

# **CHEMISTRY** A European Journal





## WILEY-VCH

# Hydrazone-Linked Heptazine Polymeric Carbon Nitrides for Synergistic Visible-Light-Driven Catalysis

### Wei Zhang, Congying Xu, Takeshi Kobayashi, Yun Zhong, Zhiyong Guo,\* Hongbing Zhan, Marek Pruski and Wenyu Huang\*

Abstract: Heptazine-based conjugated polymeric carbon nitrides (PCNs) are promising metal-free photocatalysts, yet their synthesis is very challenging due to the electron-deficiency and insolubility of heptazine units. Indeed, heptazine-containing polymers have only been prepared via nucleophilic substitution with amines, using toxic cyameluric chloride as the starting material. Herein, we report the novel and environmentally friendly method for preparing heptazinebased mesoporous PCNs with hydrazone links formed via a simple Schiff-base condensation of melem-NH<sub>2</sub> and aldehydes. Unlike cyameluric chloride, melem-NH<sub>2</sub> is nontoxic, stable and can be readily obtained from melem and hydrazine in solution. We demonstrate that the hydrazone linkages and the heptazine units synergistically enhance the photocatalytic activity of PCNs in visiblelight-driven aerobic oxidation of benzyl alcohol to benzaldehyde. In particular, the polymer constructed from melem-NH<sub>2</sub> and pphthalaldehyde shows 17 times more activity than graphitic carbon nitride  $(g-C_3N_4)$ .

Visible-light-driven photocatalysis attracts increased attention because sunlight is a clean and renewable energy source and visible light accounts for 45 % of the solar spectrum.<sup>[1]</sup> Polymeric carbon nitrides (PCNs) are of particular interest<sup>[2]</sup> as low-cost, non-toxic, metal-free polymeric semiconductors, which indeed shown promising activity in visible light-driven have photocatalytic reactions.<sup>[3]</sup> Chief among those is the family of graphitic carbon nitrides (g-C<sub>3</sub>N<sub>4</sub>), which can catalyze a variety of reactions, including water splitting, carbon dioxide conversion, oxidative coupling of amines, and degradation of Rhodamine B.<sup>[4]</sup> The photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub> is attributed to the sheptazine unit (melem, 2,5,8-triamino-tri-s-heptazine, see Scheme 1a).<sup>[5]</sup> Typically, g-C<sub>3</sub>N<sub>4</sub> is prepared by the pyrolysis of nitrogen-rich precursors including urea, thiourea, melamine, cyanamide, and dicyandiamide.<sup>[6]</sup> However, the catalytic efficiency of the resulting g-C<sub>3</sub>N<sub>4</sub> is restricted by low specific surface area and high electron-hole recombination rate.<sup>[7]</sup>

Numerous strategies have been reported to improve the surface area, dispersion, thermal/chemical stability, and

[\*] W. Zhang, C. Xu, Y. Zhong, Prof. Z. Guo, Prof. H. Zhan College of Materials Science and Engineering Fuzhou University Fuzhou 350108 (P. R. China) E-mail: guozhy@fzu.edu.cn W. Zhang Van 't Hoff Institute for Molecular Sciences University of Amsterdam Science Park 904, 1098 XH Amsterdam (The Netherlands) Prof. M. Pruski, Prof. W. Huang Department of Chemistry Iowa State University Ames, IA 50011 (USA) E-mail: whuang@iastate T. Kobayashi, Prof. M. Pruski, Prof. W. Huang Ames Laboratory, US Department of Energy Ames, IA 50011 (USA)

Supporting information for this article is given via a link at the end of the document.

chemical tunability of g-C<sub>3</sub>N<sub>4</sub>.<sup>[8]</sup> These include doping with heteroatoms, nanocasting with hard templates, and introducing heterojunctions.<sup>[9]</sup> However, these top-down approaches are typically uncontrollable and time-consuming, giving low-quality g-C<sub>3</sub>N<sub>4</sub> with low yields.<sup>[10]</sup>

The alternative, bottom-up, methods to synthesize PCNs from heptazine monomers offer better structural control but are challenged by the insolubility of most heptazine precursors in common organic solvents.<sup>[11]</sup> Moreover, the electron deficiency of heptazine rings hinders their reactivity.<sup>[12]</sup> Thus far, cyameluric chloride (C<sub>6</sub>N<sub>7</sub>Cl<sub>3</sub>, also known as trichloroheptazine) is the only reactive heptazine precursor used for the preparation of heptazine-based PCNs.<sup>[13]</sup> Cyameluric chloride is typically synthesized from melem in two steps (Scheme 1b), which use deleterious PCI<sub>5</sub> as the chlorinating reagent and release toxic POCI<sub>3</sub> byproduct.<sup>[14]</sup> Therefore, developing heptazine precursors that are environmentally friendly and suitable for the facile design of versatile heptazine-based PCNs is highly desired.<sup>[15]</sup>







c. Our work: one-pot synthesis from melem and hydrazine



Scheme 1. (a) The representative structures of g-C<sub>3</sub>N<sub>4</sub> and heptazine-based PCNs. (b) Previous and (c) our strategies for the synthesis of PCNs using two different heptazine precursors.

Here, we discovered a new, scalable, and environmentally friendly heptazine precursor, 2,5,8-trihydrazino-s-heptazine (melem-NH<sub>2</sub>), which could react with aldehydes by a simple condensation to form heptazine-based PCNs connected through COMMUNICATION

hydrazone linkages (Scheme 1c and Figure 1a). Melem-NH<sub>2</sub> is a nontoxic and stable compound that is readily prepared from melem and hydrazine in solution. Hydrazone, a trinuclear azomethine group (-N-N=C-), has been previously incorporated into covalent organic frameworks to improve their hydrolytic and oxidative stability as well as charge carrier mobility.<sup>[16]</sup> Particularly, we found *p*-phthalaldehyde to be the optimal aldehyde precursor that reacted with melem-NH<sub>2</sub> to yield a mesoporous organic polymer (MelonHP) featuring a high specific surface area, and thus more accessible active sites. Most importantly, the cross-linked hydrazone-heptazine repeating units in MelonHP synergistically enhanced its activity in the visible-light-driven oxidation of benzyl alcohol to

benzaldehyde with  $O_2$  under mild conditions. MelonHP showed a mass-specific activity enhancement factor of 17 compared to g- $C_3N_4$ . To the best of our knowledge, this is the first report of synthesis and photocatalysis studies on such hydrazone-heptazine PCNs.

Figure 1a briefly outlines the synthesis of hydrazone-linked heptazine PCNs using 2,5,8-trihydrazino-s-heptazine (melem-NH<sub>2</sub>) and aldehydes as starting materials via a Schiff-base condensation reaction (see the supporting information for details). We initially chose *p*-phthalaldehyde, *m*-phthalaldehyde, and trimesaldehyde as the aldehyde precursors, and the resulting polymers are denoted as MelonHP, MelonHM, and MelonHT, respectively.



Figure 1. (a) Schematic illustration of the synthesis of hydrazone-linked heptazine PCNs via melem-NH<sub>2</sub> condensation with different aldehydes. (b) <sup>13</sup>C<sup>{1</sup>H} CPMAS SSNMR spectra of MelonHP, MelonHM, and MelonHT (see supporting information for NMR experimental details); (c) FTIR spectra of MelonHP and the precursors (melem-NH<sub>2</sub> and *p*-phthalaldehyde).

For all three polymers, the powder X-ray diffraction (PXRD) patterns did not show peaks from Melem-NH<sub>2</sub>; instead, a broad peak was observed at  $2\theta \sim 27^{\circ}$  in line with (002) reflection of g-C<sub>3</sub>N<sub>4</sub> (Figure S1).<sup>[17]</sup> These observations suggest the formation of disordered heptazine networks with partly layered structures.<sup>[15]</sup> The transmission electron microscopy (TEM) images in Figure S2 show the representative morphology of MelonHP with the ultrathin and lamellar feature, upholding the XRD results.

We then studied the porous properties of the PCNs using nitrogen adsorption-desorption measurements (Figure S3 and

Table S1). Among all samples, only MelonHP showed a typical type-IV isotherm with an H4 hysteresis loop at relative pressures (P/P<sub>0</sub>) from 0.7 to 0.9, indicating the presence of mesopores.<sup>[18]</sup> The specific Brunauer–Emmett–Teller (BET) surface area and pore volume were calculated to be 120 m<sup>2</sup>/g and 0.44 cm<sup>3</sup>/g, respectively. By comparison, MelonHT gave a specific BET surface area of 25 m<sup>2</sup>/g, while MelonHM was non-porous. These results indicate that the type of aldehyde precursor plays a vital role in the pore formation of the hydrazone-heptazine-based organic network. Thermogravimetric analysis (TGA, Figure S4) in an N<sub>2</sub> flow showed the high thermal stability of MelonHP up to

COMMUNICATION



350 °C. Additionally, the exact elemental compositions of these polymers were confirmed by X-ray photoelectron spectroscopy (XPS, see Figure S5).

Figure 2. Indirectly-detected 2D  $^1H\{^{15}N\}$  through-space HETCOR spectra of melem-NH2 and derivative polymers. Experimental conditions are given in the supporting information.

The atomic-level structures of the three newly derived PCNs were examined by solid-state (SS)NMR and Fourier-transform infrared (FTIR) spectroscopy (Figure 1b-c). The  $^{13}\text{C}\{^{1}\text{H}\}$  crosspolarization magic-angle-spinning (CPMAS) SSNMR spectra of MelonHP, MelonHM and MelonHT displayed a distinct signal at 150 ppm, that can be assigned to the hydrazone carbon, -NHN=CH-.[19] The signals at 120-140 ppm and 155-165 ppm were attributed to the carbons in the phenyl and heptazine moieties, respectively. These assignments are in agreement with the resonances observed in a reference non-polymeric compound MelonB, prepared via condensation reaction between Melem-NH<sub>2</sub> and benzaldehyde (the synthesis details are given in the supporting information along with NMR spectra, Figure S6 and S7), and with the results of a previous study.<sup>[20]</sup> To further confirm the formation of hydrazone linkages, we performed indirectly-detected 2D <sup>1</sup>H{<sup>15</sup>N} heteronuclear correlation (HETCOR) experiments (Figure 2),<sup>[21]</sup> which showed that cross peaks assigned to -NH-NH2 and -NH-NH2 of melem-NH2 disappeared after the reaction between melem-NH $_{2}$  and aldehydes. Instead, new signal appeared at  $\delta_{N}$   $\approx$  –220 ppm and  $\delta_{H} \approx 11$  ppm, which can be assigned to the hydrazone linkages – NH-N=CH- (note that non-protonated nitrogen was not observed due to the inefficient polarization transfer under the present experimental conditions).<sup>[22]</sup>

The FTIR results are consistent with SSNMR. As shown in Figure 1c, the MelonHP polymer combines the characteristic signals of the heptazine unit and phenyl ring of its melem-NH<sub>2</sub> and *p*-phthalaldehyde precursors. Additionally, the FTIR spectra of MelonHP showed a vibration of the C=N bond at 1554 cm<sup>-1</sup>,<sup>[23]</sup> accompanied by the disappearance of the C=O stretching (1659 cm<sup>-1</sup>, *cf. p*-phthalaldehyde) and amine signals (3220 cm<sup>-1</sup>, *cf.* melem-NH<sub>2</sub>).<sup>[24]</sup> This indicates the formation of hydrazone

linkages (–NH–N=CH–) through condensation of aldehyde and amine.  $^{\left[ 25\right] }$ 

Taken together, the above SSNMR and FTIR results definitively show that all three samples consist of polymeric heptazine units cross-linked by hydrazone formed via condensation between melem-NH<sub>2</sub> and different aldehydes. The structural differences among MelonHP, MelonHM, and MelonHT derive from the locations of the formed imine bonds (or hydrazone) at either the *para* or *meta* position of the phenyl rings. The MelonHP shows the highest specific surface area, possibly due to a reduced steric hindrance between melem units connected via the *para* sites of aldehydes.

Notably, we were unable to prepare the PCNs using the abovementioned melem as precursor instead of melem-NH<sub>2</sub> (Scheme S1, see the supporting information).<sup>[26]</sup> Evidently, melem cannot react with aldehyde due to the electron-deficient heptazine ring that makes the  $-NH_2$  groups inert to electrophilic attack.<sup>[13c]</sup> This was clearly confirmed by SSNMR; indeed, the only resonances observed in the <sup>13</sup>C{<sup>1</sup>H} CPMAS spectrum of the melem-based product represented unreacted melem (Figure S8).



Figure 3. (a) Comparisons of benzyl alcohol conversion and benzaldehyde selectivity over various photocatalysts for visible-light-induced photocatalytic aerobic oxidation to benzaldehyde. (b) The mass-specific activity for benzyl alcohol oxidation under visible light irradiation calculated at <10% conversion; the apparent quantum yield (AQY) of these catalysts is measured at ca. 540 nm visible light irradiation conditions.

The MelonHM, MelonHT and MelonHP polymers were then tested in the visible-light-driven oxidation of benzyl alcohols with  $O_2$  (1 atm) to benzaldehyde, using a 26 W white LED lamp as the light source (see the supporting information for details). As shown in Figure 3a, control experiments confirmed that the reaction did not proceed in the absence of catalysts or without

## COMMUNICATION

light, whereas g-C<sub>3</sub>N<sub>4</sub> gave only 3% conversion. All three polymers proved to be active with > 99% selectivity. MelonHP with the highest surface area exhibited the best photocatalytic performance among all the catalysts tested in this study, giving a much higher conversion of 36% than MelonHM/g-C<sub>3</sub>N<sub>4</sub> (3%) and MelonHT (7%).

The mass-specific activities of these catalysts, calculated as millimole of benzaldehyde produced per gram of catalyst per hour under identical conditions, are shown in Figure 3b. The catalytic performance in this series increased as follows: MelonHP >> MelonHT > MelonHM  $\approx$  g-C<sub>3</sub>N<sub>4</sub>. Note that MelonHP outperformed g-C<sub>3</sub>N<sub>4</sub> by a factor of 17, which indicates a strong synergistic effect between the hydrazone linkers and the heptazine units in MelonHP. The apparent quantum yield (AQY) of this light-driven process is consistent with the optical absorption (see the supporting information for details). In our case, the AQY was measured as a function of incident light wavelength using bandpass filters with central wavelengths of 540 nm, which is close to the maximum absorbance of the Melon-samples determined from the UV-vis analysis (see below). MelonHP gave the highest AQY of 1.12%, showing a remarkably high activity for benzaldehyde production under this visible light irradiation.

To confirm the synergistic effect between the hydrazone linkers and heptazine units in MelonHP on the photocatalytic oxidation, we prepared a previously reported heptazine-based porous polymer without hydrazone linkages using cyameluric chloride and *p*-phenylenediamine as starting materials (Scheme S2).<sup>[13c]</sup> The resulting polymer, denoted as MelonP (Figure 4a), was indeed hydrazone-free, as confirmed by SSNMR (Figure 4b) and FTIR (Figure S9) (see the supporting information for details). The BET surface area of MelonP is 150 m<sup>2</sup>/g (Figure 4c), higher than that of MelonHP (120 m<sup>2</sup>/g). For the latter, the hydrazone linkages in the heptazine-derived network lead to a flexible structure, and thus lower crystallinity and porosity.[27] Intriguingly, in spite of a higher surface area, MelonP gave much lower benzaldehyde conversion (14%) than MelonHP (36%). Figure 4d shows that the area-specific activity for MelonHP is four times higher than that of MelonP. The higher activity of MelonHP over Melon P supports the synergistic effect between the hydrazone linkages and the heptazine units in MelonHP.

Based on the above results, it is reasonable to expect that the catalytic performance of hydrazone-linked PCNs correlates well with the amount of exposed hydrazone-heptazine pairs. To substantiate this inference, we plotted, in Figure 4e, the mass-specific activities of the studied polymers (MelonHM, MelonHT, MelonHP, MelonP, and g-C<sub>3</sub>N<sub>4</sub>) against their BET surface areas. Indeed, the activities of hydrazone-linked PCNs show a strong linear correlation with their specific surface areas ( $R^2 = 0.97$ ), which corroborates the synergistic effect between hydrazone and the heptazine units. Notably, g-C<sub>3</sub>N<sub>4</sub> and MelonP, which do not feature the hydrazone linkages, are two exceptions with relatively high surface area (see Table S1) but low activity.

Inspired by this finding, we explored the possibility to further increase the catalytic activity by preparing materials with highersurface-area than MelonHP. First, we synthesized another PCN catalyst with hydrazone-heptazine sites, denoted as MelonHBP (see Scheme S3 and Figure S10), using a larger dialdehyde precursor molecule (4,4'-biphenyldicarboxaldehyde). Although the resulting product had the surface area of only 40 m<sup>2</sup>/g, its catalytic activity followed exactly the trend discussed above (see Figure 4e). Secondly, we attempted the preparation of highsurface-area covalent organic frameworks (COFs) composed of hydrazone linkages. However, we tested various synthesis conditions and found that we could not obtain hydrazone-linked COFs, possibly due to the flexible hydrazone linkage with a sp<sup>3</sup> N.



Figure 4. (a) Schematic illustration of two heptazine-based PCNs: MelonHP and Hydrazone-free MelonP. (b)  ${}^{13}C{}^{1H}$  CPMAS SSNMR spectra and (c) nitrogen adsorption-desorption isotherms of MelonP and MelonHP. (d) Comparisons of the area-specific activity of MelonP and MelonHP. (e) The plot for the correlation between the mass-specific activity of benzyl alcohol oxidation on hydrazone-catalysts and their specific surface area, compared with porous g-C<sub>3</sub>N<sub>4</sub> and MelonP.

The synergistic effect between hydrazone linkages and heptazine units was further explored by UV-visible diffuse reflectance spectroscopy (UV-vis DRS) and density functional theory (DFT) calculations. As shown in Figure S11, the hydrazone-free MelonP exhibited an absorption edge at ca. 550 nm in the visible light region (> 400 nm). Upon introducing hydrazone to the heptazine-derived network, the absorption band became red-shifted to ca. 700 nm for MelonHP, MelonHM, and MelonHT. This indicates that the hydrazone moiety can significantly enhance visible light absorption of the PCNs. We calculated the bandgap energy ( $E_q$ ) by the plot of [ $F(R_{\infty}) hv$ ]<sup>1/2</sup> *vs. hv*, where  $F(R_{\infty})$  is the Kubelka–Munk function and *hv* is the photon energy (Figure S12). All of the hydrazone-polymers showed a narrower bandgap (2.4-2.5 eV) than that of MelonP (3.58 eV, see Figure S12 inset). This is probably due to the strong electron-donating effect caused by the lone pair of electrons on the hydrazone group, lowering the bandgap of the heptazine-based PCNs.<sup>[28]</sup>

## COMMUNICATION

Using DFT with the CP2K software package,<sup>[29]</sup> we studied the theoretical highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of these PCNs. Figure S13 showed that the HOMO of representative MelonP models is localized in the heptazine unit. For MelonHP, however, the corresponding electron density is shifted to the hydrazone moiety with a higher HOMO by 0.4 eV in comparison to that of MelonP (Figure S14). The calculated band gap of MelonHP is narrower (2.9 eV) than that of MelonP (3.8 eV), which agrees well with the UV-Vis DRS results. Therefore, the introduction of hydrazone linkages can enhance the visible-light absorption and charge separation efficiency in MelonHP for the photocatalytic oxidation of benzyl alcohol (Scheme 2). Further experiments are needed to elucidate the active oxidative species that are responsible for this photocatalytic oxidation reaction.



#### Synergistic Visible-Light-Driven Catalysis

**Scheme 2.** the synergistic effect of hydrazone linkages in visible-light-driven aerobic oxidation of benzyl alcohol to benzaldehyde over hydrazone-inked heptazine-based mesoporous polymer.

In conclusion, we have developed a facile method to synthesize a series of new heptazine-based PCNs with hydrazone linkage via the condensation of melem-NH<sub>2</sub> and different aldehydes. Our results identified p-phthalaldehyde as the optimal aldehyde precursor, giving a robust mesoporous polymer (MelonHP) with highly cross-linked hydrazoneheptazine repeating units. The synthesized MelonHP showed high efficiency as a catalyst for visible-light-driven oxidation of benzyl alcohol to benzaldehyde with oxygen under mild conditions. Control experiments and DFT calculations showed that the hydrazone linkages in the PCNs play a vital role in this photocatalytic reaction, making MelonHP 17 times more active than g-C<sub>3</sub>N<sub>4</sub>. This synergistic effect between hydrazone linkers and heptazine units is further confirmed by the much lower photocatalytic activity of an analogous heptazine-based porous polymer without the hydrazone moiety (MelonP). This work provides a new approach for designing highly efficient metal-free catalysts for photocatalytic aerobic oxidation of alcohols under visible light.

#### Acknowledgements

This work was supported by the financial support from the National Natural Science Foundation of China (Grant No. 51703031). W.Z. thanks the China Scholarship Council for a Ph.D. fellowship (201506140058). T.K. and M.P. (SSNMR) are supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences. Ames Laboratory is operated for the DOE by Iowa State University under Contract No. DE-AC02-07CH11358. We also acknowledge the support from Iowa Energy Center and Iowa State University.

#### **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** heptazine • porous polymer • hydrazone linkage • synergistic effect • visible light

- [1] J. C. Colmenares, R. Luque, *Chem. Soc. Rev.* **2014**, *43*, 765-778.
- [2] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* 2008, *8*, 76.
- a) W.-J. Ong, L.-L. Tan, Y. H. Ng, S.-T. Yong, S.-P. Chai, *Chem. Rev.* **2016**, *116*, 7159-7329; b) S. Xu, P. Zhou, Z. Zhang, C. Yang, B. Zhang,
  K. Deng, S. Bottle, H. Zhu, *J. Am. Chem. Soc.* **2017**, *139*, 14775-14782.
- [4] a) Y. Wang, X. Wang, M. Antonietti, Angew. Chem. Int. Ed. 2012, 51, 68-89; Angew. Chem. 2012, 124, 70-92; b) F. Su, S. C. Mathew, G. Lipner, X. Fu, M. Antonietti, S. Blechert, X. Wang, J. Am. Chem. Soc. 2010, 132, 16299-16301; c) Y. Xiao, G. Tian, W. Li, Y. Xie, B. Jiang, C. Tian, D. Zhao, H. Fu, J. Am. Chem. Soc. 2019, 141, 2508-2515.
- [5] a) Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, A. Du, M. Jaroniec, S. Z. Qiao, *Nat. Commun.* **2014**, 5, 3783; b) Y. Zheng, Y. Jiao, Y. Zhu, Q. Cai, A. Vasileff, L. H. Li, Y. Han, Y. Chen, S.-Z. Qiao, *J. Am. Chem. Soc.* **2017**, *139*, 3336-3339.
- Y. Dong, Q. Wang, H. Wu, Y. Chen, C.-H. Lu, Y. Chi, H.-H. Yang, Small 2016, 12, 5376-5393.
- [7] G. Marci, E. I. García-López, L. Palmisano, *Catal. Today* 2018, 315, 126-137.
- a) J. Pan, L. Guo, S. Zhang, N. Wang, S. Jin, B. Tan, *Chem. Asian J.* **2018**, *13*, 1674-1677; b) W. Zhang, T. Liu, H. Wu, P. Wu, M. He, *Chem. Commun.* **2015**, *51*, 682-684.
- [9] a) M. Antonietti, A. Savateev, I. Ghosh, B. König, *Angew. Chem. Int. Ed.* 2018, *57*, 15936-15947; *Angew. Chem.* 2018, *130*, 16164-16176; b) G. Zhang, Z.-A. Lan, X. Wang, *Chem. Sci.* 2017, *8*, 5261-5274; c) G. Peng, L. Xing, J. Barrio, M. Volokh, M. Shalom, *Angew. Chem. Int. Ed.* 2018, *57*, 1186-1192; *Angew. Chem.* 2018, *130*, 1200-1206; d) M. Zhu, S. Kim, L. Mao, M. Fujitsuka, J. Zhang, X. Wang, T. Majima, *J. Am. Chem. Soc.* 2017, *139*, 13234-13242.
- [10] Y. Zheng, L. Lin, B. Wang, X. Wang, Angew. Chem. Int. Ed. 2015, 54, 12868-12884; Angew. Chem. 2015, 127, 13060-13077.
- [11] L. Maxwell, S. Gómez-Coca, T. Weyhermüller, D. Panyella, E. Ruiz, *Dalton Trans.* 2015, 44, 15761-15763.
- [12] S. Kumar, N. Sharma, K. Kailasam, J. Mater. Chem. A 2018, 6, 21719-21728.
- [13] a) K. Kailasam, J. Schmidt, H. Bildirir, G. Zhang, S. Blechert, X. Wang, A. Thomas, *Macromol. Rapid Commun.* **2013**, *34*, 1008-1013; b) Q.-Q. Dang, Y.-F. Zhan, X.-M. Wang, X.-M. Zhang, ACS Appl. Mater. Interfaces **2015**, *7*, 28452-28458; c) K. Kailasam, M. B. Mesch, L. Möhlmann, M. Baar, S. Blechert, M. Schwarze, M. Schröder, R. Schomäcker, J. Senker, A. Thomas, *Energy Technol.* **2016**, *4*, 744-750.
- [14] A. Schwarzer, T. Saplinova, E. Kroke, Coord. Chem. Rev. 2013, 257, 2032-2062.
- [15] P. Kumar, E. Vahidzadeh, U. K. Thakur, P. Kar, K. M. Alam, A. Goswami, N. Mahdi, K. Cui, G. M. Bernard, V. K. Michaelis, K. Shankar, J. Am. Chem. Soc. 2019, 141, 5415-5436.

- COMMUNICATION
- [16] a) L. Shen, N. Cao, L. Tong, X. Zhang, G. Wu, T. Jiao, Q. Yin, y. Pan, H. Li, *Angew. Chem. Int. Ed.* **2018**, *57*, 16486-16490; *Angew. Chem.* **2018**, *130*, 16724-16728; b) D. N. Bunck, W. R. Dichtel, *J. Am. Chem. Soc.* **2013**, *135*, 14952-14955; c) P. Data, P. Pander, P. Zassowski, V. Mimaite, K. Karon, M. Lapkowski, J. V. Grazulevicius, P. Slepski, K. Darowicki, *Electrochim. Acta* **2017**, *230*, 10-21; d) H. K. Singh, B. Pradhan, S. K. Singh, R. Nandi, D. S. S. Rao, S. K. Prasad, A. S. Achalkumar, B. Singh, *ChemistrySelect* **2018**, *3*, 4027-4037.
- [17] G. Zhang, G. Li, T. Heil, S. Zafeiratos, A. Savateev, X. Wang, M. Antonietti, Angew. Chem. Int. Ed. 2019, 58, 3433-3437; Angew. Chem. 2019, 131, 3471-3475.
- [18] C. Gao, G. Chen, X. Wang, J. Li, Y. Zhou, J. Wang, *Chem. Commun.* 2015, *51*, 4969-4972.
- [19] F. J. Uribe-Romo, C. J. Doonan, H. Furukawa, K. Oisaki, O. M. Yaghi, J. Am. Chem. Soc. 2011, 133, 11478-11481.
- [20] B. V. Lotsch, M. Döblinger, J. Sehnert, L. Seyfarth, J. Senker, O. Oeckler, W. Schnick, *Chem. Eur. J.* 2007, *13*, 4969-4980.
- [21] a) T. Kobayashi, Y. Nishiyama, M. Pruski, in Modern Methods in Solidstate NMR: A Practitioner's Guide, The Royal Society of Chemistry,

**2018**, pp. 1-38; b) W. Wiench, C. E. Bronnimann, V. S.-Y. Lin, M. Pruski, *J. Am. Chem. Soc.* **2007**, *129*, 12076-12077.

- [22] P. Šimůnek, V. Bertolasi, A. Lyčka, V. Macháček, O Org. Biomol. Chem. 2003, 1, 3250-3256.
- [23] a) L. Zou, X. Yang, S. Yuan, H.-C. Zhou, *CrystEngComm* 2017, *19*, 4868-4871; b) Z.-J. Li, S.-Y. Ding, H.-D. Xue, W. Cao, W. Wang, *Chem. Commun.* 2016, *52*, 7217-7220.
- [24] a) C. R. DeBlase, K. E. Silberstein, T.-T. Truong, H. D. Abruña, W. R. Dichtel, *J. Am. Chem. Soc.* 2013, *135*, 16821-16824; b) L. Lin, H. Guan, D. Zou, Z. Dong, Z. Liu, F. Xu, Z. Xie, Y. Li, *RSC Adv.* 2017, *7*, 54407-54415.
- [25] L. Stegbauer, K. Schwinghammer, B. V. Lotsch, Chem. Sci. 2014, 5, 2789-2793.
- [26] T.-O. Do, ChemSusChem 2019, 12, 291-302.
- [27] T. Kundu, J. Wang, Y. Cheng, Y. Du, Y. Qian, G. Liu, D. Zhao, *Dalton Trans.* 2018, 47, 13824-13829.
- [28] T. W. Goh, C. Xiao, R. V. Maligal-Ganesh, X. Li, W. Huang, *Chem. Eng. Sci.* 2015, 124, 45-51.
- [29] J. Hutter, M. lannuzzi, F. Schiffmann, J. VandeVondele, J. Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2014, 4, 15-25.

#### Entry for the Table of Contents



Wei Zhang, Congying Xu, Takeshi Kobayashi, Yun Zhong, Zhiyong Guo\* Hongbing Zhan, Marek Pruski and Wenyu Huang\*

Page No. – Page No.

Hydrazone-Linked Heptazine Polymeric Carbon Nitrides for Synergistic Visible-Light-Driven Catalysis