for both redox processes.

A small molecule, 4,7-bis(phenylethynyl)benzo[c][1,2,5]-oxadiazole (B-BO-B) as a soluble and homogeneous analog was employed for the same photocatalytic reaction (entry 10). A higher conversion of 68% under the same reaction conditions was recorded. However, after the reaction, a clear decrease of the absorption maximum by  $\approx$ 30%, the so-called photobleaching effect, was observed (Figure S19, Supporting Information). In comparison, the heterogeneous counterpart B-BO-1,3,5 could be used for another five repeating cycles without significantly losing its catalytic efficiency (Figure S20, Supporting Information).

A number of benzylamine derivatives were also investigated to demonstrate the general applicability of B-BO-1,3,5 as photocatalyst (**Table 2**). To note, a 23 W household energy saving fluorescent light bulb was used as a low-cost light source. It could be determined that electron withdrawing groups such as F or Cl led to higher conversions (entries 12 and 13) than the electron donating groups such as methyl (entry 14), methoxy (entries 15 and 16). The reason could be the stabilized cationic radical by the methyl and especially methoxy groups, which decelerated the formation of the final product. However, this effect was not observed with the thiophene unit (entry 17).

In summary, we present a simple structural design principle of conjugated microporous polymers as pure organic, heterogeneous photocatalytic systems to allow the fine justification of the photoredox potential for enhanced catalytic activity. Via merely altering the substitution positions on the centered phenyl unit, which functions as the 3D center of a series of poly(benzooxadiazole) networks, the resulted valence and conduction band positions of the polymers can be optimally aligned to bracket the required reductive and oxidative potentials of the catalytic reactions, without changing the electron donor and acceptor moieties in the polymer network backbone. It was shown that the photocatalyst designed with the 1,3,5-substitution positions of the centered phenyl ring demonstrated the superior photocatalytic activity in the oxidative coupling of amines. Furthermore, the use of a house hold energy saving light bulb offered a commercially cost-saving solution for the general application of the photocatalysts. Overall this report is rather an experimental

**Table 2.** Screening experiments of the oxidative coupling of benzylamines using B-BO-1,3,5 as photocatalyst.

![](_page_4_Figure_8.jpeg)

<sup>a)</sup>Reaction conditions: B-BO-1,3,5 (6 mg), substrate (1 mmol), 1 atm  $O_2$ , 3 mL CH<sub>3</sub>CN, 23 W energy saving fluorescent light bulb, 24 h, water bath, room temperature. <sup>b)</sup>Conversion data were obtained by <sup>1</sup>H NMR.

study, for optimizing the polymer networks for high photocatalytic efficiency, molecular modeling would be helpful in guiding research directions and predicting experimental results. More theoretical studies will be conducted in future projects. Additionally, further studies on different 3D center molecules for more versatile structural design are on the way.

#### **Experimental Section**

Synthesis of B-BO-1,3,5, B-BO-1,2,4 and Synthesis of B-BO-1,2,4,5: To a solution of 0.02 mmol (23 mg) of tetrakis(triphenylphosphine) palladium(0), 0.02 mmol (4 mg) of CuI in 20 mL of DMF and Et<sub>3</sub>N (vol/vol 50/50), 0.67 mmol (100 mg) of 1,3,5-triethynylbenzene, 1 mmol (278 mg) 4,7-dibromobenzo[c][1,2,5]oxadiazole for B-BO-1,3,5 were added. To 0.67 mmol (100 mg) of 1,2,4-triethynylbenzene, 1 mmol (278 mg) 4,7-dibromobenzo[c][1,2,5]oxadiazole for B-BO-1,2,4; 0.67 mmol (117 mg) of 1,2,4,5-tetraethynylbenzene, 1.34 mmol (372 mg) 4,7-dibromobenzo[c][1,2,5]oxadiazole for B-BO-1,2,4,5 were added. The solution was degassed for 20 min with N<sub>2</sub> and then was heated to 80 °C for 12 h. The resulting CMPs were then rinsed with Milli-Q water several times and extracted with 50/50 dichloromethane and methanol solution in a Soxhlet for 24 h. The insoluble solid was then dried under vacuum conditions overnight. The final yields were 305 mg (81%), 286 mg (75%), and 379 mg (78%) for polymers B-BO-1,3,5, B-BO-1,2,4, and B-BO-1,2,4,5 respectively. Inductively coupled plasma spectrometry analysis showed that all three conjugated polymers have little or trace amounts of residual Pd (30 ppm) and Cu (20 ppm).

General Procedure for the Photooxidative Coupling of Benzylamine and Derivatives: 6 mg of photocatalyst and 1 mmol of substrate were added to 3 mL CH<sub>3</sub>CN in a glass vial, which was placed in a water bath in front of the light source: a blue LED lamp (OSA Opto Lights, 1.2 W cm<sup>-2</sup>) or a 23 W household energy saving fluorescent light bulb (Osram) www.advmat.de

![](_page_5_Picture_1.jpeg)

under 1 atm  $O_2.$  Samples were taken after a certain period of time and conversions were determined by  $^1H$  NMR using CDCl\_3 as solvent.

#### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

### Acknowledgements

The authors acknowledge the Max Planck Society for financial support. Jan Roth is acknowledged for support with the monomer synthesis. Z.J.W. is a recipient of a fellowship through funding of the Excellence Initiative (DFG/GSC 266) of the graduate school of excellence "MAINZ" (Materials Science in Mainz). K.A.I.Z. thanks Fonds der Chemischen Industrie, FCI for funding.

Received: June 8, 2015 Revised: July 17, 2015 Published online: September 10, 2015

- a) M. Oelgemoller, C. Jung, J. Mattay, *Pure Appl. Chem.* 2007, *79*, 1939; b) P. Esser, B. Pohlmann, H. D. Scharf, *Angew. Chem. Int. Ed.* 1994, *33*, 2009.
- [2] a) X. J. Lang, H. W. Ji, C. C. Chen, W. H. Ma, J. C. Zhao, Angew. Chem. Int. Ed. 2011, 50, 3934; b) X. Lang, X. Chen, J. Zhao, Chem. Soc. Rev. 2014, 43, 473; c) S. Furukawa, Y. Ohno, T. Shishido, K. Teramura, T. Tanaka, ACS Catal. 2011, 1, 1150; d) J. D. Cuthbertson, D. W. MacMillan, Nature 2015, 519, 74; e) Z. Zuo, D. T. Ahneman, L. Chu, J. A. Terrett, A. G. Doyle, D. W. MacMillan, Science 2014, 345, 437; f) M. T. Pirnot, D. A. Rankic, D. B. Martin, D. W. MacMillan, Science 2013, 339, 1593; g) D. A. Nagib, D. W. C. MacMillan, Nature 2011, 480, 224; h) A. McNally, C. K. Prier, D. W. MacMillan, Science 2011, 334, 1114; i) J. N. Du, K. L. Skubi, D. M. Schultz, T. P. Yoon, Science 2014, 344, 392; j) K. L. Skubi, T. P. Yoon, Nature 2014, 515, 45; k) D. M. Schultz, T. P. Yoon, Science 2014, 343, 985; l) C. H. Dai, J. M. R. Narayanam, C. R. J. Stephenson, Nat. Chem. 2011, 3, 140; m) J. M. R. Narayanam, C. R. J. Stephenson, Chem. Soc. Rev. 2011, 40, 102; n) A. G. Condie, J. C. Gonzalez-Gomez, C. R. Stephenson, J. Am. Chem. Soc. 2010, 132, 1464; o) D. Ravelli, M. Fagnoni, Chem-CatChem 2012, 4, 169; p) T. M. Nguyen, D. A. Nicewicz, J. Am.

Chem. Soc. 2013, 135, 9588; q) D. A. Nicewicz, T. M. Nguyen, ACS Catal. 2014, 4, 355; r) M. Neumann, S. Füldner, B. König, K. Zeitler, Angew. Chem. Int. Ed. 2011, 50, 951.

- [3] J. D. Nguyen, E. M. D'Amato, J. M. R. Narayanam, C. R. J. Stephenson, *Nat. Chem.* 2012, 4, 854.
- [4] a) X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* 2009, *8*, 76; b) X. Wang, S. Blechert, M. Antonietti, *ACS Catal.* 2012, *2*, 1596.
- [5] K. Zhang, Z. Vobecka, K. Tauer, M. Antonietti, F. Vilela, Chem. Commun. 2013, 49, 11158.
- [6] Z. J. Wang, S. Ghasimi, K. Landfester, K. A. I. Zhang, Chem. Commun. 2014, 50, 8177.
- [7] a) J.-X. Jiang, Y. Li, X. Wu, J. Xiao, D. J. Adams, A. I. Cooper, *Macro-molecules* 2013, 46, 8779; b) Z. J. Wang, S. Ghasimi, K. Landfester, K. A. I. Zhang, *Chem. Mater.* 2015, 27, 1921.
- [8] Z. J. Wang, S. Ghasimi, K. Landfester, K. A. I. Zhang, J. Mater. Chem. A 2014, 2, 18720.
- [9] J. Luo, X. Zhang, J. Zhang, ACS Catal. 2015, 5, 2250.
- [10] a) Z. J. Wang, K. Landfester, K. A. I. Zhang, *Polym. Chem.* 2014, 5, 3559; b) S. Dadashi-Silab, H. Bildirir, R. Dawson, A. Thomas, Y. Yagci, *Macromolecules* 2014, 47, 4607.
- [11] R. S. Sprick, J.-X. Jiang, B. Bonillo, S. Ren, T. Ratvijitvech, P. Guiglion, M. A. Zwijnenburg, D. J. Adams, A. I. Cooper, J. Am. Chem. Soc. 2015, 137, 3265.
- [12] a) X. H. Gao, H. B. Bin Wu, L. X. Zheng, Y. J. Zhong, Y. Hu, X. W. Lou, Angew. Chem. Int. Ed. 2014, 53, 5917; b) W. L. Yang, L. Zhang, Y. Hu, Y. J. Zhong, H. B. Wu, X. W. Lou, Angew. Chem. Int. Ed. 2012, 51, 11501; c) J. H. Yang, D. G. Wang, H. X. Han, C. Li, Acc. Chem. Res. 2013, 46, 1900.
- [13] J. R. Choi, T. Tachikawa, M. Fujitsuka, T. Majima, *Langmuir* 2010, 26, 10437.
- [14] K. Zhang, D. Kopetzki, P. H. Seeberger, M. Antonietti, F. Vilela, Angew. Chem. Int. Ed. 2013, 52, 1432.
- [15] J. Terao, A. Wadahama, A. Matono, T. Tada, S. Watanabe, S. Seki, T. Fujihara, Y. Tsuji, *Nat. Commun.* **2013**, *4*, 1691.
- [16] a) F. Su, S. C. Mathew, L. Möhlmann, M. Antonietti, X. Wang, S. Blechert, *Angew. Chem. Int. Ed.* **2011**, *50*, 657; b) N. Kang, J. H. Park, K. C. Ko, J. Chun, E. Kim, H. W. Shin, S. M. Lee, H. J. Kim, T. K. Ahn, J. Y. Lee, S. U. Son, *Angew. Chem. Int. Ed.* **2013**, *52*, 6228.
- [17] C. Su, M. Acik, K. Takai, J. Lu, S.-j. Hao, Y. Zheng, P. Wu, Q. Bao, T. Enoki, Y. J. Chabal, K. Ping Loh, *Nat. Commun.* **2012**, *3*,1298.