Supplementary Material (ESI) for Soft Matter

Controllable self-assemblies of micro/nano-tubes and vesicles from arylamides and their applications as templates to fabricate Pt micro/nano-tubes and hollow Pt nanospheres

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Experimental section

General methods：All reagents and chemicals were obtained from commercial sources and used without further purification unless otherwise noted. The solvents have been purified by standard procedures before use. Silica gel (10-40 μ) was used for all column chromatography. The NMR spectra were recorded on Varian Mercury 300 MHz, Bruker Avance 400 MHz or 500 MHz spectrometers in the indicated solvents. Chemical shifts are expressed in parts per million (δ) using residual proton resonances of the deuterated solvents as the internal standards. Atomic force microscopy (AFM) measurements were performed on a Nano scope IIIa MultiMode microscope; High-resolution transmission electron microscopy (HR-TEM) images and EDX spectra were recorded on a JEOL JEM-2010 microscope equipped with energy-dispersive X-ray spectroscopy; Low-resolution transmission electron microscopy (LR-TEM) images were recorded on a JEOL JEM-1230 microscope; Scanning electron microscopy (SEM) experiments were conducted on a JEOL JSM-6390-LV microscope; X-ray crystallography was carried on a Bruker AXS Smart apex II diffractometer; Powder XRD spectra were obtained on a X'Pert PROX system using monochromated Cu Kα (λ = 0.1542 nm) radiation; A fluorescence microscope (Olympus IX51) was used for fluorescence microscopy study.

Preparation of samples for microscopic stucies: For TEM observations, the solutions of aggregates were dropped onto the carbon/Formvar coated copper grids and excess fluid was removed carefully with a filter paper, which had been left overnight in a vacuum oven at 25 ºC; For SEM studies, one drop of solution of the aggregates was pipetted onto the silicon wafers. After natural evaporation of the solvent at room temperature (ca. 25 ºC) under ambient atmosphere, the as-prepared samples were treated in a vacuum oven at 25 ºC overnight; For AFM experiment, aliquot of solution of the aggregates was dropped onto silicon wafer and spread by using a spin-coater operating at 1500 rpm, and then dried naturally under ambient atmosphere; For fluorescence microscopy studies, aliquots of solutions of the aggregates were pipetted onto microscope glass cover slip and then dried naturally under ambient atmosphere.

Compound 2

To a stirred mixture of 2,7-diaminonaphthalene (20.6 g, 0.13 mol) and triethyl amine (19.5 mL, 0.14 mol) in dioxane (350 mL), a solution of di-tert-butyl dicarbonate (28.4 g, 0.13 mol) in dioxane (70 mL) was added in 30 minutes. The reaction mixture was stirred at room temperature for 30 hours and then concentrated with a rotavapor. The resulting residual was purified by flash column chromatography (petroleum ether/EtOAc 5:1) to afford compound 2 as grey solid (11.3 g, 34 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (s, 1 H), 7.58 (t, J = 9.0 Hz, 2 H), 7.07 (d, J = 8.7 Hz, 1 H), 6.90 (s, 1 H), 6.83 (d, J = 9.9 Hz, 1 H), 6.55 (s, 1 H), 3.83 (br, 2 H), 1.54 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.3, 144.7, 136.3, 135.6, 128.9, 128.6, 124.6, 116.8, 115.7, 112.6, 108.2, 80.5, 28.4. MS (ESI) m/z 259.2 $[M + H]^+$. HRMS (MALDI-FT): Calcd for $C_{15}H_{18}N_2O_2Na$: 281.1264 $[M + Na]^+$. Found: 281.1261.

Compound T1

To a solution of 5-(benzyloxy)isophthalic acid (0.30 g, 1.10 mmol) and oxalyl chloride (0.96 mL, 11.0 mmol) in toluene (5 mL) and THF (2 mL) was added one drop of DMF as catalyst. After stirred at room temperature for 1.3 h, the solvent was removed with a rotavapor and then pumped under high vacuum to give acid chloride 3 as a yellow solid. Compound 3 was then dissolved in anhydrous THF (10 mL) and the solution added dropwise to a solution of 2 (0.60 mL, 2.3 mmol) and triethyl amine (0.66 mL, 4.8 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature for 6 h. The resulting precipitate was filtered and dissolved in dichloromethane (30 mL). The solution was then washed with 5% hydrochloric acid (15 mL), saturated sodium bicarbonate solution (15 mL), water (15 mL) and brine (15 mL) successively. After dried over anhydrous sodium sulfate, the organic phase was concentrated under reduced pressure. The resulting residue was washed with methanol and then dried to afford compound T1 as a white solid (0.54 g, 65%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.57 (s, 2 H), 9.56 (s, 2 H), 8.31 (s, 2 H), 8.25 (s, 1 H), 7.99 (s, 2 H), 7.85-7.70 (m, 8 H), 7.56-7.37 (m, 7 H), 5.32 (s, 2 H), 1.52 (s, 18 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.4, 158.9, 153.4, 138.2, 137.5, 137.1, 134.4, 129.0, 128.5, 128.4, 126.7, 120.1, 119.5, 118.8, 117.5, 116.4, 113.6, 79.7, 70.4, 28.6. MS (MALDI-TOF): m/z 774.8 $[M + Na]^+$. HRMS (MALDI-FT): Calcd for $C_{45}H_{44}N_4O_7Na$: 775.3102 $[M + Na]^+$. Found: 775.3096.

Compound T3

A mixture of acid 4 (0.27 g, 1.00 mmol) was dissolved in dichloromethane (10 mL) and then 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) (0.46 g, 2.40 mmol) and N-hydroxybenzotrizole (HOBt) (0.32 g, 2.40 mmol) were added. The mixture was stirred at room temperature for 5 minutes until a clear solution was obtained. To this solution, 1-naphthaleneamine (0.34 g, 2.40 mmol) was added and the solution stirred at room temperature for 10 hours. The solvent was then removed with a rotavapor, the resulting solid was suspended in methanol (20 mL), filtered, washed with methanol twice (2 mL each). After dried in vacuo, compound T3 was obtained as a white solid (0.31 g, 59%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.61 (s, 2 H), 8.48 (s,

2 H), 8.28 (s, 1 H), 7.95-7.85 (m, 10 H), 7.56-7.38 (m, 9 H), 5.33 (s, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.6, 159.1, 137.3, 134.0, 130.8, 129.2, 128.9, 128.8, 128.6, 128.2, 127.1, 125.6, 121.6, 120.4, 117.7, 117.4, 70.6. MS (MALDI-TOF): m/z 523.2 $[M + H]^+$. Anal. Calcd for $C_{35}H_{26}N_2O_3$: C, 80.44; H, 5.01; N, 5.36. Found: C, 80.58; H, 4.96; N, 5.30.

Compound 6

To a stirred solution of dimethyl 5-hydroxy-isophthalate (4.00 g, 19.0 mmol), triphenylphosphine (5.24 g, 20.0 mmol) and iso-butanol (2.40 mL, 25.9 mmol) in methanol (50 mL) was added N,N-diisopropyl ethylamine (4.04 g, 20.0 mmol) at 0 ºC. The mixture was stirred at 0 ºC for 0.5 h and then at room temperature for 12 h. The solvent was then removed with a rotavapor. The resulting residue was subjected to flash column chromatography (CH_2Cl_2/petroleum ether 1:1) to give compound 6 as a white solid (3.59 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (s, 1 H), 7.73 (s, 2 H), 3.93 (s, 6 H), 3.79 (d, J = 6.9 Hz, 2 H), 2.15-2.06 (m, 1 H), 1.03 (d, J = 6.9 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 159.4, 131.7, 122.7, 119.9, 75.0, 52.3, 28.2, 19.2. MS (EI): m/z 266 $[M]^+$. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.21; H, 6.68.

Compound 7

To a stirred solution of compound 6 (0.69 g, 2.59 mmol) in THF (12 mL), methanol (4 mL) and water (4 mL) was added lithium hydroxide monohydrate (0.24 g, 5.70 mmol). The mixture was stirred at room temperature for 12 h and then concentrated with a rotavapor. The resulting residue was then acidified with diluted hydrochloric acid (0.01 N) to pH = 1 and the resulting precipitate was filtered, washed with water (20 mL × 2) and dried under vacuum to give compound 7 as a white solid (0.62 g, 100%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.05 (s, 1 H), 7.57 (s, 2 H), 4.77 (br, 2 H), 3.80 (d, J = 6.3 Hz, 2 H), 2.07-1.93 (m, 1 H), 0.96 (d, J = 6.9 Hz, 6 H). ^{13}C NMR (100 MHz, DMSO-d_6):δ 167.4, 159.2, 134.2, 122.8, 119.1, 74.7, 28.2, 19.5. MS (ESI): m/z 237.1 $[M–H]^-$. HRMS (EI): Calcd for $C_{12}H_{14}O_5$: 238.0841 $[M]^+$. Found: 238.0837.

Compound T2

A mixture of 2 (0.24 g, 0.91 mmol), 7 (90 mg, 0.38 mmol), O-(7-azabenzotriazol-1-yl)-N,N,N’,N’-tetramethyluronium hexafluorophosphate (HATU) (0.43 g, 1.14 mmol) and N,N-diisopropylethylamine (0.59 mL, 3.42 mmol) in DMF (10 mL) was stirred at room temperature for 13 h. Upon removal of the solvent with a rotavapor, the resulting residue was dissolved in chloroform (30 ml). The solution was washed with 5% hydrochloric acid (10 mL), saturated sodium bicarbonate solution (10 mL) and brine (10 mL) successively. The organic layer was then dried over anhydrous sodium sulfate and then concentrated. The resulting residue was subjected to column chromatography (CH_2Cl_2/EtOAc 20:1, then CH_2Cl_2/MeOH 100:1) to afford compound T2 as a white solid (0.17 g, 63%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.56 (s, 2 H), 9.60 (s, 2 H), 8.31 (s, 2 H), 8.20 (s, 1 H), 7.99 (s, 2 H), 7.82-7.70 (m, 8 H), 7.48 (d, J = 9.0 Hz, 2 H), 3.96 (d, J = 6.0 Hz, 2 H), 2.13-2.09 (m,

1 H), 1.51 (s, 18 H), 1.06 (d, J = 6.6 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 159.5, 153.1, 136.3, 136.2, 135.9, 134.1, 128.3, 127.4, 119.1, 118.7, 116.8, 114.8, 80.6, 74.6, 28.4, 28.0, 19.1. MS (MALDI-FT): m/z 741.3 $[M + Na]^+$, 757.3 $[M + K]^+$. HRMS (MALDI-FT): Calcd for $C_{42}H_{46}N_4O_7Na$: 741.3259 $[M + Na]^+$. Found: 741.3266.

Compound T4

A solution of isophthalic acid chloride (0.34 g, 2.00 mmol) in THF (5 mL) was added dropwise to a solution of compound 2 (1.14 g, 4.40 mmol) and triethyl amine (0.66 mL, 4.80 mmol) in THF (10 mL). The mixture was stirred at room temperature for 3 h. After the solvent was removed, the resulting solid was washed with methanol and diethyl ether and then dried in vacuum to afford compound T4 as a white solid (0.65 g, 50%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.59 (s, 2 H), 9.56 (s, 2 H), 8.62 (s, 1 H), 8.33 (s, 2 H), 8.20 (dd, J1 = 7.5 Hz, J2 = 1.2 Hz, 2 H), 7.99 (s, 2 H), 7.82-7.71 (m, 7 H), 7.49 (dd, J1 = 9.0 Hz, J2 = 1.8 Hz, 2 H), 1.52 (s, 18 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.2, 152.8, 137.7, 137.1, 135.2, 133.9, 130.7, 128.6, 127.9, 127.8, 127.0, 126.2, 118.9, 118.3, 115.8, 113.1, 79.2, 28.1. MS (MALDI-TOF): m/z 669.3 $[M + Na]^+$, 685.4 $[M + K]^+$. HRMS (MALDI-TOF): Calcd for $C_{38}H_{38}N_4O_6Na$: 669.2693 $[M + Na]^+$. Found: 669.2684.

Compound T5

This compound was prepared from acid 4 and aniline according a procedure similar to the preparation of compound T3. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.35 (s, 2 H), 8.13 (s, 1 H), 7.78-7.76 (m, 6 H), 7.50-7.32 (m, 9 H), 7.11-7.07 (m, 2 H), 5.25 (s, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.1, 158.8, 139.4, 137.0, 129.1, 129.0, 128.5, 128.3, 124.3, 120.9, 120.0, 117.3, 70.3. MS (MALDI-TOF): m/z 423.2 $[M + H]^+$. HRMS (MALDI-FT): Calcd for $C_{27}H_{22}N_2O_3$: 423.1703 $[M + H]^+$. Found: 423.1713. Anal. Calcd for $C_{27}H_{22}N_2O_3$: C, 76.76; H, 5.25; N, 6.63. Found: C, 76.44; H, 5.23; N, 6.61.

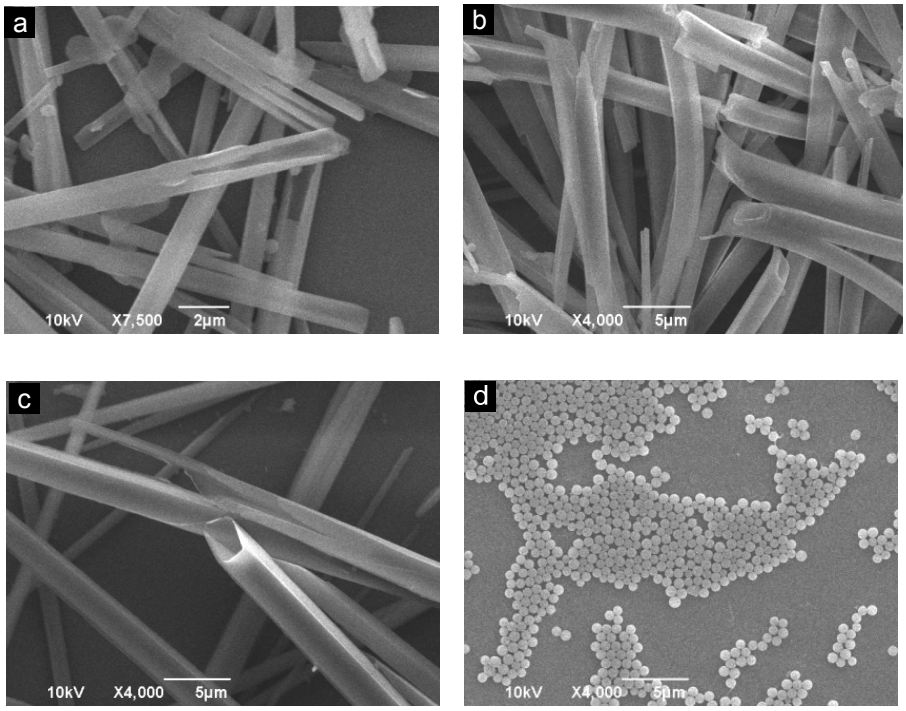

Figure S1. SEM images of **T3** fabricated from methanol solutions of different concentrations. (a) 5 mM, (b) 3 mM, (c) 1 mM, and (d) 0.5 mM.

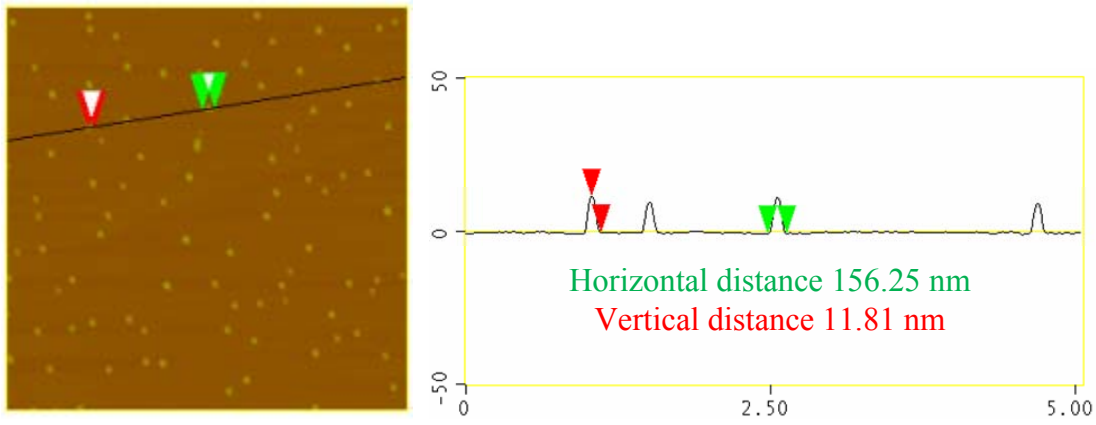

Figure S2. Tapping-mode AFM image (left) and cross-section analysis (right) of **T1** on silicon plate. The sample was obtained by evaporation of the methanol solution (0.01 mM).

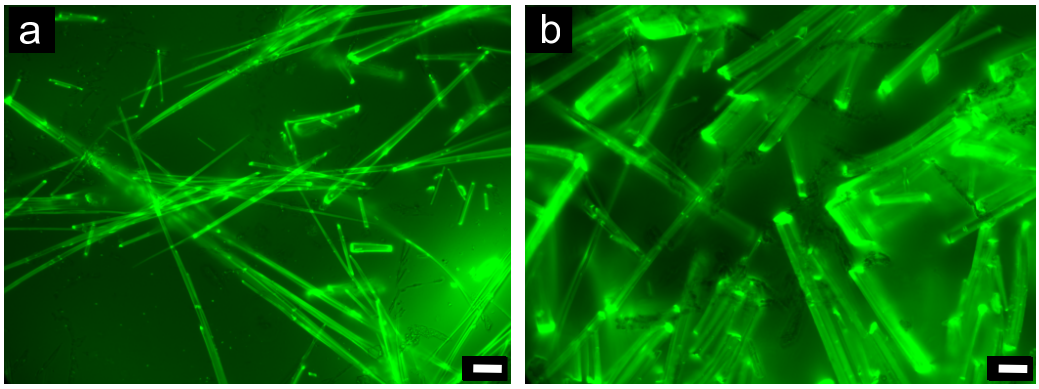

Figure S3. Fluorescence micrographs of tubes of (a) **T1** and (b) **T2** obtained from their methanol-water (5:1) solutions (5 mM). The scale bar for the fluorescent images is 10 μm.

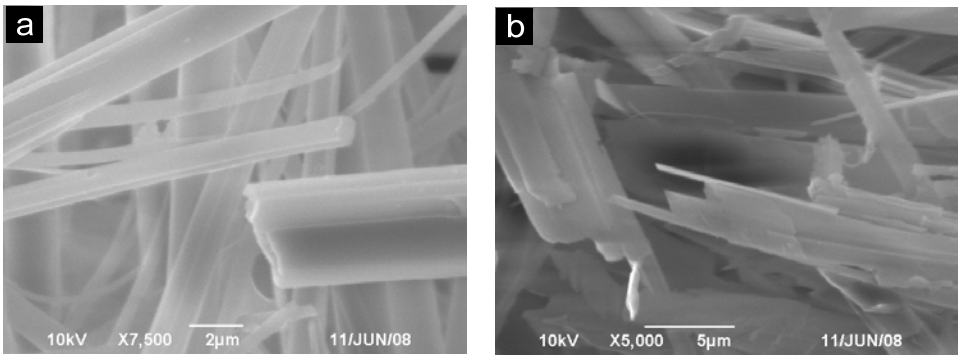

Figure S4. SEM images of (a) **T1** dried gel and (b) **T2** dried gel obtained from methanol-water (5:1).

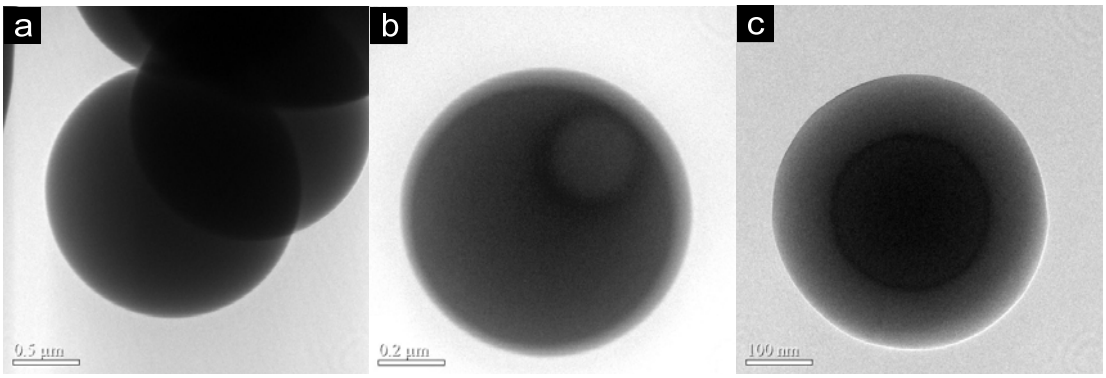

Figure S5. TEM images of vesicles of (a) T1(5 mM), (b) T2 (5mM) and (c) T3 (2 mM, all from their methanol-chloroform solution (9:1).

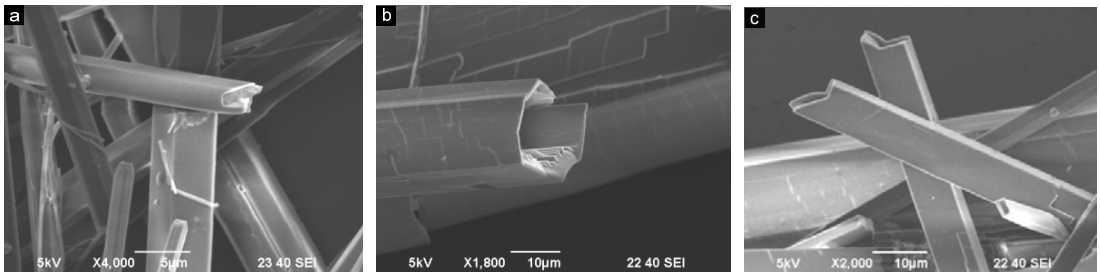

Figure S6. SEM images of tubes of **T3** fabricated from (a) methanol-water (5:1) and (b-c) methanol-chloroform (3:1) (5 mM).

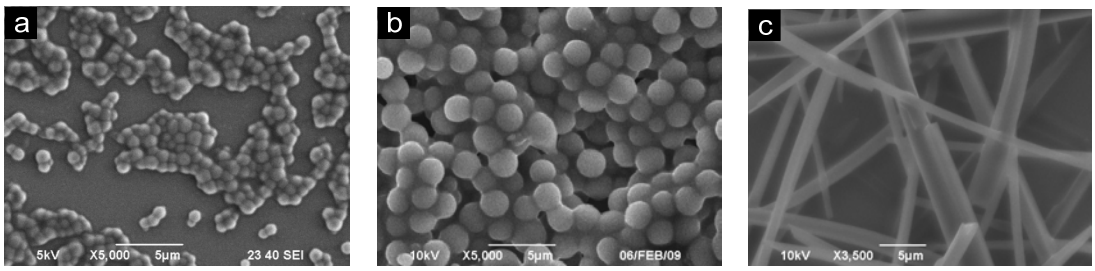

Figure S7. SEM images of (a) **T1** (5 mM), (b) **T2** (5 mM) and (c) **T3** (5 mM) obtained from their decalin solutions.

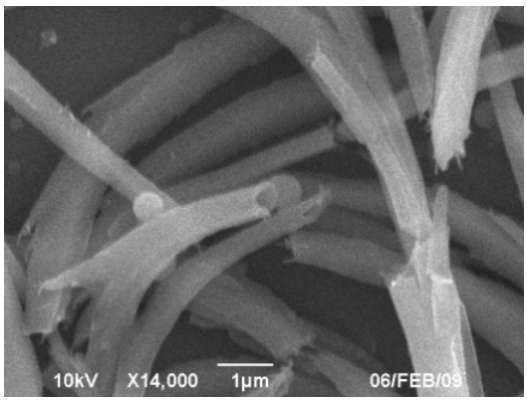

Figure S8. SEM images of **T5** (5 mM, methanol) on silicon surface after the solvent was evaporated.

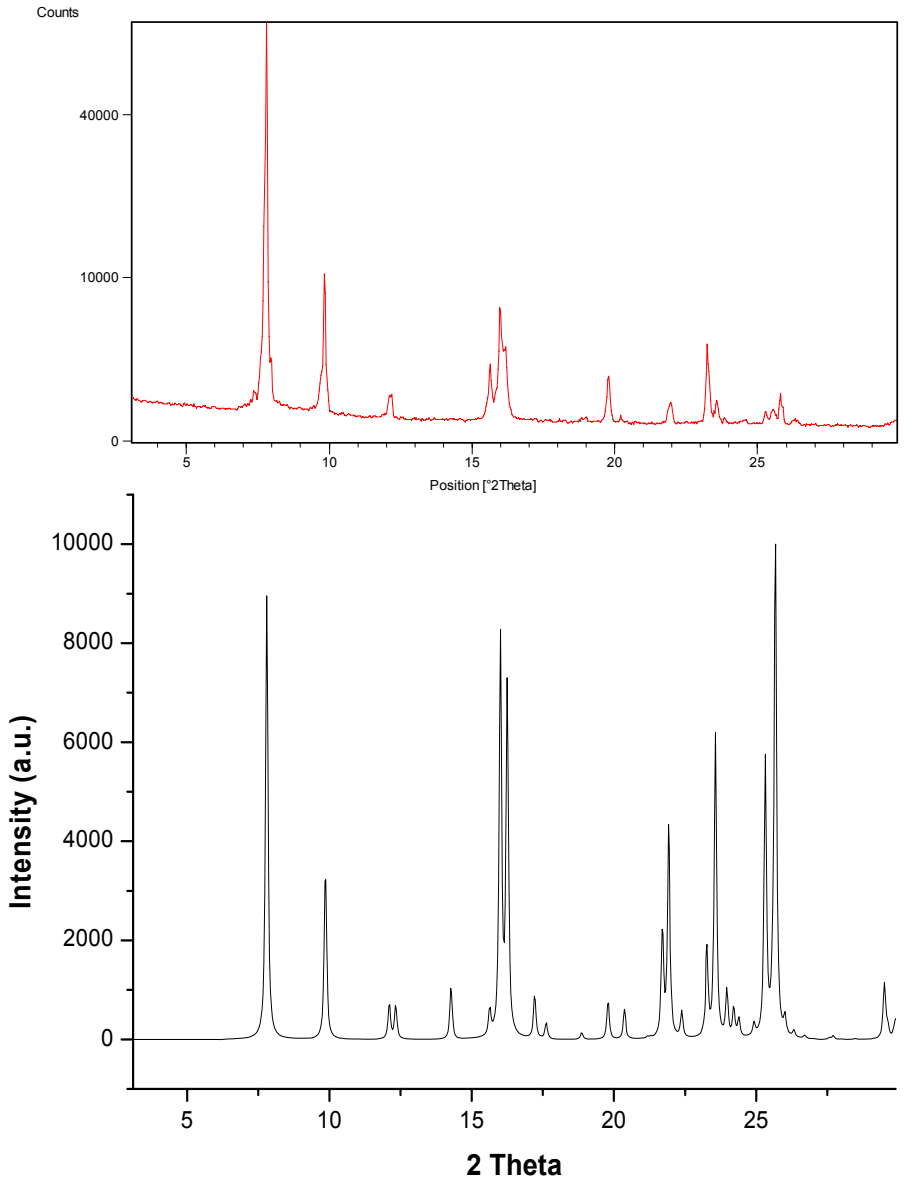

Figure S9. Powder XRD patterns of the **T5** nanotubes (top) and the theoretical profile calculated from its X-ray crystallographic data (bottom).

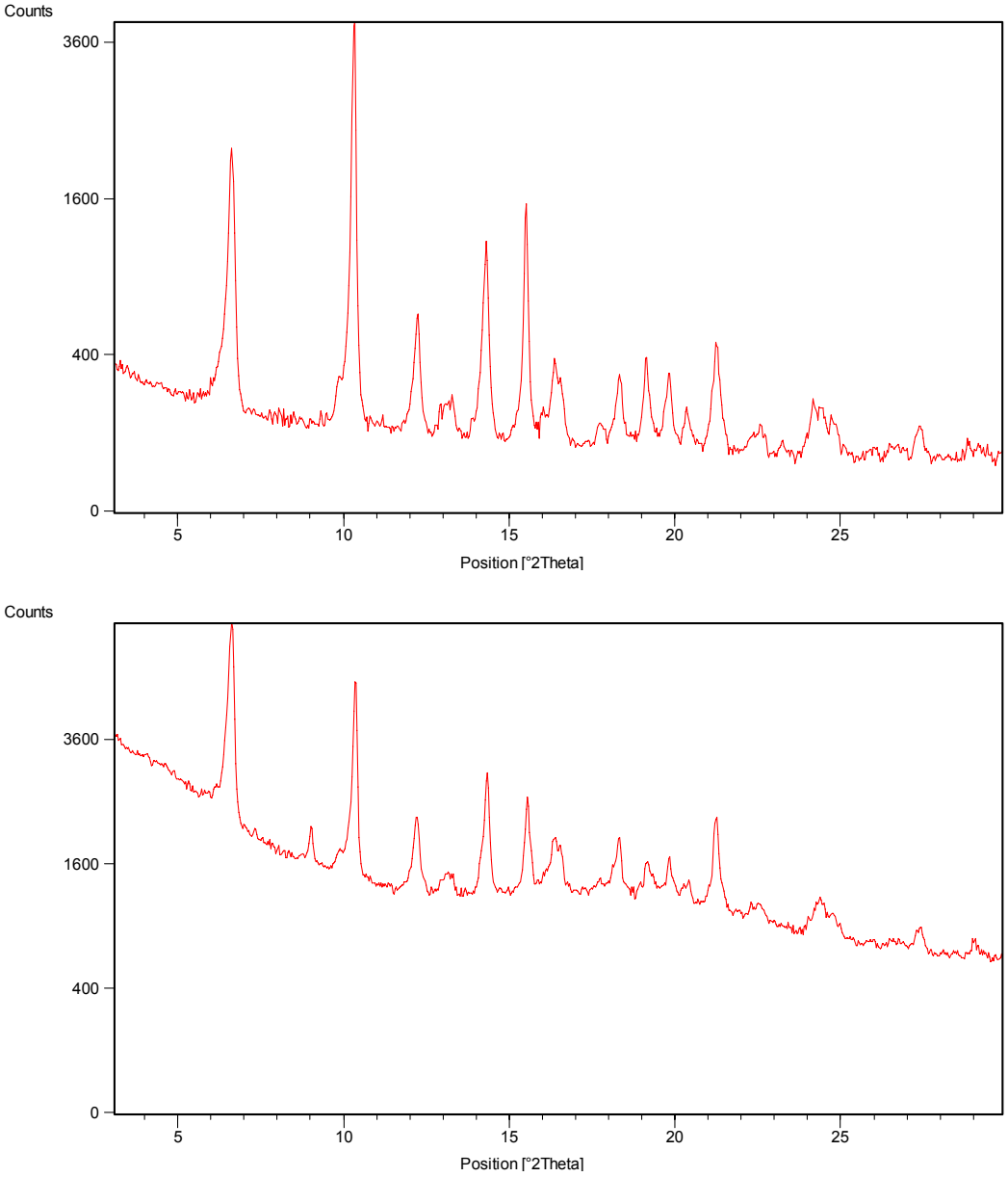

Figure S10. Powder XRD patterns of the **T1** tubes (top) and the **T1** vesicles (bottom).

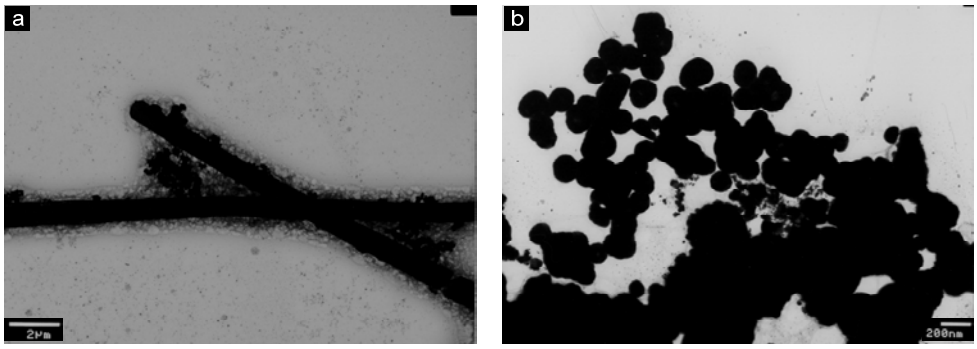

Figure S11. TEM images of (a) Pt nanotubes and (b) Pt nanospheres fabricated by using **T3** as template.