Supporting Information

Metal-free and Solvent-free Oxidative Coupling of Amines to Imines with Mesoporous Carbon from Macrocyclic Compounds

Bo Chen,[1,2] Lianyue Wang,[1] Wen Dai,[1] Sensen Shang,[1,2] Ying Lv,[1] and Shuang Gao[1]*

[1] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Dalian 116023, China.

[2] University of the Chinese Academy of Sciences, Beijing 100049, China.

To whom correspondence should be addressed. E-mail: sgao@dicp.ac.cn.

Synthesis of SBA-15:[1] A solution of P123 : 2 M HCl : TEOS : H_2O = 2 : 60 : 4.25 : 15 (mass ratio) was stirred for 12h at 40 ^oC, and then hydrothermally treated at 110 ^oC for 24 h. The obtained solid was thoroughly washed with water, dried in vacuum at 100 °C overnight, and calcined at 550 ^oC for 8 h to remove the template. (P123: Ttriblock copolymer $EO_{20}PO_{70}EO_{20}$, Mw = 5800; TEOS: tetraethyl orthosilicate).

Synthesis of mesoporous graphitic carbon nitride (mpg-C_3N_4):[2] Cyanamide was dissolved in a 40% dispersion of 12-nm SiO_2 particles (Ludox HS-40) in water with stirring at 60 °C overnight. After evaporation of the solvent at 100 ^oC, the obtained solid was pyrolyzed at 550 °C (ramp rate: 2.3 °C min^{-1}) for 4 h under flowing nitrogen. The obtained powder was treated with 10 wt % hydrofluoric acid for 12 h, and this procedure was repeated once for removing the silicon template completely. Finally, the powder was thoroughly washed to neutral with water and dried in vacuum at 100 °C overnight.

Base or hydrogenation treatment of the catalyst: The as-prepared PC-Ludox-8 was dispersed in 2.5 M NaOH solutions and stirred at 80 ^oC for 12 h. Then, the powder was separated by filtration and washed to neutral with water. The obtained sample was dried in vacuum at 100 °C overnight. The hydrogenation treatment of catalyst was conducted in the same way, except using $NaBH_4$ instead of NaOH and stirring at 25 ^oC.

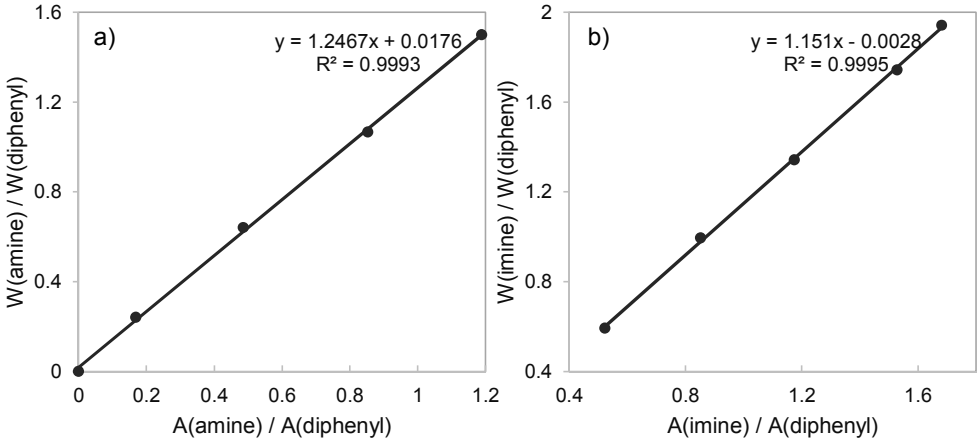


Figure S1 Standard curves for benzylamine oxidation (A: Area, W:weight).

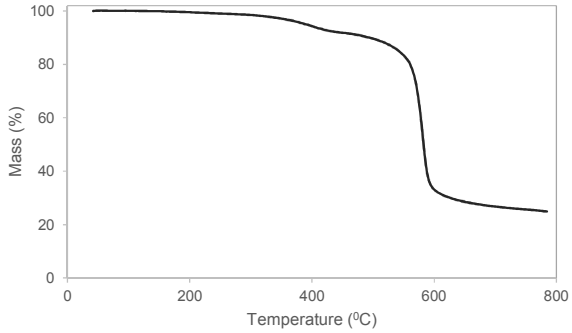


Figure S2 Thermogravimetric curve of commercially available phthalocyanine.

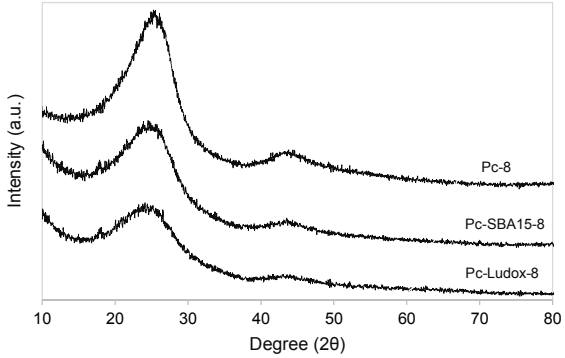


Figure S3 Powder XRD patterns of Pc-Ludox-8, Pc-SBA15-8, and Pc-8.

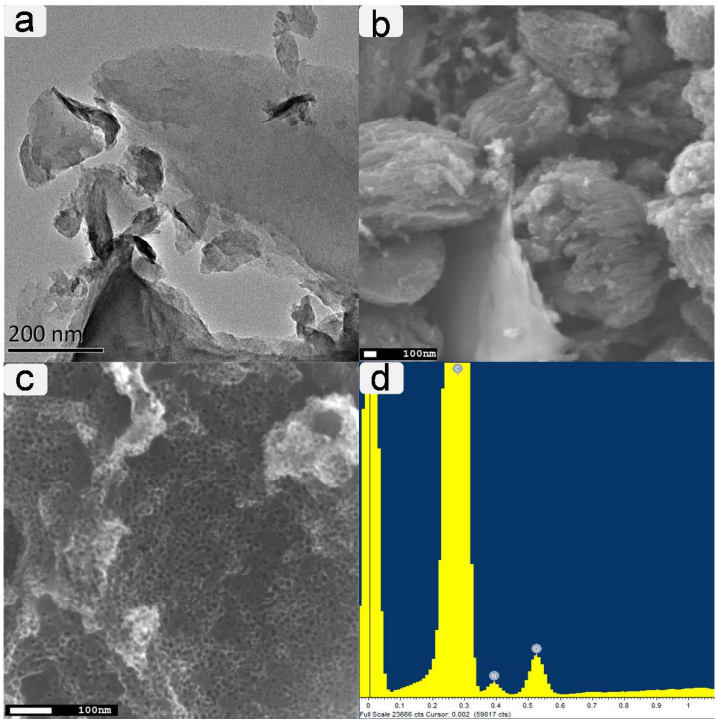


Figure S4 a) TEM image of Pc-8, b) SEM image of Pc-SBA15-8, c) SEM image of TPP-Ludox-8 and d) representative EDX spectrum of Pc-Ludox-8.

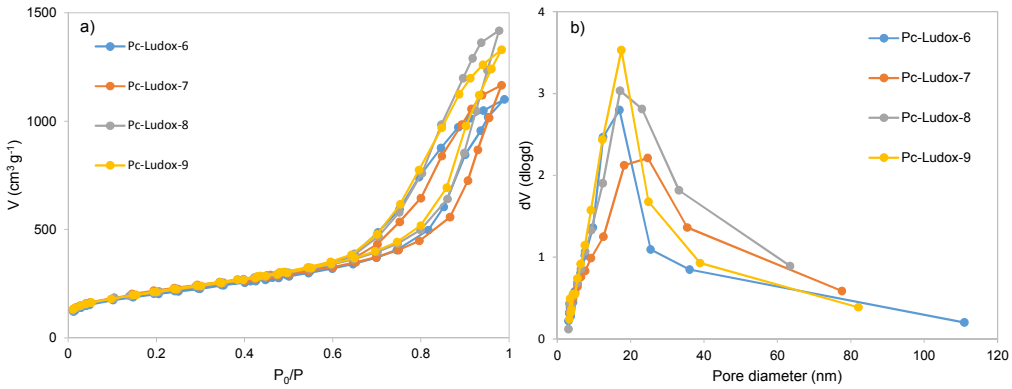


Figure S5 a) N_2 sorption isotherms, b) BJH mesopore size distribution plots of Pc-Ludox-6, 7, 8, and 9.

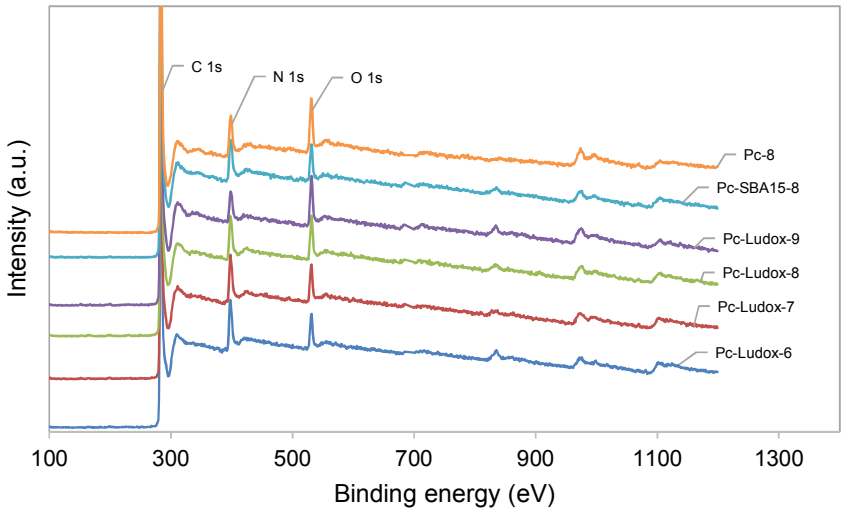


Figure S6 XPS survey spectrum of various carbon-based catalysts.

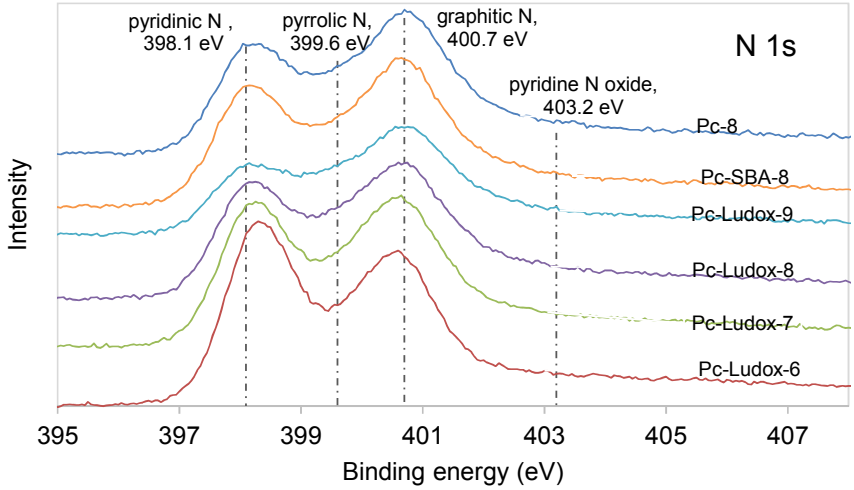


Figure S7 High-resolution N 1s spectra of various samples.

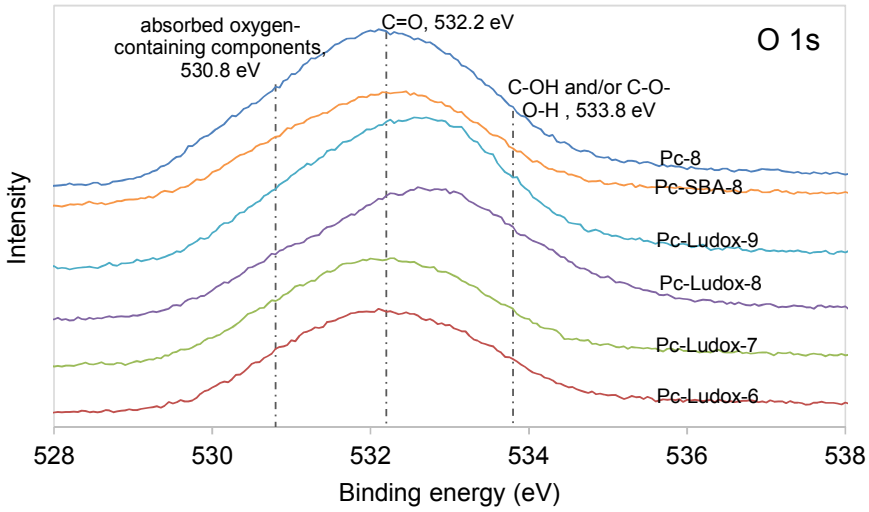


Figure S8 High-resolution O1s spectra of various samples.

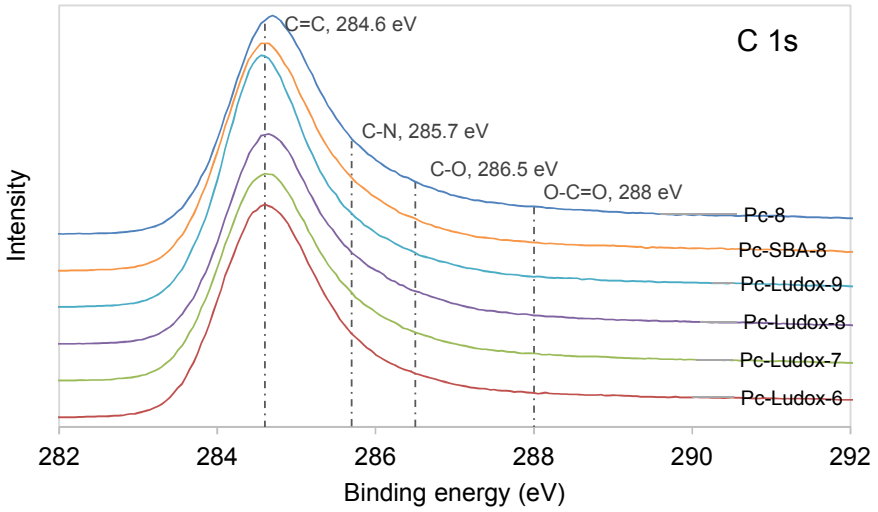


Figure S9 High-resolution C 1s spectra of various samples.

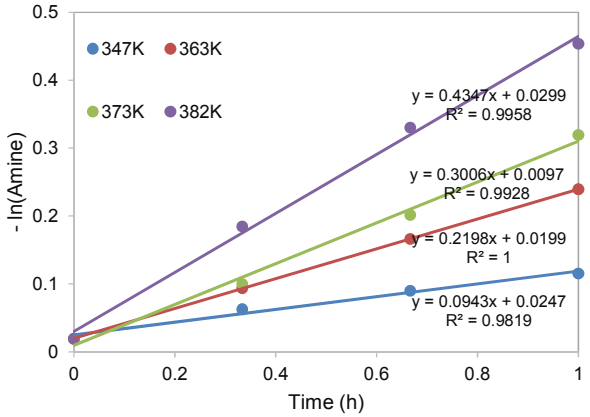
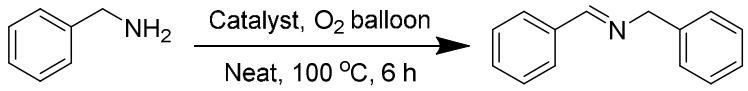


Figure S10 Time-on-stream course of conversion under different temperatures. Reaction conditions: benzylamine (5 mmol), Pc-Ludox-8 (20 mg), O_2 balloon, 100 °C.

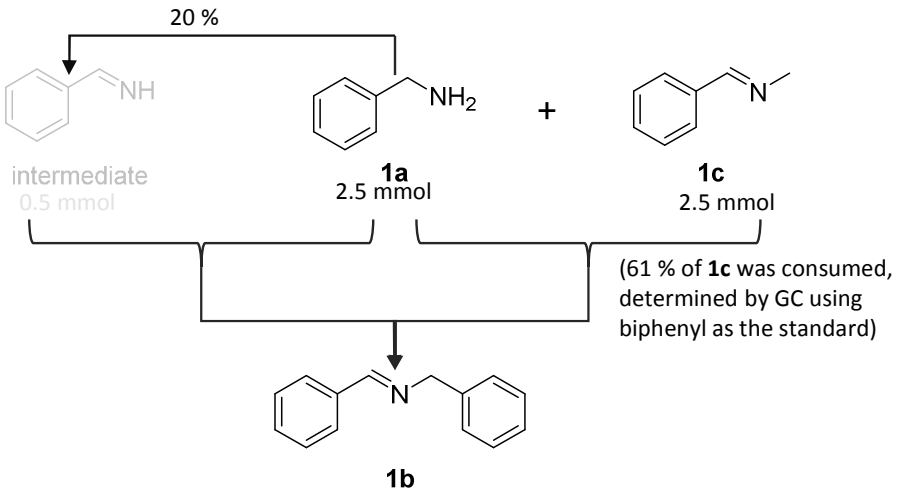
Table S1 Additional catalytic data for the oxidative coupling of benzylamine.[a]



1a **2a**

Entry	Catalyst	Conversion [%][b]	Selectivity [%][b]
1[c]	Pc-Ludox-8	95.0%	95.2%
2[d]	Pc-Ludox-8	91.4%	95.6%
3[e]	Pc-Ludox-8	91.6%	99.0%

[a] Reaction conditions: **1a** (5 mmol), catalyst (20 mg), O_2 balloon, 6 h, 100 °C. [b] Determined by GC using diphenyl as the internal standard and confirmed by GC-MS. [c] the free-radical scavenger 2,6-Di-tert-butyl-4-methylphenol (BHT, 5 mmol %) was added. [d] the catalyst was treated with NaOH. [e] the catalyst was treated with $NaBH_4$.



Schem S1 Oxidative coupling of benzylamine and *N*-benzylidenemethyl amine over Pc-Ludox-8. Reaction conditions: **1a** (2.5 mmol), **1c** (2.5 mmol), catalyst (20 mg), O_2 balloon, 5 h, 100 °C.

REFERENCES

(1) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D., *Science* **1998**, *279*, 548-552.

(2) Su, F.; Mathew, S. C.; Möhlmann, L.; Antonietti, M.; Wang, X.; Blechert, S., *Angew. Chem. Int. Ed.* **2011**, *50*, 657-660.