Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Preparation and structural control of metal coordination-assisted supramolecular architectures of porphyrins. nanocubes to microrods

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Experimental Section

General Information. H_2TCPP was purchased from Tokyo Chemical Industry (TCI). All solvents and reagents of the best grade available were purchased from commercial suppliers and were used without further purification. All experiments were performed at room temperature. FTIR measurement was performed on a KBr pellet using JASCO FT/IR 4200 spectrometer after thorough mixing.

TEM Measurement. Transmission electron micrograph (TEM) measurements were recorded on Tecnai spirit (FEI company) by applying a drop of the sample to a copper grid. TEM images were recorded on a transmission electron microscope an accelerating voltage of 120 kV for imaging.

Steady-State and Transient Spectroscopic Measurements. Steady-state absorption spectra in the visible and near-IR regions were measured on a Perkin Elmer UV-VIS-NIR spectrophotometer (Lamba 750). Nanosecond transient absorption measurements were carried out using Unisoku TSP-2000 flash spectrometer. Surelite-I Nd-YAG (Q-switched) laser with the second harmonic at 532 nm was employed for the flash photo-irradiation. A 150 W Xenon arc lamp was used as the monitor light source. All measurements were carried out in DMF.

Synthetic Details of Porphyrin Assemblies. 5,10,15,20-tetra-(4-carboxyphenyl),21*H*, 23*H*-porphyin (H_2TCPP) solutions with different concentrations (52.5 μM, 105, μM, 420 μM) were prepared in mixed solvents (DMF/Dioxane/H_2O = 4/1/1 (v/v/v). Then, $Zn(NO_3)_2{\bullet}6H_2O$ (2.0 equiv.) was added to the H_2TCPP solutions. The solutions were stirred for 3 h at 100 ^{o}C. After the solutions were cooled down to room temperature, the mother solvents were centrifuged by 14,500 rpm for 20 min. The residues were washed with H_2O and DMF at three times by centrifugation (14,500 rpm, 20 min). Finally, the porphyrin assemblies were dissolved in DMF again. H_2TCPP assemblies are very stable in DMF solution and cannot be reverted back to their monomeric forms by diluting the solution.

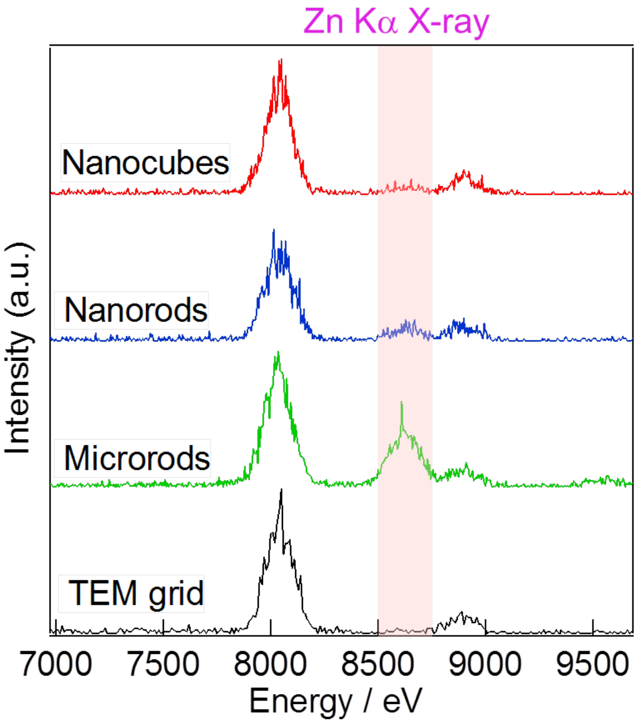

Fig. S1 Energy dispersive X-ray spectroscopy spectra of the porphyrin assemblies of nanocubes on TEM grid (red line), nanorods on TEM grid (blue line), microrods on TEM grid (green line) and pristine TEM grid (gray line). The characteristic peaks of zinc atoms appear at around 8600 eV in all systems. The other two peaks at around 8000 and 8900 eV are derived from copper atoms, which are involved in pristine TEM grid.

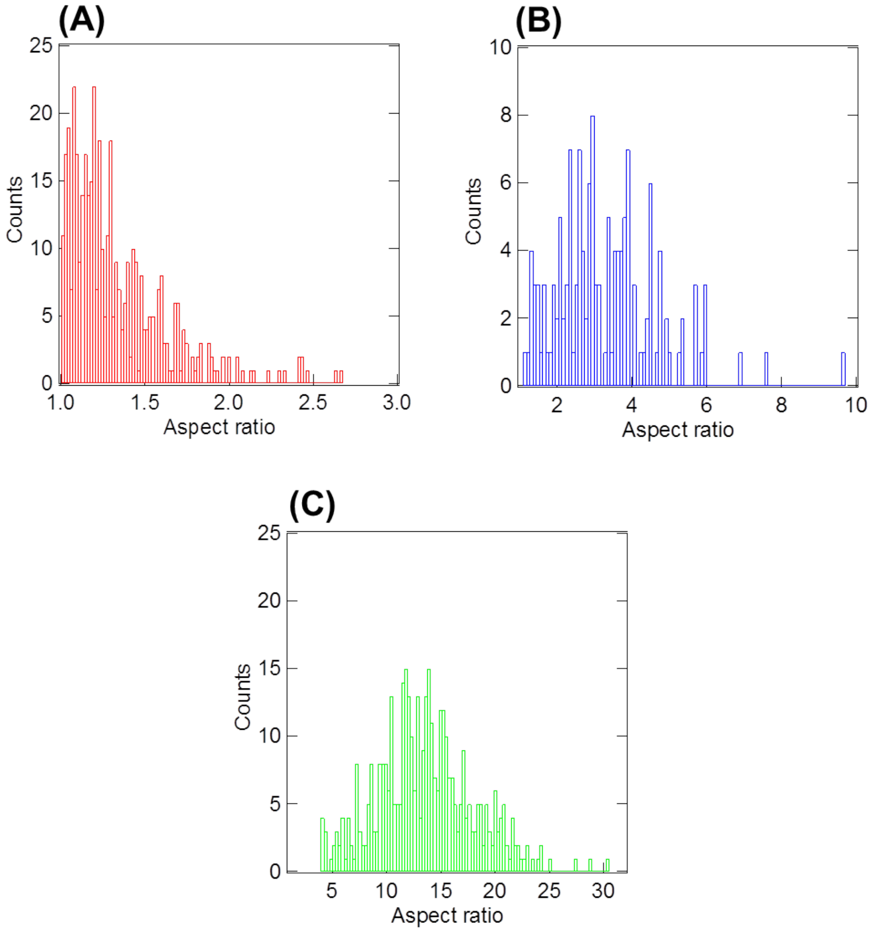

Fig. S2 Aspect ratio distributions of porphyrin assemblies. (A) nanocubes, (B) nanorods and (C) microrods.

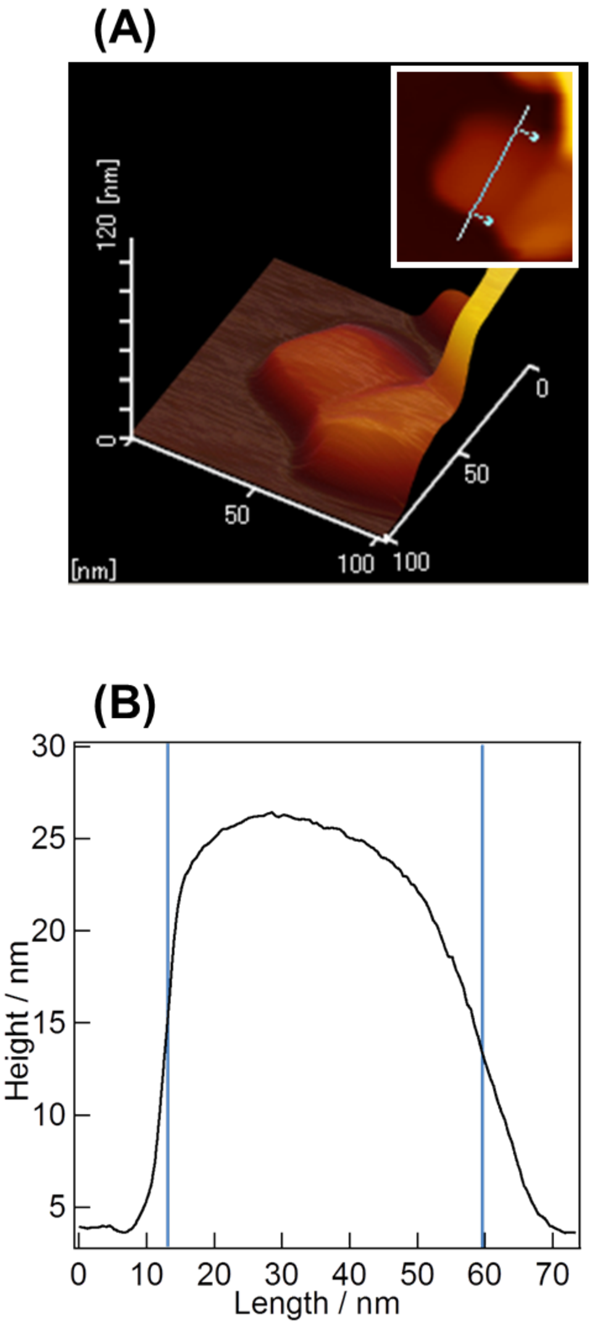

Fig. S3 (A) A AFM image of the porphyrin assemblies (nanocubes) prepared at concentration of [H_2TCPP] = 52.5 μM. (B) The information shows the length and height values of nanocubes. This indicates that the height of nanocubes is approximately estimated to be ca. 20-25 nm.

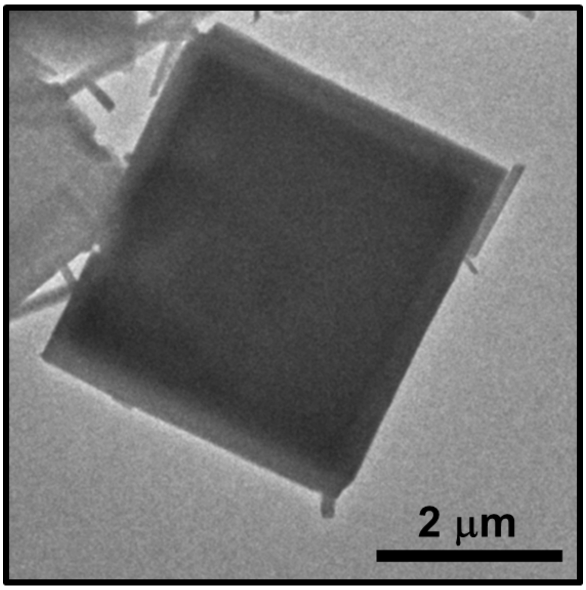

Fig. S4 A TEM image of the porphyrin assemblies prepared at concentration of [H_2TCPP] = 1.0 mM.

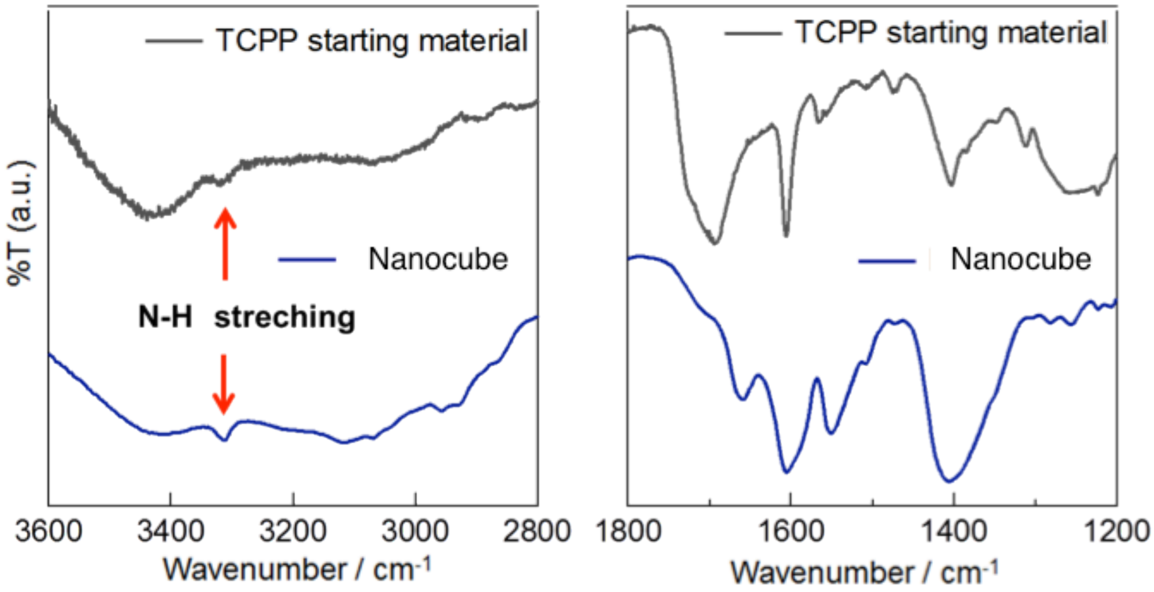

Fig. S5 Infrared absorption spectra of H_2TCPP powder (gray line) and the porphyrin assemblies (blue line) prepared at concentration of [H_2TCPP] = 52.5 μM. N-H stretching band of the assemblies remain unchanged at 3300 cm^{-1} and the carboxylic C=O stretching band shifts from ca. 1700 cm^{-1} (monomer) to 1600 cm^{-1}.

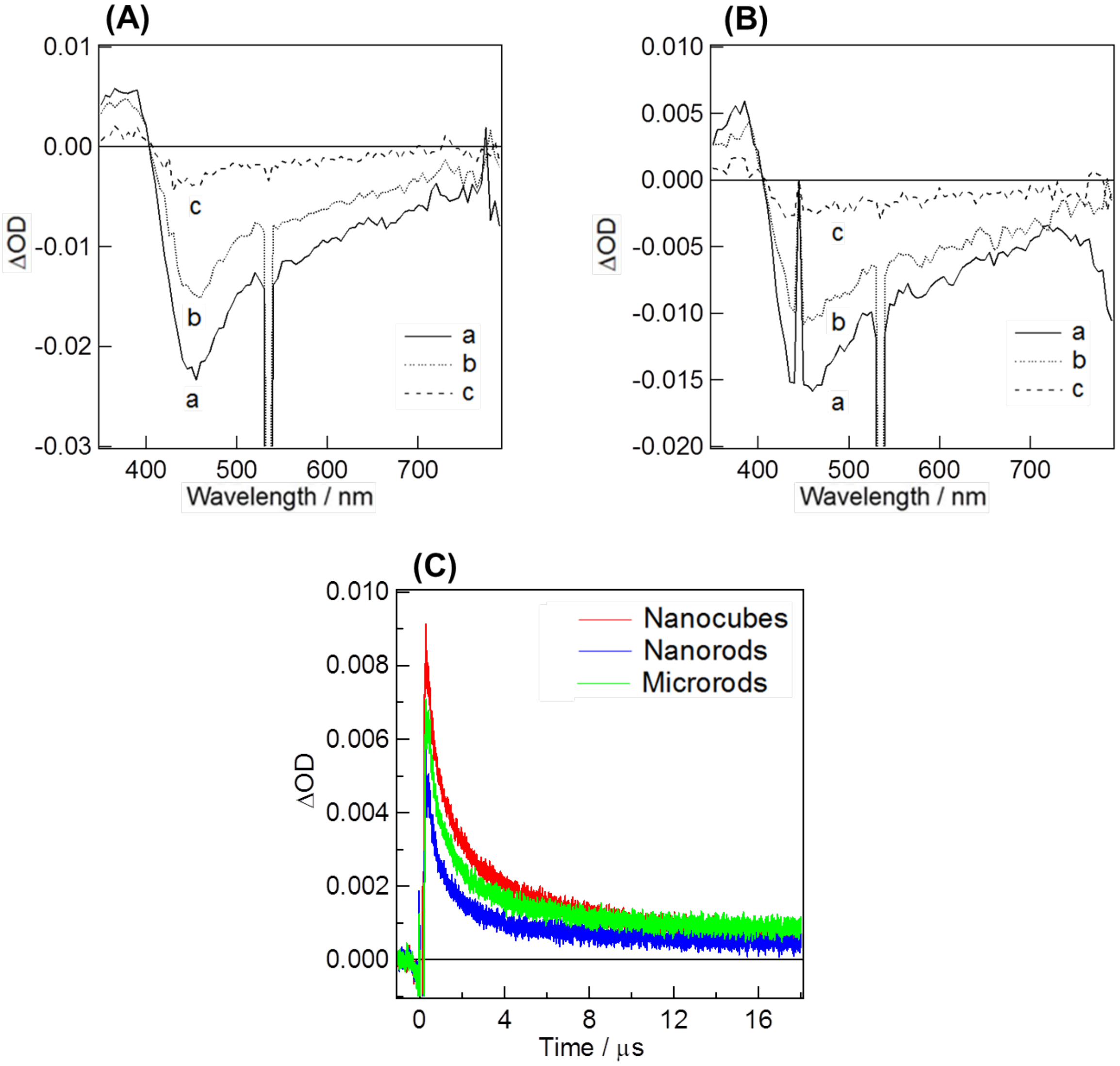

Fig. S6 Nanosecond transient absorption spectra of (A) nanorods and (B) microrods observed by 532 nm laser light (ca. 2 mJ/pulse) irradiation at (a) 0.30 μs, (b) 0.66 μs and (c) 3.3 μs. (C) Time profiles at 370 nm of nanocubes (red line), nanorods (blue line) and microrods (green line). All measurements were carried out in DMF.