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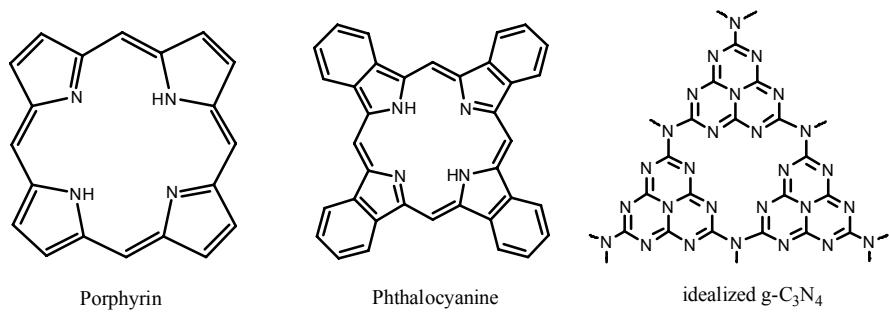
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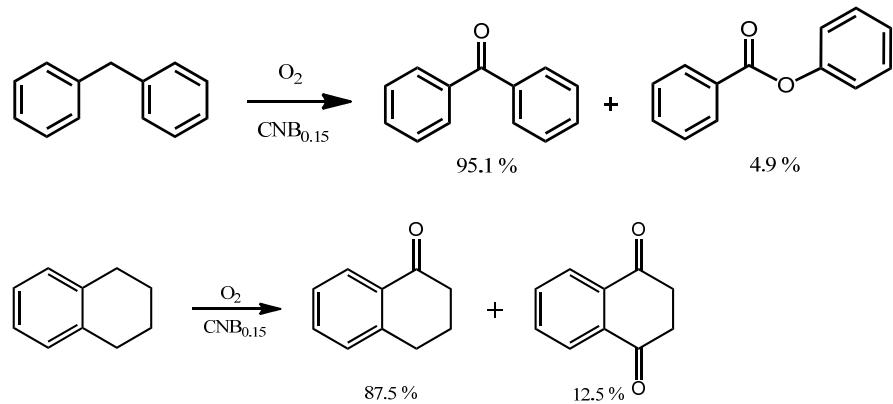
## Supporting Information:

### Synthesis of Boron Doped Carbon Nitride Solids and Their Use as Metal Free Catalyst for Aliphatic C-H Bond Oxidation

*Yong Wang,\* Haoran Li, Jia Yao, Xincheng Wang, and Markus Antonietti*



**Scheme S1.** Nitrogen-enriched  $\pi$ -conjugated macrocyclic scaffolds.



**Scheme S2.** Molecular oxygen oxidation of substituted aromatics to ketone using  $\text{CNB}_{0.15}$  as metal free heterogeneous catalyst

**Table S1.** Photocatalytic activity of Pt/CNB<sub>0.025</sub> and Pt/g-C<sub>3</sub>N<sub>4</sub> for the hydrogen evolution reaction with visible light.

| Entry                           | H <sub>2</sub> evolution rate ( $\mu$ mol/h) |      |
|---------------------------------|--|------|
|                                 | $\lambda > 420$ nm                           |      |
| g-C <sub>3</sub> N <sub>4</sub> |  | 14.1 |
| BN <sub>0.025</sub>             |  | 25.5 |

<sup>a</sup>Reaction conditions see ref. 7.

**Table S2.** Conversion and selectivity of toluene oxidation over CNB<sub>x</sub> catalysts.

| Entry | Catalyst            | Conv. [%] | Sel. [%] BA <sup>a</sup> |
|-------|---------------------|-----------|--------------------------|
| 1     | CNB <sub>0.01</sub> | 2.7       | >99.0                    |
| 2     | CNB <sub>0.05</sub> | 5.6       | >99.0                    |
| 3     | CNB <sub>0.2</sub>  | 6.0       | >99.0                    |
| 4     | CNB <sub>0.25</sub> | 6.2       | 77.0                     |

Reaction conditions: toluene 0.8ml, H<sub>2</sub>O<sub>2</sub> (30% in water solution) 0.77ml, catalyst 50mg, acetonitrile 8ml, reaction temperature 150°C, reaction time 2h. <sup>a</sup>BA=benzaldehyde.

**Table S3.** Conversion and selectivity of toluene oxidation over CNB<sub>x</sub> catalysts.

| Entry | Catalyst                        | Toluene   | H <sub>2</sub> O <sub>2</sub> |
|-------|---------------------------------|-----------|-------------------------------|
|       |                                 | Conv. [%] | Sel. (%) <sup>a</sup>         |
| 1     | g-C <sub>3</sub> N <sub>4</sub> | 2.0       | 2.8                           |
| 2     | CNB <sub>0.025</sub>            | 4.2       | 7.6                           |
| 3     | CNB <sub>0.15</sub>             | 6.3       | 12.3                          |

<sup>a</sup>moles of produced benzaldehyde/moles of reacted H<sub>2</sub>O<sub>2</sub> \* 100.

**Table S4.** Effect of different solvents on the oxidation of toluene over CNB<sub>x</sub> catalysts.

| Entry | Solvent                         | Conv. | Sel. [%] BA <sup>a</sup> |
|-------|---------------------------------|-------|--------------------------|
|       |                                 | [%]   |                          |
| 1     | Acetonitrile                    | 6.3   | >99.0                    |
| 2     | CH <sub>2</sub> Cl <sub>2</sub> | 0     | -                        |
| 3     | Pyridine                        | 0     | -                        |
| 4     | Acetone                         | 5.5   | >99.0                    |
| 5     | Ethyl acetate                   | 0.5   | >99.0                    |

Reaction conditions: toluene 0.8ml, H<sub>2</sub>O<sub>2</sub> (30% in water solution) 0.77ml, catalyst 50mg, acetonitrile 8ml, reaction temperature 150°C, reaction time 2h. <sup>a</sup>BA=benzaldehyde.

**Table S5.** Effect of the amount of CNB<sub>x</sub> catalysts.

| Entry | Amount (mg) | Conv. [%] | Sel. [%] BA <sup>a</sup> |
|-------|-------------|-----------|--------------------------|
| 1     | 25          | 3.1       | >99.0                    |
| 2     | 40          | 4.8       | >99.0                    |
| 3     | 50          | 6.3       | >99.0                    |
| 4     | 60          | 6.5       | >99.0                    |

Reaction conditions: toluene 0.8ml, H<sub>2</sub>O<sub>2</sub> (30% in water solution) 0.77ml, catalyst CNB<sub>0.15</sub>, acetonitrile 8ml, reaction temperature 150°C, reaction time 2h. <sup>a</sup>BA=benzaldehyde.

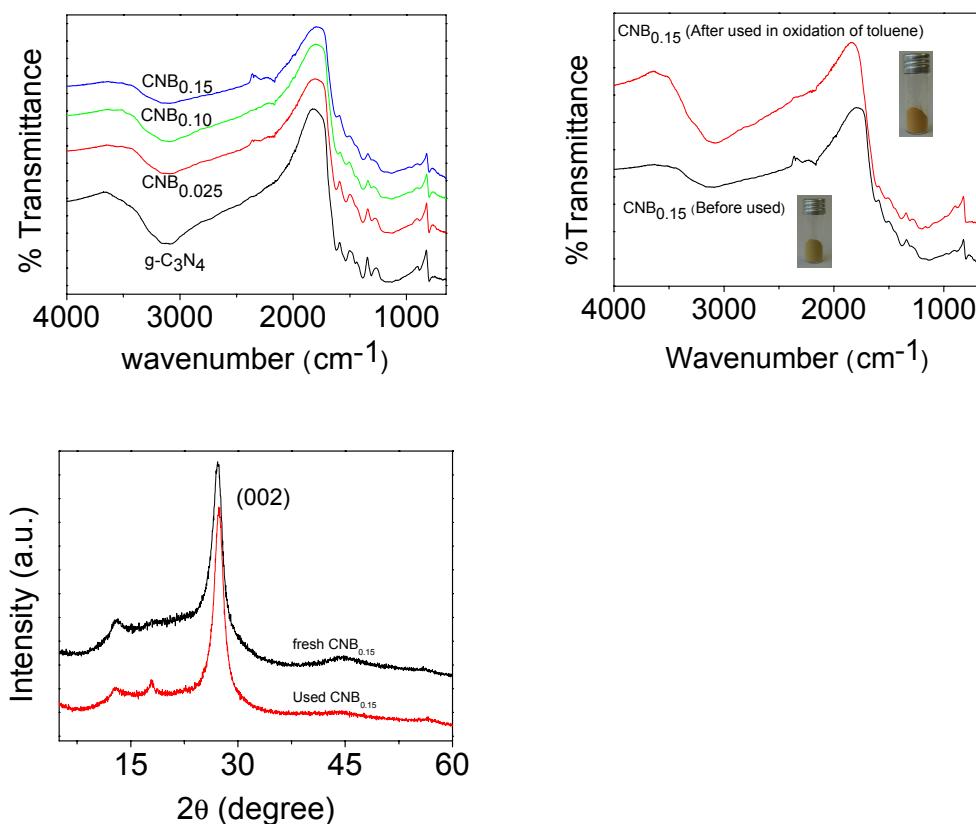
**Table S6.** Comparison of the catalytic results using different catalysts.

| Entry          | Catalyst                            | Sel. [%] benzaldehyde | Sel. [%] benzyl alcohol |
|----------------|-------------------------------------|-----------------------|-------------------------|
| 1              | CNB <sub>0.15</sub>                 | >99.0                 | -                       |
| 2 <sup>a</sup> | P450 enzyme                         | <5%                   | 95%                     |
| 3 <sup>b</sup> | FeTPP <sup>Cl</sup> <sub>8</sub> Cl | 13.2%                 | 86.8%                   |

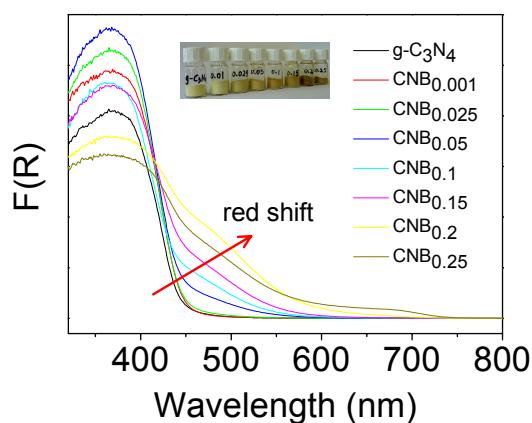
<sup>a</sup>S1. Wikipedia, see <http://en.wikipedia.org/wiki/Toluene>

<sup>a</sup>S2. H. Hanioka, M. Hamamura, K. Kakino, H. Ogata, H. Jinno, A. Takahashi, T. Nishimura, M. Ando, *Xenobiotica*, **1995**, *25*, 1207-1217.

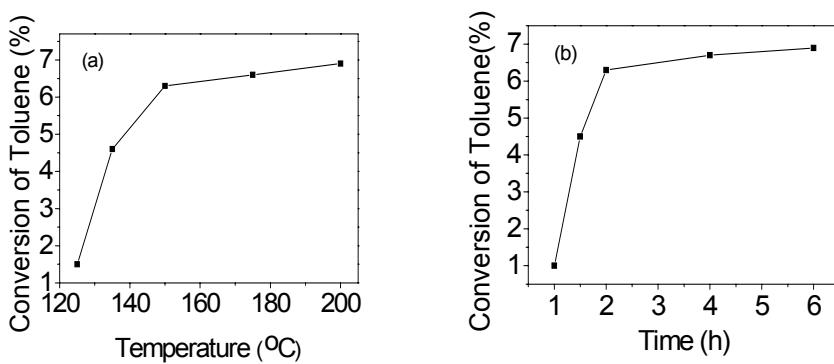
<sup>b</sup>S3. T. Nakano, N. Agatsuma, S. Kodama, H. Kakuda, and D. Dolphin, *Bull. Chem. Soc. Jpn.*, **1996**, *69*, 3513-3512.



**Figure S1.** FTIR spectra and XRD patterns of CNB<sub>x</sub> materials.



**Figure S2.** UV spectra of of  $\text{CNB}_x$  materials.



**Figure S3.** Influence of reaction temperature and time on toluene conversion (over  $\text{CNB}_{0.15}$ ).

Influence of reaction temperature and time on the toluene conversion over  $\text{CNB}_{0.15}$  was investigated. The influence of reaction temperature was studied in the temperature range between 100 and 200  $^{\circ}\text{C}$ . Indeed, no reaction takes place at 100  $^{\circ}\text{C}$  and 2h reaction time. Figure S3a shows that the conversion increases quickly with temperature, while staying constant beyond a reaction temperature of 150  $^{\circ}\text{C}$ . This is typical for the setting in of a secondary reaction consuming reactants, presumably the decomposition of  $\text{H}_2\text{O}_2$  by the catalyst into products other than benzaldehyde, e.g. oxygen. Figure S3b illustrates that the oxidation of toluene at temperature 150  $^{\circ}\text{C}$  is indeed finished after 2h, prolongation of the reaction time to 4 or 6 h give no obviously increase in the conversion of toluene.