

Supporting Information

Exploration of the Two-Step Crystallization of Organic Micro/nano Crystalline Materials by Fluorescence Spectroscopy

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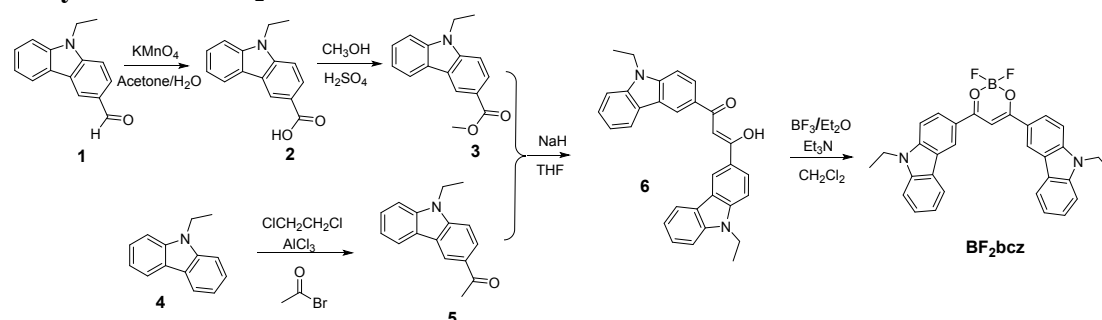
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Materials and Methods	2
Synthesis of BF₂bcz	2
The preparation of nanospheres and nanorods	2
Figure S1	4
Figure S2	4
Figure S3	5
Figure S4	5
Figure S5	5
Figure S6	6
Figure S7	6
Figure S8	6
Figure S9	7
Figure S10	7
Figure S11	8
Figure S12	8
Figure S13	9
Figure S14	9
Figure S15	10
Figure S16	10
Figure S17	11
Figure S18	12
Figure S19	12
Figure S20	13
Figure S21	13
Figure S22	14
Figure S23	14
References	14

1. Materials and Methods

Unless otherwise noted, all chemicals were commercially available and were used without further purification. High-purity water (resistivity = 18.2 M Ω .cm) was produced with Milli-Q apparatus (Millipore, America). The absorbance spectra were recorded on Hitachi U-3900 UV-Vis spectrophotometer at room temperature. The fluorescence spectra were recorded on Edinburgh instruments FLS-980 equipped with a temperature-control apparatus (TC 125, Quantum Norwest Inc.). Fluorescence quantum yields were determined on Edinburgh instruments FLS-980 with an integrating sphere system. The time-resolved fluorescence spectra were recorded by time-correlated single photon counting (Edinburgh instruments FLS-980), and the values of lifetime were analyzed by exponential function fitting with software F900. SEM images were obtained by using a Hitachi SU-8010 instrument. X-ray diffraction (XRD) patterns were recorded at room temperature with a Shimadzu XRD-7000. Fluorescence microscopy images were performed with Olympus IX 71. The photographs were shot by Nikon D7100. Dynamic light scattering (DLS) investigations were carried out on a Dynapro nanostar dynamic light scattering detector.

2. Synthesis of BF₂bcz



Scheme S1. The synthetic route of BF₂bcz.

The detailed synthetic procedure of **BF₂bcz** depicted in Scheme 1 were according to the methods reported in our previous report.^{S1}

3. The preparation of nanospheres and nanorods

1) The preparation of nanosphere

In a typical preparation procedure, a solution of BF₂bcz (1.0 mM) in THF (good solvent for BF₂bcz, 1.0 mL) was injected rapidly into 5.0 mL of deionized water (poor solvent for BF₂bcz) in a 10 mL vial under vigorous stirring. After stirring for 2 min, the samples were left standing before measurements. During the aging time, the vial was kept sealed.

2) The preparation of nanorods

In a typical preparation procedure, a solution of BF₂bcz (1.0 mM) in THF (good solvent for BF₂bcz, 1.0 mL) was injected into 5.0 mL of aqueous solution (poor solvent for BF₂bcz) containing different concentrations of surfactant in a 10 mL vial under vigorous stirring. After stirring for 2 min, 3 mL of aqueous dispersion of the sample was transferred into 4 mL of sealed cuvette, which was further placed in a temperature-control apparatus (TC 125, Quantum Norwest Inc.) equipped by Edinburgh FLS980 Fluorescence Spectrometer for the measurement of emission changes during the formation of nanorods at different temperatures. After the emission spectra kept constant, the samples were processed immediately for SEM images.

$$C_{\text{surfactant}} = m_{\text{surfactant}} / (V_{\text{THF}} + V_{\text{H}_2\text{O}}), \text{ concentration unit is mg/mL.}$$

3) The phase transition from nanosphere to nanorods

Surfactant was added to the aqueous dispersions of nanosphere. The resulting dispersions were slightly shaken to ensure the complete dissolution of surfactant. Then the dispersions were placed in a temperature-control apparatus of Edinburgh FLS980 for the spectral measurement. After the emission spectra kept constant, the samples were processed immediately for SEM images.

4) The characterization of nanospheres and nanorods

The aqueous dispersions of nanosphere were directly used for DLS measurements without further treatment. 5 μ L of the aqueous dispersions of nanosphere was dropped in a silicon wafer and dried in air at room temperature before the SEM images. For the SEM images of nanorods, the samples were firstly processed with two cycles of centrifugation/washing with water, subsequently placed onto silicon substrates and dried in air at room temperature before the SEM images. The nanospheres and nanorods were examined with a field emission SEM (Hitachi SU-8010) operated at an accelerating voltage of 5 or 10 kV. To minimize sample charging, an ultra-thin layer of Au was deposited onto the samples before SEM examination.

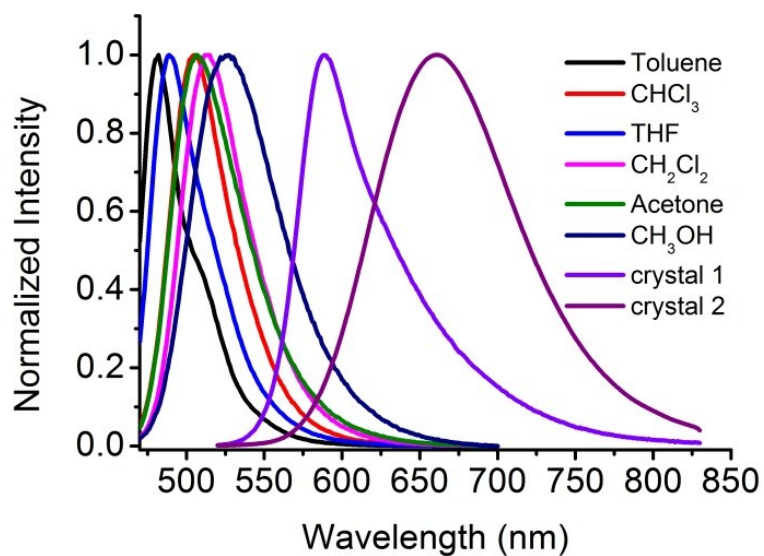


Figure S1. The normalized emission spectra of BF₂bcz in different solvents and crystals.

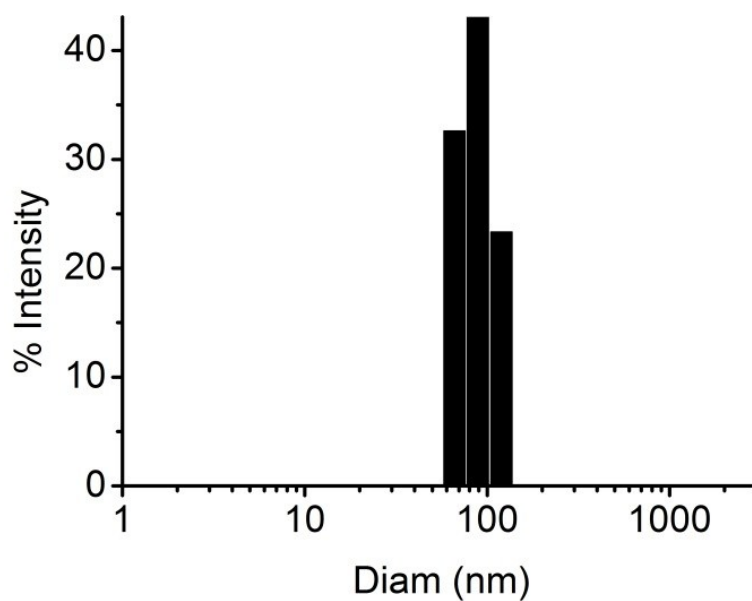


Figure S2. The DLS measurements of nanospheres.

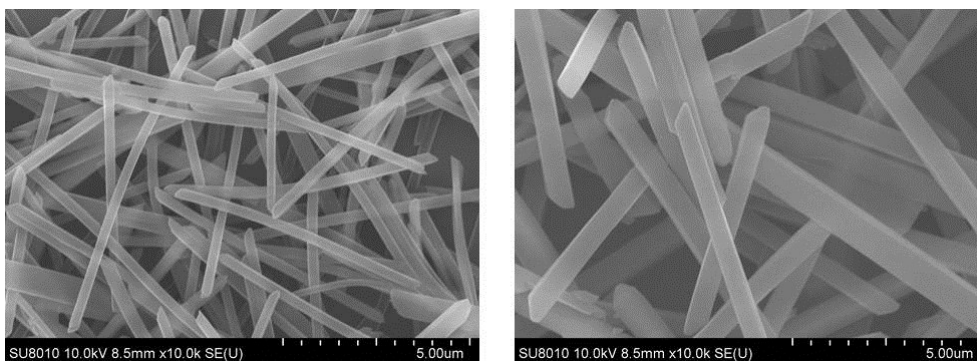


Figure S3. The SEM images of nanorods obtained by adding CTAB (left) or SDS (right) to the aqueous dispersion of BF₂bcz nanospheres.

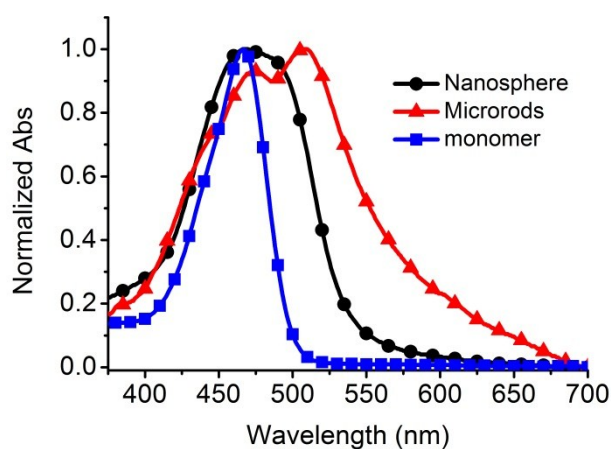


Figure S4. The normalized absorption spectra of aqueous dispersions of BF₂bcz nanospheres, nanorods and monomers in dilute THF solution. The different absorption spectra between the nanosphere and nanorods indicate the different ground-state molecular packing ways in them.

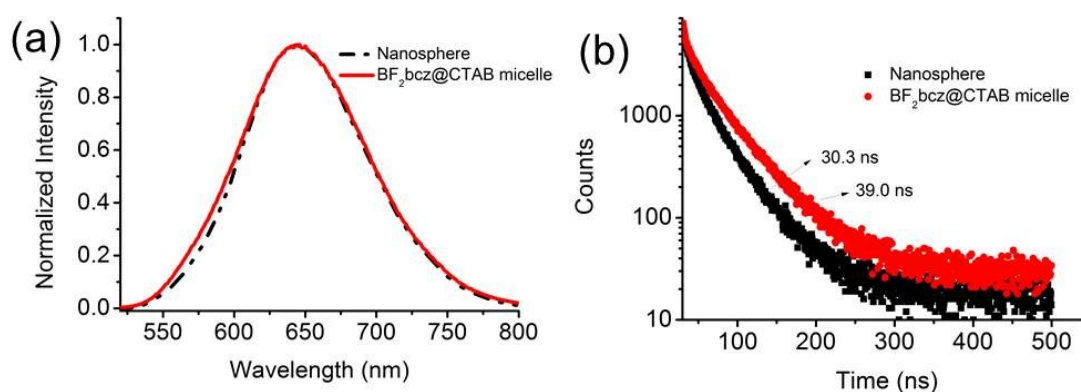


Figure S5. The normalized emission spectra (a) and fluorescence lifetime (b) of nanosphere and two BF₂bcz molecules encapsulated inside CTAB micelles monitored at $\lambda = 640$ nm.

CTAB molecules form spherical micelles with an aggregation number of 90 within the concentration range from 0.9 to 100 mM in water.^{S2} We calculated the molar ratios between the BF₂bcz molecules and CTAB micelles to be approximately 2.

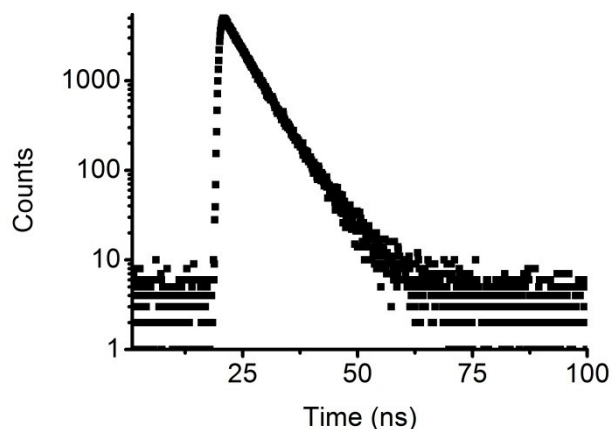


Figure S6. The fluorescence decay profile of BF₂bcz nanorod monitored at $\lambda = 580$ nm.

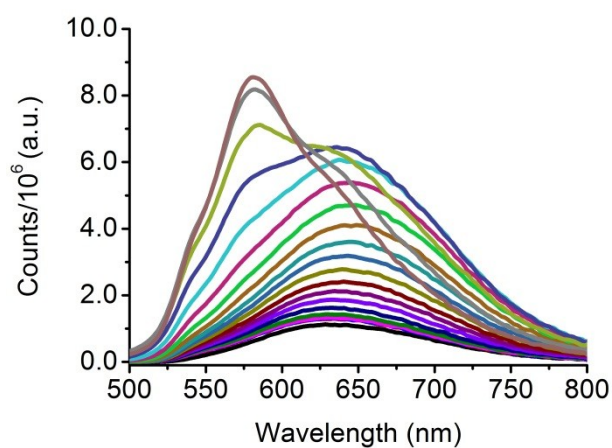


Figure S7. The fluorescence changes during the phase conversion from nanosphere to nanorods by adding CTAB (1.5 mg/mL) to the aqueous dispersion of nanosphere. The spectra were recorded every 3 min, $\lambda_{\text{ex}} = 460$ nm.

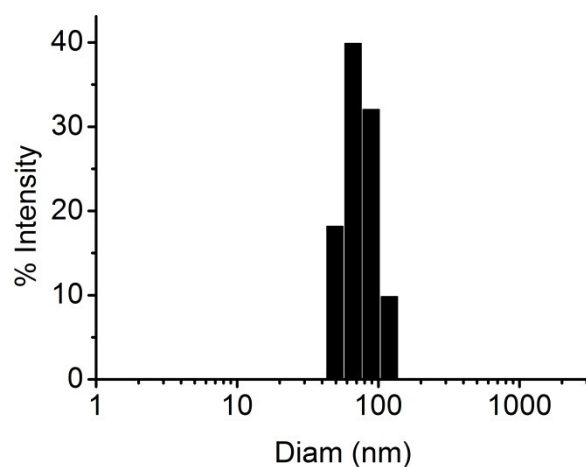


Figure S8. The DLS measurements of the initial molecular aggregates during the formation of nanorods.

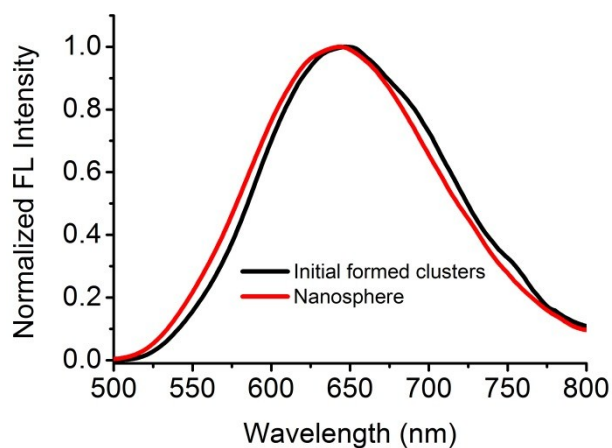


Figure S9. The emission spectra of nanosphere and the initial formed molecular aggregates during the formation of nanorods.

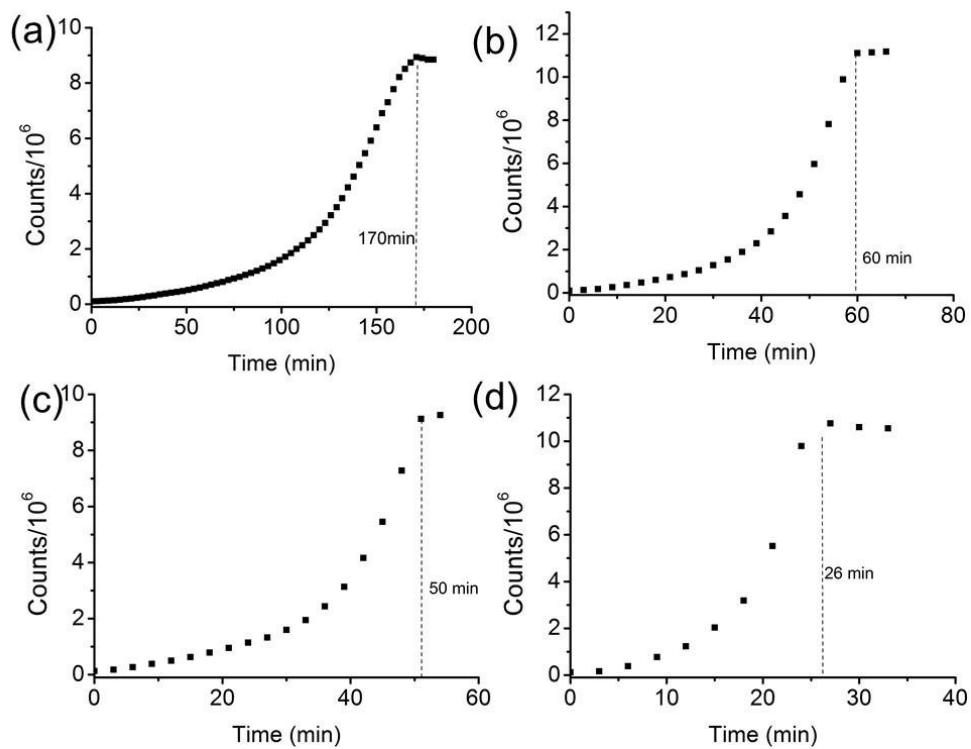


Figure S10. The time-dependent emission intensities monitored at $\lambda = 580$ nm during the formation of nanorods by using CTAB (1.0 mg/mL) as templates at different temperatures. (a) 15 °C, (b) 20 °C, (c) 25 °C, (d) 30 °C.

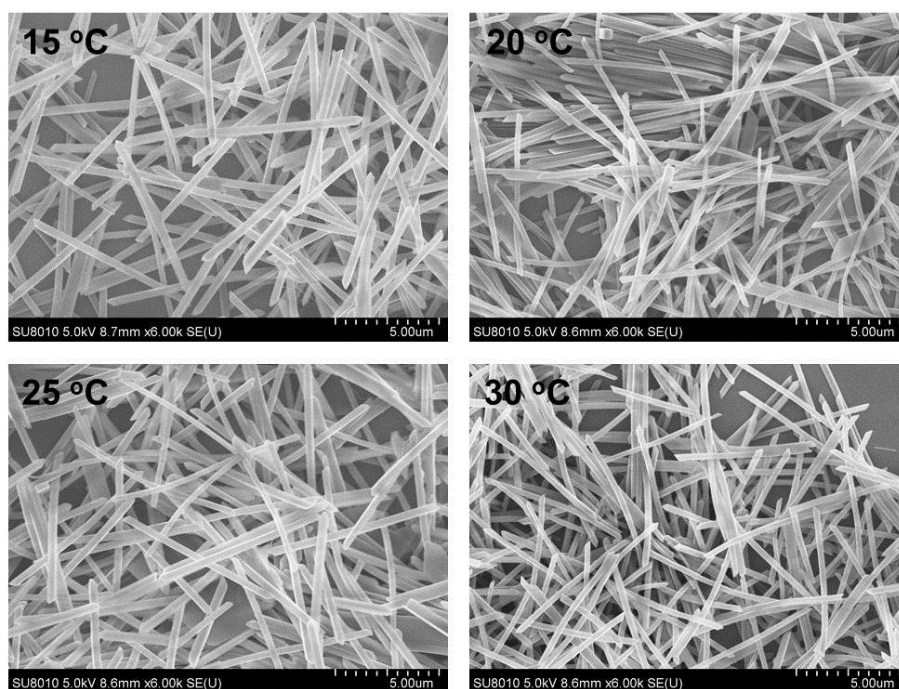


Figure S11. The SEM images of nanorods formed by using surfactant CTAB (1.0 mg/mL) as templates at different temperatures.

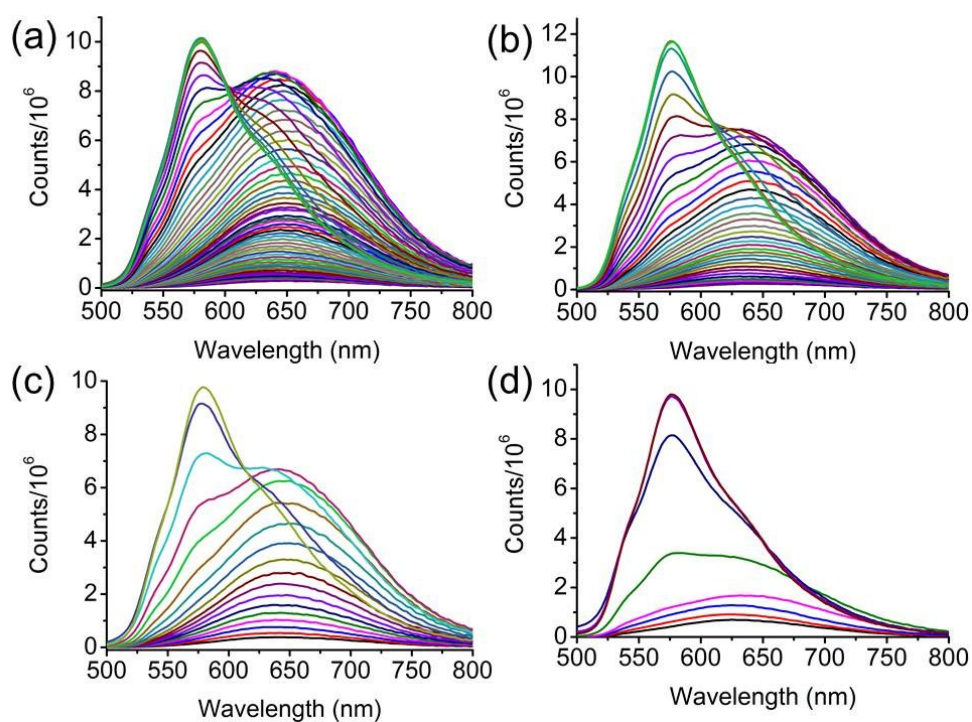


Figure S12. The emission changes during the formation of nanorods under different C_{CTAB} at 25 °C. (a) 0.5 mg/mL, (b) 0.75 mg/mL, (c) 1.0 mg/mL, (d) 2.0 mg/mL. $V_{\text{CTAB solution}} = 5.0$ mL, $V_{\text{THF}} = 1.0$ mL, $C(\text{BF}_2\text{bcz}) = 1.0$ mM. The spectra were measured every 3 min, $\lambda_{\text{ex}} = 460$ nm.

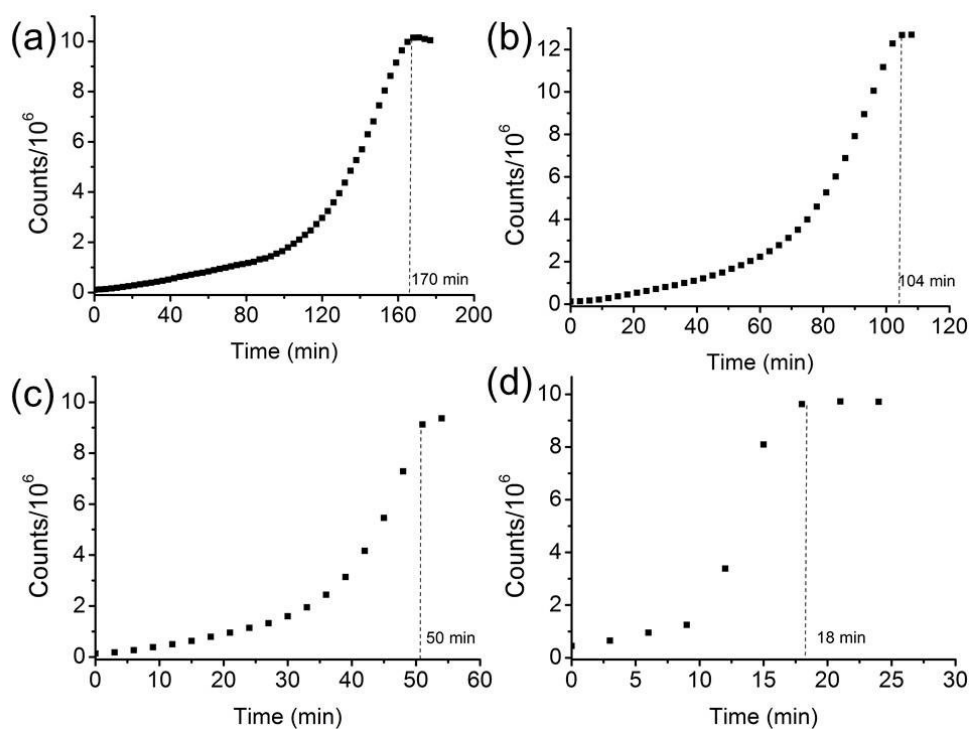


Figure S13. The time-dependent emission intensities monitored at $\lambda = 580$ nm during the formation of nanorods under different C_{CTAB} at 25 °C. (a) 0.5 mg/mL, (b) 0.75 mg/mL, (c) 1.0 mg/mL, (d) 2.0 mg/mL.

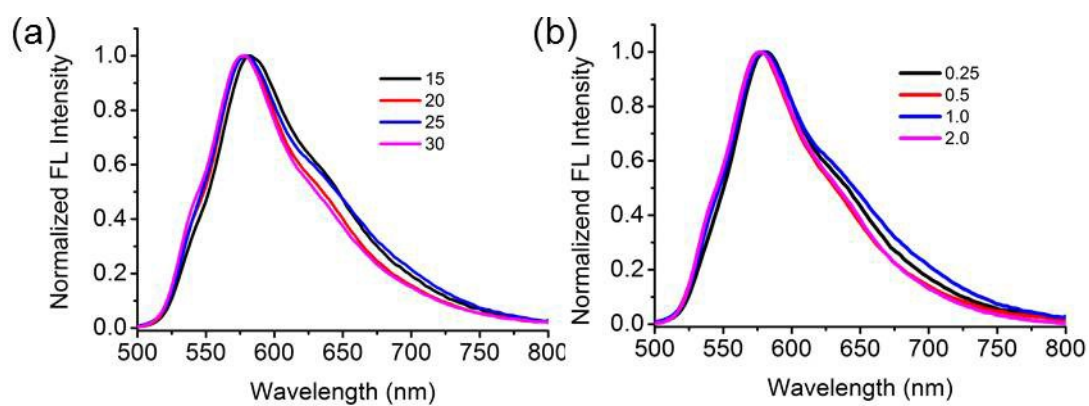


Figure S14. The normalized emission spectra of nanorods formed at different temperatures (a, $C_{CTAB} = 1.0$ mg/mL) and different concentrations of CTAB (b) at 25 °C.

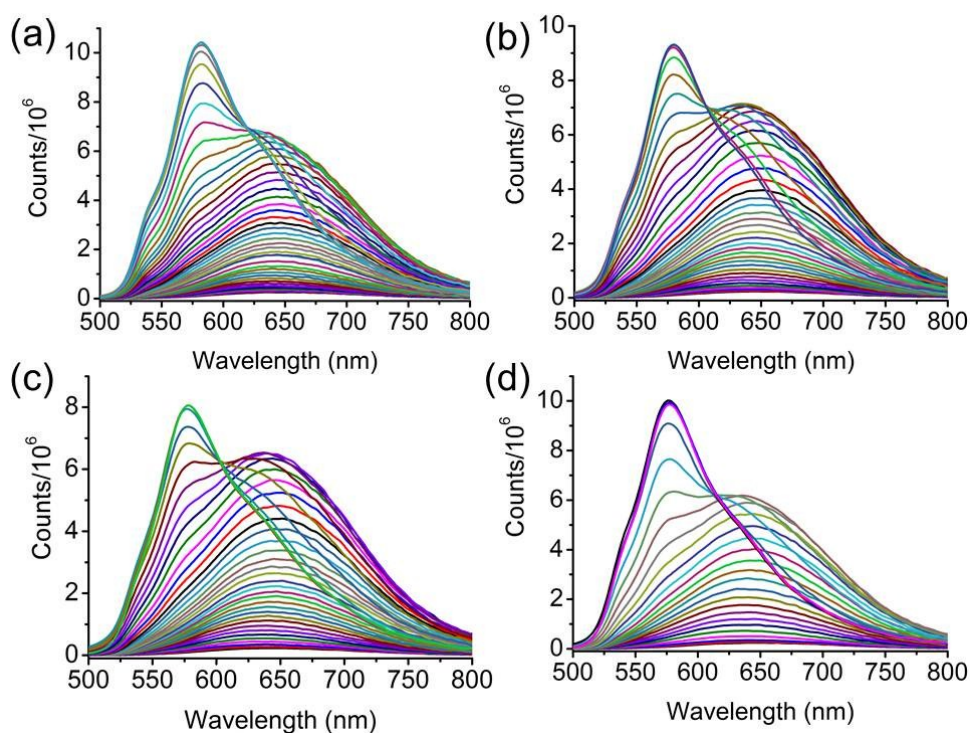


Figure S15. The emission changes during the formation of nanorods by using SDS (1.0 mg/mL) as templates under different temperatures. (a) 15 °C, (b) 20 °C, (c) 25 °C, (d) 30 °C. $V_{\text{SDS solution}} = 5.0$ mL, $V_{\text{THF}} = 1.0$ mL, $C(\text{BF}_2\text{bcz}) = 1.0$ mM. For profile a-c, the spectra were recorded every 3 min; for profile d, the spectra were recorded every 1.5 min. $\lambda_{\text{ex}} = 460$ nm.

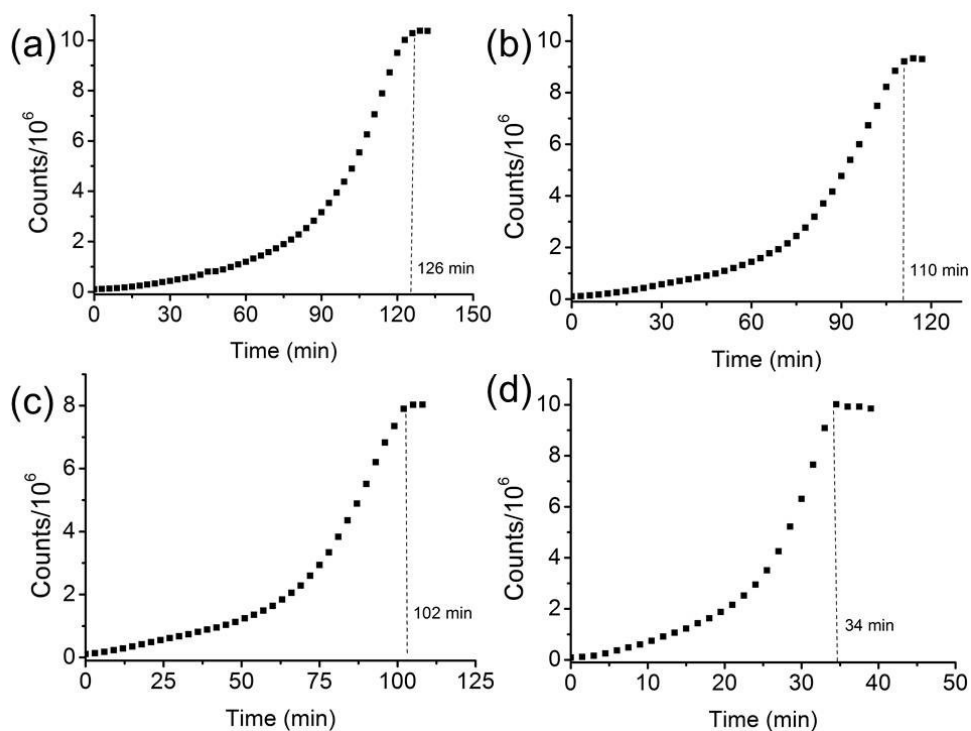


Figure S16. The time-dependent emission intensities monitored at $\lambda = 580$ nm during the formation of nanorods by using SDS (1.0 mg/mL) as template under different temperatures. (a) 15 °C, (b) 20 °C, (c) 25 °C, (d) 30 °C.

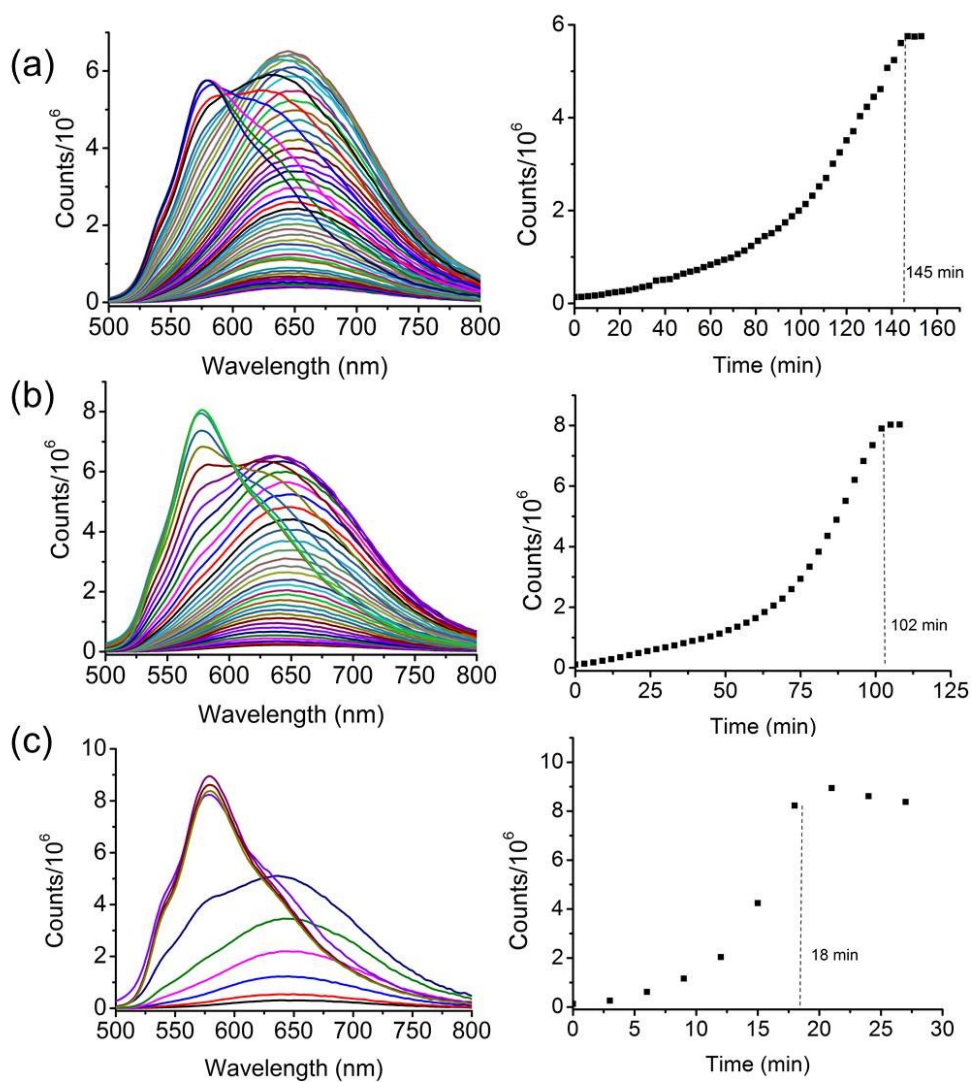


Figure S17. The emission changes (right) during the formation of nanorods under different C_{SDS} at RT 25 °C, and the time-dependent emission intensities monitored at $\lambda = 580$ nm (left). (a) 0.5 mg/mL, (b) 1.0 mg/mL, (c) 2.0 mg/mL. $V_{\text{SDS solution}} = 5.0$ mL, $V_{\text{THF}} = 1.0$ mL, $C(\text{BF}_2\text{bcz}) = 1.0$ mM. The spectra were measured every 3 min, $\lambda_{\text{ex}} = 460$ nm.

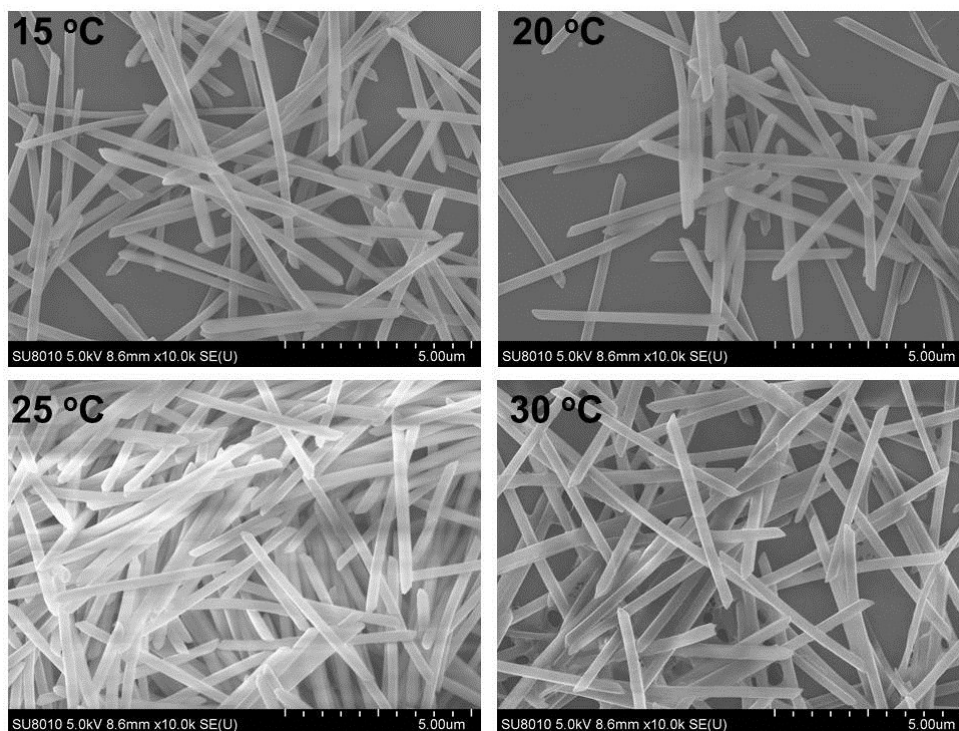


Figure S18. The SEM images of nanorods by using SDS as templates (1.0 mg/mL) at different temperatures.

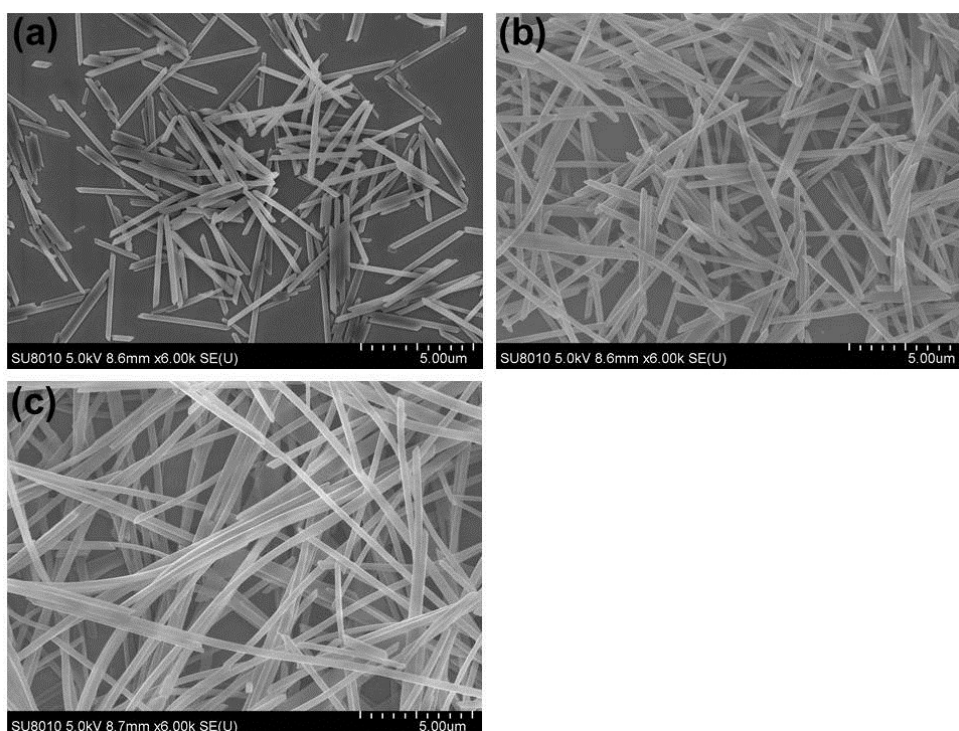


Figure S19. The SEM images of nanorods under different C_{SDS} at room temperature 25 °C. (a) 0.5 mg/mL, (b) 1.0 mg/mL, (c) 2.0 mg/mL.

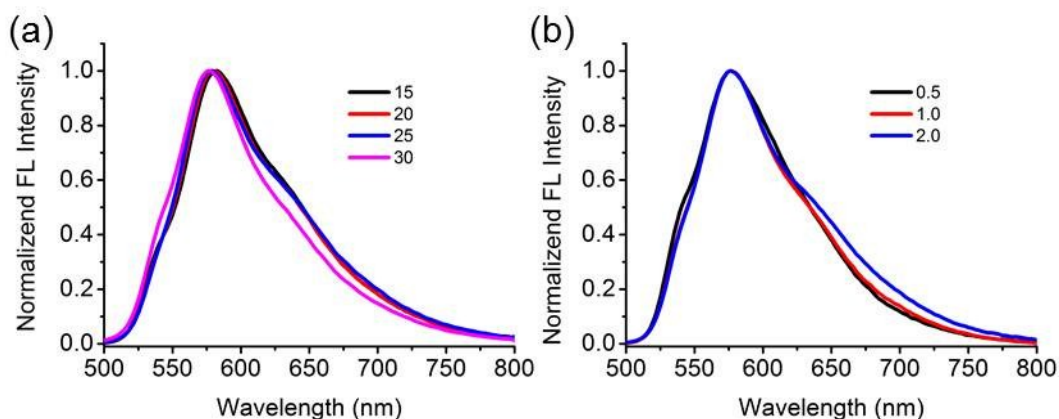


Figure S20. The normalized emission spectra of nanorods formed at different temperatures (a, $C_{\text{SDS}} = 1.0$ mg/mL) and different concentrations of SDS (b) at 25 °C.

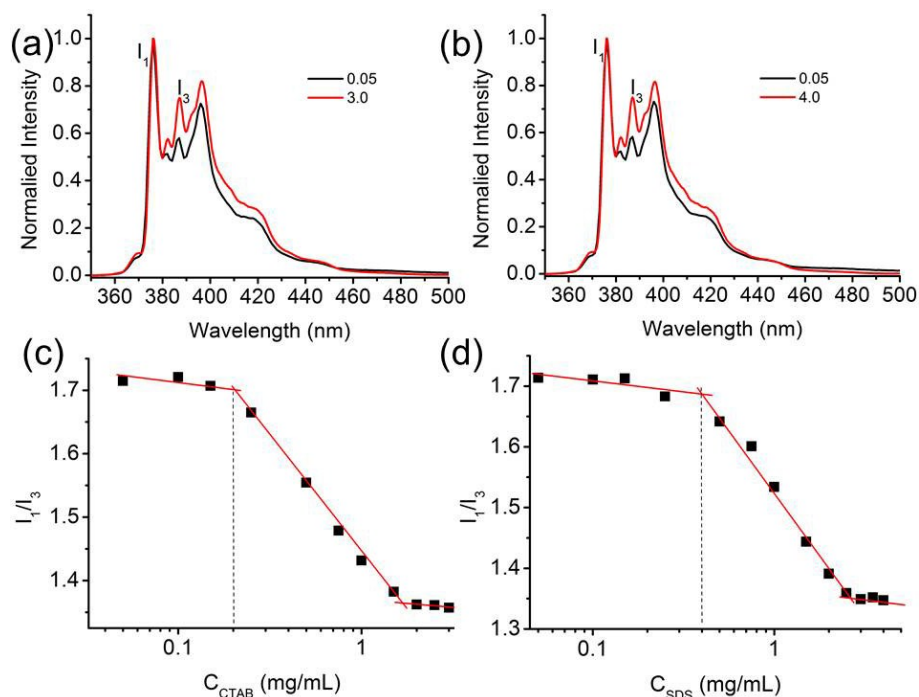


Figure S21. The normalized emission spectra of pyrene in THF/H₂O = 1/5 mixed solutions with different concentrations of CTAB (a) and SDS (b), unit mg/mL. Variation of I_1/I_3 with the concentration of CTAB (c) and SDS (d). $\lambda_{\text{ex}} = 336$ nm.

We chose pyrene as a mock hydrophobic probe because of its environmentally sensitive fluorescence.^{S3} Its five vibronic bands respond to environmental polarity differently. The intensity ratio between the first band ($I_1 \sim 376$ nm) and the third ($I_3 \sim 387$ nm) is particularly sensitive to environmental changes. Thus, the critical aggregation concentration (CAC) of CTAB and SDS in THF/H₂O = 1/5 mixed solutions were determined to be approximately 0.2 and 0.4 mg/mL, respectively.

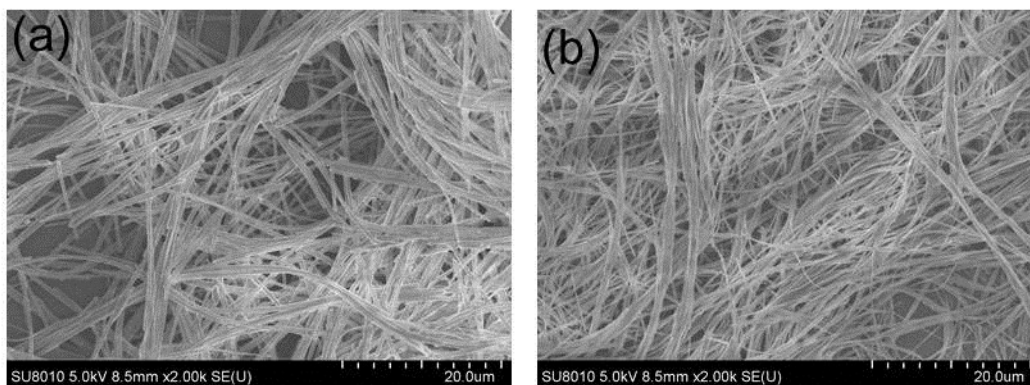


Figure S22. The SEM images of nanorods obtained from THF/H₂O (v/v = 1/5) mixed solutions containing SDS (a, 0.2 mg/mL) and CTAB (b, 0.1 mg/mL).

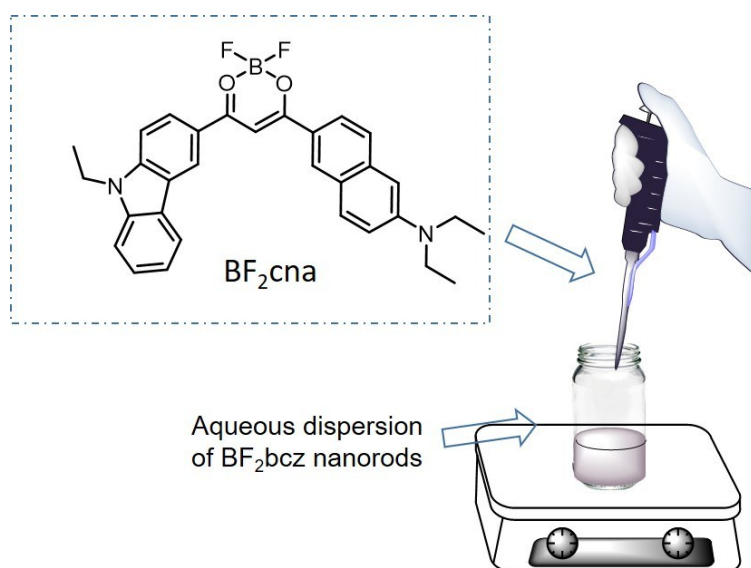


Figure S23. Schematic drawing of the addition of the 0.1 mol% BF₂cna to the aqueous dispersion of BF₂bcz nanorods.

Our previous work reported that the absorption spectra of BF₂cna showed good overlap with the emission spectra of the BF₂bcz nanorods, indicating an possible energy transfer from BF₂bcz to the BF₂cna in the nanorods.^{S1}

References

- S1. P.-Z. Chen, Y.-X. Weng, L.-Y. Niu, Y.-Z. Chen, L.-Z. Wu, C.-H. Tung and Q.-Z. Yang, *Angew. Chem. Int. Ed.*, 2016, **55**, 2759.
 S2. T. Imae, R. Kamiya and S. Ikeda, *J. Colloid Interface Sci.*, 1985, **108**, 215.
 S3. S. Zhang and Y. Zhao, *J. Am. Chem. Soc.*, 2010, **132**, 10642.