Supporting Information

Porous Organic Cage Nanostructures for Construction of Complex Sequential Reaction Networks

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Contents

1. Instrumentation ................................................................. Page: S4
2. Computational details .......................................................... Page: S5
3. Additional data and figures .................................................... Page: S6

Figure S1. The $^1$H NMR spectrum of the CC3 in the CDCl$_3$. Page: S6
Figure S2. The $^1$H NMR spectrum of the RCC3 in the CDCl$_3$. Page: S6
Figure S3. The $^1$H NMR spectrum of the C-Cage$^+$ in the D$_2$O. Page: S7
Figure S4. The synthesis process of the C-Cage$^+$. Page: S7
Figure S5. The synthesis process of C$_3$N$_4^-(a)$ and C$_3$N$_4^+(b)$. Page: S8
Figure S6. Particle size distribution of C$_3$N$_4^-$ and dispersed C-Cage$^+/C_3$N$_4^-$ composite evaluated by dynamic light scattering (DLS). Page: S8
Figure S7. Evolution of the distance of C-Cage$^+$ and C$_3$N$_4^+/C_3$N$_4^-$ during the MD process. Page: S9
Figure S8. Interaction energies experienced by C-Cage$^+$ and C$_3$N$_4^+/C_3$N$_4^-$. Page: S10
Figure S9. The PXRD patterns of the bulk C$_3$N$_4^-$, C-Cage$^+$ and C-Cage$^+/C_3$N$_4^-$ composite. Page: S11
Figure S10. The SEM image of the C-Cage$^+/C_3$N$_4^-$. Page: S11
Figure S11. Standard curve of iodometric titration. Page: S12
Figure S12. Photocatalytic performance of H$_2$O$_2$ generation via C-Cage$. Page: S12
Figure S13. Photocatalytic performance of H$_2$O$_2$ generation via Pd@C-Cage$. Page: S13
Figure S14. The UV-vis diffuse reflectance spectra of C$_3$N$_4^-$, C-Cage$^+$ and C-Cage$^+/C_3$N$_4^-$. Page: S13
Figure S15. The $^1$H NMR spectrum of pure 4-NPBA in the CD$_2$OD. Page: S14
Figure S16. The $^1$H NMR spectrum of pure 4-NP in the CD$_2$OD. Page: S14
Figure S17. The $^1$H NMR spectrum of pure 4,4'-dinitro-1,1'-biphenyl in CDCl$_3$. Page: S15
Figure S18. The $^1$H NMR spectrum (CD$_2$OD) of the further purified product after a two-step sequential reaction over the C-Cage$^+/C_3$N$_4^-$ catalyst. Page: S15
Figure S19. Time-dependent conversion of the 4-NPBA substrate over the C-Cage$^+/C_3$N$_4^-$ catalyst. Page: S16
Figure S20. HAADF-STEM images and the size distribution histograms of Pd@C-Cage$. Page: S16
Figure S21. The XPS spectrum of Pd@C-Cage$^+$ shows Pd 3d5/2 (335.5 eV) and 3d3/2 (340.6 eV) peaks of metallic Pd. Page: S17
Figure S22. Time-dependent conversion of 4-NP over the integrated catalyst Pd@C-Cage$^+/C_3$N$_4^-$. Page: S17
Figure S23. Time-dependent conversion of 4-NP over the C₃N₄⁻ and C-Cage⁺ catalysts. Page: S18

Figure S24. Photocatalytic performance of H₂O₂ generation via C₃N₄⁻ and C₃N₄⁺ catalysts in solution...........................................................................................................................................Page: S18

Figure S25. Time-dependent conversion of 4-NP over the mixture of Pd@C-Cage⁺ and C₃N₄⁺ catalysts .......................................................................................................................................Page: S19

Figure S26. The ¹H NMR spectrum (CDCl₃) of neutralized C-Cage⁺ (N-Cage) after treating C-Cage⁺ with NaOH ........................................................................................................................................Page: S19

Figure S27. TEM image of Pd nanoparticles produced without any support....................Page: S20

Figure S28. Time-dependent conversion of 4-NP over the mixture of Pd nanoparticles and C₃N₄⁻ catalysts ........................................................................................................................................Page: S20

Figure S29. Three-input Boolean AND logic gate. ...........................................................Page: S21

Figure S30. Time course plots of H₂ generation for the methanolsysis of AB over the Pd@C-Cage⁺ catalyst at 298 K (Pd/AB = 0.033) .......................................................................................................................................Page: S21

Figure S31. The conversion of 4-NP with AB over the Pd@C-Cage⁺/C₃N₄⁻ catalyst.......Page: S22

Figure S32. Durability test of the integrated Pd@C-Cage⁺/C₃N₄⁻ catalyst in the convergent cascade. ........................................................................................................................................Page: S22

Scheme S1. Reaction scheme for the C-Cage⁺ being neutralized by adding a stoichiometric NaOH (12 eq to C-Cage⁺). ........................................................................................................................................Page: S23

4. Supporting Movie legends ..........................................................................................Page: S23

References ...................................................................................................................Page: S24-S25
1. Instrumentation

Scanning electron microscopy (SEM) was performed on a JEOL JSM-7500F scanning electron microscope operated at 5 kV. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2200FS transmission electron microscope operated at 120 kV. Scanning TEM (STEM) was performed on a JEOL JEM-2200FS transmission electron microscope operated at 200 kV and equipped with a high-angle annular dark-field (HAADF) STEM detector. X-ray photoelectron spectroscopy (XPS) studies were performed on a Thermo Fisher ESCALAB250 X-ray photoelectron spectrometer (powered at 150 W) using Al Ka radiation (1/4 8.357 A). To compensate for surface charging effects, the XPS spectrum was referenced to the C 1s neutral carbon peak at 284.6 eV. The solution UV-vis absorption measurements were recorded on a Lambda 900 spectrophotometer. $^1$H nuclear magnetic resonance ($^1$H-NMR) measurements were carried out at room temperature on a Bruker ascend-400/700 spectrometer in D$_2$O, CD$_3$OH and CDCl$_3$. Dynamic light scattering (DLS) and zeta potential measurements were performed on a Zetasizer Nano ZS90 (Malvern). Powder X-ray diffraction (PXRD) patterns were measured on a Bruker D8 Advance instrument using Cu Kα radiation. Fourier transform infrared (FT-IR) spectra were obtained on a Varian1000 FT-IR spectrometer. The UV-vis diffuse reflectance absorbance spectroscopy (UV-vis DRS) was performed on a TU-1901 Dual Beam UV-vis Spectrophotometer.
2. Computational details

All simulations were performed with the Gromacs 2020.4 package \(^1\). The $\text{C}_3\text{N}_4^+/\text{C}_3\text{N}_4^-$ and $\text{C-Cage}^+$ systems were placed in a box with dimensions of $4 \times 4 \times 10$ nm\(^3\). Subsequently, both models were solvated with solvents (methanol and water). Chloride ions were added to maintain charge neutrality. The number of solvate molecules was adjusted to reproduce the standard density of methanol (methanol-water mixture). CGenFF \(^2\) (CHARMM General Force Field) was used to generate the parameters of $\text{C-Cage}^+$ and $\text{C}_3\text{N}_4^+/\text{C}_3\text{N}_4^-$. All RESP charges were generated as follows: All molecules were optimized at the B3LYP \(^3\) level using the 6-31+g** basis set with the Gaussian 09 program,\(^4\) where the solvent effect was corrected using a SMD method. The RESP charges were fitted from the optimized geometry and wave function using Multiwfn software.\(^5\) The figures were made with VMD software.\(^6\)

The cut-off for the neighbor list of the Verlet method and that for short-range interactions is 1.2 nm in all calculations with periodic boundary conditions in all three directions. The modified Berendsen thermostat (V-rescale in Gromacs) is used for temperature control. A Berendsen pressure bath is used for possible pressure control. The particle mesh Ewald (PME) method is used for electrostatics.

The $\text{C}_3\text{N}_4^+/\text{C}_3\text{N}_4^-$ were frozen in the system, and each system was subjected to energy minimization (with the steepest descent algorithm), NVT and NPT equilibration phases (each 6 ns long), and a final production phase (12 ns), from which the average density and other parameters were collected.
3. Additional data and figures

**Figure S1.** The $^1$H NMR spectrum of the CC3 in the CDCl$_3$.

**Figure S2.** The $^1$H NMR spectrum of the RCC3 in the CDCl$_3$. 
**Figure S3.** The $^1$H NMR spectrum of the C-Cage$^+$ in the D$_2$O.

**Figure S4.** The synthesis process of the C-Cage$^+$. 
Figure S5. The synthesis process of $C_3N_4^-$ (a) and $C_3N_4^+$ (b).

Figure S6. Particle size distribution of $C_3N_4^-$ and dispersed C-Cage$^+$/C$_3N_4^-$ composite evaluated by dynamic light scattering (DLS).
Figure S7. Evolution of the distance of C-Cage\(^+\) and C\(_3\)N\(_4\)^+/C\(_3\)N\(_4\)^− during the MD process, which can be used to illustrate how C-Cage\(^+\) and C\(_3\)N\(_4\)^+/C\(_3\)N\(_4\)^− interact during molecular dynamics. (a, c) C-Cage\(^+\)/C\(_3\)N\(_4\)^− (Movie S1) and (b, d) C-Cage\(^+\) + C\(_3\)N\(_4\)^+ (Movie S2) (In each system, each C\(_3\)N\(_4\) sheet was placed with two cages on both sides). Blue VDW mod = C\(_3\)N\(_4\)^+/C\(_3\)N\(_4\)^−; Gray licorice mod = C-Cage\(^+\); Cyan MSMS mod = Water; Red MSMS mod = Methanol. The distance between C-Cage\(^+\) and C\(_3\)N\(_4\)^+/C\(_3\)N\(_4\)^− is expressed by measuring the distance between the centroid of C-Cage\(^+\) and C\(_3\)N\(_4\)^+/C\(_3\)N\(_4\)^−.
Figure S8. Interaction energies experienced by C-Cage$^+$ and C$_3$N$_4^+/C_3$N$_4^-$ In the chart, light-colored lines represent the ‘raw’ data points, whereas the darker, solid lines mark the corresponding running averages. $E_{int}$, Total short-range interaction energies (both Coulomb interaction and Lennard-Jones potential).

Values for the interaction energy were computed using the Gromacs tool, gmx energy. The interaction energy between molecules was calculated by summing Lennard-Jones (LJ) and Coulombic potentials. In line with the experimental results, we found that the interaction in C-Cage$^+/C_3$N$_4^-$ (-1026.7 kJ mol$^{-1}$) was much larger than that in C-Cage$^+$ + C$_3$N$_4^+$ (-3.6 kJ mol$^{-1}$). Regarding the source of intermolecular forces, the difference in charge between C$_3$N$_4^+/C_3$N$_4^-$ accounts for the interaction with C-Cage$^+$. 
Figure S9. The PXRD patterns of the bulk $\text{C}_3\text{N}_4^-$, C-Cage$^+$ and C-Cage$^+$/C$_3$N$_4^-$ composite.

Figure S10. The SEM image of the C-Cage$^+$/C$_3$N$_4^-$.
**Figure S11.** Standard curve of iodometric titration.

**Figure S12.** Photocatalytic performance of $\text{H}_2\text{O}_2$ generation via C-Cage$^+$. 
Figure S13. Photocatalytic performance of H$_2$O$_2$ generation via Pd@C-Cage$^+$. A neglectable H$_2$O$_2$ was produced by Pd@C-Cage$^+$, indicating that neither Pd nor C-Cage$^+$ can catalyze the H$_2$O$_2$ generation.

Figure S14. The UV-vis diffuse reflectance spectra of C$_3$N$_4^-$, C-Cage$^+$ and C-Cage$^+/C_3$N$_4^-$. 
Figure S15. The $^1$H NMR spectrum of pure 4-NPBA in the CD$_3$OD. δ 8.16 (d, $J = 8$ Hz, 2H), δ 7.91 (d, $J = 8$ Hz, 2H).

Figure S16. The $^1$H NMR spectrum of pure 4-NP in the CD$_3$OD. δ 8.12 (d, $J = 8$ Hz, 2H), δ 6.89 (d, $J = 8$ Hz, 2H).
**Figure S17.** The $^1$H NMR spectrum of pure 4,4′-dinitro-1,1′-biphenyl in CDCl$_3$. δ 8.37 (d, $J = 8$ Hz, 4H), δ 7.79 (d, $J = 8$ Hz, 4H).

**Figure S18.** The $^1$H NMR spectrum (CD$_3$OD) of the further purified product after a two-step sequential reaction over the C-Cage$^3$/C$_3$N$_4$ catalyst, which is consistent with...
Figure S16, indicating of the formation of 4-NP. Note: the formation of byproduct 4,4'-dinitro-1,1'-biphenyl was excluded from the $^1$H NMR spectrum. δ 8.12 (d, $J = 8$ Hz, 2H), δ 6.90 (d, $J = 8$ Hz, 2H).

Figure S19. Time-dependent conversion of the 4-NPBA substrate over the C-Cage$^+$/C$_3$N$_4^-$ catalyst. Note: this is the last step in the two-step sequential reactions.

Figure S20. HAADF-STEM images and the size distribution histograms of Pd@C-Cage$^+$. 
Figure S21. The XPS spectrum of Pd@C-Cage* shows Pd 3d$_{5/2}$ (335.5 eV) and 3d$_{3/2}$ (340.6 eV) peaks of metallic Pd.

Figure S22. Time-dependent conversion of 4-NP over the integrated catalyst Pd@C-Cage*/C$_3$N$_4^-$. Note: this is the last step in the three-step sequential reactions. The 4-NP as the intermediate product was obtained by oxidative hydroxylation of 4-NPBA in the sequential reaction.
**Figure S23.** Time-dependent conversion of 4-NP over the C$_3$N$_4^-$ and C-Cage$^+$ catalysts.

**Figure S24.** Photocatalytic performance of H$_2$O$_2$ generation via C$_3$N$_4^-$ and C$_3$N$_4^+$ catalysts in solution.
**Figure S25.** Time-dependent conversion of 4-NP over the mixture of Pd@C-Cage$^+$ and C$_3$N$_4^+$ catalysts. Note: this is the last step in the three-step sequential reactions. The 4-NP as the intermediate product was obtained by oxidative hydroxylation of 4-NPBA in the sequential reaction.

**Figure S26.** The $^1$H NMR spectrum (CDCl$_3$) of neutralized C-Cage$^+$ (N-Cage) after treating C-Cage$^+$ with NaOH, which is consistent with Figure S2, indicating the formation of RCC3.
**Figure S27.** TEM image of Pd nanoparticles produced without any support.

**Figure S28.** Time-dependent conversion of 4-NP over the mixture of Pd nanoparticles and C₃N₄⁻ catalysts. Note: this is the last step in the three-step sequential reactions. The 4-NP as the intermediate product was obtained by oxidative hydroxylation of 4-NPBA in the sequential reaction.
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**Figure S29.** Three-input Boolean AND logic gate, by $C_3N_4^-$, Pd and C-Cage$^+$ as the chemical inputs.

![Diagram](image)

**Figure S30.** Time course plots of $H_2$ generation for the methanolysis of AB over the Pd@C-Cage$^+$ catalyst at 298 K (Pd/AB = 0.033).
Figure S31. The conversion of 4-NP with AB over the Pd@C-Cage$^{+}$/C$_3$N$_4$$^{-}$ catalyst. Note: this is the last step in the convergent reactions. The 4-NP as the intermediate product was obtained by oxidative hydroxylation of 4-NPBA in the sequential reaction.

Figure S32. Durability test of the integrated Pd@C-Cage$^{+}$/C$_3$N$_4$$^{-}$ catalyst in the convergent cascade.
Scheme S1. Reaction scheme for the C-Cage$^+$ being neutralized by adding a stoichiometric NaOH (12 eq to C-Cage$^+$).

4. Supporting Movie legends

Movie S1. MD simulation of C$_3$N$_4^-$ interacts with C-Cage$^+$ in a mixture of water and methanol. The water and methanol molecules were used MSMS mod for a better view of the target molecules. The running time is 12 ns. Initially, C-Cage$^+$ was placed about 1.4 nm away from the center of C$_3$N$_4^-$. After 6 ns, the average distance of C-Cage$^+$ was stable in the system, was 1.1 nm.

Movie S2. MD simulation of C$_3$N$_4^+$ interacts with C-Cage$^+$ in a mixture of water and methanol. The water and methanol molecules were used MSMS mod for a better view of the target molecules. The running time is 12 ns. Initially, C-Cage$^+$ was placed about 3.2 nm away from the center of C$_3$N$_4^+$. After 6 ns, the average distance of C-Cage$^+$ was stable in the system, was 4.3 nm.
References


