Supporting Information:

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

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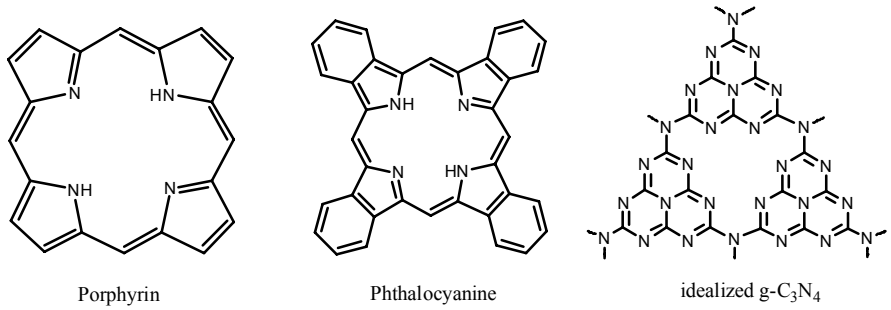
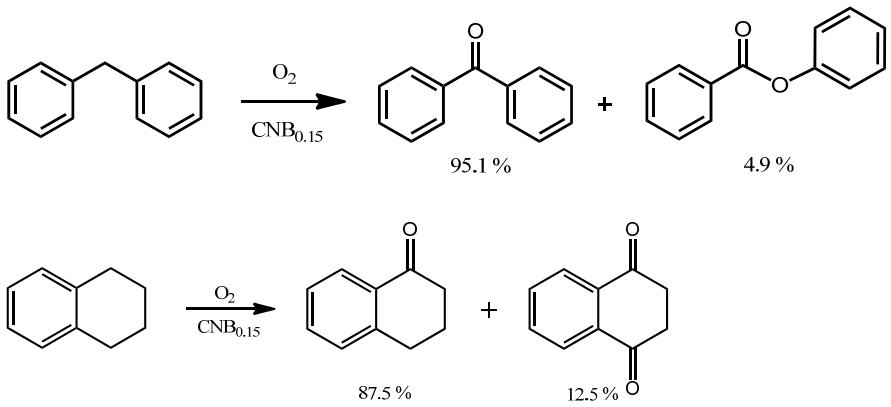


Scheme S1. Nitrogen-enriched π-conjugated macrocyclic scaffolds.



Scheme S2. Molecular oxygen oxidation of substituted aromatics to ketone using $CNB_{0.15}$ as metal free heterogeneous catalyst

Table S1. Photocatalytic activity of $Pt/CNB_{0.025}$ and $Pt/g\text{-}C_3N_4$ for the hydrogen evolution reaction with visible light.

Entry	H_2 evolution rate (μ mol/h)
	$\lambda > 420$ nm
$g\text{-}C_3N_4$	14.1
$BN_{0.025}$	25.5

[a]Reaction conditions see ref. 7.

Table S2. Conversion and selectivity of toluene oxidation over CNB_x catalysts.

Entry	Catalyst	Conv. [%]	Sel. [%] BA[a]
1	$CNB_{0.01}$	2.7	>99.0
2	$CNB_{0.05}$	5.6	>99.0
3	$CNB_{0.2}$	6.0	>99.0
4	$CNB_{0.25}$	6.2	77.0

Reaction conditions: toluene 0.8ml, H_2O_2 (30% in water solution) 0.77ml, catalyst 50mg, acetonitrile 8ml, reaction temperature 150°C, reaction time 2h. [a]BA=benzaldehyde.

Table S3. Conversion and selectivity of toluene oxidation over CNB_x catalysts.

Entry	Catalyst	Toluene Conv. [%]	H_2O_2 Sel. (%)[a]
1	$g\text{-}C_3N_4$	2.0	2.8
2	$CNB_{0.025}$	4.2	7.6
3	$CNB_{0.15}$	6.3	12.3

[a]moles of produced benzaldehyde/moles of reacted H_2O_2 * 100.

Table S4. Effect of different solvents on the oxidation of toluene over CNB_x catalysts.

Entry	Solvent	Conv. [%]	Sel. [%] BA[a]
1	Acetonitrile	6.3	>99.0
2	CH_2Cl_2	0	-
3	Pyridine	0	-
4	Acetone	5.5	>99.0
5	Ethyl acetate	0.5	>99.0

Reaction conditions: toluene 0.8ml, H_2O_2 (30% in water solution) 0.77ml, catalyst 50mg, acetonitrile 8ml, reaction temperature 150^{o}C, reaction time 2h. [a]BA=benzaldehyde.

Table S5. Effect of the amount of CNB_x catalysts.

Entry	Amount (mg)	Conv. [%]	Sel. [%] BA[a]
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_2O_2 (30% in water solution) 0.77ml, catalyst $CNB_{0.15}$, acetonitrile 8ml, reaction temperature 150^{o}C, reaction time 2h. [a]BA=benzaldehyde.

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

Entry	Catalyst	Sel. [%] benzaldehyde	Sel. [%] benzyl alcohol
1	$CNB_{0.15}$	>99.0	-
2[a]	P450 enzyme	<5%	95%
3[b]	$FeTPPCl_8Cl$	13.2%	86.8%

[a]S1. Wikipedia, see http://en.wikipedia.org/wiki/Toluene

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

[b]S3. T. Nakano, N. Agatsuman, S. Kodama, H. Kakuda, and D. Dolphin, *Bull. Chem. Soc. Jpn.*, 1996, *69*, 3513-3512.

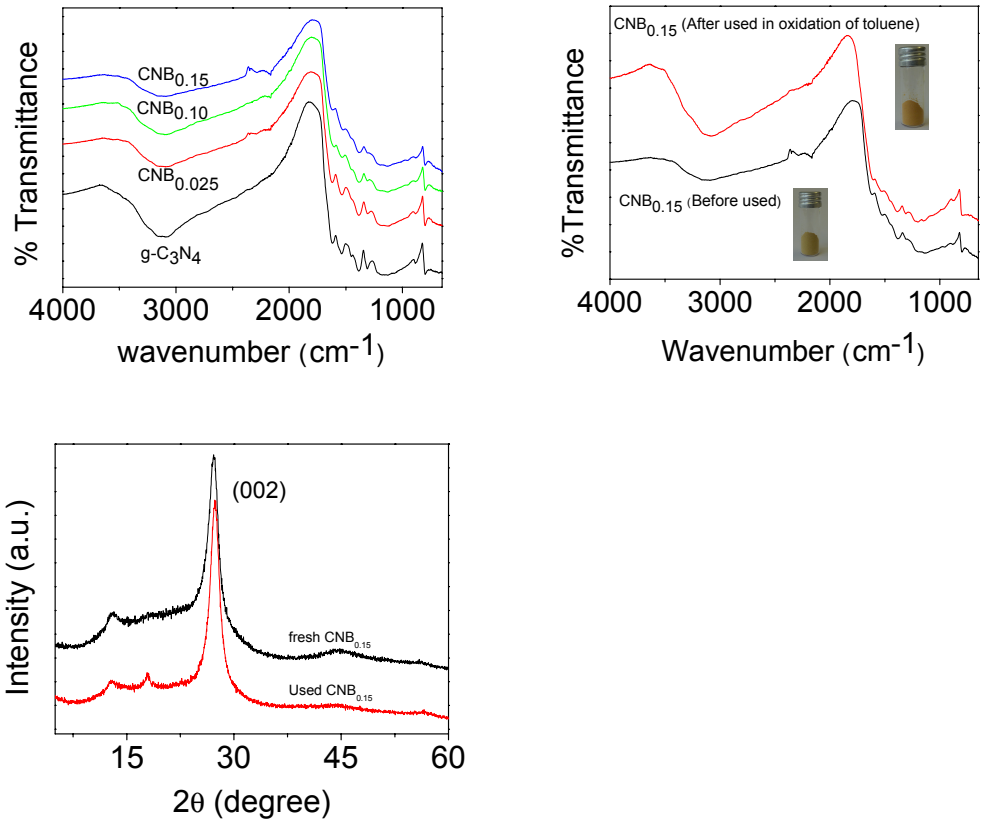


Figure S1. FTIR spectra and XRD patterns of CNB_x materials.

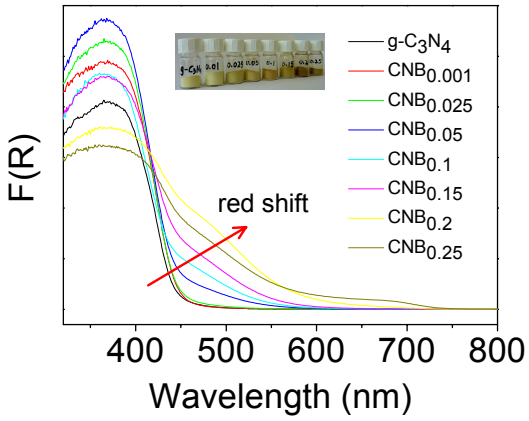


Figure S2. UV spectra of of CNB_x materials.

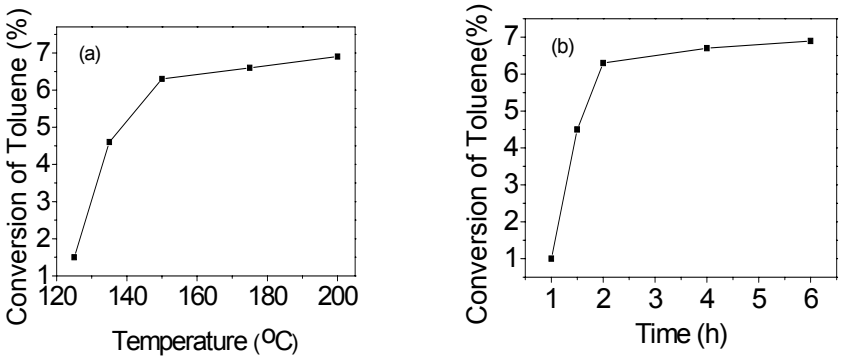


Figure S3. Influence of reaction temperature and time on toluene conversion (over $CNB_{0.15}$).

Influence of reaction temperature and time on the toluene conversion over $CNB_{0.15}$ was investigated. The influence of reaction temperature was studied in the temperature range between 100 and 200 °C. Indeed, no reaction takes place at 100 °C and 2h reaction time. Figure S3a shows that the conversion increases quickly with temperature, while staying constant beyond a reaction temperature of 150°C. This is typical for the setting in of a secondary reaction consuming reactants, presumably the decomposition of H_2O_2 by the catalyst into products other than benzaldehyde, e.g. oxygen. Figure S3b illustrates that the oxidation of toluene at temperature 150 °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.