

Supporting Information

Ionic Porous Porphyrin Cage as a Superior Catalyst for Photocatalytic Oxidization

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Computational Details

DFT calculations were performed using the Gaussian 09 software package.^[1] The model structure was extracted from the crystallographic data of **TPPCage•8PF₆** or **TPPCage•8I** in CIF format, including one porphyrin unit, one pyridinium unit, and one corresponding counterion. The model structure was then optimized, and the distributions and energy levels of the involved molecular orbitals were evaluated at the PBE0/def2tzvp level of theory.^[2] The SMD was chosen to mimic the solvent (water) effect in all calculations.^[3] Dispersion energies between two fragments are given from Grimme's D3 correction.^[4] Molecular orbital was implemented in Multiwfn,^[5] and visualized with VMD.^[6] Electron density distribution (EDD) of **TPPCage•8PF₆** or **TPPCage•8I** structure was analyzed with Multiwfn and visualized by VMD.

Titration of Iodine Ion. **TPPCage•8I** (10.00 mg, 0.00336 mmol) was dissolved in 2.0 mL of DMF. Then, the AgNO₃ solution (0.250 mmol/mL) was added dropwise to the above solution, with continuous stirring. Following the reaction, the mixture underwent centrifugation, and the resulting product, AgI, was obtained after vacuum drying. By performing calculations, it can be deduced that all iodide ions have undergone exchange, leading to the formation of AgI. The yield of AgI was determined to be 6.340 mg.

Synthesis of TPPCage•8Cl. **TPPCage•8PF₆** (40.00 mg, 0.0129 mmol) was dissolved in 20.0 mL of acetonitrile, while KCl (38.32 mg, 0.514 mmol) was dissolved in 2.0 mL of H₂O. The aqueous solution of KCl was added slowly to the acetonitrile solution containing **TPPCage•8PF₆**. The mixture was stirred for 12 h. Following the completion of the reaction, **TPPCage•8Cl** was collected after centrifugation and subsequently subjected to vacuum drying.

¹H NMR (400MHz, (CD₃)₂SO): δ =9.73 (d, 16H), 8.80 (s, 16H), 8.77 (d, 16H), 8.26 (m, 8H), 8.21-8.18 (m, 16H), 7.94 (t, 8H), 6.47 (s, 16H), -3.31 (s, 4H)

Titration of Chloride Ion. **TPPCage•8Cl** (10.00 mg, 0.00447 mmol) was dissolved

in 2.0 mL of DMF. Then, the AgNO₃ solution (0.250 mmol/mL) was added dropwise to the above solution, with continuous stirring. Following the reaction, the mixture underwent centrifugation, and the resulting product, AgCl, was obtained after vacuum drying. By performing calculations, it can be deduced that all chloride ions have undergone exchange, leading to the formation of AgCl. The yield of AgCl was determined to be 5.210 mg.

Synthesis of TPPCage•4PF₆•4I. TPPCage•8PF₆ (10.00 mg, 0.00323mmol) was dissolved in 3 mL of acetonitrile, while KI (2.13 mg, 0.0129 mmol) was dissolved in 0.3 mL of H₂O. The aqueous solution of KI was added slowly to the acetonitrile solution containing TPPCage•8PF₆. The mixture was stirred for 12 h. Following the completion of the reaction, TPPCage•4PF₆•4I was collected after centrifugation and subsequently subjected to vacuum drying.

¹H NMR (400MHz, (CD₃)₂SO): δ =9.39 (d, 16H), 8.80 (s, 16H), 8.42 (d, 16H), 8.32 (d, 8H), 8.16 (d, 8H), 8.06 (s, 8H), 7.97 (t, 8H), 6.25 (s, 16H), -3.30 (s, 4H)

Titration of Iodine Ion. TPPCage•4PF₆•4I (10.00 mg, 0.00447 mmol) was dissolved in 2.0 mL of DMF. Then, the AgNO₃ solution (0.250 mmol/mL) was added dropwise to the above solution, with continuous stirring. Following the reaction, the mixture underwent centrifugation, and the resulting product, AgI, was obtained after vacuum drying. By performing calculations, it can be deduced that four PF₆⁻ ions have undergone exchange, leading to the formation of AgI. The yield of AgI was determined to be 3.140 mg.

Synthesis of TPPCage•8SDS. TPPCage•8I (20.00 mg, 0.00672 mmol) was dissolved in 10.0 mL of DMF, while sodium dodecyl sulfate (38.76 mg, 0.1344 mmol) was dissolved in 2.0 mL of H₂O. The aqueous solution of sodium dodecyl sulfate was added slowly to the DMF solution containing TPPCage•8I. The mixture was stirred for 12 h. Following the completion of the reaction, TPPCage•8SDS was collected after centrifugation and subsequently subjected to vacuum drying.

^1H NMR (400MHz, $(\text{CD}_3)_2\text{SO}$): δ =9.37 (d, 16H), 8.80 (s, 16H), 8.41 (d, 16H), 8.34 (d, 8H), 8.19 (d, 8H), 8.06 (s, 8H), 7.98 (t, 8H), 6.24 (s, 16H), 1.33-0.67 (m, 204H), -3.29 (s, 4H)

Recycle of TPPCage•8I. TPPCage•8SDS (20.00 mg, 0.0049 mmol) was dissolved in 10.0 mL of DMF, while KI (16.29 mg, 0.098 mmol) was dissolved in 1.0 mL of H_2O . The aqueous solution of KI was added slowly to the DMF solution containing TPPCage•8SDS. The mixture was stirred for 12 h. Following the completion of the reaction, TPPCage•8I was collected after centrifugation and subsequently subjected to vacuum drying.

^1H NMR (400MHz, $(\text{CD}_3)_2\text{SO}$): δ =9.43 (d, 16H), 8.80 (s, 16H), 8.47 (d, 16H), 8.33 (d, 8H), 8.17 (d, 8H), 8.08 (s, 8H), 7.97 (t, 8H), 6.29 (s, 16H), -3.30 (s, 4H)

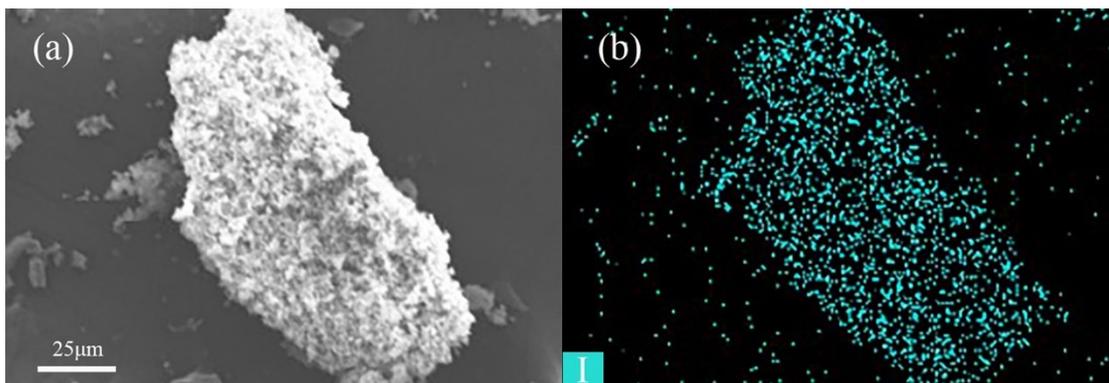


Figure S1. (a, b) EDS spectra of TPPCage•8I.

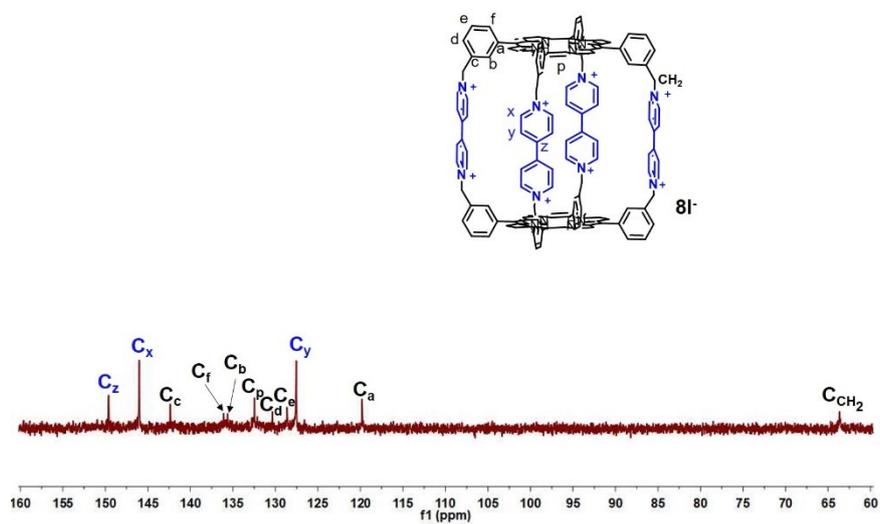


Figure S2. ^{13}C NMR spectra of TPPCage•8I.

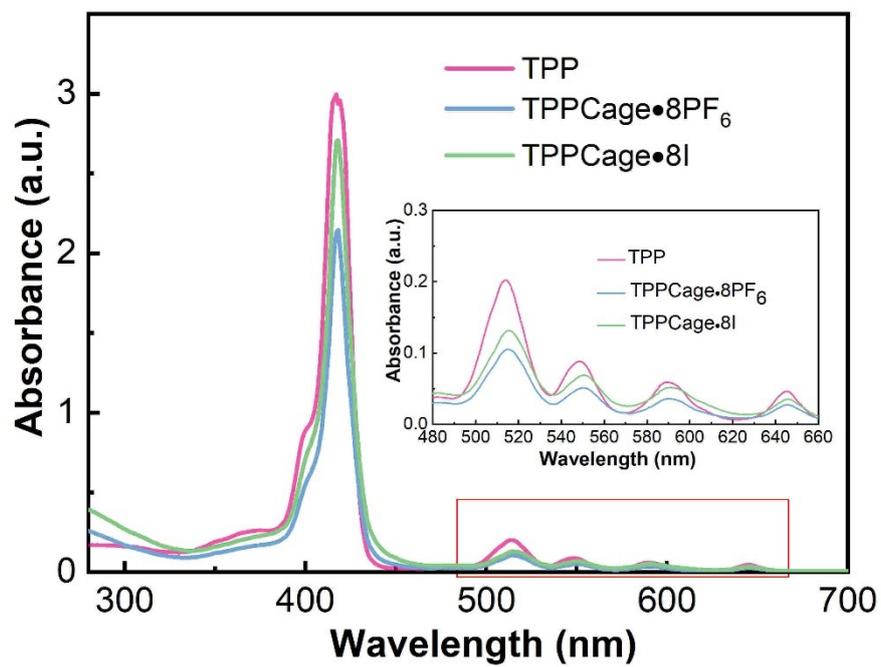


Figure S3. UV-vis spectra of TPP, TPPCage•8PF₆ and TPPCage•8I.

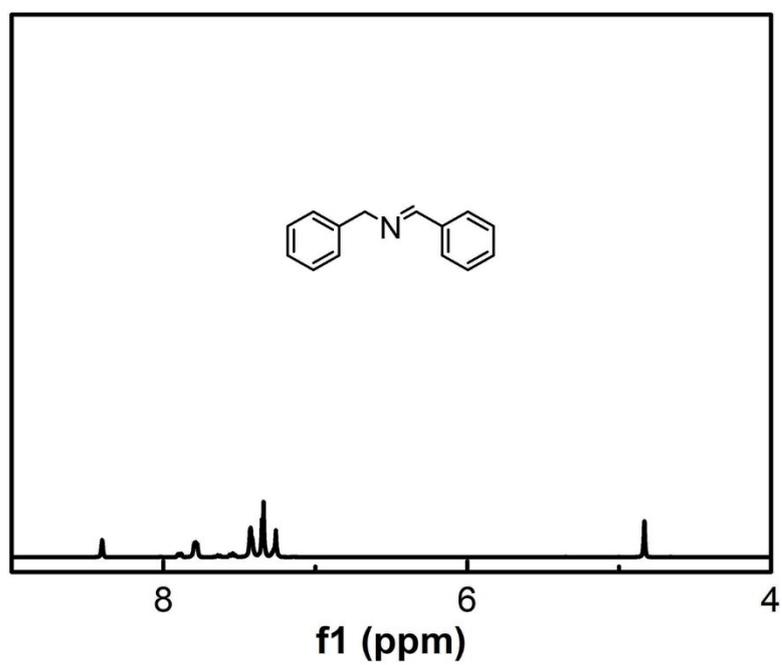


Figure S4. ¹H NMR spectra of N-benzylidenezylamine.

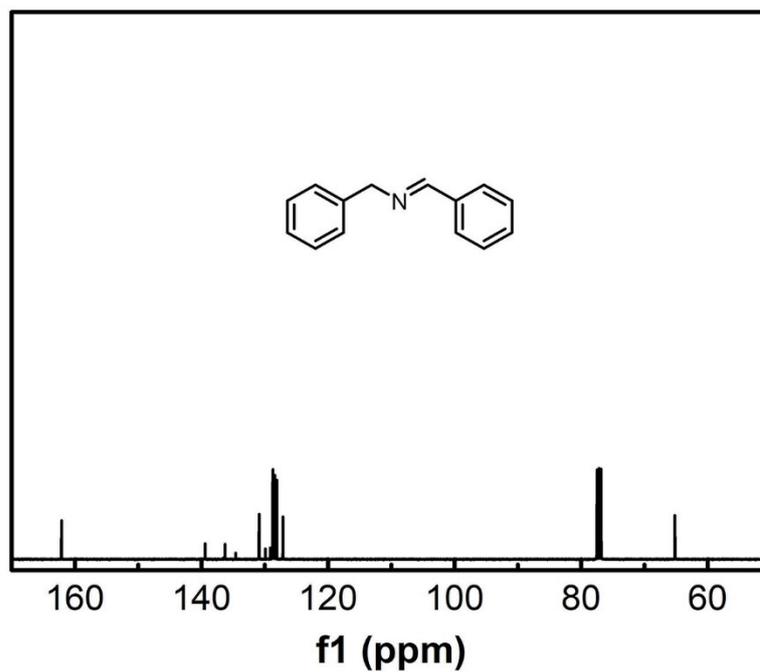


Figure S5. ^{13}C NMR spectra of N-benzylidenezylamine.

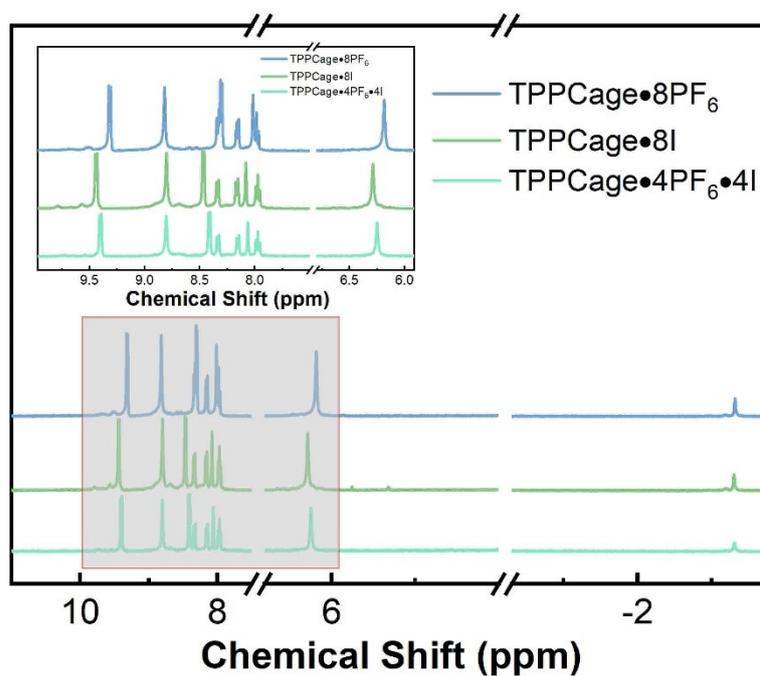


Figure S6. ^1H NMR spectra of TPPCage•8PF₆, TPPCage•8I and TPPCage•4PF₆•4I.

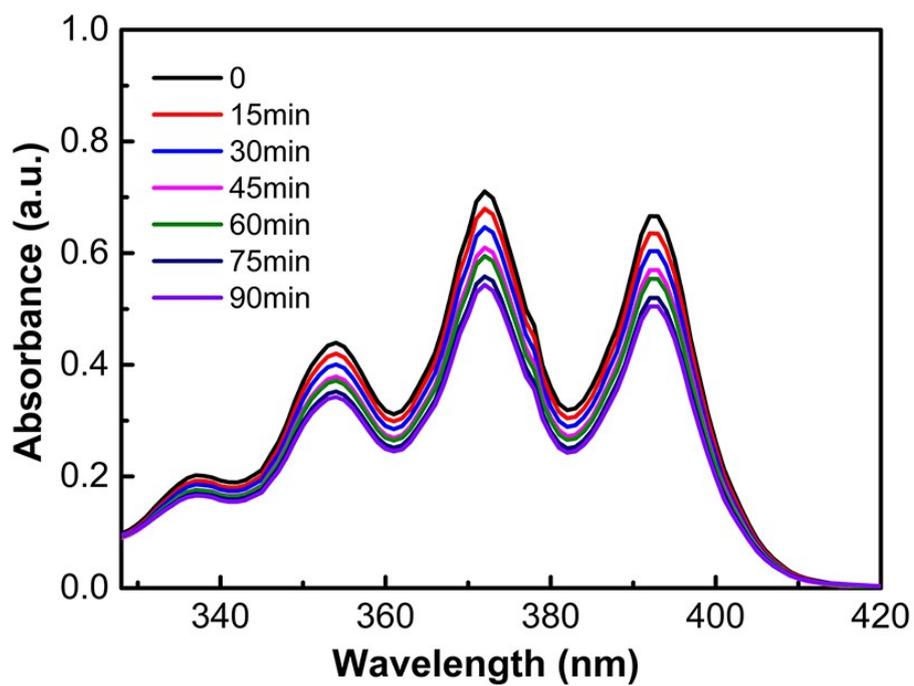


Figure S7. Photo-bleach experiments based on the oxidation of DPA in ethyl acetate upon irradiation at $\lambda > 420$ nm.

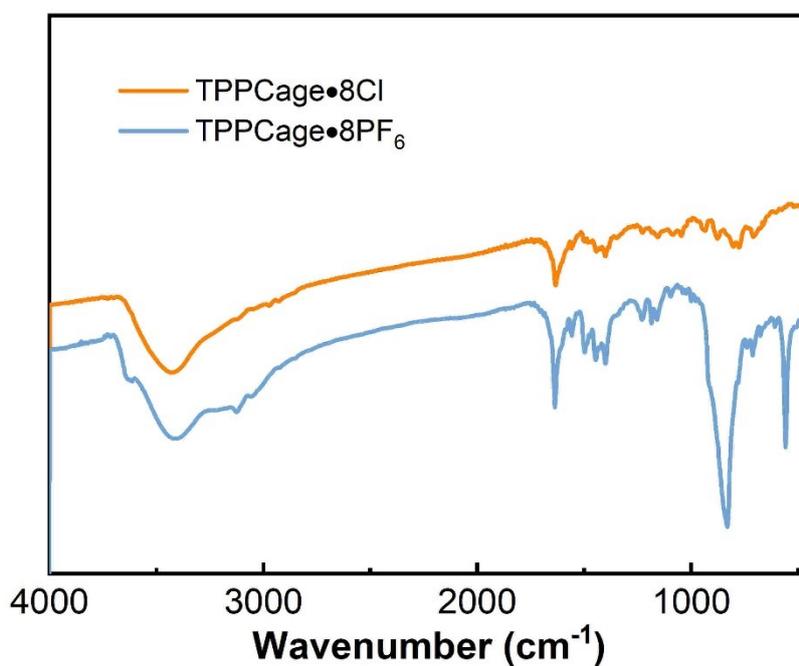


Figure S8. FT-IR spectra of TPPCage•8PF₆ and TPPCage•8Cl.

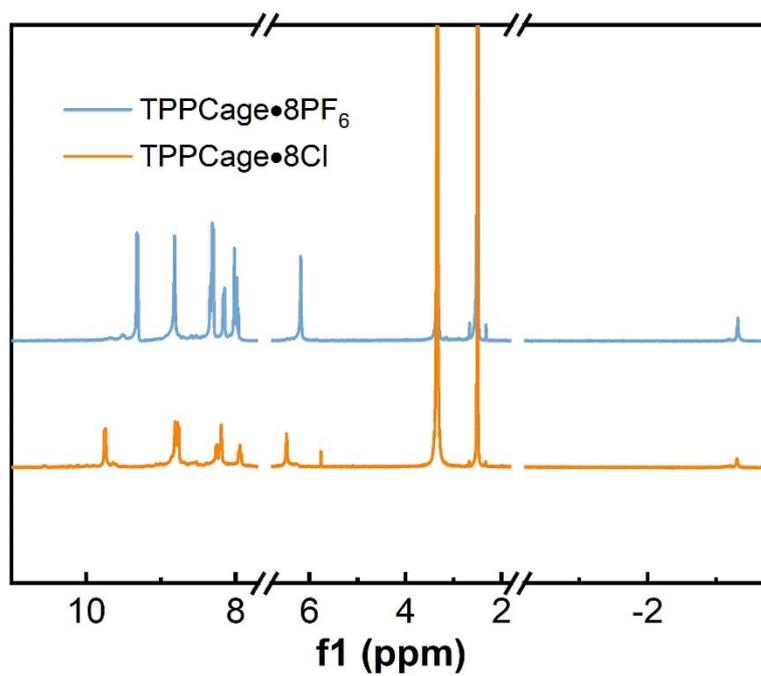


Figure S9. ¹H NMR spectra of TPPCage•8PF₆ and TPPCage•8Cl.

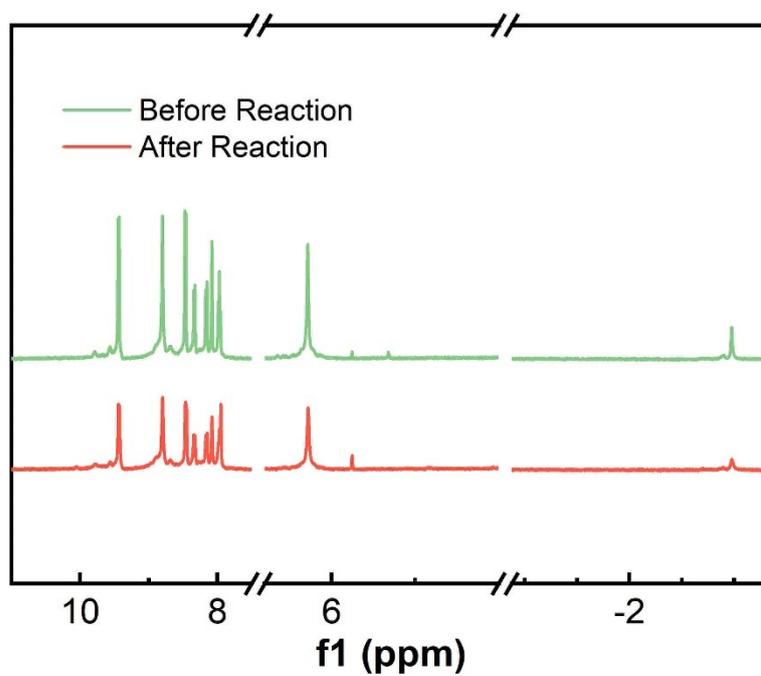


Figure S10. ¹H NMR spectra of TPPCage•8I before and after five repeating cycles.

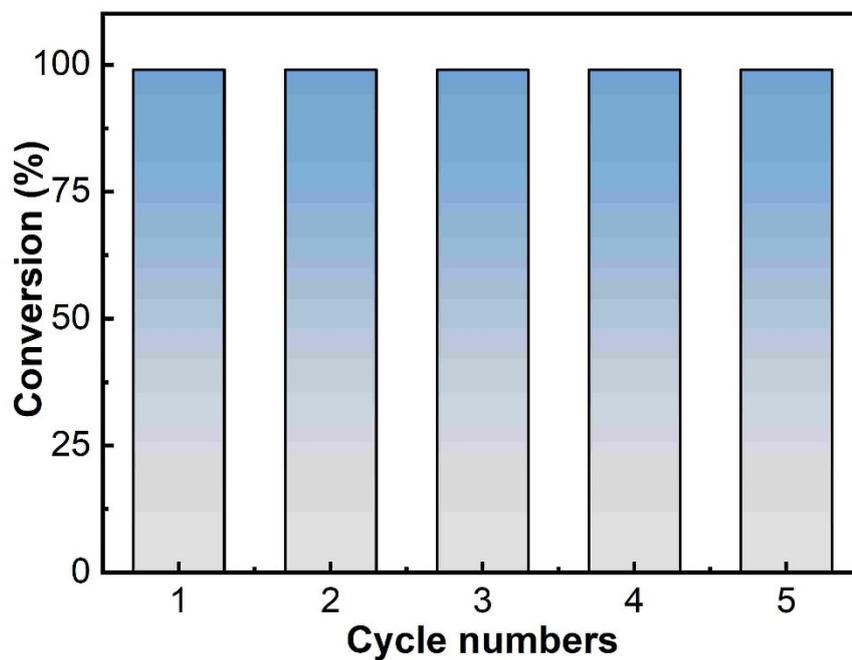


Figure S11. The conversion of photocatalytic oxidative coupling of benzylamines with TPPCage•8I under blue LED light in five repeating cycles.

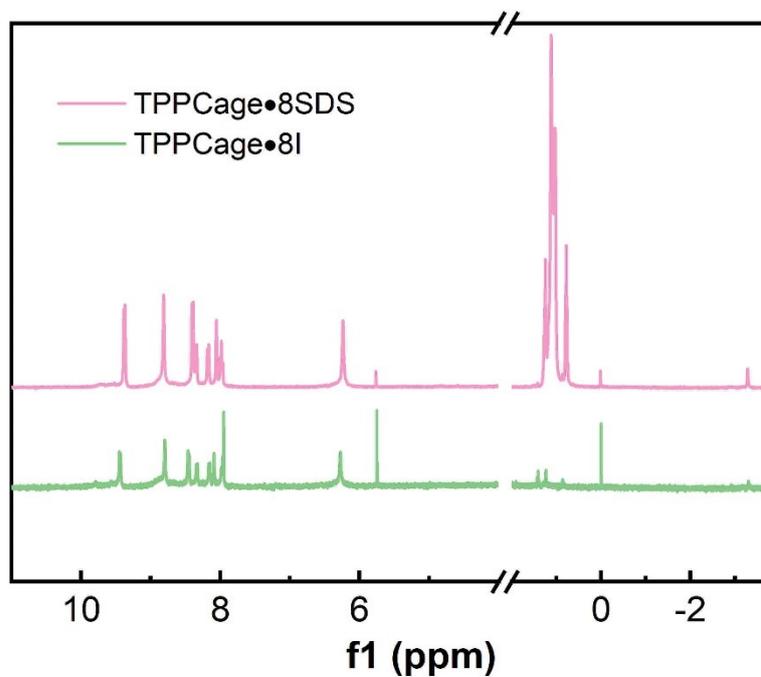


Figure S12. ^1H NMR spectra of TPPCage•8SDS and TPPCage•8I.

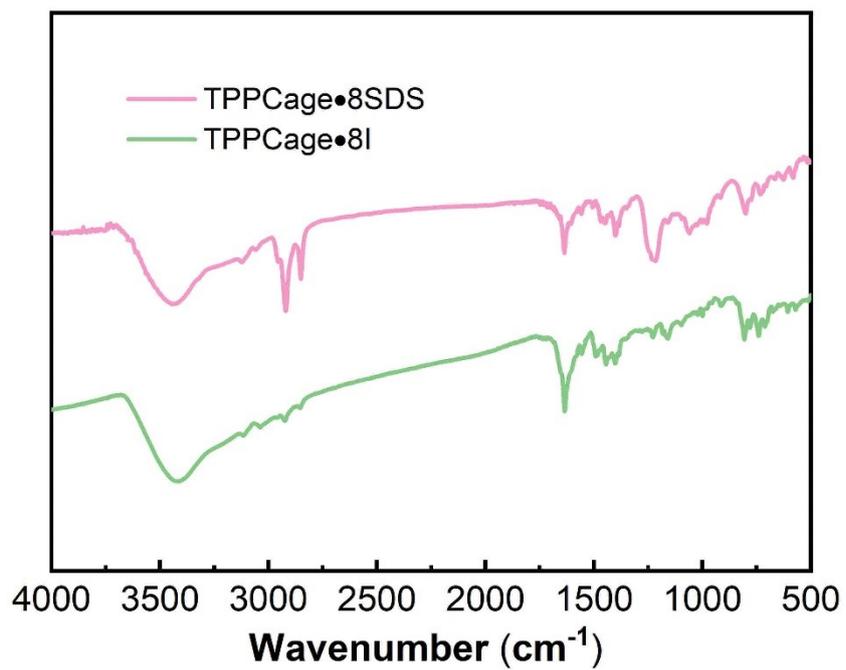


Figure S13. FT-IR spectra of TPPCage•8SDS and TPPCage•8I.

Table S1. Comparison of the catalytic performance of various photocatalysts in amines oxidation in visible light.

Entry	Photocatalysts	Reaction conditions ^a	Conversion (%)	Selectively (%)	TOF (h ⁻¹) ^b	Ref.
1	[Au ₂₅]/TiO ₂	0.2mmol[B]+ 10mg[C] +CH ₃ CN	98	99	878	7
2	In-MOF	0.2mmol[B]+ 4mg[C] +DMSO	99	99	16.7	8
3	PTC-1(2H)	0.1mmol[B]+ 0.1μmol[C] +CH ₃ CN	99	99	1320	9
4	Por-BC-COF	0.2mmol[B]+ 10mg[C] + CH ₃ CN	99	97	22.5	10
5	CoP@POC	1mmol[B]+3 mg[C]+ CH ₃ CN	99	99	1389	11
6	TPPCage•8I	1mmol[B]+3 mg[C]+ CH₃CN/DM F	99	99	1980	This work

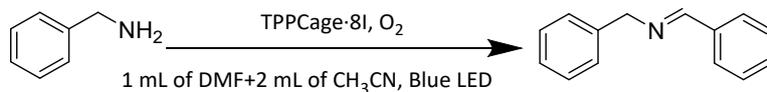
^a[B] is short for benzylamine, [C] is short for photocatalyst. ^bTOF is calculated based on mole of amine converted per mole of catalyst per hour.

Table S2. Comparison of the catalytic performance of various photocatalysts in amines oxidation in visible light.

Entry	Photocatalysts	Reaction conditions ^a	Conversion (%)	Selectivity (%)	TOF (mmol.g ⁻¹ .h ⁻¹) ^b	Ref.
1	Cd(dcbpy)	0.48mmol[B] +10mg[C] +DMF	41.8	99	5.016	12
2	CS@MF-3	0.2mmol[B]+ 10mg[C] +CH ₃ CN	99	95	19	13
3	CoSAS@CD	1mmol[B]+3 mg[C] +CH ₃ CN	83	99	23.1	14
4	Pc-Ludox-8	5mmol[B]+20 mg[C]+ solvent free	90.9	99.1	45.45	15
5	<i>o</i> -COF	0.1mmol[B]+ 2mg[C]+ CH ₃ CN	99	99	49.5	16
6	TPPCage•8I	1mmol[B]+3 mg[C]+ CH₃CN/DM F	99	99	666.7	This work

^a[B] is short for benzylamine, [C] is short for photocatalyst. ^bTOF is calculated based on mole of amine converted per gram of catalyst per hour.

Table S3. Photocatalytic oxidation coupling of benzylamines with TPPCage·8I under different reaction conditions^a.



Entry	Photocatalyst	Reaction condition	Time (h)	Conversion (%)
1	TPPCage·8I	Standard	0.5	>99
2	TPPCage·8I	With 1 mg photocatalyst	0.5	85.5
3	TPPCage·8I	With 5 mg photocatalyst	0.5	>99
4	TPPCage·8I	With benzylamine 0.5 mmol	0.33	>99
5	TPPCage·8I	With benzylamine 2.0 mmol	0.5	35.2
6	TPPCage·8I	In 3 mL DMF	0.5	60.0
7	TPPCage·8I	In 3 mL CH ₃ CN	0.5	91.12
8 ^b	TPPCage·8I	In Air	1.0	63.52
9 ^c	TPPCage·8I	In N ₂	1.0	–
10	TPPCage·8I	Under 5 W LED light	0.5	77.11

^aStandard Reaction conditions: photocatalyst (3 mg), substrate (1 mmol), 1 mL of DMF and 2 mL of CH₃CN, O₂ balloon, blue LED light (10 W). ^bReaction carried out in Air condition. ^cReaction carried out in N₂ condition.

References

- 1 A. Frisch, gaussian 09W Reference, Wallingford, USA, 2009, **470**, 25p.
- 2 C. Adamo, V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158-6170.
- 3 A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 4538-4543.
- 4 S. Grimme, C. Bannwarth, P. Shushkov, *J. Chem. Theory. Comput.*, 2017, **13**, 1989-2009.
- 5 T. Lu, F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.
- 6 W. Humphrey, A. Dalke, K. Schulten, *J. Mol. Graph.*, 1996, **14**, 33-38.
- 7 H. Chen, C. Liu, M. Wang, C. Zhang, N. Luo, Y. Wang, H. Abroshan, G. Li, F. Wang, *ACS Catal.*, 2017, **7**, 3632-3638.
- 8 H. Wei, Z. Guo, X. Liang, P. Chen, H. Liu, H. Xing, *ACS Appl. Mater. Inter.*, 2019, **11**, 3016-3023.
- 9 C. Liu, K. Liu, C. Wang, H. Liu, H. Wang, H. Su, X. Li, B. Chen, J. Jiang, *Nat. Commun.*, 2020, **11**, 1047.
- 10 H. He, X. Fang, D. Zhai, W. Zhou, Y. Li, W. Zhao, C. Liu, Z. Li, W. Deng, *Chem. Eur. J.*, 2021, **27**, 14390-14395.
- 11 F. Zhang, J. Ma, Y. Tan, G. Yu, H. Qin, L. Zheng, H. Liu, R. Li, *ACS Catal.*, 2022, **12**, 5827-5833.
- 12 J. Shi, J. Zhang, T. Liang, D. Tan, X. Tan, Q. Wan, X. Cheng, B. Zhang, B. Han, L. Liu, F. Zhang, G. Chen, *ACS Appl. Mater. Inter.*, 2019, **11**, 30953-30958.
- 13 K. Gao, H. Li, Q. Meng, J. Wu, H. Hou, *ACS Appl. Mater. Inter.*, 2021, **13**, 2779-2787.
- 14 Q. Wang, J. Li, X. Tu, H. Liu, M. Shu, R. Si, C.T.J. Ferguson, K.A.I. Zhang, R. Li, *Chem. Mater.*, 2019, **32**, 734-743.
- 15 B. Chen, L. Wang, W. Dai, S. Shang, Y. Lv, S. Gao, *ACS Catal.*, 2015, **5**, 2788-2794.
- 16 N. Sun, Y. Jin, H. Wang, B. Yu, R. Wang, H. Wu, W. Zhou, J. Jiang, *Chem. Mater.*, 2022, **34**, 1956-1964.