

Supporting Information for

Amphiphilic polymeric micelles as microreactors: improving photocatalytic hydrogen production of [FeFe]-hydrogenase mimic in water

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1. Instruments and methods

^1H NMR spectra were recorded on a Bruker400 FT-NMR spectrometer and chemical shifts are given relative to tetramethylsilane. Mass spectra were recorded with ApexIII (7.0 tesla) FTICR mass spectrometer (Bruker). UV-vis spectra were measured on a Shimadzu UV-1601PC spectrophotometer. Emission spectra were recorded on a Perkin Elmer LS50B spectrofluorimeter. The IR spectra were recorded by Excalibur 3100, the spectra of **PDT**, **P-NB** was obtained by analysis of solid sample in KBr, the spectra of **PDT@P-NB**, **PDT@P-NB** + $\text{Ru}(\text{bpy})_3\text{Cl}_2$, $\text{Ru}(\text{bpy})_3\text{Cl}_2$, and $\text{Ru}(\text{bpy})_3\text{Cl}_2$ + **P-NB** were obtained by analysis of corresponding aqueous solution in cell. The transient absorption spectroscopy and the lifetime of $\text{Fe}^{\text{I}}\text{Fe}^0$ species were measured by Edinburgh LP920 apparatus. The samples were purged with argon for 30 min. Excitation was provided by using an Nd:YAG laser (third harmonic, 10 ns) at 355 nm. The detector was a xenon lamp. Quinine in 0.5 M H_2SO_4 aqueous solution was used as a reference for determination of quantum yield (QY) of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ with known QY of 0.546 as excited at 365 nm.

The preparation of PDT@P-NB micellar aqueous solution:

- 1) A certain amount of **PDT** (50.0 mg, red solid) was dissolved in a mixed solution of dichloromethane and petroleum ether ($v/v = 1/1$, total volume = 10 mL) in a round-bottomed flask, then evaporated solvent by rotary evaporator to make **PDT** as a red film attached in the bottom of flask.
- 2) A certain amount of **P-NB** (150.0 mg, colorless solid), water (100 mL), and a magnetic bar were added into the flask, and then put the flask on a magnetic stirrer for long time stirring.
- 3) A small amount of solution in flask was extracted during stirring at certain time for UV-vis absorption to determine the loading amount of **PDT** in **P-NB** micelle; caution: the extracted solution was filtered by 0.45 μm filter before doing UV-vis absorption testing.
- 4) After completion of self-assembly, which was monitored by UV-vis absorption,

the **PDT@P-NB** micellar aqueous solution was filtered by 0.45 μm filters as stock solution for further analysis and photocatalysis.

Photocatalytic Hydrogen Production Experiment:

The experiments were conducted in a Schlenk tube containing corresponding components. The pH of the sample was adjusted by aqueous NaOH or HCl solution prior irradiation. The sample was saturated by nitrogen gas to eliminate oxygen. The CH_4 (500 μL) was injected as the internal standard for quantitative GC-TCD analysis. The light sources was blue LED lamp (0.3 A, $\lambda = 450$ nm). The generated photoproduct of H_2 was characterized by GC-TCD analysis (TIANMEI 7890-II) using nitrogen as the carrier gas with a molecular sieve column (5 \AA ; 2 m \times 2 mm) and a thermal conductivity detector. 500 μL of mixed gas was extracted from the sample tube and injected into the GC. The response factor for H_2/CH_4 was about 5.12 under the experimental conditions, which was established by calibration with known amounts of H_2 and CH_4 , and determined before and after a series of measurements.

Control experiments of photocatalytic hydrogen production^[a]

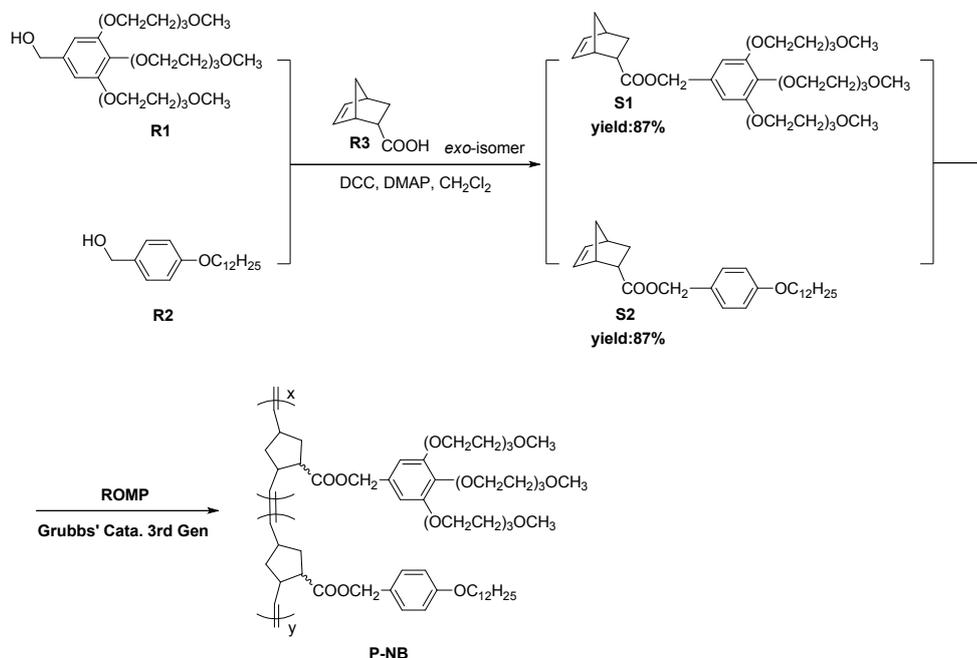
Entry ^[b]	PDT@P-NB	Ru(bpy) ₃ Cl ₂	H ₂ A	irradiation	TON (H ₂)
1	P	P	P	P	48
2 ^[c]	P	P	P	P	trace
3	A	P	P	P	trace
4	P	A	P	P	null
5	P	P	A	P	null
6	P	P	P	A	null

[a]. P = presence, A = absence; [b]. the concentration of each component: $[\text{PDT}] = 3.0 \times 10^{-5}$ M, $[\text{Ru}(\text{bpy})_3\text{Cl}_2] = 3.0 \times 10^{-5}$ M, $[\text{H}_2\text{A}] = 4.5 \times 10^{-2}$ M, pH = 4.0-4.1; irradiation time: 2 h; light source: LED lamp, $\lambda_{\text{max}} = 450$ nm; [c]. No **PDT** in **P-NB** micelle;

2. Synthesis

All moisture-sensitive reactions were performed under an atmosphere of dry argon. All solvents were dried and distilled prior to use according to the standard methods. All chemicals were obtained from commercial suppliers and used without further purification unless otherwise noted. The synthesis and characterization of amphiphilic polymer **P-NB** were reported by our group in literature.^[1] The catalyst **PDT** were synthesized according to literature.^[2]

1) Synthesis of **P-NB**

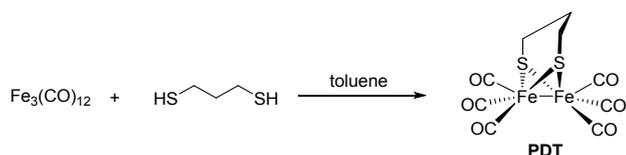


S1: ¹H NMR (400 MHz, CDCl₃, ppm) δ : 6.57 (s, 2H), 6.10 (m, 2H), 4.99 (s, 2H), 4.14 (t, 6H, $J = 4.6$ Hz), 3.83 (m, 4H), 3.77 (m, 2H), 3.70 (m, 6H), 3.63 (m, 12H), 3.52 (m, 6H), 3.35 (s, 9H), 3.04 (m, 1H), 2.91 (m, 1H), 2.25 (m, 1H), 1.91 (m, 1H), 1.50 (m, 1H), 1.36 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ : 175.49, 152.30, 137.99, 137.69, 135.31, 131.24, 107.49, 71.91, 71.55, 70.43, 70.30, 70.14, 69.33, 68.53, 65.83, 58.58, 46.24, 45.95, 42.74, 41.25, 30.02. EI-MS: $m/z = 714$ [M⁺].

S2: ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 7.28 (d, 2H, $J = 8.4$ Hz), 6.87 (d, 2H, $J = 8.8$ Hz), 6.10 (m, 2H), 5.07 (s, 2H), 3.96 (t, 2H, $J = 6.4$ Hz), 3.05 (m, 1H), 2.92 (m, 1H), 2.25 (m, 1H), 1.94 (m, 1H), 1.78 (m, 2H), 1.53 (m, 1H), 1.46 (m, 2H), 1.28 (s, 18H), 0.90 (t, 3H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ : 176.04, 159.11, 138.00, 135.70, 129.85, 128.11, 114.45, 67.98, 66.07, 46.59, 46.31, 43.16, 41.62, 31.89, 30.32, 29.60 (2C), 29.56 (2C), 29.36, 29.32, 29.22, 26.01, 22.66, 14.09. EI-MS: $m/z = 412$ [M^+].

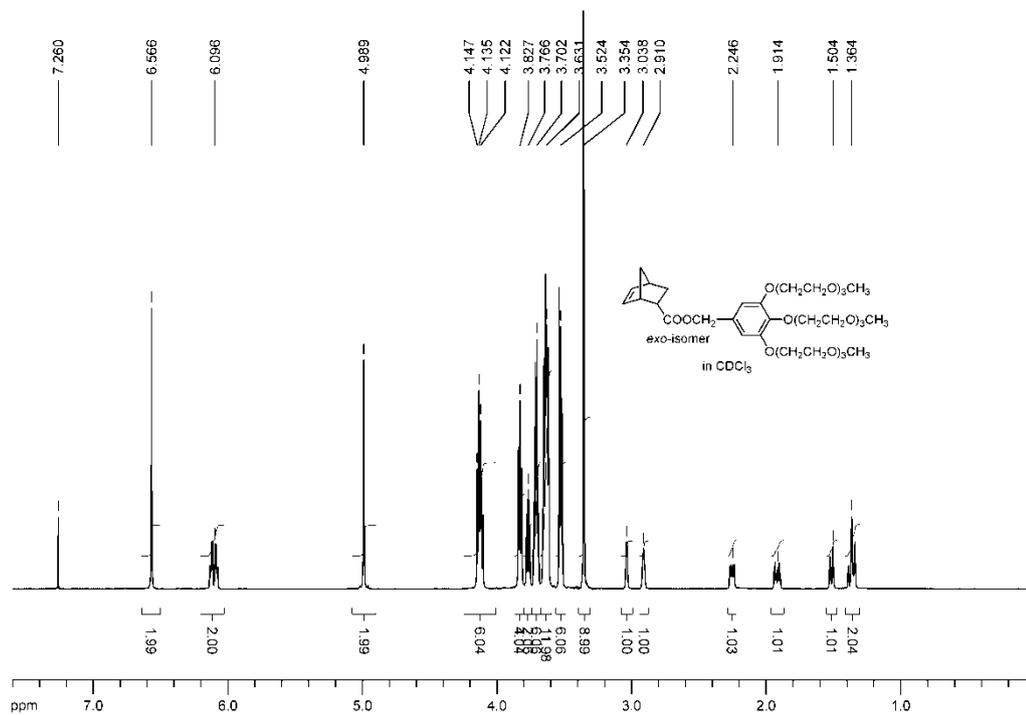
P-NB: ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 7.20 (br, 1H), 6.80 (br, 1H), 6.52 (br, 1H), 5.33 (m, 2H), 4.98 (br, 2H), 4.09 (br, 3H), 3.88 (br, 1H), 3.80 (m, 2H), 3.75 (m, 1H), 3.68 (m, 3H), 3.61 (m, 6H), 3.51 (m, 3H), 3.33 (br, 4.5H), 3.09 (m, 1H), 2.71 (m, 1H), 2.51 (br, 1H), 2.03 (br, 2H), 1.72 (br, 1H), 1.62 (br, 1H), 1.40 (br, 1H), 1.23 (br, 8H), 1.10 (br, 1H), 0.85 (t, 1.5H, $J = 6.6$ Hz).

2) Synthesis of PDT

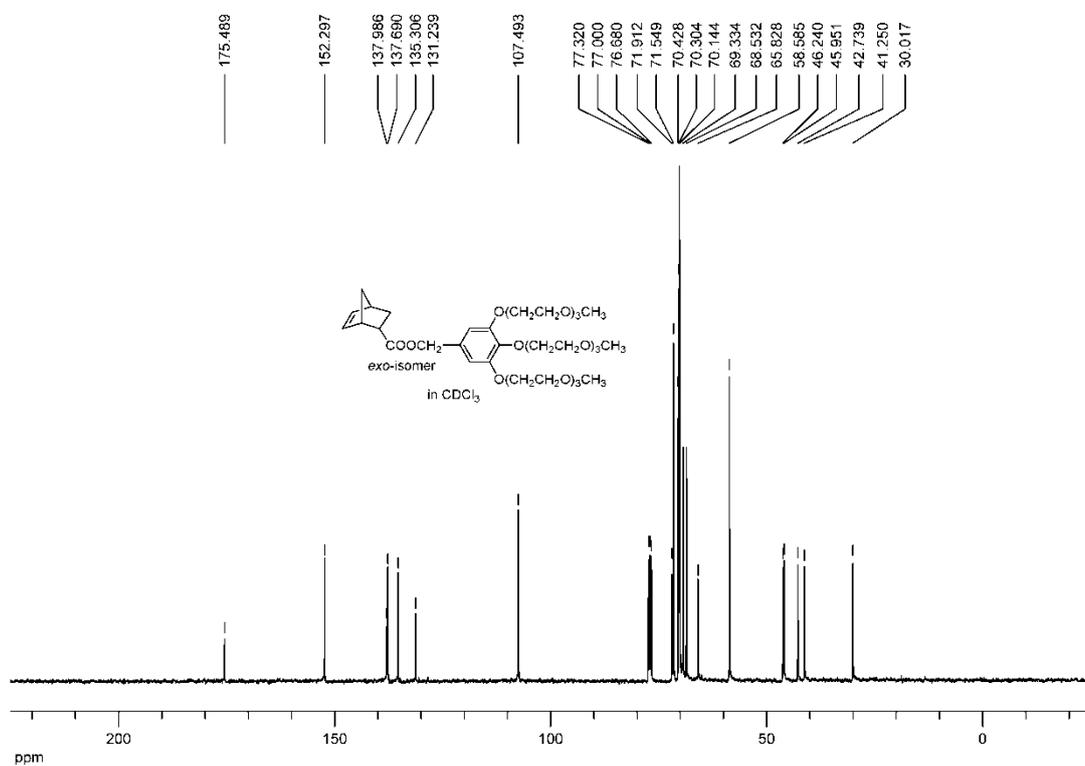


PDT: ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 2.14 (m, 4H), 1.81 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 30.56, 23.43.

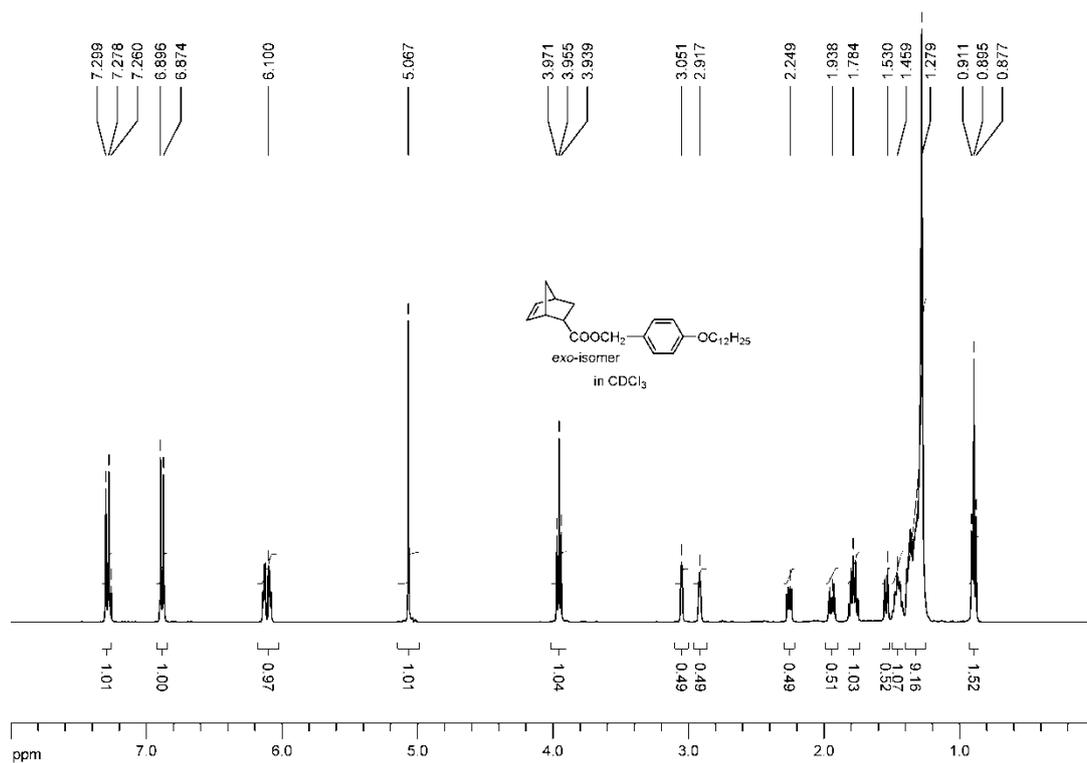
3) NMR spectra for compounds



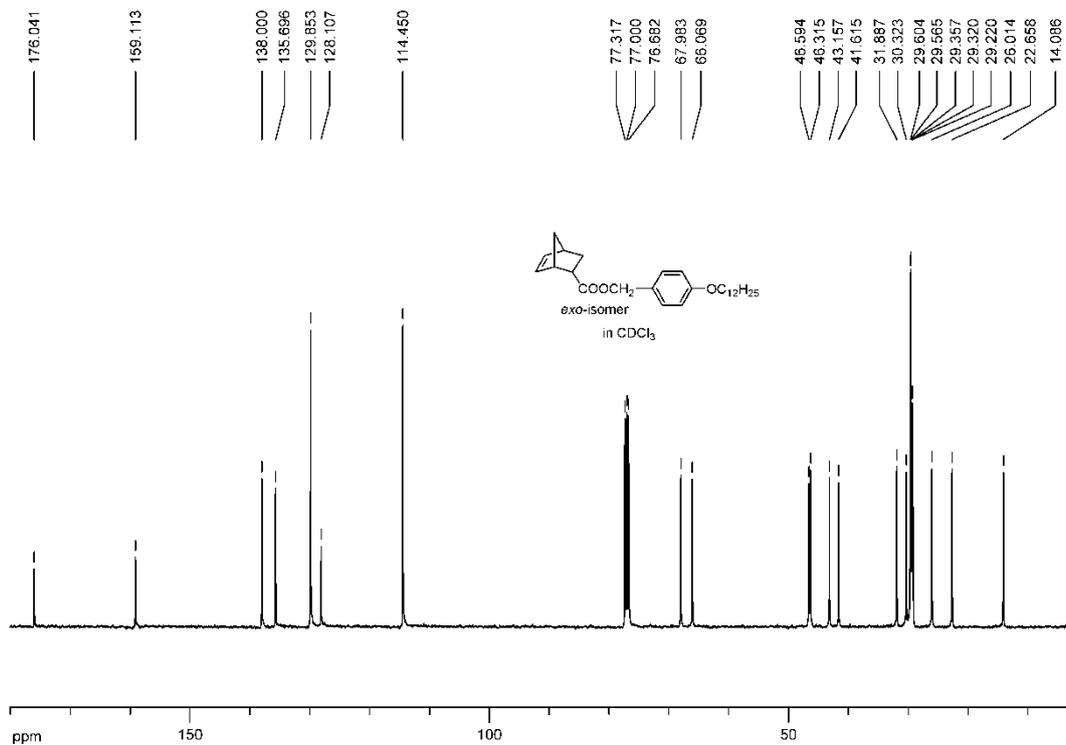
¹H NMR spectrum for S1



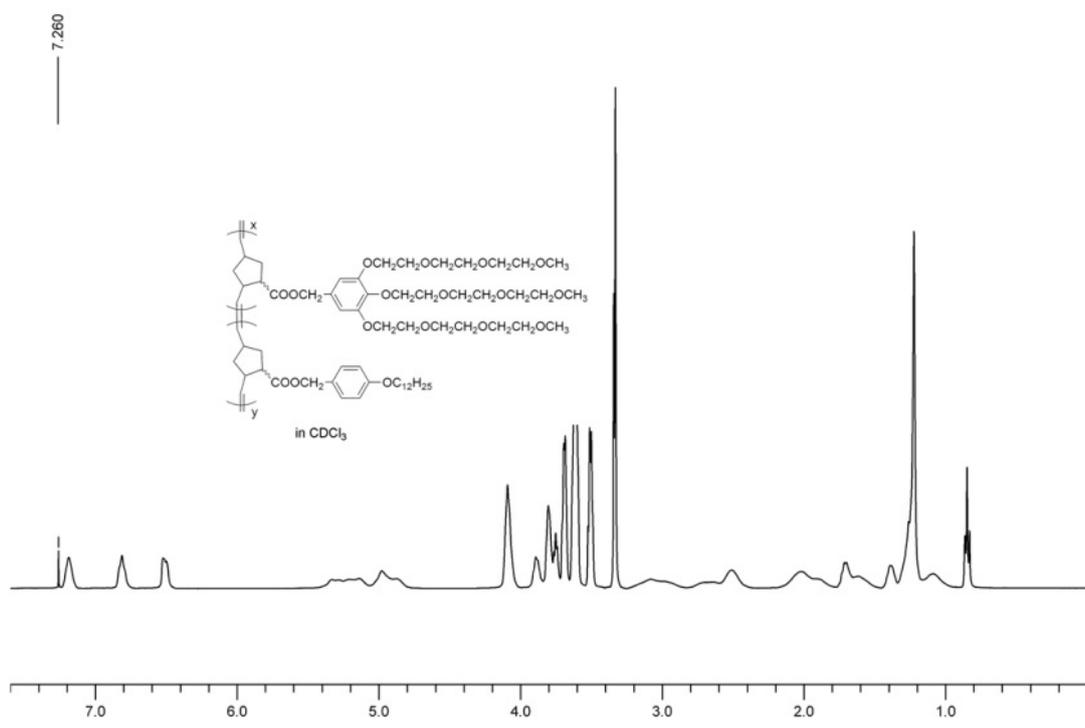
¹³C NMR spectrum for S1



¹H NMR spectrum for S2



¹³C NMR spectrum for S2



3. The IR spectra

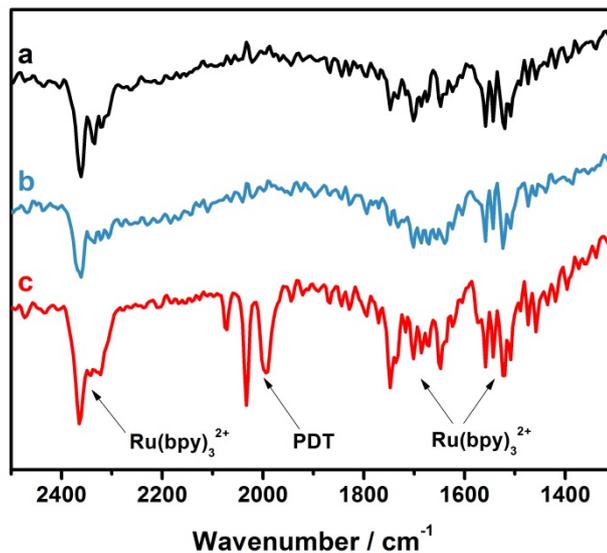


Figure S1. The IR spectra of (a) Ru(bpy)₃Cl₂, (b) Ru(bpy)₃Cl₂ in **P-NB** micellar aqueous solution, and (c) **PDT@P-NB** + Ru(bpy)₃Cl₂ in water

4. The determination of PDT concentration in P-NB micelle

1) Methods:

The relationship between characteristic absorption of **PDT** (328 nm) and its concentration was determined by Lambert-Beer Law (Figure S2 and S3) in CH₃CN, and the equation (1) was given below. The equation (1) was used to calculate the initial concentration of **PDT** in **P-NB** micellar aqueous solution by measuring the characteristic absorption at 328 nm of **PDT@P-NB** solution. By stepwise dilution of **PDT@P-NB** aqueous solution, and using Lambert-Beer Law to fit the characteristic absorptions of **PDT** at 328 nm and corresponding concentration (Figure S4 and S5), we obtained equation (2) for calculation of concentration of **PDT** in **P-NB** micellar aqueous solution.

$$C_{PDT} = \frac{A_{328 \text{ nm}}}{13797} \quad (1)$$

$$C_{PDT} = \frac{A_{328 \text{ nm}}}{13669} \quad (2)$$

2) The UV-vis absorption of PDT in CH₃CN and linear fitting by using Lambert-Beer Law

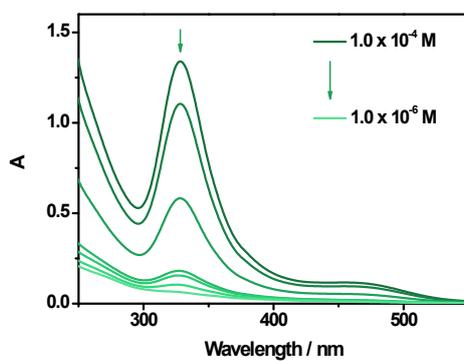


Figure S2. The UV-vis absorption of **PDT** of different concentration (1.00×10^{-4} M - 1.00×10^{-6} M) in CH₃CN

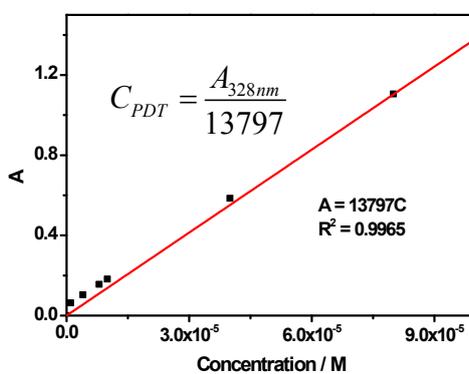


Figure S3. The linear fitting of the characteristic absorption at 328 nm of **PDT** in CH₃CN by Lambert-Beer Law

3) The UV-vis absorption of PDT@P-NB in H₂O and linear fitting by using Lambert-Beer Law

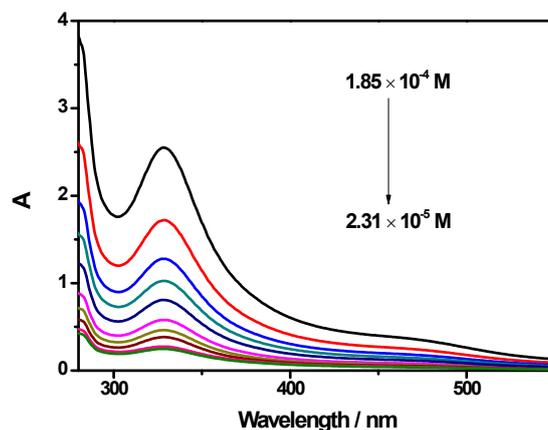


Figure S4. The UV-vis absorption of PDT@P-NB of different concentration (1.85×10^{-4} M - 2.31×10^{-5} M) in H₂O

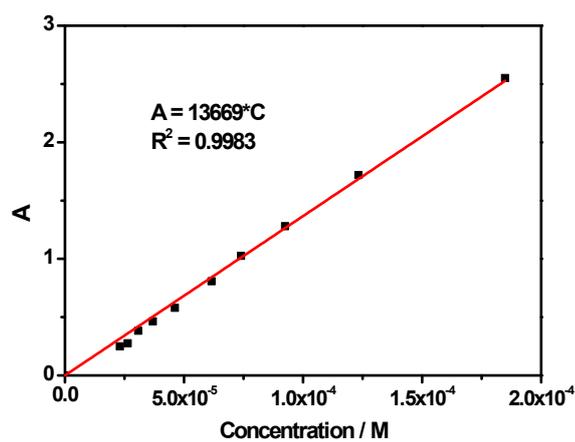


Figure S5. The linear fitting of the characteristic absorption at 328 nm of PDT@P-NB in H₂O by Lambert-Beer Law

5. The UV-vis absorption spectra of PDT in P-NB micelle in the course of self-assembly

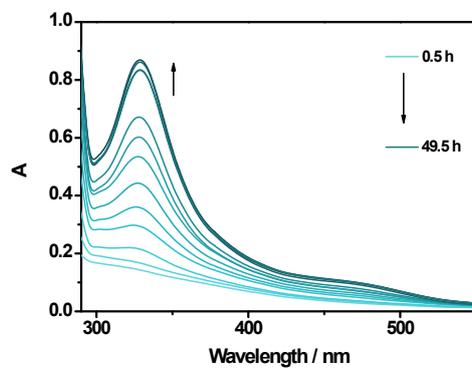


Figure S6. The UV-vis absorption spectra of **PDT** in **P-NB** micelle in water in the course of self-assembly

6. The emission quenching of $\text{Ru}(\text{bpy})_3^{2+}$ by NaHA in P-NB micellar aqueous solution

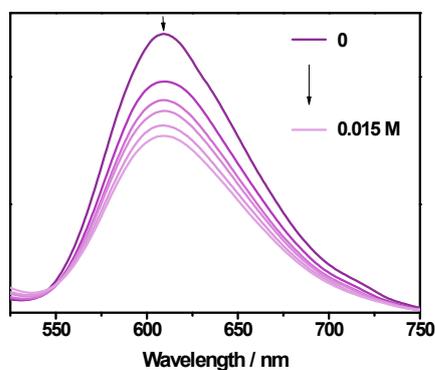


Figure S7. The emission quenching of $\text{Ru}(\text{bpy})_3^{2+}$ (1.00×10^{-5} M) by NaHA in **P-NB** (1.5 mg/mL) micellar aqueous solution, excitation wavelength: 400 nm

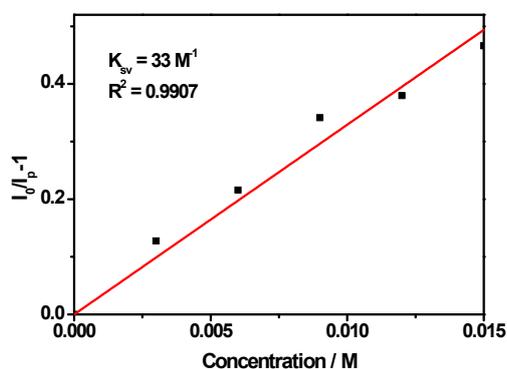


Figure S8. The Stern-Volmer equation fitting for the emission quenching of $\text{Ru}(\text{bpy})_3^{2+}$ (1.00×10^{-5} M) by NaHA in **P-NB** (1.5 mg/mL) micellar aqueous solution

7. The transient absorption spectrum of sample with $\text{Ru}(\text{bpy})_3^{2+}$ and NaHA in P-NB micellar aqueous solution

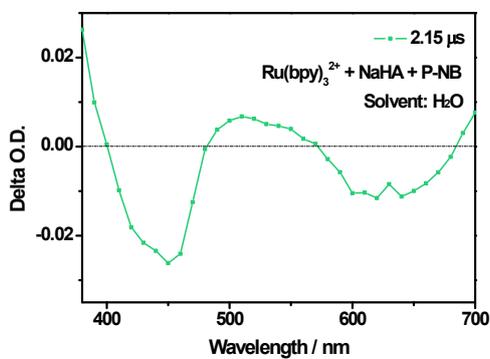


Figure S9. The transient absorption spectrum of sample with $\text{Ru}(\text{bpy})_3^{2+}$ (3.33×10^{-5} M) and NaHA (1.68×10^{-3} M) in P-NB (1.5 mg/mL) micellar aqueous solution, excited wavelength: 355 nm

8. The kinetics of sample with $\text{Ru}(\text{bpy})_3^{2+}$ and NaHA in PDT@P-NB micellar aqueous solution

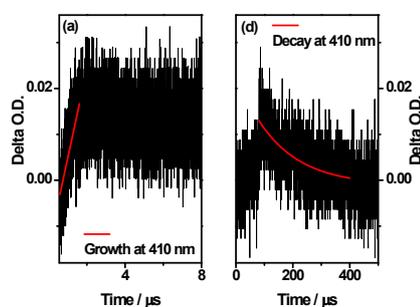


Figure S10. The growth (a) and decay (b) kinetics at 410 nm of the sample with $\text{Ru}(\text{bpy})_3^{2+}$ (3.33×10^{-5} M) and NaHA (1.68×10^{-3} M) in PDT@P-NB (the concentration of PDT and P-NB are 1.18×10^{-4} M and 1.5 mg/mL, respectively) micellar aqueous solution

9. References

- [1]. K. Feng, N. Xie, B. Chen, L.-P. Zhang, C.-H. Tung, L.-Z. Wu, *Macromolecules*, 2012, **45**, 5596-5603.
- [2]. D. Seyferth, G. B. Womack, M. K. Gallagher, M. Cowie, B. W. Hanmes, *Organometallics*, 1987, **6**, 283-294.