

## Fluoroalkylation

# Graphitic Carbon Nitride Polymer as a Recyclable Photoredox Catalyst for Fluoroalkylation of Arenes

Moritz Baar and Siegfried Blechert\*<sup>[a]</sup>

**Abstract:** Heterogeneous catalysis for trifluoromethylations and perfluoroalkylations has been performed. Through the usage of cheap, metal-free and recyclable mesoporous graphitic carbon nitride (mpg-CN) it was possible to fluoroalkylate various arenes by the reductive activation of sulfonyl chlorides with visible light. Thus, we were able to demonstrate the robustness and versatility of mpg-CN as a photoredox catalyst beyond water splitting and the activation of oxygen.

Using visible light for photoredox catalysis in organic synthesis has aroused great interest in the last couple of years.<sup>[1]</sup> In particular, light sensitizers like Ru(bpy)<sub>3</sub><sup>2+</sup>,<sup>[2]</sup> Ir<sup>III</sup> complexes,<sup>[3]</sup> or Eosin Y<sup>[4]</sup> are often employed to initiate organic reactions.

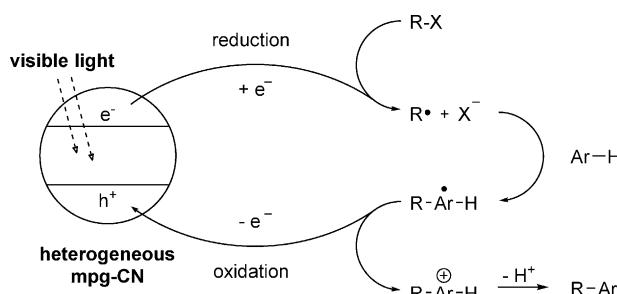
However, the homogeneous nature of these dyes makes their separation from the product as well as their recycling difficult. This is where heterogeneous catalysts show major advantages. In this context, mesoporous graphitic carbon nitride (mpg-CN), a metal-free solid-state organocatalyst that is easily accessible by thermal polymerisation of cheap precursors like dicyandiamide and cyanamide, holds great potential. Higher activity was achieved through the introduction of a high mesopore surface area ( $\approx 200 \text{ m}^2 \text{ g}^{-1}$ ) with silica nanoparticles as templates.<sup>[5]</sup> Initially established for photocatalytic water splitting,<sup>[6]</sup> a large variety of morphologies and applications have been developed.<sup>[7]</sup> Recently its potential in organic catalysis was demonstrated, especially for aerobic oxidations.<sup>[8]</sup>

Within this research we were able to generate a highly reactive superoxide radical anion ( $\text{O}_2^-$ ) photocatalytically through a one-electron reduction of oxygen. This enabled a variety of photoredox oxidations or oxidative couplings of alcohols and amines. Very recently, several of those transformations have also been performed by using heterogeneous metal catalysts such as TiO<sub>2</sub> or CdS.<sup>[9]</sup>

Motivated by the possibilities provided by the reductive activation of oxygen, we intended to expand the application of mpg-CN towards additional reducible precursors. In this aspect

the redox potential and the robustness of the employed catalyst hold a crucial role.

Unlike TiO<sub>2</sub>, mpg-CN absorbs light in the visible area (band gap of 2.7 eV) and is not dependent on a surface complexation with electron-rich substrates for visible light catalysis. With an oxidation potential of the conduction band at  $-1.3 \text{ V}$  and a reduction level of the valence band at  $1.4 \text{ V}$  (vs. NHE, pH 7),<sup>[8b]</sup> mpg-CN also features an appropriate electrochemical behavior for the photocatalytic activation of a variety of reagents. In this regard reactive alkyl radicals are of particular interest as they allow direct C–H functionalization of arenes and olefins (Scheme 1). In particular, fluorinated alkyl radicals play an important role in the design of new pharmaceutical agents, because fluorinated compounds often show improved cellular membrane permeability and metabolic stability.



Scheme 1. Photocatalytic generation of alkyl radicals for C–H functionalization of arenes.

Recently, different kinds of precursors have been used for the photocatalytic fluoroalkylation of arenes and olefins. Examples of these precursors are CF<sub>3</sub>I, as well as Umemoto's and Togni's reagents, which are activated with homogeneous photoredox catalysts.<sup>[10]</sup> To the best of our knowledge there is no application of heterogeneous catalysts for fluoroalkylation reactions so far. Hence, we took this as a starting point for our research.

After less successful attempts with gaseous CF<sub>3</sub>I we decided to have a closer look at the oxidation potential of feasible reagents. As it turned out, trifluoromethanesulfonyl chloride **1** (TfCl) presents a more convenient oxidation potential of  $-0.18 \text{ V}$  (vs. SCE)<sup>[11]</sup> and an enhanced driving force due to evolving SO<sub>2</sub> after reduction (CF<sub>3</sub>SO<sub>2</sub>Cl + e⁻ → CF<sub>3</sub> + SO<sub>2</sub> + Cl⁻). First presented by the MacMillan group<sup>[11]</sup> as a cheap and easy-to-handle alternative to CF<sub>3</sub>I, several reports demonstrated the versatility of reagent **1** in various applications.<sup>[12]</sup> Together with

[a] M. Baar, Prof. Dr. S. Blechert  
Institut für Chemie  
Technische Universität Berlin  
Straße des 17. Juni 135  
10623 Berlin (Germany)  
E-mail: blechert@chem.tu-berlin.de

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201405505>.

the advantages of a heterogeneous catalyst, we were delighted to see that it was possible to perform fluoroalkylations of various arenes with mpg-CN as a photoredox catalyst. Additionally, the reusability could be demonstrated with recycle experiments (see Figure S-1 in the Supporting Information).

We started our investigation with the trifluoromethylation of benzene in acetonitrile (8 M) using trifluoromethanesulfonic chloride (**1**, 2 eq), mpg-CN (25 mg/0.25 mmol substrate) and K<sub>2</sub>HPO<sub>4</sub> (3 eq) under visible light irradiation with a 60 W energy saving bulb, based on the conditions which proved optimal for homogeneous catalysts. After 48 h reaction time, a conversion of 50% to the desired product was obtained (Table 1).

**Table 1.** Screening and control experiments for the trifluoromethylation of benzene.

| Entry |  | t [h] | GC yield [%] |
|-------|--|-------|--------------|
| 1     | conditions <sup>[a]</sup>  | 48    | 50           |
| 2     | without mpg-CN   | 48    | <0.1         |
| 3     | no light   | 48    | <0.1         |
| 4     | O <sub>2</sub> atm.  | 20    | trace        |
| 5     | K <sub>2</sub> CO <sub>3</sub> /DBU <sup>[b]</sup> /Disodiummalonate as base | 60    | 31/28/25     |
| 6     | DCM as solvent   | 64    | 21           |
| 7     | DMF, DMSO or THF as solvent  | 64    | trace        |
| 8     | conditions <sup>[a]</sup>  | 60    | 65           |
| 9     | CdS (1.5 equiv) instead of mpg-CN  | 64    | 1            |
| 10    | TiO <sub>2</sub> (1.5 equiv) instead of mpg-CN                               | 64    | 9            |
| 11    | BiVO <sub>4</sub> (1.5 equiv) instead of mpg-CN                              | 64    | <0.1         |

[a] Benzene (0.25 mmol), TfCl **1** (0.5 mmol), mpg-CN (25 mg), K<sub>2</sub>HPO<sub>4</sub> (0.75 mmol), MeCN (2 mL). [b] DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

To verify the role of mpg-CN, further control experiments in the absence of light or catalyst were conducted. No conversion was observed under these conditions (Table 1, entries 2 and 3). This unambiguously proves the catalytic activity of mpg-CN.

Oxygen can easily be reduced photocatalytically by mpg-CN<sup>[8]</sup> and thus compete with the reduction of TfCl **1**. To analyse its influence, the reaction was carried out under an oxygen atmosphere. Almost no substrate conversion was observed (Table 1, entry 4); hence the reaction is quenched by oxygen and should be carried out under inert gas.

In order to optimise the reaction conditions, further parameter variations were tested. Differ-

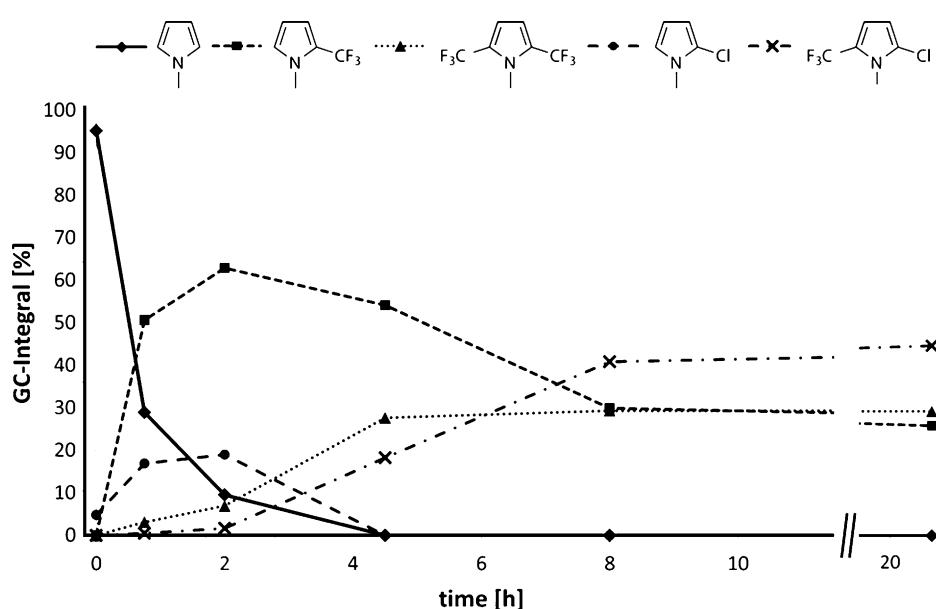
ent bases and solvents did not lead to higher yields (Table 1, entries 5–7). A prolongation of the reaction time, however, increased the yield. A conversion of 65% to the desired product was obtained without detectable side-products after 60 h (Table 1, entry 8); subsequent irradiation caused only slow conversion and unselective double trifluoromethylation.

To examine whether other heterogeneous photocatalysts can compete with this result, we took three examples to test their reactivity in this reaction. CdS and TiO<sub>2</sub> have been used under comparable conditions with visible light in previous applications,<sup>[13]</sup> whereas BiVO<sub>4</sub> is often used as a visible light photocatalyst for water oxidation,<sup>[14]</sup> but not for photoredox catalysis in organic synthesis. No conversion was observed for BiVO<sub>4</sub>, probably due to its low activity in photoreduction. In this respect CdS and TiO<sub>2</sub> have a higher reduction potential<sup>[9a]</sup> but show only low conversions for trifluoromethylation (Table 1, entries 9–11).

During the screening of the reaction conditions, we observed that the conversion was nearly the same when the amount of TfCl **1** was doubled (Table S-1 in the Supporting Information). However, altering the stoichiometry of the base decreased the yield, which is why we suspected the oxidation process to be the rate-limiting step. Compared to benzene, this oxidation step should be enhanced for heteroaromatic substrates.

To prove this theory we decided to use *N*-methylpyrrole (**3**) as a substrate, and indeed much higher reaction rates could be achieved. Figure 1 demonstrates that we faced two problems when using *N*-methylpyrrole (**3**) as substrate: beside over-reaction causing double trifluoromethylation, chlorinated side products **6** and **7** occurred during the reaction.

In contrast to benzene, unselective conversion even takes place without the catalyst. However, the presence of mpg-CN increases reactivity and selectivity significantly. The appearance



**Figure 1.** Kinetic studies of the trifluoromethylation of *N*-methylpyrrole (**3**). Reaction conditions: substrate **3** (0.25 mmol), TfCl **1** (0.5 mmol), mpg-CN (15 mg), K<sub>2</sub>HPO<sub>4</sub> (0.75 mmol), MeCN (2 mL).

**Table 2.** Screening and control experiments for the trifluoromethylation of *N*-methylpyrrole (**3**).<sup>[a]</sup>

| Entry            | mpg-CN<br>[mg] | TfCl<br>[equiv] | <i>t</i><br>[h] | conv. <sup>[c]</sup><br>[%] | 6  |    | select. <sup>[c]</sup> [%] |    |
|------------------|----------------|-----------------|-----------------|-----------------------------|----|----|----------------------------|----|
|                  |                |                 |                 |                             | 4  | 5  | 6                          | 7  |
| 1                | 15             | 2               | 2.5             | 88                          | 73 | 1  | 20                         | 6  |
| 2 <sup>[b]</sup> | 15             | 2               | 2.5             | 57                          | —  | —  | 91                         | —  |
| 3                | 15             | 2               | 17              | 100                         | 21 | 47 | 1                          | 31 |
| 4                | —              | 2               | 17              | 94                          | 29 | 1  | 29                         | 30 |
| 5 <sup>[b]</sup> | —              | 2               | 17              | 90                          | 4  | —  | 51                         | 9  |
| 6                | 15             | 1               | 4.5             | 89                          | 87 | 2  | 6                          | 4  |
| 7                | 15             | 1.5             | 4.5             | 98                          | 74 | 5  | 9                          | 11 |
| 8                | 45             | 2               | 2               | 100                         | 77 | 12 | 2                          | 10 |
| 9                | 25             | 1.2             | 1.5             | 100                         | 81 | 8  | 3                          | 5  |

[a] Reaction conditions: substrate **3** (0.25 mmol), TfCl **1** (0.25–0.5 mmol), mpg-CN (0–45 mg), MeCN (2 mL). [b] Absence of light. [c] Determined by GC-FID.

of chlorinated side products, especially in the absence of light (Table 2, entries 2 and 5), suggests an ionic side reaction process which correlates to early reports<sup>[15]</sup> that presented TfCl **1** as a mild, electrophilic chlorination agent: a fact that has not been discussed for photoredox reactions with TfCl **1** so far.

More electron-rich arenes required higher amounts of catalyst to suppress ionic chlorination. Together with a lower amount of TfCl **1** to prevent overreaction it was possible to achieve a good selectivity towards the desired product **4** (Table 2, entry 9).

With these optimised conditions the substrate scope of the reaction was studied. It was possible to trifluoromethylate various heteroaromatic compounds like pyrroles, oxazoles, furanes, thiophenes, indoles, and pyrazines in moderate to excellent yields. In the course of these investigations, we were delighted to observe that different kinds of functional groups were tolerated, namely aldehydes, esters, halides, and amides (Table 3). Depending on the substrate, the reaction time varied between 90 min and 3 days, as well as the optimal amount of TfCl **1** (1.2–2.5 equiv), and catalyst loading (15–25 mg/0.25 mmol substrate). Only in the case of caffeine the tribasic potassium phosphate turned out to be the best base instead of the di-basic one.

Synthetic procedures for direct couplings with perfluoroalkyl groups are relatively limited compared to trifluoromethylations. As a model, we decided to employ the higher fluorinated sulfonyl chloride **22**. With this reagent a fast perfluorobutylation of pyrrole (**21**) was achieved, demonstrating that the chain length of sulfonyl chlorides can be varied without losing reactivity; a higher reactivity was even observed for reagent **22** (Scheme 2). Double fluoroalkylation at positions 2 and 5 of pyrrole (**21**) was observed for higher reagent stoichiometries.

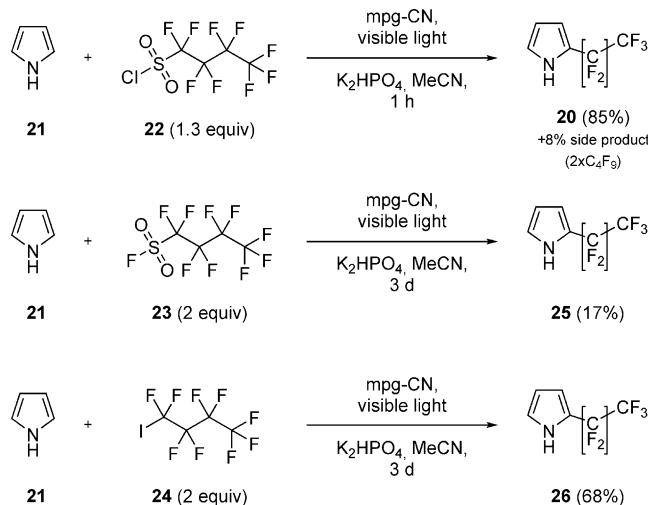
**Table 3.** Reaction scope for the fluoroalkylation through photoredox catalysis with mpg-CN.<sup>[a]</sup>

|   |  |  |  |
|---|--|--|--|
| (Het)Ar-H   | + Cl-SO <sub>2</sub> -CF <sub>3</sub>                            | mpg-CN,<br>visible light   | (Het)Ar-CF <sub>3</sub> + SO <sub>2</sub> + Cl <sup>-</sup>                              |
| 1   |  | K <sub>2</sub> HPO <sub>4</sub> , MeCN,<br>90 min – 3 d                                  |  |
|   |  |  |  |
| <b>2</b> , 65% <sup>[c]</sup>   | <b>3</b> , 81%<br>+8% side product<br>(2xCF <sub>3</sub> )       | <b>8</b> , 81%<br>+8% side product<br>(2xCF <sub>3</sub> )                               | <b>9</b> , 88%<br>C1:C2 9:1<br>+9% side product<br>(2xCF <sub>3</sub> )                  |
|   |  |  |  |
| <b>10</b> , 91%<br>C1:C2 10:1<br>+6% side product<br>(2xCF <sub>3</sub> ) | <b>11</b> , 63%  | <b>12</b> , 94%  | <b>13</b> , 84% <sup>[b]</sup><br>C1:C2 7:1<br>+11% side product<br>(2xCF <sub>3</sub> ) |
|   |  |  |  |
| <b>14</b> , quant.  | menthofurane-CF <sub>3</sub> ( <b>15</b> )<br>55% <sup>[b]</sup> | <b>16</b> , 49% <sup>[b]</sup>   | <b>17</b> , 72%<br>+14% side product<br>(2xCF <sub>3</sub> )                             |
|   |  |  |  |
| <b>18</b> , 75% <sup>[b,d]</sup>  | <b>19</b> , 51% <sup>[b]</sup>                                   | <b>20</b> , 85% <sup>[e]</sup><br>+8% side product<br>(2xC <sub>2</sub> F <sub>5</sub> ) |  |

[a] Reaction conditions: substrate (0.25 or 0.5 mmol), TfCl **1** (1.2–2.0 equiv), mpg-CN (15–25 mg/0.25 mmol substrate), K<sub>2</sub>HPO<sub>4</sub> (3 equiv), MeCN (2 mL/0.25 mmol substrate), 60 W energy saving bulb, 90 min–3 d.

[b] Isolated yield. [c] Determined by GC-FID. Other substrates: determined by <sup>1</sup>H NMR or <sup>19</sup>F NMR. [d] K<sub>3</sub>PO<sub>4</sub> (3 equiv) as base. [e] Perfluoro-1-butane-sulfonyl chloride **22** (1.3 equiv) was used as reagent.

For higher fluorinated reagents, the sulfonyl fluorides are often much cheaper than the corresponding chloride. In particular, nonafluoro-1-butanesulfonyl fluoride (**23**, NfF) is a cheap and popular perfluorinated reagent in organic synthesis.<sup>[16]</sup> Such compounds are therefore very attractive as reagents in photoredox catalysis. However, sulfonyl fluorides have not been investigated in photoredox catalysis so far. The experiment with NfF **23** showed only a slow reaction with a low conversion of 17% to the desired product. This can be explained by the stronger S–F bond of **23** compared to the S–Cl bond in **22** that inhibits a fast degradation after reduction to generate the perfluoroalkyl radical. Perfluorinated alkyl iodides, on the other hand, should have a more challenging reduction poten-



tial. There are few reports that use perfluorinated alkyl iodides in photoredox catalysis for fluoroalkylations of arenes.<sup>[17]</sup> Using mpg-CN as a photocatalyst, perfluoroalkylation with iodide **24** was slower than with **22**, but a good yield of 68% of the desired product was achieved.

Both reagents **23** and **24** showed a certain degree of reactivity, illustrating the great potential for broad applicability in further investigations.

In summary, we have reported a new photoredox system for graphitic carbon nitride, in which a photoreductive activation of sulfonyl chlorides for perfluoroalkylation was achieved. We were able to demonstrate the high potential and broad applicability in organic synthesis for these kinds of metal-free heterogeneous catalysts beyond oxygen activation. With the developed method it was possible to trifluoromethylate benzene and a great variety of heteroaromatic compounds. Additionally, promising prospects for various reagents for perfluoroalkylation have been pointed out.

## Experimental Section

### General procedure for the trifluoromethylation reaction

Powdered potassium phosphate (3 equiv) and mpg-CN (15–25 mg/0.25 mmol substrate) were added to a vacuum-dried 10 mL Schlenk tube with a septum under nitrogen atmosphere. A solution of trifluoromethanesulfonyl chloride **1** (1.2–2.0 equiv) in dry acetonitrile (2 mL/0.25 mmol substrate) was prepared in a glovebox and added to the Schlenk tube, together with the substrate (0.25 or 0.5 mmol). The resulting suspension was shaken under irradiation with visible light using a Philips cool daylight energy-saving bulb (60 W). The optimal reaction time was determined by GC-FID. The reaction mixture was filtered and the filtrate concentrated under reduced pressure. For volatile products water was added to the filtrate, extracted with diethyl ether and washed with brine before concentration to wash out acetonitrile. The residue was pu-

rified by column chromatography on silica using either cyclohexane/ethyl acetate or pentane/diethyl ether (volatile products) as eluent.

## Acknowledgements

This work was supported by the Cluster of Excellence UniCat (financed by the Deutsche Forschungsgemeinschaft and administered by the TU Berlin) and the “Light2Hydrogen” Project of the BMBF (03IS2071D). M.B. thanks the Berlin International Graduate School of Natural Sciences and Engineering (BIGNSE).

**Keywords:** C<sub>3</sub>N<sub>4</sub> • carbon nitride • fluoroalkylation • heterogeneous photoredox catalysis • trifluoromethylation • visible light

- [1] For reviews about photoredox catalysis see: a) M. Reckenthaler, A. G. Griesbeck, *Adv. Synth. Catal.* **2013**, *355*, 2727–2744; b) D. A. Nicewicz, T. M. Nguyen, *ACS Catal.* **2014**, *4*, 355–360; c) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322–5363; d) L. Shi, W. Xia, *Chem. Soc. Rev.* **2012**, *41*, 7687–7697; e) J. Xie, H. Jin, P. Xu, C. Zhu, *Tetrahedron Lett.* **2014**, *55*, 36–48; f) J. Xuan, L.-Q. Lu, J.-R. Chen, W.-J. Xiao, *Eur. J. Org. Chem.* **2013**, *2013*, 6755–6770.
- [2] For examples of Ru(bpy)<sub>3</sub><sup>2+</sup> catalysed reactions see: a) M. A. Cismesia, M. A. Ischay, T. P. Yoon, *Synthesis* **2013**, *45*, 2699–2705; b) C. Dai, J. M. R. Narayanan, C. R. J. Stephenson, *Nat. Chem.* **2011**, *3*, 140–145; c) D. A. DiRocco, T. Rovis, *J. Am. Chem. Soc.* **2012**, *134*, 8094–8097; d) Y.-X. Liu, D. Xue, J.-D. Wang, C.-J. Zhao, Q.-Z. Zou, C. Wang, J. Xiao, *Synlett* **2013**, *24*, 507–513; e) P. Schroll, D. P. Hari, B. König, *ChemistryOpen* **2012**, *1*, 130–133; f) G. Zhao, C. Yang, L. Guo, H. Sun, C. Chen, W. Xia, *Chem. Commun.* **2012**, *48*, 2337–2339; g) Y.-Q. Zou, J.-R. Chen, X.-P. Liu, L.-Q. Lu, R. L. Davis, K. A. Jørgensen, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2012**, *51*, 784–788; *Angew. Chem.* **2012**, *124*, 808–812.
- [3] For examples of reactions catalysed by Ir<sup>III</sup>-complexes see: a) Y. Cheng, X. Gu, P. Li, *Org. Lett.* **2013**, *15*, 2664–2667; b) A. G. Condie, J. C. González-Gómez, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2010**, *132*, 1464–1465; c) H. Jiang, Y. Cheng, R. Wang, M. Zheng, Y. Zhang, S. Yu, *Angew. Chem. Int. Ed.* **2013**, *52*, 13289–13292; *Angew. Chem.* **2013**, *125*, 13531–13534; d) J. D. Nguyen, E. M. D’Amato, J. M. R. Narayanan, C. R. J. Stephenson, *Nat. Chem.* **2012**, *4*, 854–859; e) S. Paria, O. Reiser, *Adv. Synth. Catal.* **2014**, *356*, 557–562; f) K. Kvortrup, D. A. Rankic, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2014**, *136*, 626–629; g) L. J. Rono, H. G. Yayla, D. Y. Wang, M. F. Armstrong, R. R. Knowles, *J. Am. Chem. Soc.* **2013**, *135*, 17735–17738; h) S. Zhu, A. Das, L. Bui, H. Zhou, D. P. Curran, M. Rueping, *J. Am. Chem. Soc.* **2013**, *135*, 1823–1829.
- [4] For examples of reactions catalysed by Eosin Y see: a) D. P. Hari, P. Schroll, B. König, *J. Am. Chem. Soc.* **2012**, *134*, 2958–2961; b) M. Neumann, S. Füldner, B. König, K. Zeitler, *Angew. Chem. Int. Ed.* **2011**, *50*, 951–954; *Angew. Chem.* **2011**, *123*, 981–985; c) V. P. Srivastava, A. K. Yadav, L. D. S. Yadav, *Synlett* **2013**, *24*, 2758; d) D.-T. Yang, Q.-Y. Meng, J.-J. Zhong, M. Xiang, Q. Liu, L.-Z. Wu, *Eur. J. Org. Chem.* **2013**, *2013*, 7528–7532.
- [5] a) X. Wang, K. Maeda, X. Chen, K. Takanabe, K. Domen, Y. Hou, X. Fu, M. Antonietti, *J. Am. Chem. Soc.* **2009**, *131*, 1680–1681; b) F. Goettmann, A. Fischer, M. Antonietti, A. Thomas, *Angew. Chem. Int. Ed.* **2006**, *45*, 4467–4471; *Angew. Chem.* **2006**, *118*, 4579–4583.
- [6] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* **2009**, *8*, 76–80.
- [7] a) J. Zhu, P. Xiao, H. Li, S. A. C. Carabineiro, *ACS Appl. Mater. Interfaces* **2014**, *6*, 16449–16465; b) K. Kailasam, J. D. Epping, A. Thomas, S. Losse, H. Junge, *Energy Environ. Sci.* **2011**, *4*, 4668–4674; c) N. Cheng, P. Jiang, Q. Liu, J. Tian, A. M. Asiri, X. Sun, *Analyst* **2014**, *139*, 5065–5068; d) J. Tian, Q. Liu, A. M. Asiri, K. A. Alamry, X. Sun, *ChemSusChem* **2014**, *7*, 2125–2130; e) J. Tian, Q. Liu, C. Ge, Z. Xing, A. M. Asiri, A. O. Al-Youbi, X. Sun, *Nanoscale* **2013**, *5*, 8921–8924.

- [8] a) L. Möhlmann, M. Baar, J. Rieß, M. Antonietti, X. Wang, S. Blechert, *Adv. Synth. Catal.* **2012**, *354*, 1909–1913; 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) F. Su, S. C. Mathew, L. Möhlmann, M. Antonietti, X. Wang, S. Blechert, *Angew. Chem. Int. Ed.* **2011**, *50*, 657–660; *Angew. Chem.* **2011**, *123*, 683–686; d) Y. Wang, X. Wang, M. Antonietti, *Angew. Chem.* **2012**, *124*, 70–92.
- [9] a) M. Cherevatskaya, B. König, *Russ. Chem. Rev.* **2014**, *83*, 183; b) X. Lang, X. Chen, J. Zhao, *Chem. Soc. Rev.* **2014**, *43*, 473–486; c) C. Vila, M. Rueping, *Green Chem.* **2013**, *15*, 2056–2059.
- [10] For examples of trifluoromethylations by photoredox catalysis see: a) N. Iqbal, J. Jung, S. Park, E. J. Cho, *Angew. Chem. Int. Ed.* **2014**, *53*, 539–542; b) S. Mizuta, S. Verhoog, K. M. Engle, T. Khotavivattana, M. O'Duill, K. Wheelhouse, G. Rassias, M. Médebielle, V. Gouverneur, *J. Am. Chem. Soc.* **2013**, *135*, 2505–2508; c) D. A. Nagib, M. E. Scott, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2009**, *131*, 10875–10877; d) D. J. Wilger, N. J. Gesmundo, D. A. Nicewicz, *Chem. Sci.* **2013**, *4*, 3160–3165; e) Y. Yasu, Y. Arai, R. Tomita, T. Koike, M. Akita, *Org. Lett.* **2014**, *16*, 780–783.
- [11] D. A. Nagib, D. W. C. MacMillan, *Nature* **2011**, *480*, 224–228.
- [12] a) D. Cantillo, O. de Frutos, J. A. Rincón, C. Mateos, C. O. Kappe, *Org. Lett.* **2014**, *16*, 896–899; b) H. Jiang, X. Chen, Y. Zhang, S. Yu, *Adv. Synth. Catal.* **2013**, *355*, 809–813; c) H. Jiang, Y. Cheng, Y. Zhang, S. Yu, *Eur. J. Org. Chem.* **2013**, *2013*, 5485–5492; d) S. H. Oh, Y. R. Malpani, N. Ha, Y.-S. Jung, S. B. Han, *Org. Lett.* **2014**, *16*, 1310–1313.
- [13] a) X. Lang, W. Ma, Y. Zhao, C. Chen, H. Ji, J. Zhao, *Chem. Eur. J.* **2012**, *18*, 2624–2631; b) T. Mitkina, C. Stanglmair, W. Setzer, M. Gruber, H. Kisch, B. Konig, *Org. Biomol. Chem.* **2012**, *10*, 3556–3561; c) Y. Zhang, N. Zhang, Z.-R. Tang, Y.-J. Xu, *Chem. Sci.* **2012**, *3*, 2812–2822.
- [14] N. Aiga, Q. Jia, K. Watanabe, A. Kudo, T. Sugimoto, Y. Matsumoto, *J. Phys. Chem. C* **2013**, *117*, 9881–9886.
- [15] G. Hosein Hakimelahi, G. Just, *Tetrahedron Lett.* **1979**, *20*, 3643–3644.
- [16] R. Zimmer, M. Webel, H.-U. Reiβig, *Journal Prakt. Chem.* **1998**, *340*, 274–277.
- [17] a) N. Iqbal, S. Choi, E. Ko, E. J. Cho, *Tetrahedron Lett.* **2012**, *53*, 2005–2008; b) Y. Ye, M. S. Sanford, *J. Am. Chem. Soc.* **2012**, *134*, 9034–9037.

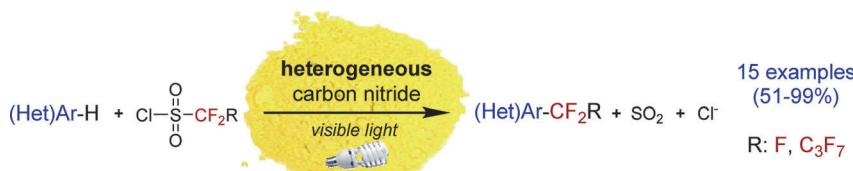
Received: October 2, 2014

Published online on ■■■, 0000

## COMMUNICATION

**Fluoroalkylation**

M. Baar, S. Blechert\*

 **Graphitic Carbon Nitride Polymer as a Recyclable Photoredox Catalyst for Fluoroalkylation of Arenes**

**Heterogeneous catalysis for trifluoromethylations** and perfluoroalkylations has been performed. Through the usage of cheap, metal-free and recyclable mesoporous graphitic carbon nitride (mpg-CN), it was possible to fluoroalkylate various arenes by the reductive ac-

tivation of sulfonyl chlorides with visible light (see scheme). Thus, the robustness and versatility of mpg-CN as a photoredox catalyst was demonstrated beyond water splitting and the activation of oxygen.