Supporting information

Porphyrin-Based Multicomponent Metallacage: Host–Guest Complexation towards Photooxidation-Triggered Reversible Encapsulation and Release

Zeyuan Zhang,† Lingzhi Ma,† Fang Fang,‡ Yali Hou,‡ Chenjie Lu,‡ Chaoqun Mu,‡ Yafei Zhang,† Haifei Liu,† Ke Gao,† Ming Wang,† Zixi Zhang,⊥ Xiaopeng Li,‡ Mingming Zhang*†

†State Key Laboratory for Mechanical Behavior of Materials, Shaanxi International Research Center for Soft Matter, School of Materials Science and Engineering Xian Jiaotong University, Xi’an, 710049, P. R. China
‡Instrumental Analysis Center of Shenzhen University, Shenzhen, 518055, P. R. China
‡Key Laboratory of Adsorption and Separation Materials and Technologies of Zhejiang Province, Zhejiang University, Hangzhou, 310027, P. R. China
†State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, 130012, P. R. China
⊥Department of Dermatology, The First Affiliated Hospital of Xi’an Jiaotong University, Xi’an, 710061, P. R. China
‡College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, 518055, P. R. China

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1. Materials and methods

All reagents and deuterated solvents were used as purchased without further purification. Compounds 1, G_{1-7}, G_{9-10} were purchased from commercial suppliers. Compounds 2, G_{8}^{[S1]} G_{9}^{[S2]} and G_{11}^{[S2]} were prepared according to the literature procedures. NMR spectra were recorded on a Bruker Avance 600 MHz spectrometer. $^1$H NMR chemical shifts were recorded relative to residual solvent signals. $^{31}$P{$^1$H} NMR chemical shifts were referenced to an external unlocked sample of 85% H$_3$PO$_4$ ($\delta$ 0.0). Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. The UV/vis experiments were conducted on a Lambda 950 absorption spectrophotometer. The fluorescent experiments were conducted on a Hitachi F-7000 fluorescence spectrophotometer. X-ray diffraction analysis was conducted a Bruker D8 VENTURE PHOTON II MetalJet, in which crystals were frozen in paratone oil inside a cryoloop under a cold stream of N$_2$. An empirical absorption correction using SADABS was applied for all data. The structures were solved and refined to convergence on F2 for all independent reflections by the full-matrix least squares method using the OLEX2 1.2.

2. Synthetic procedures and characterization data

2.1 Synthesis of compound 3

![Chemical structure of compound 3]

[1,1'-biphenyl]-3,3',5,5'-tetracarboxylic acid (1.65 g, 5.00 mmol) and NaOH (840 mg, 21 mmol) were added in H$_2$O (50 mL) and stirred at room temperature for 0.5 h. Then the mixture was concentrated to 10 mL and acetone was added to afford a white precipitate which was collected and further dried to give 3 (2.00 g, 95.7%) as a white solid. $^1$H NMR (600 MHz, CD$_3$OD) $\delta$ 8.48 (s, 1H), 8.37 (s, 2H).
Figure S1. $^1$H NMR spectra (600 MHz, CD$_3$OD, 295 K) recorded for 3.

2.2 Synthesis of metallacage 4

Scheme S1. Self-assembly of metallacage 4.

Compounds 1 (6.19 mg, 10.00 µmol) and 2 (19.73 mg, 40.00 µmol) were dissolved in acetone (4.0 mL) and heated at 50 °C for 12 h. Then 3 (4.18 mg, 10.00 µmol in 1 mL deionized water) was added to the reaction mixture and the system was heated at 50 °C for another 12 h. After cooling, the solvent was removed by nitrogen flow. The residue was redissolved in acetone (2.0 mL), filtered and the filtrate was poured into ethyl ether (8.0 mL) to give a precipitate, which was collected by centrifugation to give metallacage 4 (31.03 mg, 95%) as a dark brown powder. $^1$H NMR (600 MHz, CD$_3$CN, 295 K) $\delta$ 9.13 (m, 8H), 9.07 (m, 8H), 8.88 (s,
8H), 8.66 (s, 4H), 8.62 (s, 8H), 8.15 (s, 8H), 8.12 (d, \( J = 4.3 \) Hz, 8H), 7.74 (d, \( J = 4.3 \) Hz, 8H), 1.54-1.29 (m, 114H). \(^{31}\)P{\(^{1}\)H} NMR (243 MHz, CD\(_3\)CN, 295 K) \( \delta \) 7.14 ppm (d, \( ^{2}J_{P-P} = 18.3 \) Hz, \(^{195}\)Pt satellites, \( ^{1}J_{P-P} = 3459.1 \) Hz), 1.11 ppm (d, \( ^{2}J_{P-P} = 18.3 \) Hz, \(^{195}\)Pt satellites, \( ^{1}J_{P-P} = 3459.1 \) Hz). ESI-TOF-MS: \( m/z \) 939.8862 \([4 - 6OTf]^6+\), 1157.6560 \([4 - 5OTf]^5+\), 1484.3114 \([4 - 4OTf]^4+\), 2028.7831 \([4 - 3OTf]^3+\).

Figure S2. \(^{1}\)H NMR spectra (600 MHz, CD\(_3\)CN, 295 K) recorded for metallacage 4.

Figure S3. \(^{31}\)P{\(^{1}\)H} NMR spectra (243 MHz, CD\(_3\)CN, 295 K) recorded for metallacage 4.
Figure S4. ESI-TOF-MS spectra of metallacage 4.

Figure S5. The side view (a) and top views (b-d) of crystal structure of metallacage 4. Crystal packing model of metallacage 4 viewed from (e) c axis, (f) a axis, and (g) b axis. Triethylphosphine units, hydrogen atoms, counterions, and solvent molecules were omitted for clarity. The CCDC number is 2102359.
**Figure S6.** The angle between diphenyl and porphyrin face in metallacage 4.

**Table S1.** Crystallographic data and refinement details for metallacage 4.

| Compound | 4 |
|----------|---|
| **Empirical formula** | C$_{212}$H$_{300}$F$_{12}$N$_{16}$O$_{28}$P$_{16}$Pt$_8$S$_4$ |
| **Fw** | 5933.14 |
| **Crystal system** | Triclinic |
| **Space group** | P-1 |
| **a/Å** | 18.646(2) |
| **b/Å** | 19.391(2) |
| **c/Å** | 22.255(3) |
| **α/°** | 83.426(3) |
| **β/°** | 69.021(3) |
| **γ/°** | 88.082(3) |
| **V/Å$^3$** | 7463.6(17) |
| **Z** | 1 |
| **$D_{calc}$/g cm$^{-3}$** | 1.320 |
| **F (000)** | 2944.0 |
| **μ/mm$^{-1}$** | 3.906 |
| **θ max** | 27.340 |
| **Independent reflns** | 32957 |
| **S** | 1.019 |
| **$R_1$; wR$_2$ [I>2σ(I)]** | 0.0880; 0.2764 |
**Figure S7.** Normalized absorption and emission spectra of the compounds 1 and metallacage 4 in CH$_3$CN/CHCl$_3$ (v/v = 9/1).

**Figure S8.** Near-infrared singlet oxygen phosphorescent emission spectra sensitized by ligand 1 and metallacage 4.
Figure S9. Time dependent UV/Vis absorption of the mixture of DPBF with 1 (a) and 4 (d) in CH$_3$CN/CHCl$_3$ (ν/ν = 9/1) upon light irradiation ($\lambda_{ex}$ = 405 nm). The concentration was 60 mM for DPBF, 10 mM for 1 and 5 mM for 4.

Figure S10. The plotting of $A(0)-A(t)$ at 417 nm against time (s) for the measurement in CH$_3$CN/CHCl$_3$ (ν/ν = 9/1), $A(t)$ is the absorbance at time t at 417 nm.
3. Host-guest complexation of metallacage 4 and polycyclic aromatic hydrocarbons

Scheme S2. Cartoon representations of host-guest complexation of metallacage 4 and polycyclic aromatic hydrocarbons (PAHs).

3.1 Determination of stoichiometry by UV-vis absorption spectra

Figure S11. (a) UV-vis absorption of metallacage 4 with G₁ in different molar ratios ([4] + [G₁] = 10 μM); (b) Job’s plot of the complex 4⋯G₁ in CH₃CN, showing a 1:1 stoichiometry.
Figure S12. (a) UV-vis absorption of metallacage 4 with G₂ in different molar ratios ([4] + [G₂] = 10 μM); (b) Job’s plot of the complex 4⊃G₂ in CH₃CN, showing a 1:1 stoichiometry.

Figure S13. UV-vis absorption of metallacage 4 with G₃ in different molar ratios ([4] + [G₃] = 10 μM); (b) Job’s plot of the complex 4⊃G₃ in CH₃CN, showing a 1:1 stoichiometry.
Figure S14. (a) UV-vis absorption of metallacage 4 with G₄ in different molar ratios ([4] + [G₄] = 10 μM); (b) Job’s plot of the complex 4⊃G₄ in CH₃CN, showing a 1:1 stoichiometry.

Figure S15. (a) UV-vis absorption of metallacage 4 with G₅ in different molar ratios ([4] + [G₅] = 10 μM); (b) Job’s plot of the complex 4⊃G₅ in CH₃CN, showing a 1:1 stoichiometry.
**Figure S16.** (a) UV-vis absorption of metallacage 4 with G₆ in different molar ratios ([4] + [G₆] = 10 μM); (b) Job’s plot of the complex 4⊃G₆ in CH₃CN, showing a 1:1 stoichiometry.

3.2 ESI-TOF-MS spectra of host-guest complexes

**Figure S17.** ESI-TOF-MS spectra of host-guest complexes.
3.3 Partial $^1$H NMR spectra of 4⊃PAHs

**Figure S18.** $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) recorded for $G_1$ (a), 4⊃$G_1$ (b), and 4 (c).

**Figure S19.** $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) recorded for $G_2$ (a), 4⊃$G_2$ (b), and 4 (c).
Figure S20. $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) recorded for $G_3$ (a), $4 \supset G_3$ (b), and 4 (c).

Figure S21. $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) recorded for $G_4$ (a), $4 \supset G_4$ (b), and 4 (c).
**Figure S22.** $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) recorded for $G_5$ (a), $4\supset G_5$ (b), and 4 (c).

**Figure S23.** $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) recorded for $G_6$ (a), $4\supset G_6$ (b), and 4 (c).
3.4 Determination of binding constant (K_a) by fluorometric titration method [S3]

**Figure S24.** Fluorescent emission of metallacage 4 at the fixed concentration of 80 µM in CH₃CN upon the addition of G₁.

**Figure S25.** Fluorescent emission of metallacage 4 at the fixed concentration of 80 µM in CH₃CN upon the addition of G₂.

**Figure S26.** Fluorescent emission of metallacage 4 at the fixed concentration of 40 µM in CH₃CN upon the addition of G₃.
Figure S27. Fluorescent emission of metallacage 4 at the fixed concentration of 40 µM in CH$_3$CN upon the addition of G$_4$.

Figure S28. Fluorescent emission of metallacage 4 at the fixed concentration of 50 µM in CH$_3$CN/CHCl$_3$ (v/v = 9/1) upon the addition of G$_1$.

Figure S29. Fluorescent emission of metallacage 4 at the fixed concentration of 50 µM in CH$_3$CN/CHCl$_3$ (v/v = 9/1) upon the addition of G$_2$. 
**Figure S30.** Fluorescent emission of metallacage 4 at the fixed concentration of 50 μM in CH$_3$CN/CHCl$_3$ (ν/ν = 9/1) upon the addition of G$_3$.

**Figure S31.** Fluorescent emission of metallacage 4 at the fixed concentration of 40 μM in CH$_3$CN/CHCl$_3$ (ν/ν = 9/1) upon the addition of G$_4$.

**Figure S32.** Fluorescent emission of metallacage 4 at the fixed concentration of 20 μM in CH$_3$CN/CHCl$_3$ (ν/ν = 9/1) upon the addition of G$_5$. 
Figure S33. Fluorescent emission of metallacage 4 at the fixed concentration of 10 μM in CH$_3$CN/CHCl$_3$ (v/v = 9/1) upon the addition of $G_6$. 

$K_a = (2.37 \pm 0.99) \times 10^7$ M$^{-1}$
3.5 Determination of X-ray structure of host-guest complexes

Table S2. Crystallographic data and refinement details for compounds 4⊃G₁, 4⊃G₂, 4⊃G₃, 4⊃G₄, 4⊃G₅, and 4⊃G₆.

| Compound | 4⊃G₁ | 4⊃G₂ | 4⊃G₃ | 4⊃G₄ | 4⊃G₅ | 4⊃G₆ |
|----------|------|------|------|------|------|------|
| Empirical formula | C₂₁₈.₅₀H₃₁₂.₅₀N₁₆O₁₆ | C₂₁₇H₃₁₁F₆N₁₆O₂₂ | C₂₂₆H₃₂₃F₆N₁₆O₂₂ | C₂₂₂H₃₅₆F₁₅N₁₆O₃₁ | C₂₃₂H₃₁₂F₁₂N₁₆O₂₈ | C₂₃₆H₃₁₄F₁₂N₁₆O₂₈ |
| Fw | 5475.57 | 5730.16 | 5851.35 | 6196.35 | 6185.44 | 6235.49 |
| Crystal system | Triclinic | Triclinic | Triclinic | Triclinic | Triclinic | Triclinic |
| Space group | P-1 | P-1 | P-1 | P-1 | P-1 | P-1 |
| a/Å | 21.961(3) | 22.3059(16) | 26.164(3) | 22.521(2) | 24.1802(9) | 19.0386(10) |
| b/Å | 23.310(3) | 22.1992(16) | 37.964(4) | 23.845(2) | 22.1123(9) | 18.9986(9) |
| c/Å | 33.005(4) | 32.445(2) | 33.015(4) | 33.434(3) | 33.3226(14) | 41.733(2) |
| α/° | 92.633(7) | 90 | 90 | 89.418(5) | 90 | 90 |
| β/° | 92.871(7) | 106.818(2) | 94.838(3) | 84.325(5) | 98.037(2) | 99.533(2) |
| γ/° | 111.856(7) | 90 | 90 | 63.202(4) | 90 | 90 |
| V/Å³ | 15624(3) | 15378.5(19) | 32678(7) | 15936(3) | 17641.9(12) | 14886.5(13) |
| Z | 2 | 2 | 4 | 2 | 2 | 2 |
| D_calcd/g cm⁻³ | 1.164 | 1.237 | 1.189 | 1.291 | 1.164 | 1.391 |
|                | 5455.0 | 5702.0 | 11672.0 | 6154.0 | 6152.0 | 6204.0 |
|----------------|--------|--------|---------|--------|--------|--------|
| $F (000)$      |        |        |         |        |        |        |
| $\mu \text{mm}^{-1}$ | 5.369  | 3.772  | 3.552   | 5.427  | 4.854  | 5.756  |
| $\theta \text{max}$ | 51.702 | 26.476 | 27.487  | 57.460 | 51.450 | 57.016 |
| Independent reflns | 51593  | 31541  | 37047   | 65213  | 29168  | 30003  |
| $S$            | 1.099  | 1.027  | 1.284   | 0.996  | 1.175  | 1.019  |
| $R_I$; $wR_2$ [$I>2\sigma(I)$] | 0.1200; 0.3058 | 0.0880; 0.2764 | 0.1100; 0.3025 | 0.0846; 0.2744 | 0.0720; 0.2114 | 0.0671; 0.1720 |
4. The photooxidation of $G_1$ by metallacage 4

Scheme S3. Cartoon representations of photooxidation of $G_1$ by metallacage 4

Figure S34. $^1$H DOSY NMR spectra (400 MHz, CD$_3$CN, 295 K) recorded for $4\supset G_1$.

Figure S35. $^1$H DOSY NMR spectra (400 MHz, CD$_3$CN, 295 K) recorded for metallacage $4\supset G_1$ irradiated by light at 405 nm in 10 min.
**Figure S36.** Partial $^1$H NMR spectra (600 MHz, 295 K) of metallacage 4 at the fixed concentration of 500 μM in CD$_3$CN upon the addition of G$_1$.

**Figure S37.** Plot of the chemical shifts of H$_{2o}$ and H$_{2i}$ of metallacage 4 versus the concentration of G$_1$.$^{[S3]}$
5. The construction of reversible host-guest complexation

5.1 Synthesis of $G_8$

![Chemical structure](image)

9,10-Dibromoanthracene (333 mg, 1 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (120 mg, 0.16 mmol), CuI (200 mg, 1.04 mmol), and but-3-yn-1-ol (210 mg, 3 mmol) were placed in a round bottom flask and dissolved in dry THF (15 mL) and dry i-Pr$_2$NH (15 mL). After degassing by three freeze-pump-thaw cycles the flask was filled with argon. The mixture was further stirred at 80 °C for 18 h. Chromatography (hexane) afforded the product which was further recrystallized by dichloromethane and petroleum ether to give $G_8$ as orange crystals (265 mg, 84.3%). $^1$H NMR (600 MHz, CD$_3$CN) $\delta$ 8.60 (dd, $J = 6.6$, 3.3 Hz, 4H), 7.65 (dd, $J = 6.7$, 3.2 Hz, 4H), 3.89 (m, 4H), 3.17 (t, $J = 5.9$ Hz, 2H), 2.94 (t, $J = 6.5$ Hz, 4H).

![Figure S38. $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) recorded for $G_8$.](image)

5.2 Synthesis of $G_{11}$

![Chemical structure](image)
9-Bromo-10-phenlanthracene (333 mg, 1 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (60 mg, 0.08 mmol), CuI (100 mg, 0.52 mmol), and phenylacetylene (122 mg, 1.2 mmol) were placed in a round bottom flask and dissolved in dry THF (10 mL) and dry $i$-Pr$_2$NH (10 mL). After degassing by three freeze-pump-thaw cycles the flask was filled with argon. The mixture was further stirred at 80 °C for 6 h. Chromatography (hexane) afforded the product which was further recrystallized by dichloromethane and methanol to give $G_{11}$ as yellow crystals (282 mg, 80%).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.74 (d, $J = 8.6$ Hz, 2H), 7.80 (d, $J = 7.1$ Hz, 2H), 7.68 (d, $J = 8.8$ Hz, 2H), 7.59-7.54 (m, 5H), 7.46-7.38 (m, 7H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 138.52, 138.42, 132.28, 131.69, 131.67, 131.17, 129.95, 128.57, 128.51, 128.40, 128.39, 127.68, 127.42, 126.92, 126.34, 125.61, 123.71, 117.44, 100.95, 86.54. The NMR spectra of $G_{11}$ match well with reported results.$^{52}$

Figure S39. $^1$H NMR spectra (600 MHz, CDCl$_3$, 295 K) recorded for $G_{11}$. 
$^{13}$C NMR spectra (150 MHz, CDCl$_3$, 295 K) recorded for G$_{11}$.

Figure S40.

5.3 The screen of guests for the construction of reversible host-guest complexation.

Owing to the low thermal stability of epidioxyanthracene (G$_{1}$-O$_2$), it cannot be converted to anthracene G$_1$ efficiently. Therefore, we screened a series of anthracene derivatives to get a suitable guest molecule for the construction of a reversible host-guest complexation. 9,10-bis(2-phenylethynyl)anthracene (G$_7$) showed good host-guest interactions with metallacage 4 (Figure S41). It can also be converted into epidioxyanthracene analogue by irradiation with light at 405 nm. However, the endoperoxide is not stable at room temperature and quickly went back to G$_7$, which is not suitable for the construction of a bistable host-guest complexation. Compound G$_9$ also showed good interactions with metallacage 4 (Figure S44), but the encapsulated guest failed to convert into endoperoxide by irradiation, owing to the
high stability of $G_9$. Due to steric hindrance of the benzene rings on both sides, $G_{10}$ showed a poor host-guest interaction with metallacage $4$ (Figure S45), so it is not suitable for the reversible complexation. Compound $G_8$ showed good host-guest interactions with metallacage $4$ (Figure S42). However, the photoirradiation of $4\supset G_8$ for $3.0$ h cannot fully convert $G_8$ into its epidioxy form (Figure S43). Finally, $10$-phenyl-$9$-(2-phenylethynyl)anthracene ($G_{11}$) was chosen as the guest for construction of this reversible host-guest complex because its endoperoxide $G_{11}$-$O_2$ showed moderate stability at room temperature and could be converted back to $G_{11}$ upon heating quickly. (Figure S46 and S52)

![Diagram](image)

**Figure S41.** Partial $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) of $G_7$, $4\supset G_7$, and $4$. $[4] = [G_7] = 1.00$ mM.
Figure S42. Partial $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) of G$_8$, 4$\uparrow$G$_8$, and 4. [4] = [G$_8$] = 1.00 mM.

Figure S43. Partial $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) of 4$\uparrow$G$_8$ irradiated by light at 405 nm in different times. [4] = [G$_8$] = 1.00 mM.
Figure S44. Partial $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) of $G_9$, $4 \supset G_9$, and $4$. $[4] = [G_9] = 1.00$ mM.

Figure S45. Partial $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) of $G_{10}$, $4 \supset G_{10}$, and $4$. $[4] = [G_{10}] = 1.00$ mM.
Figure S46. (a) UV-vis absorption of metallacage 4 with G_{11} in different molar ratios ([4] + [G_{11}] = 10 \mu M); (b) Job’s plot of the complex 4\supset G_{11} in CH\textsubscript{3}CN, showing a 1:1 stoichiometry; (c) ESI-TOF-MS spectra of the complex 4\supset G_{11}; The side view (d) and top views (e) of crystal structure of complex 4\supset G_{11}. 
**Figure S47.** Partial $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) of G$_{11}$ at the fixed concentration of 1.00 mM in CD$_3$CN upon the addition of metallacage 4.

**Figure S48.** Partial $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) of G$_{11}$, $G_{11}$, and 4. [4] = [G$_{11}$] = 1.00 mM.
**Figure S49.** Partial $^1$H NMR spectra (600 MHz, CD$_3$CN, 295 K) of metallacage 4 at the fixed concentration of 0.5 mM in CD$_3$CN upon the addition of G$_{11}$.

**Figure S50.** Plot of the chemical shift of H$_b$ and H$_{3o}$ of metallacage 4 versus the concentration of G$_{11}$ added.$^{[S3]}$
**Figure S51.** Fatigue cycles for reversible host-guest system based on metallacage 4 and $G_{11}$ characterized by fluorescence spectroscopy ($\lambda_{ex} = 405$ nm).

6. **References**

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