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Electronic Supplementary Information

BODIPY Directed One-Dimensional Self-assembly of Gold Nanorods

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Experimental section

1. Chemicals

Tetrachloroauric (III) acid, cetyltrimethylammonium bromide (CTAB), silver nitrate, pyrrole, 2,4dimethyl pyrrole, Pd on carbon, chloroform-d and acetonitrile-d₃ were purchased from Sigma Aldrich. Sodium borohydride and L-ascorbic acid were purchased from Spectrochem. 2,4,6-Trimethylbenzaldehyde and trifluoroacetic acid was purchased from TCI Chemicals. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), triethyl amine, boron trifluorate dietherate ester, Nbromosucciniamide and 4-nitrophenyl boronic pinacol ester were purchased from Alfa-Aesar. Dichloromethane, hexane, acetone, acetonitrile, tetrahydrofuran, and dimethylformamide were purchased from Merck. DCM was dried using P_2O_5 and stored over molecular sieves (4A).

2. Characterization

Absorption spectra were recorded on a Shimadzu UV-2700 UV-Vis spectrophotometer in 3 mL quartz cuvettes having a path length of 1 cm at room temperature. NMR spectra were measured on a 400 MHz Bruker Avance Neo spectrometer. Chemical shifts are reported in parts per million (δ) calibrated using tetramethyl silane as an internal standard for samples in CDCl₃ and using the residual solvent signals at 1.940 ppm for CD₃CN. HR-TEM images were acquired on a Jeol-2100 plus operating at 120 kV. Fluorescence spectra were recorded on a fluorolog 3-221 fluorimeter equipped with 450 W Xenon lamp. Raman measurements were conducted using an Oxford Instruments Witec-alpha 300 R equipped with an upright optical Zeiss microscope using 633 nm excitation with a 100× objective (NA = 0.9) at room temperature.

3. Photothermal conversion efficiency

The photothermal conversion efficiency of end-to-end assembled gold nanorods was measured by irradiating the sample with a 750 nm laser at 0.526 W for six minutes. Temperature changes were recorded during the irradiation and for another six minutes after irradiation with a FLIR ONE thermal imaging camera. Photothermal conversion efficiency was calculated using the formula given below by following previously reported methods.^{1,2}

$$\eta = \frac{hs(T_{max} - T_{surr}) - Q_{diss}}{I(1 - 10^{-A_{750}})}$$

where *h* is the heat transfer coefficient (water), *s* is the surface area of the container (vial, 1 mL, 11.6 × 32 mm), and the maximum steady temperature of the solution containing end-to-end assembled gold nanorods was 53 °C, and the environmental temperature (T_{surr}) was 28 °C. So, the temperature change ($T_{max} - T_{surr}$) of the solution was 25 °C. The laser power *I* was 0.526 W. The absorbance of the end-to-end assembled gold nanorods at 750 nm A₇₅₀ was 0.8345. Q_{diss} expresses heat dissipated from the light absorbed by the solvent and container (0.015 W). Thus, by substituting values of each parameter to the above-mentioned formula, the photothermal conversion efficiency (η) of the solution containing end-to-end assembled gold nanorods was calculated to be 70%. The maximum steady temperature of the solution containing gold nanorods alone was 33 °C. So, the temperature change of the solution was 5 °C. The absorbance of gold nanorods alone at 750 nm A₇₅₀ is 0.3905, then the photothermal conversion efficiency (η) of solution containing gold nanorods alone was calculated to be 20%.

4. Procedure for protonation of molecule 1

Molecule **1** was protonated by adding a drop of HCl (1 mM) to the solution of **1** in acetone. The protonation was readily observed by the visible colour change of the solution and a blue-shift in the absorption maximum.

5. Synthesis

Synthesis of Gold Nanorods (AuNRs)

Gold nanorods were synthesized by a seed-mediated method by following previous reports.^{3,4} For the synthesis of gold nanoseeds, HAuCl₄.3H₂O (5.0 mL, 0.0005 M) in water was added to a solution of CTAB (5.0 mL, 0.2 M) in water and stirred for one minute. To the stirring solution, icecold NaBH₄ (0.60 mL, 0.01M) in water was added and the solution was stirred vigorously for two minutes. The color of the solution changed from pale yellow to brownish-yellow. Then, the solution was kept at a constant temperature of 30 °C in a water bath for two hours. To synthesize gold nanorods, a growth solution was prepared by adding AgNO₃ (0.2 mL, 0.004M) in water into an aqueous CTAB (5.0 mL, 0.2M) solution with gentle stirring at 450 rpm. Then HAuCl₄.3H₂O (5.0 mL, 0.001 M) in water was added to the solution, followed by aqueous L-ascorbic acid (0.070mL, 0.1 M) resulting in a colorless solution. In the end, 12 μ L of the prepared seed solution was injected to the mixture of HAuCl₄, silver nitrate, CTAB and ascorbic acid, and the solution was kept undisturbed at 30 °C in water bath for 12 hours to ensure the full growth of gold nanorods. The gold nanorods were then purified by centrifugation at 8000 rpm for 10 minutes (twice) and re-dispersed in water and the same was used for further experiments.

Synthesis of 1-3

Molecules 1-3 were synthesized by following the previously reported procedures.^{5,6}

Characterization data

1:¹H NMR (400 MHz, CD₃CN), δ (ppm) 2.12 (s, 6H), 2.38 (s, 3H), 4.27 (s, 4H), 6.61 (d, J = 8 Hz, 4H), 6.70 (s, 2H), 7.06 (s, 2H), 7.32 (d, J = 8.0 Hz, 4H), 8.26 (s, 2H); ¹³C NMR (400 MHz, CD₃CN), δ (ppm) 20.0, 21.2, 115. 5, 122.3, 127.5, 129.0, 130.7, 135.8, 137.0, 137.3, 139.8, 142.5, 145.7, 148.8; HRMS m/z calculated for C₃₀H₂₈BF₂N₄ (M+H)⁺: 493.2368, found: 493.2381.

2: ¹H NMR (400 MHz, CDCl₃), δ (ppm) 2.10 (s, 6H), 2.36 (s, 3H), 6.46 (d, 2H), 6.67 (d, 2H), 6.95 (s, 2H,), 7.91 (s, 2H); ¹³C NMR (400 MHz, CDCl₃) δ (ppm) 19.9, 21.1, 118.5, 128.1, 129.6, 130.1, 135.3, 136.2, 138.8, 144.2, 147.6; HRMS m/z calculated for C₁₈H₁₈BF₂N₂ (M+H)⁺: 311.1621, found: 311.1543.

3: ¹H NMR (400 MHz, CD₃CN), δ (ppm) 2.34 (s, 6H), 2.39 (s, 6H), 2.75 (s, 3H), 4.24 (s, 4H), 6.73 (dt, 4H, $J_1 = 6.8$ Hz, $J_2 = 2.0$ Hz), 6.98 (dt, 4H, $J_1 = 6.8$ Hz, $J_2 = 2.0$ Hz); ¹³C NMR (400 MHz, CD₃CN): δ (ppm) 13.48, 15.65, 17.82, 115.20, 122.34, 131.98, 132.82, 134.59, 138.25, 143.80, 148.18, 152.71; HRMS m/z calculated for C₂₆H₂₈BF₂N₄ (M+H)⁺: 445.2370, found: 445.2394.

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Fig. S1. (a) Absorption spectrum (20 $\mu g/mL$) and (b) HR-TEM micrograph of gold nanorods in water.



Fig. S2. Absorption spectra of **1-3** (20 μ M) in (a) acetonitrile and (b) their aggregates in water. Absorption spectrum of **AuNRs** (15 μ g/mL) in water is also shown for reference.



Fig. S3. HR-TEM image of the end-to-end assembled **AuNRs** used for the calculation of gap between two gold nanorods.



Fig. S4. EDX analyses of the end-to-end assembled **AuNRs** carried out (a) on the surface and (b) in the gap between gold nanorods. The line on the adjacent TEM images show the region analysed.



Fig. S5 EDX analysis of end-to-end assembled AuNRs in the gap between two gold nanorods.



Fig. S6. Changes in the extinction spectrum of gold nanorods (20 μ g/mL) in water upon the addition of **1H**. [**1H**], (a-d) 0-10 μ M.



Fig. S7. HR-TEM micrographs of gold nanorods (20 μ g/mL) in the presence of **1H** (10 μ M). Scale is (a) 200 and (b, c) 100 nm.



Fig. S8. Fluorescence spectra of **1H** in the absence and presence of gold nanorods. [**1H**] 10 μ M, gold nanorods, (20 μ g/mL). Excitation wavelength, 583 nm.



Fig. S9. Changes in extinction spectrum of end-to-end assembled gold nanorods (containing 20 μ g/mL of gold nanorods and 10 μ M of **1**) in water upon the addition of 1,6-hexane dithiol (HDT).



Fig. S10. HR-TEM micrographs of end-to-end assembled gold nanorods (containing 20 μ g/mL of gold nanorods and 10 μ M of **1**) after the addition of 1,6-hexane dithiol (13 μ M). Scale is (a) 200, (b) 100 and (c, d) 50 nm.



Fig. S11. Changes in the extinction spectra of end-to-end assembled gold nanorods (containing $20 \ \mu\text{g/mL}$ of gold nanorods and $10 \ \mu\text{M}$ of **1**) in water upon the addition of HCl.



Fig. S12. HR-TEM micrographs of end-to-end assembled gold nanorods (containing 20 μ g/mL of gold nanorods and 10 μ M of **1**) in the presence of HCl. Scale is (a, c) 100, and (b, d) 50 nm.



Fig. S13. Absorption spectrum of molecule 1H (10 μ M) in acetonitrile.



Fig. S14. Raman spectra of (a) 2 (10 μ M) and (b) 3 (10 μ M) in the presence of AuNRs in water.



Fig. S15. Time versus $-\ln(\theta)$ plotted from the cooling period of end-to-end assembled gold nanorods (containing 20 µg/mL of gold nanorods and 10 µM of **1**) in water irradiated with 750 nm laser. θ was calculated by formula

$$(\theta) = \frac{T - T_{Surr}}{T_{Max} - T_{Surr}}$$

where T, T_{max} and T_{surr} are the temperature of the medium, maximum steady temperature attained upon irradiation and the surrounding temperature, respectively.



Fig. S16. Changes in the temperature of a solution of **AuNRs** (20 μ g/mL) in water and **1** (10 μ M) in acetonitrile upon irradiation with 750 nm laser for six minutes.



Fig. S17. Extinction spectra of end-to-end assembled gold nanorods (containing 20 μ g/mL of gold nanorods and 10 μ M of **1**) in water at different temperatures.