

Supporting Information

Sewage Remediation Using Solar Energy and a Triply Fused Zn-Porphyrin Dimer Molecular Graphene Photocatalytic Agent

Fei Cheng,^a Taotao Qiang,^{a*} Mingli Li,^a Tony D. James^{b,c*}

^a College of Bioresources and Materials Engineering, Shaanxi Collaborative Innovation Center of Industrial Auxiliary Chemistry & Technology, Shaanxi University of Science & Technology, Xi'an, 710021, China.

^b Department of Chemistry, University of Bath, Bath, BA27AY, UK.

^c School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China.

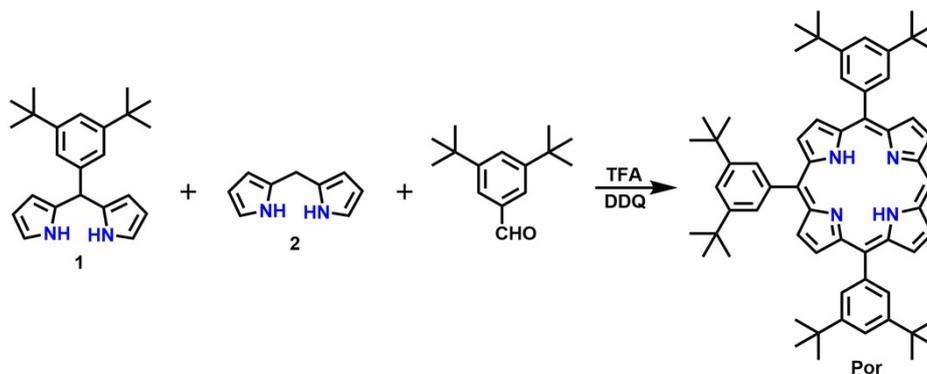
Table of Contents

<u>Instrumentation and Materials</u>	3
<u>General Procedures</u>	4
<u>Compounds Data</u>	6
<u>NMR spectra</u>	7
<u>Mass Spectra</u>	11
<u>Absorption spectra</u>	12
<u>Application Experimental Data</u>	13
<u>References</u>	25

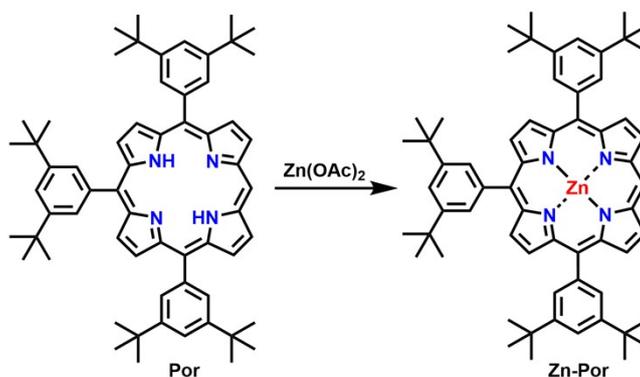
Instrumentation and Materials

^1H NMR (600 MHz) spectra were recorded on a Bruker AVANCE NEO 600MHz spectrometer, and chemical shifts were reported using the delta scale in ppm relative to CHCl_3 as internal reference for ^1H NMR ($\delta = 7.260$ ppm). Absorption spectra were recorded on a Cary 5000 spectrometer. MALDI-TOF mass spectra were obtained with a Bruker ultraflex extreme MALDI-TOF/TOF spectrometer with matrix. Material surface morphology were observed on a FEI Verios 460 spectrometer. Dispersion of materials in aqueous solution were taken on an ALV/C spectrometer. Photogenic charge lifetime was recorded on an ultrafast systems helios spectrometer. Electrochemical data were measured by cyclic voltammetry on a PGSTAT 302N scanning electrochemical microscope. Free radical species were recorded on a CIQTEK EPR200-Plus spectrometer. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

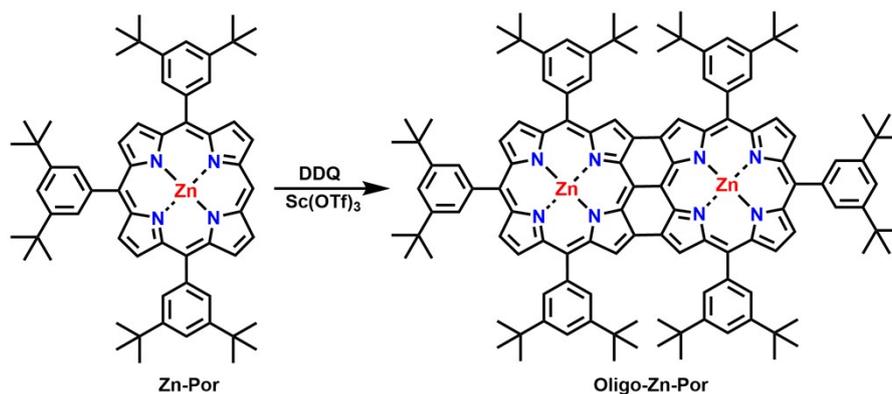
General Procedures



Synthesis of Por^{S1}: 3,5 *di-tert*-butylphenyl-dipyrrromethane **1** (3.34 g, 10.00 mmol), dipyrromethene **2** (1.46 g, 10.00 mmol), and 3,5 *di-tert*-butylbenzaldehyde (4.36 g, 20.00 mmol) were dissolved in CH₂Cl₂ (1.5 L) and degassed for 15 min (bubbling N₂ through the solution). Boron fluoride ethyl ether (0.15 mL) was added and the reaction was stirred for 2 h at rt under the exclusion of light. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (6.80 g, 30.00 mmol) was added and the mixture was stirred for further 4 h under air. The acid was quenched via the addition of NEt₃ (5 mL), the solvent was removed and the crude product purified by silica-gel column chromatography (CH₂Cl₂/petroleum ether as an eluent) and recrystallized from CH₂Cl₂/MeOH, **Por** (1.05 g, 1.20 mmol, 12% yield) was obtained as a purple solid.



Synthesis of Zn-Por^{S2}: **Por** (1.00 g, 1.10 mmol) was added to a round-bottomed 250 mL flask containing a magnetic stirring bar, and dissolved in CH₂Cl₂ (100 mL)/MeOH (10 mL). Zn(OAc)₂ (0.61 g, 3.30 mmol) was added, after being stirred at 25 °C for 3 h. The reaction mixture was poured in to water and the products were extracted with CH₂Cl₂. The organic extracts were combined, washed with water, and dried over anhydrous sodium sulfate. The solvent was evaporated, and the product was recrystallization with CH₂Cl₂/MeOH, **Zn-Por** (1.02 g, 1.08 mmol, 99% yield) was obtained as a red solid.



Synthesis of Oligo-Zn-Por^{S3}: A flask containing **Zn-Por** (0.10 g, 0.11 mmol), DDQ (0.12 g, 0.55 mmol), and Sc(OTf)₃ (0.27 g, 0.55 mmol) was purged with argon, and then charged with toluene (10 mL). The mixture was stirred at 50 °C for 2 h. The reaction was quenched by the addition of a saturated aqueous NaHCO₃ solution. Then, the mixture was poured in to water and the products were extracted with CHCl₃. The organic extracts were combined, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by gel column chromatography (CHCl₃ as an eluent) and recrystallization from CH₂Cl₂/MeOH, **Oligo-Zn-Por** (0.08 g, 0.04 mmol, 80% yield) was obtained as a purple solid.

Photocatalytic process^{S4}: The photocatalytic reduction of heavy metal Cr(VI) was carried out in an outdoor environment (Longitude 108.977° and latitude 34.378° of Xi 'an Campus, Shaanxi University of Science and Technology, Xi 'an City, Shaanxi Province, China) in 50 mL quartz tube. The effects of the amount of photocatalyst (5-40 mg), the concentration of Cr(VI) (10-70 mg/L), pH (2-8), the sunlight catalysis in different time periods (8:00-16:00) in a day and the climate change in four seasons on the catalytic reduction of Cr(VI) by sunlight were studied. The amount of Cr(VI) aqueous solution was 30mL, and the pH value was adjusted with 1M H₂SO₄ and 1M NaOH. After stirring in the dark for 30 min, the photocatalyst and Cr(VI) aqueous solution reached adsorption equilibrium, and the suspension was irradiated by sunlight. During the catalysis process, 2 mL suspension was collected at an interval of 30 min, and the suspended catalyst was removed with a stream filter (0.22μm). The content of Cr(VI) was determined by Agilent Cary 5000 UV-vis spectrophotometer at 540 nm.

Compounds Data

Por: ^1H NMR (600 MHz, CDCl_3): δ = 10.31 (s, 1H, *meso*-H), 9.46 (d, J = 4.8 Hz, 2H, β -H), 9.27 (d, J = 4.8 Hz, 2H, β -H), 9.20 (d, J = 4.8 Hz, 2H, β -H), 9.16 (d, J = 4.8 Hz, 2H, β -H), 8.35 (s, 4H, Ar-H), 8.32 (s, 2H, Ar-H), 8.03 (s, 2H, Ar-H), 8.01 (s, 1H, Ar-H), 1.76 (s, 36H, *t*-Bu-H), 1.73 (s, 18H, *t*-Bu-H), -2.64 (s, 2H, NH-H) ppm.

Zn-Por: ^1H NMR (600 MHz, CDCl_3): δ = 10.26 (s, 1H, *meso*-H), 9.41 (d, J = 4.8 Hz, 2H, β -H), 9.15 (d, J = 4.8 Hz, 2H, β -H), 9.05 (d, J = 4.8 Hz, 2H, β -H), 9.03 (d, J = 4.8 Hz, 2H, β -H), 8.12 (d, J = 1.8 Hz, 4H, Ar-H), 8.09 (d, J = 1.8 Hz, 2H, Ar-H), 7.82 (s, 2H, Ar-H), 7.79 (s, 1H, Ar-H), 1.55 (s, 36H, *t*-Bu-H), 1.52 (s, 18H, *t*-Bu-H) ppm; UV/Vis (CHCl_2): λ_{max} (ϵ [$\text{M}^{-1}\text{cm}^{-1}$]) = 422 (177000), 549 (6270), 588 (1640) nm.

Oligo-Zn-Por: ^1H NMR (600 MHz, CDCl_3): δ = 7.75 (d, J = 4.8 Hz, 4H, β -H), 7.71 (d, J = 4.8 Hz, 4H, β -H), 7.67 (d, J = 1.8 Hz, 8H, Ar-H), 7.64 (d, J = 1.8 Hz, 4H, Ar-H), 7.62 (s, 4H, Ar-H), 7.59 (s, 2H, Ar-H), 7.35 (s, 4H, β -H), 1.46 (s, 72H, *t*-Bu-H), 1.42 (s, 36H, *t*-Bu-H) ppm; ^{13}C NMR (151 MHz, CDCl_3): δ = 153.95, 153.53, 153.43, 153.03, 149.10, 148.78, 140.05, 135.67, 131.37, 131.12, 128.19, 127.46, 127.29, 126.18, 120.88, 120.78, 34.86, 31.62, 31.56 ppm; HR-MS (MALDI-TOF-MS) m/z = 1867.0891 [M] $^+$, calcd for $(\text{C}_{124}\text{H}_{138}\text{N}_8\text{Zn}_2)^+$ = 1866.9627; UV/Vis (CHCl_3): λ_{max} (ϵ [$\text{M}^{-1}\text{cm}^{-1}$]) = 413 (91000), 458 (32700), 576 (84000), 916 (11100), 1040 (22700) nm.

NMR spectra

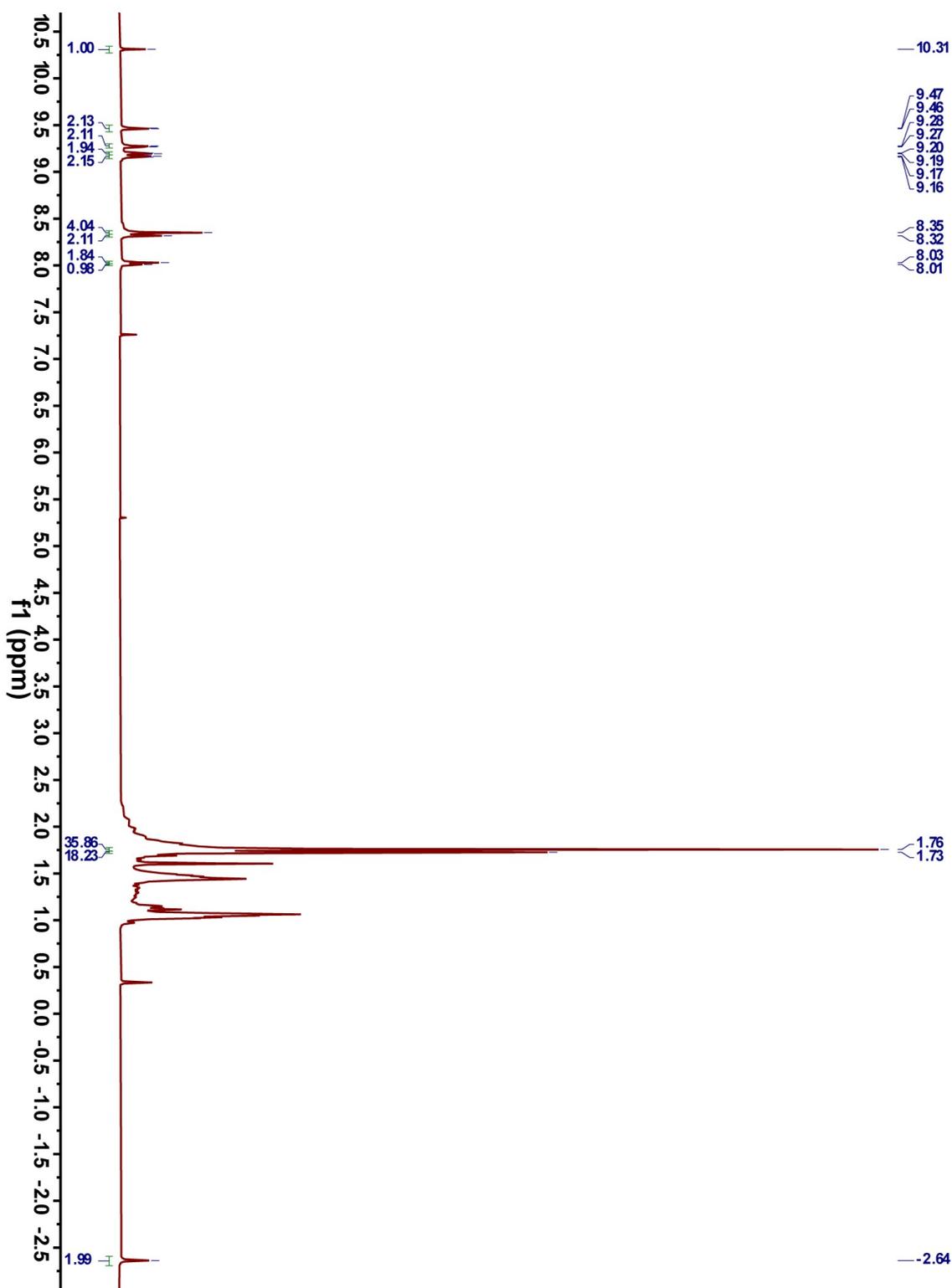


Figure S1. ^1H NMR spectrum of **Por** in CDCl_3 .

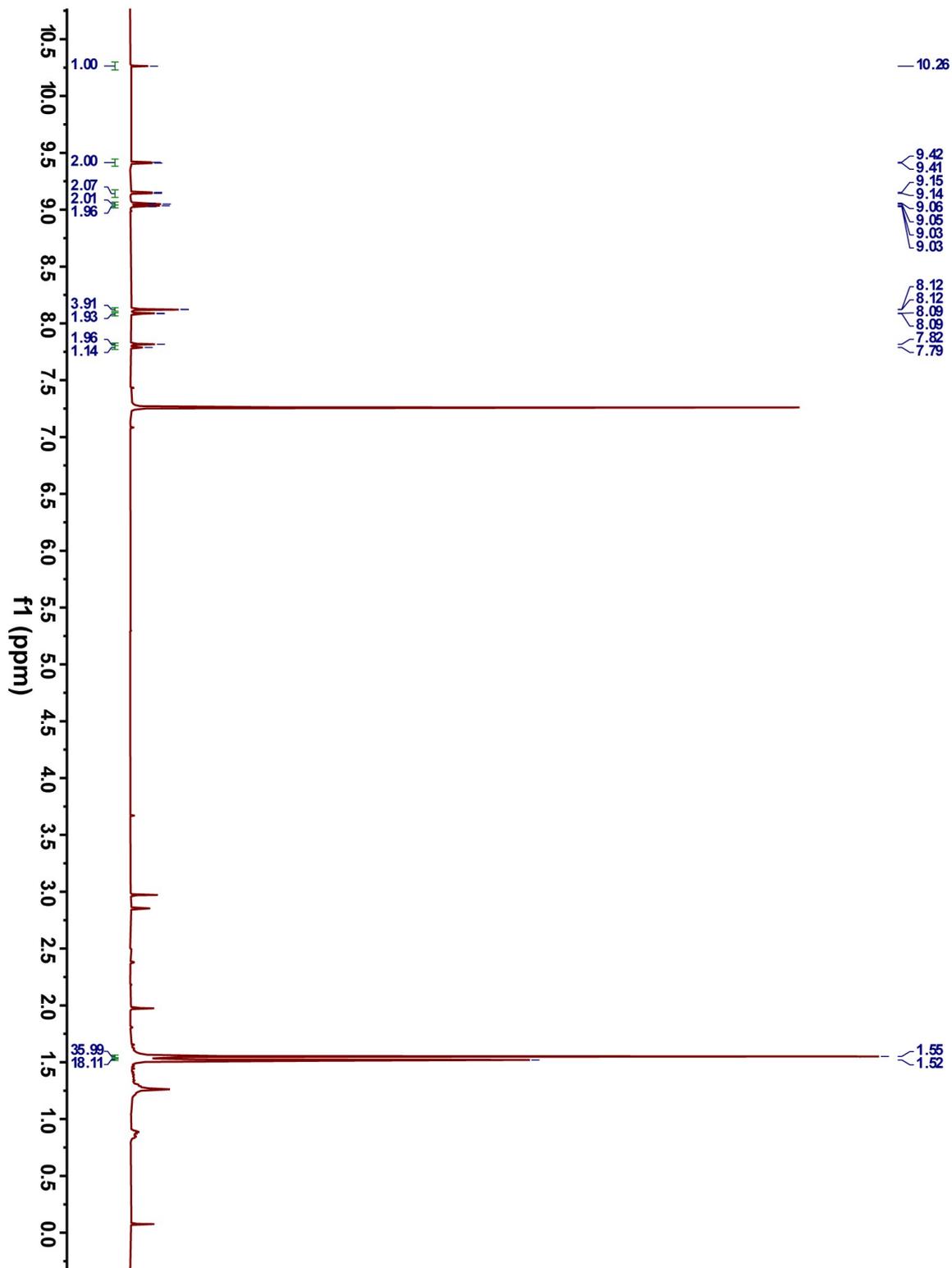


Figure S2. ¹H NMR spectrum of Zn-Por in CDCl₃.

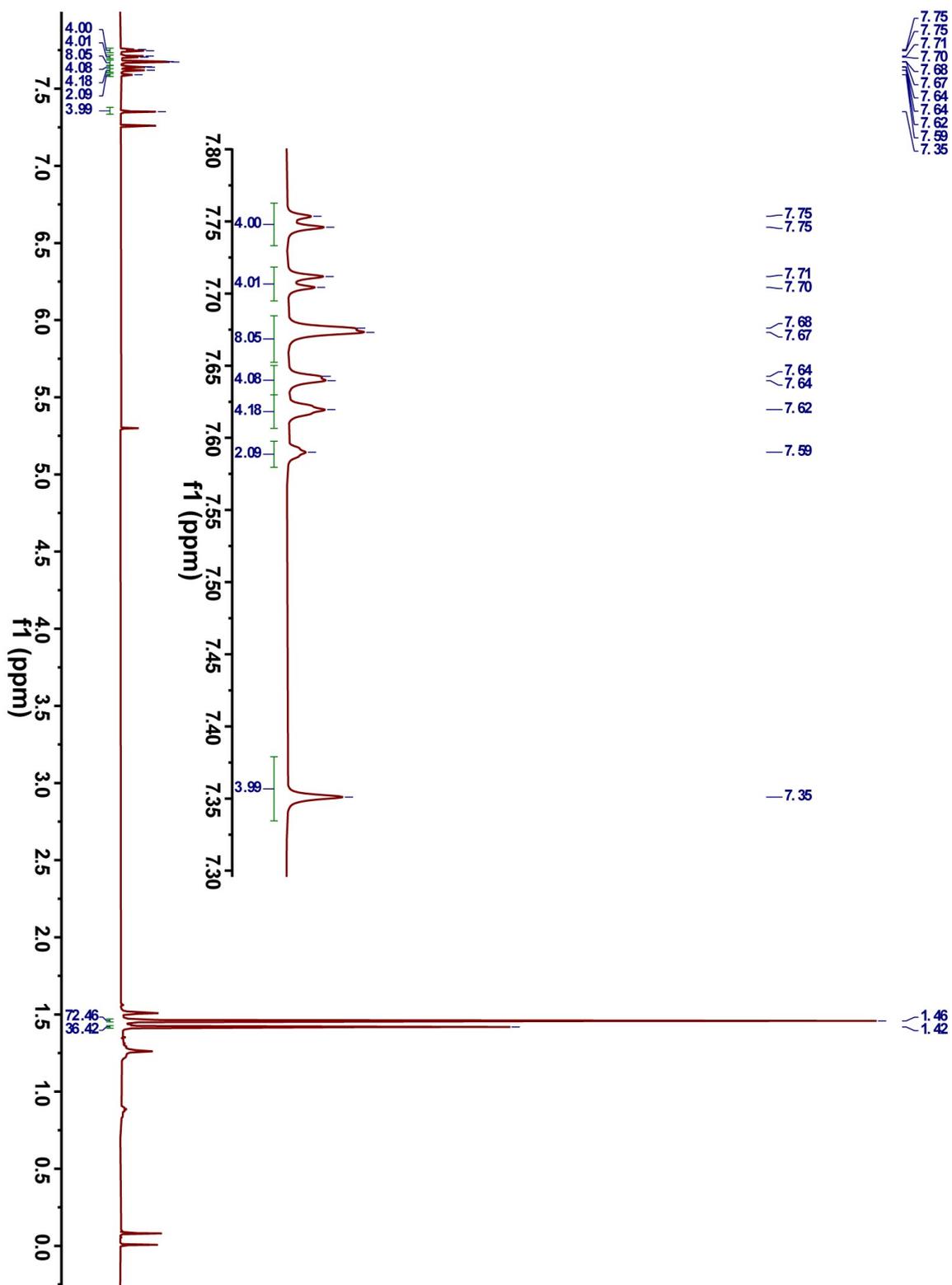


Figure S3. ^1H NMR spectrum of Oligo-Zn-Por in CDCl_3 .

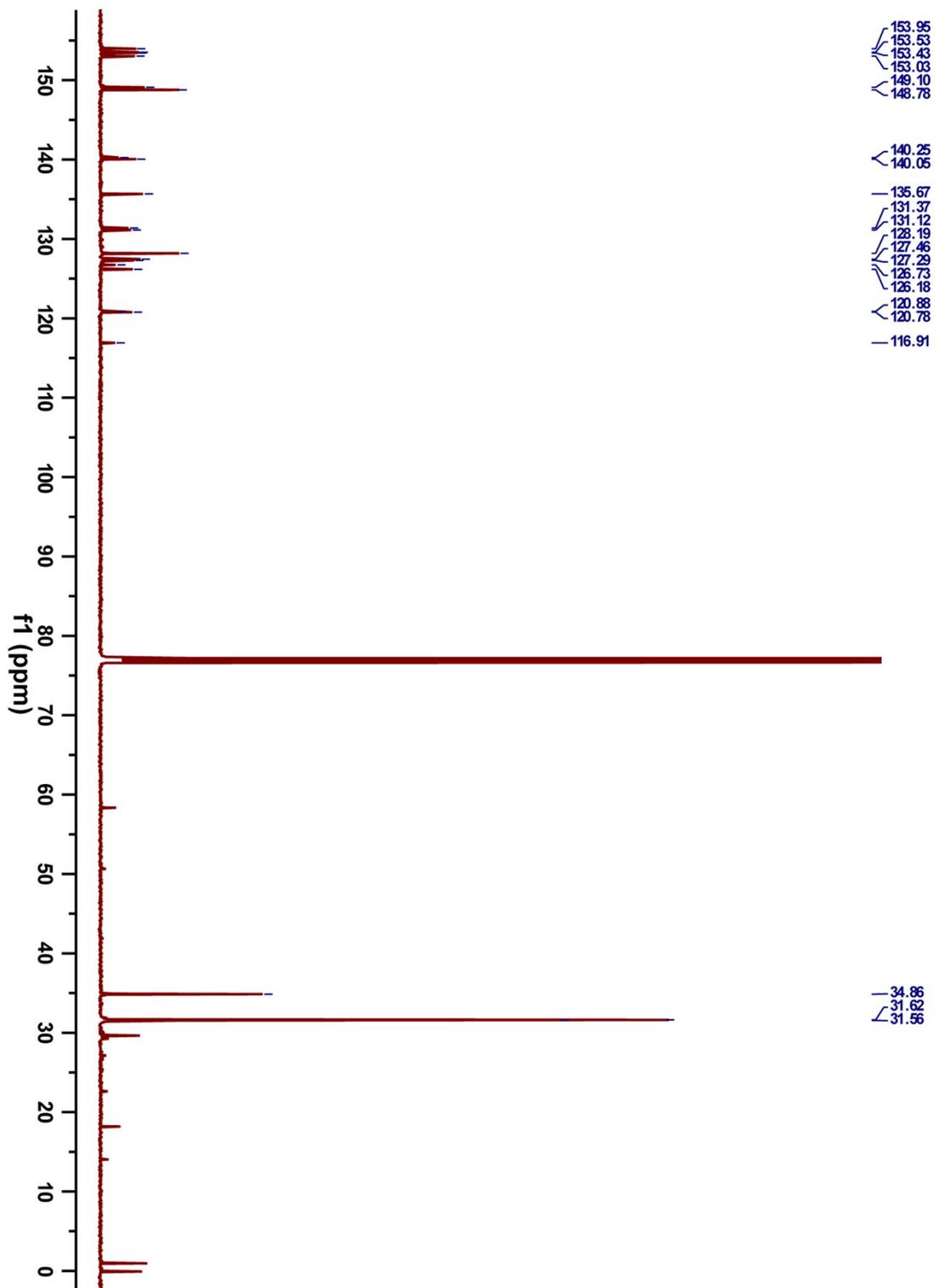


Figure S4. ^{13}C NMR spectrum of **Oligo-Zn-Por** in CDCl_3 .

Mass Spectrum

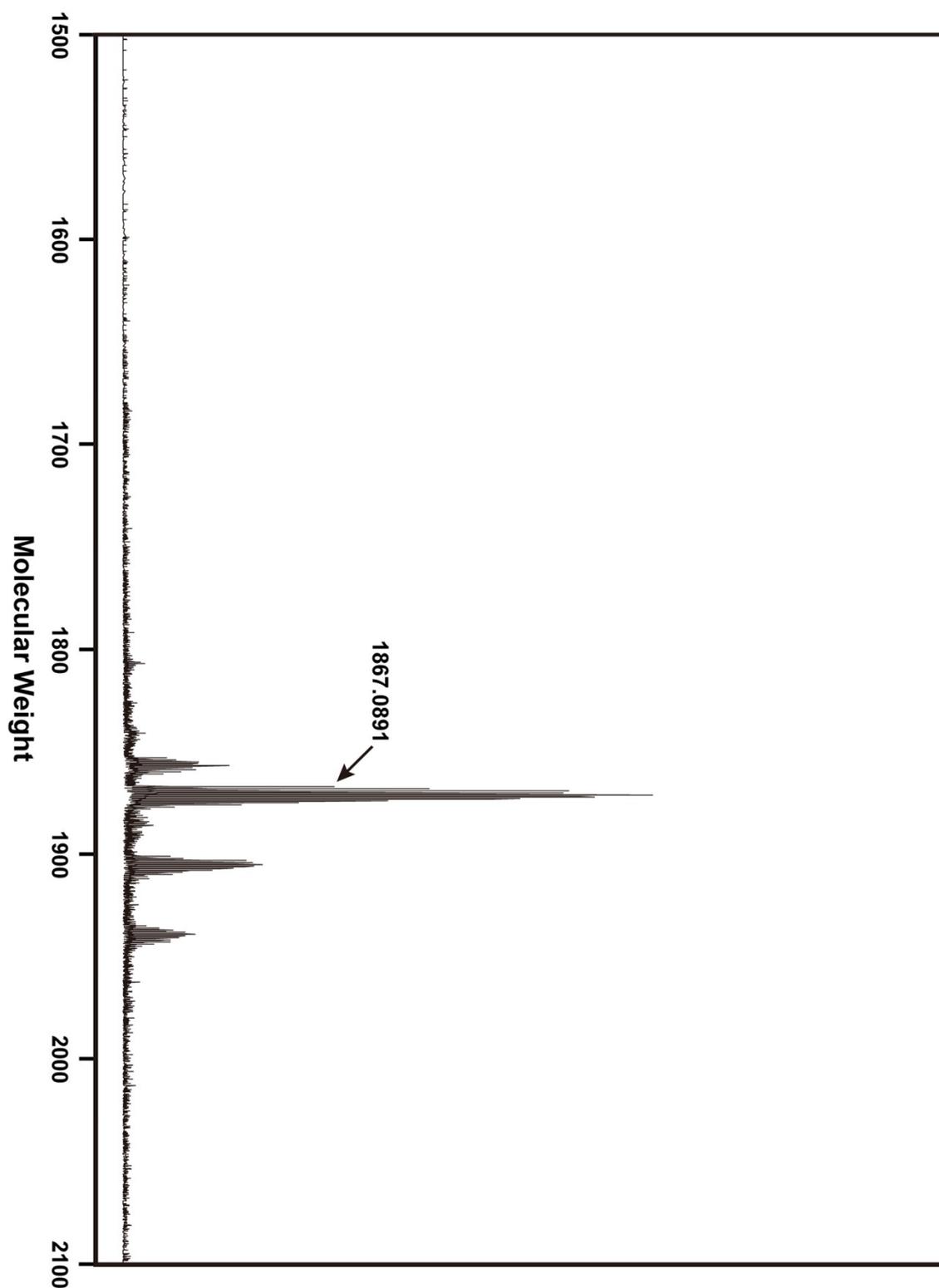


Figure S5. HR-MS spectrum of Oligo-Zn-Por

Absorption spectra

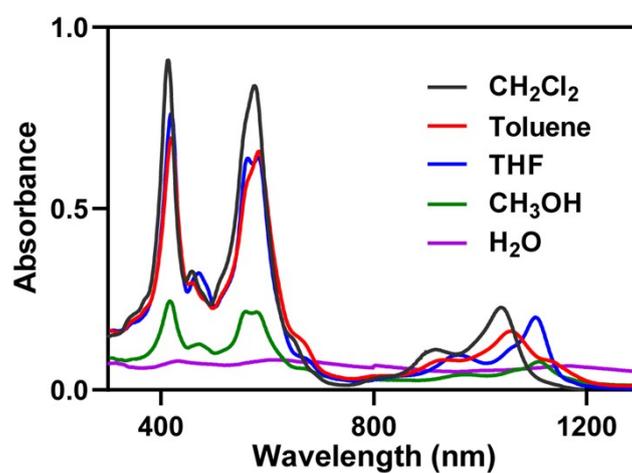


Figure S6. Absorption spectra of **Oligo-Zn-Por** in different solvent.

Application Experimental Data

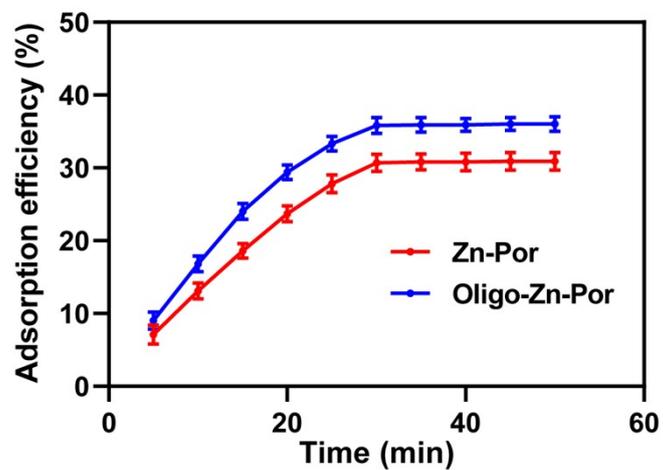


Figure S7. Effect of the amount of photocatalyst on the adsorption rate of Cr(VI) (The catalytic period was July, 2022, photocatalyst dosage of 5 mg, Cr(VI) concentration of 10 mg/L).

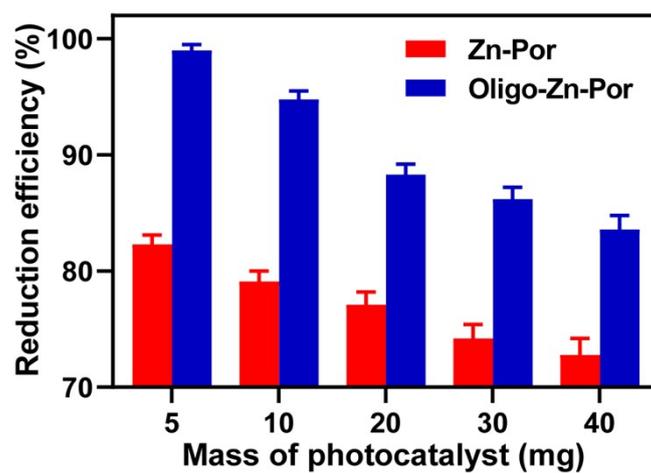


Figure S8. Effect of the amount of photocatalyst on the reduction rate of Cr(VI) (The catalytic period was July, 2022, Cr(VI) concentration is 10 mg/L).

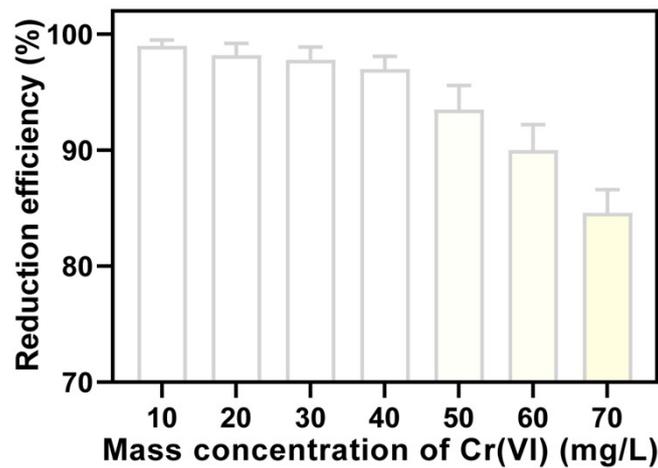


Figure S9. Effect of Cr(VI) concentration on reduction rate(The catalytic period was July, 2022, **Oligo-Zn-Por** dosage is 5 mg).

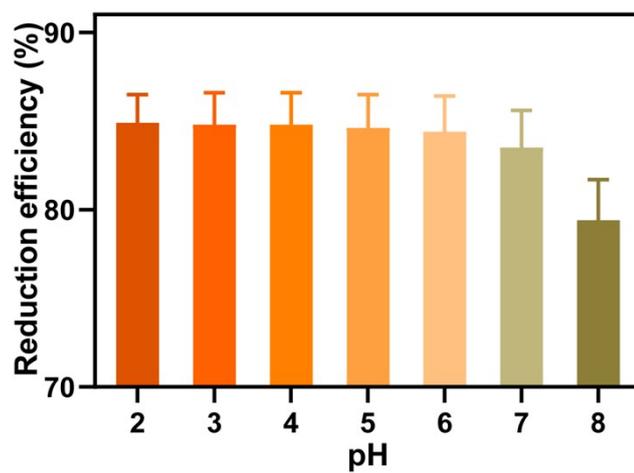


Figure S10. Effect of pH on reduction rate of Cr(VI) (The catalytic period was July, 2022, **Oligo-Zn-Por** dosage is 5 mg, Cr(VI) concentration is 70 mg/L).

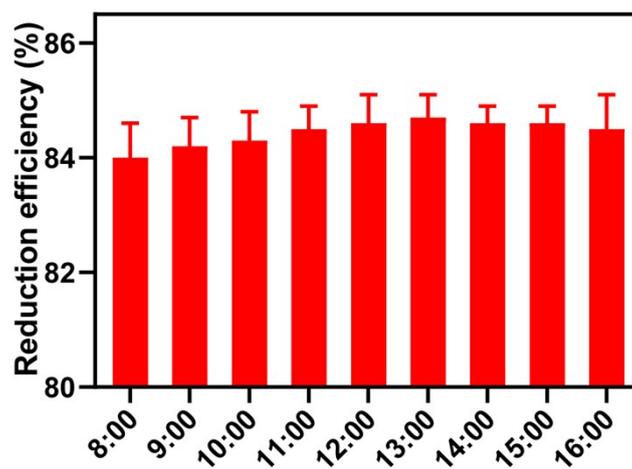


Figure S11. Effect of sunlight catalyzes at different times of the day on reduction rate of Cr(VI) (The catalytic period was July 15, 2022, **Oligo-Zn-Por** dosage is 5 mg, Cr(VI) concentration is 70 mg/L).

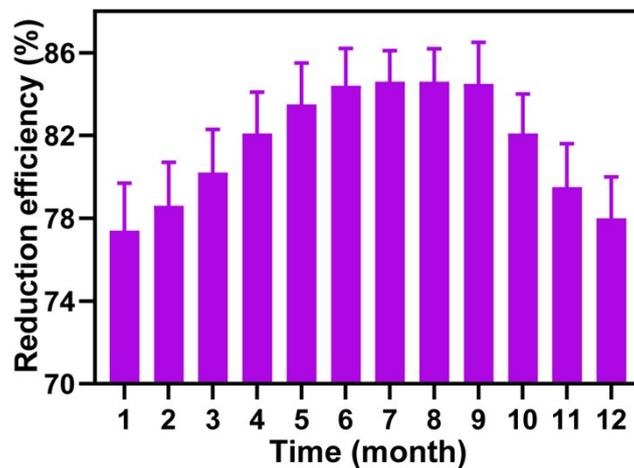


Figure S12. Effect of sunlight catalyzes at different times of the year on reduction rate of Cr(VI) (The catalytic period was July 2022, **Oligo-Zn-Por** dosage is 5 mg, Cr(VI) concentration is 70 mg/L).

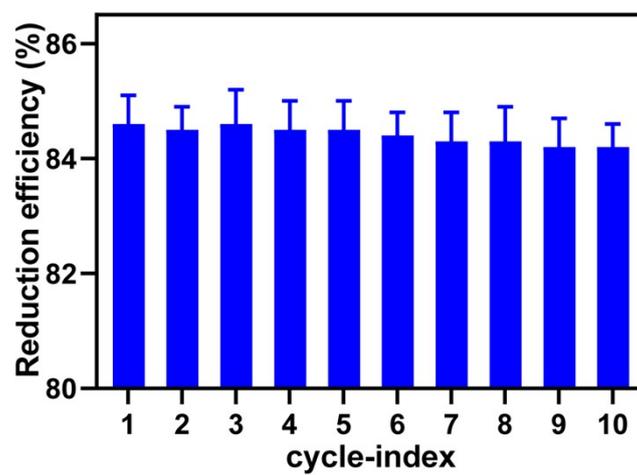


Figure S13. Effect of cycle-index on reduction rate of Cr(VI) (The catalytic period was July, 2022, **Oligo-Zn-Por** dosage is 5 mg, Cr(VI) concentration is 70 mg/L).

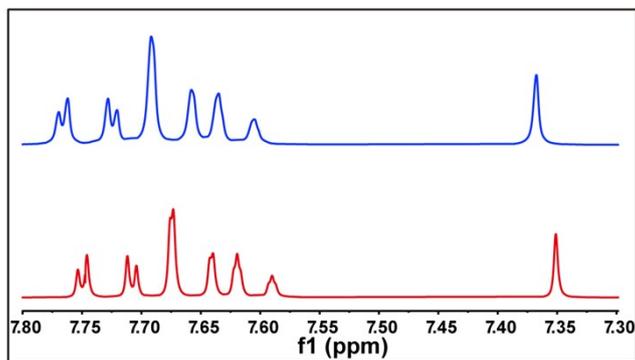


Figure S14. The cyclic stability of **Oligo-Zn-Por** was verified by ¹H NMR (Red is the ¹H NMR of **Oligo-Zn-Por** before the photocatalytic reaction, blue is the ¹H NMR of **Oligo-Zn-Por** after photocatalytic reaction).

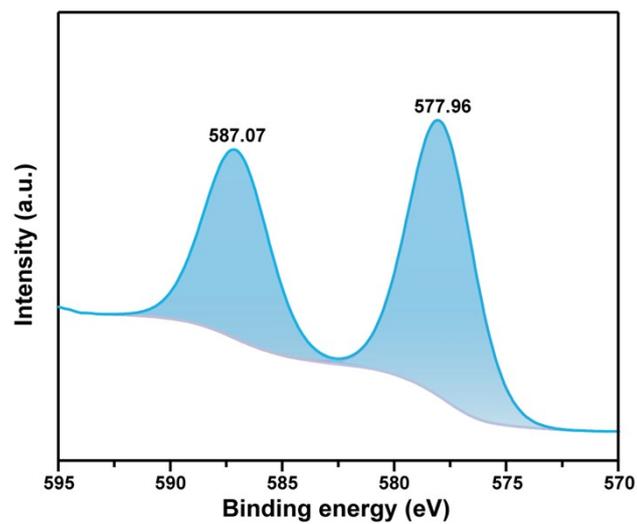


Figure S15. High-resolution Cr 2p XPS spectrum of **Oligo-Zn-Por** after the Cr(VI) reduction cyclic experiment.

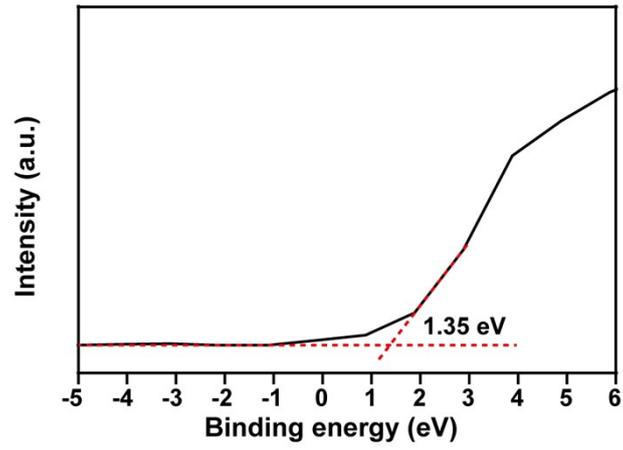


Figure S16. XPS valence band spectrum of Oligo-Zn-Por.

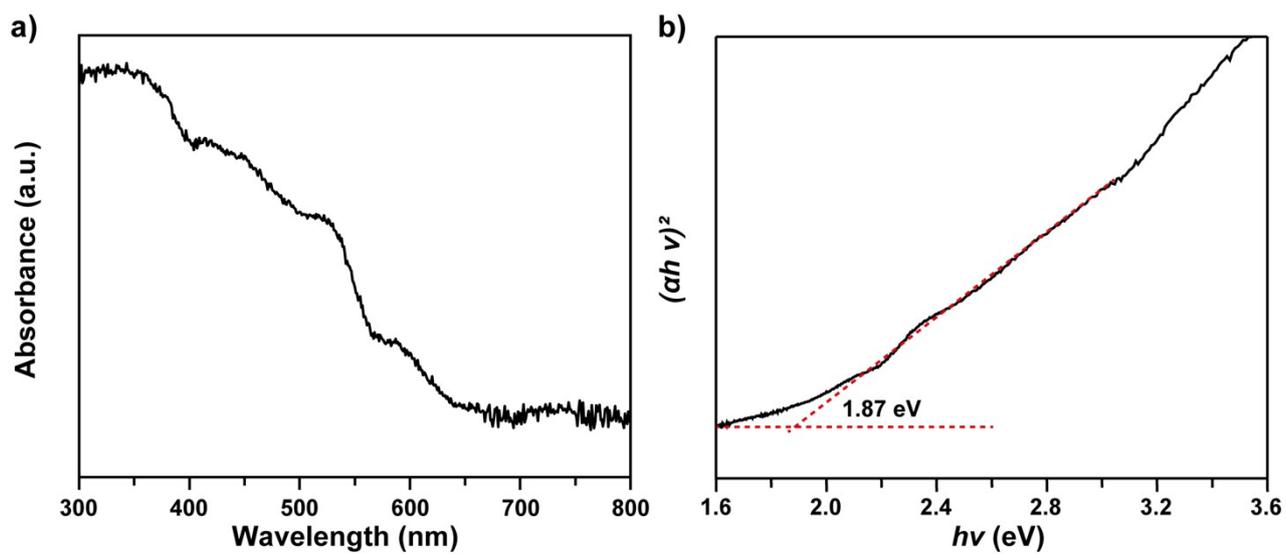


Figure S17. (a) Solid UV-visible absorption spectra of **Oligo-Zn-Por**, (b) the band edges of **Oligo-Zn-Por**.

Table S1

Comparison of reported literature on the photo-reduction of Cr(VI).

Photocatalyst	Catalyst dosage (mg)	Initial Cr(VI) concentration (mg/L)	Solution volume (mL)	Photosource	Reduction efficiency	Refs.
BCG-5	30	20	50	Xe lamp	81.51%	9
ZnO/Bi ₂ S ₃	50	20	50	Xe lamp	95%	S1
Carbon dots-TiO ₂	50	10	50	Xe lamp	99.2%	S5
RGO/ α -MnO ₂	50	10	50	Xe lamp	76%	S6
Bi ₂ WO ₆	60	10	50	Xe lamp	78%	S7
CoS ₂	10	20	20	Xe lamp	10.2%	S8
CdS	30	10	150	Xe lamp	13%	S9
Bi ₂ O ₃ /Bi ₂ S ₃	25	80	50	Xe lamp	91.8%	S10
CoS ₂ /g-C ₃ N ₄ -rGO	10	20	20	Xe lamp	72%	S11
Oligo-Zn-Por	5	70	30	Sunlight	84.6%	This study

References

- S1 M. M. Martin, D. Lungerich, P. Haines, F. Hampel and N. Jux, *Angew. Chem., Int. Ed.*, 2019, **58**, 8932-8937.
- S2 M. J. Plater, S. Aiken and G. Bourhill, *Tetrahedron*, 2002, **58**, 2415-2422.
- S3 A. Tsuda and A. Osuka, *Science*, 2001, **293**, 79-82.
- S4 F. P. Zhao, Y. P. Liu, S. B. Hammoud, B. Doshi, N. Guijarro, X. B. Min, C. J. Tang, M. Sillanpää, K. Sivulad and S. B. Wang, *Appl. Catal., B*, 2020, **272**, 119033.
- S5 Y. R. Li, Z. M. Liu, Y. C. Wu, J. T. Chen, J. Y. Zhao, F. M. Jin and P. Na, *Appl. Catal., B*, 2018, 224, 508-517.
- S6 D. k. Padhi, A. Baral, K. Parida, S. K. Singh and M. K. Ghosh, *J. Phys. Chem. C*, 2017, 121, 6039-6049.
- S7 F. Xu, H. M. Chen, C. Y. Xu, D. P. Wu, Z. Y. Gao, Q. Zhang and K. Jiang, *J. Colloid Interface Sci.*, 2018, 525, 97-106.
- S8 Y. J. Wang, S. Y. Bao, Y. Q. Liu, W. W. Yang, Y. S. Yu, M. Feng and K. F. Li, *Appl. Surf. Sci.*, 2020, 510, 145495.
- S9 F. Deng, X. Y. Lu, Y. B. Luo, J. Wang, W. J. Che, R. J. Yang, X. B. Luo, S. L. Luo and D. D. Dionysiou, *Chem. Eng. J.*, 2019, 361, 1451-1461.
- S10 Y. Sang, X. Cao, G. D. Dai, L. X Wang, Y. Peng and B. Y. Geng, *J. Hazard. Mater.*, 2020, 381, 120942.
- S11 X. Zhang, W. W. Yang, M. Y. Gao, H. Liu, K. F. Li, Y. S. Yu, *Green, Energy Environ.*, 2022, 7, 66-74.