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Electronic Supplementary Information

Controllable Synthesis of Ultrafine One-dimensional Small-Molecule Semiconductor Nanocrystals in Surfactant-assisted Wet Chemical Reaction and Confinement Effect

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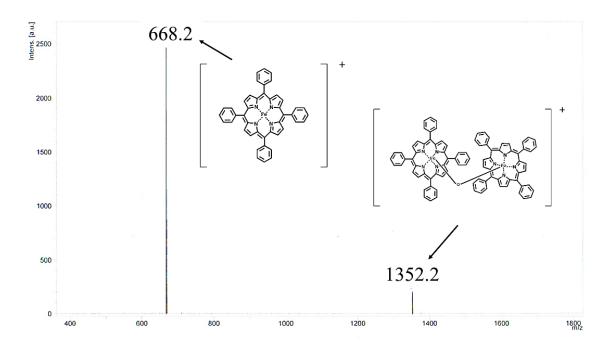


Figure. S1 MALDI-TOF-MS spectra of ultrafine nanorods. The calculation result: $C_{88}H_{56}N_8Fe_2O$, m/z=1353.13; MALDI-TOF-MS experimental result: m/z=668.4 and 1352.2. It proves the existence of (FeTPP) $_2O^+$ and FeTPP $^+$ from (FeTPP) $_2O$.

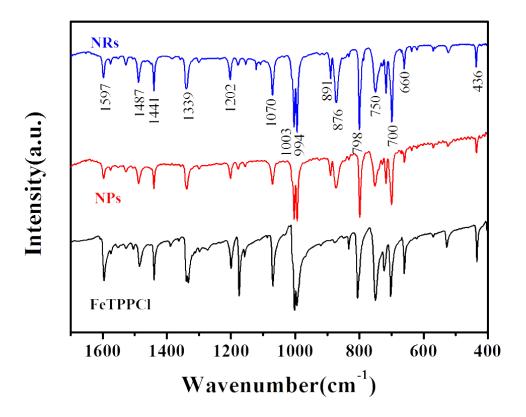


Figure. S2 IR spectra of FeTPPCI (black), (FeTPP)₂O nanoparticles (red) and (FeTPP)₂O nanorods (blue). IR (KBr): As compared with the raw material of FeTPPCI, the obvious difference in the spectra of samples is the appearance of vibration band at 876 and 891 cm⁻¹, which can be assigned to the stretching vibration of Fe-O-Fe from μ-oxo dimeric iron(III) porphyrin [(FeTPP)₂O].¹⁻⁴ The bands range from 1600 to 1005 cm⁻¹ can be respectively ascribed to the stretch vibration of C=C, C-C, C=N, C-N and C-H in-plane bending modes. The bands at 1003 and 994 cm⁻¹ in FT-IR spectra are the vibration modes related to the skeleton of metal porphyrin (MTPP) ring. The bands from 650 to 800 cm⁻¹ are usually assigned to the out-plane bending vibration of C-H from pyrrole and benzene rings, such as the band at 798 cm⁻¹ from pyrrole C-H, the bands at 700, 717 and 750 cm⁻¹ from the bending vibration modes of o-, m-, p- C-H on benzene ring.

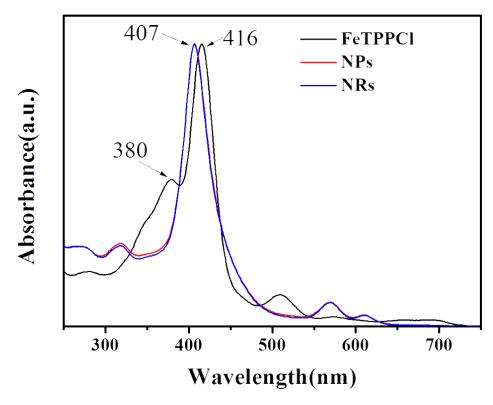
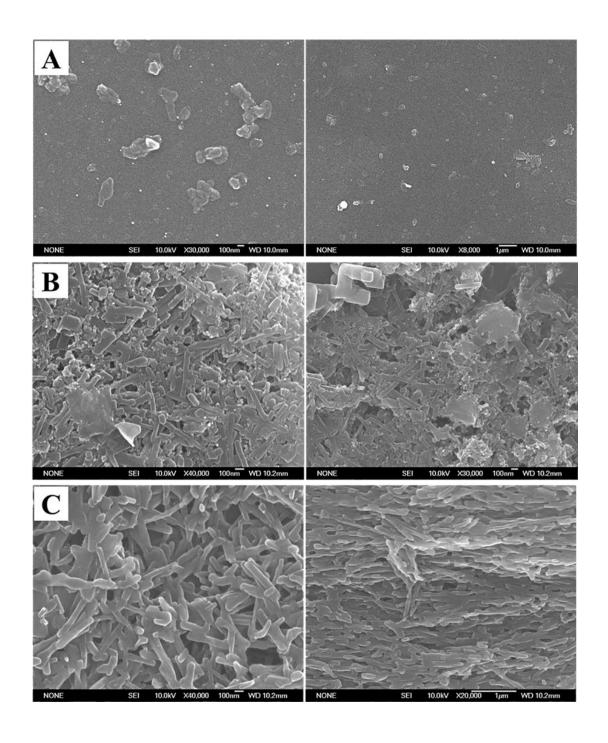


Figure. S3 UV-Vis absorption spectra of FeTPPCl (black line), (FeTPP)₂O nanoparticles (NPs, red line) and (FeTPP)₂O nanorods (NRs, blue line) dissolved in CH_2Cl_2 . λ _{FeTPPCl}: 380, 416, 509, 572, 690 nm. λ _{(FeTPP)2O}: 318, 407, 570, 610 nm. 2,4



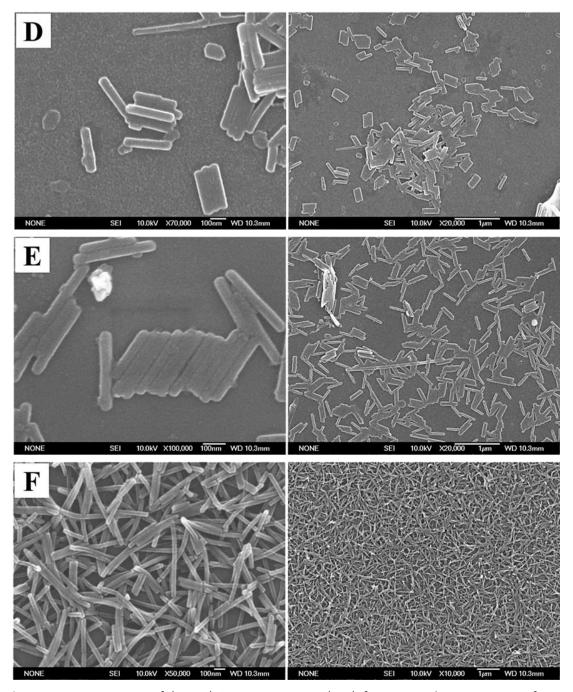


Figure. S4 SEM images of $(FeTPP)_2O$ nanostructures (NSs) from amorphous NSs to uniform ultrafine 1D organic nanorods (ONRs) obtained when the aging time is (A), 3 h (B), 12h (C), 24 h (D), 72 h (E) and 360 h (F), respectively.

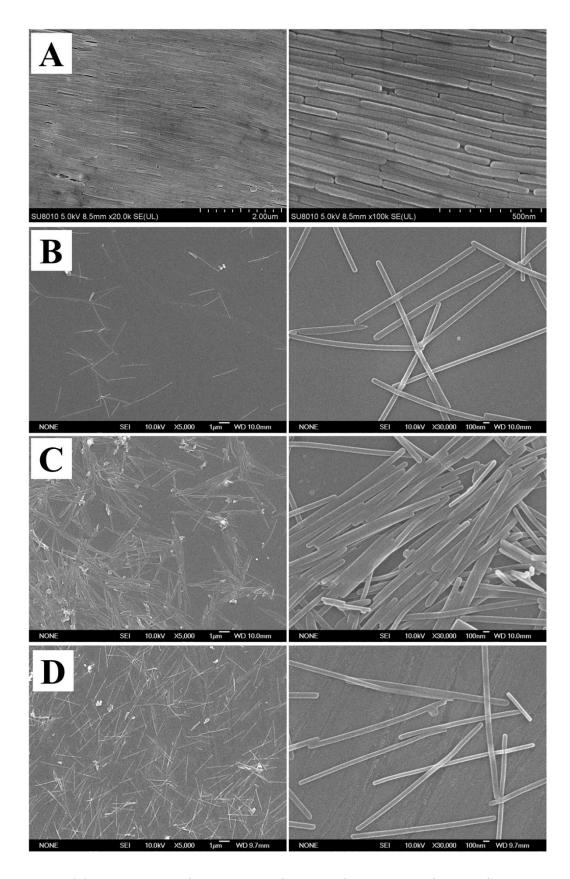


Figure. S5 (A) Larger scale self-organization of the ultrafine 1D ONRs formed after the 360 h-sample was casted on Si substrate. (B-D) SEM images of 1D ONRs formed after aging for 360 h, samples were casted on mica substrate, SiO_2 substrate and sapphire substrate, respectively.

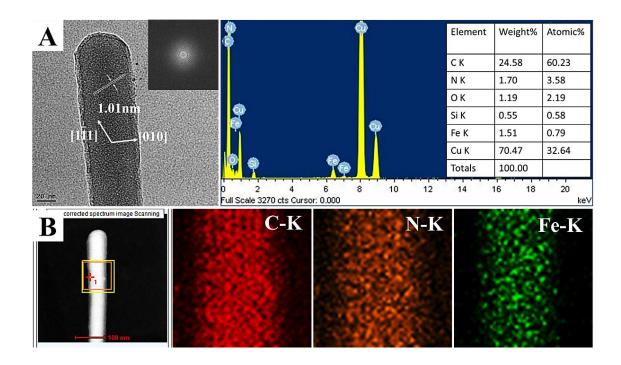


Figure. S6 (A) HRTEM image and the corresponding EDS (right), and (B) TEM image and the corresponding mapping images (right) of the ultrafine nanorod.

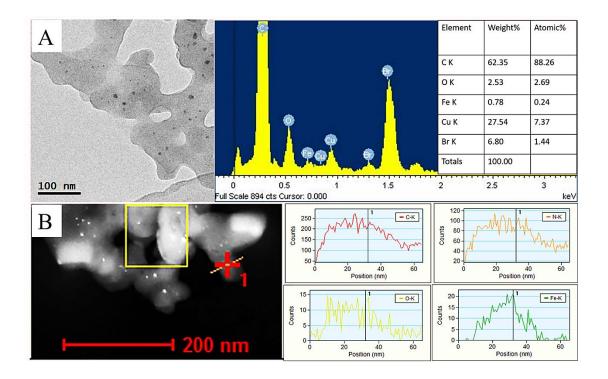


Figure. S7 (A) TEM images and the corresponding EDS (right), and (B) TEM images and the corresponding linear scanning images (right) of the samples obtained after aging for 1 h.

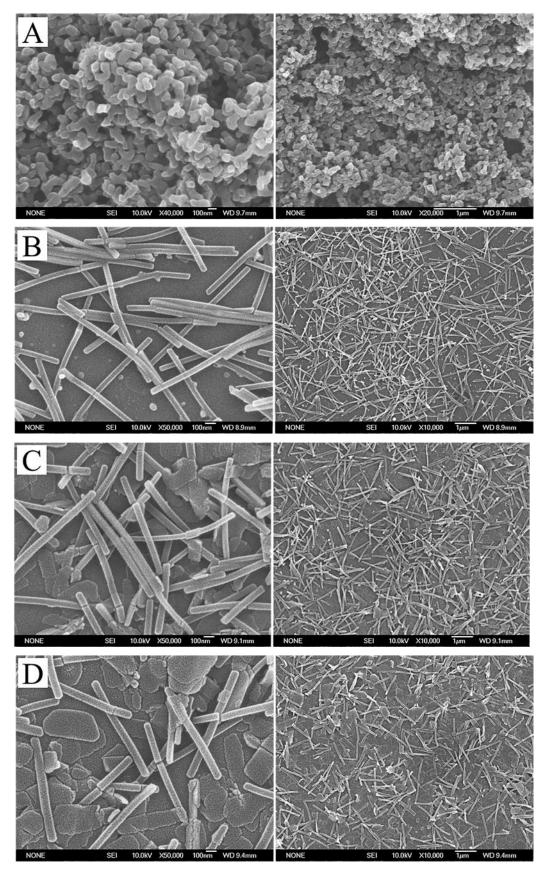
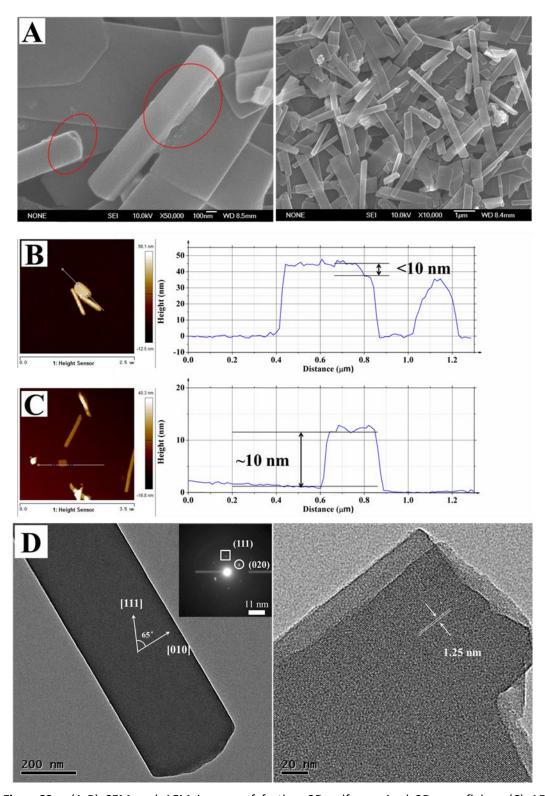


Figure. S8 SEM images of $(FeTPP)_2O$ samples obtained by adjusting the concentration of CTAB from (A) 0 mM , (B) 5.0 mM t, (C) 10.0 mM, (D)15.0 mM.



FigureS9. (A-B) SEM and AFM images of further 3D self-organized 2D nanoflakes. (C) AFM image of ultrathin 2D nanoflake. (D) TEM images of nanoflakes obtained by changing the concentration of CTAB, inset shows the corresponding SAED pattern. The SEM images in Figure S9A show the 3D self-organization of ultrathin nanoflakes. The Figure S9B proves the ultrathin nanoflakes, which constitute the 3D self-organization sample, is as thin as \sim 10 nm. Besides, the Figure S9C also proves the thickness of the ultrathin nanoflake is about 10 nm. Figure S9D shows

that the lattice fringes in the HRTEM image and the selected area electron diffraction (SAED) pattern are consisted with those of the nanorods. Therefore, we can come to the conclusion that the orientation of the nanoflakes is the same with the nanorods. The (FeTPP)₂O nanocrystals that we synthesized belong to orthorhombic system (CCDC No.: PPORFE10) with space group Aba2. The unit cell parameters are a = 15.197 Å, b = 25.077 Å, c = 18.074 Å, $\alpha = \beta = \gamma = 90^{\circ}$. Unfortunately, the diffraction spot of (101) facet disappears in SAED pattern according to the space-group extinction rule. However, we can get some useful information from the selected area electron diffraction (SAED) pattern. If the growth direction of 1D (FeTPP)₂O nanocrystal is [hkl], the surface angle between (hkl) and (111) facets is 25°, and the angle between (hkl) and (010) facets is 90°. In addition, the three facets of (hkl), (111) and (020) are perpendicular to the substrate. Based on these conditions and the surface angle formula of orthorhombic system, we can know that the growth direction should be [101].

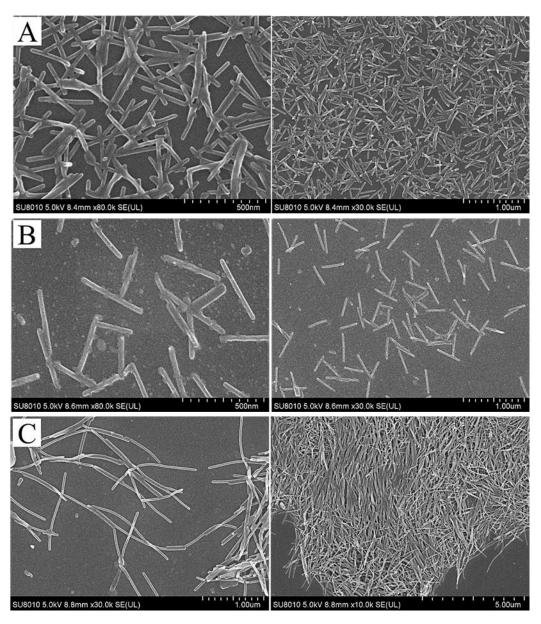
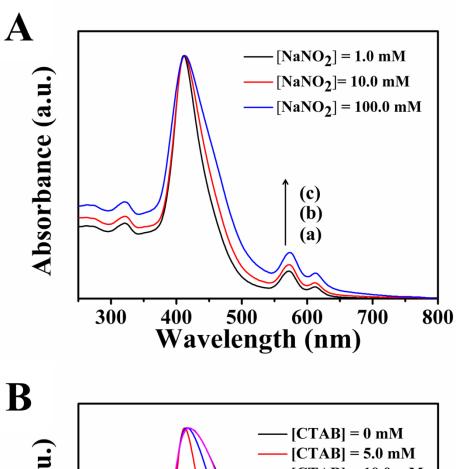


Figure S10. SEM images of $(FeTPP)_2O$ samples obtained by adjusting the concentration of NaNO₂ from (A)1.0 mM ,(B) 10.0 mM to (C) 100.0 mM..



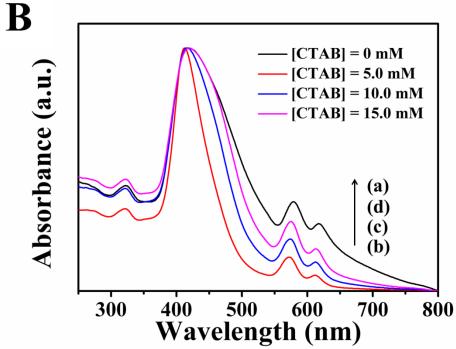


Figure. S11 The change of UV-vis spectra of $(FeTPP)_2O$ nanostructures in aqueous dispersion with the concentration of (A) NaNO₂ from (a) 1.0 mM, (b) 10.0 mM to (c) 100.0 mM and (B) CTAB from (a) 0 mM, (b) 5.0 mM, (c) 10.0 mM to (d) 15.0 mM.

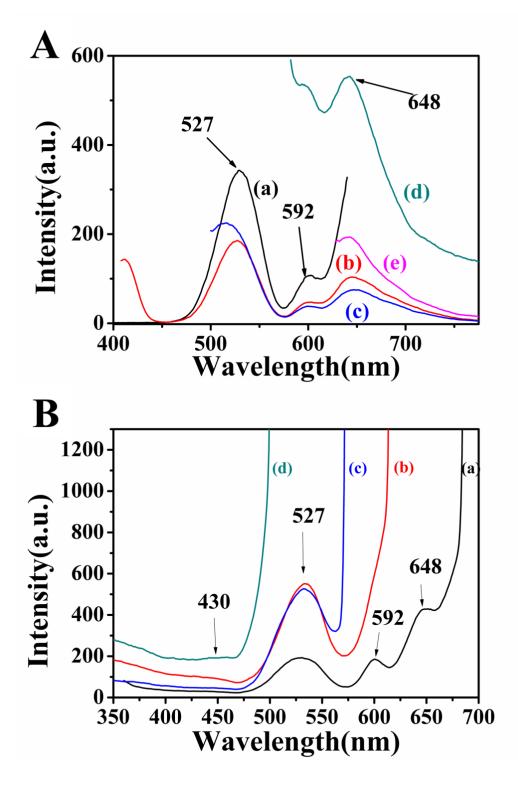


Figure. S12 (A) PL spectra of the 1D ultrafine NRs in aqueous dispersion excited at (a) 320 nm, (b) 408 nm, (c) 457 nm, (d) 527 nm and (e) 570 nm. (B) PLE spectra of the 1D ultrafine NRs in aqueous dispersion monitored at (a) 710 nm, (b) 648 nm, (c) 592 nm and (d) 527 nm.

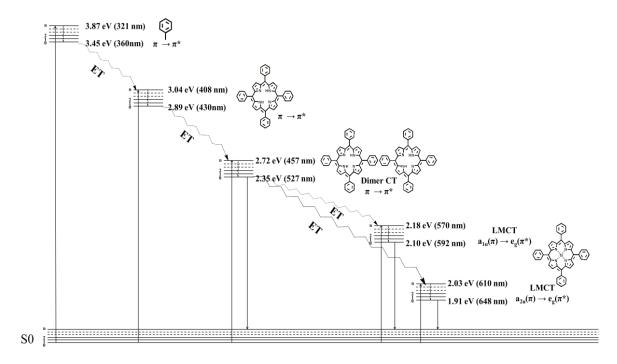


Figure. \$13 The energy-level diagram of (FeTPP)₂O.

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