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Supporting Information

Broadening the Range of Vesicle Formation by Heating

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Experimental Section

1. Materials. All chemical reagents were purchased from commercial suppliers and used without further purification. Amphiphilic block copolymers poly(styrene)-*b*-poly(acrylic acid) (PS_{154}-*b*-PAA_{49}, Mn = 16000 for the PS block and Mn = 3500 for the PAA block, Mw/Mn = 1.15; PS_{192}-*b*-PAA_{13}, Mn = 20000 for the PS block and Mn = 900 for the PAA block, Mw/Mn = 1.07), poly(styrene)-*b*-poly(4-vinylpyridine) (PS_{222}-*b*-$P4VP_{43}$, Mn = 23000 for the PS block and Mn = 4500 for the P4VP block, Mw/Mn = 1.10; PS_{230}-*b*-$P4VP_{90}$, Mn = 24000 for the PS block and Mn = 9500 for the P4VP block, Mw/Mn = 1.10; $P4VP_{43}$-*b*-PS_{260}-*b*-$P4VP_{43}$, Mn = 27000 for the PS block and Mn = 4500 for the P4VP blocks, Mw/Mn = 1.09), and poly(styrene)-*b*-poly(ethylene oxide) (PS_{1442}-*b*-PEO_{795}, Mn = 150000 for the PS block and Mn = 35000 for the PEO block, Mw/Mn = 1.09) were purchased from Polymer Source, Inc. Deionized water (resistance > 18.2 $M\Omega\cdot cm^{-1}$) was used in all experiments. Copper specimen grids (200 mesh) with carbon support film (referred to as TEM grids in the text) were purchased from Beijing XXBR Technology co., ltd.

2. TEM characterization and sample preparation. TEM images were collected from a JEM-1400 Transmission Electron Microscope (JEOL) operated at 100 kV. TEM grids were treated with oxygen plasma in a Harrick plasma cleaner for 45 seconds to increase surface hydrophilicity. One drop of sample solution was added to the hydrophilic surface of the TEM grid, and excess solution was wicked off with a filter paper. After drying in a desiccator for 30 min, the grid was used for TEM characterization.

3. Synthesis of BCP vesicles with the heating method. In the heating method, all the reagents and solvents were mixed in one shot, and then heated under high temperature. In a typical experiment, BCP powder was first dissolved in 1 mL DMF or THF in a 4 mL glass vial, and water of corresponding amount was directly injected into the mixture followed by vortex to give thorough mixing of the ingredients. (In preparing vesicles from the long-hair ionic BCP, PS_{154}-*b*-PAA_{49}, different volumes of HCl aqueous solution (2 M) were first mixed with water before its injection.) Then the vial was capped and sealed to avoid solvent loss, and the mixture was placed in a silicon oil bath and incubated under 110 ^{o}C (for DMF/H_2O mixtures) or 90 ^{o}C (for THF/H_2O mixtures) for a corresponding period of time. After heating, the vial was taken out of the oil bath, and slowly cooled down in air to room temperature. After cooling, 100 μL of the product solution was extracted and mixed with 1 mL water. Then the mixture was centrifuged at 14000 rpm for 20 min to isolate the BCP micelles from the solution, and these concentrated micelles were further used for TEM characterization.

4. Synthesis of BCP vesicles with the water addition method. In the water addition method, water was introduced at an extremely slow rate to other pre-mixed. Typically, BCP powder was first dispersed in 1 mL DMF or THF in a 4 mL vial, and the mixture was sonicated for 10 min to ensure complete dissolution. Then a corresponding amount of water was added to the above solution through a syringe pump under vigorous stirring. The flow rate of water was set at 10 μL/min for all experiments. In the PS_{154}-*b*-PAA_{49} case, different volumes of HCl aqueous solution (2 M) were first mixed with the water to be added by the syringe pump. After the water addition, the resultant mixture was kept under stirring for another 12 h before TEM sample preparation. After this period of time, the product solution was treated in the same way as in the heating method for TEM characterization.

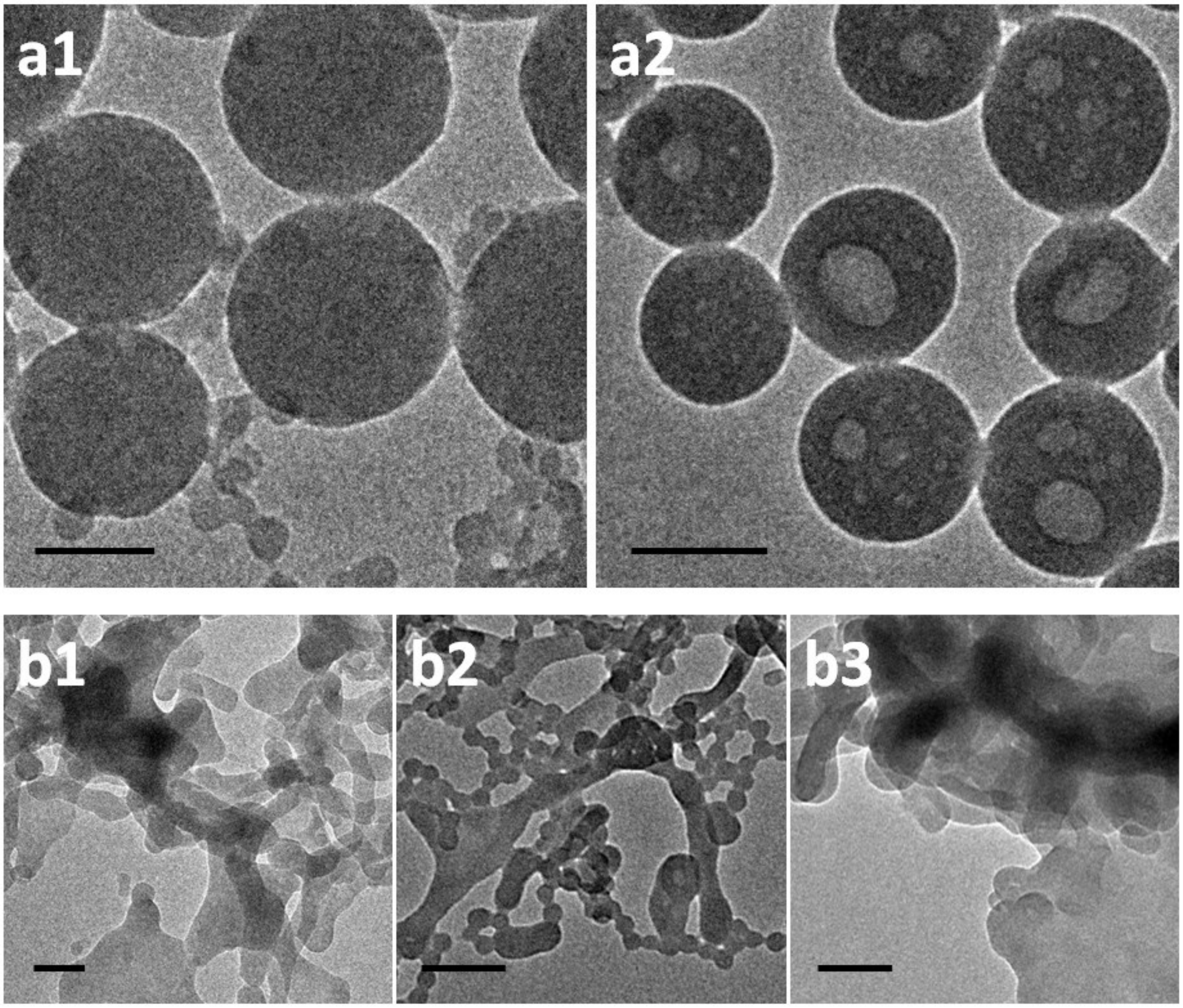


Figure S1. Another 3 added points for Figure 3 in the main text. The products of the heating method: (a1) 0.4 wt%, DMF/H_2O = 10:1, and (a2) 1.6 wt%, DMF/H_2O = 10:8. The products of the water addition method: (b1) 0.4 wt%, DMF/H_2O = 10:1, (b2) 1.2 wt%, DMF/H_2O = 10:4, and (b3) 1.6 wt%, DMF/H_2O = 10:8. Scale bar: 100 nm.

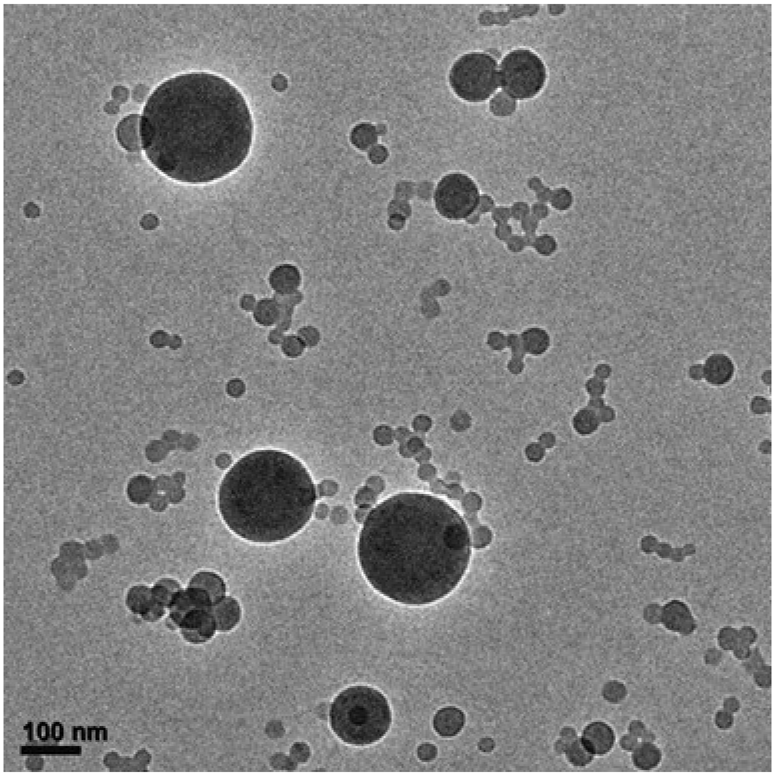


Figure S2. Large-area view of Figure 1. a1.

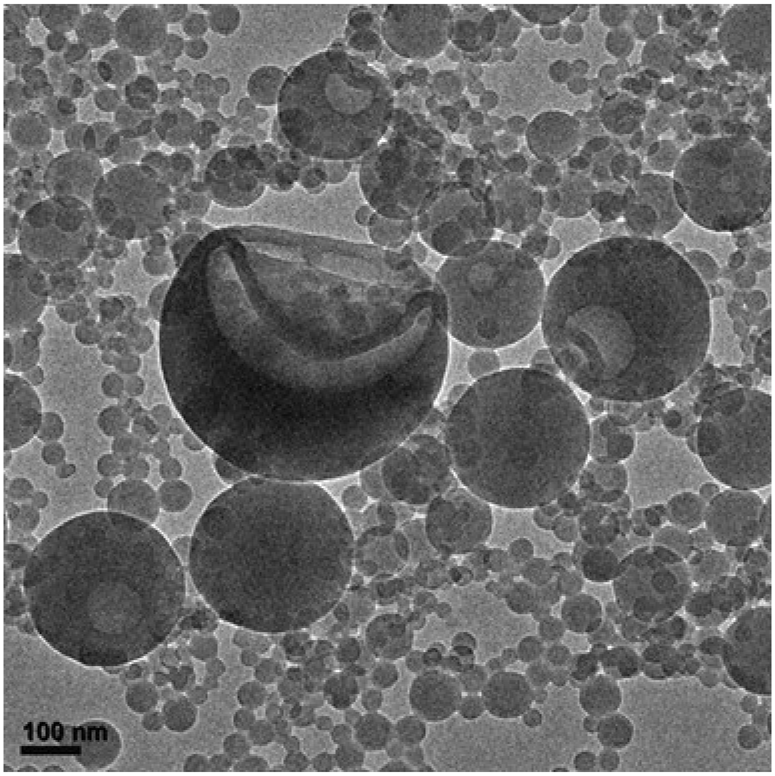


Figure S3. Large-area view of Figure 1. a2.

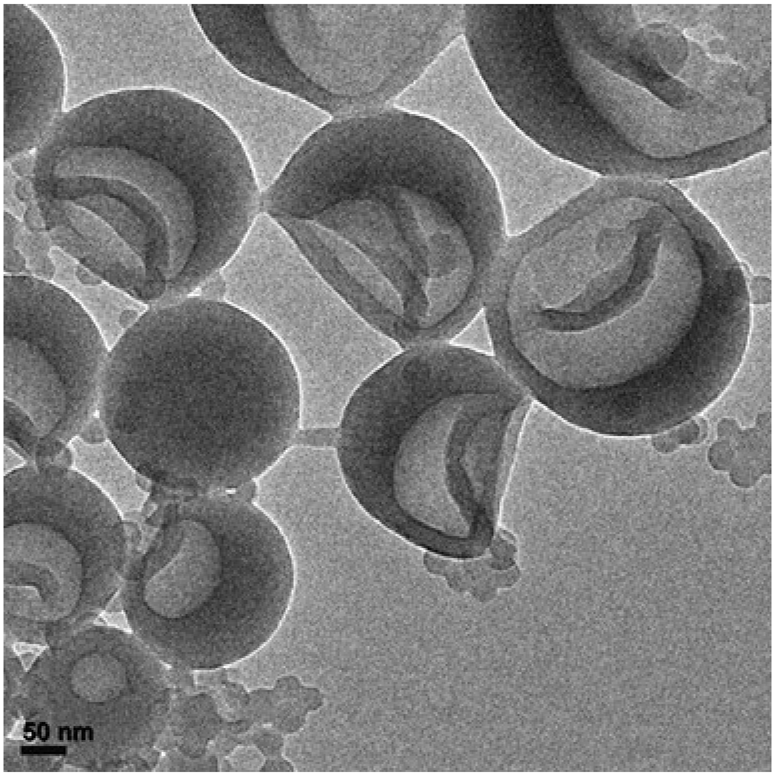


Figure S4. Large-area view of Figure 1. a3.

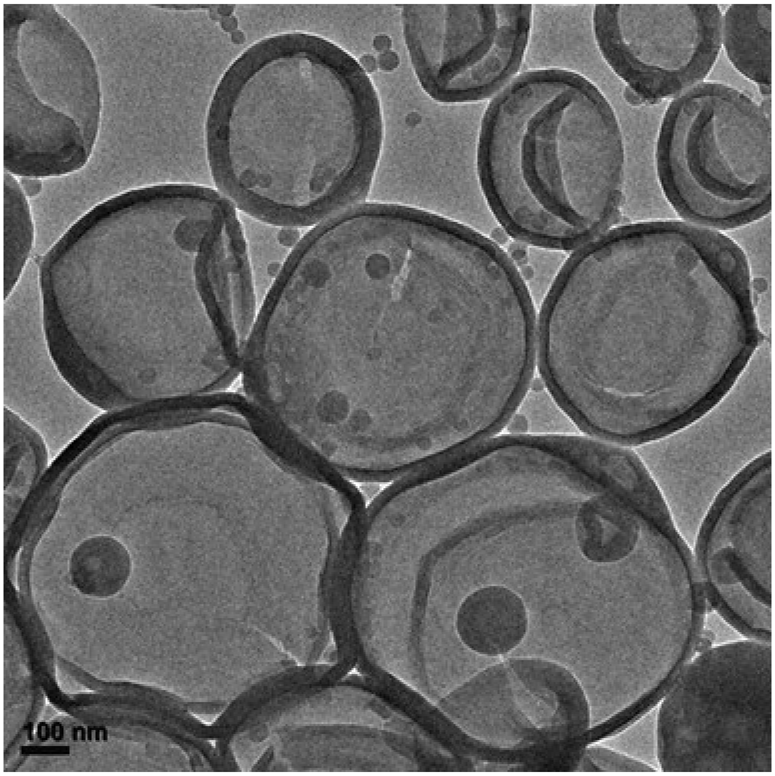


Figure S5. Large-area view of Figure 1. a4.

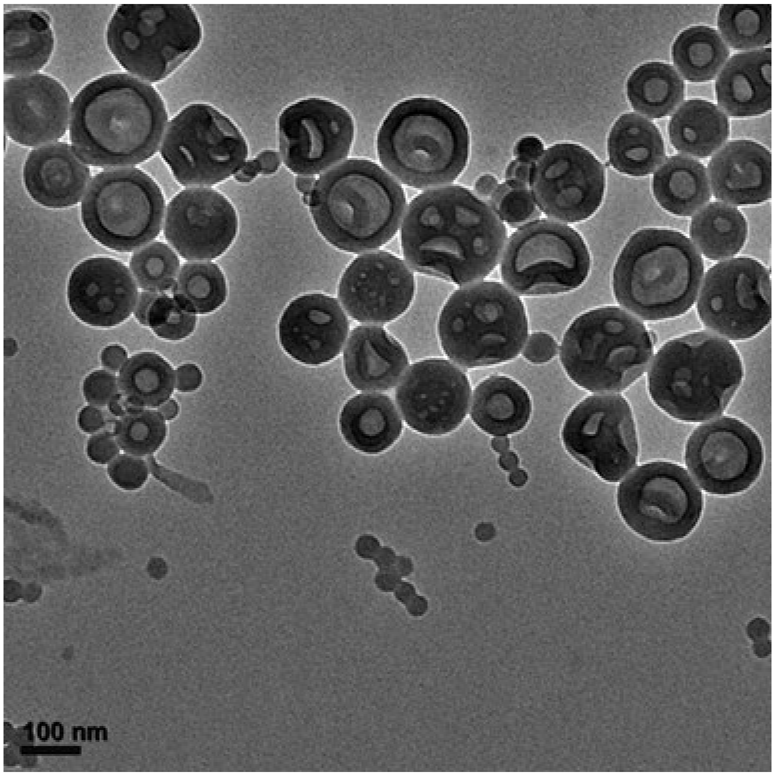


Figure S6. Large-area view of Figure 1. a5. Approximate Yield = 90%

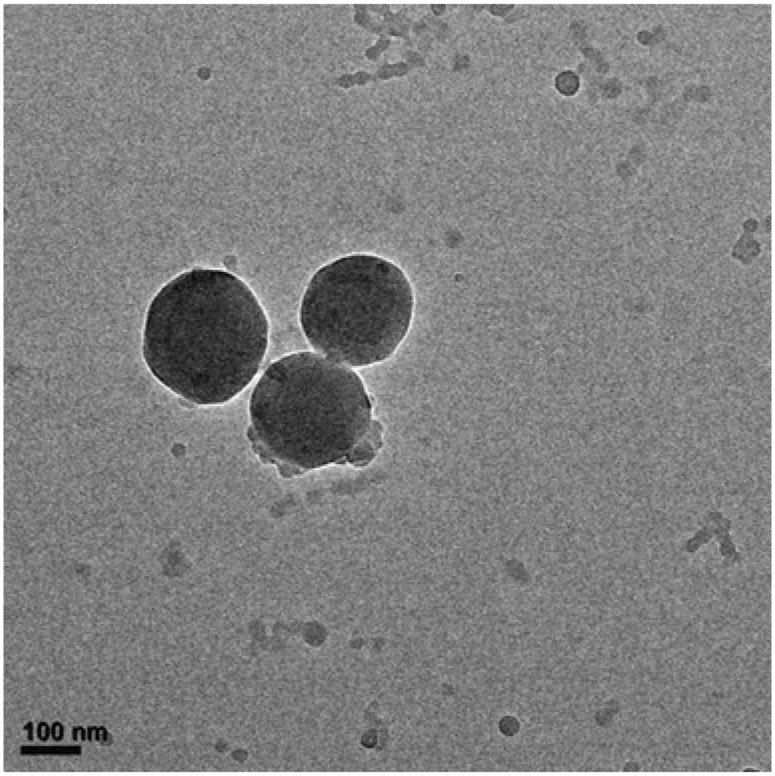


Figure S7. Large-area view of Figure 1. b1.

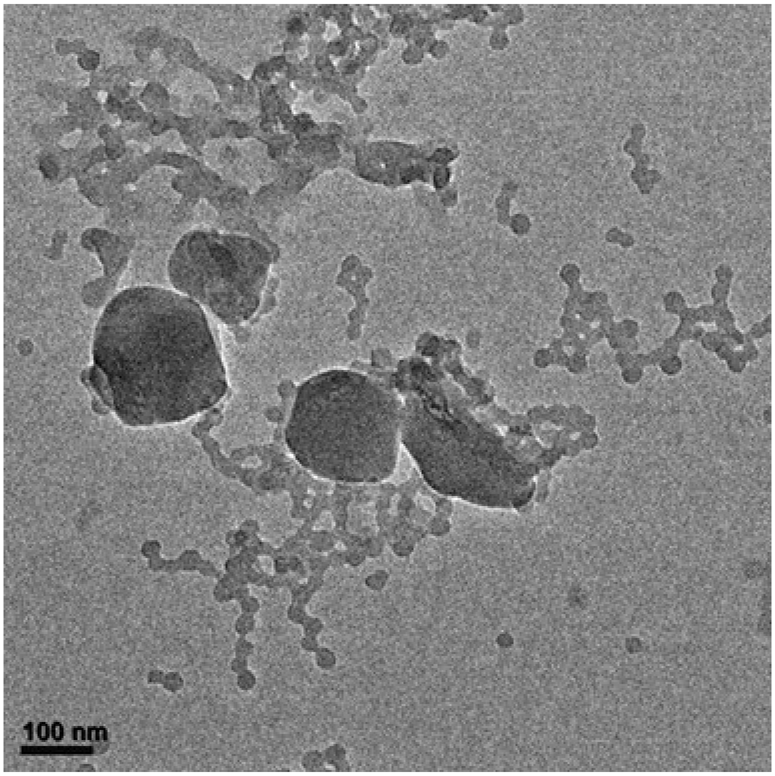


Figure S8. Large-area view of Figure 1. b2.

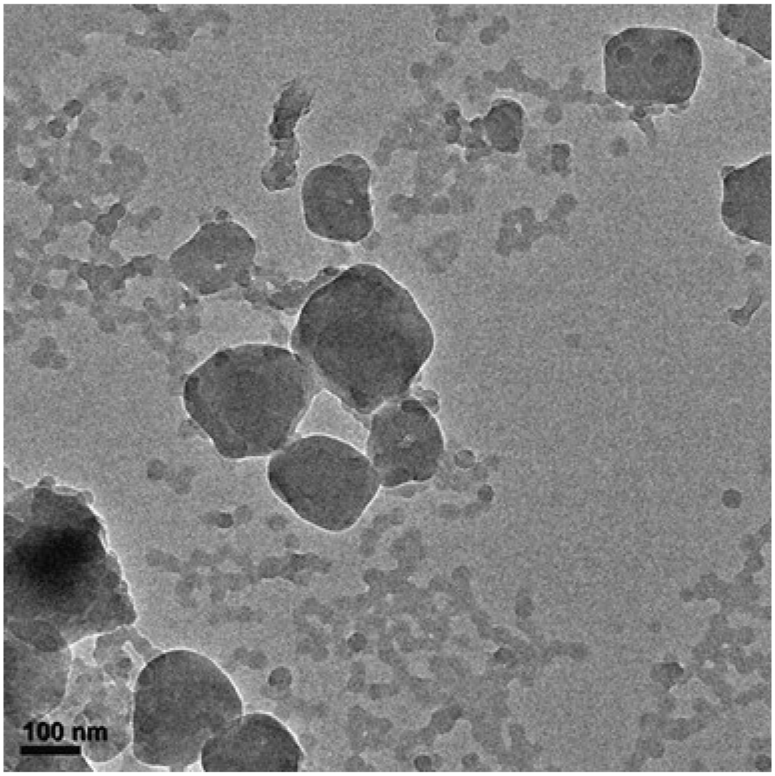


Figure S9. Large-area view of Figure 1. b3.

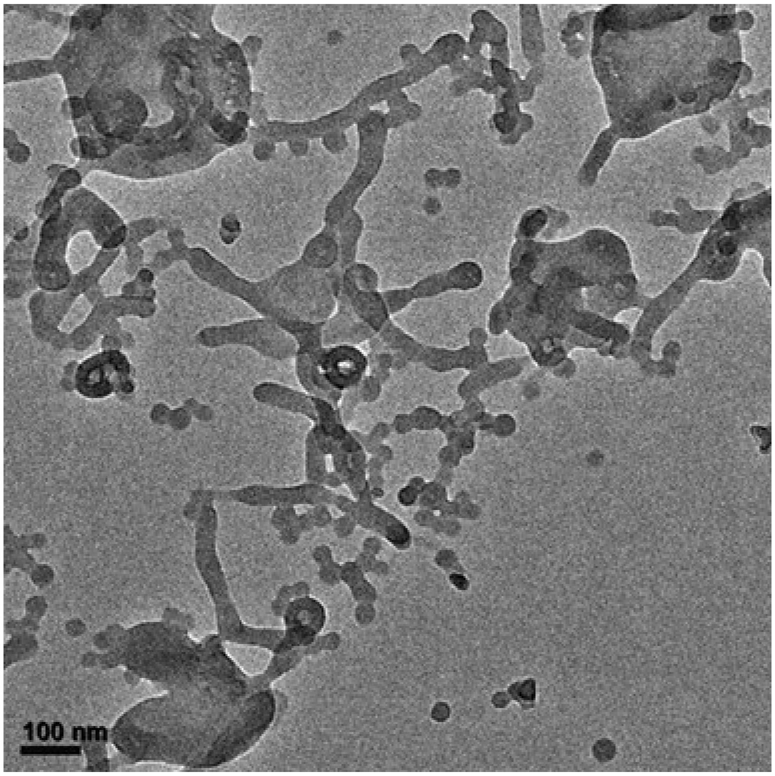
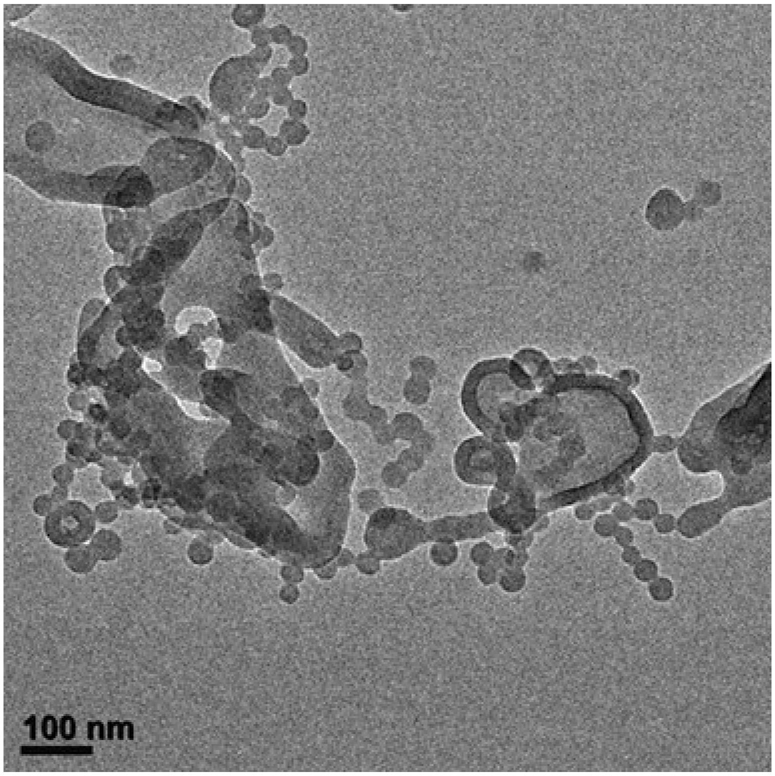


Figure S10. Large-area view of Figure 1. b4.



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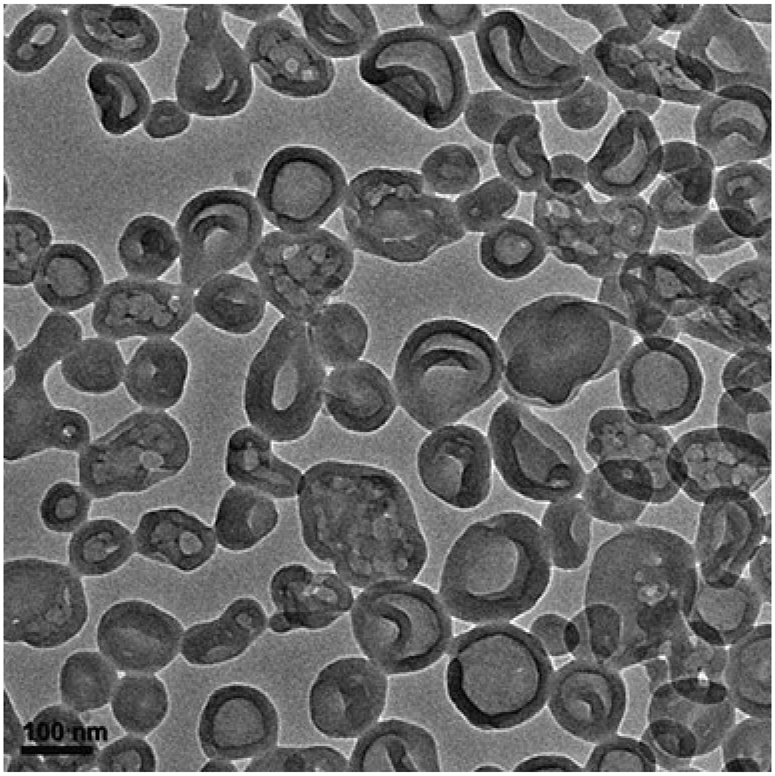


Figure S12. Large-area view of Figure 1. b6. Approximate Yield = 72%

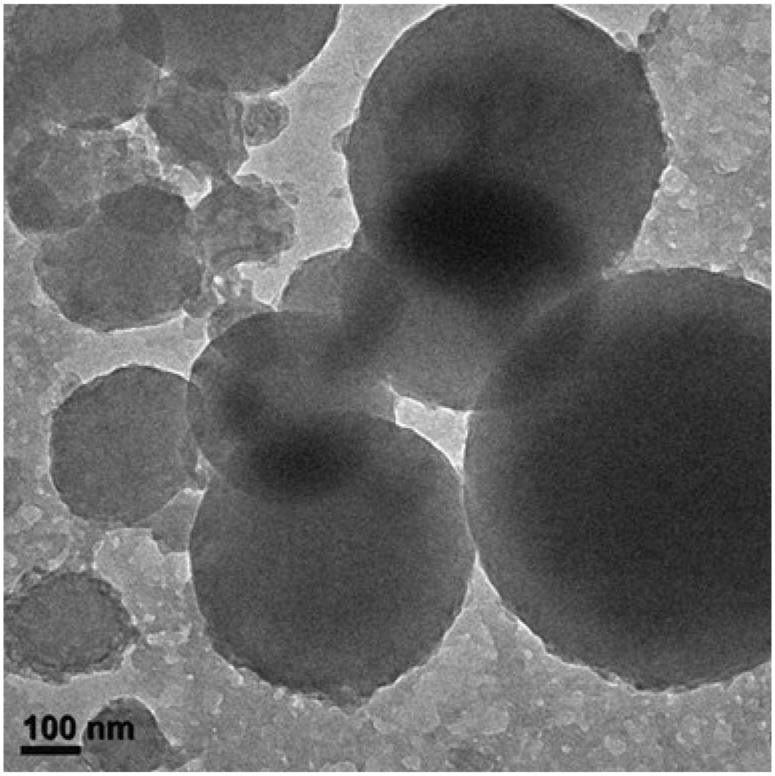


Figure S13. Large-area view of Figure 2. a1.

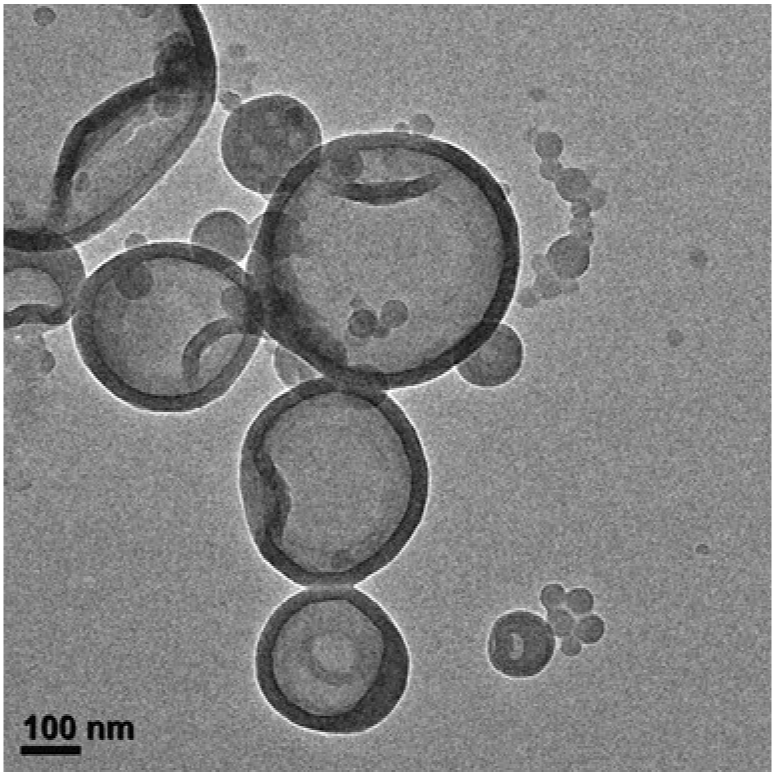
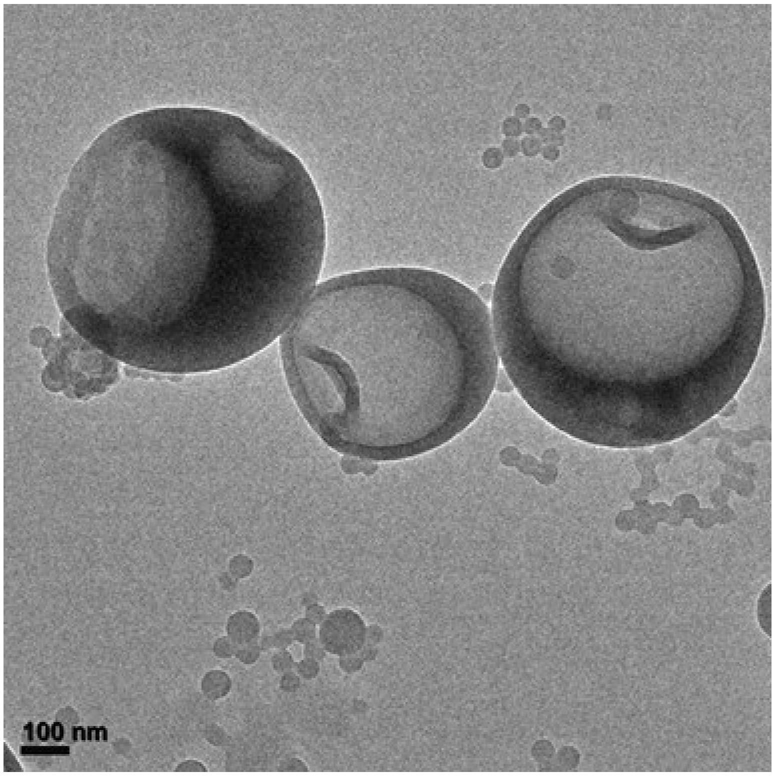


Figure S14. Large-area view of Figure 2. a2. Approximate Yield = 82%



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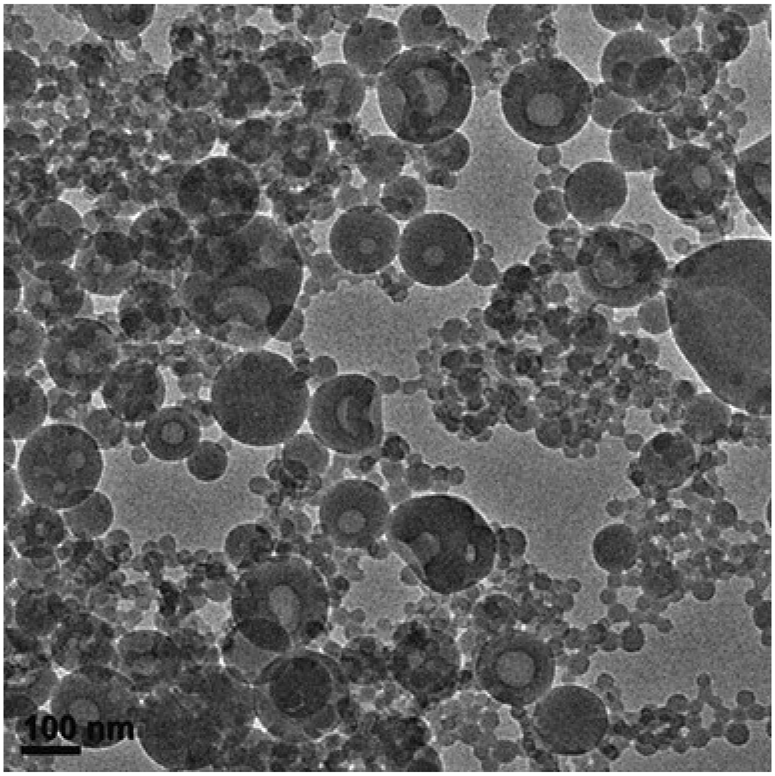

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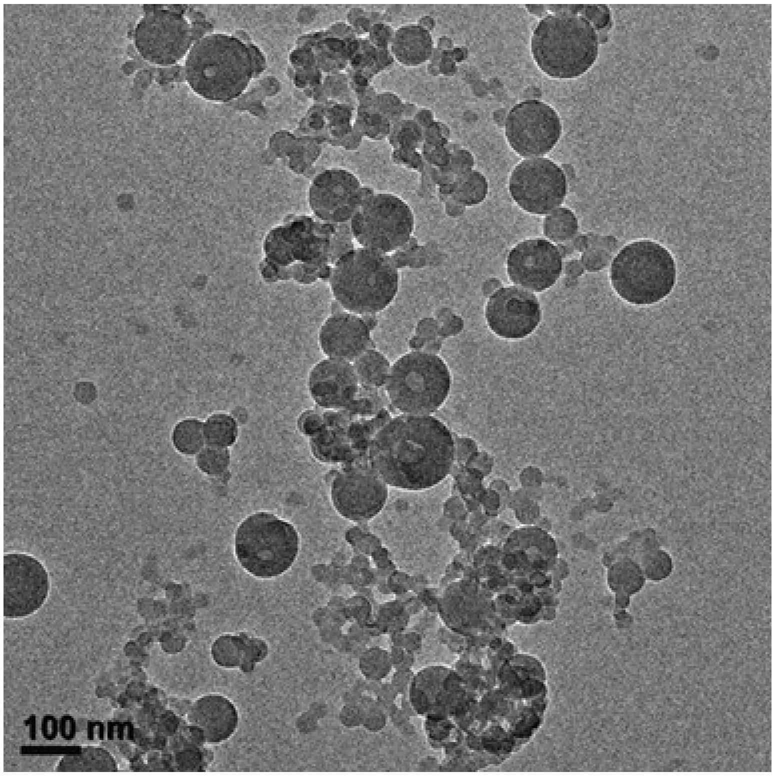


Figure S17. Large-area view of Figure 2. a5.

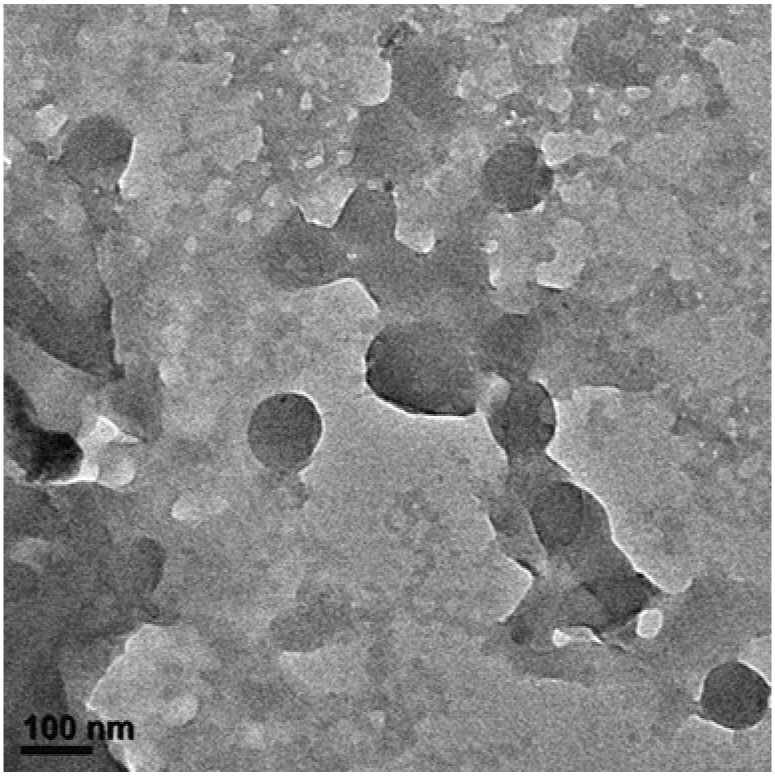


Figure S18. Large-area view of Figure 2. b1.

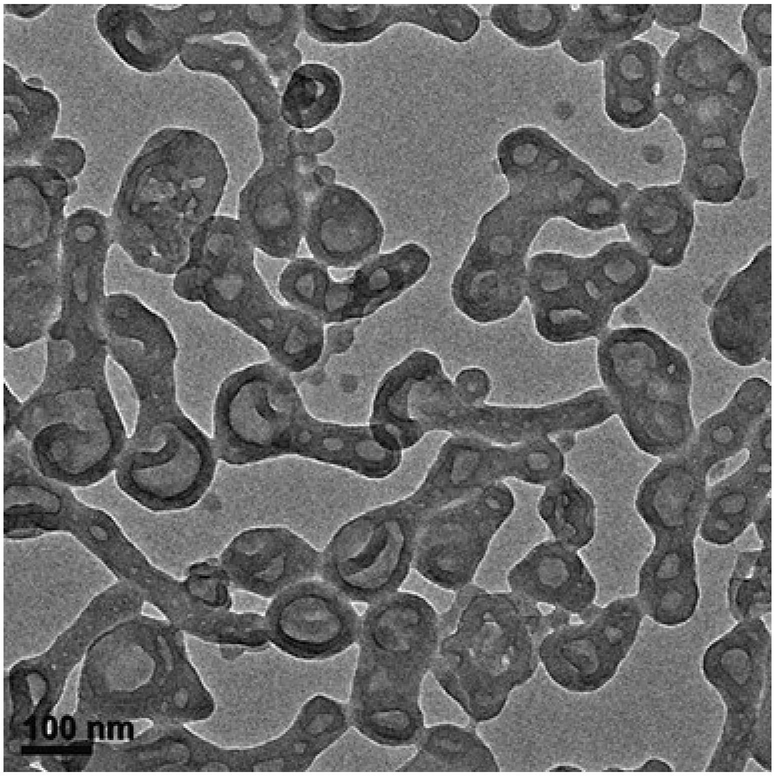


Figure S19. Large-area view of Figure 2. b2. Approximate Yield = 67%

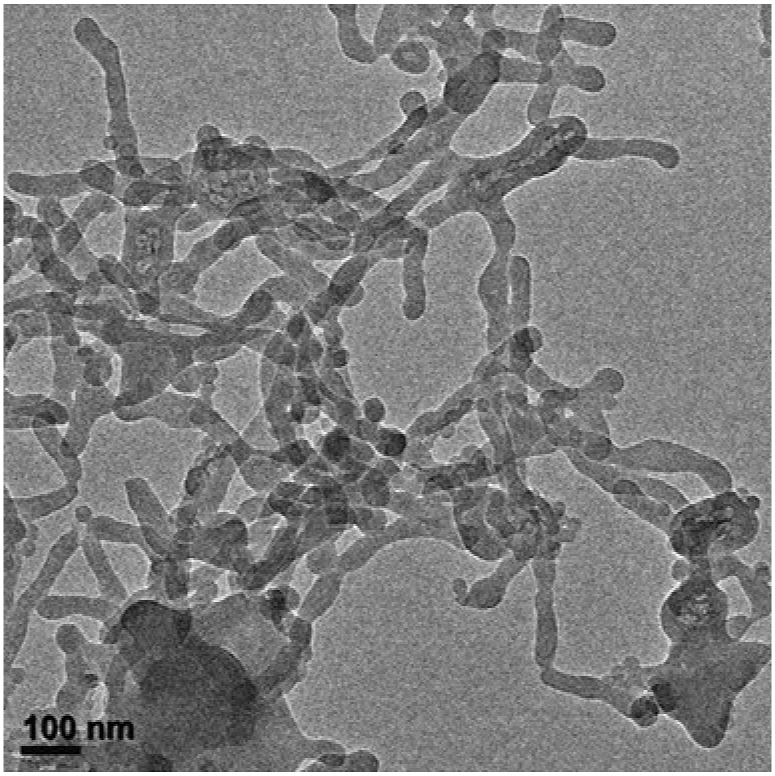


Figure S20. Large-area view of Figure 2. b3.

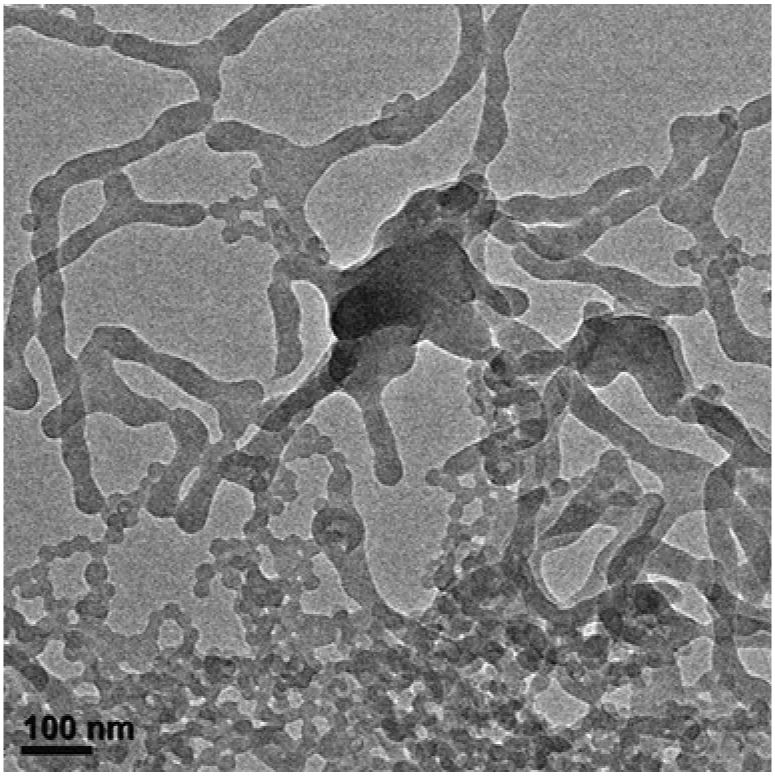


Figure S21. Large-area view of Figure 2. b4.

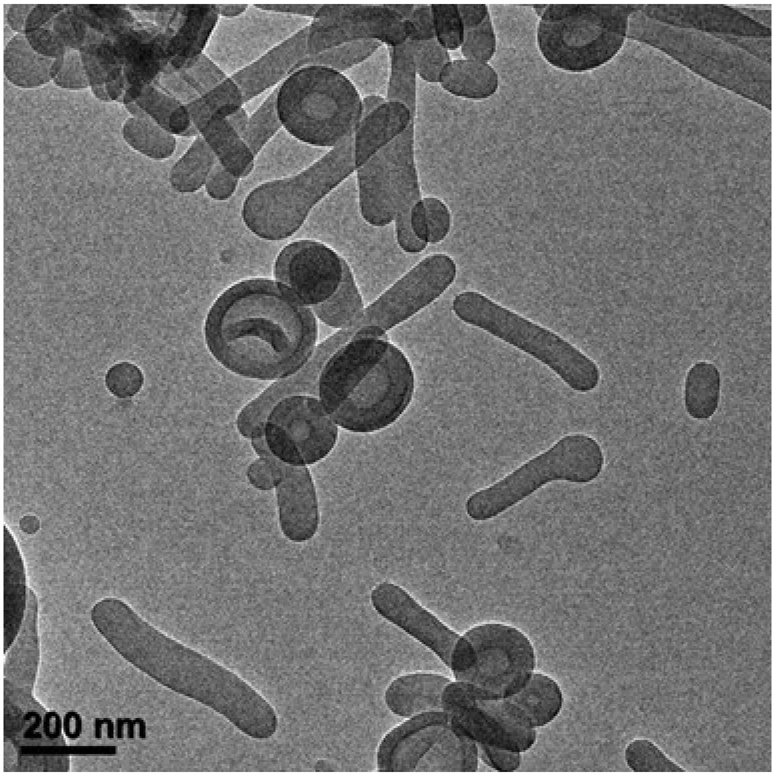
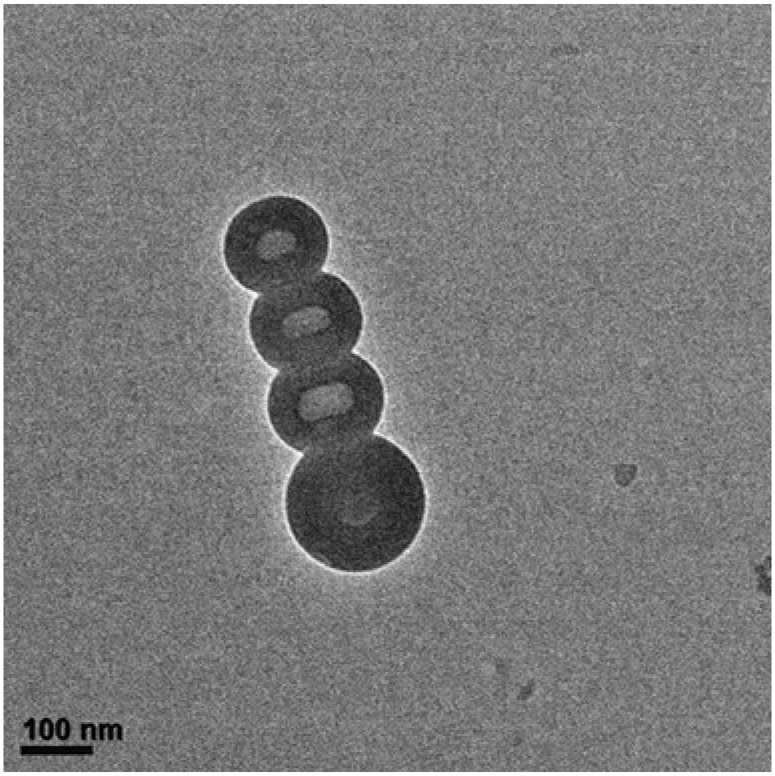


Figure S22. Large-area view of Figure 4. a1.



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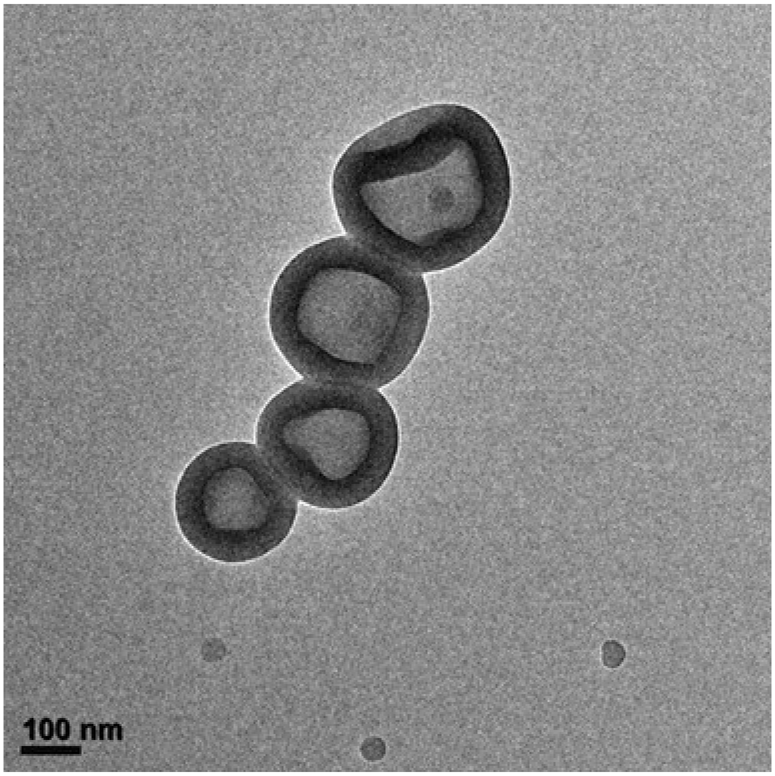

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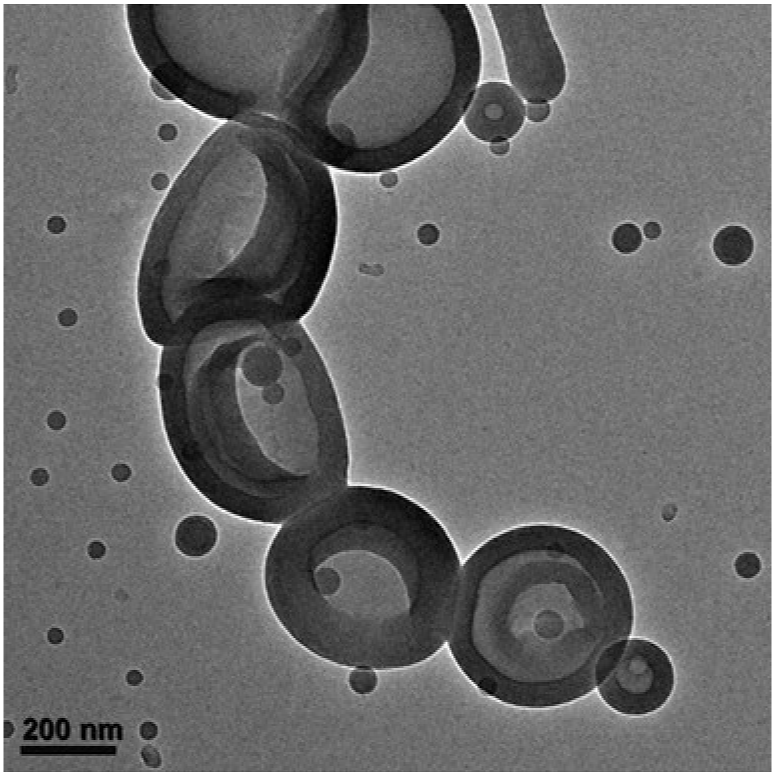

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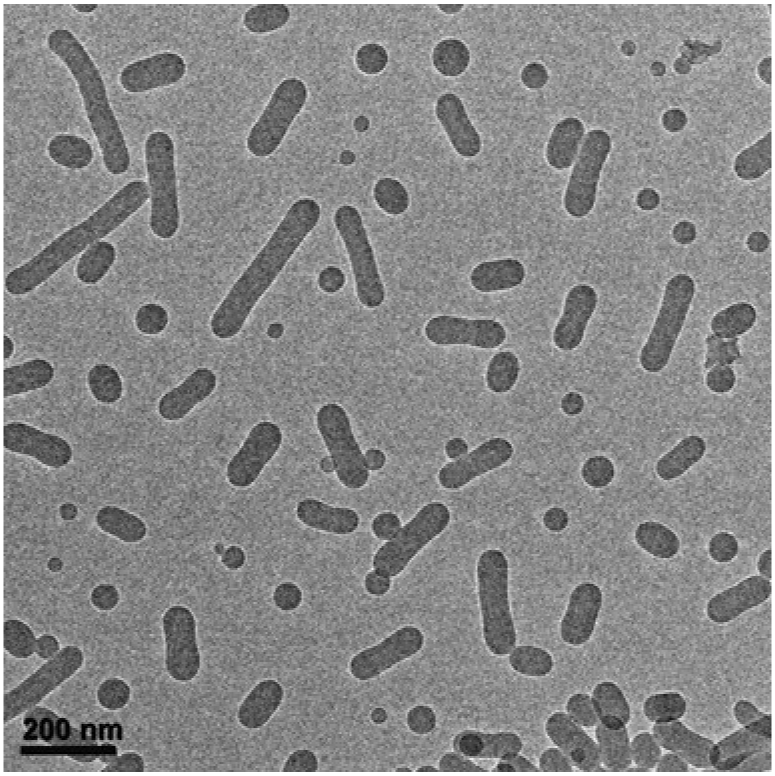


Figure S26. Large-area view of Figure 4. b1.

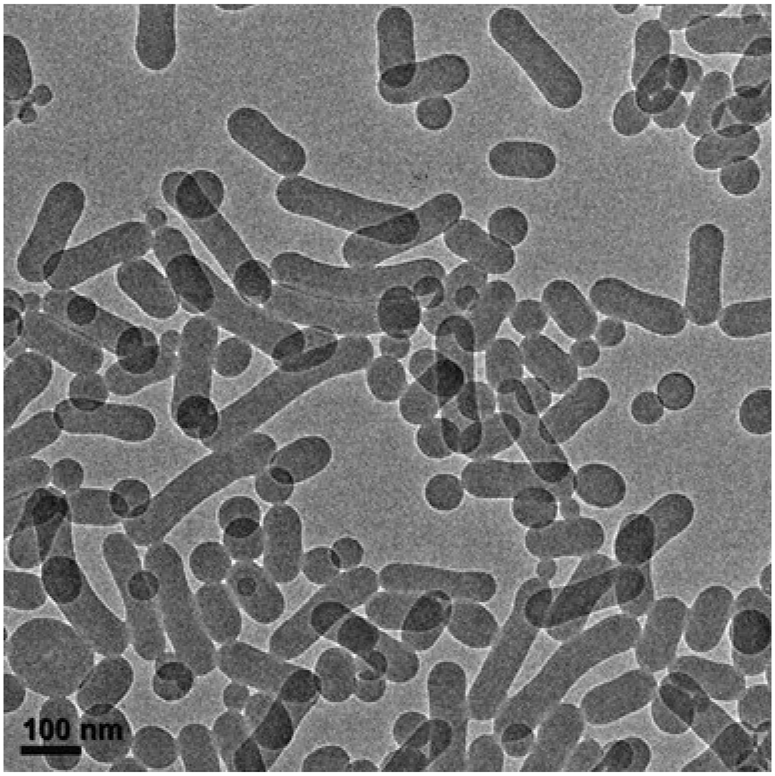
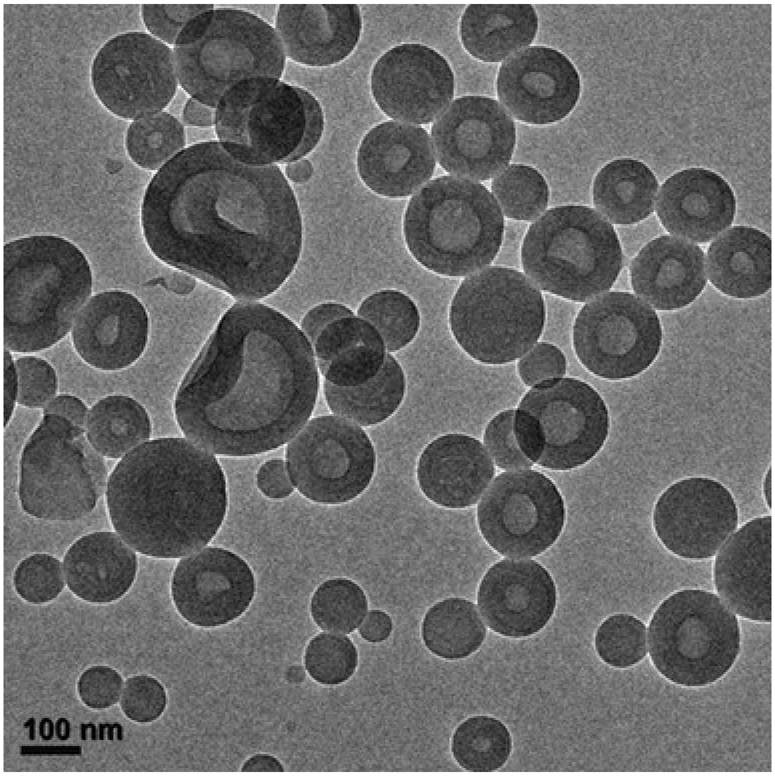


Figure S27. Large-area view of Figure 4. b2.



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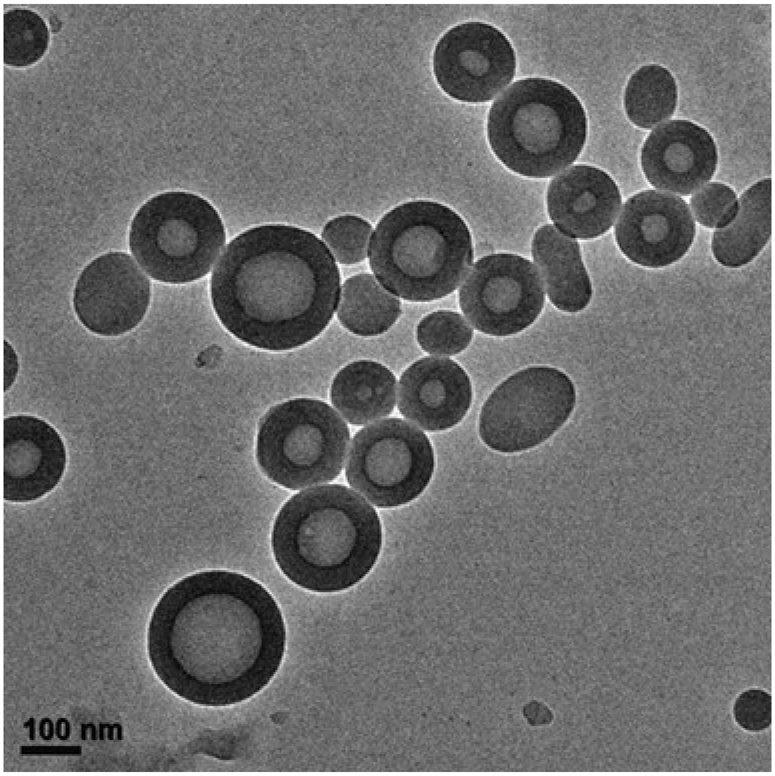


Figure S29. Large-area view of Figure 4. b4. Approximate Yield = 63%

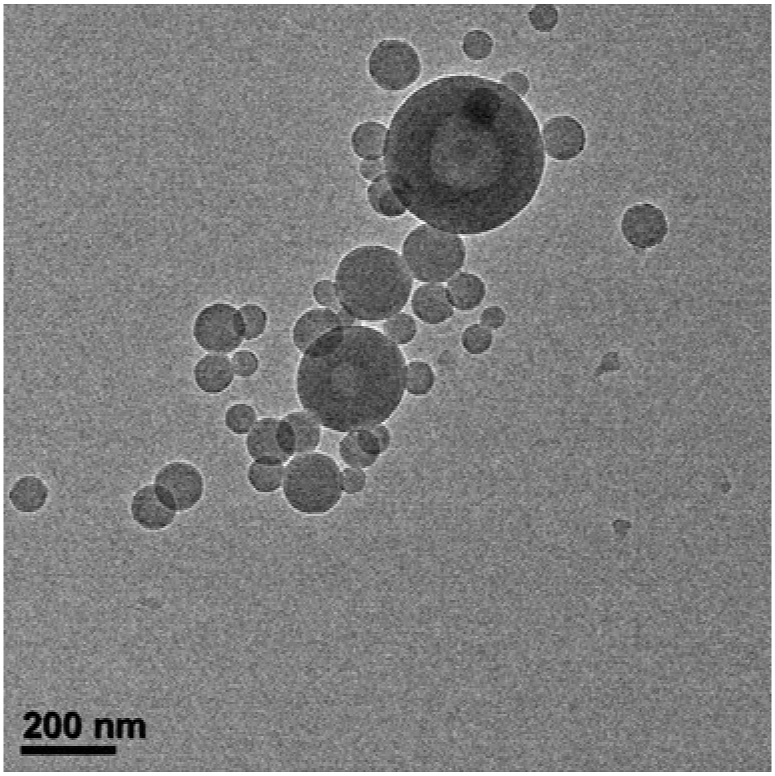


Figure S30. Large-area view of Figure 4. c1.

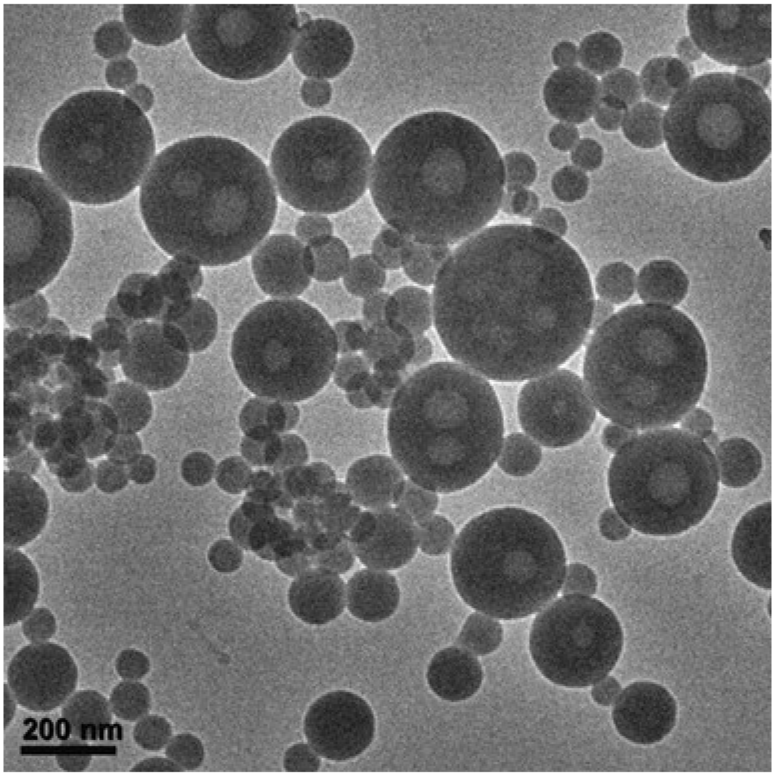


Figure S31. Large-area view of Figure 4. c2.

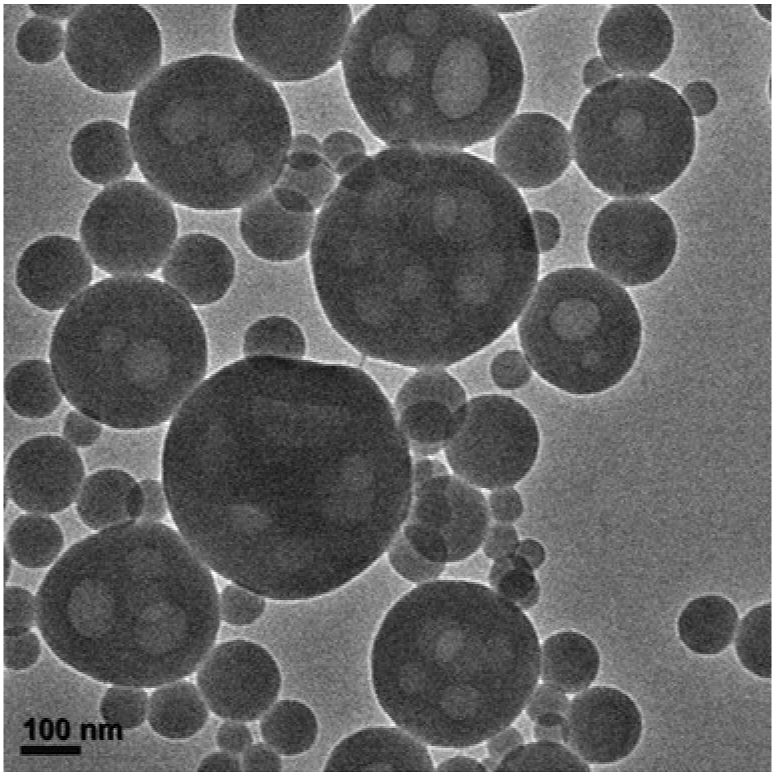
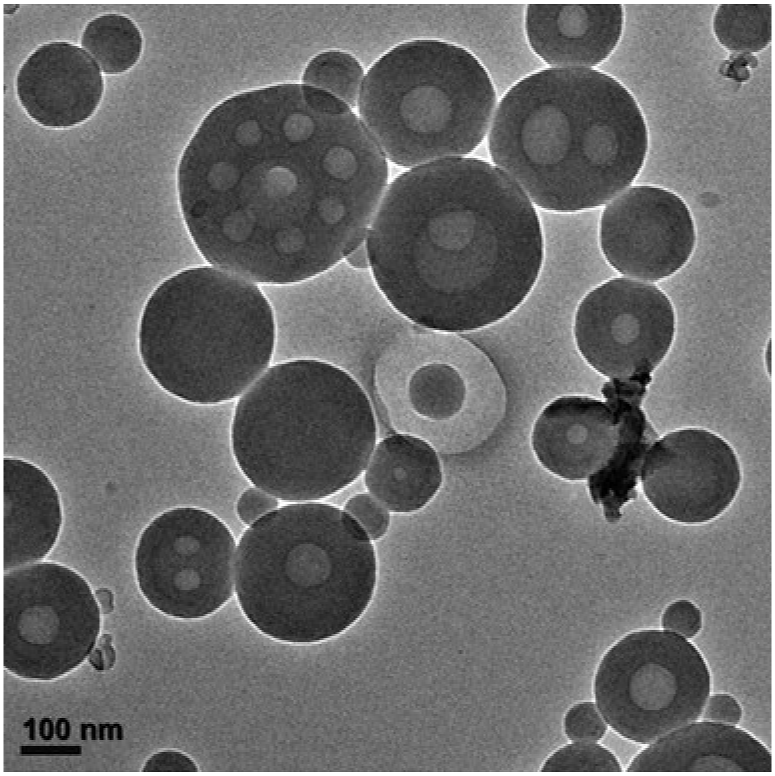


Figure S32. Large-area view of Figure 4. c3.



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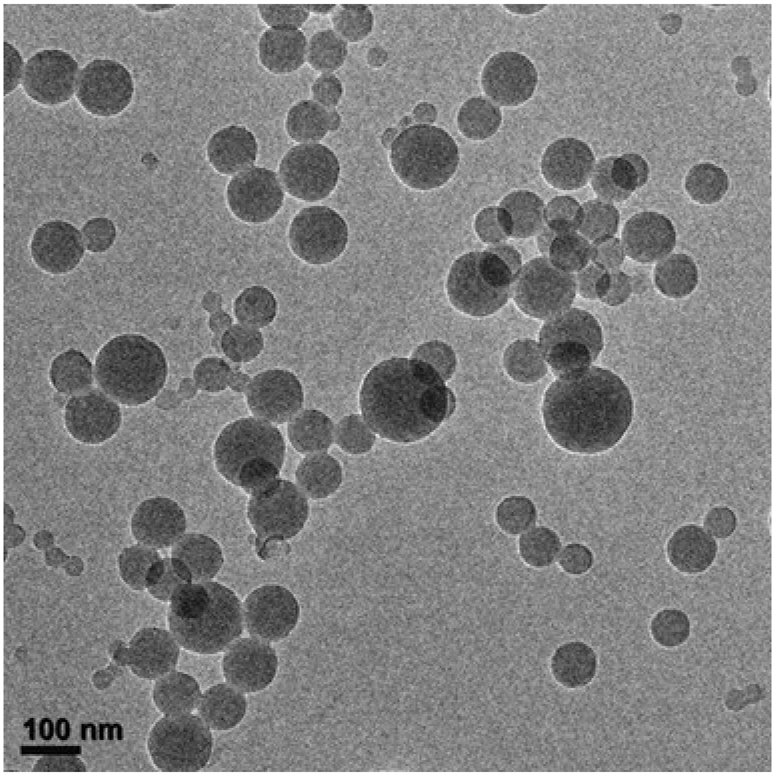
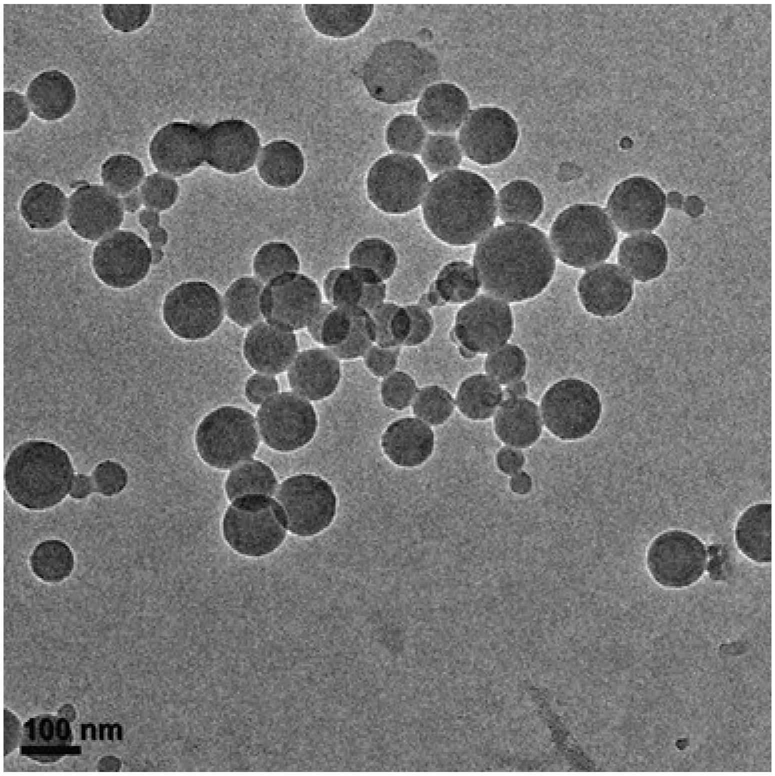


Figure S34. Large-area view of Figure 4. d1.



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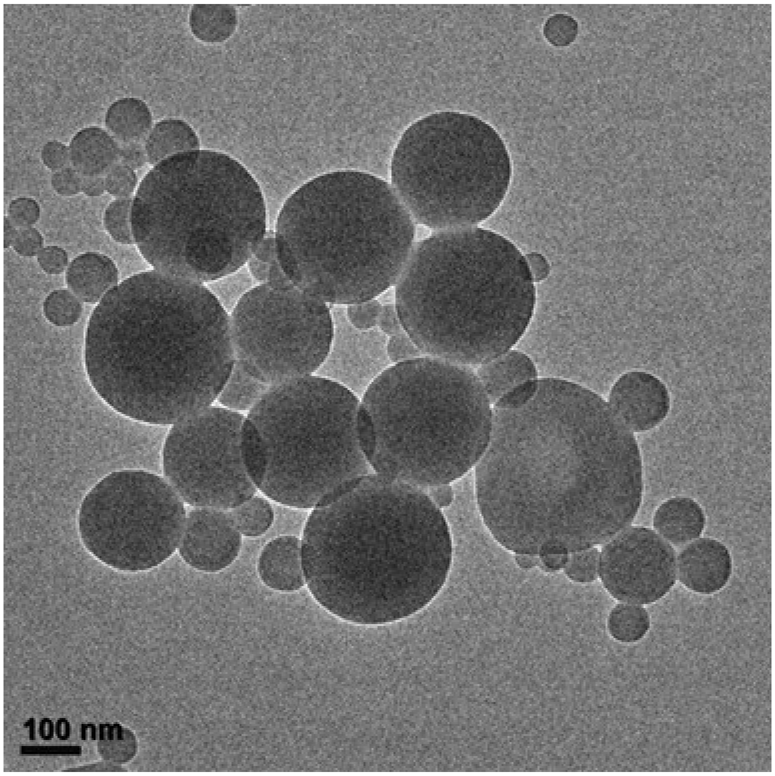
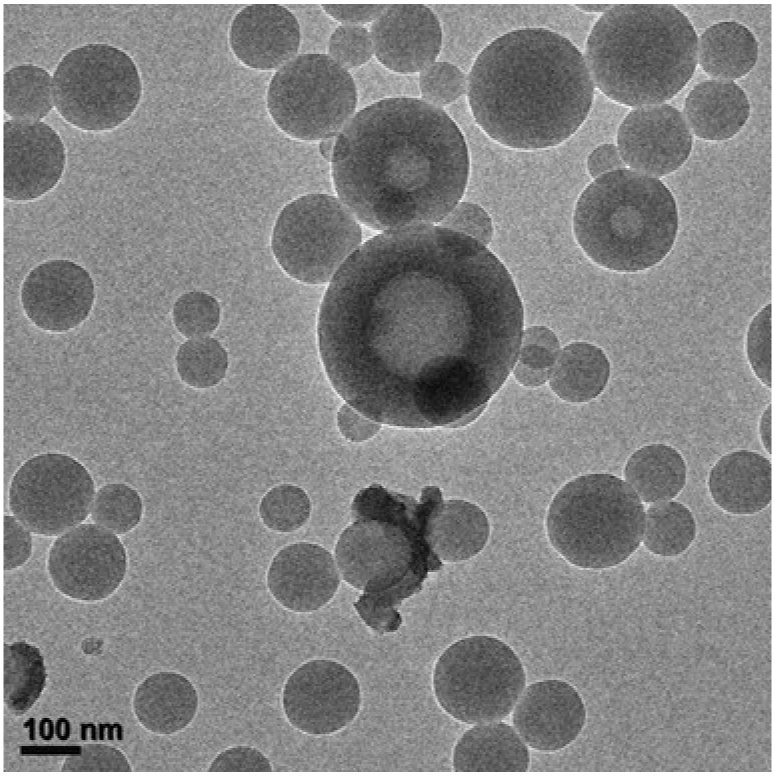


Figure S36. Large-area view of Figure 4. d3.



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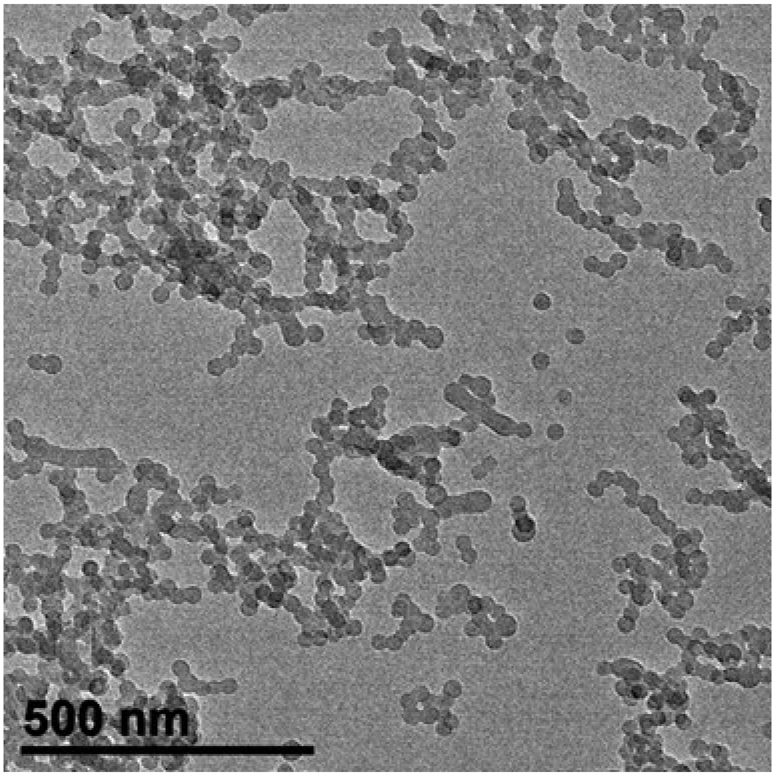


Figure S38. Large-area view of Figure 5. a1.

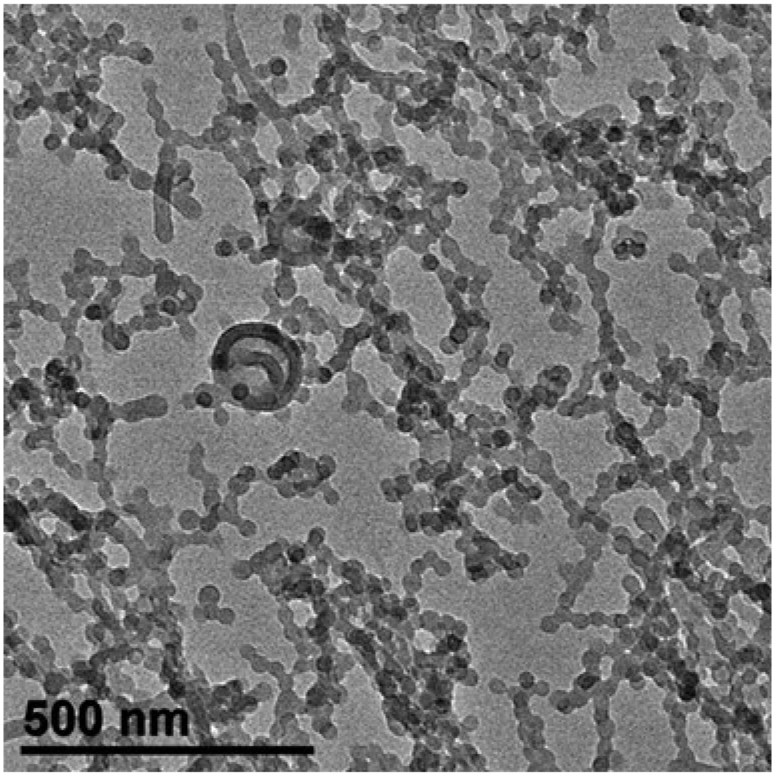
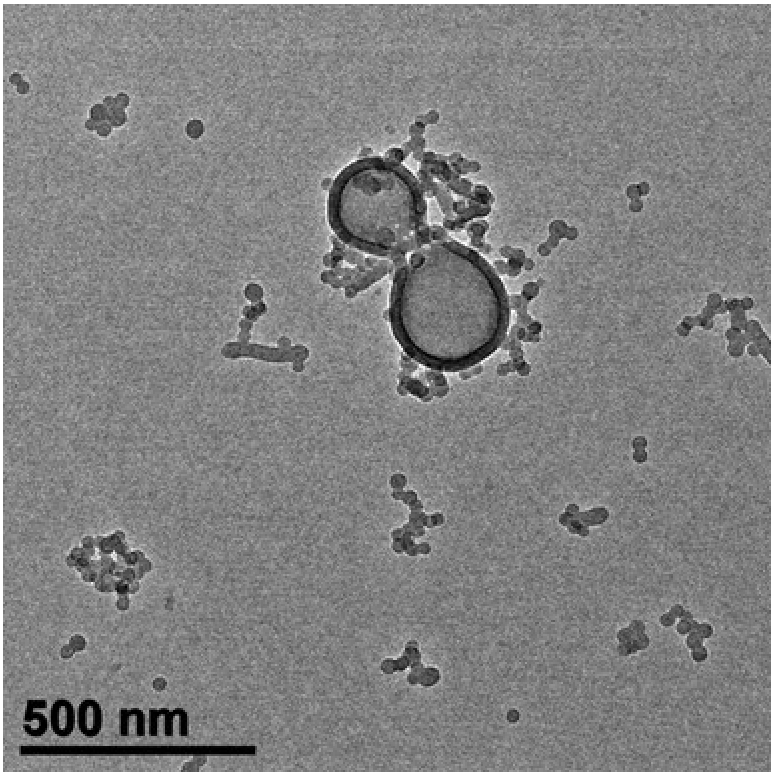


Figure S39. Large-area view of Figure 5. a2.



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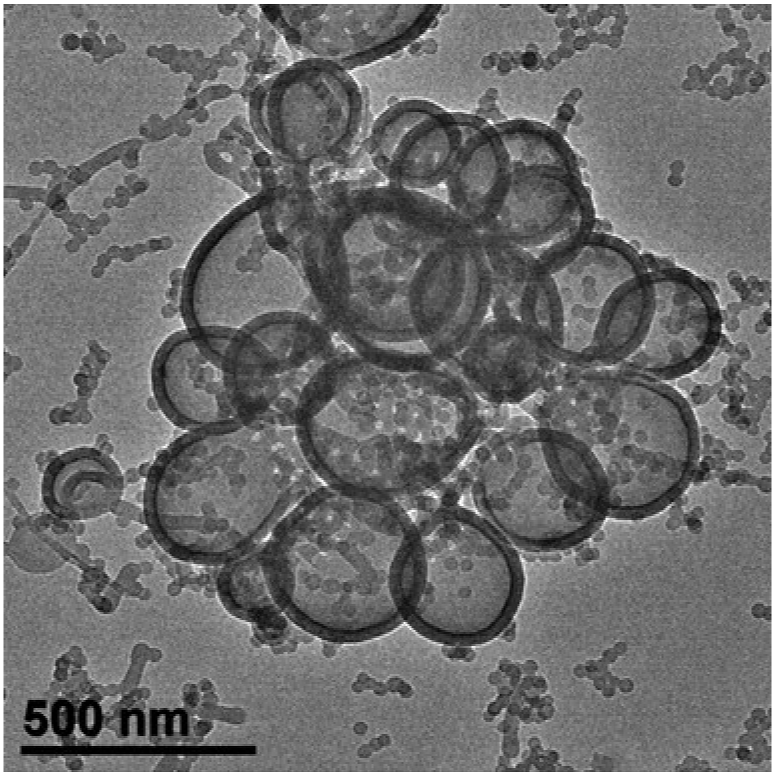

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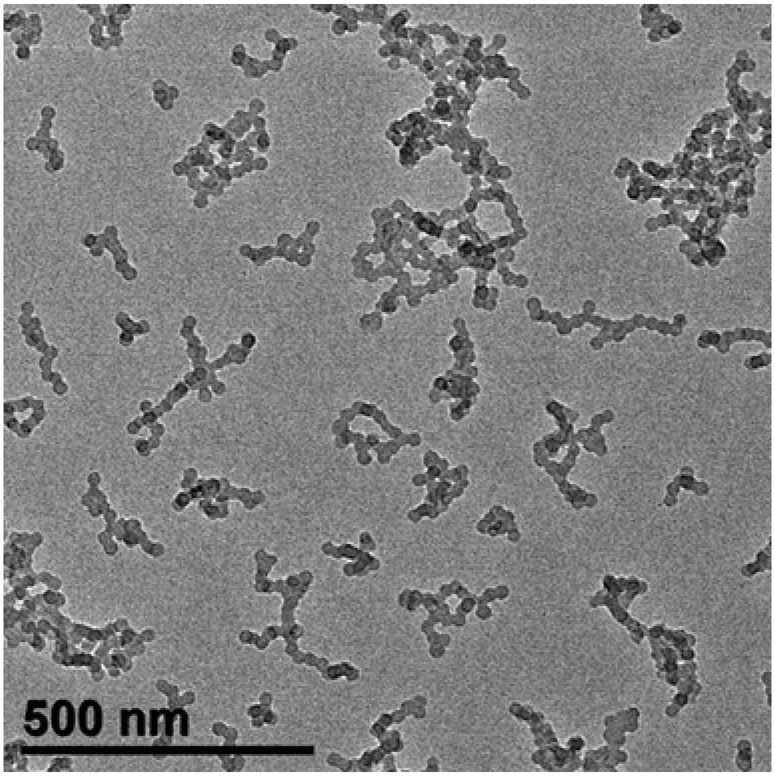

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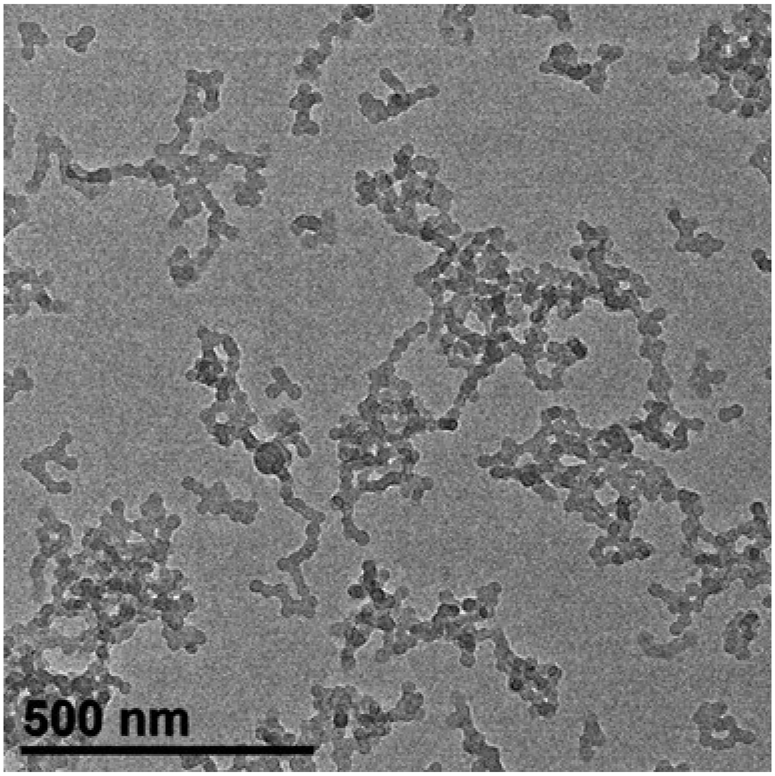

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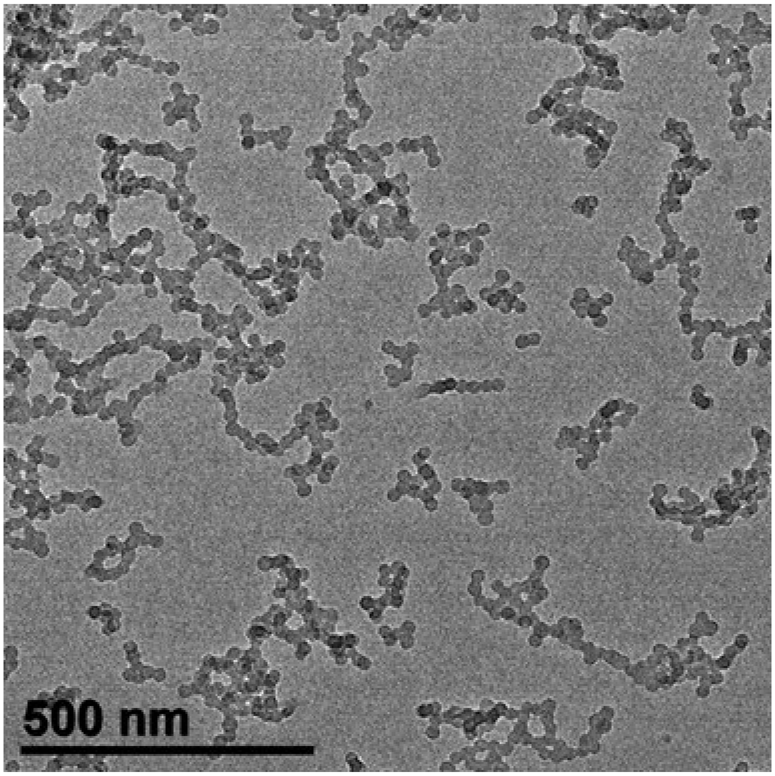


Figure S44. Large-area view of Figure 5. b3.

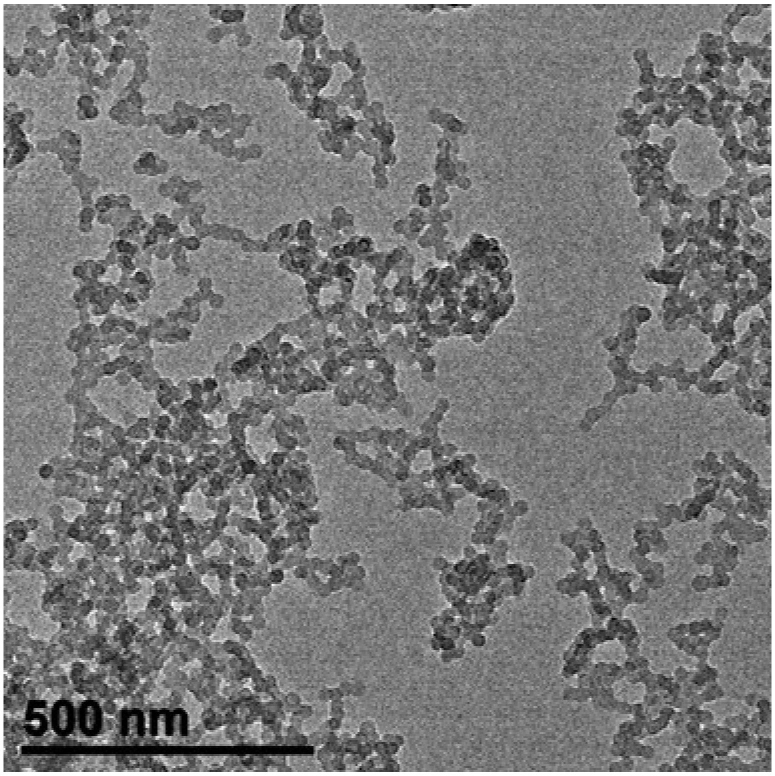
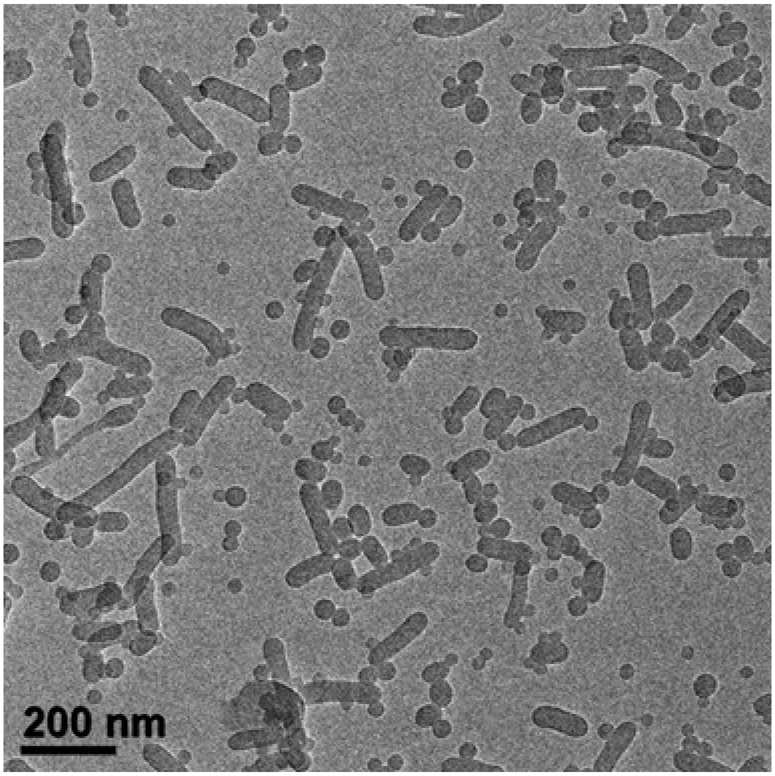


Figure S45. Large-area view of Figure 5. b4.



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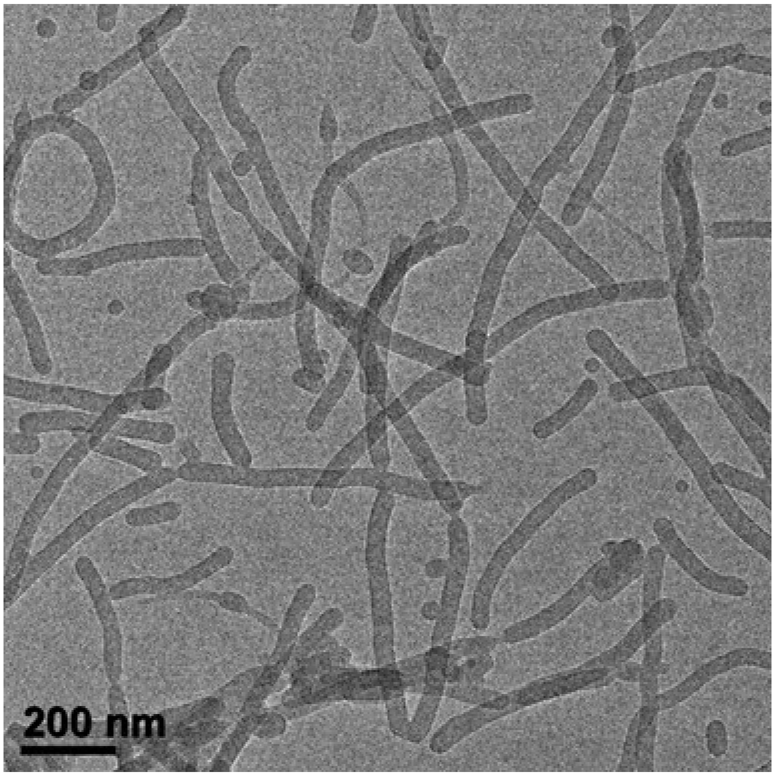


Figure S47. Large-area view of Figure 5. c2.

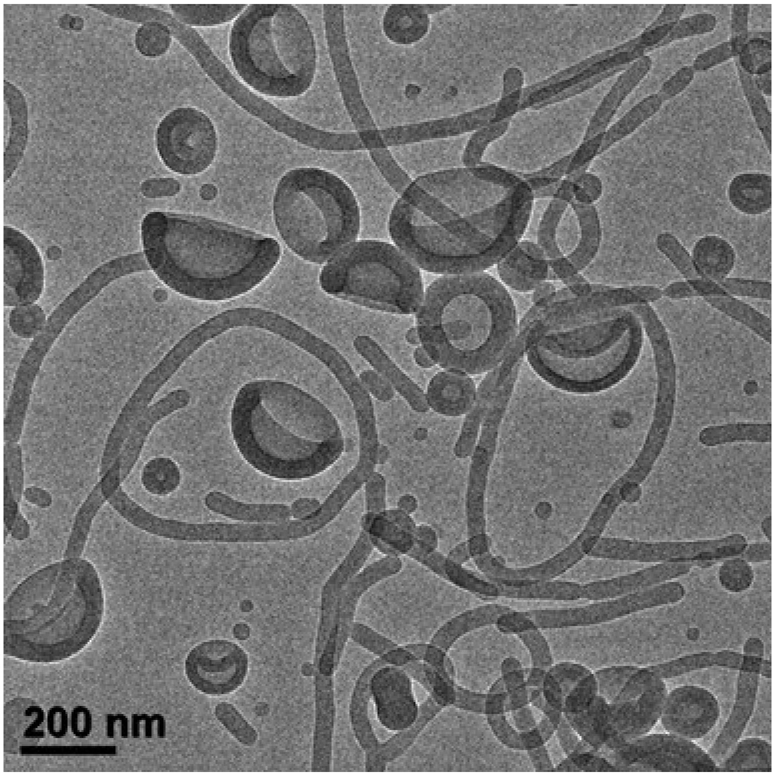


Figure S48. Large-area view of Figure 5. c3.

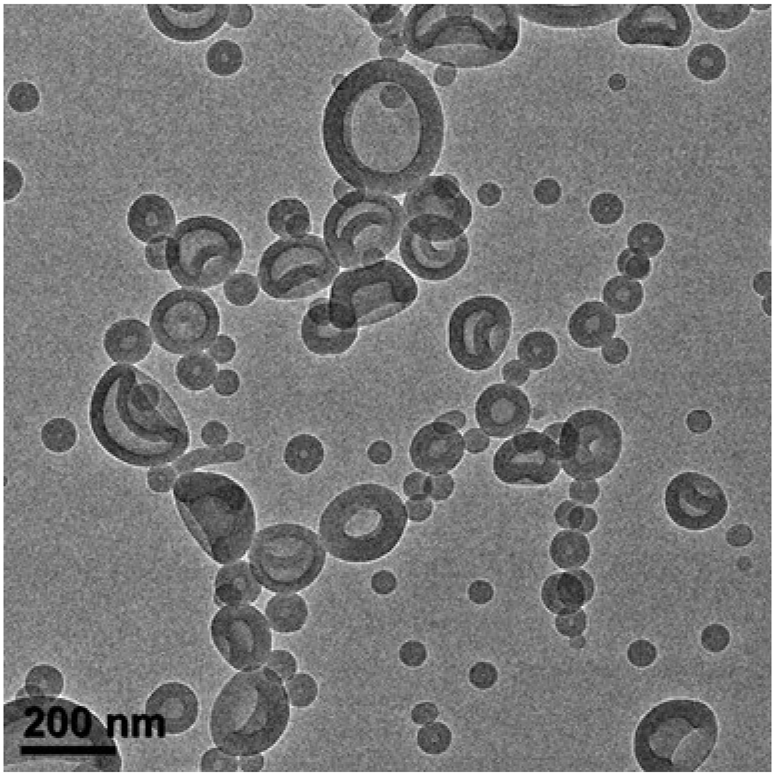


Figure S49. Large-area view of Figure 5. c4.

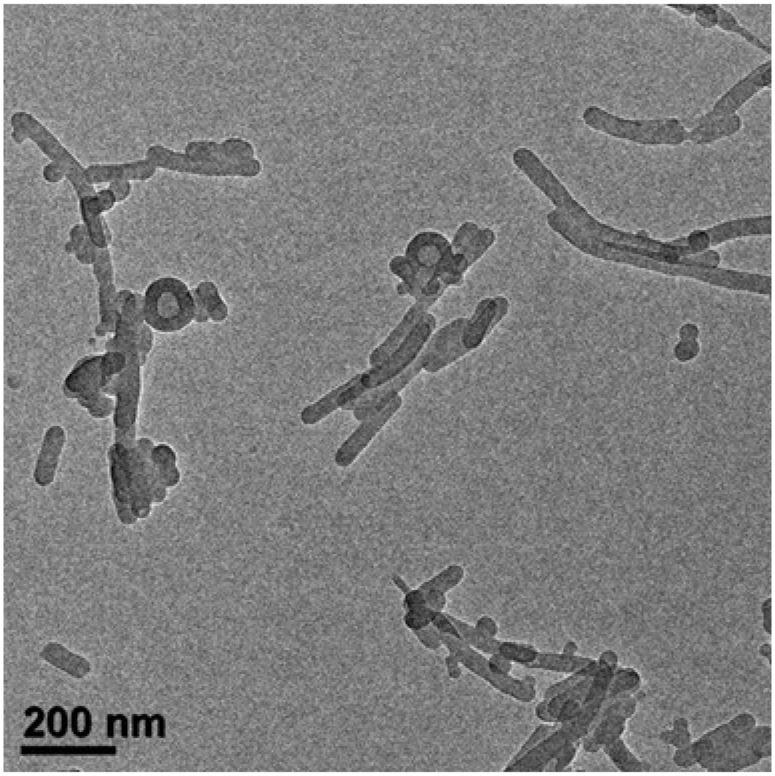


Figure S50. Large-area view of Figure 5. d3.

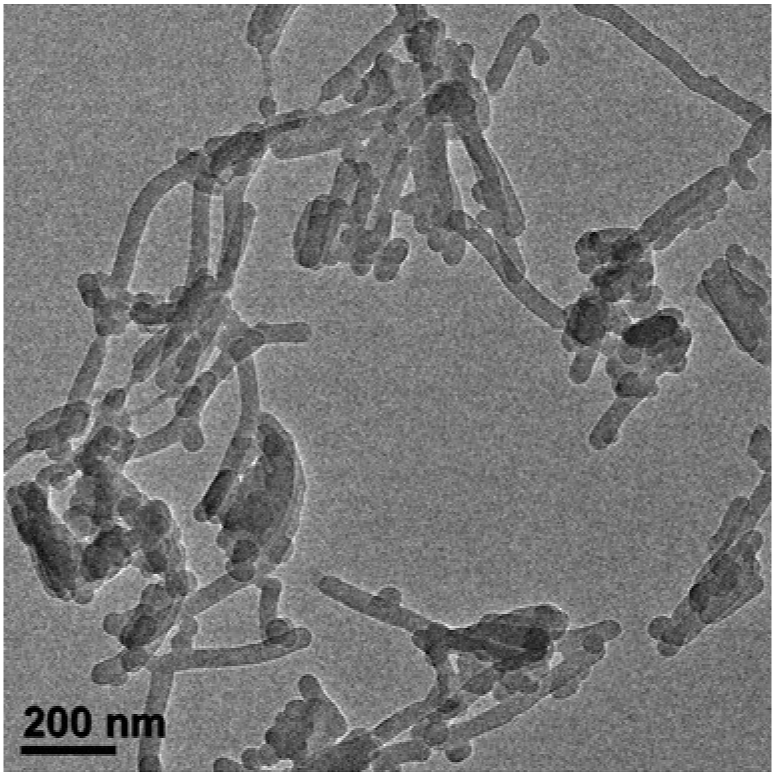


Figure S51 Large-area view of Figure 5. d4.

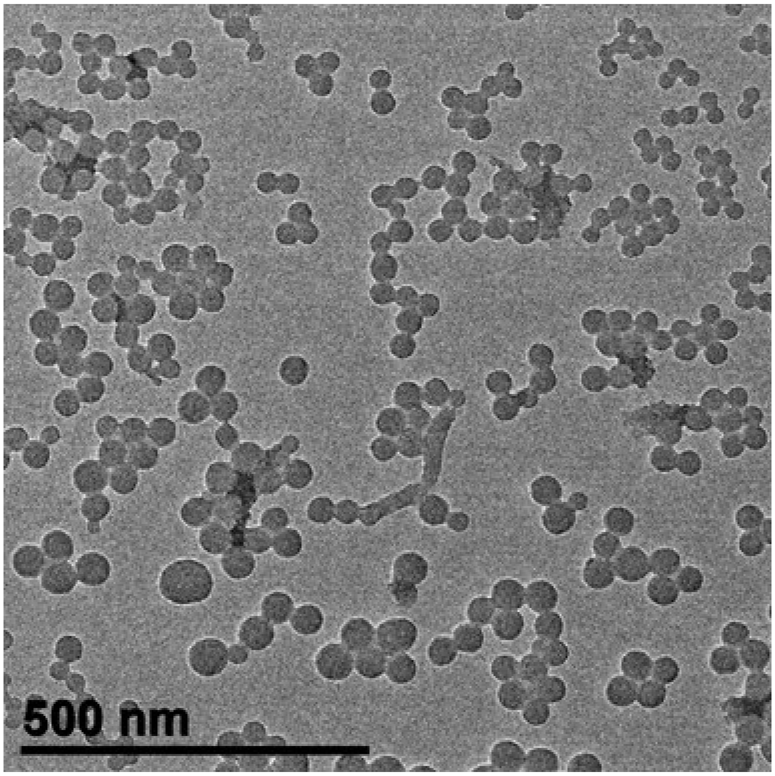
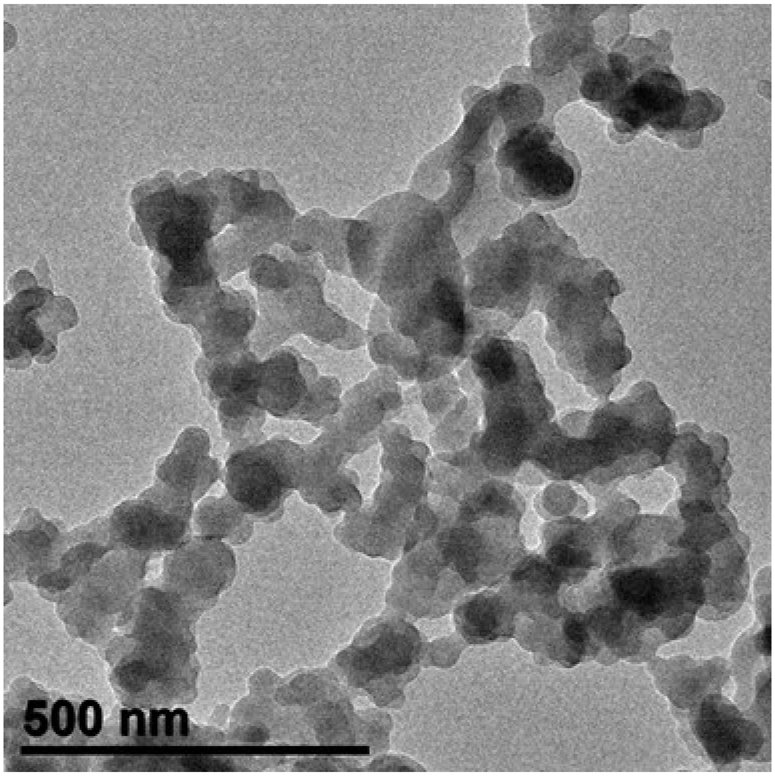


Figure S52. Large-area view of Figure 6. a1.



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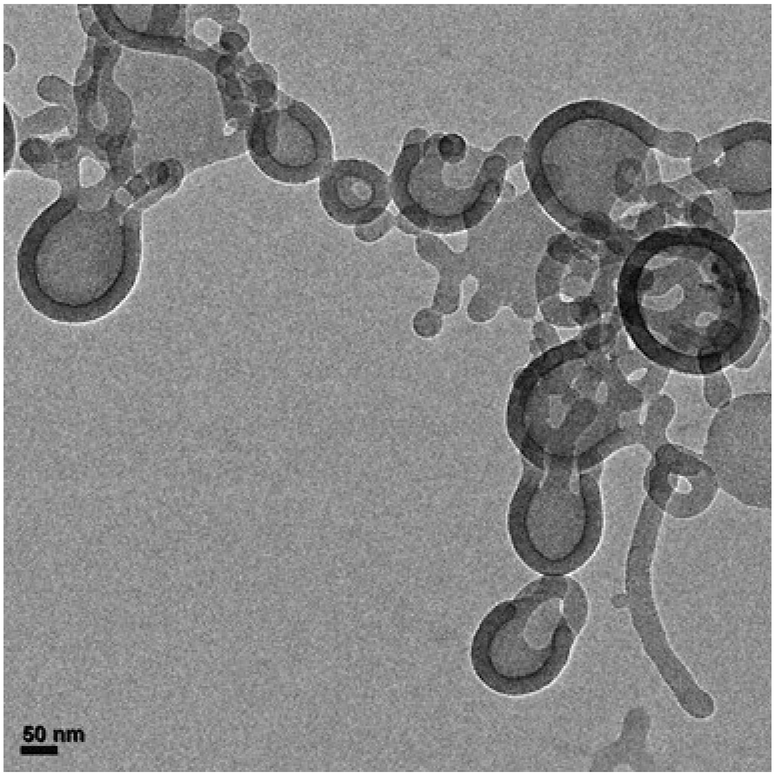

Figure S54. Large-area view of Figure 6. a3.

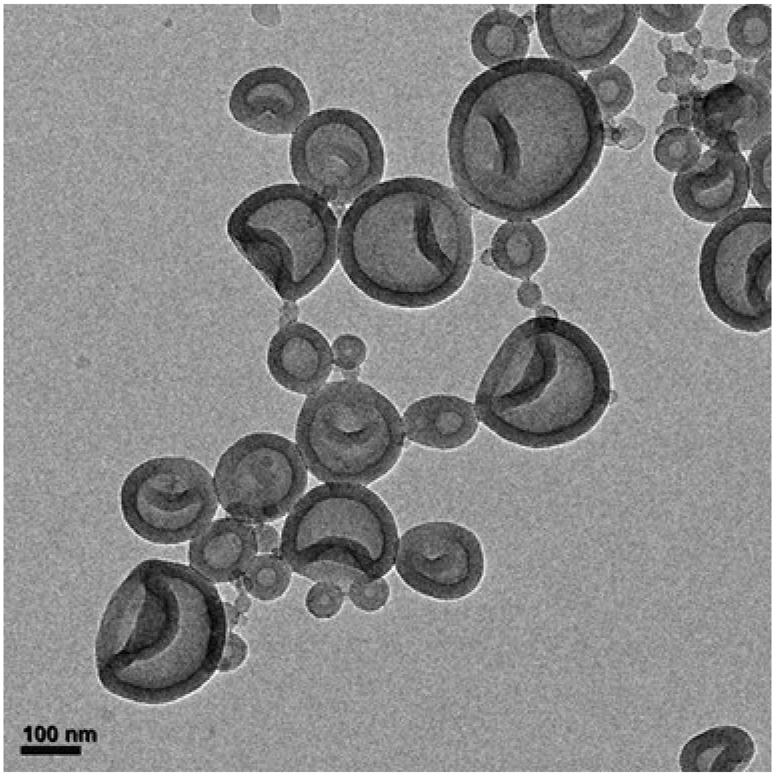

Figure S55. Large-area view of Figure 6. a4.

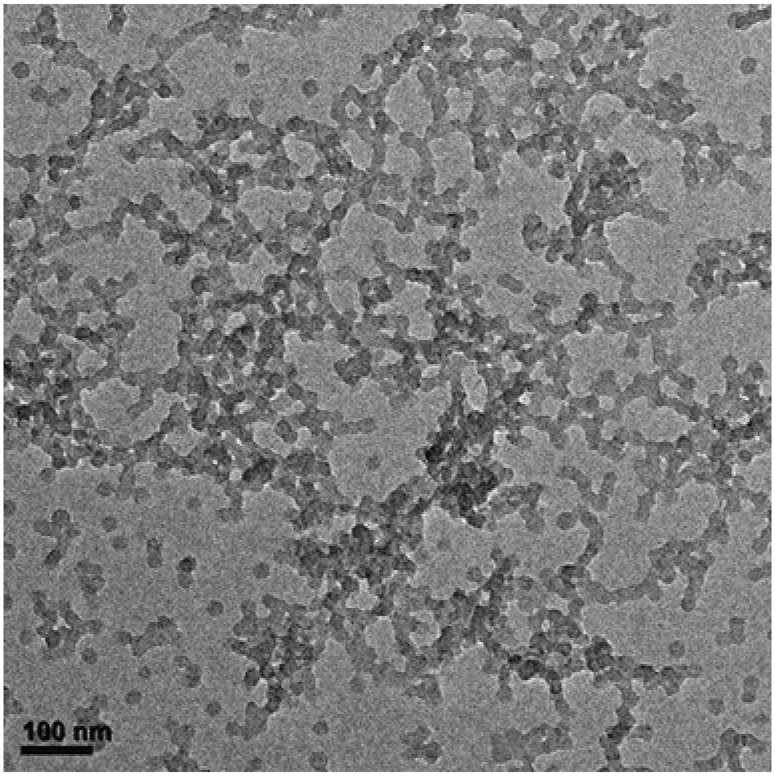

Figure S56. Large-area view of Figure 6. b4.

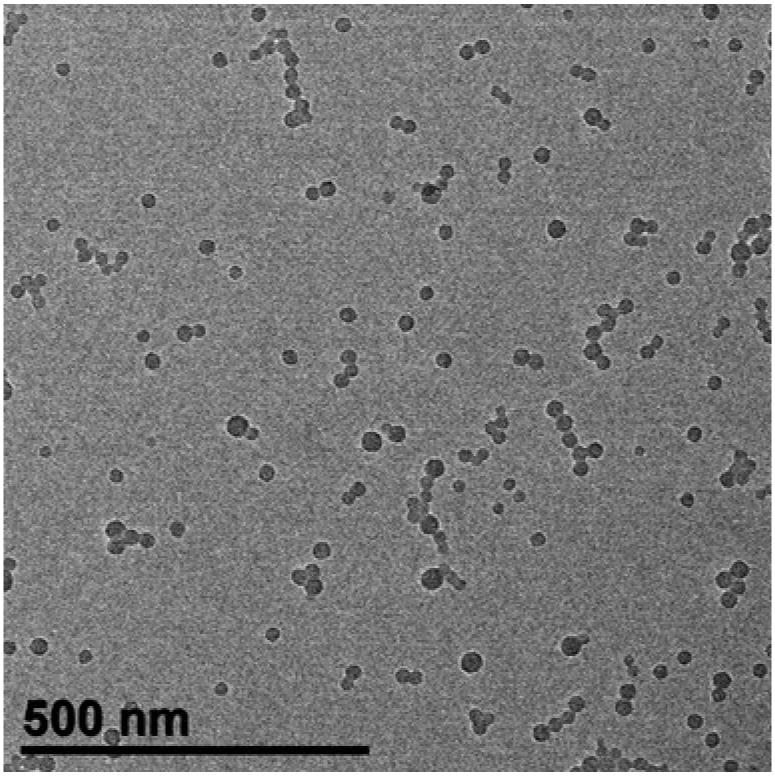

Figure S57. Large-area view of Figure 6. c1.

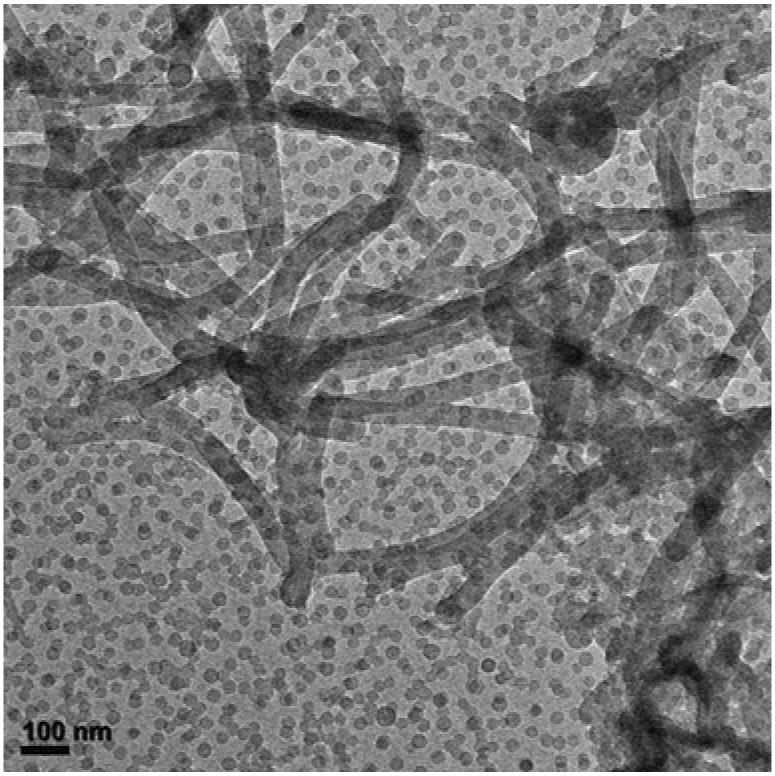

Figure S58. Large-area view of Figure 6. c2.

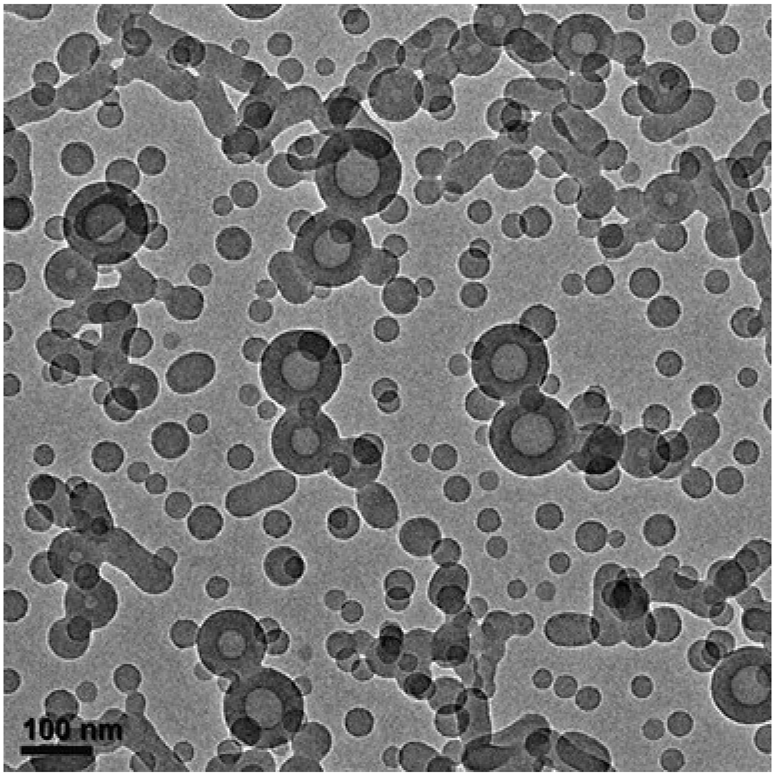

Figure S59. Large-area view of Figure 6. c3.

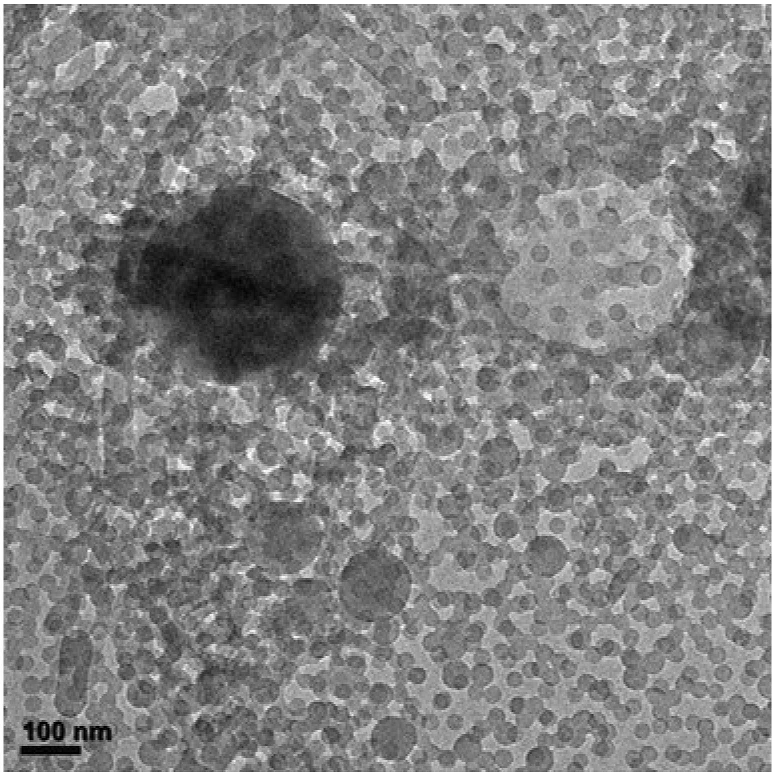

Figure S60. Large-area view of Figure 6. d3.