

Supplementary Information

Cooperative cage hybrids enabled by electrostatic marriage

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Materials:

The following chemical reagents were used directly if not specified. Methanol and dichloromethane were purchased from Beijing Daishi Zede Technology Development Co., LTD, cobaltous nitrate, formic acid, methyl red and methyl orange were purchased from Shanghai Aladdin Biochemical Technology Co.,Ltd., (R,R)-1,2-diaminocyclohexane and 2,4,6-trinitrophenol were purchased from Sigma-Aldrich Co. LLC., 1,3,5-triformylbenzene was purchased from Beijing Kaida Technology Development Co., Ltd., trifluoroacetic acid was bought from TCI Shanghai, sodium borohydride, hydrogen peroxide and potassium dichromate were purchased from Xilong Scientific Co.,Ltd., hydrochloric acid was purchased from Tian in Fuyu Fine Chemical Co., Ltd., potassium ferricyanide and sodium carbonate were purchased from Shanghai Titan Scientific Co.,Ltd., ferrous sulfate, basic red 46 and potassium hexachloropalladate(IV) were purchased from Shanghai Maclin Biochemical Technology Co., Ltd., nickel nitrate and cupric nitrate were purchased from Sinopharm Chemical Reagent Co. Ltd., cesium chloride was purchased from Beijing Mreda Technology Co., Ltd., and acid orange was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd..

Methods:

Synthesis of CC3 (porous imine cage): CC3 was synthesized according to a previous method.¹ First, 0.5 g 1, 3, 5-triformylbenzene was dispersed in 10 mL of CH₂Cl₂, and then, 10 μL of trifluoroacetic acid was added directly. Next, 0.5 g (R, R)-1, 2-diaminocyclohexane was dissolved in 10 mL of CH₂Cl₂. Finally, the two solutions were mixed and left to stand for a week to crystallize. The crystals grown on the sides of the vessel were cleaned several times with a mixed solution of CH₃OH:CH₂Cl₂=19:1, and further dried at 60 °C overnight. The ¹H NMR spectrum proved that CC3 was successfully synthesized (Figure S1).

Reduce CC3 to RCC3: RCC3 was also synthesized according to a previous method.² 463 mg of CC3 was completely dissolved in a 25 mL mixture (

$V_{CH_3OH}:V_{CH_2Cl_2} = 1:1$). After that, 0.5 g of NaBH₄ was added to the mixed solution and stirred at room temperature for 15 h. Then, 1 mL of water was added, and the solution was stirred for 9 h continuously. The solvent was removed under vacuum, and the solid was washed several times with water. Finally, the solid was dried at 60 °C overnight.

Synthesis of C-Cage-Cl: RCC3 (100 mg) was added to 5 mL of water, 0.3 mL of concentrated HCl was added, and ultrasonic dissolution was performed. The ¹H NMR spectrum is consistent with our reported C-Cage-Cl. (Figure S1a)

Synthesis of C-Cage-PB: C-Cage-Cl (15 mg) was dissolved in 3 mL of H₂O, and precipitation occurred after adding 2 ml of 0.02 M K₃[Fe(CN)₆] solution. The resulting solid was collected by centrifugation and washed with water to remove additional salt. Then, the precipitate was evenly dispersed in 2 mL of H₂O followed by 1 mL solution of FeSO₄ (0.02 M). The blue precipitate formed quickly and was collected by centrifugation. The resulting solid C-Cage-PB was washed with deionized water and dried at 80 °C overnight .

Synthesis of C-Cage-PB analogs: C-Cage-Cl (15 mg) was dissolved in 3 mL of H₂O, and precipitation occurred after adding 2 mL of K₃[Fe(CN)₆] solution (0.02 M). The resulting solid was collected by centrifugation and washed with water to remove additional salt. Then, the precipitate was evenly dispersed in 2 mL of H₂O followed by 1 mL solution of Co(NO₃)₂, Ni(NO₃)₂ or Cu(NO₃)₂ (0.02 M). The precipitate formed quickly and was collected by centrifugation. The resulting solid washed with deionized water and dried at 80 °C overnight was C-cage-PBA(Co), C-cage-PBA(Ni) or C-cage-PBA(Fe).

Process of Cs⁺ adsorption: CsCl solution (0.25 mg mL⁻¹) was added to 4 sample bottles, and C-cage-PB (25 mg) was added to the bottles and shaken on the shaker for 1.5 h, 3 h, 4.5 h and 6 h. Then, 3 mL of each supernatant was taken for ICP testing.

Dissociation-regeneration of C-Cage-PB: C-cage-PB (10 mg) was dissolved in 80 μL of concentrated HCl (3 M), then dispersed by ultrasonication for 10 minutes and statically dissociated for 0.5 h (the NMR ¹H spectrum after disassociation is shown in Figure S1b). After the solution gradually turned green, the solution was adjusted to

pH=2 with deionized water, and HCl was volatilized at 80 °C and then absorbed with a saturated Na₂CO₃ solution to avoid polluting the air. The C-Cage-PB was regenerated in the process.

Fenton degradation of TNP: C-Cage-PB (6 mg) was added into 5.32 mL of deionized H₂O, followed by 60 μL of TNP (1 mg mL⁻¹), 0.6 mL of HCl solution (pH=2) and 20 μL of H₂O₂ (30 %) (note: the PB⁻ cage part is stable under the current acidic condition). UV-vis spectroscopy was used to monitor the degradation process until complete. After centrifugation, the obtained solid repeated the above process and started the next cycle.

Fenton degradation of Organic Pollutants: C-Cage-PB (3 mg) was added into 2.62 mL of deionized water followed by separately adding 60 μL of different organic pollutants (methyl red (0.25 mg mL⁻¹ in ethanol), acid orange (2 mg mL⁻¹) and basic red 46 (1 mg mL⁻¹)), 0.3 mL of HCl solution (pH=2) and 20 μL of H₂O₂ (30 %). The digestion process was monitored by UV-vis.

Preparation of soluble PB: 10 mL of 2 M aqueous solution of K₃Fe(CN)₆ and 10 mL of 2 M aqueous solution of FeSO₄ were slowly mixed evenly. After that, the dispersion was subjected to ultrafiltration against a 1000 Da regenerated cellulose membrane to remove K₂SO₄. The soluble PB was obtained by treatment with vacuum freeze-drying over 48 h. The resultant material was characterized by PXRD measurement, as shown in Figure 2b.

Control experiment using a physical mixture of C-Cage⁺ and PB⁻: The C-Cage-Cl and KPB mixture (molar ratio: 1:12) was ground in an agate mortar over 10 min. The resultant physical mixture of C-Cage⁺ and PB⁻ was subjected to the same experimental procedure as C-Cage-PB for the Cs⁺ adsorption and Fenton degradation of waste pollutants.

Synthesis of catalyst for sequential reaction:

Synthesis of Pd@C-Cage-Cl: Pd@C-cage-Cl was synthesized according to a previous method.³ 15 mg of C-Cage-Cl dissolved in 9 mL of water and 0.75 mL of K₂PdCl₆ solution (2 mg mL⁻¹) were added. Then, 0.5 mL of solution containing 2 mg of NaBH₄ was quickly added and vortexed. Finally, the light gray solution was freeze-

dried to obtain the resulting solid Pd@C-Cage-Cl.

Synthesis of Pd@C-Cage-PB: The Pd@C-Cage-PB was synthesized in the same way as C-Cage-PB.

Pd@C-Cage-PB for the sequential degradation of waste pollutants: Pd@C-Cage-PB (3 mg) was added to 2.6 mL of deionized water. Then, 60 μ L of methyl orange (0.5 mg mL^{-1}), 30 μ L of $\text{K}_2\text{Cr}_2\text{O}_7$ (20 mg mL^{-1}) and 0.3 mL of HCl solution (pH=2) were added, followed by 3 μ L of H_2O_2 (30 %) to perform the Fenton reaction, which was monitored by UV-vis until the end of degradation. Then, 30 μ L of HCOOH (1 M) was added and heated to 45 °C for the catalytic reduction of Cr(VI), and the reduction process of $\text{K}_2\text{Cr}_2\text{O}_7$ was further monitored by UV-vis spectra. After centrifugation, the obtained solid was washed with deionized water for the next cycle.

Control experiment using a physical mixture of Pd@C-Cage⁺ and PB⁻: The Pd@C-Cage-Cl and KPB mixture (molar ratio: 1:12) was ground in an agate mortar over 10 min. The resultant physical mixture of Pd@C-Cage⁺ and PB⁻ was subjected to the same experimental procedure as Pd@C-Cage-PB for the sequential degradation of waste pollutants.

Characterization:

Nuclear magnetic resonance (NMR) ^1H was performed on a Bruker Ascend 400 M (AvanceIIIHD 400 MHz). Fourier transform infrared spectroscopy (FTIR) was tested on a Nicolet iS10 FT-IR spectrometer. X-Ray Diffraction (XRD) pattern was obtained on a Bruker D8 Advance. Scanning electron microscopy (SEM) was performed on a JSM-7500F, followed by element mapping and Energy dispersive spectroscopy (EDS) measurements. High-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) was performed on a Talos F200X G2X-Ray. Elemental analysis was performed on a EUROVECTER (EA3000). Photoelectron spectroscopy (XPS) spectra were obtained on a PHI (5000 Versaprobe III). Inductively coupled plasma emission spectrometry (ICP) was performed on an Agilent 7800 ICP-MS. Ultraviolet-visible spectrophotometer (UV-vis) spectra were obtained on a MAPADA INSTRUMENTS UV-6100 double beam spectrophotometer.

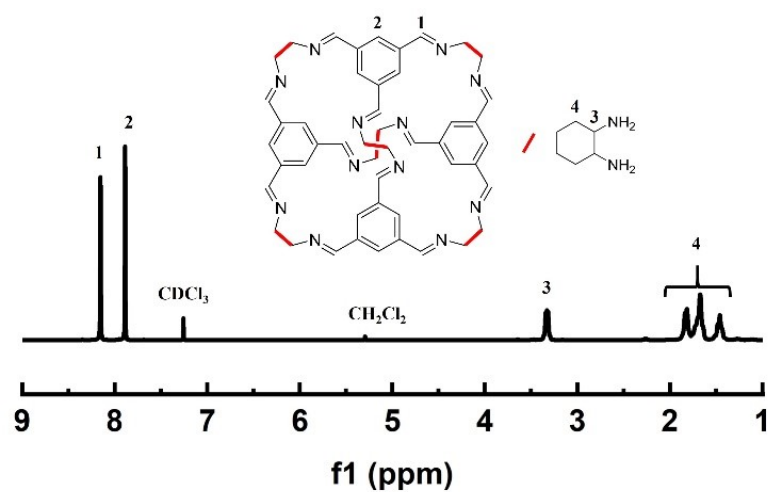


Figure S1. ^1H NMR of CC3 in CDCl_3 .

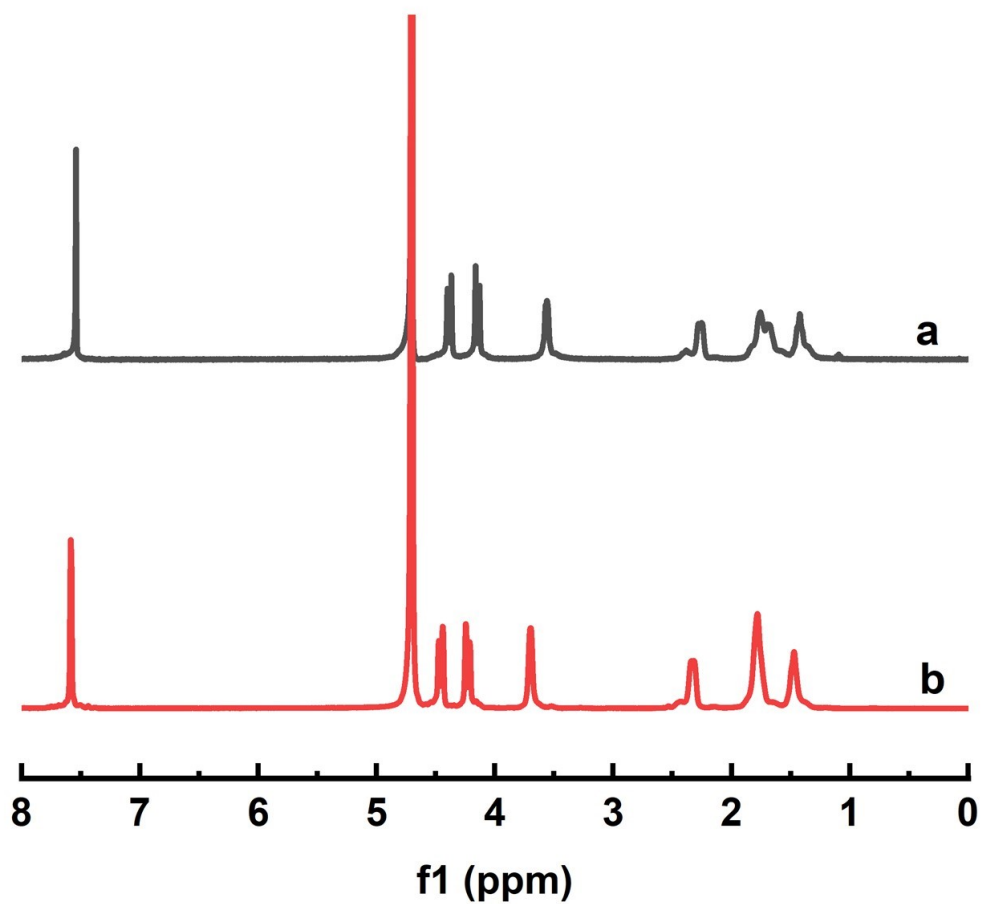


Figure S2. ^1H -NMR spectra in D_2O of (a) C-Cage-Cl and (b) dissociated C-Cage-PB.

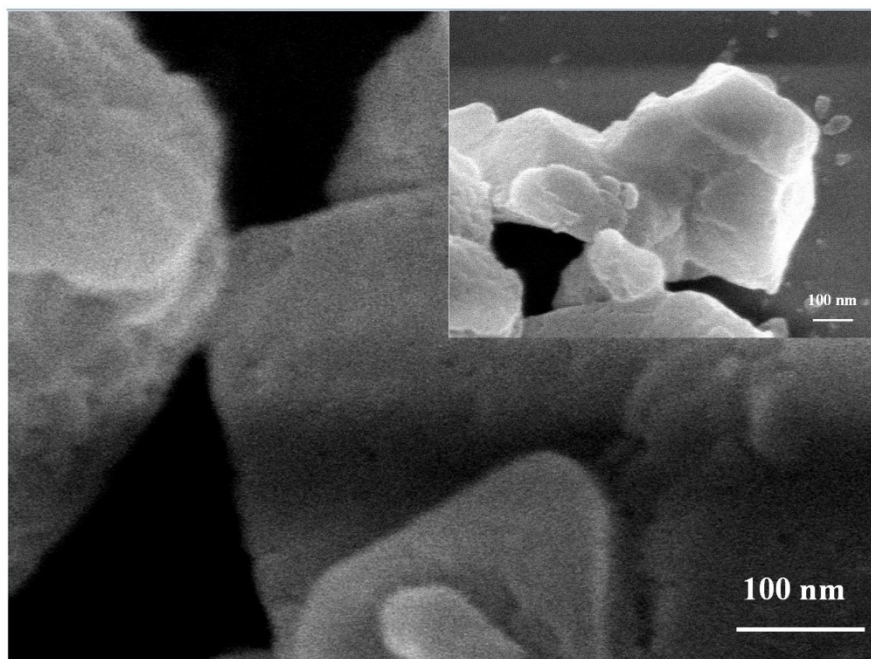


Figure S3. SEM image of C-Cage-PB.

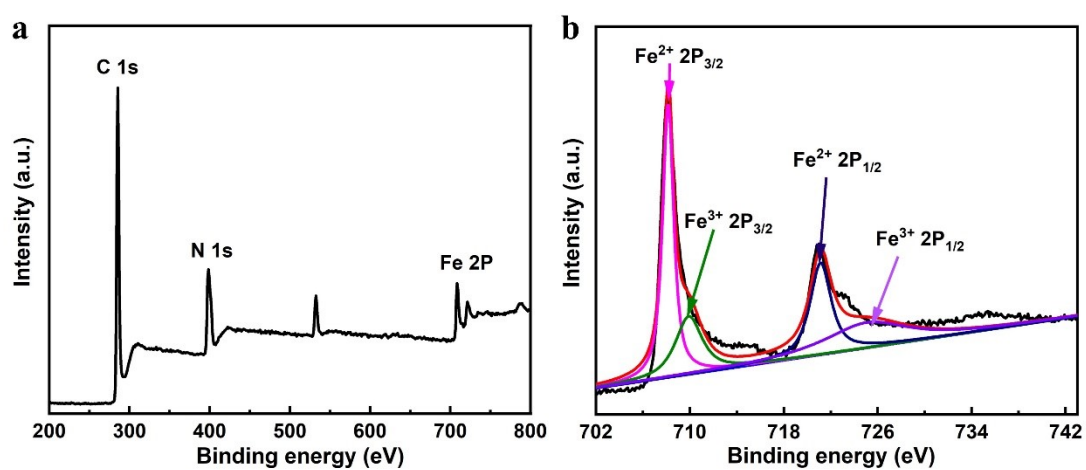


Figure S4. XPS spectrum of (a) C-cage-PB and (b) Fe 2p_{3/2} and 2p_{1/2} peaks of Fe²⁺ and Fe³⁺.

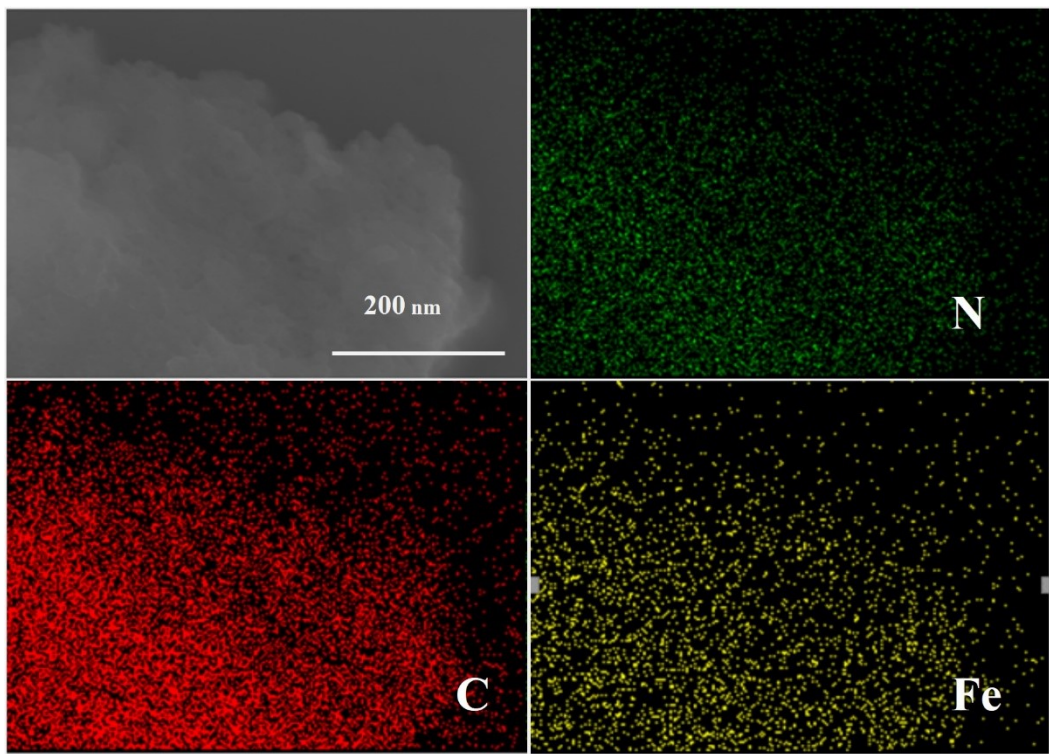


Figure S5. SEM image and element mapping for C, N and Fe.

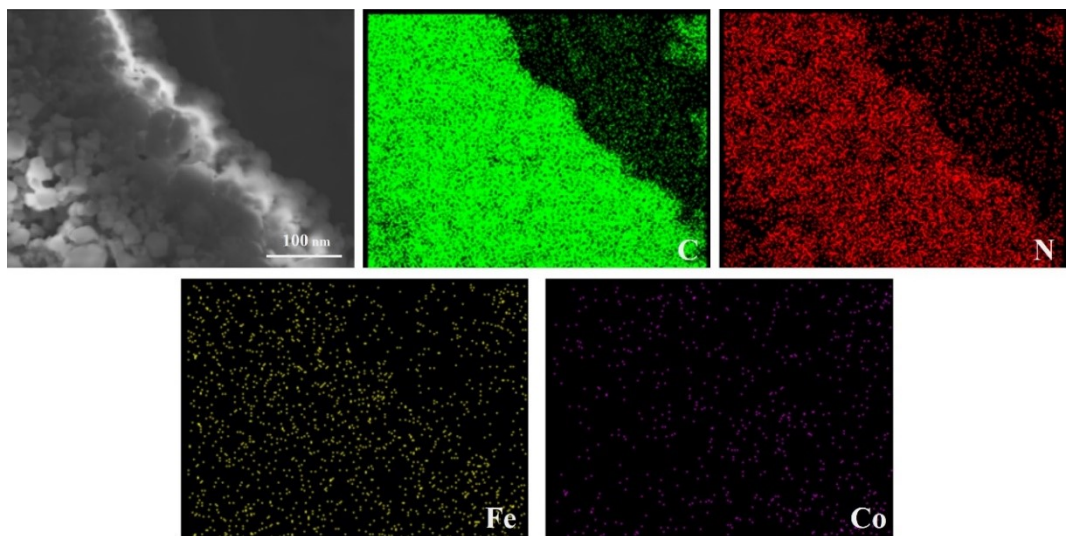


Figure S6. Element mapping for C, N, Fe and Co of C-Cage-PB(Co).

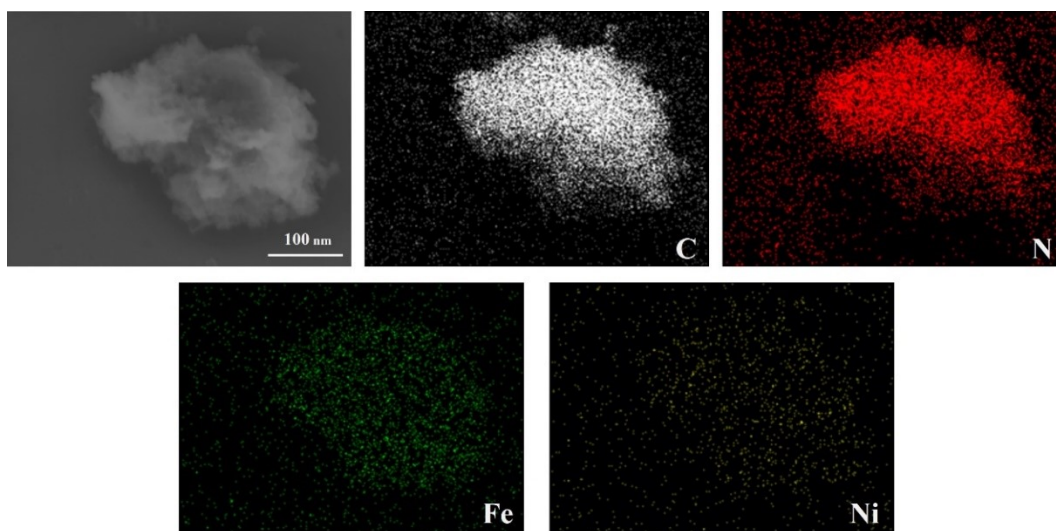


Figure S7. Element mapping for C, N, Fe and Ni of C-Cage-PB(Ni).

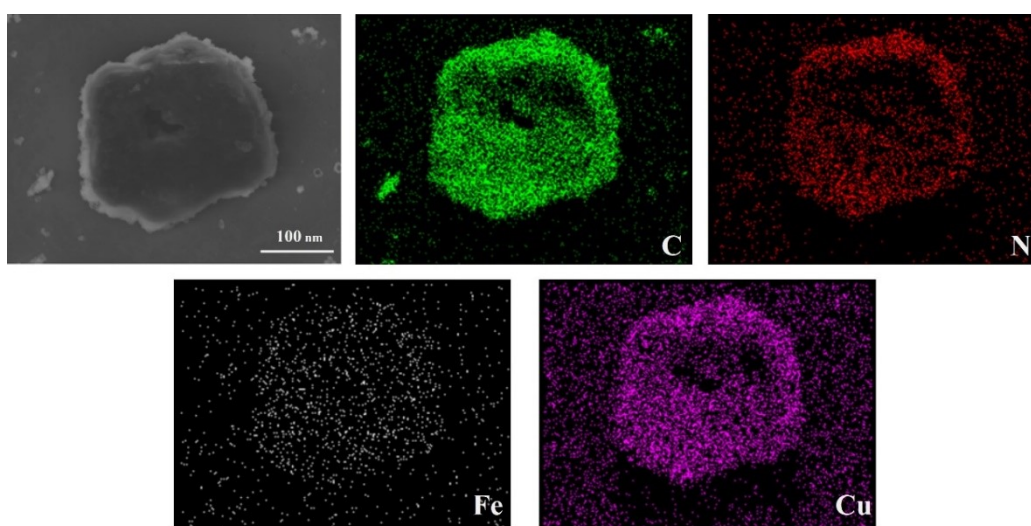


Figure S8. element mapping for C, N, Fe and Cu of C-Cage-PB(Cu).

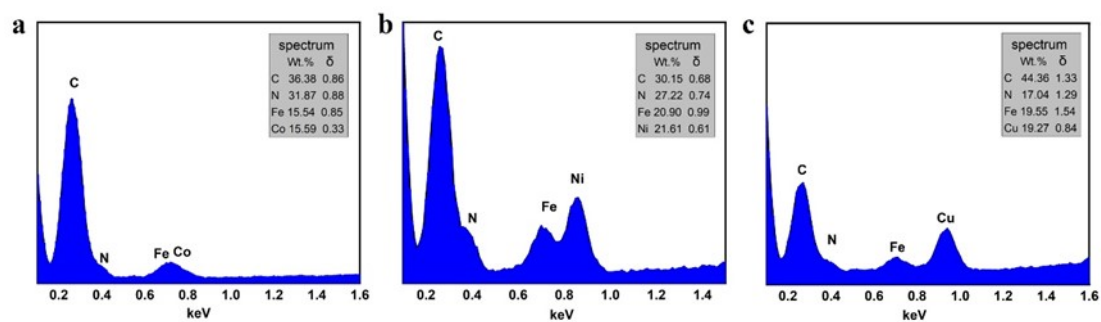


Figure S9. EDS results and elemental analysis of (a) C-Cage-PB(Co), (b) C-Cage-PB(Ni) and (c) C-Cage-PB(Cu).

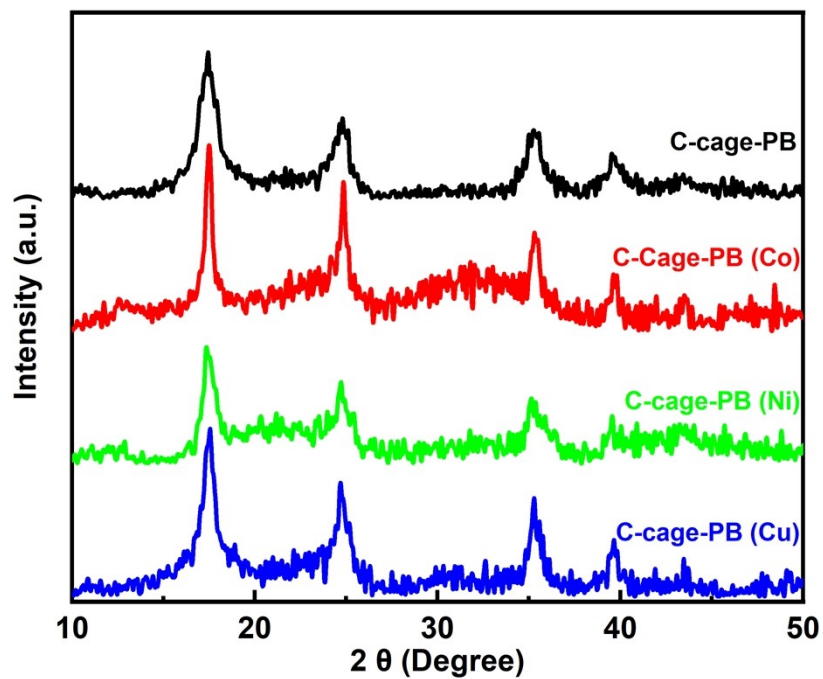


Figure S10. XRD pattern of C-Cage-PB (analogs).

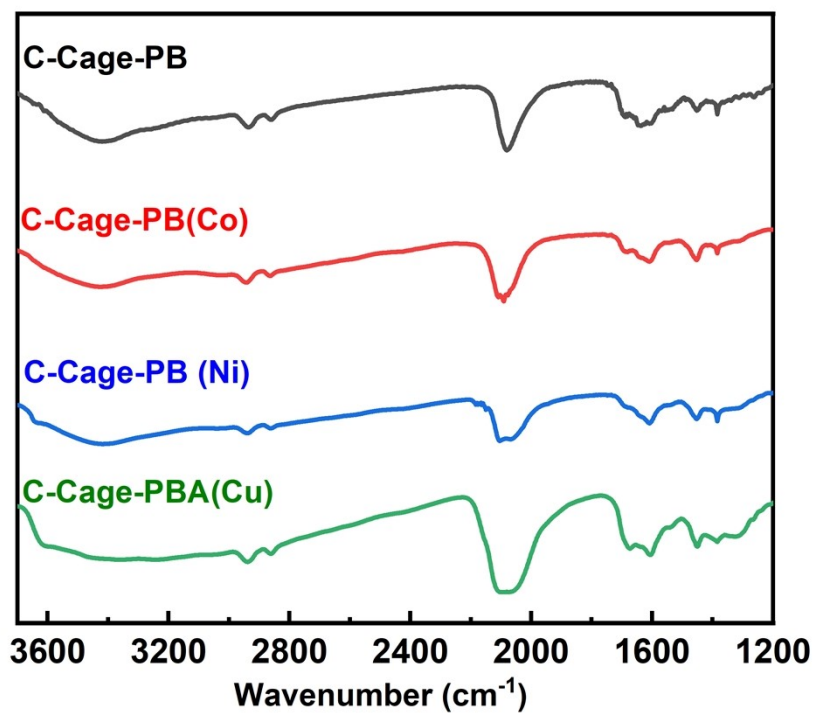


Figure S11. FTIR spectra of C-Cage-PB (analogs).

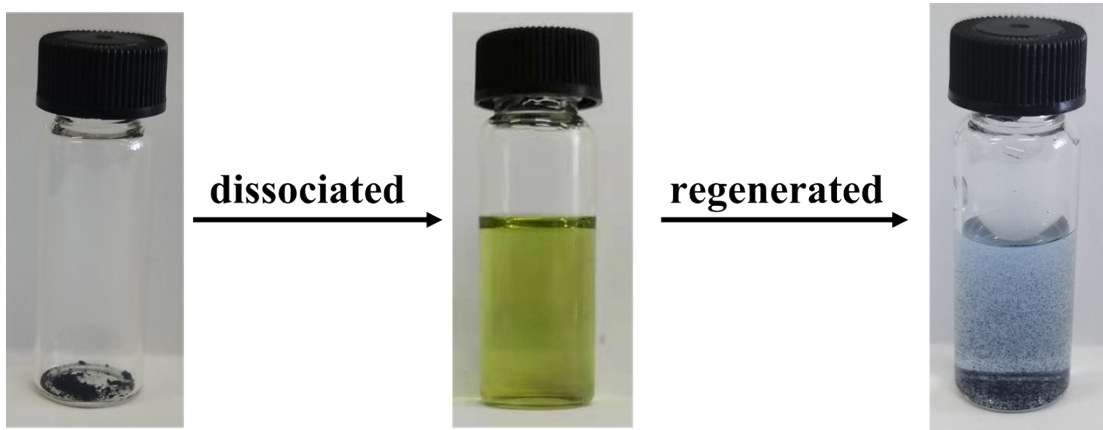


Figure S12. The state of stimuli-responsive dissociation-regeneration of C-Cage-PB.

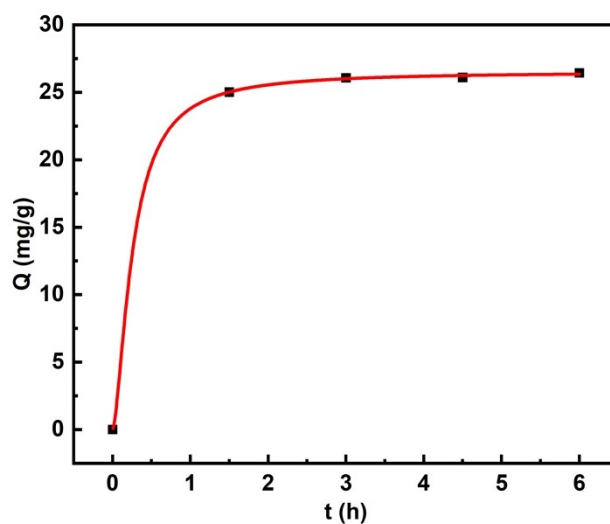
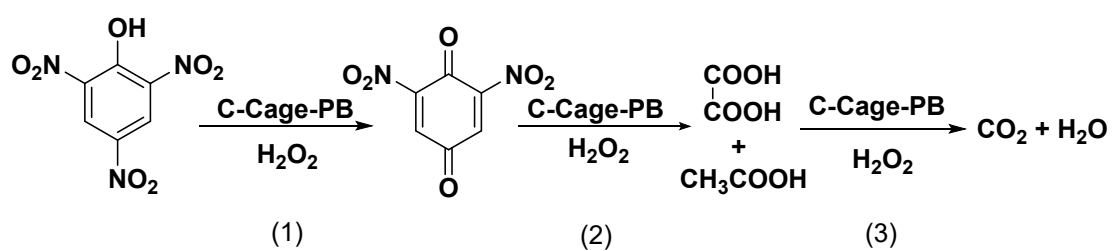


Figure S13: Time dependent adsorption of Cs^+ ions by the physical mixture of C-Cage⁺ and PB⁻.



Scheme S1. Chemical reaction process of Fenton degradation of TNP.

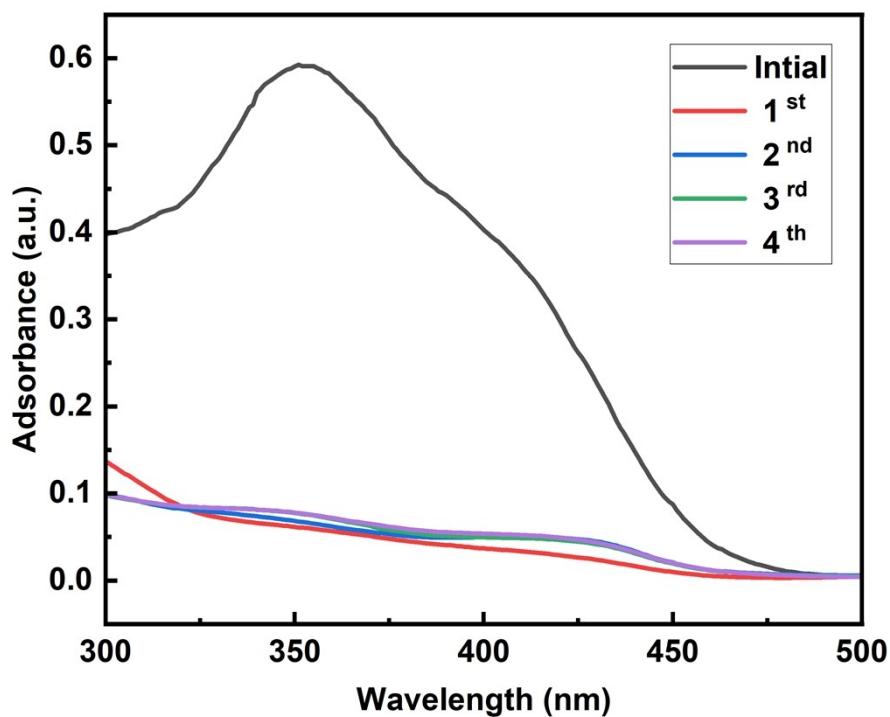


Figure S14. UV-vis spectra record the durability of C-Cage-PB for 4 successive cycles in the Fenton oxidation of TNP.

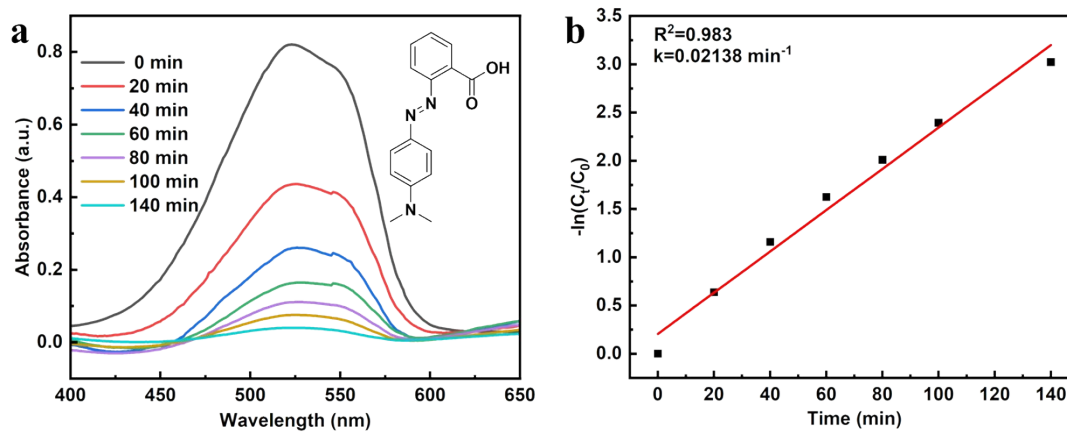


Figure S15. (a) UV-vis spectra of C-Cage-PB in the Fenton degradation of methyl red. (b) Kinetic plot of $-\ln(C_t/C_0)$ versus time for the corresponding reaction.

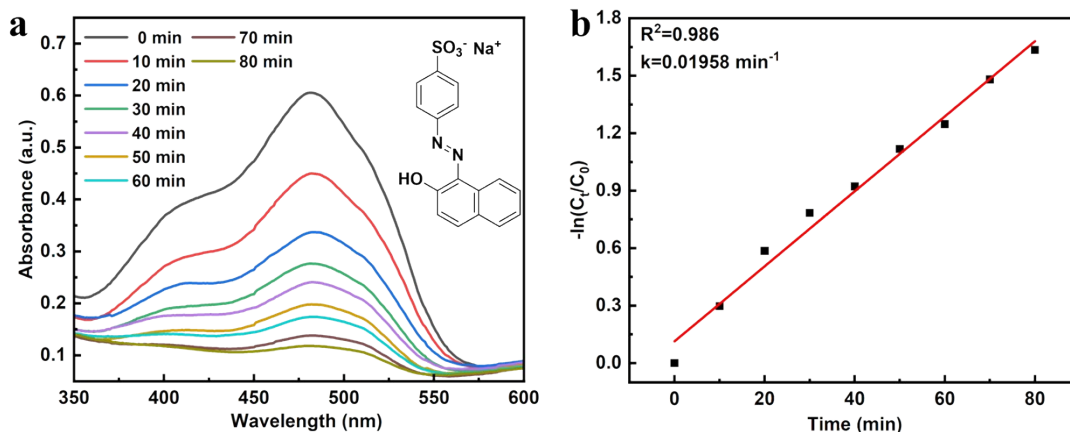


Figure S16. (a) UV-vis spectra of C-Cage-PB in the Fenton degradation of acid orange. (b) Kinetic plot of $-\ln(C_t/C_0)$ versus time for the corresponding reaction.

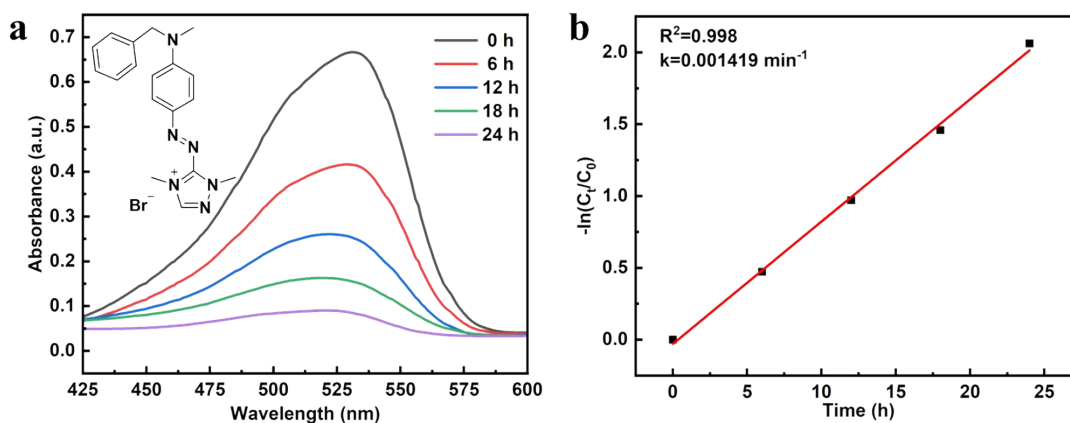


Figure S17. (a) UV-vis spectra of C-Cage-PB in the Fenton degradation of basic red 46. (b) Kinetic plot of $-\ln(C_t/C_0)$ versus time for the corresponding reaction.

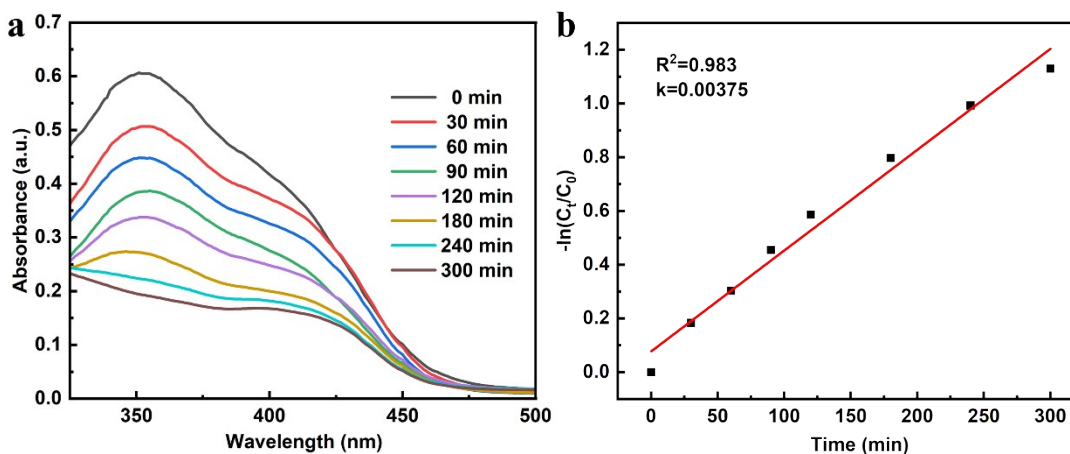


Figure S18. (a) UV-vis spectra of Fenton degradation of the TNP by the physical mixture of C-Cage⁺ and PB⁻; (b) kinetic plot of $-\ln(C_t/C_0)$ versus time for the corresponding reaction.

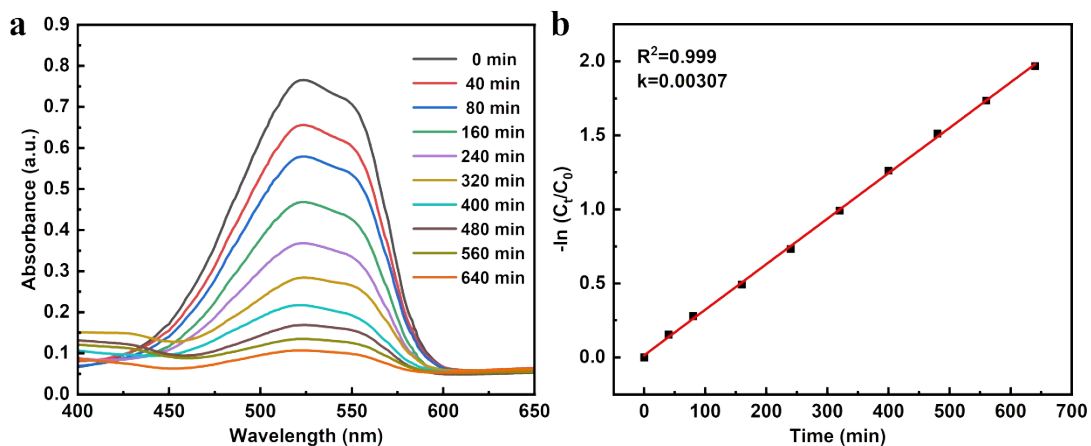


Figure S19. (a) UV-vis spectra of the physical mixture of C-Cage⁺ and PB⁻ in the Fenton degradation of methyl red. (b) Kinetic plot of $-\ln(C_t/C_0)$ versus time for the corresponding reaction.

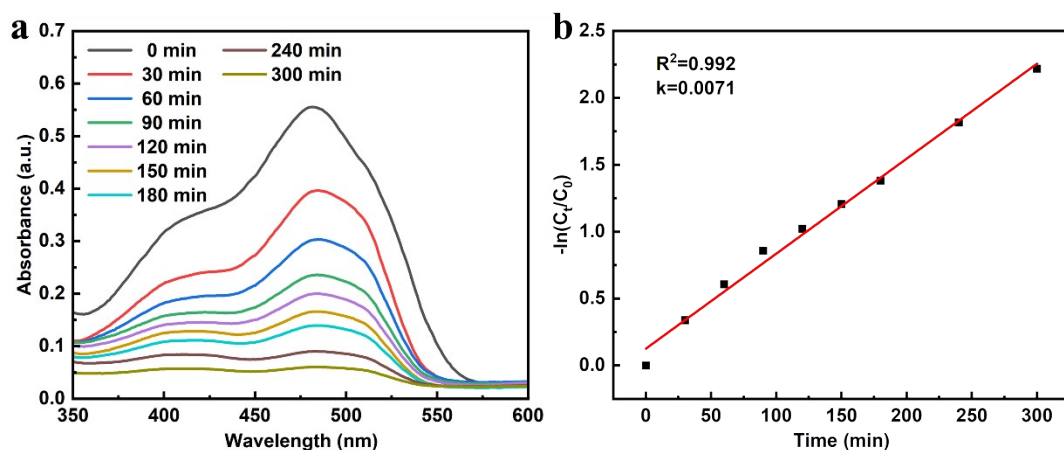


Figure S20. (a) UV-vis spectra of the physical mixture of C-Cage⁺ and PB⁻ in the Fenton degradation of acid orange. (b) Kinetic plot of $-\ln(C_t/C_0)$ versus time for the corresponding reaction.

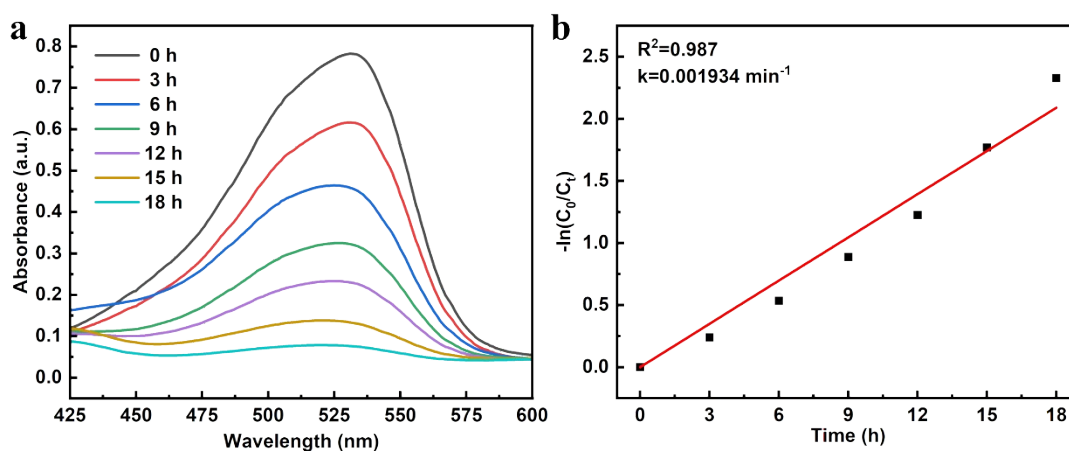


Figure S21. (a) UV-vis spectra of the physical mixture of C-Cage⁺ and PB⁻ in Fenton degradation of basic red 46. (b) Kinetic plot of $-\ln(C_t/C_0)$ versus time for the corresponding reaction.

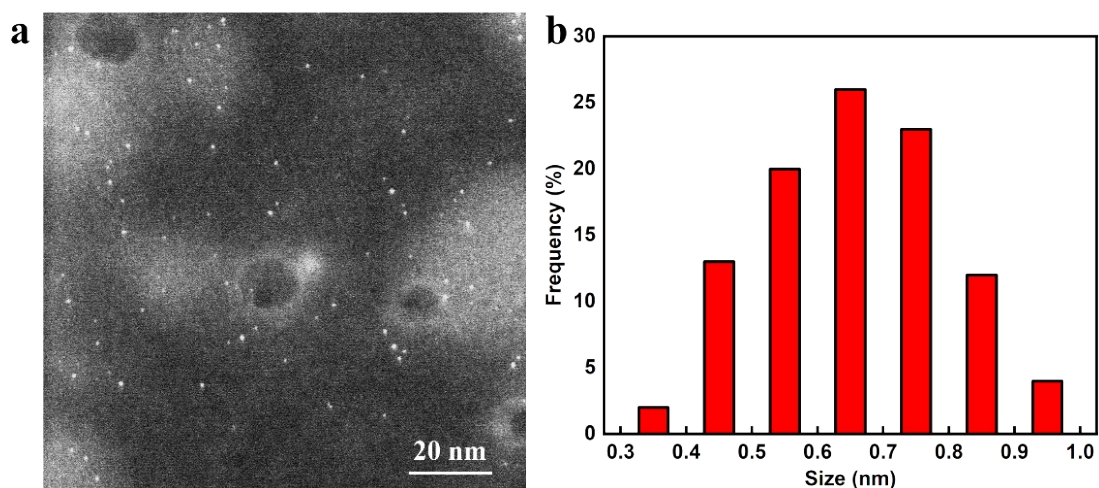


Figure S22. (a) HAADF-STEM image of Pd clusters encapsulated in C-Cage-Cl and (b) the corresponding size distribution histogram of Pd clusters.

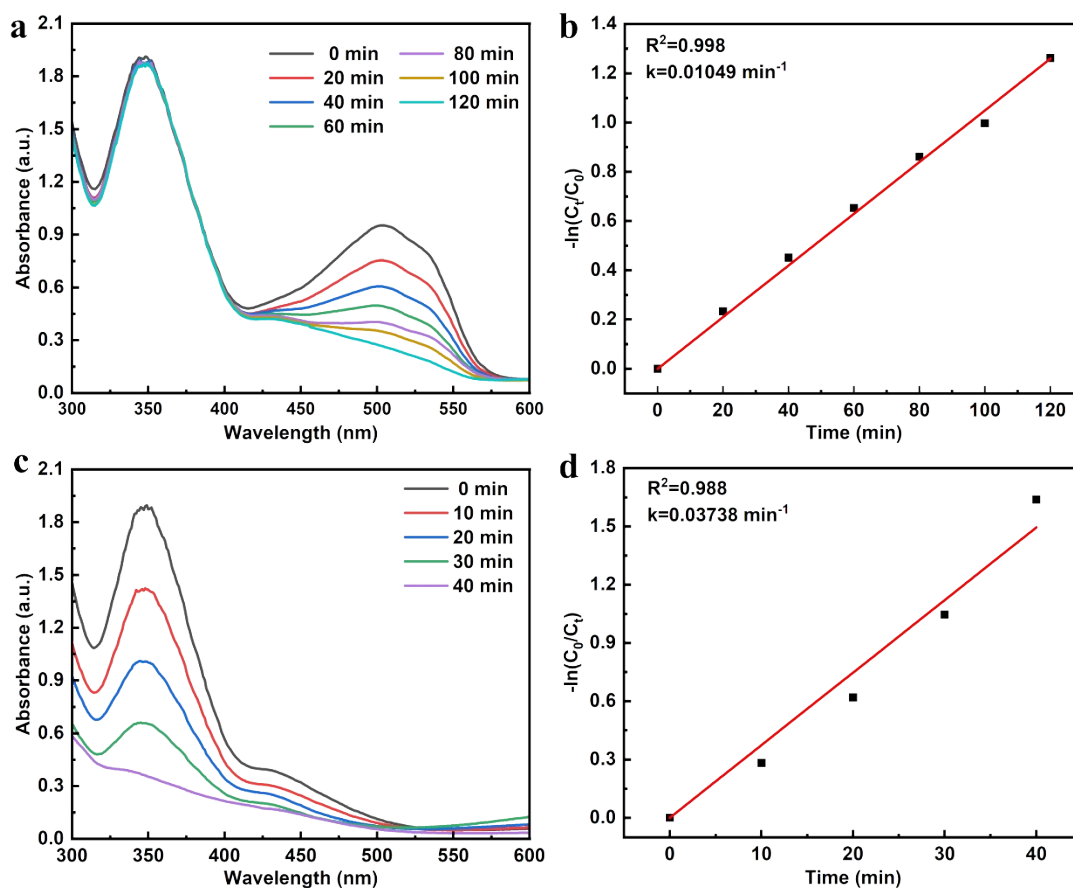


Figure S23. (a) UV-vis spectra of Fenton degradation of methyl orange by the physical mixture of Pd@C-Cage⁺ and PB⁻ and (b) kinetic plot of $-\ln(C_t/C_0)$ versus time for the corresponding reaction; (c) UV-vis spectra of reduction of $K_2Cr_2O_7$ by the physical mixture of Pd@C-Cage⁺ and PB⁻ and (d) kinetic plot of $-\ln(C_0/C_t)$ versus time for the corresponding reaction. Note: the physical mixture of Pd@C-Cage⁺ and PB⁻ displayed a lower catalytic activity toward the negatively charged methyl orange than Pd@C-Cage-PB in the first step. It is reasonable that soluble PB⁻ prevents the intimate

contact with the negatively charged substrates. In contrast, the soluble Pd@C-Cage⁺ in the physically mixed catalyst favors intimate contact with negatively charged Cr₂O₇²⁻, which displayed a higher catalytic activity in the second step. However, such a physically mixed system also suffered from the drawback of recycling issues.

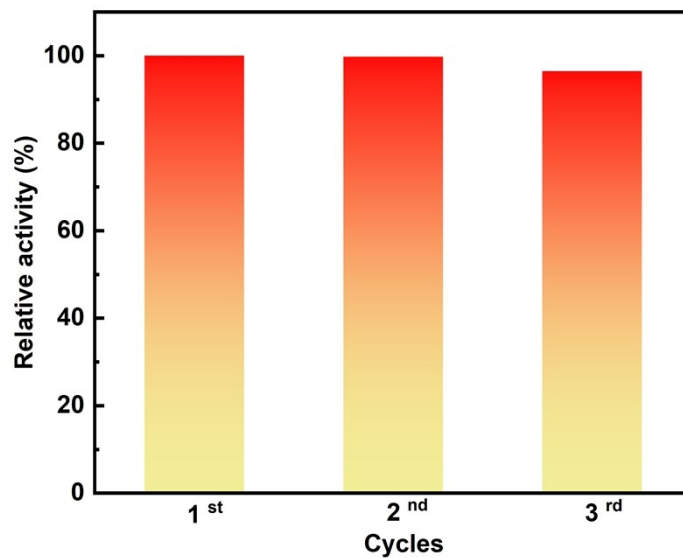


Figure S24. Durability test of Pd@C-Cage-PB for 3 successive cycles in sequential degradation of methyl orange and K₂Cr₂O₇.

Table S1. Elemental analysis of C-Cage-PB (the chemical formula is $C_{72}N_{12}H_{120}[FeFe(CN)_6]_{12}\cdot H_2O$) and recycled C-Cage-PB.

Elements	C (%)	N (%)	H (%)
Samples			
C-Cage-PB	39.98	26.02	3.38
1 st cycle	39.61	26.20	3.08
2 nd cycle	39.31	26.39	3.13
Calculated	39.44	26.83	2.80

Table S2. ICP analysis of Fe ions in C-Cage-PB and recycled C-Cage-PB.

Samples	Fe (%)
C-Cage-PB	30.12
1 st cycle	30.34
2 nd cycle	30.16
Calculated	30.56

References

- 1 L. Zhu, S. Zhang, X. C. Yang, Q. Zhuang and J. K. Sun, *Small Methods*, 2022, **6**, e2200591.
- 2 L. Tan, J. H. Zhou, J. K. Sun and J. Yuan, *Nat Commun*, 2022, **13**, 1471.
- 3 (a) W. Cao, J. Zhou, Z. Kochovski, H. Miao, Z. Gao, J. K. Sun and J. Yuan, *Cell. Rep. Phys. Sci.*, 2021, **2**, 100546; (b) Y. J. Du, J. H. Zhou, L. X. Tan, S. H. Liu, K. Zhao, Z. M. Gao and J. K. Sun, *ACS Appl. Nano. Mater.*, 2022, **5**, 7974-7982.