

Supplementary Information

**Metallacage-Crosslinked Free-Standing Supramolecular Networks via
Photo-induced Copolymerization for Photocatalytic Water
Decontamination**

Rongrong Li,^{#,1} Haixin Zhang,^{#,2} Yali Hou,¹ Lingyan Gao,^{*,2} Dake Chu,^{*,3} and Mingming Zhang^{*,1}

Supplementary Methods

General materials and instrumentation

Reagents and deuterated solvents were used as received. NMR spectra were recorded with Bruker Avance spectrometers operating at 400 MHz or 600 MHz. ^1H NMR shifts were measured relative to residual solvent signals, while $^{31}\text{P}\{^1\text{H}\}$ NMR shifts were referenced to an external 85% H_3PO_4 sample. Mass spectra were obtained using a Micromass Quattro II spectrometer with electrospray ionization, controlled by MassLynx software. UV-Vis spectroscopy was performed with a Lambda 950 spectrophotometer, and fluorescence measurements were conducted using either an Edinburgh FLS9 or a Hitachi F-7000 spectrophotometer. X-ray diffraction was carried out on a Bruker D8 VENTURE PHOTON II MetalJet, with crystal samples cryoprotected in paratone oil and cooled with nitrogen. Data were corrected for absorption with SADABS, and structures were solved and refined using OLEX2 1.2, applying F2 for all reflections. Scanning electron microscopy (SEM) images were acquired with a Hitachi SU8010. The stress-strain tests were taken with an INSTRON 3343 universal mechanical test machine. Differential Scanning Calorimetry (DSC) was carried out on a DSC250 analyzer in an N_2 atmosphere from room temperature to 200 $^\circ\text{C}$ (5 $^\circ\text{C}/\text{min}$). Electron spin resonance (ESR) measurements were conducted with a Bruker EMXplus-6/1 spectrometer. Fluorescence titration experiments involved adding varying amounts of guest molecules to $\text{CH}_3\text{CN}/\text{CHCl}_3$ (1:1) or CH_3CN solutions of metallacages, with the metallacage concentration fixed at 10.0 μM . The data were fitted using the following equation:

$$\delta = (\Delta\delta_{\text{max}}/[\text{H}]_0) (0.5[\text{G}] + 0.5 ([\text{H}]_0 + 1/K_a) - (0.5([\text{G}]^2 + (2[\text{G}](1/K_a - [\text{H}]_0)) + (1/K_a + [\text{H}]_0)^2)^{0.5}))$$

In these equations, δ represents the fluorescence change of the metallacages upon the addition of guest molecules, $\Delta\delta_{\text{max}}$ denotes the maximum fluorescence intensity change when the metallacages are fully complexed, $[\text{H}]_0$ is the constant concentration of the metallacages (10.0 μM), and $[\text{G}]$ is the concentration of the guest molecules. Each fluorescence titration experiment was conducted in triplicate.

Singlet oxygen measurements

Singlet oxygen generation studies were conducted using ESR with TEMP (0.2 M) as the spin trapping agent under light irradiation.

Singlet oxygen quantum yields were measured in acetonitrile with a LED lamp ($\lambda = 520$ nm) as the light source. Prior to the experiment, the absorption of the photosensitizers **1**, **4**, **6a**, **6b**, **6c** and **7** at the excitation wavelength of 520 nm was adjusted to approximately 0.25. Quantum yields for singlet oxygen generation were determined by monitoring the decrease in absorption of 1,3-diphenylisobenzofuran (DPBF) at 410 nm, which is caused by its photooxidation. Time-dependent absorption spectra of DPBF were recorded at 1-minute intervals for the homogeneous phase. Singlet oxygen quantum yields (Φ_{Δ}) were calculated using a relative method with optically matched solutions, comparing the decrease in absorbance of DPBF sensitized by the photosensitizers to that sensitized by rose bengal (RB) ($\Phi_{\Delta} = 0.54$) as a reference, according to the following equation:

$$\Phi_{\Delta}^S = \Phi_{\Delta}^{RB} \frac{m^{SF^{RB}}}{m^{RBF^S}}$$

Superscripts “S” and “RB” refer to the photosensitizers and rose bengal, respectively. “ Φ_{Δ} ” represents the quantum yield of singlet oxygen. The parameter “m” denotes the slope of the plot showing the change in DPBF absorbance at 410 nm over irradiation time, while “F” is the absorption correction factor, defined as $F=1-10^{-OD}$, where OD is the absorbance of the photosensitizer.

DPBF could react with $^1O_2$ in a 1:1 molar ratio, which was a valuable tool for $^1O_2$ quantification¹. Therefore, the standard curve (Supplementary Fig. 38) can also be obtained from the absorbance of a series of DPBF solutions sensitized by the photosensitizers in the above experiments.

Cell culture

In this study, Gram-negative bacterial strain *E. coli* (*E. coli*, ATCC25922) and Gram-positive bacterial strain *S. aureus* (*S. aureus*, ATCC25923) were utilized. The bacteria were initially streaked from -20 °C glycerol stocks on lysogeny broth (LB or TSB) agar plates. After growth on LB agar plates, the cells were cultured from a fresh single colony in LB. All experiments were conducted at 37 °C, and all glassware used in this study was sterilized prior to testing.

Antibacterial activity of dyes

The final concentrations of *S. aureus* and *E. coli* bacterial suspensions used in the antibacterial test were 10^5 CFU/mL in phosphate-buffered saline (PBS). Two dye solutions, **G**₃ and **G**₅, were initially prepared at a concentration of 0.1 g/L in water and then diluted with the bacterial suspension to a final

concentration of 0.01 g/L in a 96-well culture plate. The cultures were then incubated at 37 °C for 24 h. Following incubation, 100 µL of the planktonic bacterial suspensions were serially diluted and plated onto nutrient agar plates. The bacterial colonies were recorded after 24 h of incubation at 37 °C. Each experiment was performed in triplicate.

Antibacterial activity of dye mixed with network under light irradiation

S. aureus and *E. coli* bacterial suspensions used in the antibacterial test were prepared at a concentration of 10^8 CFU/mL in phosphate-buffered saline (PBS) (CFU stands for colony-forming units). A 3 mL portion of the prepared dye solution was mixed with 0.5 mL of the bacterial suspension for illumination. After exposure to light, 100 µL of the planktonic bacterial suspensions were serially diluted and plated onto nutrient agar plates. The bacterial colonies were counted after incubation at 37 °C for 24 h. Each experiment was conducted in triplicate.

Scanning electron microscopy (SEM)

SEM was used to observe the morphological changes in *S. aureus* and *E. coli* after treatment with different ligands or networks, with or without 520 nm irradiation for 30 min. The treated bacteria were washed twice with PBS and then fixed with 4 % glutaraldehyde overnight at 4 °C. Following fixation, the bacteria were washed with sterile PBS and sequentially dehydrated using increasing concentrations of ethanol (30 %, 50 %, 70 %, 80 %, 90 %, and 100 %) for 15 min each. The dehydrated bacteria were then placed onto a silicon wafer and dried under vacuum conditions overnight. Prior to observation, the specimens were coated with platinum.

Statistical analysis

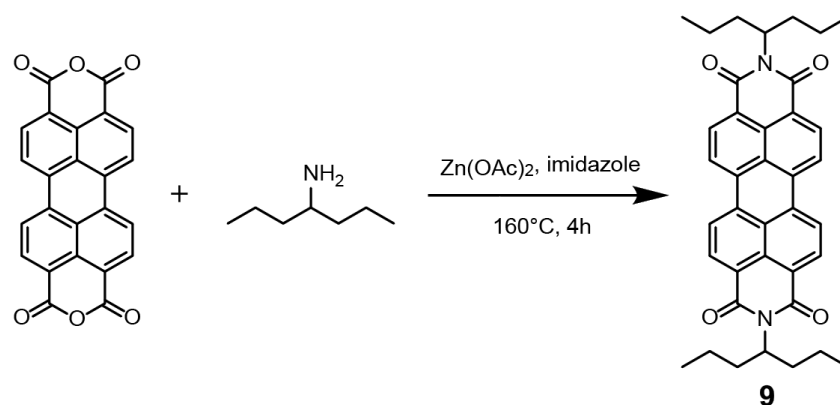
Data are represented as mean $\pm$ standard deviation (S.D). Group differences were conducted by one-way ANOVA with Tukey's post-hoc test. *P*-values < 0.05 were considered as statistically significant (**p* < 0.05 , ***p* < 0.01 , ****p* < 0.001 , *****p* < 0.0001). All statistical analyses were performed with GraphPad Prism 9.

Plant Cultivation

Green pea seeds were selected as the research subject. First, the seeds were cleaned and any damaged seeds were removed. The remaining seeds were then soaked in an appropriate amount of water for 12

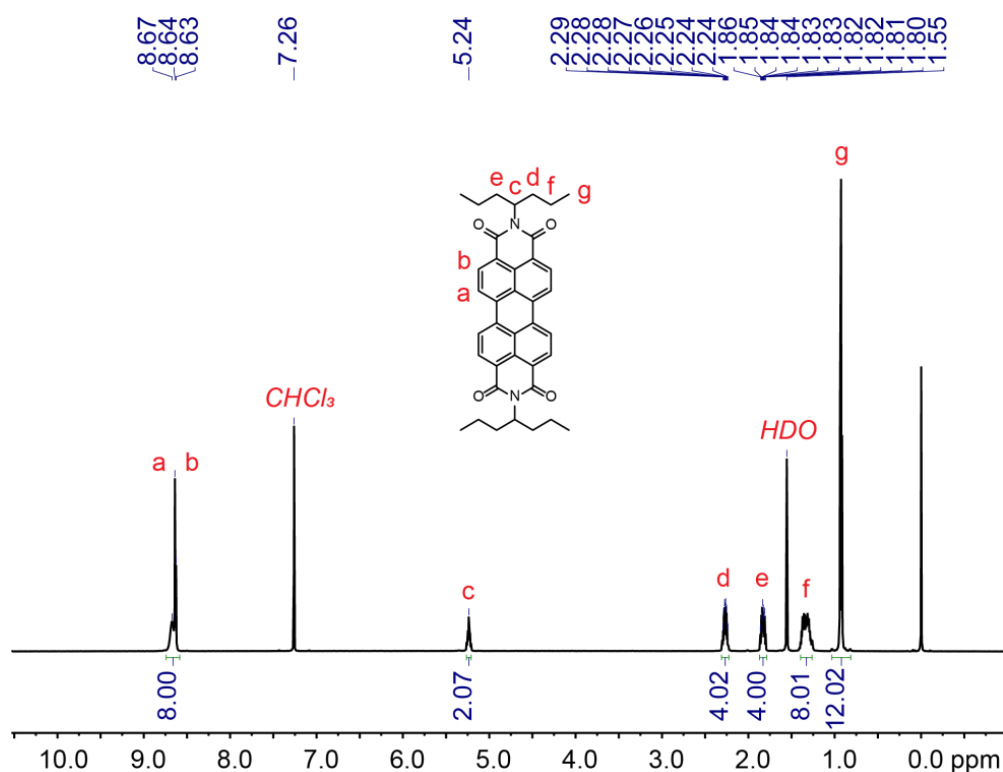
h. Wastewater (**G**₃, **G**₄, **G**₅ and **G**₆ aqueous solution with the concentration of 0.02 g/L, *S. aureus* and *E. coli* solution with the concentration of 10⁸ CFU/mL) and degraded water (wastewater treated by **6c** after 520 nm illumination for 30 min) were poured into two separate trays, each covered with a perforated grid tray. Equal amounts of the soaked seeds were evenly spread on the two grid trays, ensuring that the seeds did not overlap. The seeds were then sprayed with water and covered with a layer of seedling paper to maintain humidity. After the seeds sprouted to about 1 cm, the seedling papers were removed. The growth of the plants and the condition of the roots were recorded on the 4th and 7th days for both groups. The entire growth process was carried out at room temperature under natural light.

Supplementary Notes 1. Synthetic procedures and characterization data

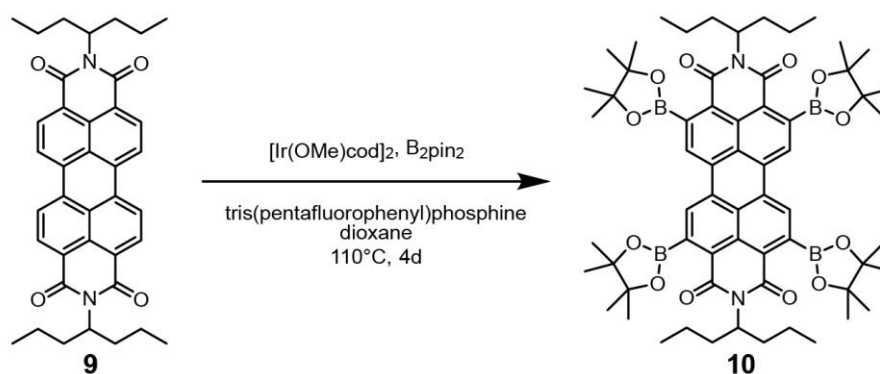


Supplementary Fig. 1 Synthesis of compound **9**.

3,4,9,10-Perylenetetracarboxylic dianhydride (5.00 g, 12.70 mmol), Zn(OAc)₂ (3.85 g, 20.40 mmol) and imidazole (34.69 g, 510 mmol) were added in 4-heptylamine (4.80 g, 42.00 mmol) under a N₂ atmosphere and the whole system was stirred at 160 °C for 5 h. After being cooled to room temperature, the reaction mixture was filtrated and the residue was washed with methanol. The crude product was purified by flash column chromatography (CH₂Cl₂) to give compound **9** (6.75 g, 89%) as a red solid. ¹H NMR (600 MHz, CDCl₃) δ 8.65 (t, *J* = 14.0 Hz, 8H), 5.24 (s, 2H), 2.26 (ddd, *J* = 14.9, 9.6, 4.9 Hz, 4H), 1.87 – 1.79 (m, 4H), 1.39 – 1.26 (m, 8H), 0.93 (t, *J* = 7.4 Hz, 12H). The ¹H NMR spectrum of **9** matches well with reported results ².

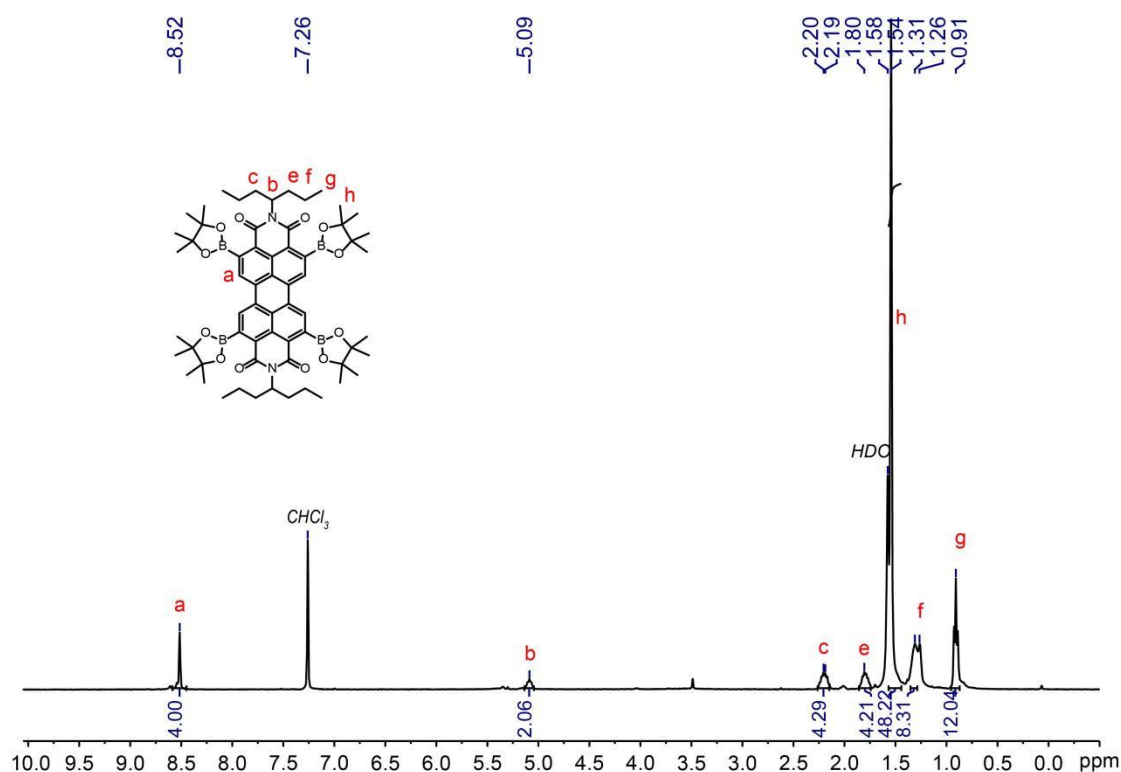


Supplementary Fig. 2 ^1H NMR spectrum (600 MHz, CDCl_3 , 295 K) recorded for **9**.

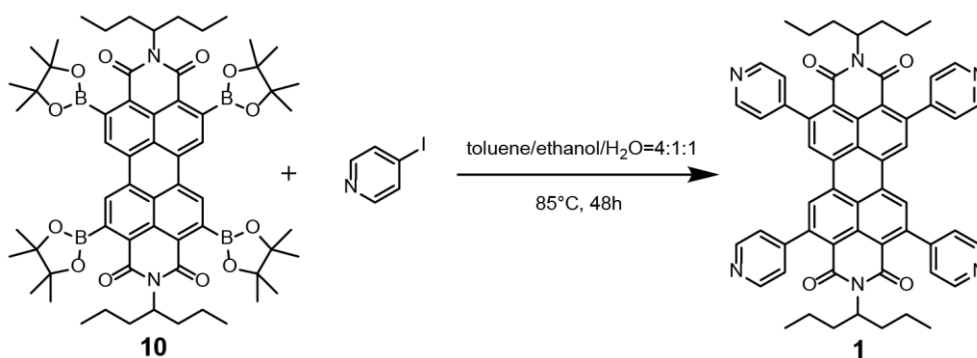


Supplementary Fig. 3 Synthesis of compound **10**.

A mixture of compound **9** (1.32 g, 2.25 mmol), $[\text{Ir}(\text{OMe})\text{cod}]_2$ (0.15 g, 0.23 mmol), tris(pentafluorophenyl)phosphine (0.48 g, 0.90 mmol), and bis(pinacolato)diboron (4.57 g, 18.00 mmol) in 30.0 mL of dry dioxane was stirred under nitrogen at 120 °C for 4.5 days. After being cooled to room temperature, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (dichloromethane : ethyl acetate = 1:1) to give compound **10** (0.30 g, 61%) as a red solid. ^1H NMR (400 MHz, CDCl_3 , 295 K) δ 8.52 (s, 4H), 5.04 – 5.13 (m, 2H), 2.15 – 2.24 (m, 4H), 1.75 – 1.84 (m, 4H), 1.54 (s, 48H), 1.31 – 1.39 (m, 8H), 0.91 (t, J = 7.3 Hz, 12H). The ^1H NMR spectrum of **10** matches well with reported results².

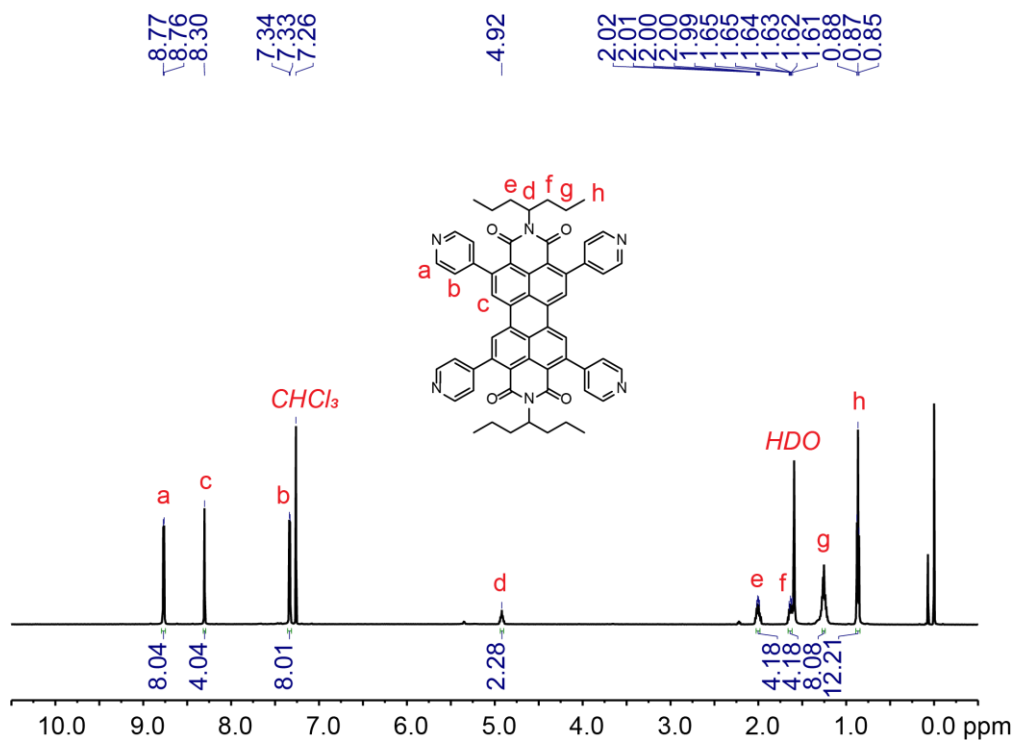


Supplementary Fig. 4 ^1H NMR spectrum (600 MHz, CDCl_3 , 295 K) recorded for **10**.

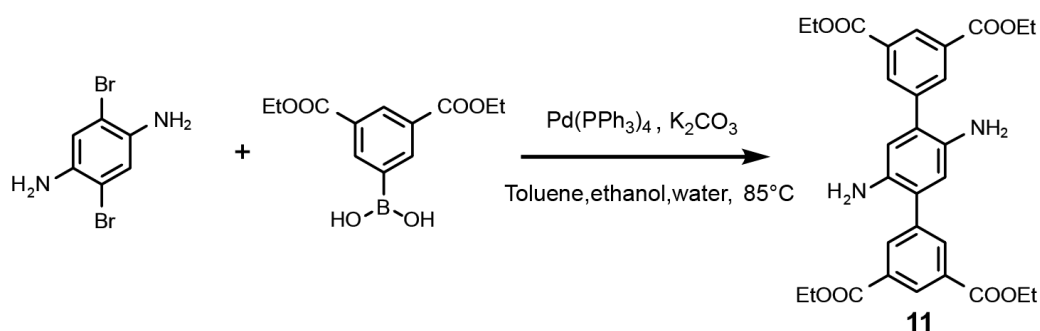


Supplementary Fig. 5 Synthesis of compound **1**.

To compound **10** (1.50 g, 1.40 mmol), 4-pyridylboronic acid (3.40 g, 16.8 mmol), anhydrous Cs_2CO_3 (9.50 g, 69.00 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.32 g, 0.25 mmol) in toluene (70.0 mL), H_2O (15.0 mL) and ethanol (15.0 mL) were added. Then the reaction mixture was stirred at 85 °C for 48 h under nitrogen atmosphere. After being cooled to room temperature, the product was concentrated to give a crude product which was purified by flash column chromatography with $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ (50:1, v/v) as the eluent to afford compound **1** (0.75 g, 60%) as a red powder. ^1H NMR (600 MHz, CDCl_3) δ 8.77 (s, 8H), 8.30 (s, 4H), 7.33 (d, J = 4.9 Hz, 8H), 4.92 (s, 2H), 2.04 – 1.97 (m, 4H), 1.64 – 1.60 (m, 5H), 1.26 (s, 8H), 0.87 (t, J = 7.3 Hz, 12H). The ^1H NMR spectrum of **1** matches well with reported results³.

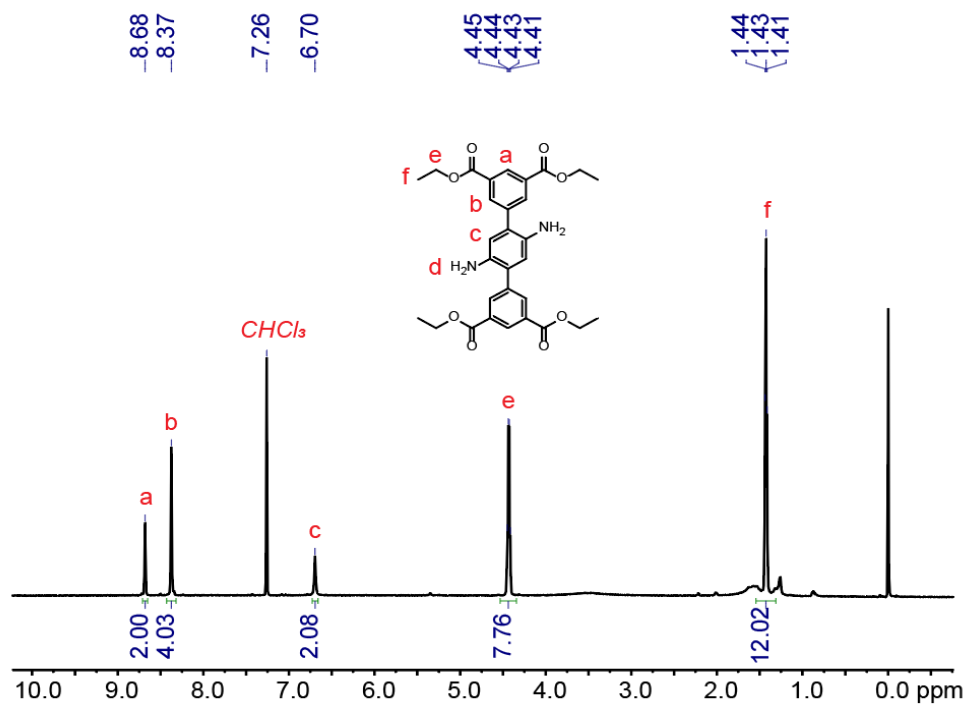


Supplementary Fig. 6 ^1H NMR spectrum (600 MHz, CDCl_3 , 295 K) recorded for **1**.

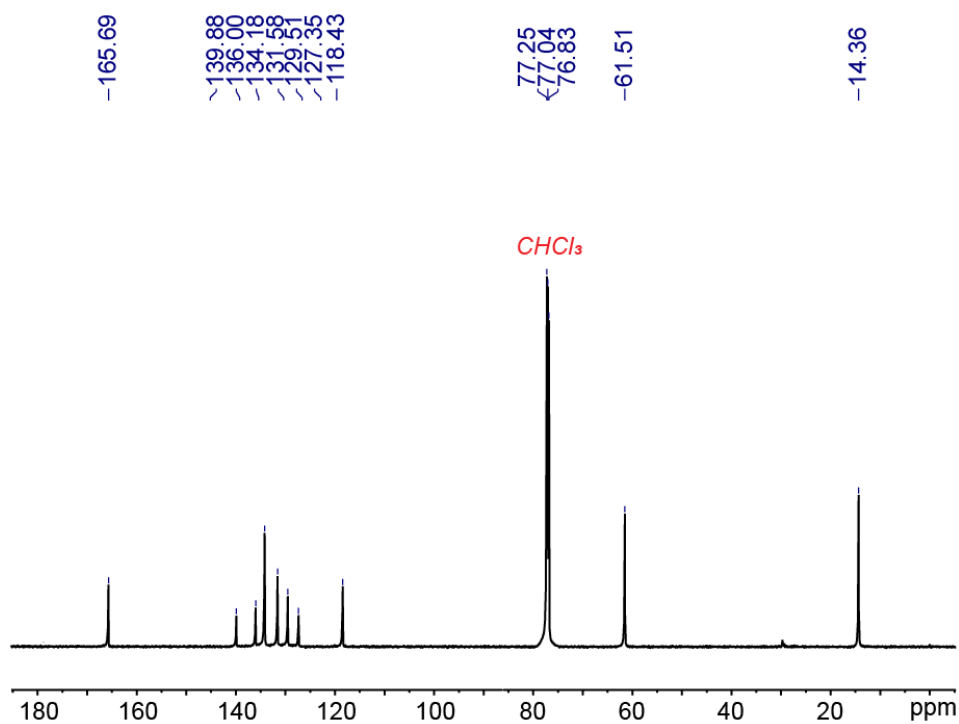


Supplementary Fig. 7 Synthesis of compound **11**.

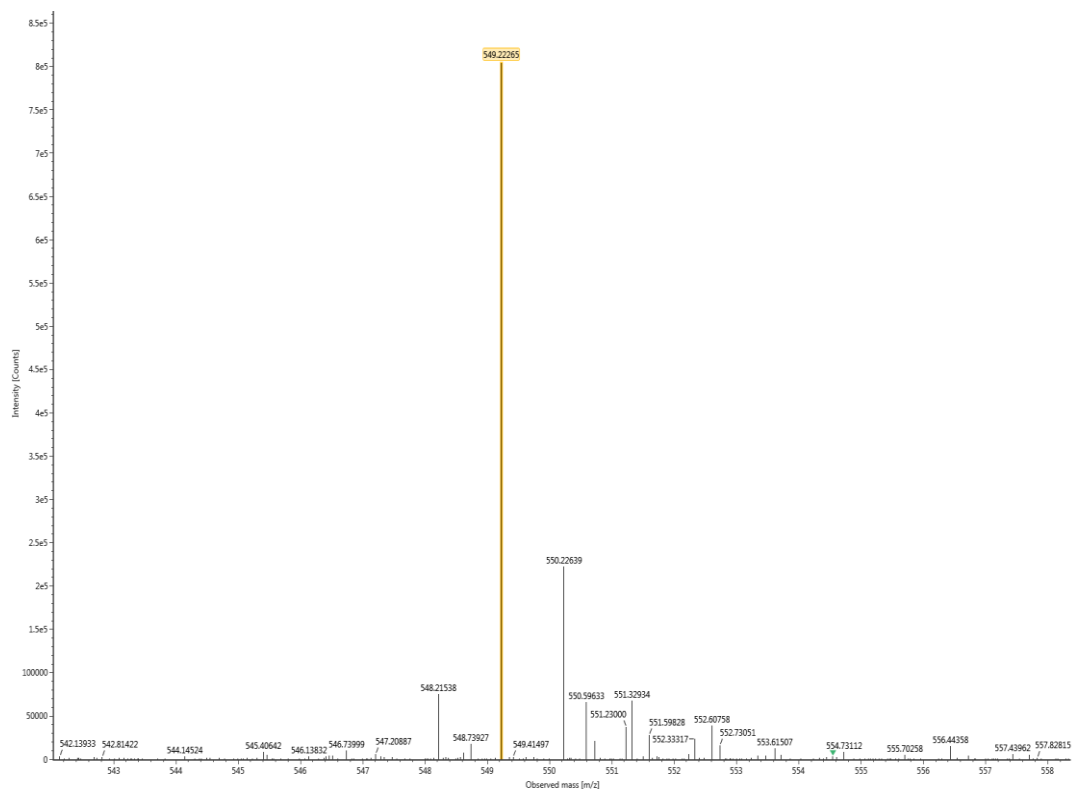
2,5-Dibromobenzene-1,4-diamine (1.00 g, 3.76 mmol), (3,5-bis(ethoxycarbonyl)phenyl) boronic acid (3.00 g, 11.28 mmol), K_2CO_3 (2.08 g, 15.04 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.22 g, 0.19 mmol) were added to a 250 mL flask. Then toluene, ethanol and water (4:1:1, 120 mL) were added to the flask under nitrogen. The system was degassed and purged with nitrogen by freeze-pump-thaw 3 times. The mixture was heated at 85 °C for 2 days. After cooling, the solvents were removed and the residue was washed with acetone to give a crude product which was purified by flash column chromatography (CH_2Cl_2 : CH_3OH = 200:1) to give compound **11** (1.82 g, 88.3%) as a solid. ^1H NMR (600 MHz, CDCl_3 , 295 K) δ 8.68 (s, 2H), 8.37 (s, 4H), 6.70 (s, 2H), 4.43 (dd, J = 14.1, 7.0 Hz, 8H), 1.43 (t, J = 7.1 Hz, 12H). ESI-HR-MS: m/z 549.2227 [**11** + H] $^+$, calcd. for $[\text{C}_{30}\text{H}_{33}\text{N}_2\text{O}_8]^+$, 549.2231.



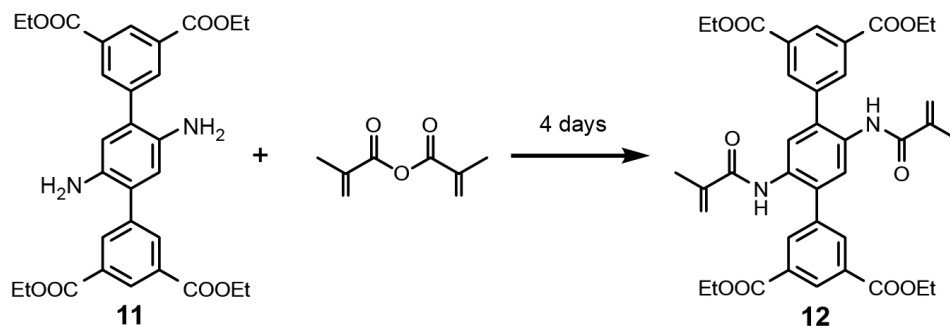
Supplementary Fig. 8 ¹H NMR spectrum (600 MHz, CDCl₃, 295 K) recorded for **11**.



Supplementary Fig. 9 ¹³C NMR spectrum (151 MHz, CDCl₃, 295 K) recorded for **11**.

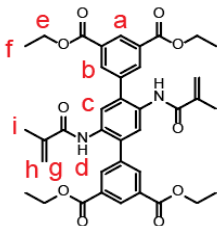


Supplementary Fig. 10 ESI-HR-MS spectrum of **11**.



Supplementary Fig. 11 Synthesis of compound **12**.

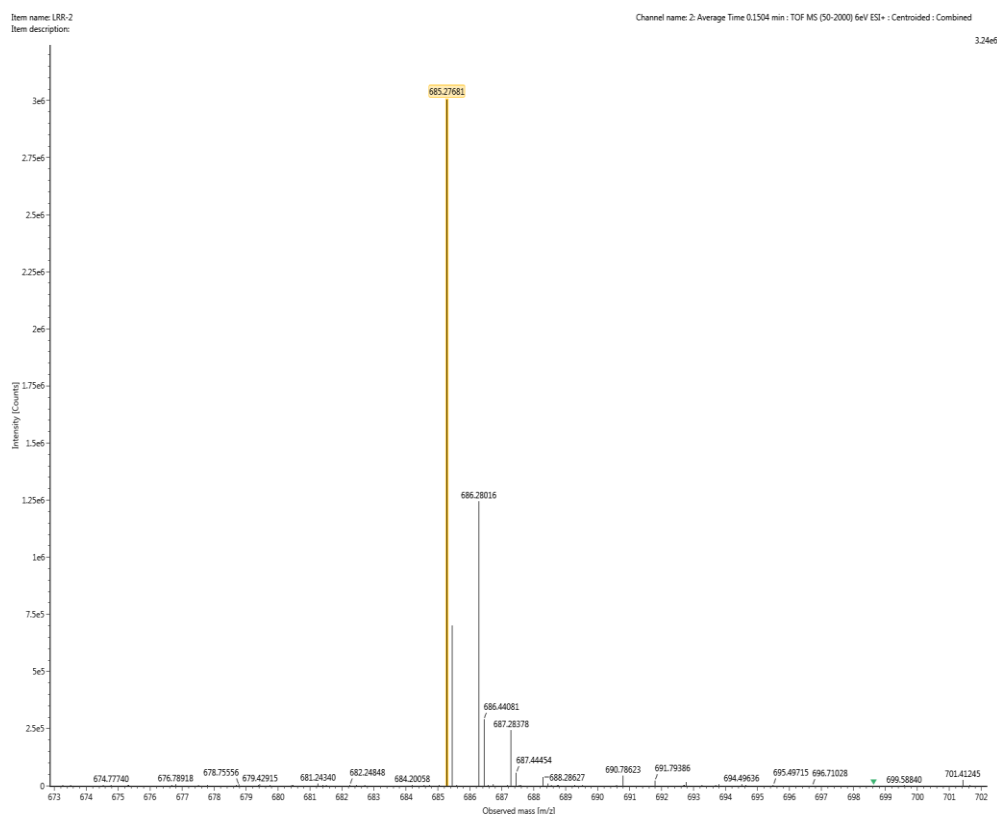
The as-synthesized compound **11** was mixed with methacrylic anhydride in CH_2Cl_2 and kept in a closed vial for 4 days. The solids were washed several times with fresh CH_2Cl_2 and then dried under vacuum at 50°C for 12 h to obtain the compound **12**. ^1H NMR (600 MHz, CDCl_3 , 295 K) δ 8.78 – 8.75 (m, 2H), 8.43 (s, 2H), 8.34 (d, $J = 1.5$ Hz, 4H), 7.49 (s, 2H), 5.58 (s, 2H), 5.33 (s, 2H), 4.44 (dd, $J = 14.3, 7.1$ Hz, 8H), 1.86 (s, 6H), 1.42 (t, $J = 7.1$ Hz, 12H). ESI-HR-MS: m/z 685.2768 [**12** + H] $^+$, calcd. for $[\text{C}_{38}\text{H}_{41}\text{N}_2\text{O}_{10}]^+$, 685.2756.



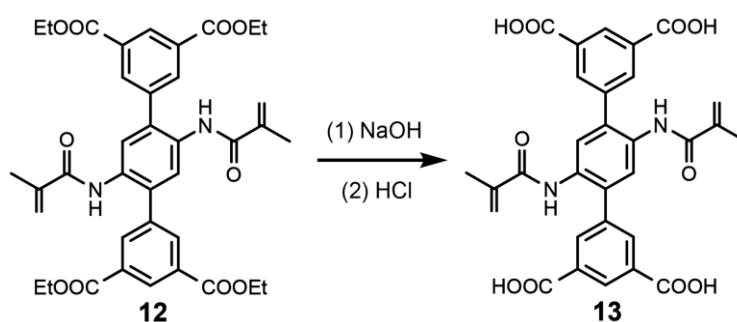
Supplementary Fig. 12 ^1H NMR spectrum (600 MHz, CDCl_3 , 295 K) recorded for **12**.



Supplementary Fig. 13 ^{13}C NMR spectrum (151 MHz, CDCl_3 , 295 K) recorded for **12**.

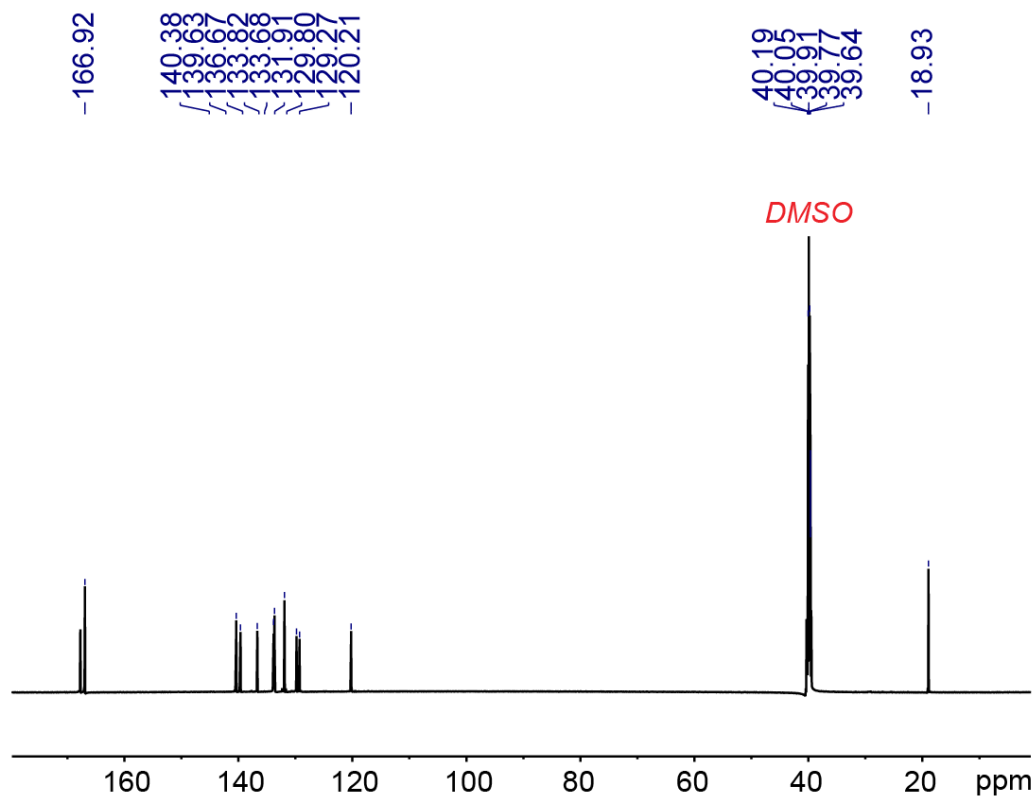
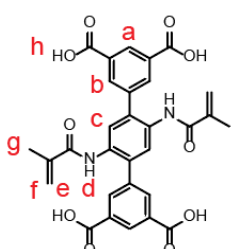


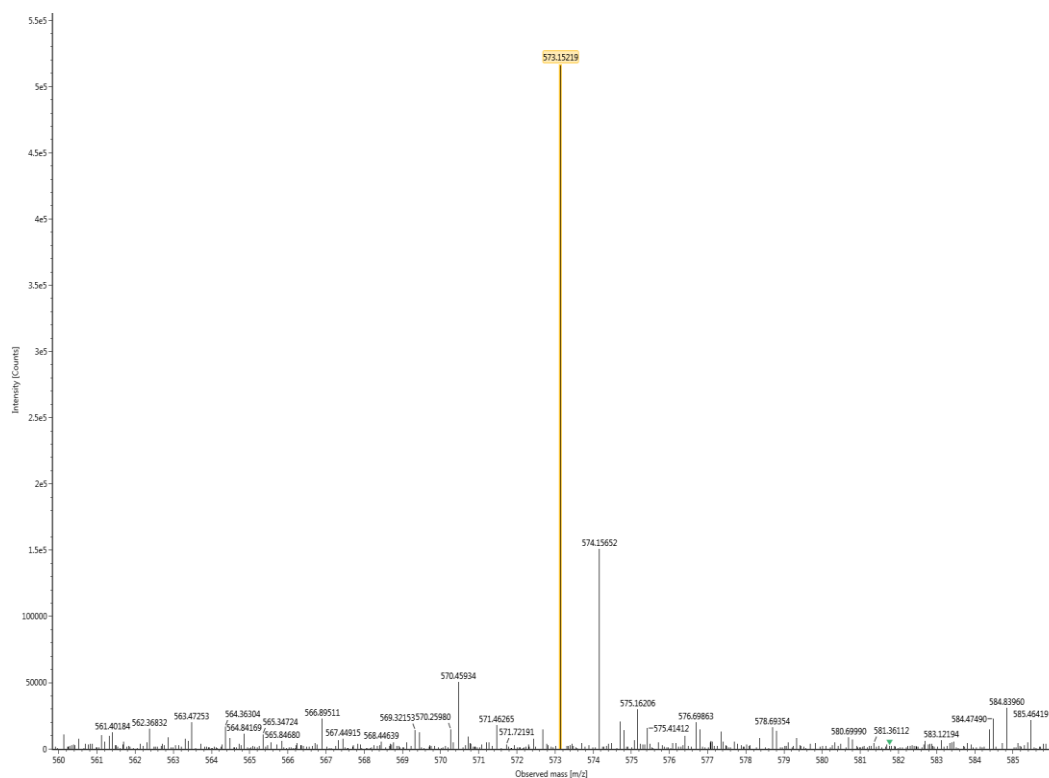
Supplementary Fig. 14 ESI-HR-MS spectrum of **12**.



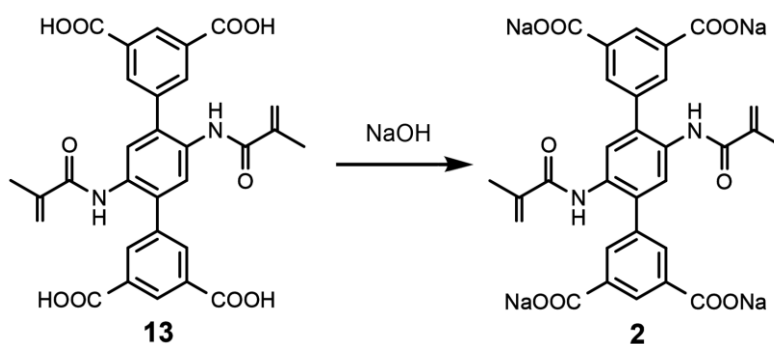
Supplementary Fig. 15 Synthesis of compound **13**.

Compound **12** (0.05 g, 0.07 mmol) and NaOH (0.04 g, 1.10 mmol) were added in ethanol (12 mL), THF (12 mL) and H₂O (4 mL). The mixture was stirred in 70 °C for 12 h. Then the solvent were evaporated under reduced pressure and the pH was adjusted to 1 with using 1 M HCl to give a white precipitate. The precipitate was filtered and washed with H₂O to give **13** (0.04 g, 96%) as a white solid. ¹H NMR (600 MHz, DMSO, 295 K) δ 13.35 (s, 4H), 9.71 (s, 2H), 8.45 (s, 2H), 8.23 (d, J = 1.5 Hz, 4H), 7.50 (s, 2H), 5.61 (s, 2H), 5.37 (s, 2H), 1.81 (s, 6H). ESI-HR-MS: m/z 573.1522 [**13** + H]⁺, calcd. for [C₃₀H₂₅N₂O₁₀]⁺, 573.1522.



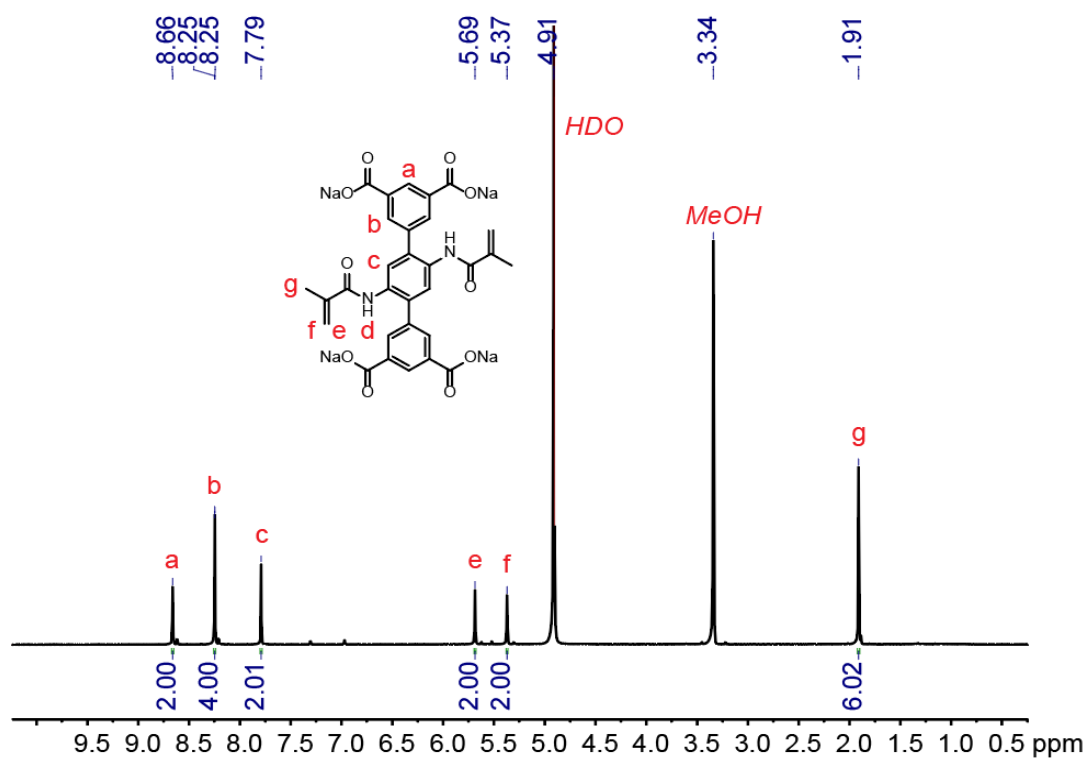


Supplementary Fig. 18 ESI-HR-MS spectrum of **13**.

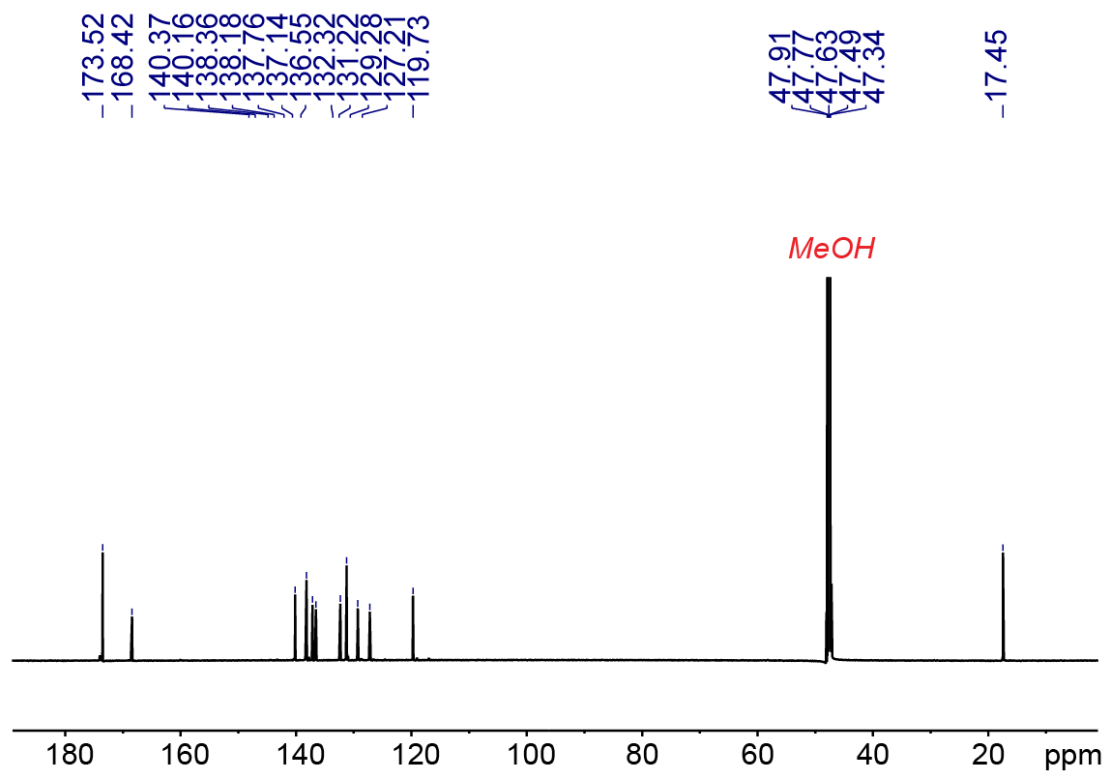


Supplementary Fig. 19 Synthesis of compound **2**.

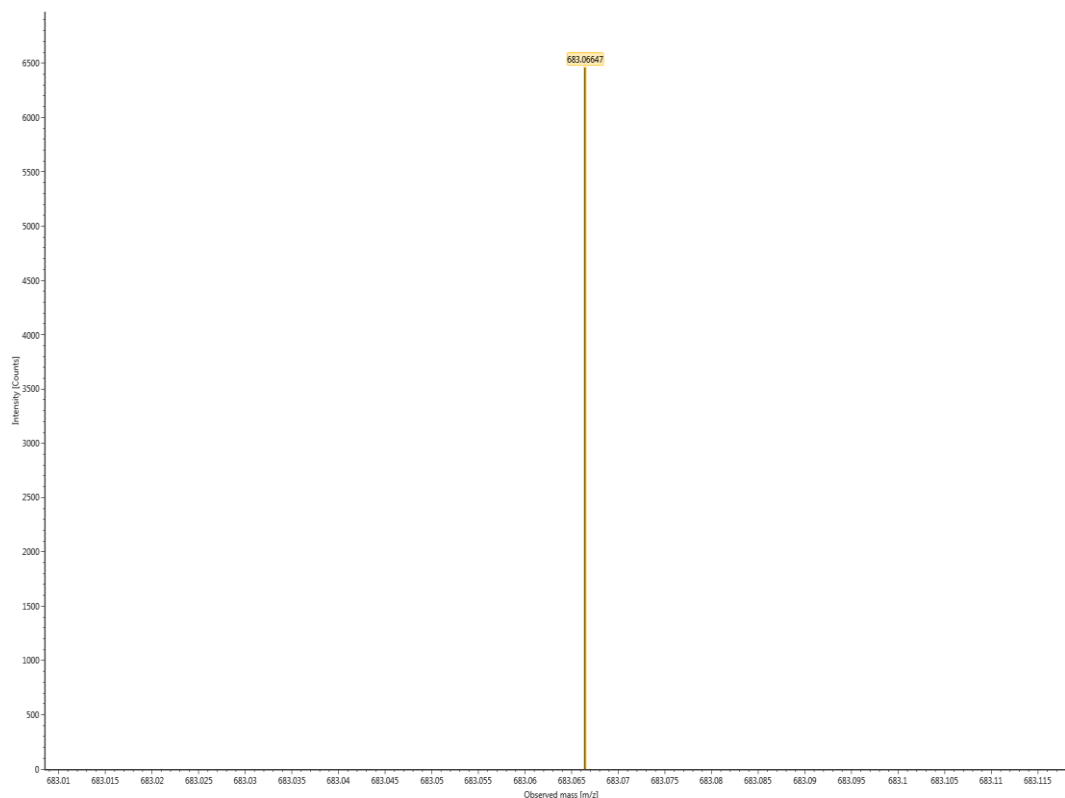
Compound **13** (0.50 g, 0.87 mmol) and NaOH (0.15 g, 3.67 mmol) were added to H₂O (50 mL) and stirred at room temperature for 3 h. Then the mixture was concentrated and washed by acetone to give **2** (0.55 g, 95%) as a white solid. ¹H NMR (600 MHz, MeOD, 295 K) δ 8.65 (s, 4H), 8.65 (s, 3H), 8.19 (s, 8H), 8.19 (s, 6H), 7.85 (s, 4H), 7.85 (s, 3H), 5.68 (s, 5H), 5.68 (s, 3H), 5.35 (s, 5H), 5.35 (s, 3H), 1.90 (s, 6H). ESI-HR-MS: m/z 683.0665 [**2** + Na]⁺, calcd. for [C₃₀H₂₀N₂Na₅O₁₀]⁺, 683.0660.



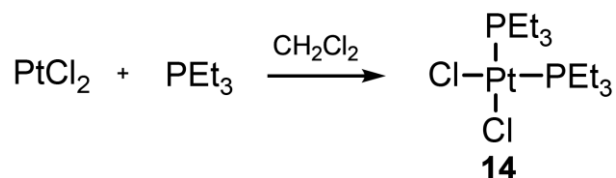
Supplementary Fig. 20 ¹H NMR spectrum (600 MHz, CD₃OD, 295 K) recorded for 2.



Supplementary Fig. 21 ¹³C NMR spectrum (151 MHz, CD₃OD, 295 K) recorded for 2.

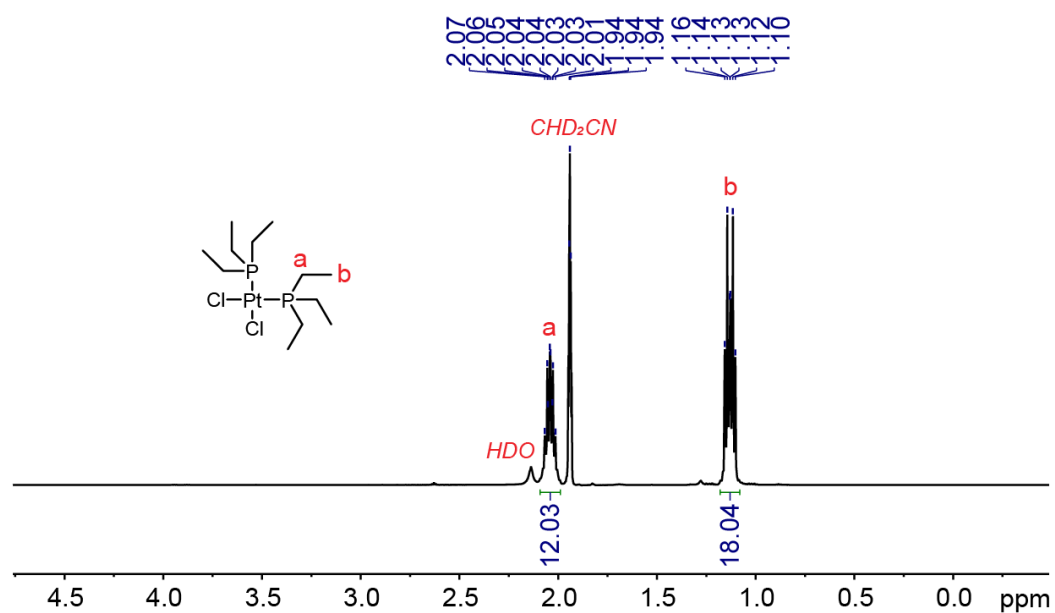


Supplementary Fig. 22 ESI-HR-MS spectrum of **2**.

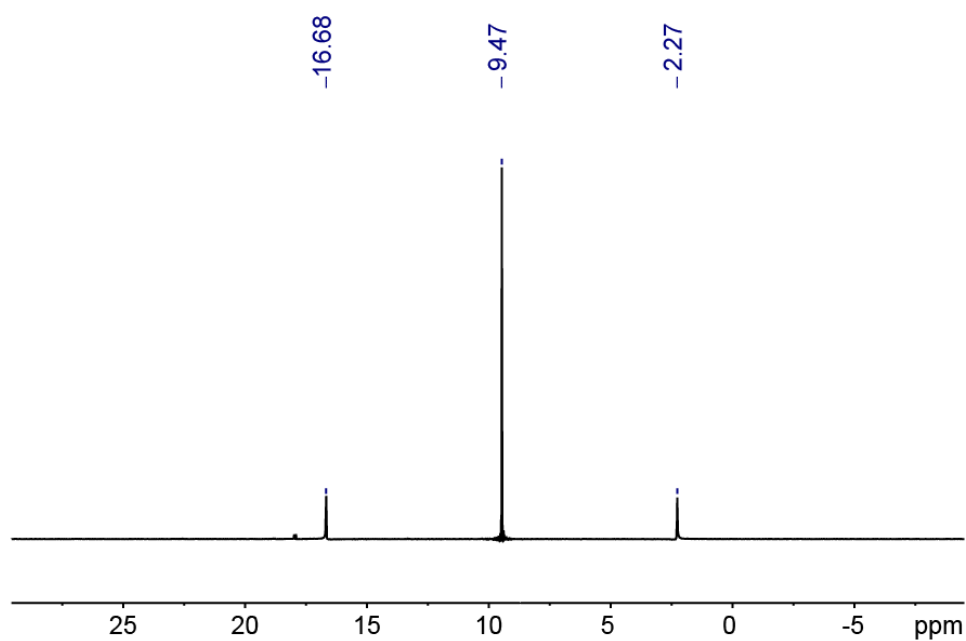


Supplementary Fig. 23 Synthesis of compound **14**.

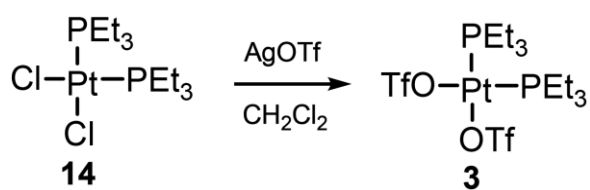
PtCl_2 (5.00 g, 18.80 mmol) was introduced under N_2 atmosphere, followed by the slow addition of CH_2Cl_2 (150 mL). Upon the dropwise addition of triethylphosphine (6.66 g, 56.39 mmol), the mixture was stirred in the dark for 48 h. The solvent was evaporated at reduced pressure and the residue was crystallized with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give a white solid that was collected by filtration, yielding compound **10** (8.40 g, 89%) as white crystals. ^1H NMR (600 MHz, CD_3CN) δ 2.04 (dq, $J = 9.5, 7.5$ Hz, 12H), 1.13 (dt, $J = 17.1, 7.6$ Hz, 18H). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CD_3CN , 295 K): 9.47 ppm (s, ^{195}Pt satellites, $^1J_{\text{Pt-P}} = 1750.8$ Hz). The ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **14** matches well with reported results ⁴.



Supplementary Fig. 24 ¹H NMR spectrum (600 MHz, CDCl₃, 295 K) recorded for **14**.

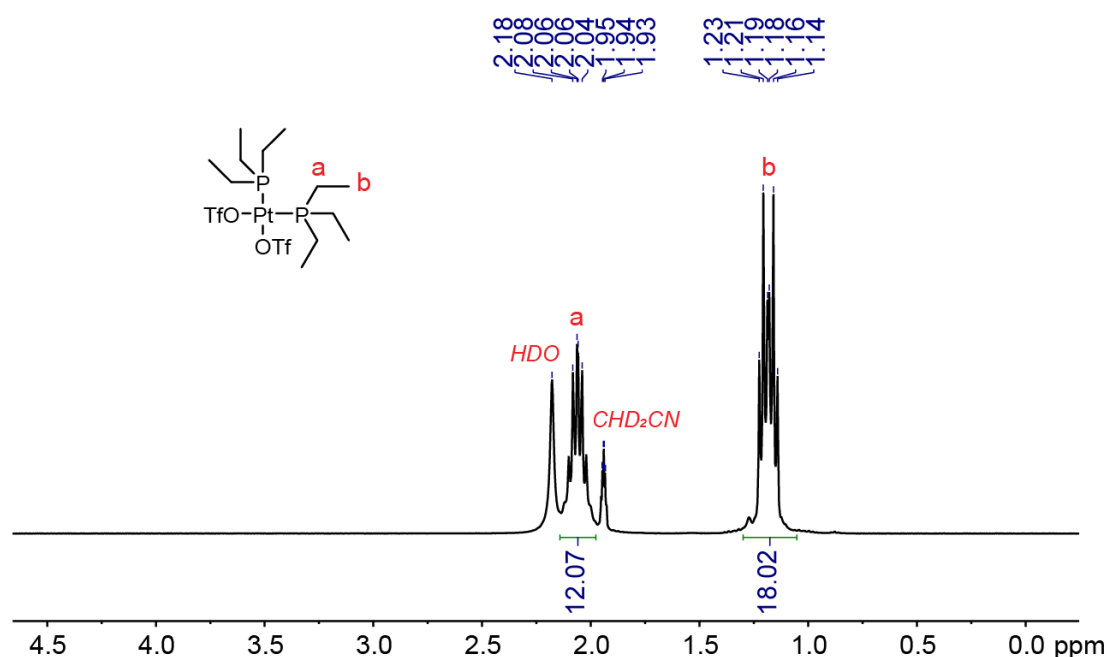


Supplementary Fig. 25 ³¹P{¹H} NMR spectrum (243 MHz, CDCl₃, 295 K) recorded for **14**.

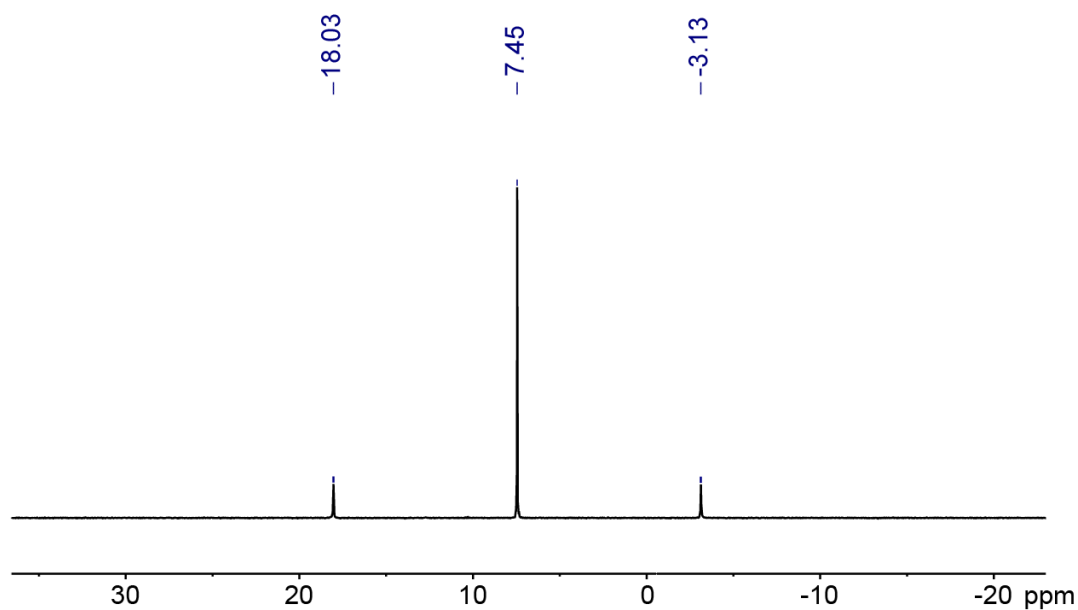


Supplementary Fig. 26 Synthesis of compound **3**.

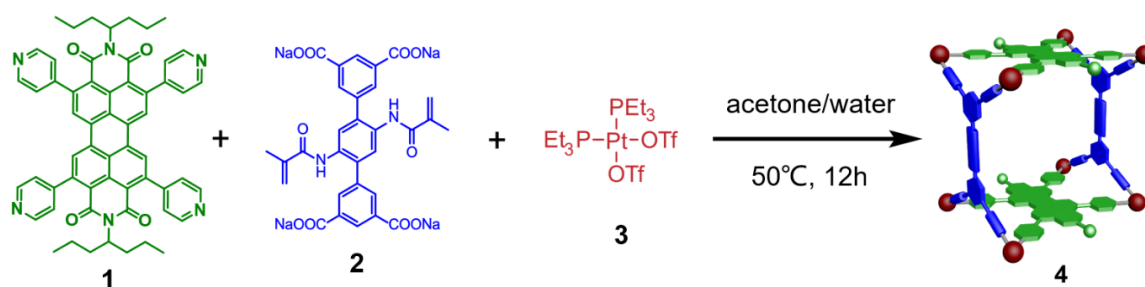
Compound **14** (500 mg, 1 mmol) and AgOTf (1.28 g, 6 mmol) were dissolved in 100 mL of anhydrous CH₂Cl₂. The mixture was stirred in the dark at room temperature for 24 h. Afterward, the solvent was centrifuged, and the supernatant then dried at 60 °C to yield compound **3** (610 mg, 84%). ¹H NMR (600 MHz, CD₃CN) δ 2.04 (dq, *J* = 9.5, 7.5 Hz, 12H), 1.13 (dt, *J* = 17.1, 7.6 Hz, 18H). ³¹P{¹H}NMR (243 MHz, CD₃CN, 295 K): 7.45 ppm (s, ¹⁹⁵Pt satellites, ¹*J*_{Pt-P} = 2570.9 Hz). The ¹H NMR and ³¹P{¹H} NMR spectrum of **3** matches well with reported results ^{S4}.



Supplementary Fig. 27 ¹H NMR spectrum (600 MHz, CDCl₃, 295 K) recorded for **3**.

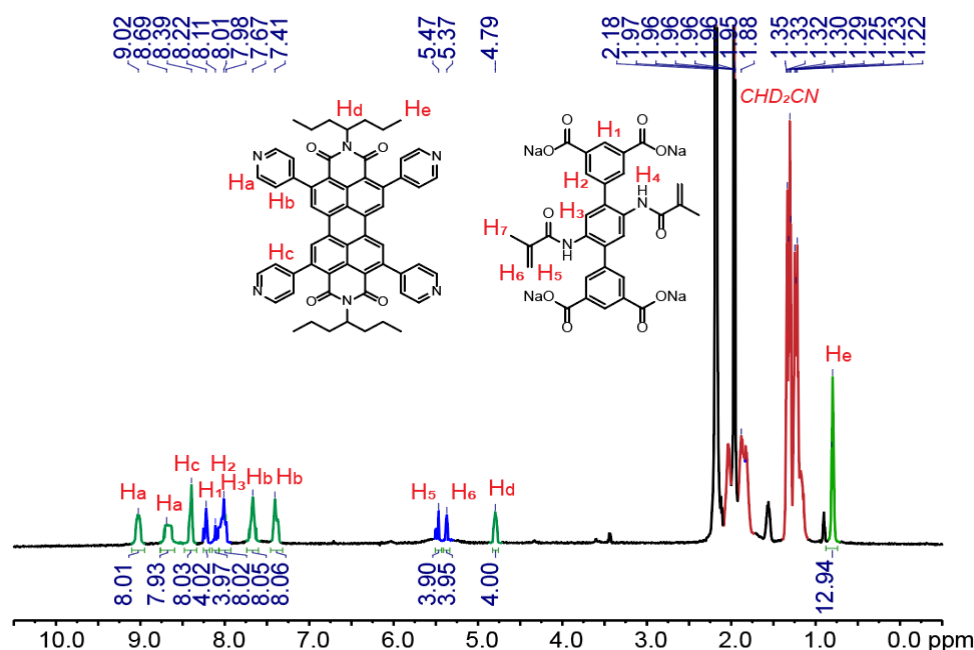


Supplementary Fig. 28 ³¹P{¹H} NMR spectrum (243 MHz, CDCl₃, 295 K) recorded for **3**.

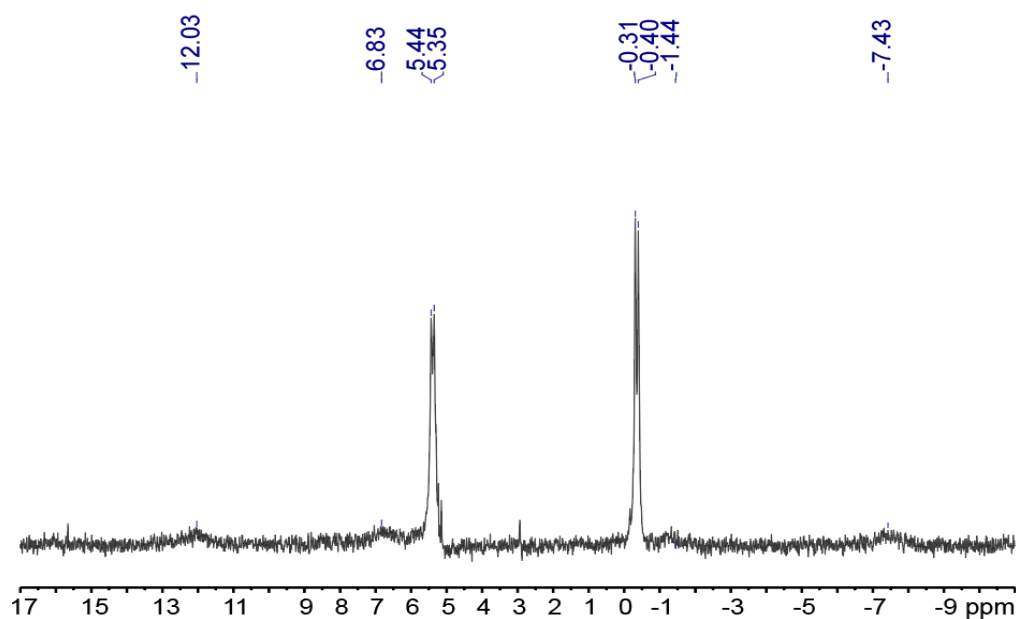


Supplementary Fig. 29 Synthesis of metallacage **4**

Compound **1** (5.00 mg, 5.59 μmol), tetracarboxylate ligand **2** (3.69 mg, 5.59 μmol), and cis-(PEt_3) $_2\text{Pt}(\text{OTf})_2$ **3** (16.30 mg, 22.34 μmol) were mixed in a 1:1:4 molar ratio and dissolved in acetone/water (6.0 mL, 4:1, v/v). The whole reaction mixture was heated at 60 $^\circ\text{C}$ for 8 h and then cooled to room temperature. The solvent was removed by nitrogen flow. The residue was redissolved in CH_3CN (1.0 mL) and filtered, and the filtrate was poured into ethyl ether (10.0 mL) to give a precipitate, which was collected by centrifugation to give **4** (15.00 mg, 93%) as a red powder. ^1H NMR (600 MHz, CD_3CN , 295 K) δ 9.02 (s, 8H), 8.69 (s, 8H), 8.39 (s, 8H), 8.22 (s, 4H), 8.11 (s, 4H), 8.00 (d, $J = 17.0$ Hz, 8H), 7.67 (s, 8H), 7.41 (s, 8H), 5.47 (s, 4H), 5.37 (s, 4H), 4.79 (s, 4H), 0.80 (d, $J = 6.7$ Hz, 12H). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CD_3CN , 295 K): 5.40 ppm (d, $^2J_{\text{P-P}} = 21.9$ Hz, ^{195}Pt satellites, $^1J_{\text{Pt-P}} = 1636.6$ Hz), -0.36 ppm (d, $^2J_{\text{P-P}} = 21.9$ Hz, ^{195}Pt satellites, $^1J_{\text{Pt-P}} = 1732.6$ Hz). ESI-TOF-MS: m/z 797.8333 [**4** – 8OTf] $^{8+}$, 932.3615 [**4** – 7OTf] $^{7+}$, 1365.0142 [**4** – 5OTf] $^{5+}$ and 1743.5010 [**4** – 4OTf] $^{4+}$.



Supplementary Fig. 30 ^1H NMR spectrum (600 MHz, CD_3CN , 295 K) recorded for **4**.



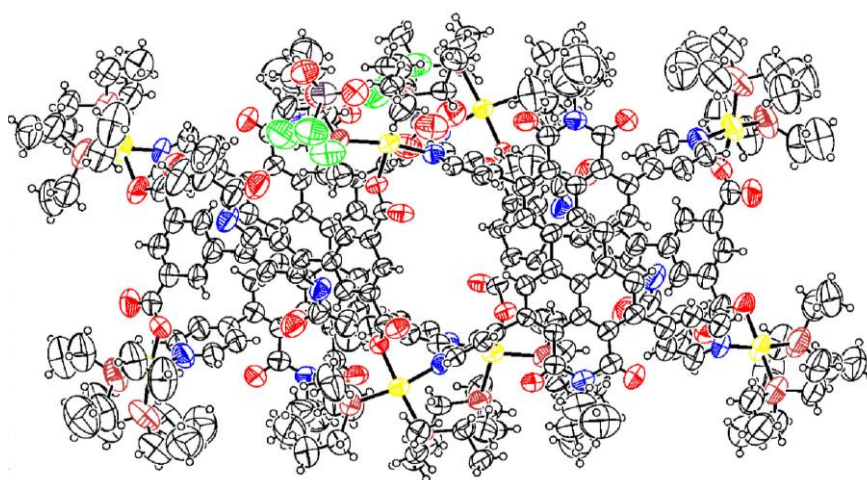
Supplementary Fig. 31 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (243 MHz, CD_3CN , 295 K) recorded for **4**.

Supplementary Notes 2. Crystallographic data and refinement details

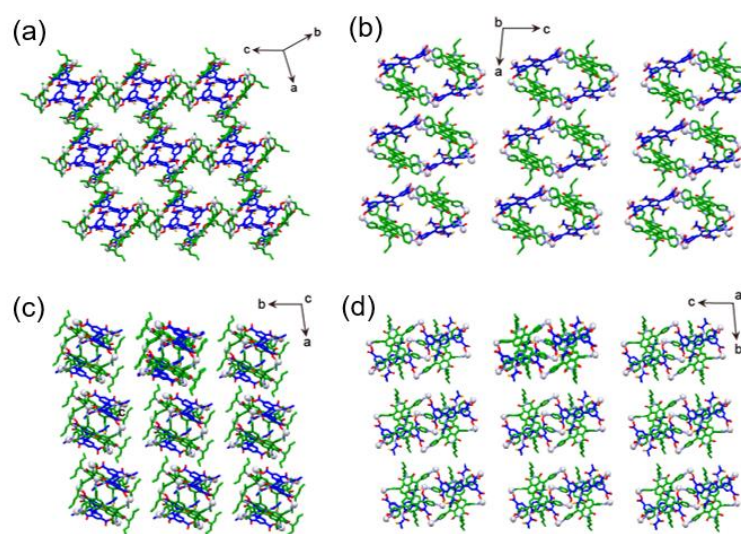
Supplementary Table 1. Crystallographic data and refinement details for metallacage **4**

Compound	Metallacage 4
Empirical formula	$\text{C}_{276}\text{H}_{376}\text{F}_{12}\text{N}_{16}\text{O}_{40}\text{P}_{16}\text{Pt}_8\text{S}_4$
Formula weight	6970.39
Temperature/K	193.00
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	17.7584(12)
<i>b</i> /Å	20.7711(15)
<i>c</i> /Å	34.884(3)
α /°	94.939(4)
β /°	95.437(4)
γ /°	98.224(4)
Volume /Å ³	12612.7(15)

Z	1
$D_{\text{calc}} / \text{g cm}^{-3}$	0.918
μ / mm^{-1}	3.434
F (000)	3500
Theta (max)	51.669
Reflections collected	134817
Independent reflns	41878
$R_1; wR_2 [I > 2\sigma(I)]$	0.0765; 0.1937

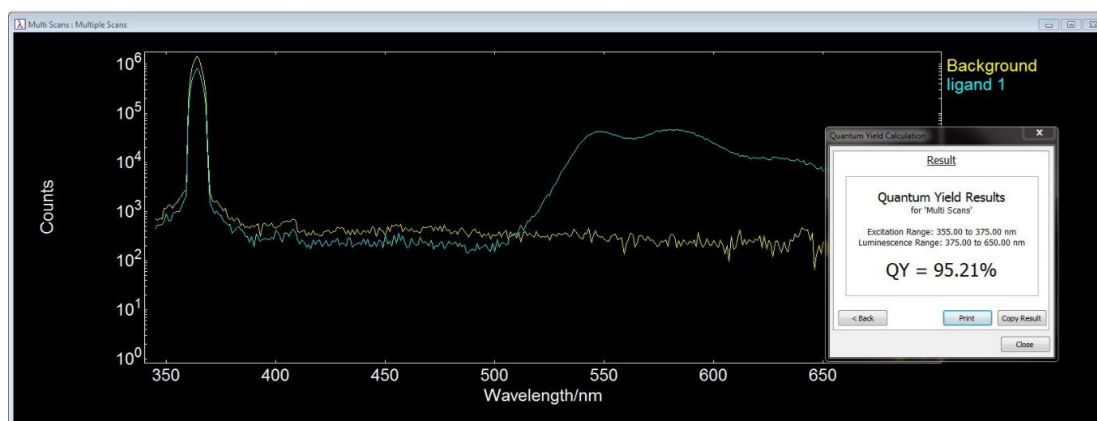


Supplementary Fig. 32 ORTEP-style illustration of crystal structure of metallacage **4**.

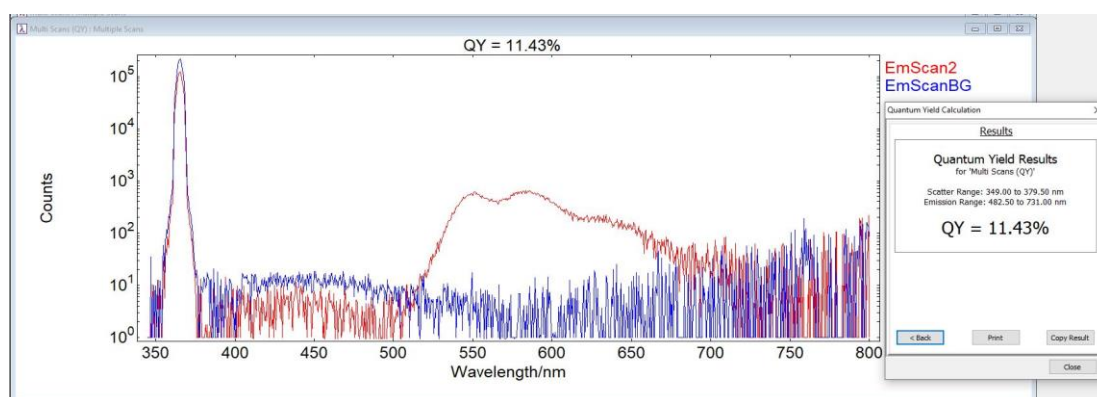


Supplementary Fig. 33 Packing mode of crystal structure of metallacage **4**. Hydrogen atoms, counterions and solvent molecules were omitted for clarity.

Supplementary Notes 3. Photophysical property

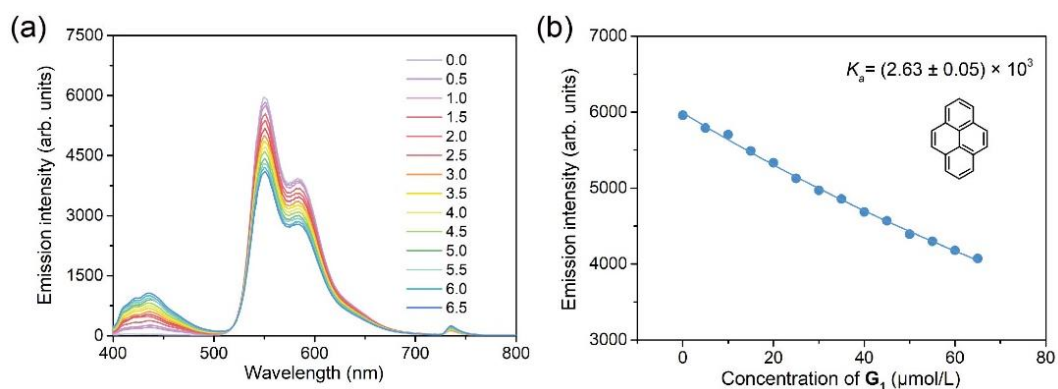


Supplementary Fig. 34 Absolute fluorescence quantum yield of ligand 1.

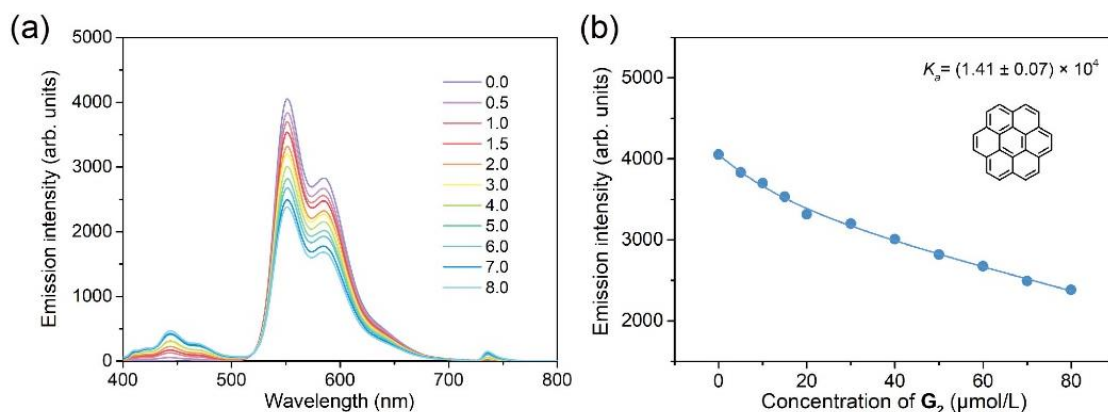


Supplementary Fig. 35 Absolute fluorescence quantum yield of metallacage 4.

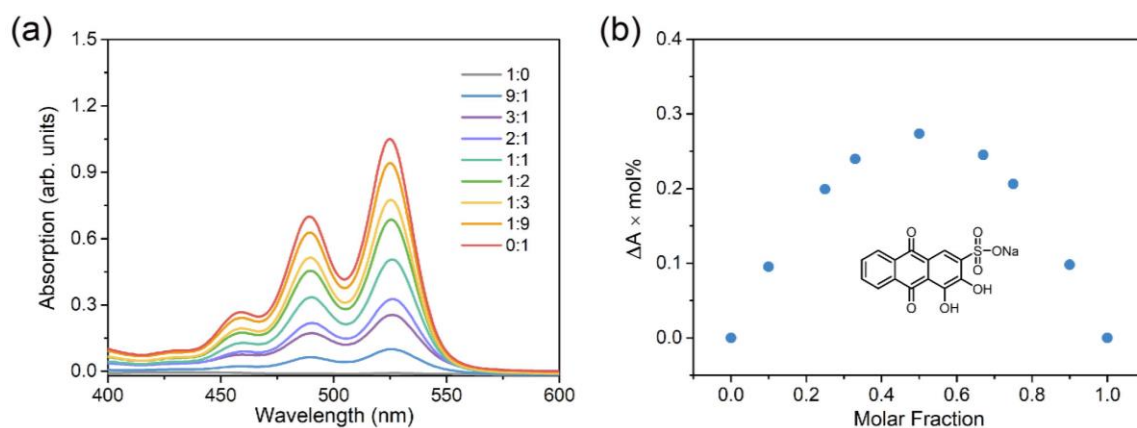
Supplementary Note 4. Host-guest complexation study



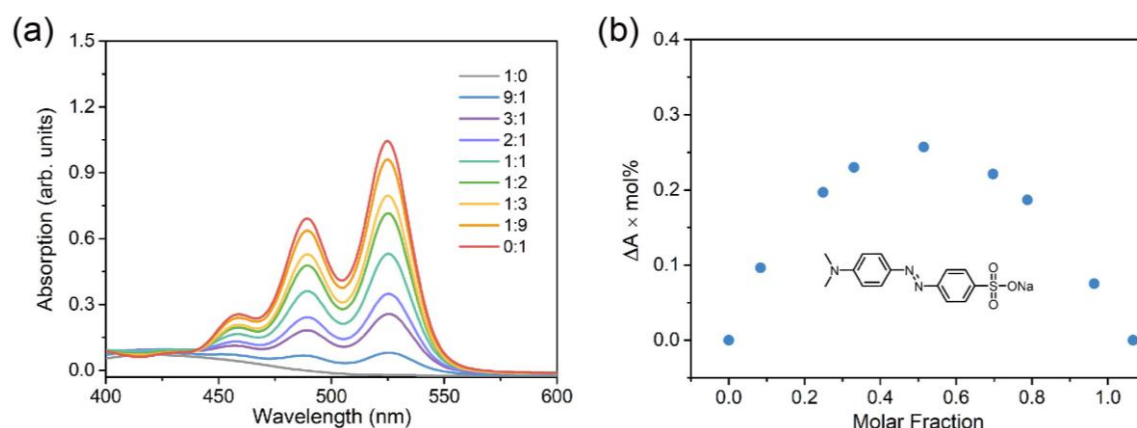
Supplementary Fig. 36 (a) Fluorescence spectra of metallacage 4 at a fixed concentration upon the addition of **G**₁ in CH₃CN ([Host] = 10 μM, [Guest] = 500 μM). (b) Nonlinear fitting curves of the emission intensity at 365 nm of 4 versus the concentrations of **G**₁.



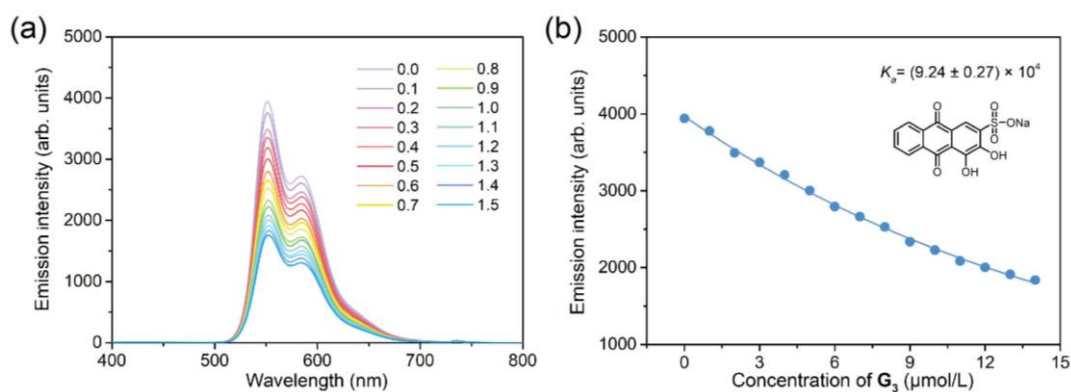
Supplementary Fig. 37 (a) Fluorescence spectra of metallacage **4** at a fixed concentration upon the addition of **G₂** in CH₃CN ([Host] = 10 μM, [Guest] = 500 μM). (b) Nonlinear fitting curves of the emission intensity at 365 nm of **4** versus the concentrations of **G₂**.



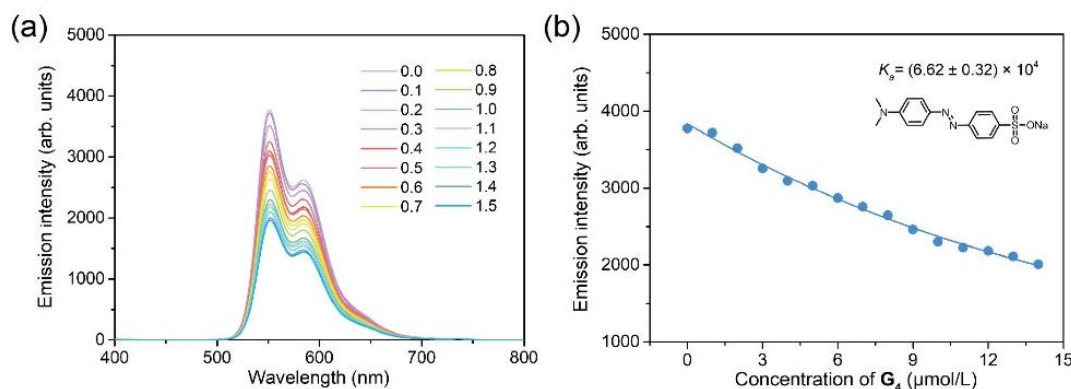
Supplementary Fig. 38 (a) UV-vis absorption of metallacage **4** with guest **G₃** in different molar ratios ([**4a**] + [**G₃**] = 10 μM). (b) Job's plot of the complex **4**⊃**G₃** in CH₃CN, showing a 1:1 stoichiometry.



Supplementary Fig. 39 (a) UV-vis absorption of metallacage **4** with guest **G₄** in different molar ratios ([**4a**] + [**G₄**] = 10 μM). (b) Job's plot of the complex **4**⊃**G₄** in CH₃CN, showing a 1:1 stoichiometry.

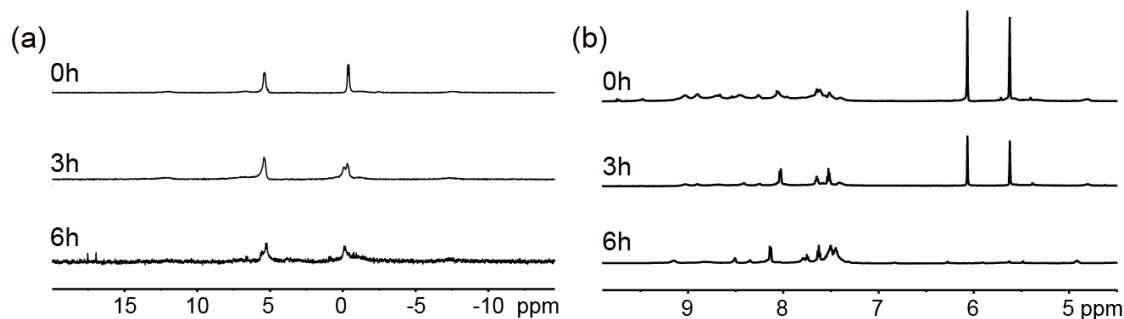


Supplementary Fig. 40 (a) Fluorescence spectra of metallacage **4** at a fixed concentration upon the addition of **G₃** in CH₃CN ([Host] = 10 μM, [Guest] = 500 μM). (b) Nonlinear fitting curves of the emission intensity at 365 nm of **4** versus the concentrations of **G₃**.

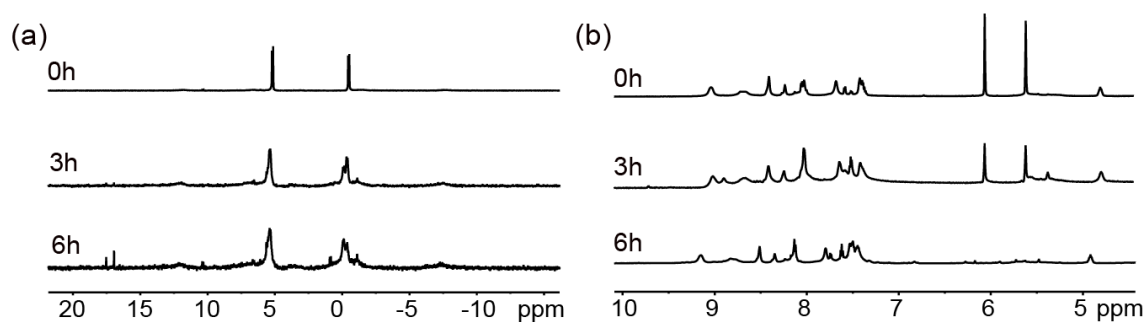


Supplementary Fig. 41 (a) Fluorescence spectra of metallacage **4** at a fixed concentration upon the addition of **G₄** in CH₃CN ([Host] = 10 μM, [Guest] = 500 μM). (b) Nonlinear fitting curves of the emission intensity at 365 nm of **4** versus the concentrations of **G₄**.

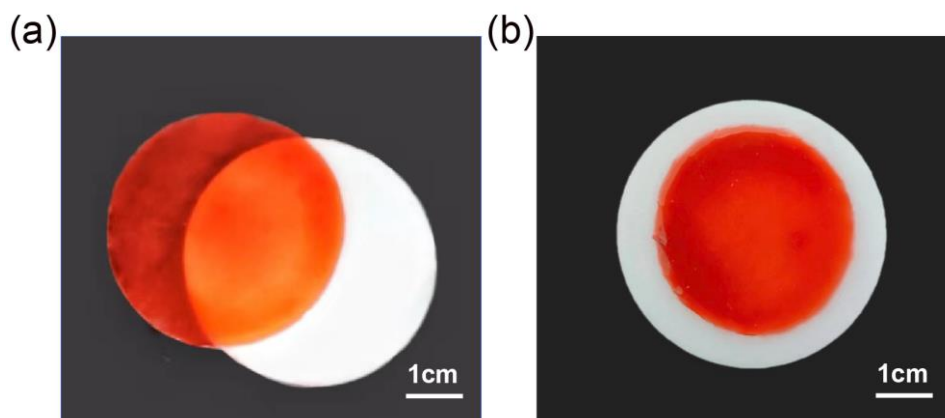
Supplementary Notes 5. Preparation and characterization of supramolecular networks



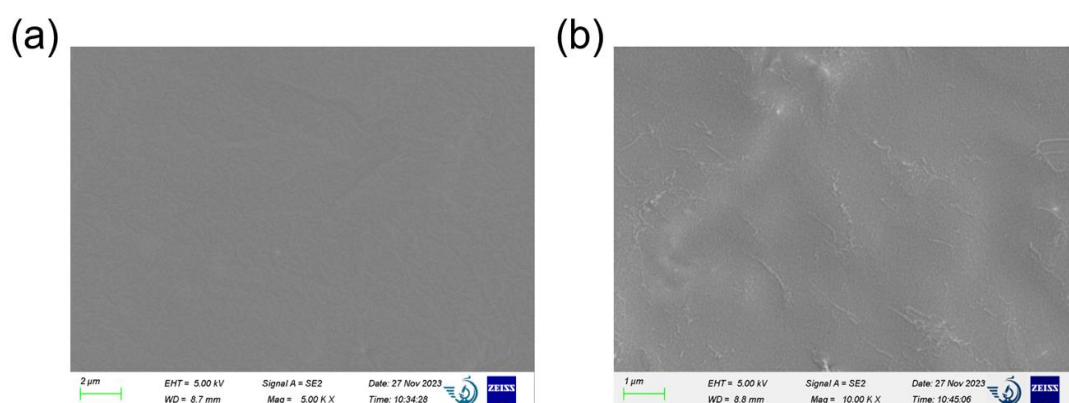
Supplementary Fig. 42 (a) Partial ³¹P{¹H} NMR (right, 243 MHz, CD₃CN, 295 K) spectra and (b) partial ¹H NMR spectra (left, 600 MHz, CD₃CN, 295 K) of network **6a** with 1 wt% **4** loading after 0 h, 3 h and 6 h upon light irradiation.



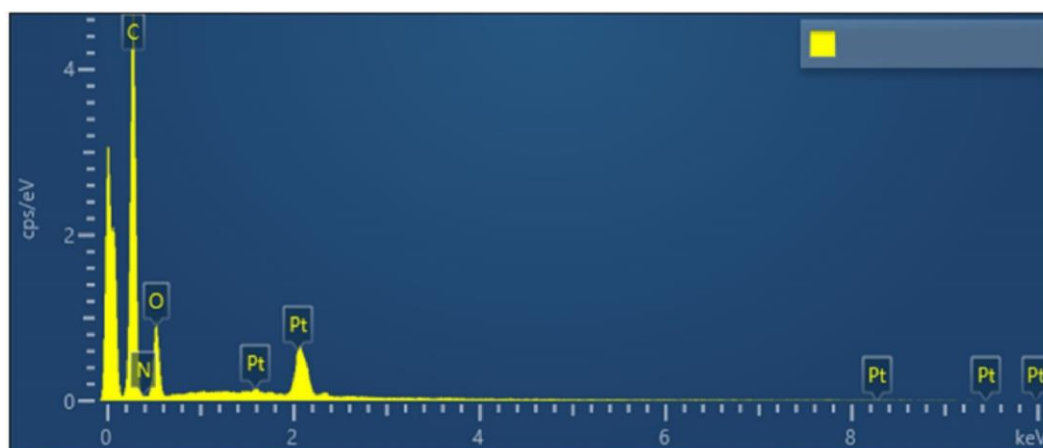
Supplementary Fig. 43 (a) Partial $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CD_3CN , 295 K) spectra and (b) partial ^1H NMR spectra (600 MHz, CD_3CN , 295 K) of network **6b** with 3 wt% **4** loading after 0 h, 3 h and 6 h upon light irradiation.



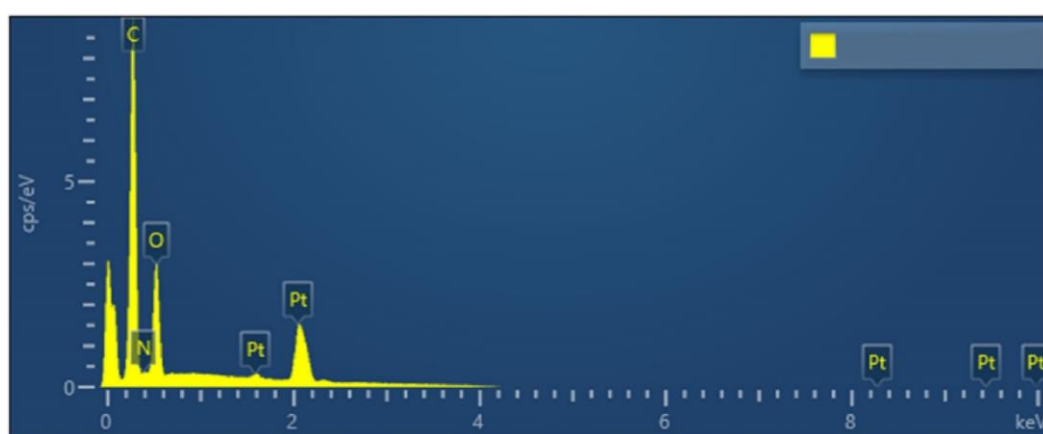
Supplementary Fig. 44 Photographs of (a) **6a** and (b) **6b**.



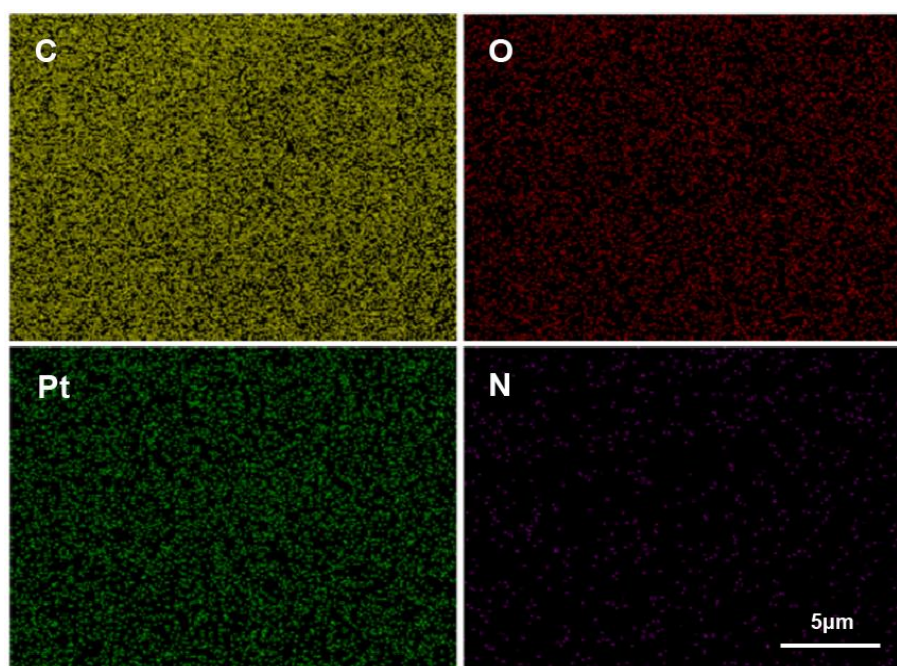
Supplementary Fig. 45 (a) SEM images of (a) **6a** and (b) **6b**.



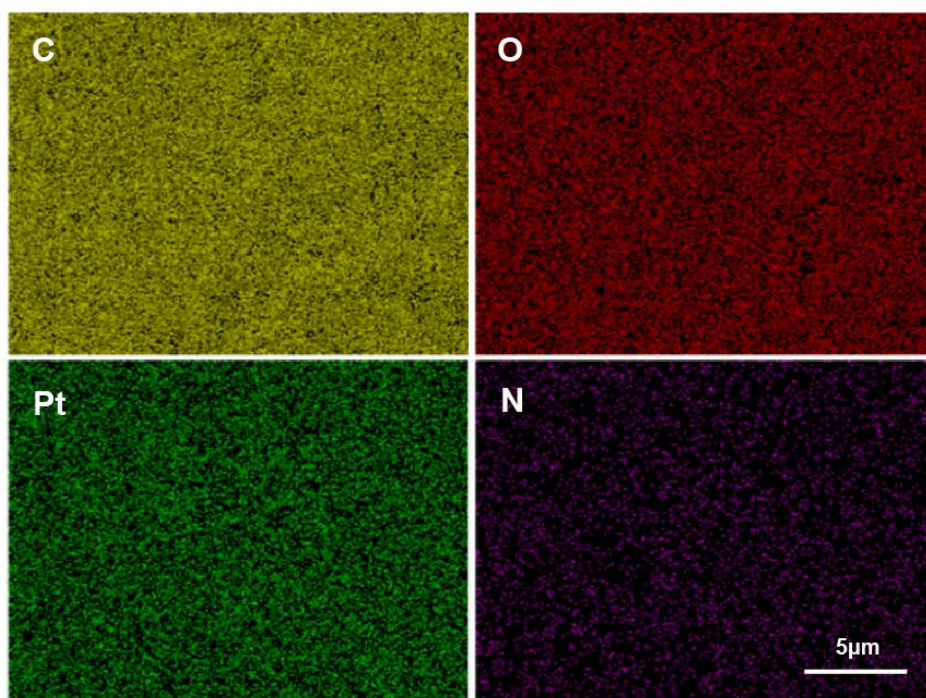
Supplementary Fig. 46 EDS spectroscopy of **6a**.



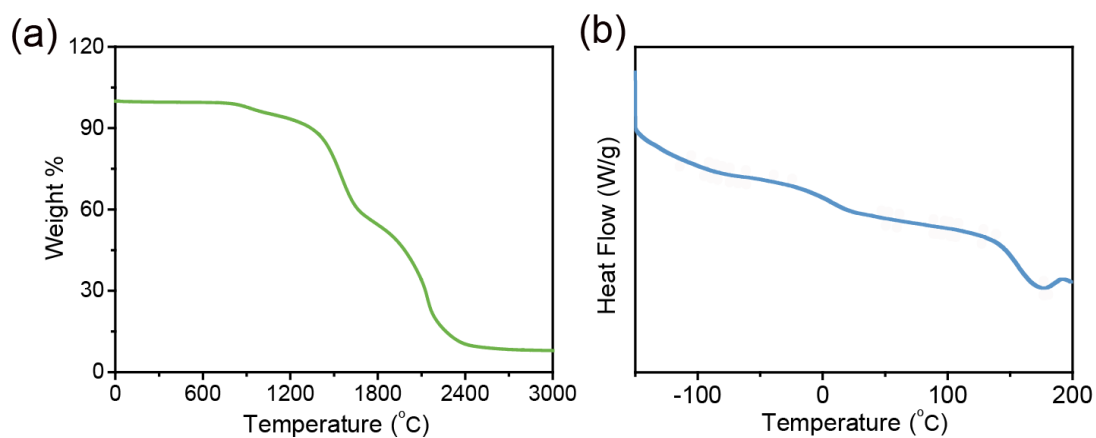
Supplementary Fig. 47 EDS spectroscopy of **6b**.



Supplementary Fig. 48 EDS elemental mapping of C, O, Pt, N for **6a**.

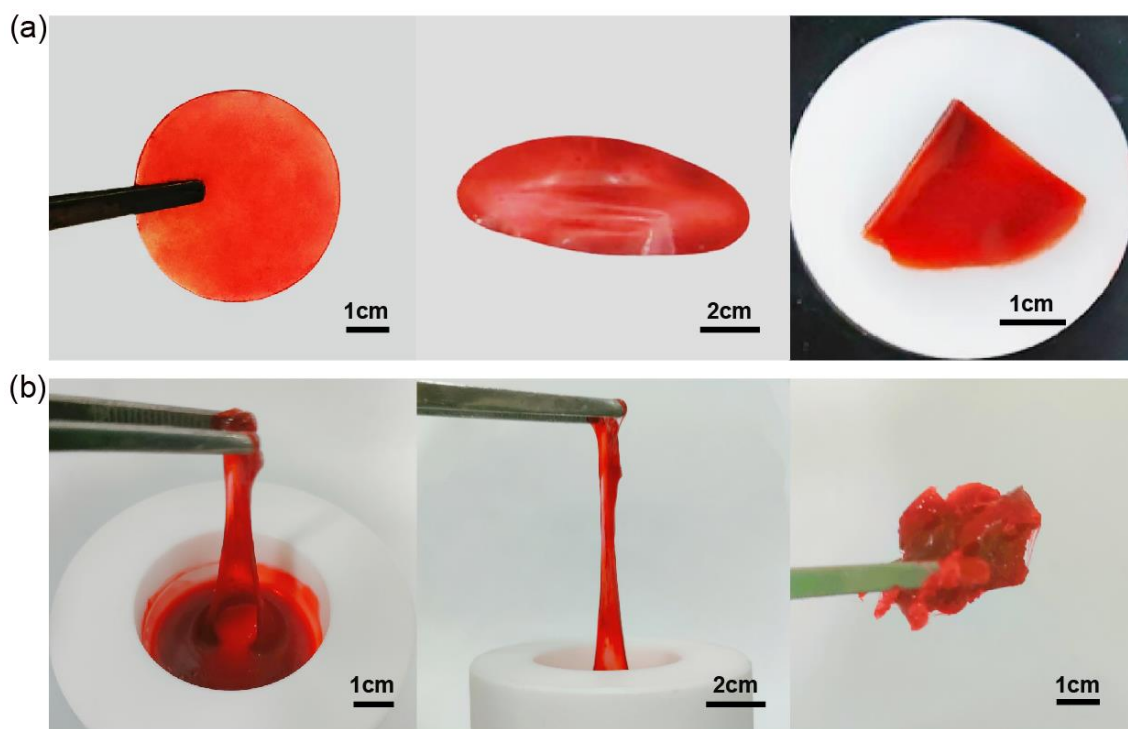


Supplementary Fig. 49 EDS elemental mapping of C, O, Pt, N for **6b**.

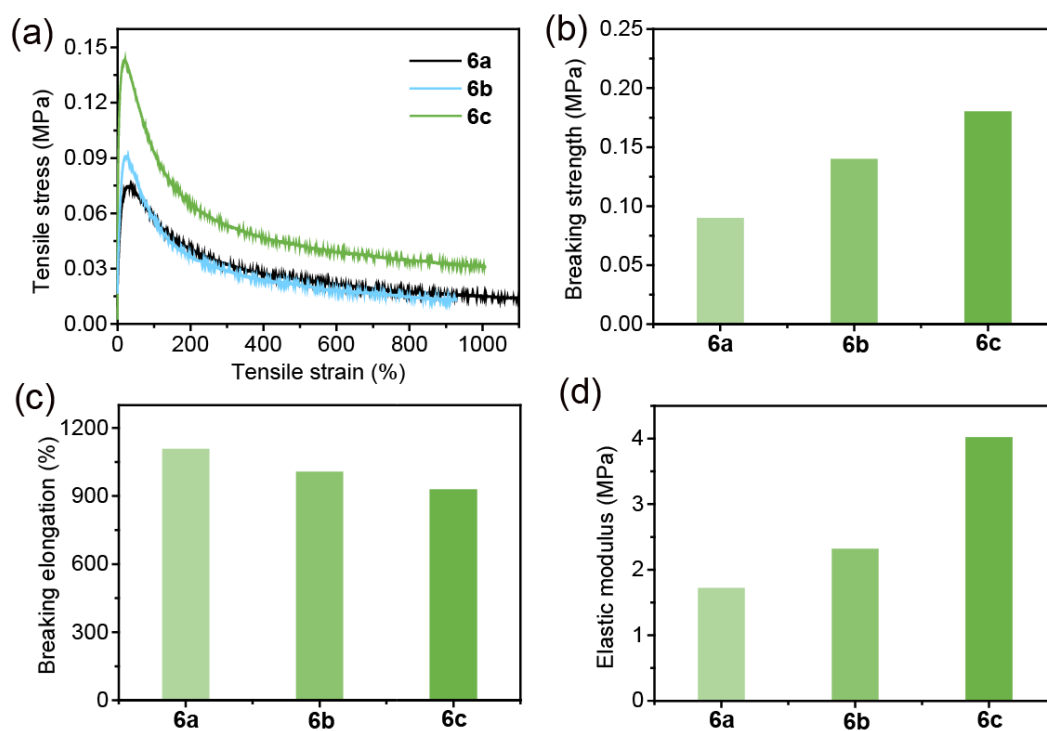


Supplementary Fig. 50 (a) TGA and (b) DSC curves of **6c**.

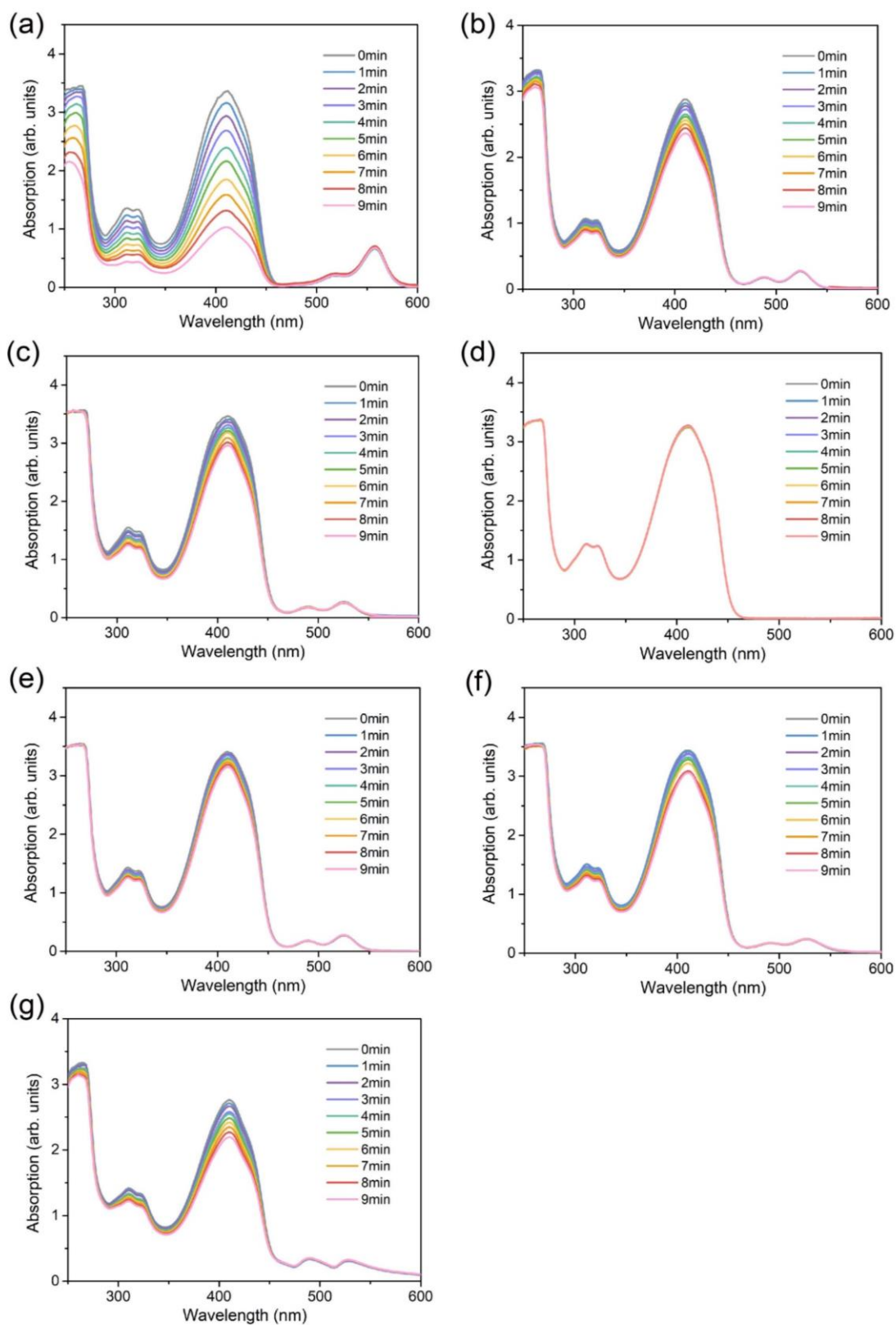
Supplementary Discussion: The discrete, rigid and nano-sized metallacages can act as fillers to improve the mechanical strength of polymeric materials. The introduction of metallacage **4** as crosslinks into PBMA would benefit the supramolecular network good mechanical properties. As shown in Fig. S51a, supramolecular network **6c** shows a certain degree of flexibility and good processability. It can be easily stretched, folded and reshaped. In contrast, we prepared the product after mixing PBMA with the ligand **1** and labeled it as polymer **8** (Fig. S51b). In contrast, for polymer **8**, when it is removed from the mold, only a viscous polymer are formed.



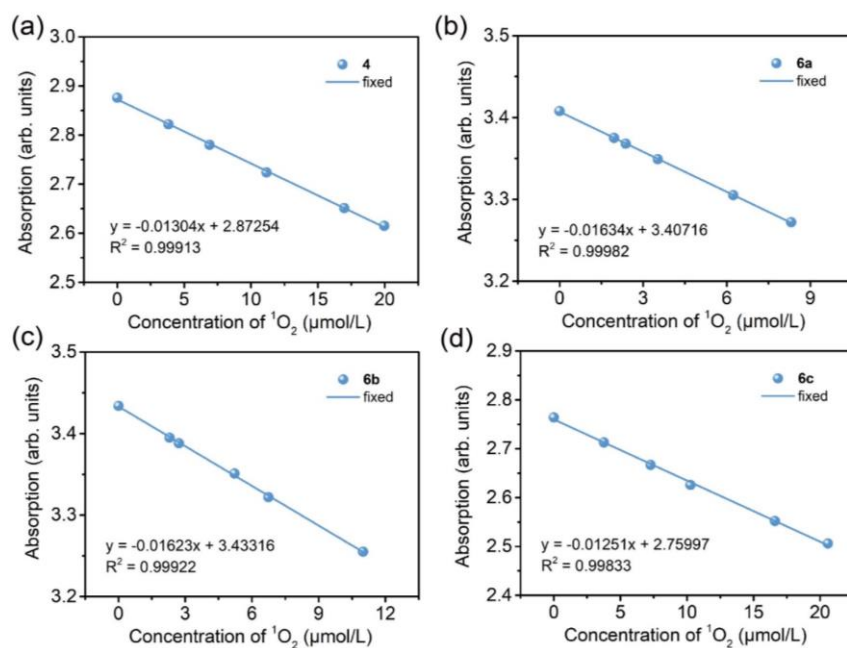
Supplementary Fig. 51 Optical photograph of (a) network **6c** and (b) polymer **8**.



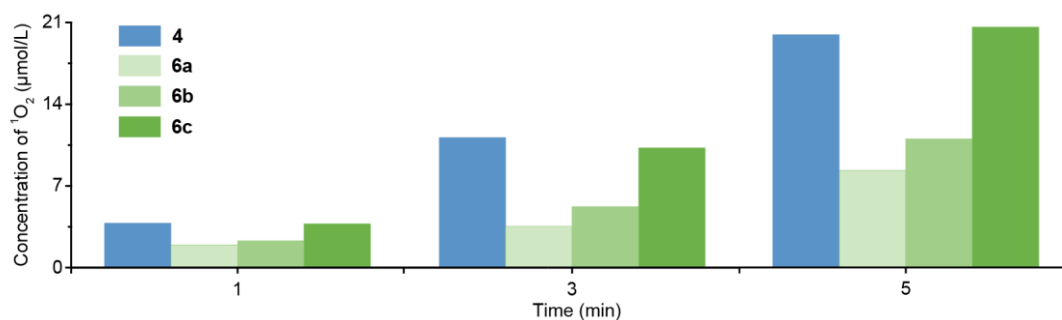
Supplementary Fig. 52 (a) Tensile stress-strain curves, (b) breaking strength, (c) breaking elongation and (d) elastic modulus of **6a**, **6b** and **6c**.



Supplementary Fig. 53 The absorbance of DPBF at 410 nm vs irradiation time in the presence of (a) **RB**, (b) **1**, (c) **4**, (d) **7**, (e) **6a**, (f) **6b**, (g) **6c** upon irradiation in acetonitrile ($\lambda_{\text{ex}} = 520 \text{ nm}$).

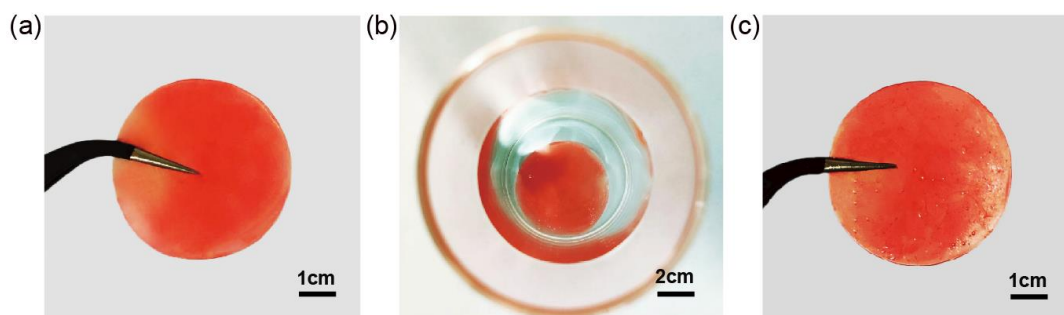


Supplementary Fig. 54 The standard curves of $^1\text{O}_2$ treated with (a) **4**, (b) **6a**, (c) **6b** and (d) **6c**.



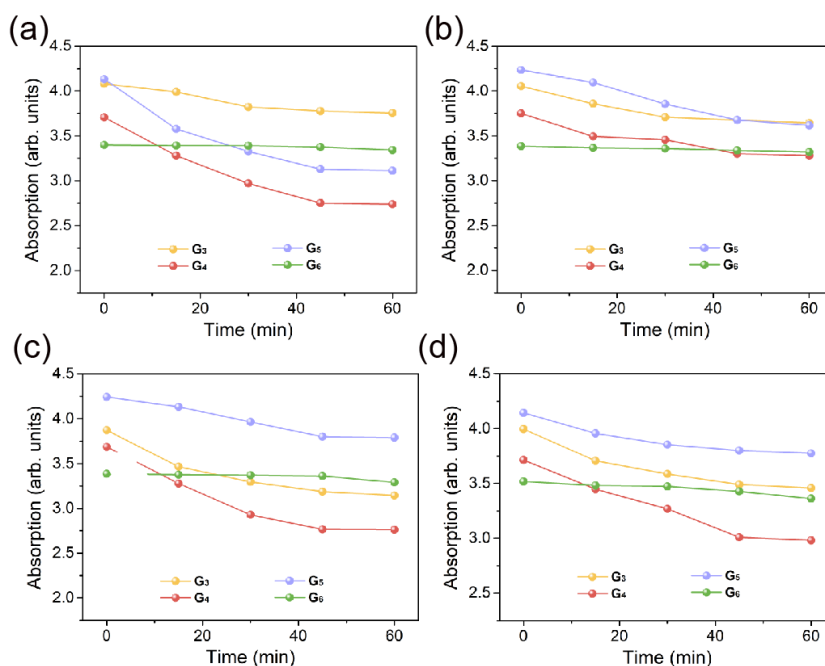
Supplementary Fig. 55 The concentration of $^1\text{O}_2$ treated with **4**, **6a**, **6b** and **6c** for different times upon irradiation in acetonitrile ($\lambda_{\text{ex}} = 520 \text{ nm}$).

Supplementary Notes 6. Photodegradation properties

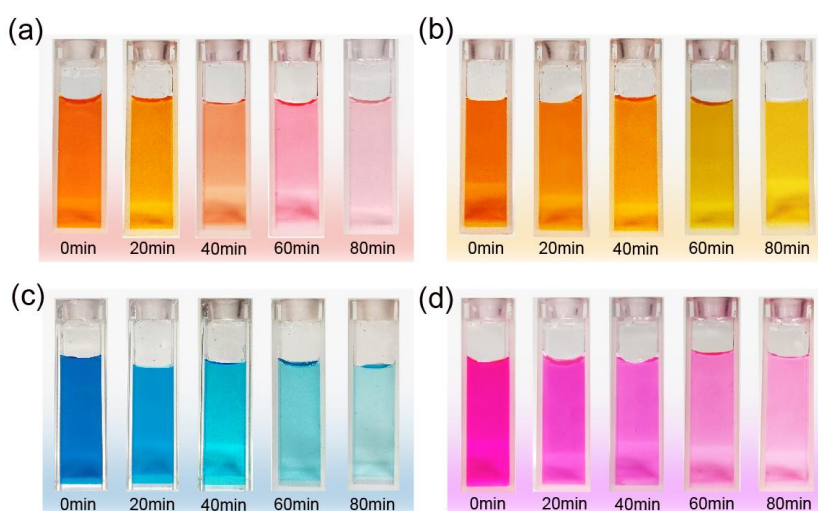


Supplementary Fig. 56 Optical photograph of (a) **6c** before being immersed in water, (b) **6c** immersed in water and (c) **6c** after being immersed in water for 30 min.

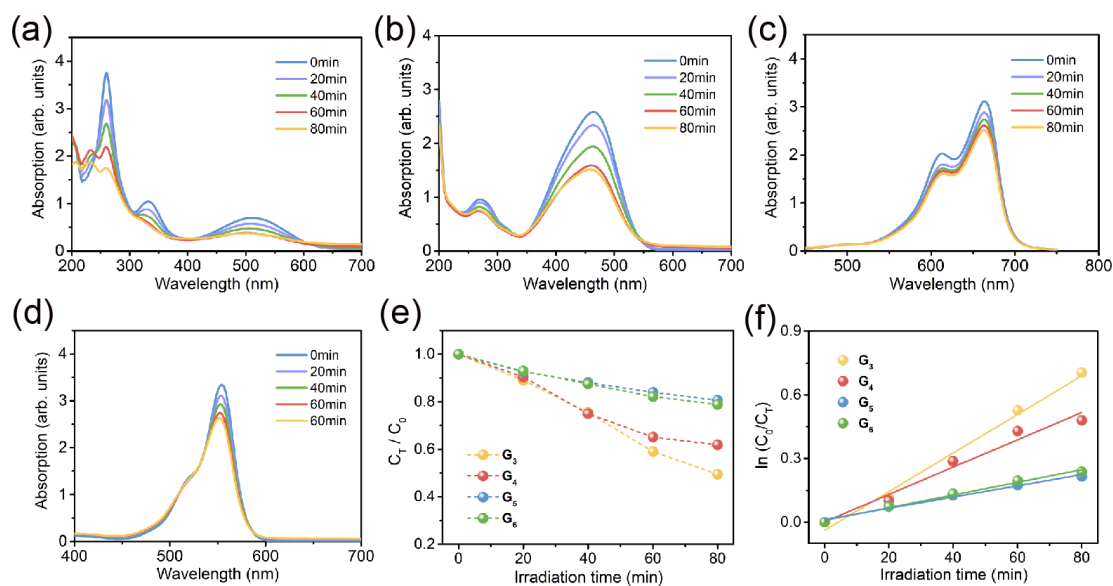
Supplementary Discussion: Since the dyes tend to undergo certain self-degradation in aqueous solution, an adsorption-desorption equilibrium test was conducted to ensure that the solution reached a relatively stable state before photocatalytic degradation. First, **4**, **6a**, **6b** and **6c** were added separately in the aqueous solution of dyes, then each solution was stirred for different times in the dark and the absorptions of each sample were measured. The results indicated that all these dyes reached equilibrium after 60 min in aqueous solution (Fig. S57), which was then used as the samples for examining the photocatalytic efficiency.



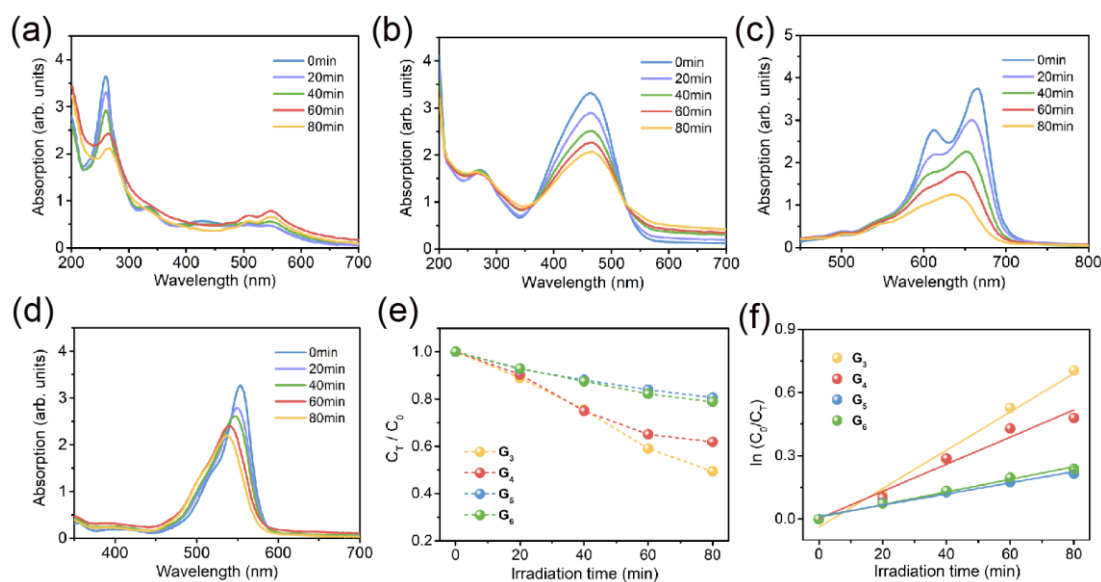
Supplementary Fig. 57 Adsorption dissociation equilibrium images of **G3**, **G4**, **G5** and **G6** carried out in aqueous solution using (a) **4**, (b) **6a**, (c) **6b** and (d) **6c** after stirred for different times in the dark.



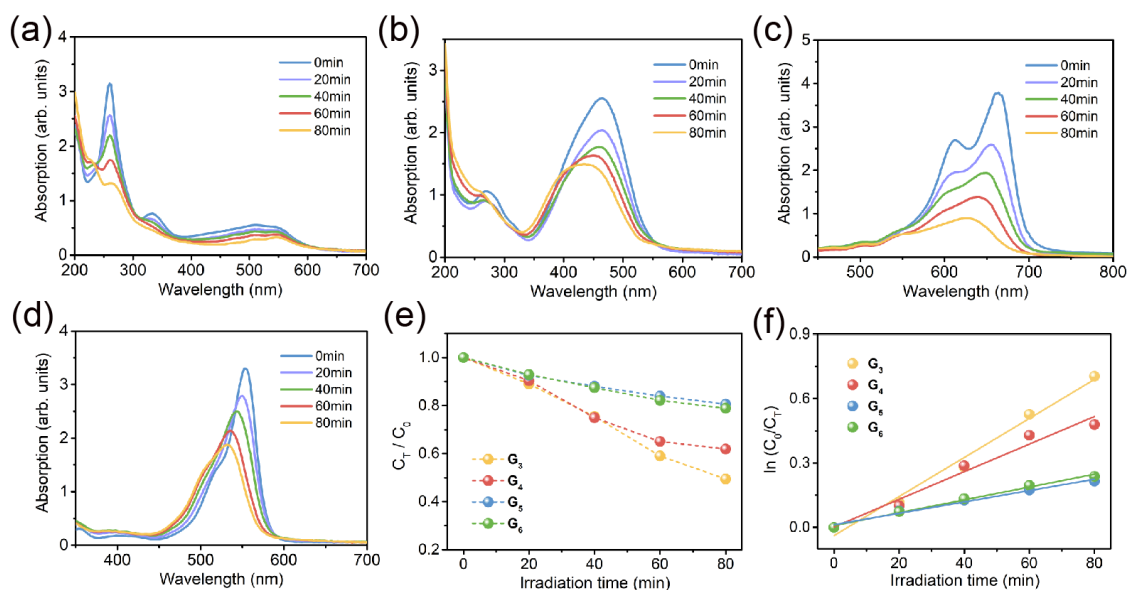
Supplementary Fig. 58 Optical photograph of (a) **G3**, (b) **G4**, (c) **G5** and (d) **G6** treated by **6c** after different times of light irradiation ($\lambda_{\text{ex}} = 520 \text{ nm}$).



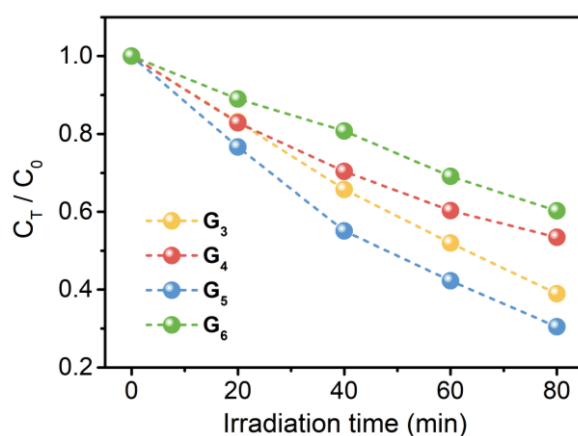
Supplementary Fig. 59 Time-dependent UV/vis absorption spectra following the photodegradation of (a) G_3 , (b) G_4 , (c) G_5 and (d) G_6 carried out in aqueous solution using **4**. (e) Photodegradation performances and (f) degradation kinetics fitted curves of G_3 , G_4 , G_5 and G_6 with **4** under 520 nm light irradiation. C_0 and C_T indicate the initial and intermediate concentrations of dyes, while T is the reaction time.



Supplementary Fig. 60 Time-dependent UV/vis absorption spectra following the photodegradation of (a) G_3 , (b) G_4 , (c) G_5 and (d) G_6 carried out in aqueous solution using **6a**. (e) Photodegradation performances and (f) degradation kinetics fitted curves of G_3 , G_4 , G_5 and G_6 with **6a** under 520 nm light irradiation. C_0 and C_T indicate the initial and intermediate concentrations of dyes, while T is the reaction time.



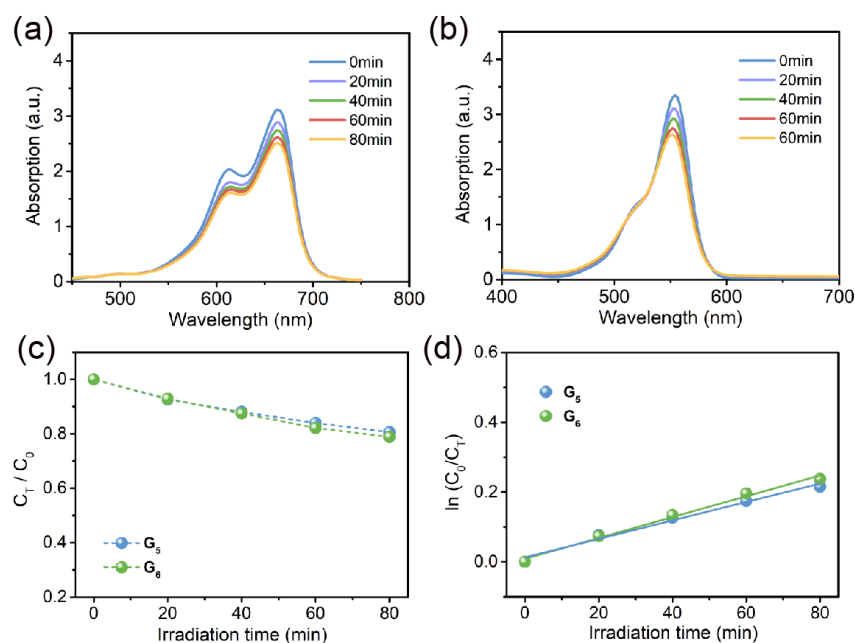
Supplementary Fig. 61 Time-dependent UV/vis absorption spectra following the photodegradation of (a) **G**₃, (b) **G**₄, (c) **G**₅ and (d) **G**₆ carried out in aqueous solution using **6b**. (e) Photodegradation performances and (f) degradation kinetics fitted curves of **G**₃, **G**₄, **G**₅ and **G**₆ with **6b** under 520 nm light irradiation, respectively. C_0 and C_T indicate the initial and intermediate concentrations of dyes, while T is the reaction time.



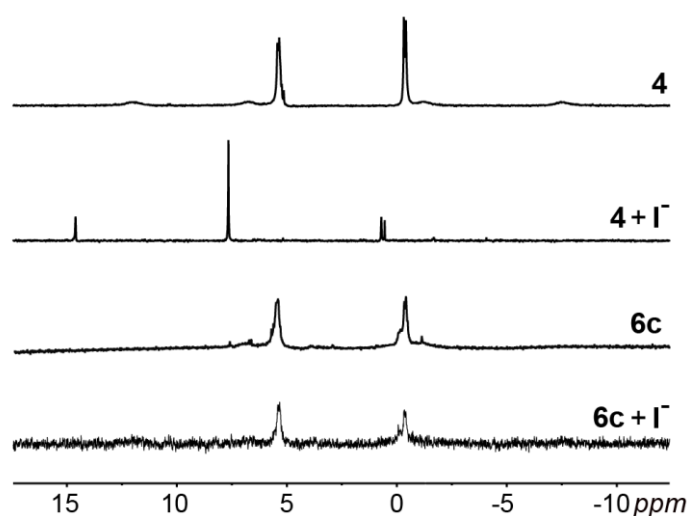
Supplementary Fig. 62 Photodegradation performances of **G**₃, **G**₄, **G**₅ and **G**₆ with **6c** under 520 nm light irradiation, respectively. C_0 and C_T indicate the initial and intermediate concentrations of dyes, while T is the reaction time.

Supplementary Discussion: The cavities of the metallacages can engage in effective host-guest interactions with the dyes, increasing the diffusion of the dyes and $^1\text{O}_2$, and thus enhancing the efficiency of the photodegradation reaction. For example, the degradation rate constants, which were calculated from the kinetic curves of **G**₅ and **G**₆ with **1** were only 4.48×10^{-5} and $4.95 \times 10^{-5} \text{ s}^{-1}$,

respectively (Fig. S63). The photodegradation efficiency of **G**₅ and **G**₆ by metallacage **4** and **6a–6c** significantly increased. The degradation rate constants of **G**₅ by **6a**, **6b** and **6c** were 1.70×10^{-4} , 2.23×10^{-4} and $2.48 \times 10^{-4} \text{ s}^{-1}$, respectively, much higher than **1**. Based on these results, it could be concluded that the incorporation of ligand **1** in the polymer network can not achieve the same photodegradation performance as that of metallacage **4** in the polymer network.



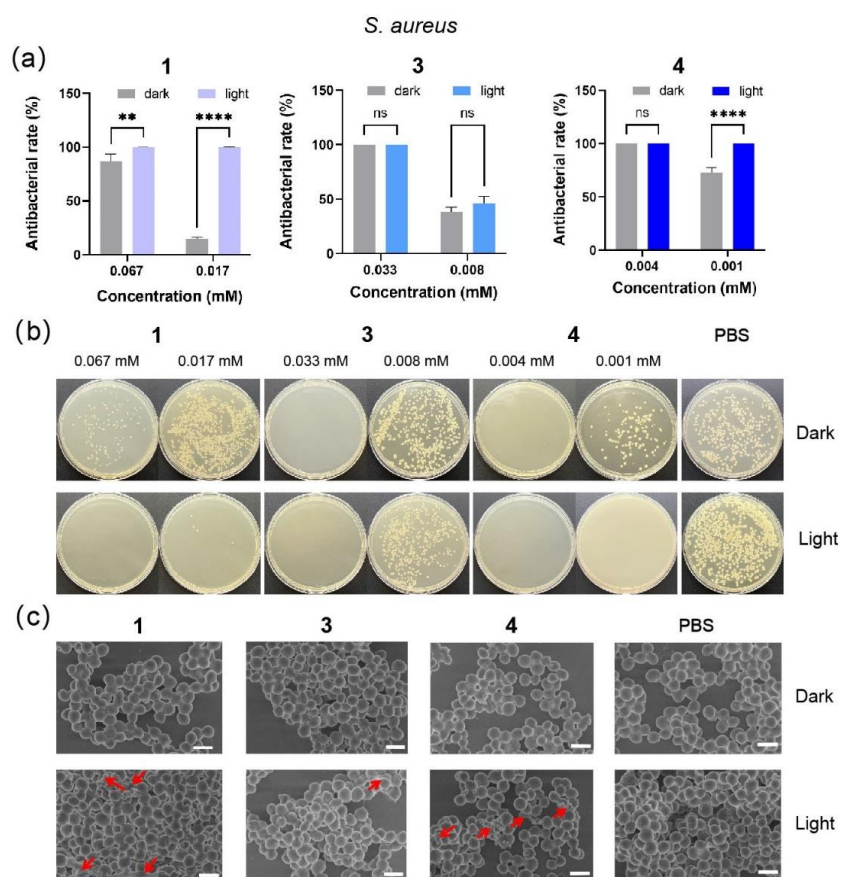
Supplementary Fig. 63 Time-dependent UV/vis absorption spectra following the photodegradation of (a) **G**₅, (b) **G**₆ carried out in aqueous solution using **1**. (c) Photodegradation performances and (d) degradation kinetics fitted curves of **G**₅ and **G**₆ with **1** under 520 nm light irradiation, respectively. C_0 and C_T indicate the initial and intermediate concentrations of dyes, while T is the reaction time.



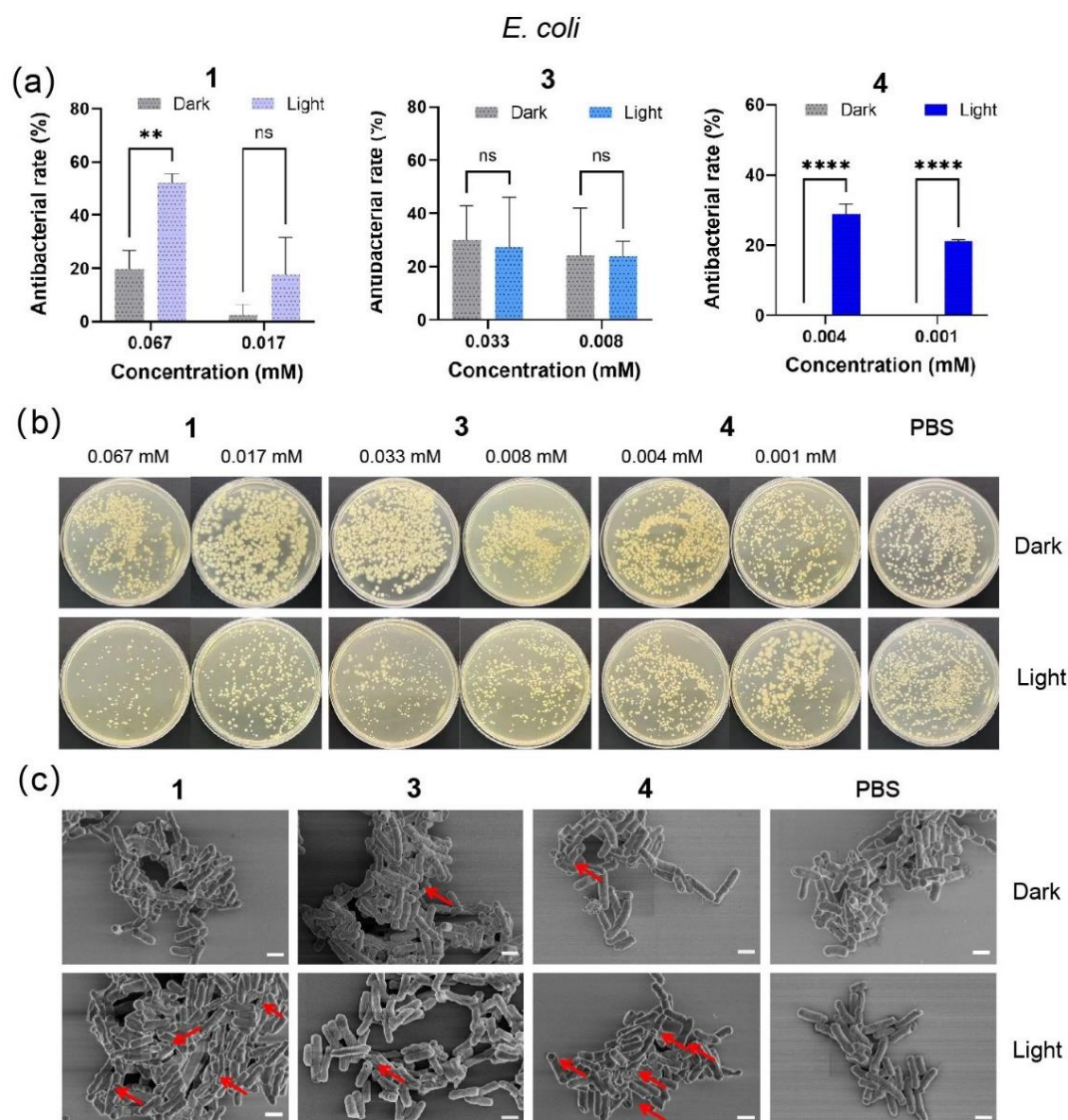
Supplementary Fig. 64 Partial ³¹P{¹H} NMR (243 MHz, CD₃CN, 295 K) spectra of metallacage **4**, **4** + I⁻, **6c** and **6c** + I⁻. Tetrabutylammonium iodide was denoted as I⁻.

Supplementary Notes 7. Antibacterial Activity

Supplementary Discussion: Compared with compound **1**, the metal-coordination bonds in metallacage **4** would promote the intersystem crossing from singlet state to triplet state, which increases the generation of $^1\text{O}_2$ and thus enhances the photocatalytic antibacterial performance. The antibacterial activity of compound **1** was evaluated, and its minimal bactericidal concentration (MBC) was about 0.067 mM against *S. aureus* and *E. coli* under light irradiation (Figs. S65a, 66a). Based on the MBC values of three supramolecular networks **6a-6c**, the concentration of incorporated compound **1** amount was 2.6×10^{-5} , 4.0×10^{-7} and 2.5×10^{-7} mM in **6a**, **6b** and **6c**, respectively, which were much lower than that of its MBC value. The antibacterial effect of metallacage comes from the synergistic effect of compound **1** and the potential toxicity of Pt-based complexes. Therefore, metallacage-based networks exhibit better antibacterial ability than compound **1** inside a PBMA film.

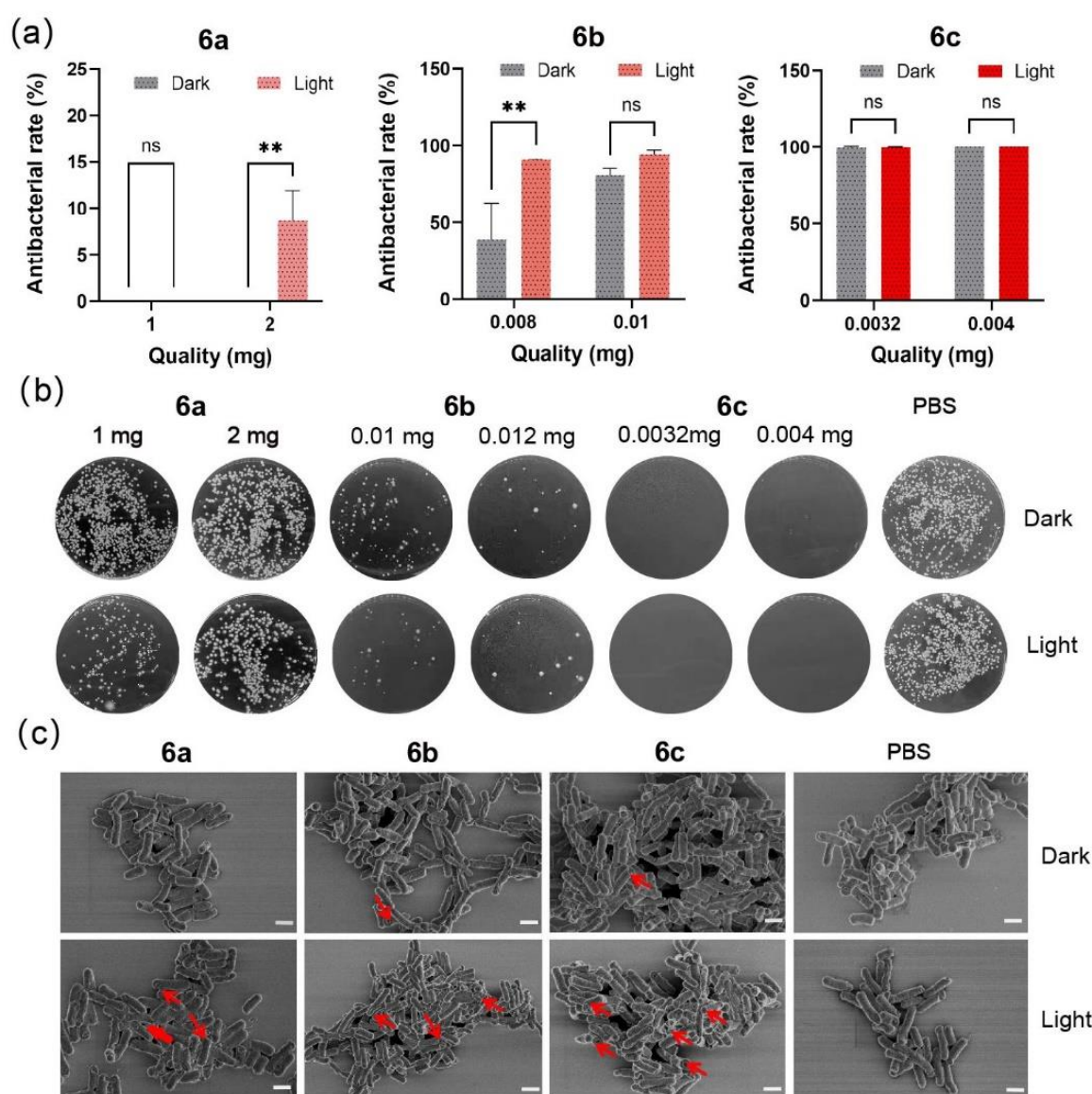


Supplementary Fig. 65 (a) Antibacterial activities of **1**, **3** and **4** against *S. aureus*. Data are presented as the mean $\pm$ SD, $n = 3$. Group difference were conducted by one-way ANOVA with Tukey's post-hoc test. The statistical test was one-sided and no adjustments were made for multiple comparisons. ns indicates not significant; P -values < 0.05 were considered statistically significant, $**p < 0.01$, $****p < 0.0001$. (b) The remaining bacterial colony-forming units (the diameter of the agar plate was 90 mm) and (c) SEM images of *S. aureus* after the treatment with **1**, **3**, **4** and PBS with or without 520 nm light irradiation for 30 min. Scale bar, 1 μm .

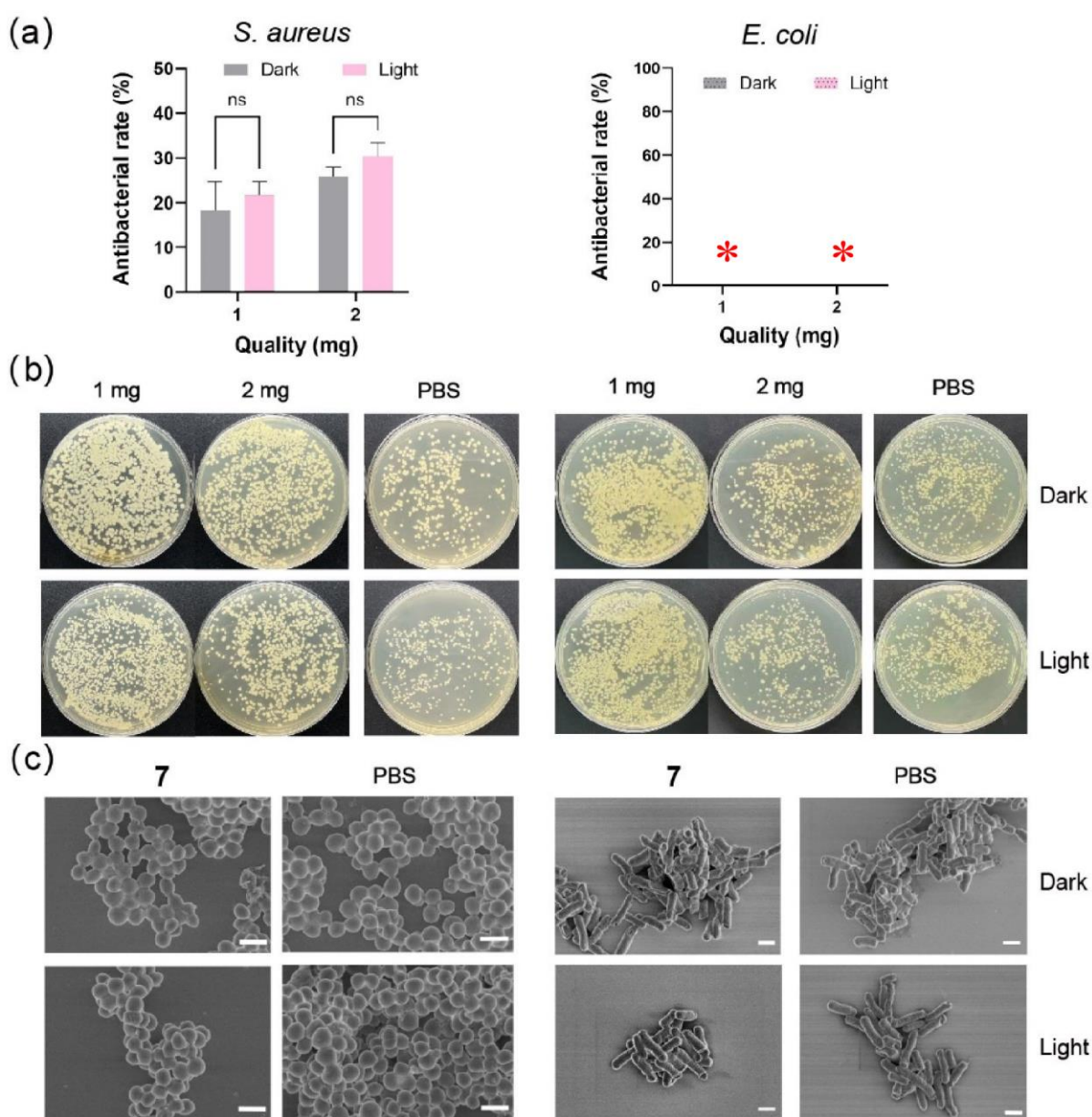


Supplementary Fig. 66 (a) Antibacterial activities of **1**, **3** and **4** against *E. coli*. Data are presented as the mean $\pm$ SD, $n = 3$. Group difference were conducted by one-way ANOVA with Tukey's post-hoc test. The statistical test was one-sided and no adjustments were made for multiple comparisons. ns indicates not significant; P -values < 0.05 were considered statistically significant, $**p < 0.01$. (b) The remaining bacterial colony-forming units (the diameter of the agar plate was 90 mm) and (c) SEM images of *E. coli* after the treatment with **1**, **3**, **4** and PBS with or without 520 nm light irradiation for 30 min. Scale bar, 1 μ m.

E. coli



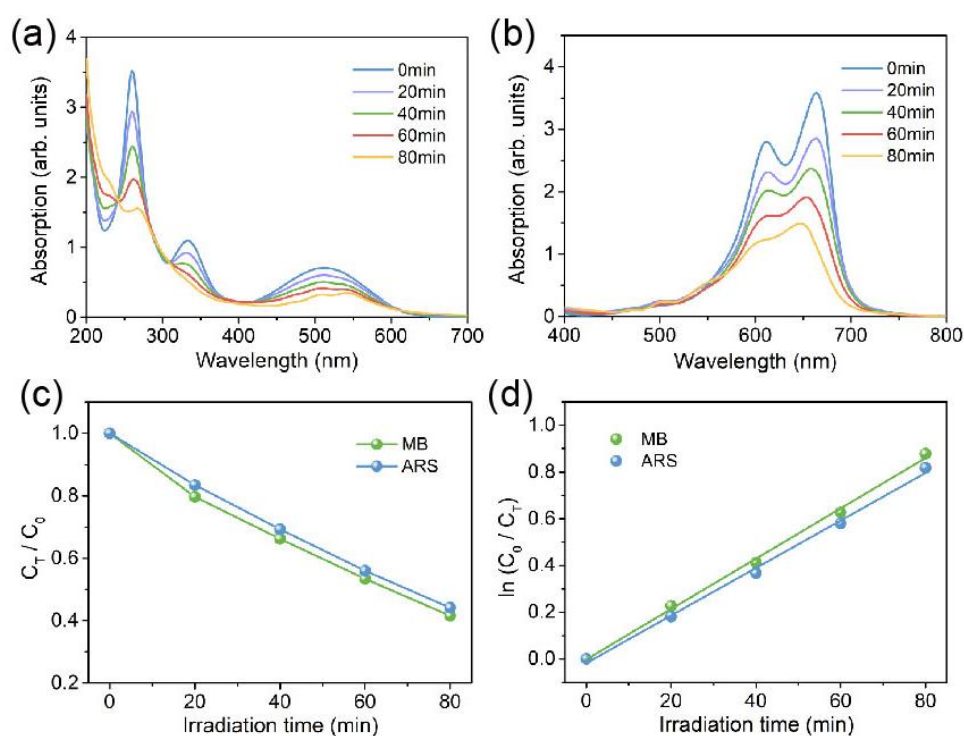
Supplementary Fig. 67 (a) Antibacterial activities of **6a**, **6b** and **6c** against *E. coli*. Data are presented as the mean $\pm$ SD, $n = 3$. Group difference were conducted by one-way ANOVA with Tukey's post-hoc test. The statistical test was one-sided and no adjustments were made for multiple comparisons. ns indicates not significant; P -values < 0.05 were considered statistically significant, $**p < 0.01$, $****p < 0.0001$. (b) The remaining bacterial colony-forming units (the diameter of the agar plate was 90 mm) and (c) SEM images of *E. coli* after the treatment with **6a**, **6b**, **6c** and PBS with or without 520 nm light irradiation for 30 min. Scale bar, 1 μ m.



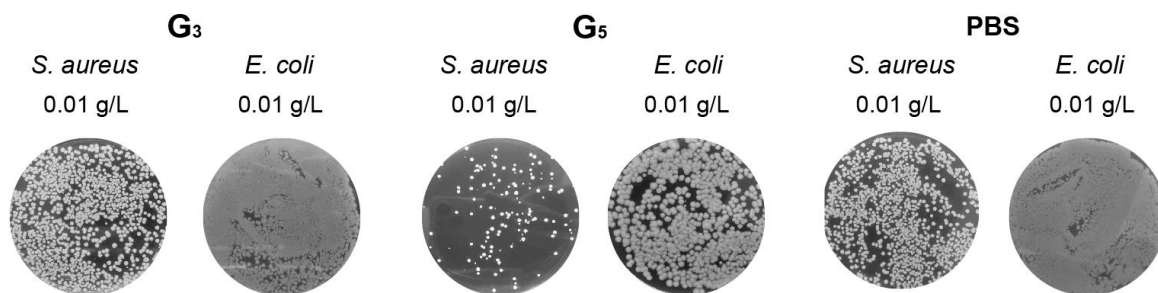
Supplementary Fig. 68 (a) Antibacterial activities of 7 against *S. aureus* and *E. coli*. * represents no antibacterial ability of 7 against *E. coli*. Data are presented as the mean $\pm$ SD, $n = 3$. Group difference were conducted by one-way ANOVA with Tukey's post-hoc test. The statistical test was one-sided and no adjustments were made for multiple comparisons. ns indicates not significant. (b) The remaining bacterial colony-forming units (the diameter of the agar plate was 90 mm) and (c) SEM images of *S. aureus* and *E. coli* after the treatment with 7 and PBS with or without 520 nm light irradiation for 30 min. Scale bar, 1 μ m. ns indicates not significant; P -values < 0.05 were considered statistically significant, ** $p < 0.01$, **** $p < 0.0001$.



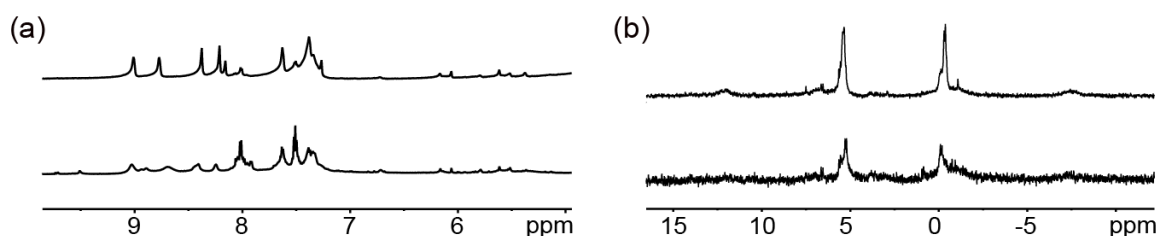
Supplementary Fig. 69 Optical photograph of the water decontamination setup.



Supplementary Fig. 70 Time-dependent UV/vis absorption spectra following the photodegradation of (a) G_3 and (b) G_5 carried out in *S. aureus* and *E. coli* solution using **6c**. (c) Photodegradation performances and (d) degradation kinetics fitted curves of **6c** for photodegradation in *S. aureus* and *E. coli* solution. C_0 and C_T indicate the initial and intermediate concentrations of dyes, while T is the reaction time.



Supplementary Fig. 71 The remaining bacterial colony-forming units of *S. aureus* or *E. coli* and dye (G_3 or G_5) solution after the treatment under 520 nm light irradiation for 30 min. The diameter of the agar plate was 90 mm.



Supplementary Fig. 72 (a) Partial ^1H NMR spectra (left, 600 MHz, CD_3CN , 295 K) and (b) partial $^{31}\text{P}\{^1\text{H}\}$ NMR (right, 243 MHz, CD_3CN , 295 K) spectra of network **6c** with 6 wt% **4** loading before (top) and after (bottom) water decontamination.

Supplementary References

1. Liu, S. et al. Peroxydisulfate activation by sulfur-doped ordered mesoporous carbon: Insight into the intrinsic relationship between defects and $^1\text{O}_2$ generation. *Water Res.* **221**, 118797 (2022).
2. Takuro Teraoka, S. H., and Hiroshi Shinokubo, Iridium-Catalyzed Direct Tetraborylation of Perylene Bisimides. *Org. Lett.* **13**, 2532 (2011).
3. Hou, Y. et al. Highly emissive perylene diimide-based metallacages and their host-guest chemistry for information encryption. *J. Am. Chem. Soc.* **142**, 18763-18768 (2020).
4. Zheng, Y. et al. A facile approach toward multicomponent supramolecular structures: Selective self-assembly via charge separation. *J. Am. Chem. Soc.* **132**, 16873 (2010).