Supporting Information

A supramolecular diazapyrene radical assembly with NIR absorption for selective photothermal antibacterial

Xiang Yu,[a] Chunmei Wang,[a] Dongdong Sun,[a] Simin Liu*[a,b]

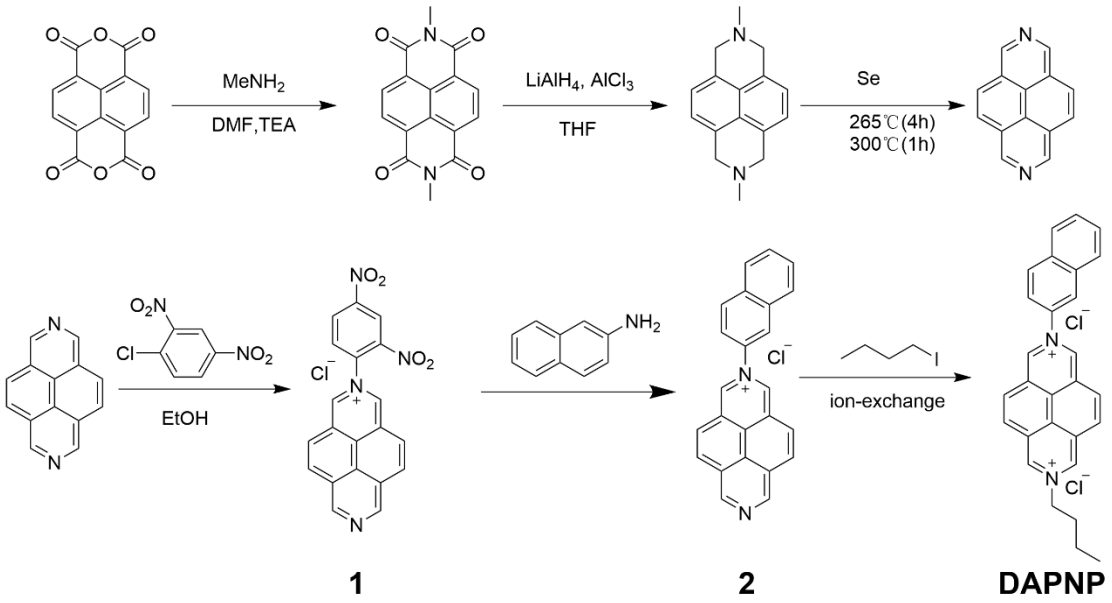
Table of Contents

1. Materials and Instrumentation

All chemical reagents were obtained from commercial suppliers and were used without further purification. CB[10] and **DAPNP** were prepared using the corresponding literature methods.[1, 2]

^{1}H NMR spectra were performed using an Agilent 600 MHz apparatus. The UV-Vis absorption spectra were studied using a Shimadzu UV-Vis-NIR spectrophotometer (UV-3600). Fluorescence profiles were recorded on a PerkinElmer LS-55 instrument. Scanning electron microscope (SEM) images were acquired on a FEI Nova 400 Nano instrument. The potentiometric diagram was performed on the Nicomp 380 Z3000. EPR experiments were performed on a Bruker A300 Xband EPR spectrometer.

2. The synthesis and characterization of DAPNP



Scheme S1. Synthetic route of **DAPNP**

Synthesis of 2,7-diazapyrene were adapted from previously reported procedures.[2]

The synthesis of compound **1**

2, 7-diazapyrene (1 g, 5 mmol) and 1-chloro-2,4-dinitrobenzene (1 g, 5 mmol) were added to ethanol solution (60 mL) and heated to reflux for 72 h. After the reaction, the reaction system is evaporated under reduced pressure, which was re-dissolved in MeOH (10 mL) and was added dropwise into diethyl ether (150 mL) to precipitate products. The precipitated product was washed three times with ether and dried to obtain yellow solid (1.5 g, 89%). ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm) : 10.47 (s, 2H), 10.06 (s, 2H), 9.25 (d, *J* = 2.6 Hz, 1H), 9.10 (dd, *J* = 8.6, 2.6 Hz, 1H), 8.94 (d, *J* = 9.0 Hz, 2H), 8.72 (d, *J* = 9.0 Hz, 2H), 8.57 (d, *J* = 8.6 Hz, 1H).

The synthesis of compound **2**

Compound **1** (406 mg,1 mmol) and 2-naphthylamine (430 mg, 3 mmol) were added to ethanol solution (20 mL) and heated for reflux for 24 h. The precipitated product was obtained by adding 50 mL of ether to the reaction solution. The solid was washed three times with ether and dried to obtain a gray solid (420 mg, 88%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.54 (s, 2H), 9.97 (s, 2H), 8.86 (d, *J* = 9.0 Hz, 2H), 8.76 – 8.70 (m, 3H), 8.43 (d, *J* = 8.8 Hz, 1H), 8.24 – 8.17 (m, 3H), 7.82 – 7.76 (m, 2H).

The synthesis of **DAPNP**

Compound **2** (200 mg, 0.42 mmol) was added to acetonitrile solution (10 mL), followed by 1 mL iodobutane solution, and the reactants were heated to reflux for 24 h. 50 mL of ether was added to the reaction solution to obtain the precipitated product, and the solid was washed three times with ether, and then the product (170 mg, 88%) was obtained by anion exchange. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.85 (s, 2H), 10.48 (s, 2H), 9.04 – 8.96 (m, 4H), 8.81 (d, J = 2.3 Hz, 1H), 8.47 (d, J = 8.8 Hz, 1H), 8.26 (ddd, J = 23.2, 8.5, 3.3 Hz, 4H), 7.84 – 7.80 (m, 2H), 5.15 (t, J = 7.5 Hz, 2H), 2.25 – 2.19 (m, 2H), 1.47 (q, J = 7.5 Hz, 2H), 1.00 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 131.15, 130.71, 130.59, 129.49, 129.32, 129.28, 128.90, 128.62, 125.80, 122.75, 63.20, 40.51, 40.38, 40.34, 33.67, 19.47, 13.90. HRMS (ESI): m/z [M-2Cl$^-$]$^{2+}$ calcd. for $C_{28}H_{24}N_2^{2+}$:194.255, found : 194.0961.

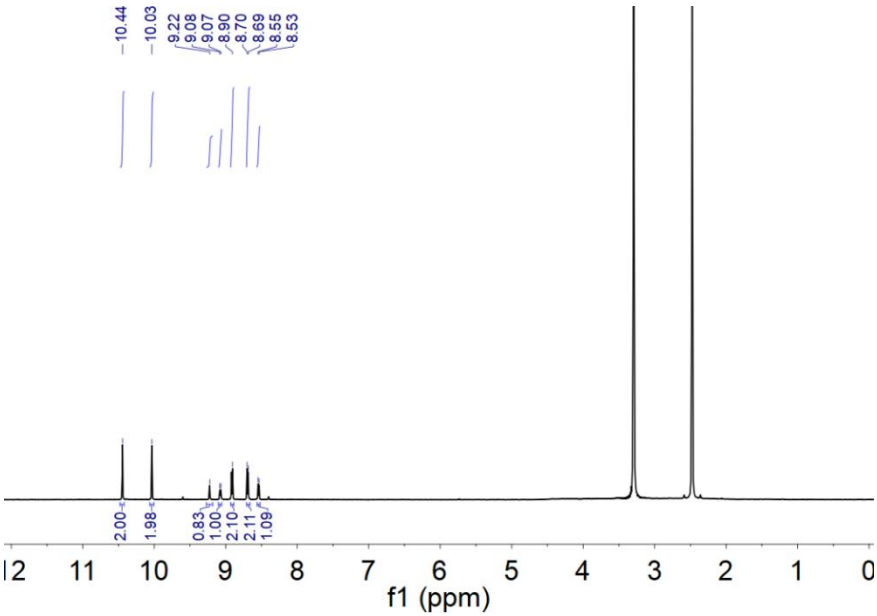


Figure S1. ^{1}H NMR spectrum of compound **1** (600 MHz, 298 K, DMSO-d_6).

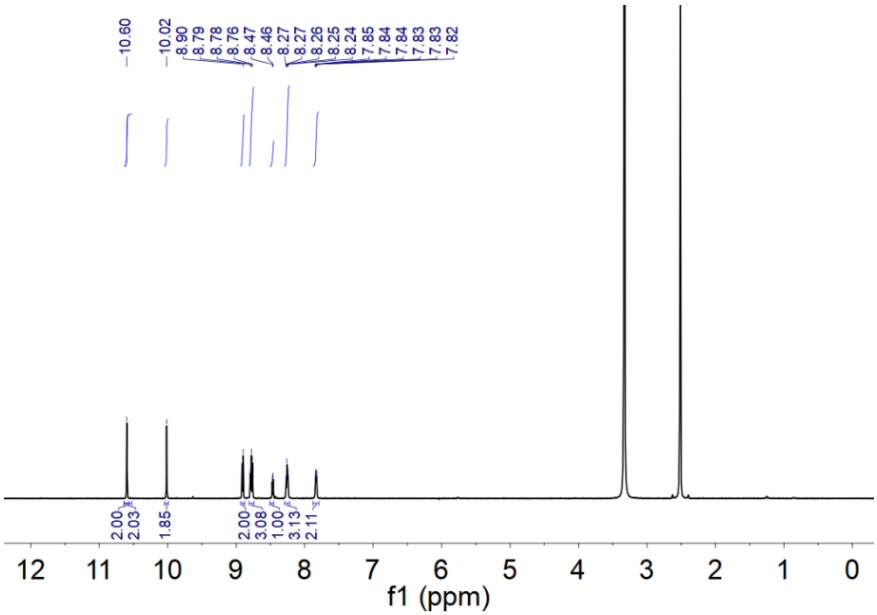


Figure S2. ^{1}H NMR spectrum of compound **2** (600 MHz, 298 K, DMSO-d_6).

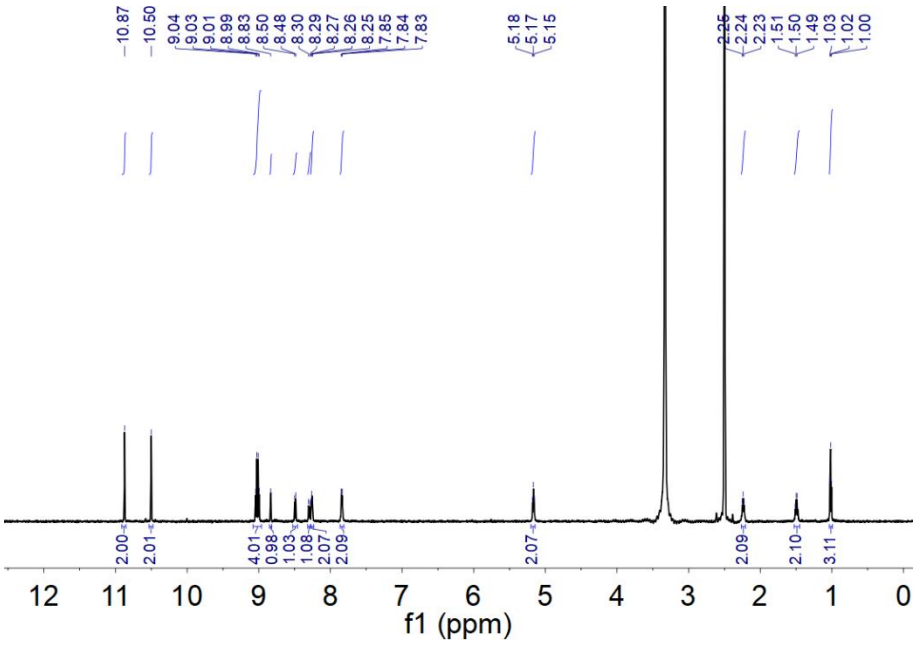


Figure S3. ^{1}H NMR spectrum of **DAPNP** (600 MHz, 298 K, DMSO-d_6).

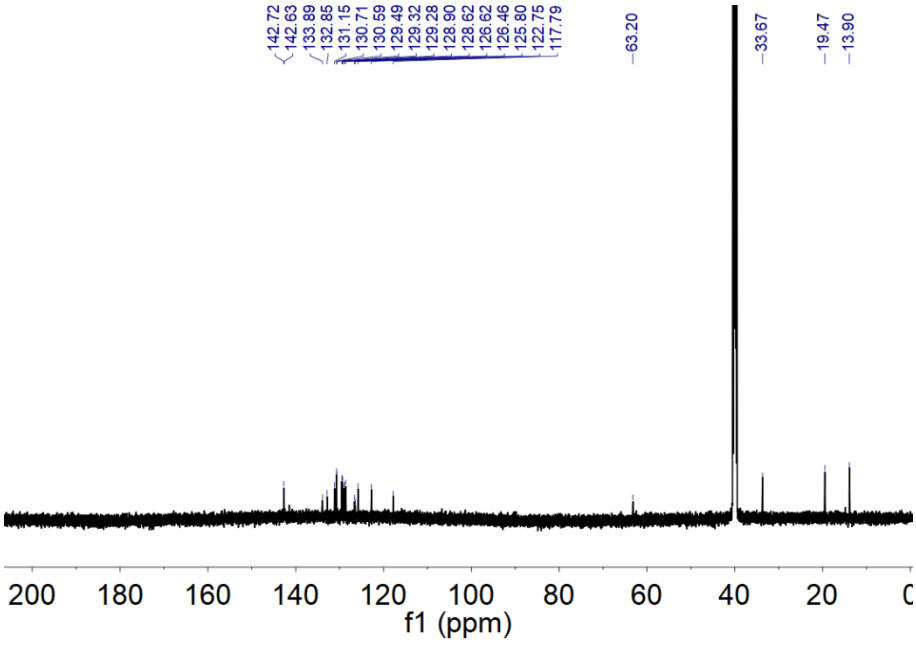


Figure S4. ^{13}C NMR spectrum of **DAPNP** (600 MHz, 298 K, DMSO-d_6).

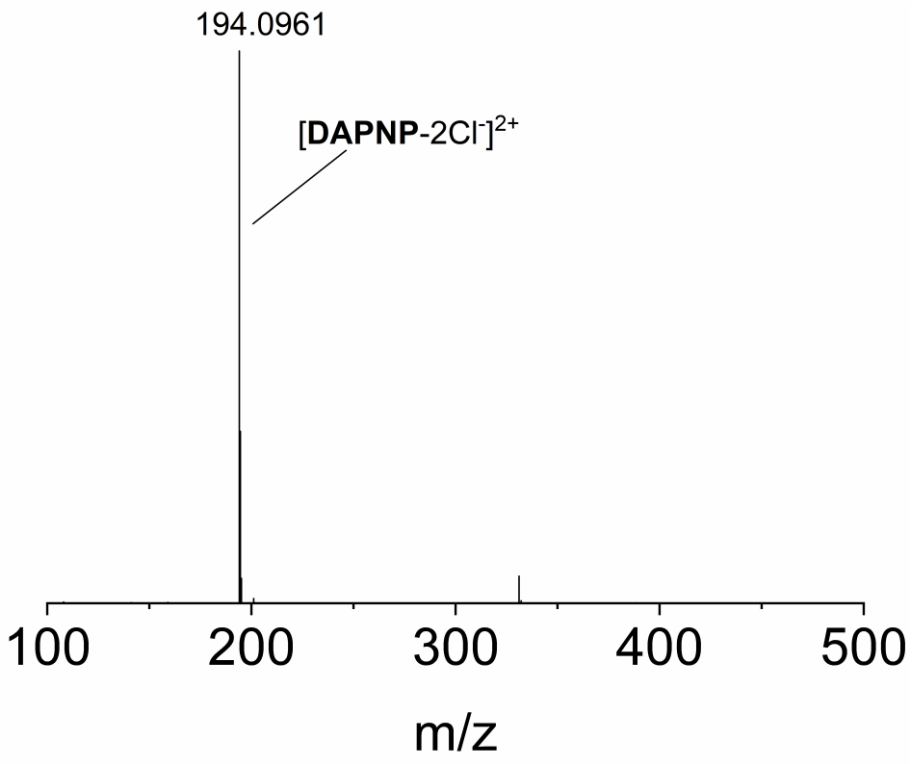


Figure S5. ESI-MS spectrum of **DAPNP**.

3. Experimental procedures

3.1 The Characterization of host-guest recognition between DAPNP and CB[10]

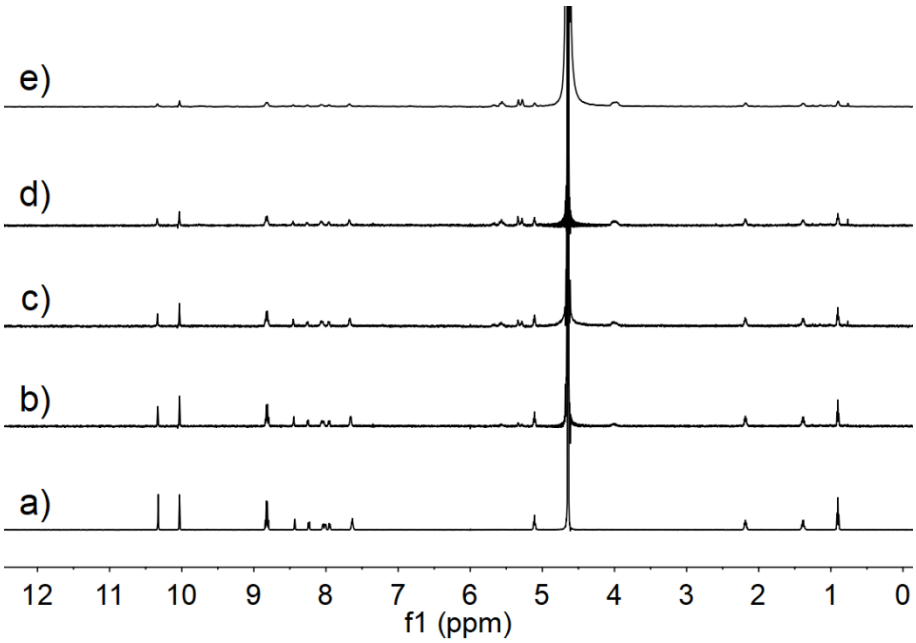


Figure S6. ^{1}H NMR spectra of **DAPNP** (0.5 mM, 600 MHz, D_2O, 298 K) with a) 0, b) 0.25, c) 0.5, d) 0.75, e) 1.00 equiv. of CB[10].

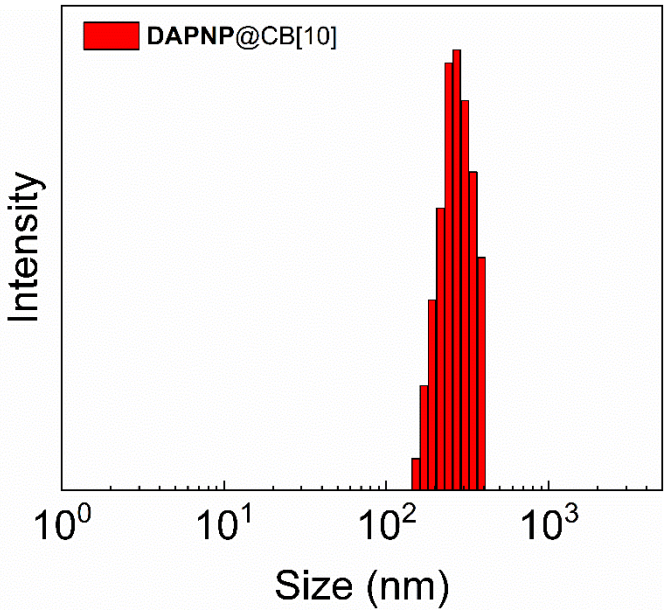


Figure S7. Dynamic light scattering (DLS) analysis of **DAPNP**@CB[10].

3.2 Formation and photothermal properties of DAPNP radical cations

$Na_2S_2O_4$ solution was freshly prepared and injected into **DAPNP** or **DAPNP**@CB[10] aqueous solution. The characteristic absorption peak of free radical was measured by UV-Vis spectrophotometer after free radical generation. Then a 660 nm laser was used to irradiate the solution, and a photothermal imager was used to detect the temperature change of the solution in real time. Similar photothermal experiments were carried out with aqueous solution as blank control.

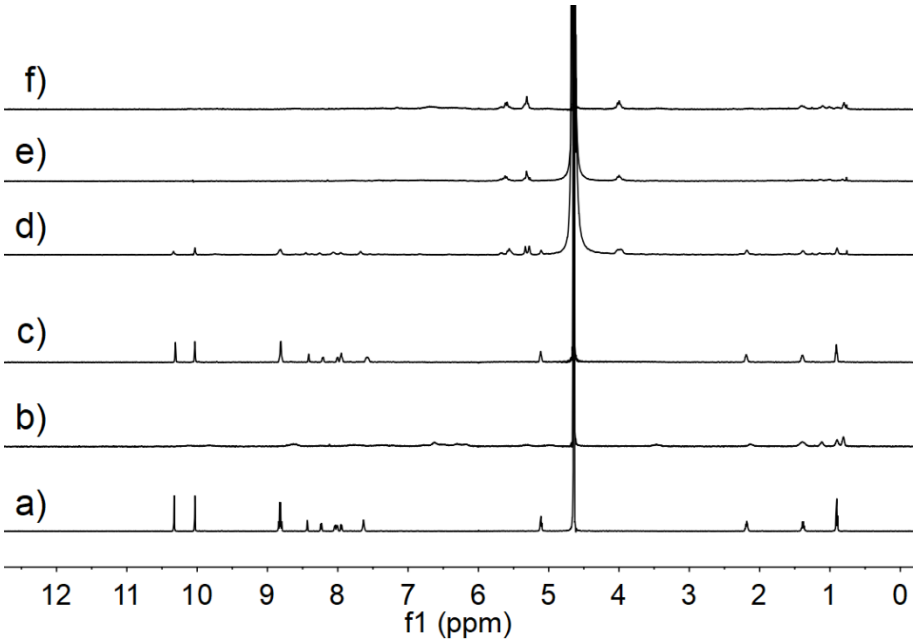


Figure S8. ^{1}H NMR spectra (600 MHz, D_2O, 298 K) of a) **DAPNP**, b) **DAPNP** with $Na_2S_2O_4$, c) **DAPNP** placed for 2 days after reduction, d) **DAPNP**@CB[10], e) **DAPNP**@CB[10] with $Na_2S_2O_4$, f) **DAPNP**@CB[10] placed for 2 days after reduction, ([**DAPNP**]=0.5 mM).

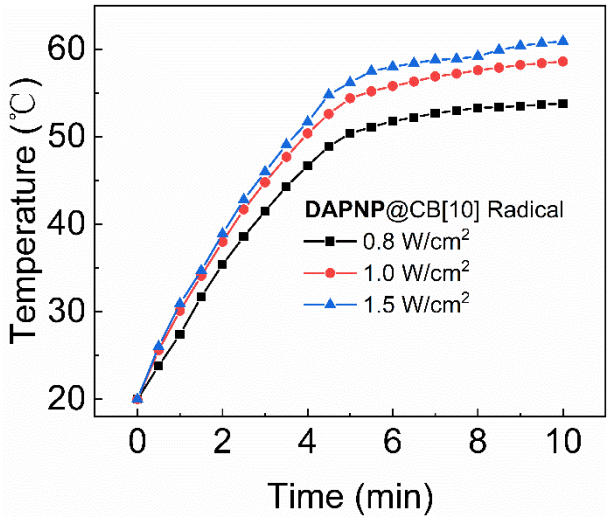


Figure S9. Heating curves of **DAPNP**@CB[10] radicals solution under different light intensities, ([**DAPNP**] = 0.2 mM).

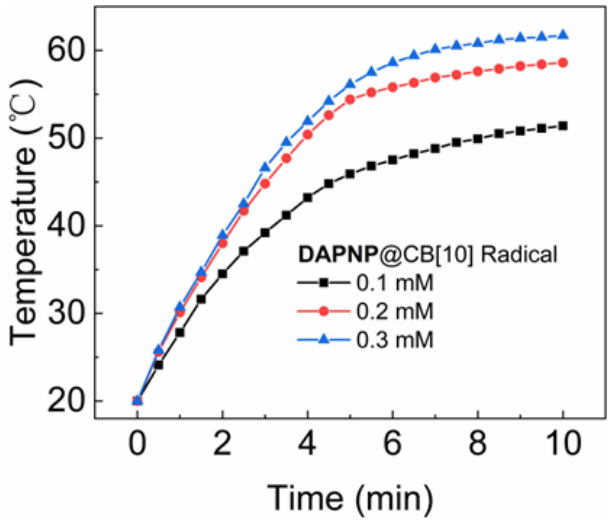


Figure S10. Heating curves of **DAPNP**@CB[10] radicals solution under different concentrations.

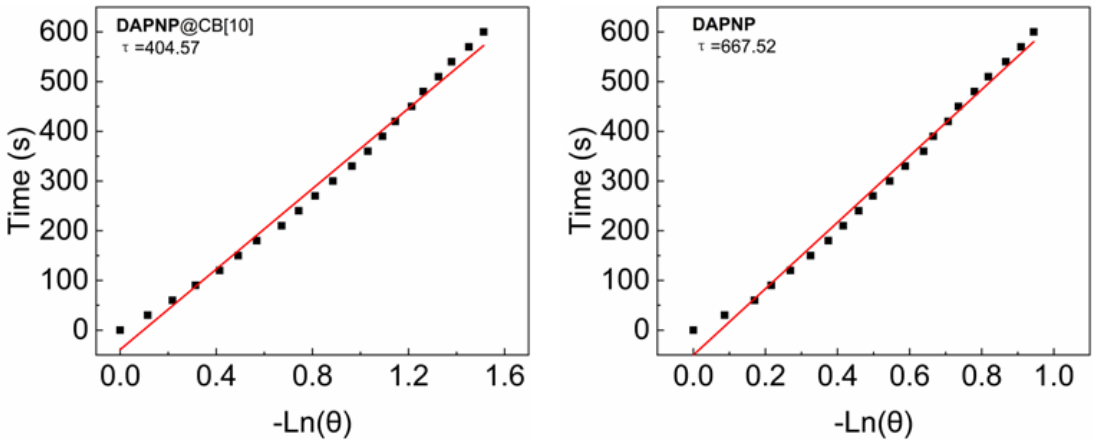


Figure S11. Calculation of photothermal conversion rate of **DAPNP**@CB[10] radicals and **DAPNP**

radical cations solution under the irradiation of 660 nm laser at 1.0 W/cm^2.

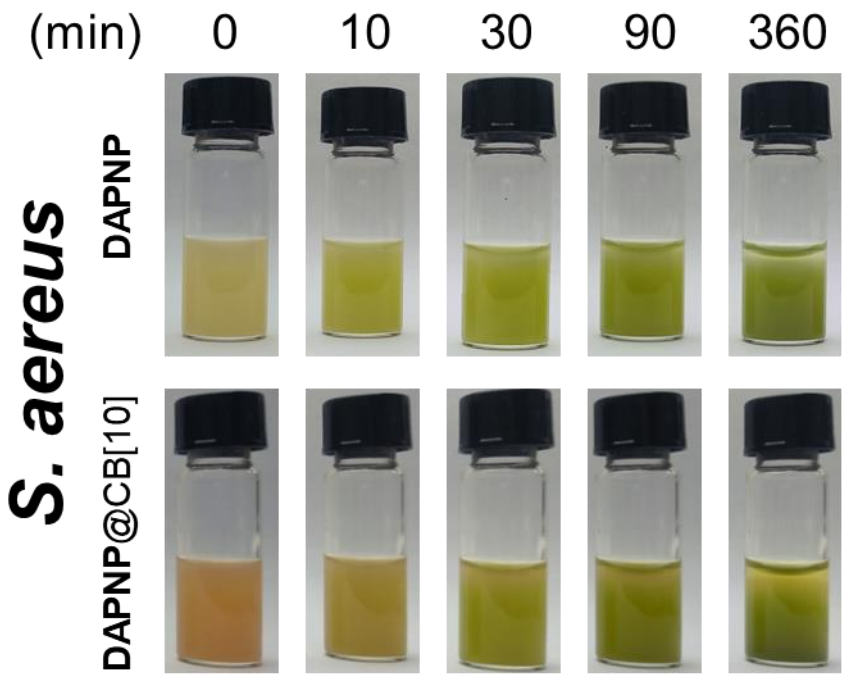


Figure S12. Optical photograph of the samples after incubation with *S. aureus*.

3.3. Photothermal antibacterial experiment

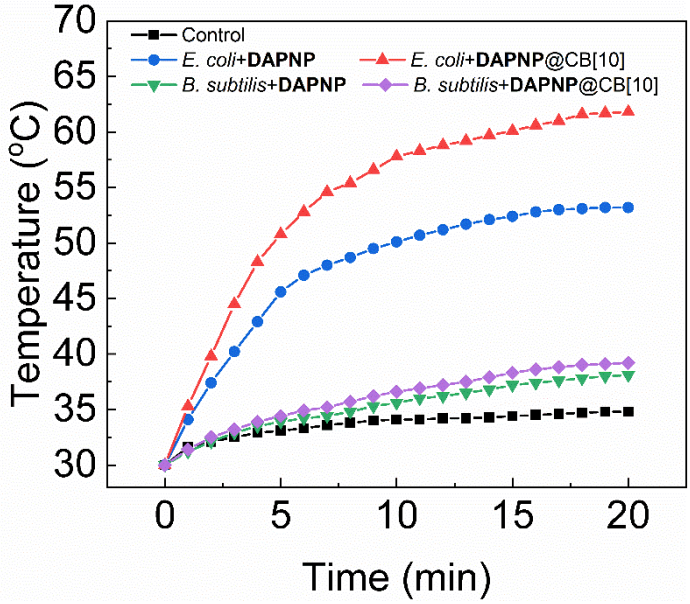


Figure S13. Heating curves of **DAPNP** and **DAPNP**@CB[10] solutions in the presence of *E. coli* and *B. subtilis* under irradiation, ([**DAPNP**] = 0.2 mM).

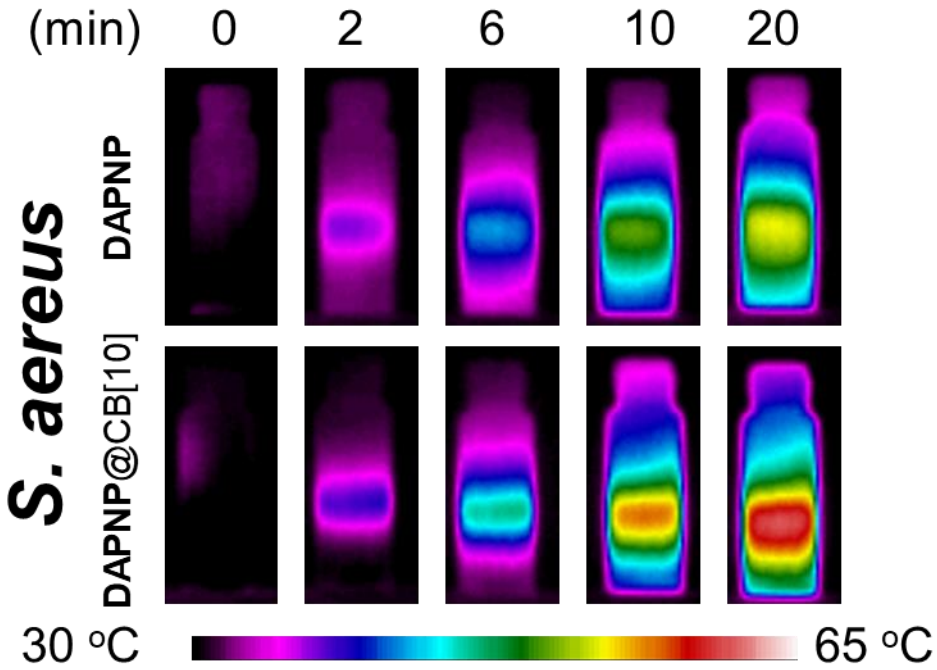


Figure S14. Temperature images of the aqueous solution of the samples in the presence of *S. aureus* under irradiation of 660 nm laser, ([**DAPNP**] = 0.2 mM).

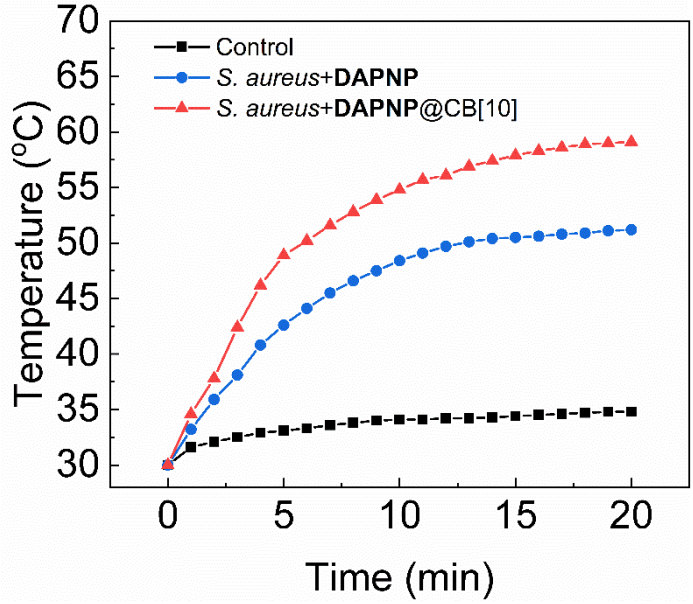


Figure S15. Heating curves of **DAPNP** and **DAPNP**@CB[10] solutions in the presence of *S. aureus* under irradiation, ([**DAPNP**] = 0.2 mM).

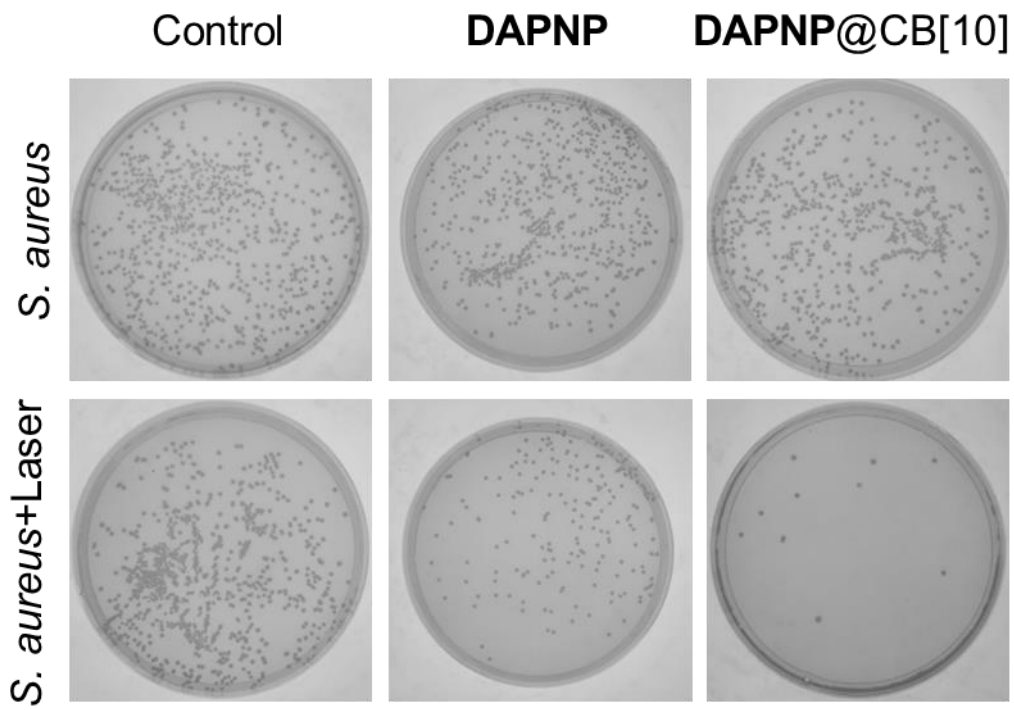


Figure S16. Photographs of bacterial colonies formed by *S. aureus* after being treated with PBS, **DAPNP** or **DAPNP**@CB[10] in the presence or absence of 660 nm laser irradiation.

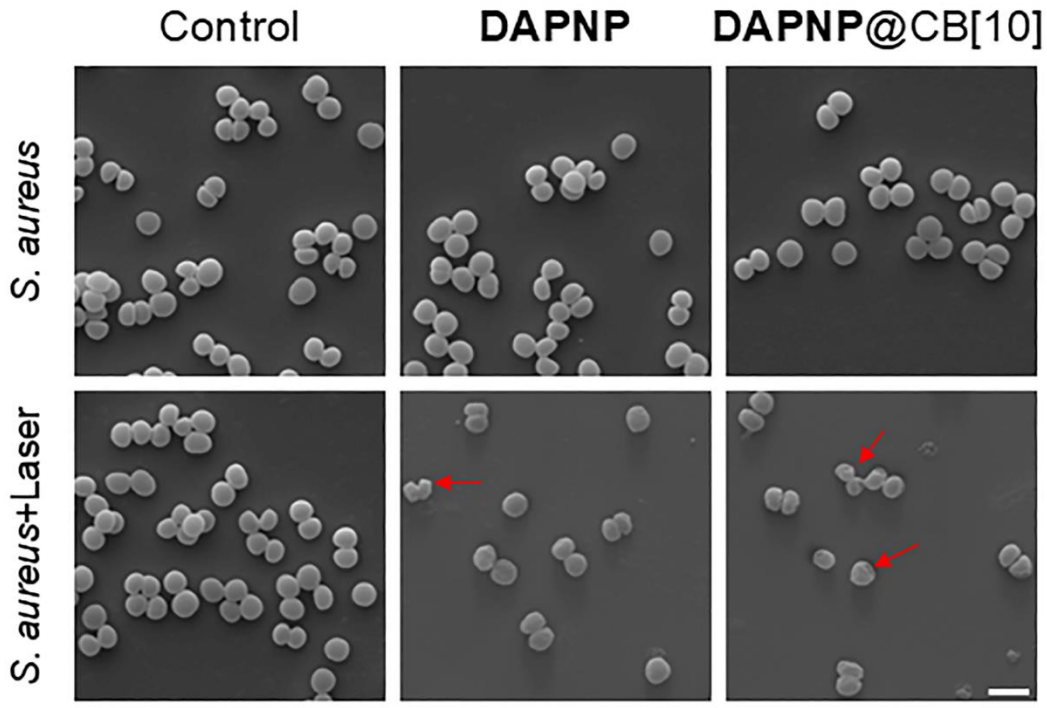


Figure S17. SEM images of *S. aureus* treated with PBS, **DAPNP** or **DAPNP**@CB[10] in the presence or absence of 660 nm irradiation, scale bar = 1 μm.

3.4. The cytotoxicity of materials

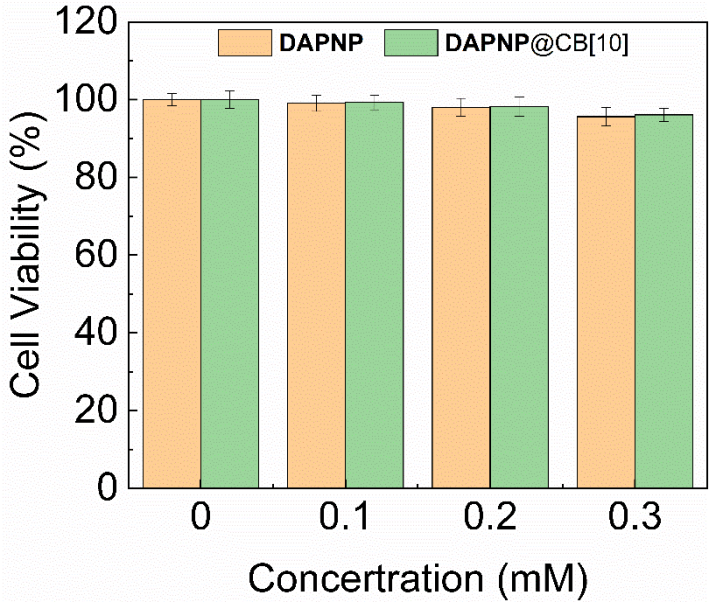


Figure S18. The cell viability of 3T3 cells treated with various concentrations of the samples.

4. References

1. X. Yang, Z. Zhao, X. Zhang and S. Liu, *Sci. China Chem.*, 2018, **61**, 787-791.
2. G. Fan, X. Yu, X. Han, Z. Zhao and S. Liu, *Org. Lett.*, 2021, **23**, 6633-6637.