Supporting Information

for

Tube-*graft*-Sheet Nano-Objects Created by A Stepwise Self-Assembly of Polymer-Polyoxometalate Hybrids

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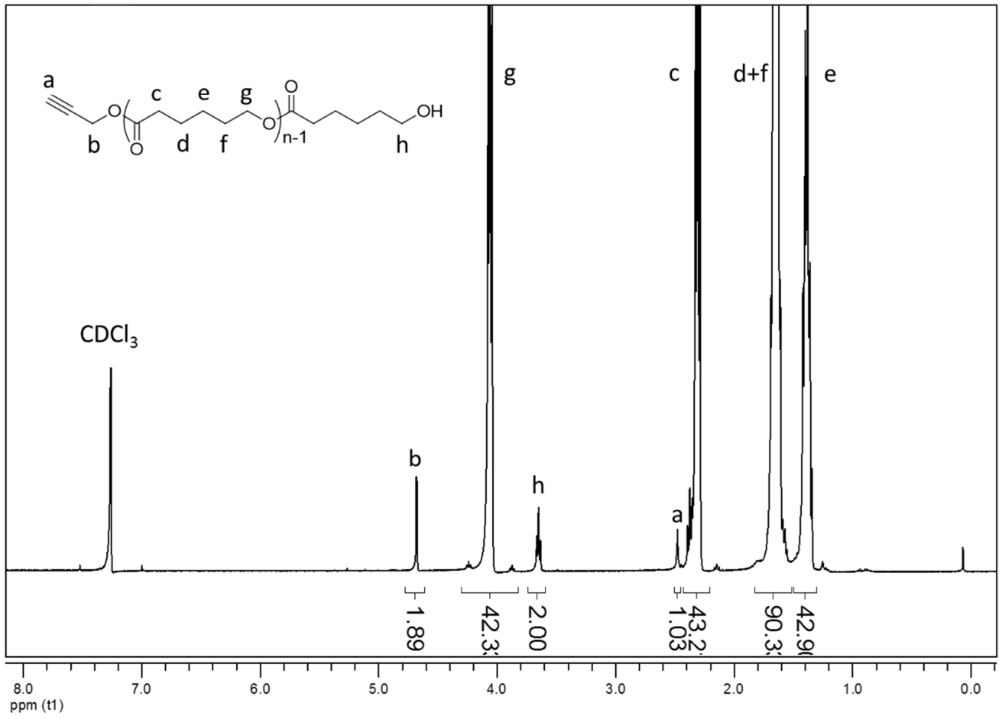


Figure S1. ^{1}H NMR spectrum of PCL_{19}-OH.

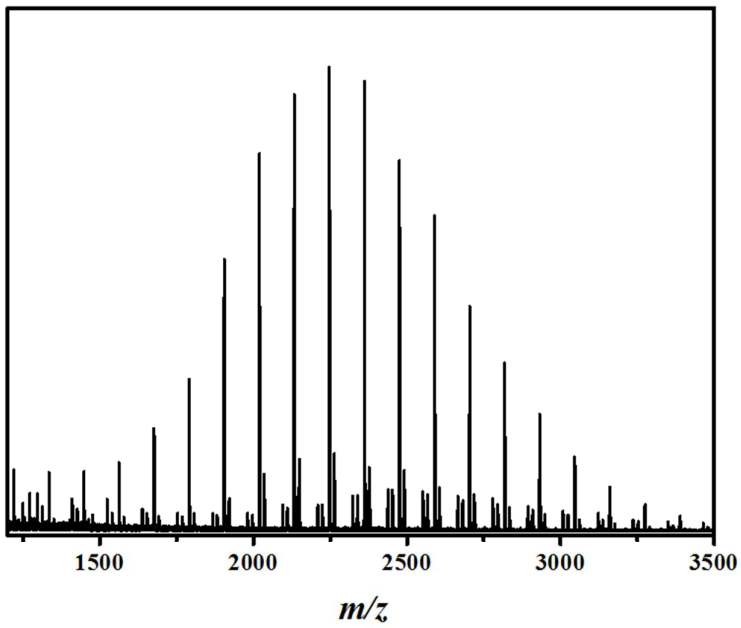


Figure S2. MALDI-TOF mass spectra of PCL_{19}.The calculated monoisotopic mass for the 19-mer of PCL_{19} is 2247.0 Da ($[M_{19} \cdot Na]^+$) and the observed m/z equals 2247.3.

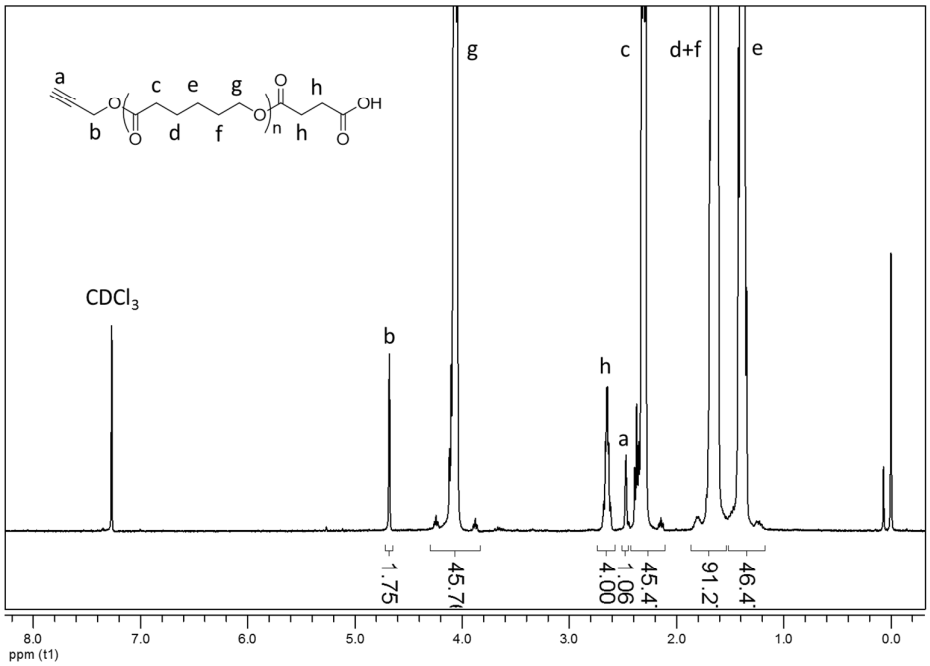


Figure S3. ^{1}H NMR spectrum of PCL_{19}-COOH.

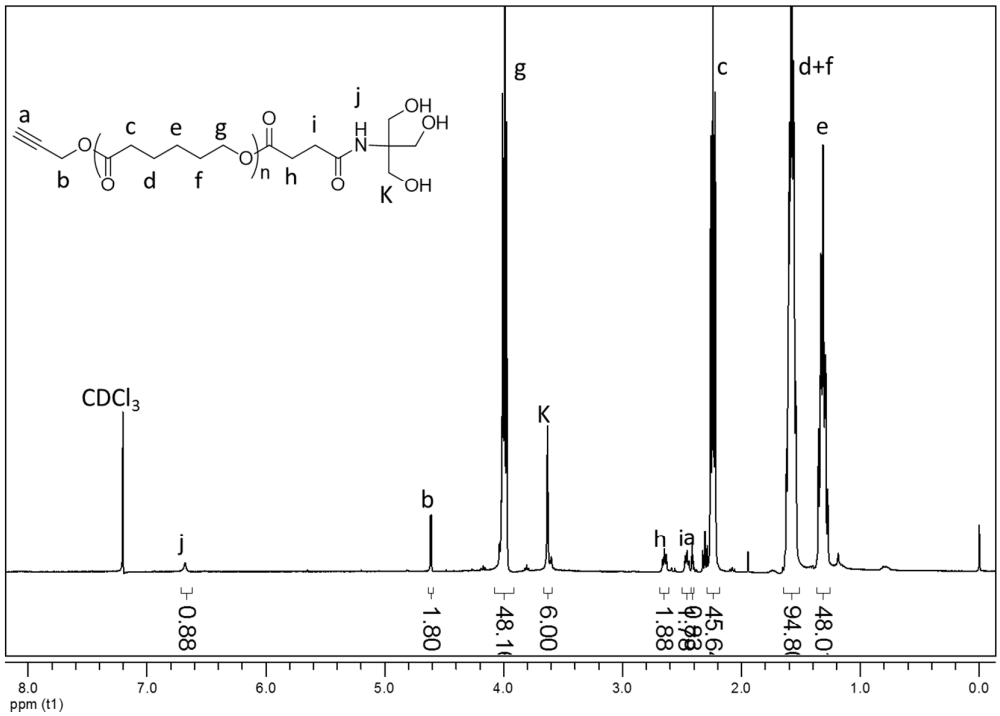


Figure S4. ^{1}H NMR spectrum of PCL_{19}-Tris.

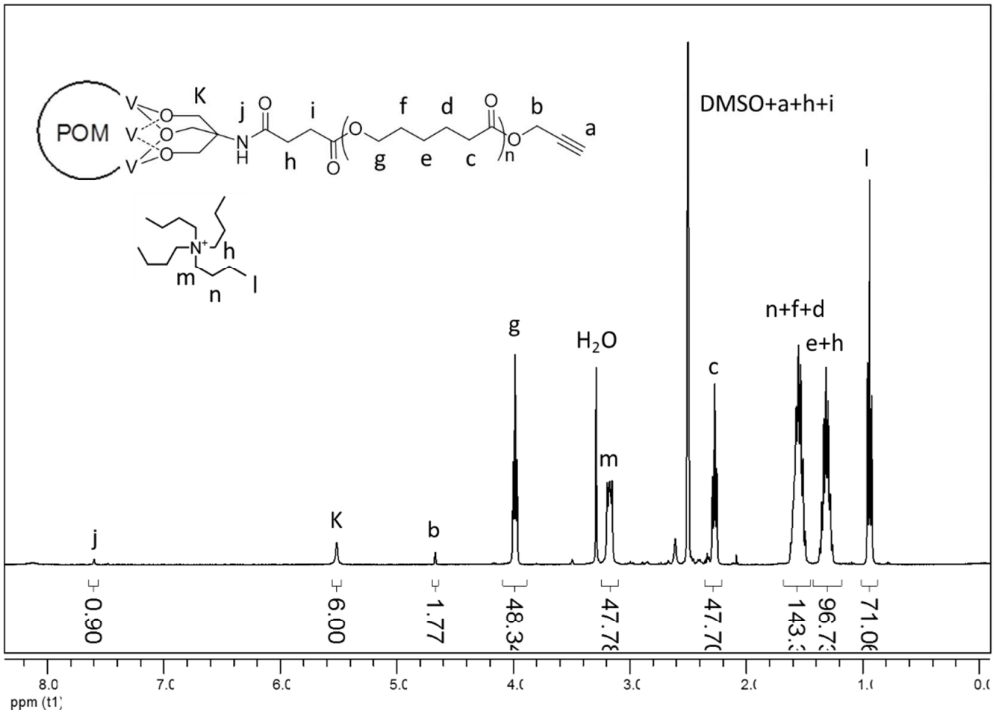


Figure S5. ^{1}H NMR spectrum of PCL_{19}-POM.

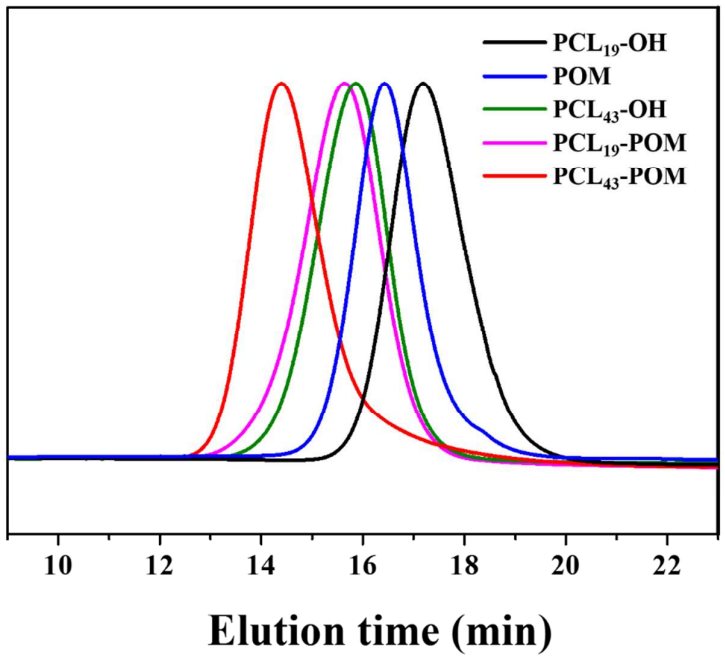


Figure S6. SEC chromatograms of the POM, PCL_{19}-OH, PCL_{43}-OH, PCL_{19}-POM and PCL_{43}-POM measured in DMF.

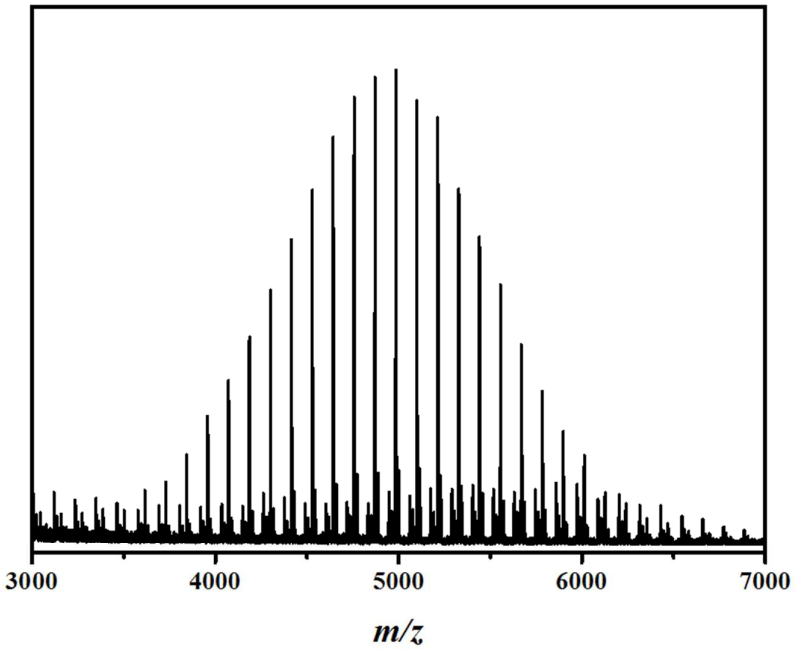


Figure S7. MALDI-TOF mass spectra of PCL_{43}. The calculated monoisotopic mass for the 43-mer of PCL_{43} is 4985.4 Da ($[M_{43} \cdot Na]^+$) and the observed m/z equals 4985.7.

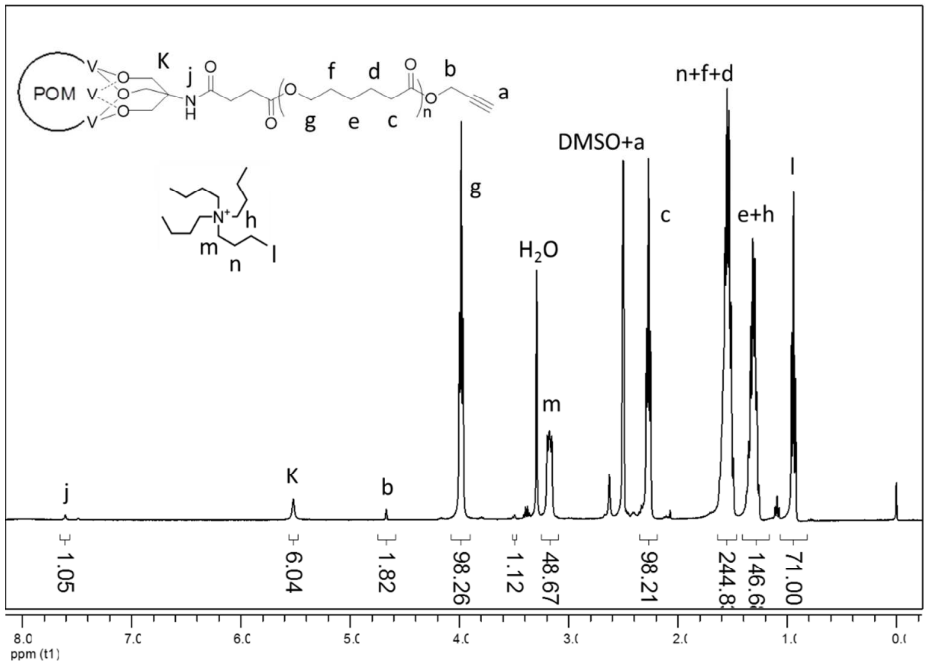
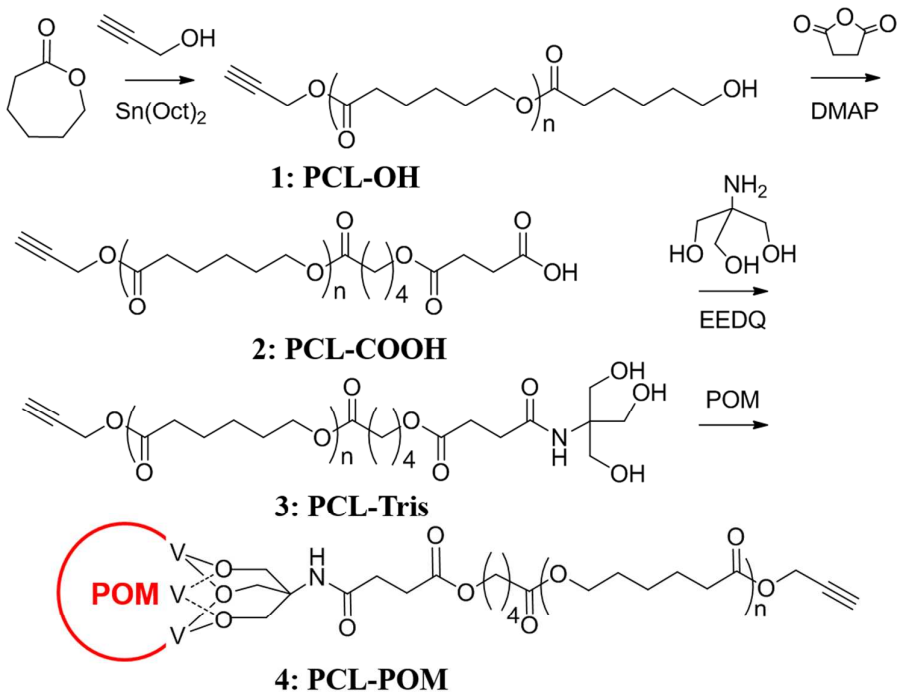


Figure S8. ^{1}H NMR spectrum of PCL_{43}-POM.

Table S1. Summary of molecular weights and molecular weight distributions (PDI= $\overline{M}_n / \overline{M}_w$) of POM-PCL hybrid.

Sample	$\overline{M}_n$ kg/mol	$\overline{M}_w$ kg/mol	$\overline{M}_z$ kg/mol	PDI
POM	4.9	5.6	---	---
PCL_{19}-OH	2.0	2.3	3.5	1.15
PCL_{19}-POM	7.5	8.6	10.1	1.14
PCL_{43}-OH	5.1	6.1	6.5	1.19
PCL_{43}-POM	11.0	12.5	14.5	1.14



Scheme S1. Synthetic route of the PCL-POM hybrids.

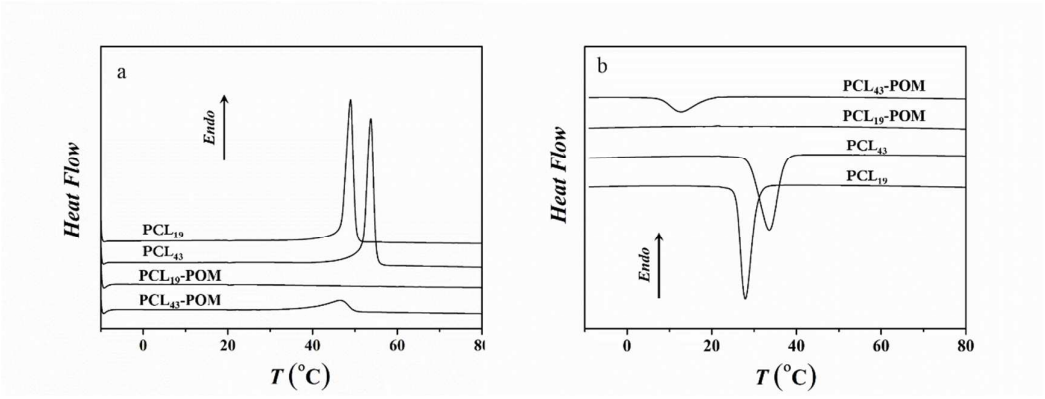


Figure S9. DSC thermographs of (a) second heating flow and (b) cooling flow for PCL_{19}, PCL_{43}, PCL_{19}-POM, and PCL_{43}-POM.

Table S2. DSC data of PCL_{19}, PCL_{43}, PCL_{19}-POM, and PCL_{43}-POM.

Sample	T_m (°C)	T_c (°C)	ΔH(J/g)	f_{PCL}[a]
PCL_{19}	49.0	27.9	93.5	0.69
PCL_{43}	53.7	33.6	92.8	0.69
PCL_{19}-POM	---	---	---	---
PCL_{43}-POM	46.5	12.7	27.3	0.42

[a] f_{PCL} is the degree of crystallinity of PCL. $f_{PCL}=\Delta H_c/\Delta H_{100}$, $H_c=\Delta H_{DSC}/PCL\%$, ΔH_{100} is the heat of crystallization of 100% crystalline PCL.

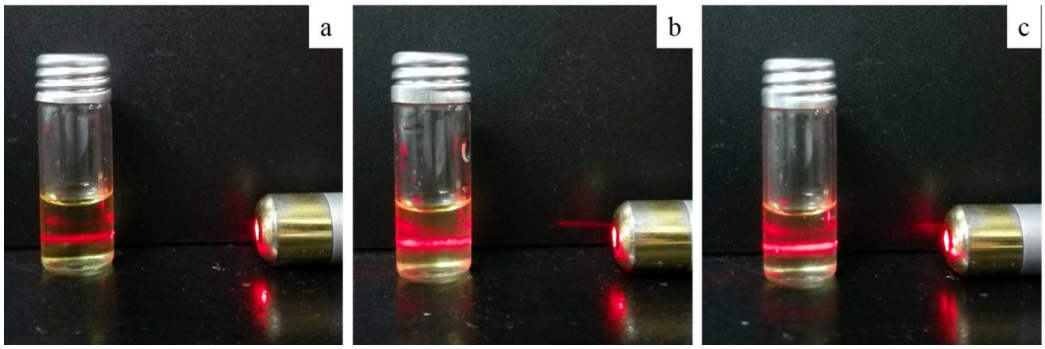


Fig. S10. Tyndall scattering of the solutions. (a) Solution of PCL_{43}-POM at r = 5:1 v/v of DMF/water. (b) Solution of PCL_{19}-POM at r = 2:1 v/v. (b) Solution prepared following a procedure: Dropping the DMF solution of PCL_{19}-POM into a suspension of the PCL_{43}-POM nanosheets at r = 5:1 v/v, and then immediately adding water into the suspension to change the ratio to r = 2:1 v/v.

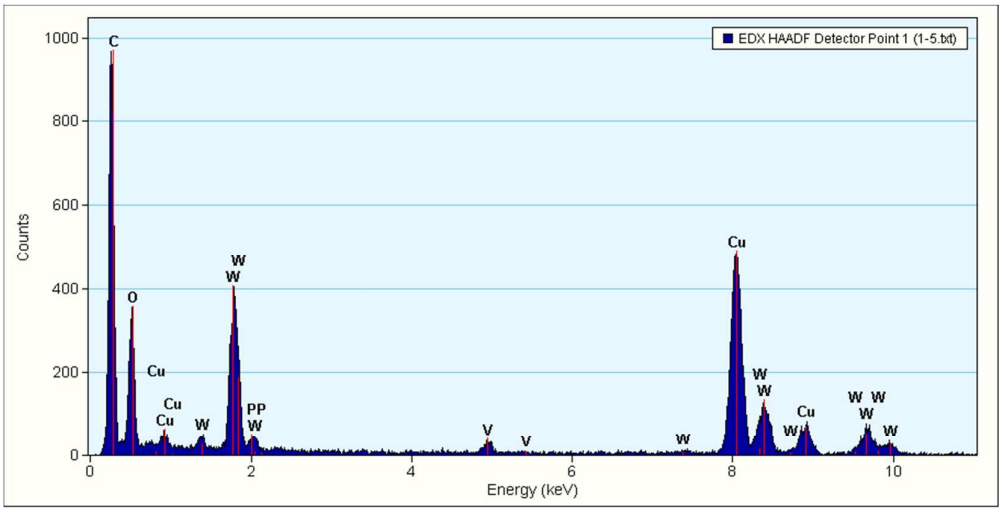


Figure S11. EDX spectrum taken on the nanosheets.

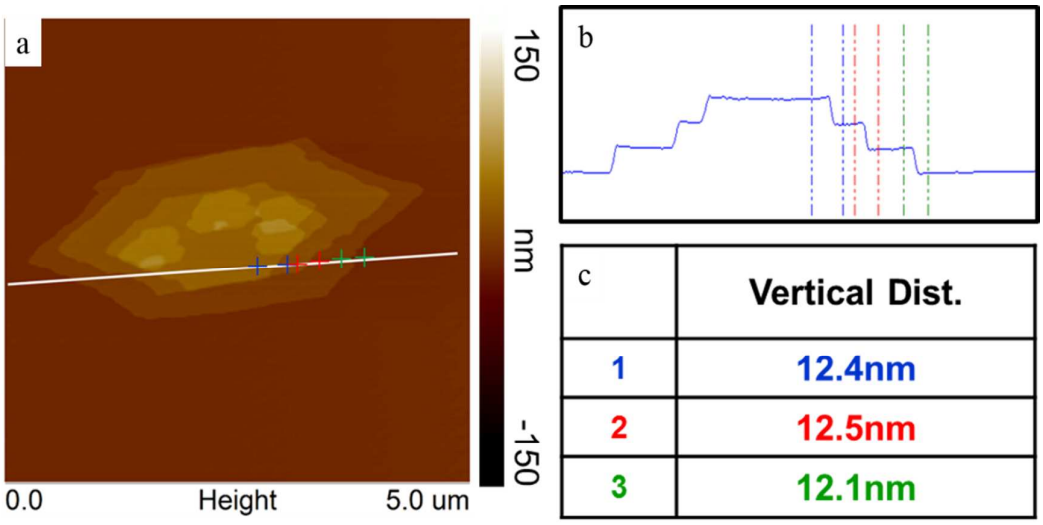


Figure S12. (a) AFM height images showing the PCL_{43}-POM nanosheets. (b) Height profiles of the nanosheets. (c) Measured vertical distance (or height) of the nanosheets.

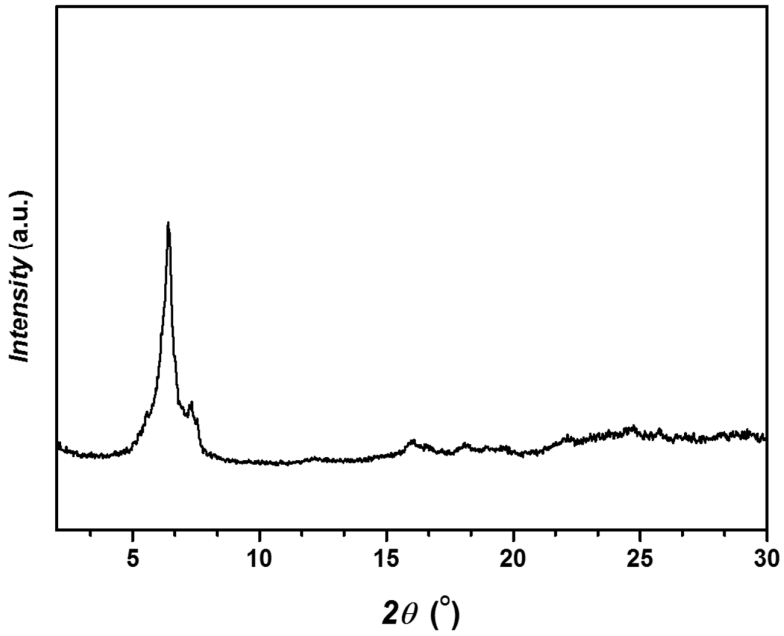


Figure S13. XRD pattern of the crystalline sample of the pure POM cluster.

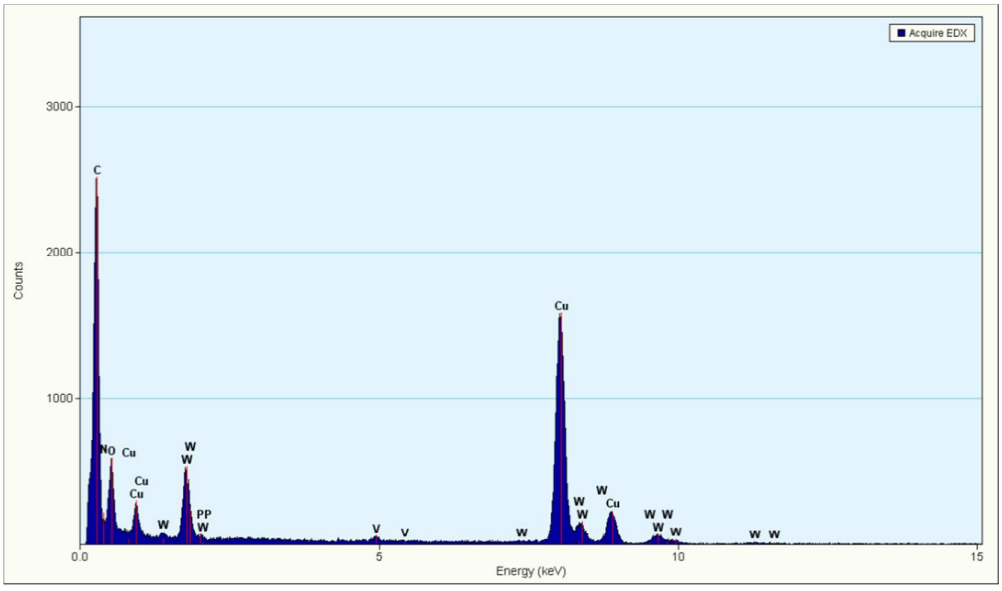


Figure S14. EDX spectrum taken on the nanotubes.

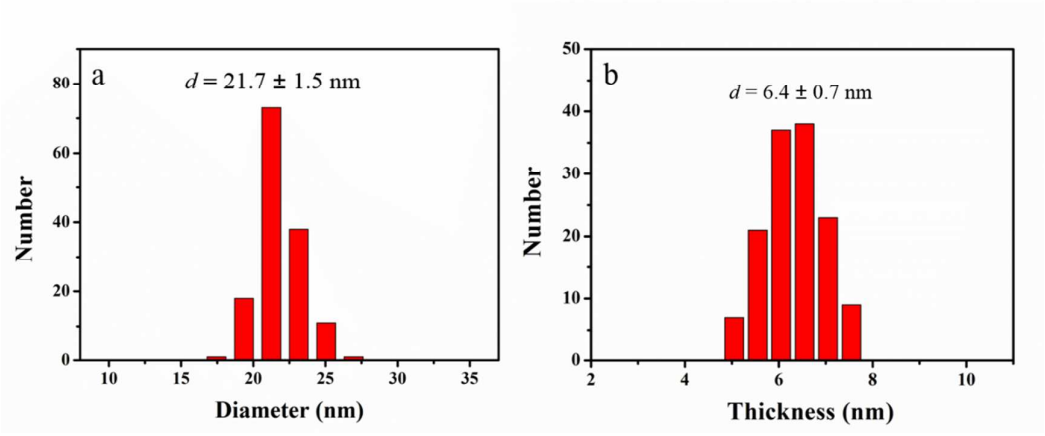


Figure S15. (a) The outside diameter distribution of nanotubes. (b) The outside diameter distribution of nanotubes.

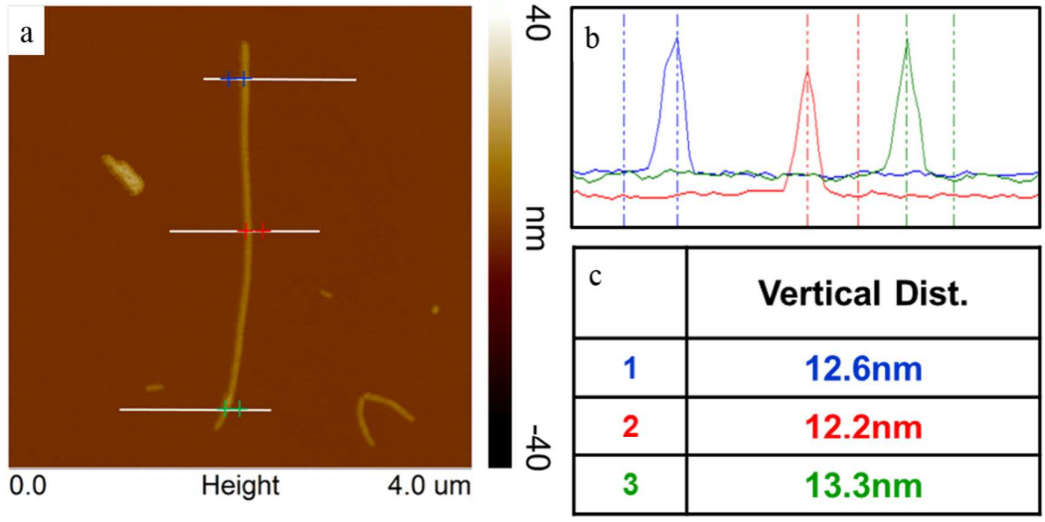


Figure S16. (a) AFM height images showing the PCL_{19}-POM nanotubes. (b) Height profiles of the nanotubes. (c) Measured vertical distance (or height) of the nanotubes.

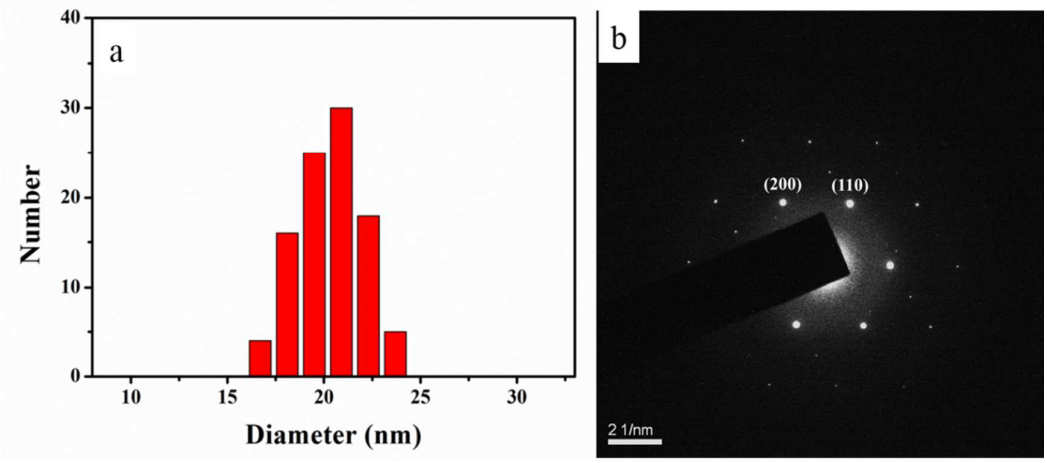


Figure S17. (a) The outside diameter distribution of grown nanotubes. (b) The ED pattern of the darker zone.

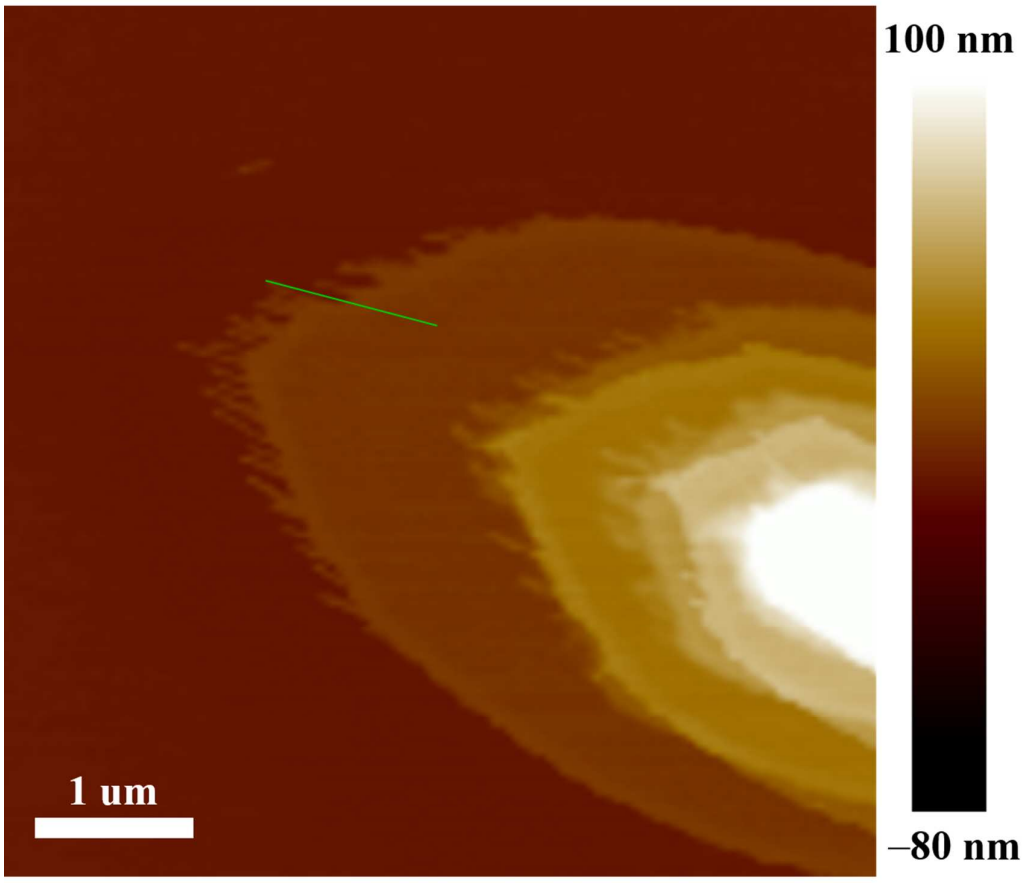


Figure S18. AFM height image showing the complex tube-*graft*-sheet nano-objects. The height profile in Figure 4c corresponds to the green line.