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
2. Synthesis
3. The IR spectra
4. The determination of PDT concentration in P-NB micelle
5. The UV-vis absorption spectra of PDT in P-NB micelle in the course of self-assembly
6. The emission quenching of Ru(bpy)$_3^{2+}$ by NaHA in P-NB micellar aqueous solution
7. The transient absorption spectrum of sample with Ru(bpy)$_3^{2+}$ and NaHA in P-NB micellar aqueous solution
8. The kinetics of sample with Ru(bpy)$_3^{2+}$ and NaHA in PDT@P-NB micellar aqueous solution
9. References
1. Instruments and methods

$^1$H 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 + Ru(bpy)$_3$Cl$_2$, Ru(bpy)$_3$Cl$_2$, and Ru(bpy)$_3$Cl$_2$ + P-NB were obtained by analysis of corresponding aqueous solution in cell. The transient absorption spectroscopy and the lifetime of Fe$^1$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$_2$SO$_4$ aqueous solution was used as a reference for determination of quantum yield (QY) of Ru(bpy)$_3$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 CH₄ (500 μL) was injected as the internal standard for quantitative GC-TCD analysis. The light sources was blue LED lamp (0.3 A, λ = 450 nm). The generated photoproduct of H₂ was characterized by GC-TCD analysis (TIANMEI 7890-II) using nitrogen as the carrier gas with a molecular sieve column (5 Å; 2 m × 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 H₂/CH₄ was about 5.12 under the experimental conditions, which was established by calibration with known amounts of H₂ and CH₄, and determined before and after a series of measurements.

Control experiments of photocatalytic hydrogen production[a]

<table>
<thead>
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<th>Entry[b]</th>
<th>PDT@P-NB</th>
<th>Ru(bpy)₃Cl₂</th>
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<th>irradiation</th>
<th>TON (H₂)</th>
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</table>

[a]. P = presence, A = absence; [b]. the concentration of each component: [PDT] = 3.0 × 10⁻⁵ M, [Ru(bpy)₃Cl₂] = 3.0 × 10⁻⁵ M, [H₂A] = 4.5 × 10⁻² M, pH = 4.0-4.1; irradiation time: 2 h; light source: LED lamp, λₘₐₓ = 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

\[ \text{R1} \xrightarrow{\text{DCC, DMAP, CH}_2\text{Cl}_2} \text{R3} \]

\[ \text{R2} \xrightarrow{\text{S1: yield:87\%}} \text{S1} \]

\[ \text{R3} \xrightarrow{\text{S2: yield:87\%}} \text{S2} \]

\[ \xrightarrow{\text{Grubbs' Cata. 3rd Gen}} \text{P-NB} \]

S1: \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\): 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). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm) \(\delta\): 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: $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$: 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) $\delta$: 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: $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$: 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

![Synthesis of PDT](image)

**PDT**: $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$: 2.14 (m, 4H), 1.81 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 30.56, 23.43.
3) NMR spectra for compounds

$^1$H NMR spectrum for S1

$^{13}$C NMR spectrum for S1
$^1$H NMR spectrum for S2

$^{13}$C NMR spectrum for S2
$^1$H NMR spectrum for P-NB
$^1$H NMR spectrum for PDT

$^{13}$C NMR spectrum for PDT
3. The IR spectra

Figure S1. The IR spectra of (a) Ru(bpy)$_3$Cl$_2$, (b) Ru(bpy)$_3$Cl$_2$ in P-NB micellar aqueous solution, and (c) PDT@P-NB + Ru(bpy)$_3$Cl$_2$ 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 CH$_3$CN, 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 CH$_3$CN and linear fitting by using Lambert-Beer Law

**Figure S2.** The UV-vis absorption of PDT of different concentration ($1.00 \times 10^{-4}$ M - $1.00 \times 10^{-6}$ M) in CH$_3$CN

**Figure S3.** The linear fitting of the characteristic absorption at 328 nm of PDT in CH$_3$CN by Lambert-Beer Law
3) The UV-vis absorption of PDT@P-NB in H$_2$O and linear fitting by using Lambert-Beer Law

**Figure S4.** The UV-vis absorption of PDT@P-NB of different concentration (1.85 $\times$ 10$^{-4}$ M - 2.31 $\times$ 10$^{-5}$ M) in H$_2$O

**Figure S5.** The linear fitting of the characteristic absorption at 328 nm of PDT@P-NB in H$_2$O 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 Ru(bpy)$_3^{2+}$ by NaHA in P-NB micellar aqueous solution

**Figure S7.** The emission quenching of Ru(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 Ru(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 Ru(bpy)$_3^{2+}$ and NaHA in P-NB micellar aqueous solution

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

![Graph showing growth and decay kinetics at 410 nm](image)

**Figure S10.** The growth (a) and decay (b) kinetics at 410 nm of the sample with Ru(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
