

Electronic Supplementary Information (ESI) for Materials Horizons

Supporting Information

Molecular Engineering of Porphyrin-Based Hierarchical Superstructure: Planarity Control of Discotic Metallomesogen for High Thermal Conductivity

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Synthesis

Synthesis of Vinyl Tosylate (VTs: dec-9-en-1-yl 4-methylbenzenesulfonate): A solution of *p*-toluenesulfonyl chloride (12 mmol), dec-9-en-1-ol (10 mmol), and TEA (12 mmol) in dried MC was stirring at room temperature for 8 h. After reaction, crude solution was washed with distilled water and saturated NH₄Cl solution several times. The organic layer was evaporated and then dissolved in MeOH for recrystallization during overnight. The re-crystalline solid was filtered and washed with cold MeOH. Resulting product is white solid (yield = 80 %). ¹H NMR (400 MHz, CDCl₃): δ 7.80-7.78 (d, 2H), 7.36-7.34 (d, 2H), 5.75-5.68 (m, 1H), 4.95-4.93 (m, 2H), 4.15-4.12 (t, 2H), 2.44 (s, 3H), 2.05-1.99 (m, 2H), 1.66 (m, 2H), 1.41 (m, 2H), 1.27 (m, 8H).

Synthesis of Vinyl Dendron (Den: methyl 3,4,5-tris(dec-9-en-1-yloxy)benzoate): A solution of VTs (5 mmol), methyl 3,4,5-trihydroxybenzoate (1 mmol) and K₂CO₃ in dried butanone was refluxed at 80 °C for four days. The solvent was removed by evaporation and the residue solid was dissolved in EA and then washed with distilled water several times. The organic layer was dried over MgSO₄. It was purified by column chromatography with silica gel using EA:Hex = 1:15. Resulting product is white solid (yield = 45 %). ¹H NMR (400 MHz, CDCl₃):

δ 7.26 (s, 2H), 5.84-4.92 (m, 3H), 5.02-4.92 (m, 6H), 4.05 (t, 6H), 3.89 (s, 3H), 2.07-2.02 (m, 6H), 1.82-1.79 (m, 6H), 1.47-1.28 (m, 6H), 0.90-0.87 (m, 24H).

Synthesis of Vinyl Dendron Acid (Den-OH: 3,4,5-tris(dec-9-en-1-yloxy)benzoic acid): A solution of Den (10 mmol), in THF/MeOH (10 mL/ 20 mL) was added aqueous NaOH (ca. 10 M, 2.15 mL). The mixture was refluxed at 60 °C for 4 h and then neutralized with an aqueous hydrochloric acid to obtain a precipitate. The precipitate was filtered off and washed with water. The crude product was dissolved in MC and then washed with distilled water several times. The organic layer was dried over MgSO₄. A white waxy solid (yield = 95 %). ¹H NMR (400 MHz, CDCl₃): δ 7.26 (s, 2H), 5.84-4.92 (m, 3H), 5.02-4.92 (m, 6H), 4.05 (t, 6H), 2.07-2.02 (m, 6H), 1.82-1.79 (m, 6H), 1.47-1.28 (m, 6H), 0.90-0.87 (m, 24H).

Synthesis of Porphyrin-based Vinyl Supramolecule (PorV-2H): A solution of Den-OH (7 mmol), 4-(Dimethylamino)pyridine (1.4 mmol), Porphyrin-OH (1 mmol), and 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (14 mmol) in dried acetone was stirring at room temperature for 1 day. After reaction, CHCl₃ was poured into mixture, and washed with distilled water and saturated NaOH several times. The organic layer was dried over MgSO₄. It was purified by column chromatography with silica gel using THF:Hex = 1:8. A purple solid (yield = 68 %). ¹H NMR (400 MHz, CDCl₃): δ 8.95 (s, 8H), 8.3 (d, 8H), 7.63 (d, 8H), 7.26 (s, 2H), 5.84-4.92 (m, 3H), 5.02-4.92 (m, 6H), 4.05 (t, 6H), 2.07-2.02 (m, 6H), 1.82-1.79 (m, 6H), 1.47-1.28 (m, 6H), 0.90-0.87 (m, 24H).

Synthesis of Metalloporphyrin-based Vinyl Supramolecules (PorV-x: x = Ni, Cu, Zn): The PorV-Ni, -Cu, -Zn compounds were synthesized according to the basis of reference.^{S1}

[S1] J. W. Buchler, *Porphyryns* **1978**, *1*, 389.

Film preparation

All of PorV-x molecules (16 mol%) are mixed with 1,6-hexanedithiol (84 mol%) and a general photo-initiator (DMPA, 5 wt% >) and DCM (because of low boiling point) in vials. To prevent polymerization during evaporation, using N₂ gas all solvent was evaporated with stirring. General glass with 4 x 4 cm was coated with water-soluble polymer (sort of Dextran) and then fabricated by using 0.6 mm cell gap tape. Homogeneously mixed compounds were carefully injected into the cell without any residual solvent. Filled cell was placed on hot plate and under 365 nm UV light for 1 hr and then flipped and continuously irradiated for 1 hr. Robust films could be obtained after removal of scarified layer in water.

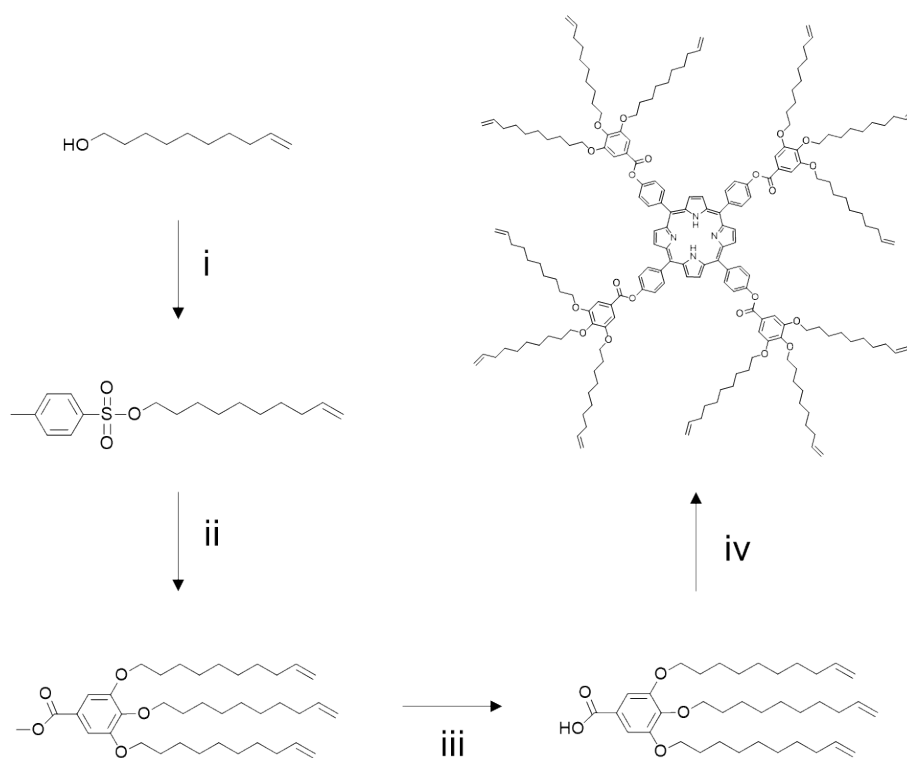


Figure S1. Synthetic route of PorV-2H. i) Ts-Cl, TEA, MC, 25 °C, 8 h; ii) K_2CO_3 , KI, butanone, 80 °C, 4 days; iii) NaOH, THF, MeOH, 60 °C, 4 h; iv) EDC, DMAP, Acetone, 25 °C, 1 day.

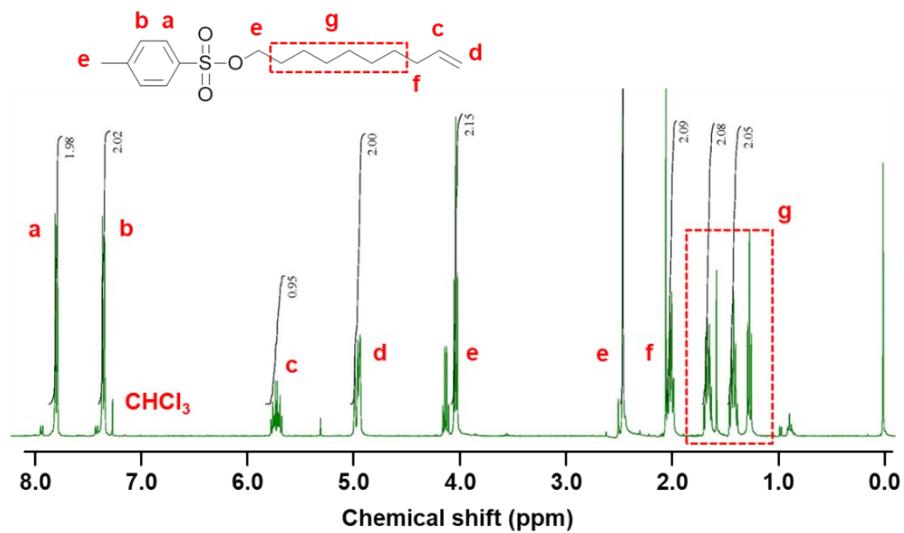


Figure S2. ^1H NMR spectrum of vinyl tosylate.

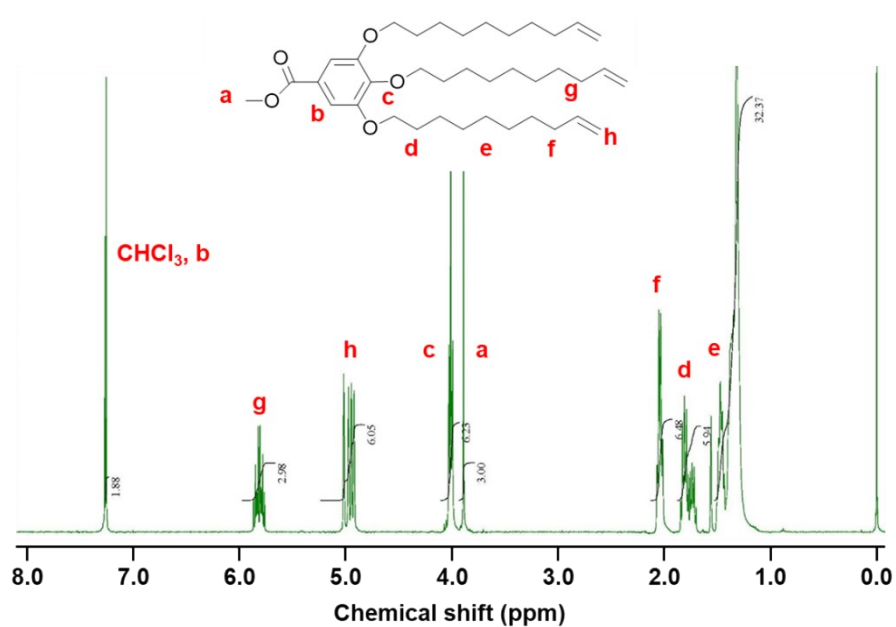


Figure S3. ^1H NMR spectrum of Den.

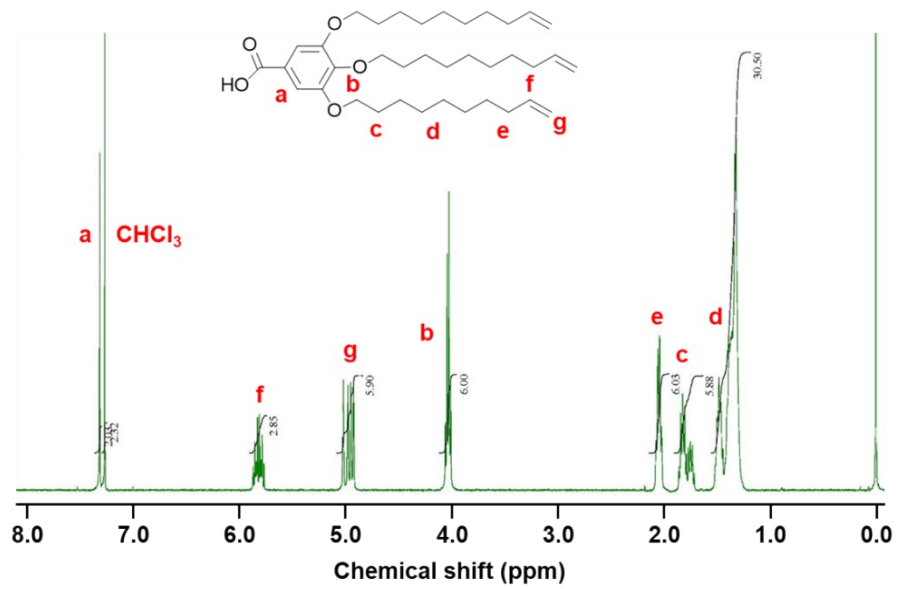


Figure S4. ^1H NMR spectrum of Den-OH.

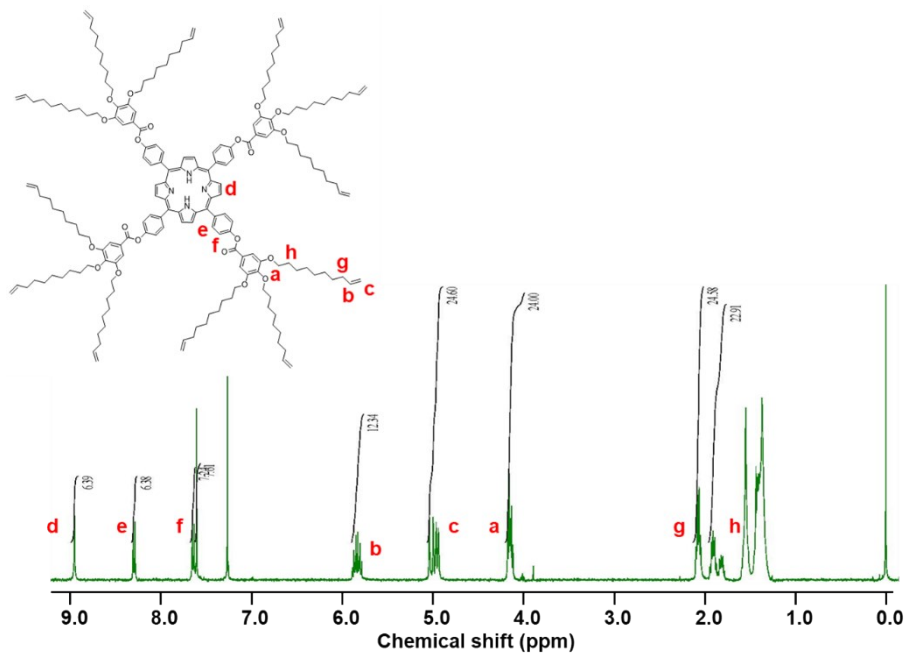


Figure S5. ^1H NMR spectrum of PorV-2H.

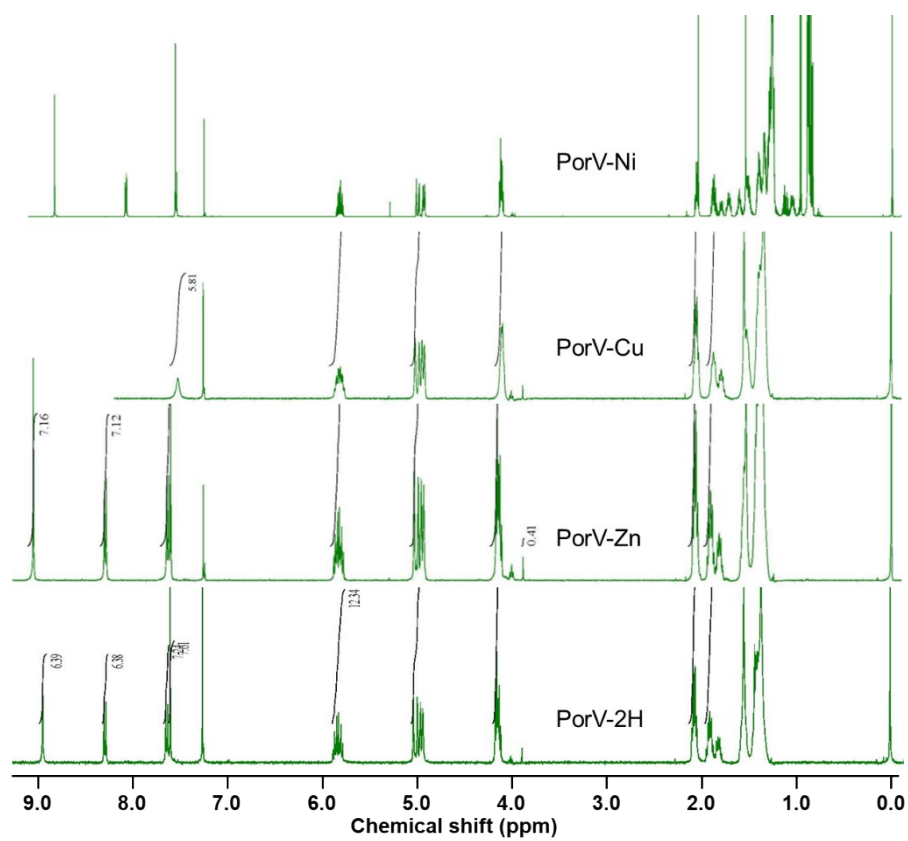


Figure S6. ^1H NMR spectra of PorV-x compounds (x = -2H, -Ni, -Cu, and -Zn).

	Experimental Content (%)	Calculated Content (%)
C	78.44	78.27
	77.94	
	78.48	
H	8.99	8.96
	9.09	
	9.01	
N	2.10	1.9
	1.94	
	2.06	
O	11.30	10.86
	11.34	
	11.32	

Figure S7. Elemental analysis of PorV-2H.

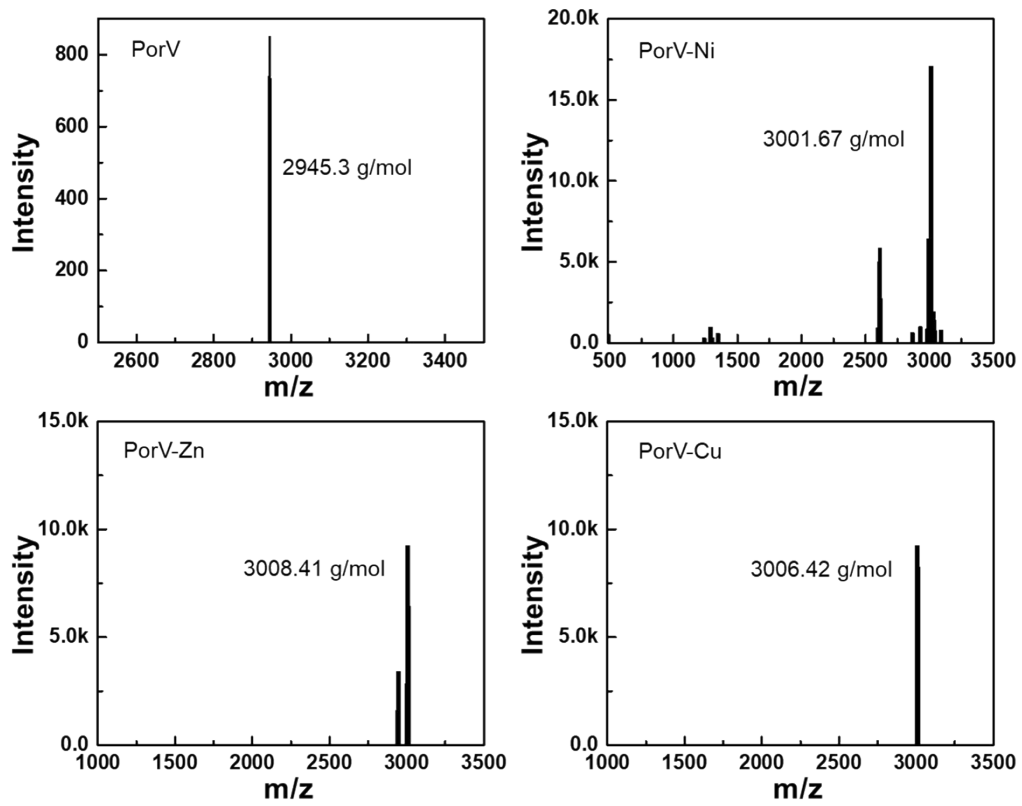


Figure S8. MALDI-ToF MS spectra of PorV-x compounds.

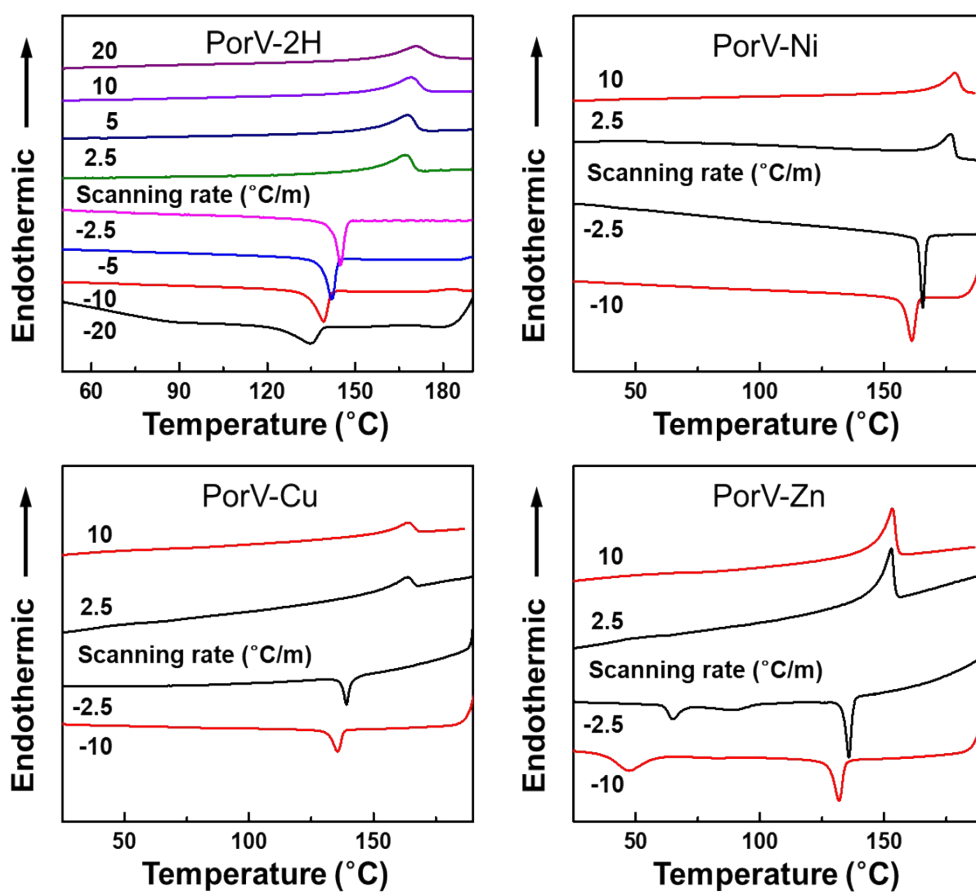


Figure S9. Sets of DSC cooling and subsequent heating diagrams for PorV-x compounds at different scanning rates.

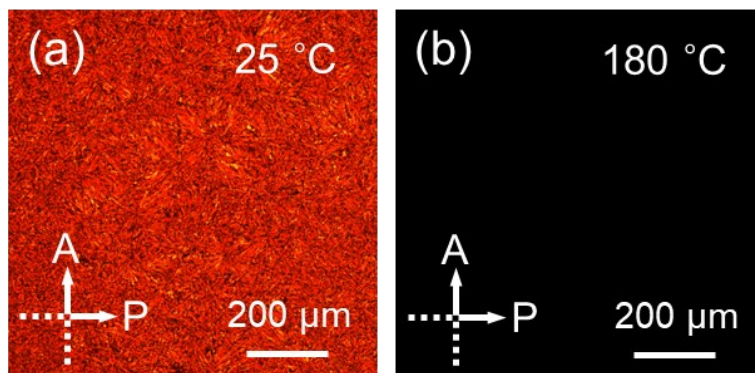


Figure S10. POM images of Por-2H observed at (a) 25 °C and (b) 180 °C during 2.5 °C min⁻¹ cooling process.

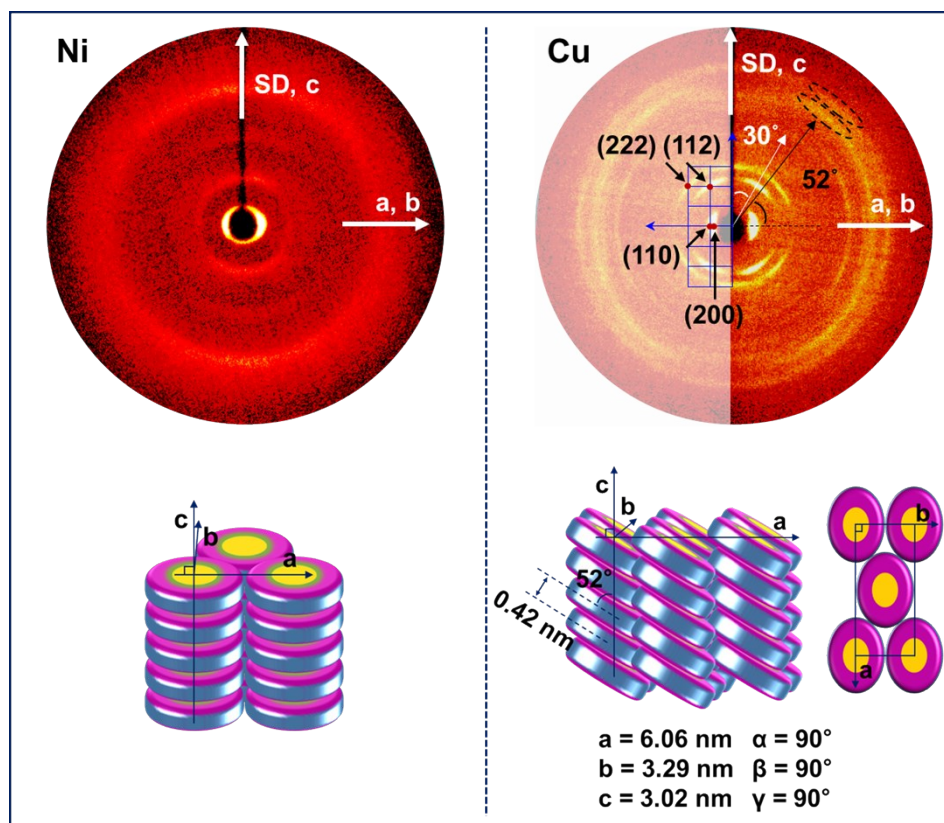


Figure S11. 2D WAXD patterns of the uniaxially oriented PorV-Ni and -Cu mesophase obtained with the X-ray beam perpendicular to shear direction (SD) and its schematic illustration with unit cell.

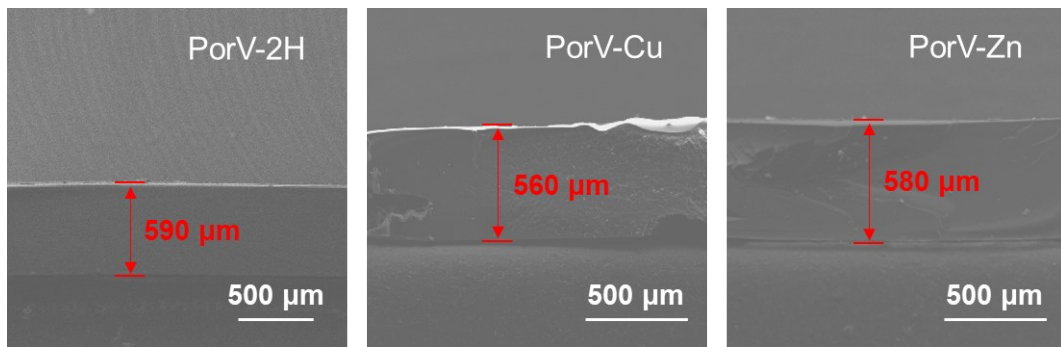


Figure S12. SEM cross-sectional observation of PorV-x films.

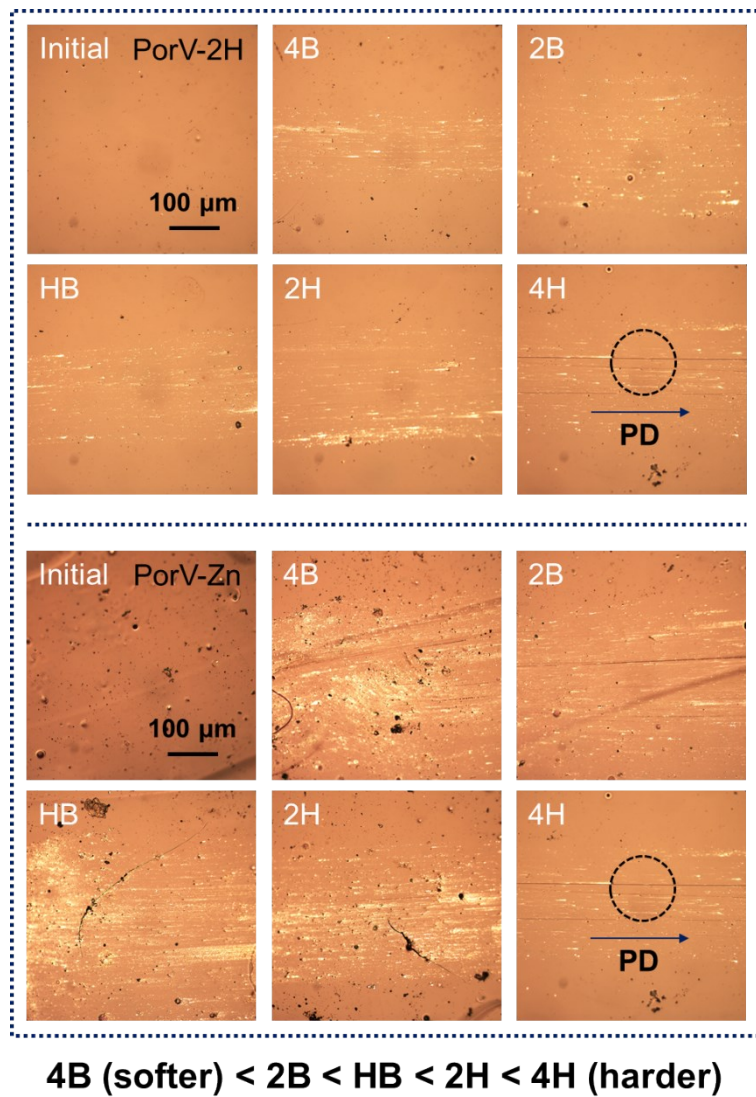


Figure S13. Optical microscopic images of PorV-2H and -Zn films scratched by the carbon pencil at various hardness. PD is pencil direction.

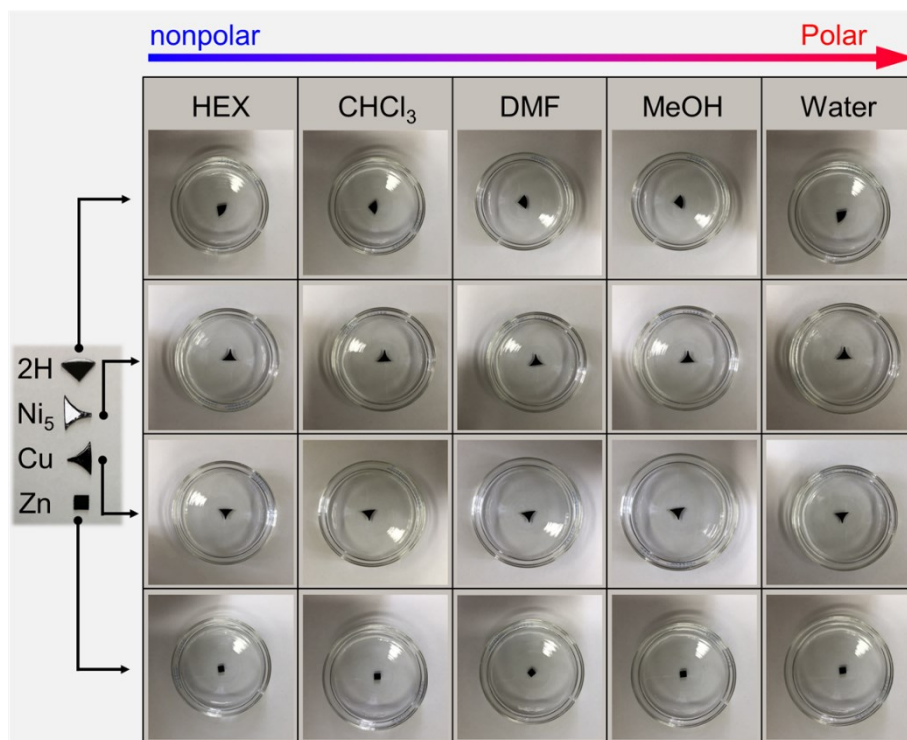


Figure S14. Photographs of PorV-x films after the chemical stability test in organic solvents.

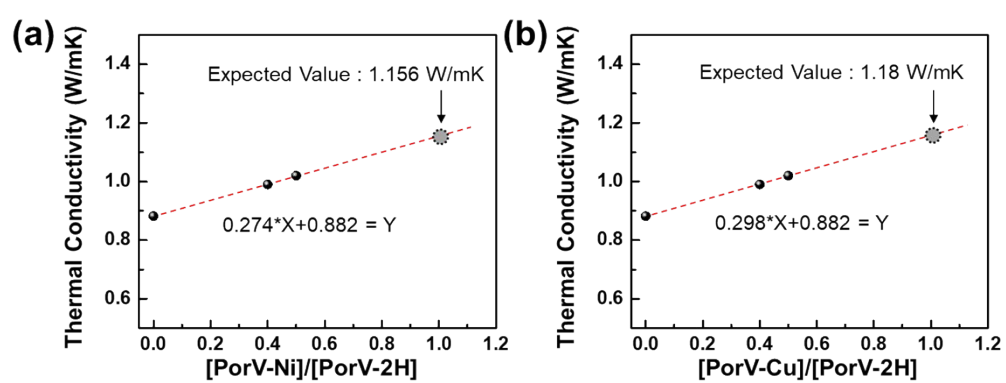


Figure S15. Thermal conductivity of mixed films (PorV-Ni/-2H and PorV-Cu/-2H) and expected values obtained by the extrapolation.

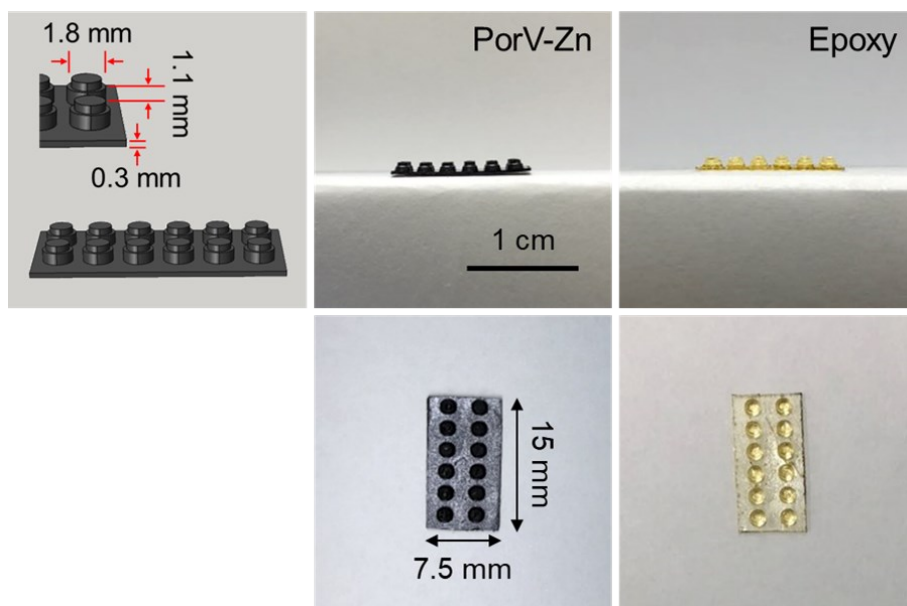


Figure S16. Photographs of heat sinks consisting of PorV-Zn and Epoxy.

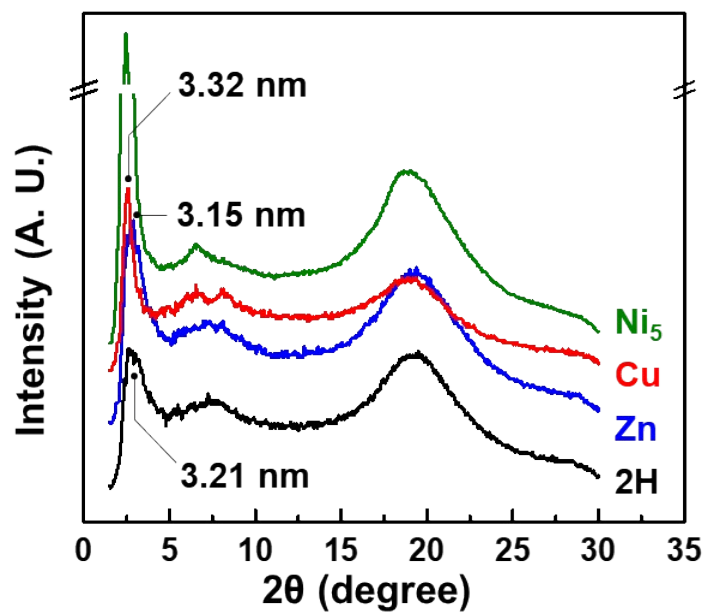


Figure S17. 1D WAXD patterns of free-standing PorV-x films polymerized at 50 °C.

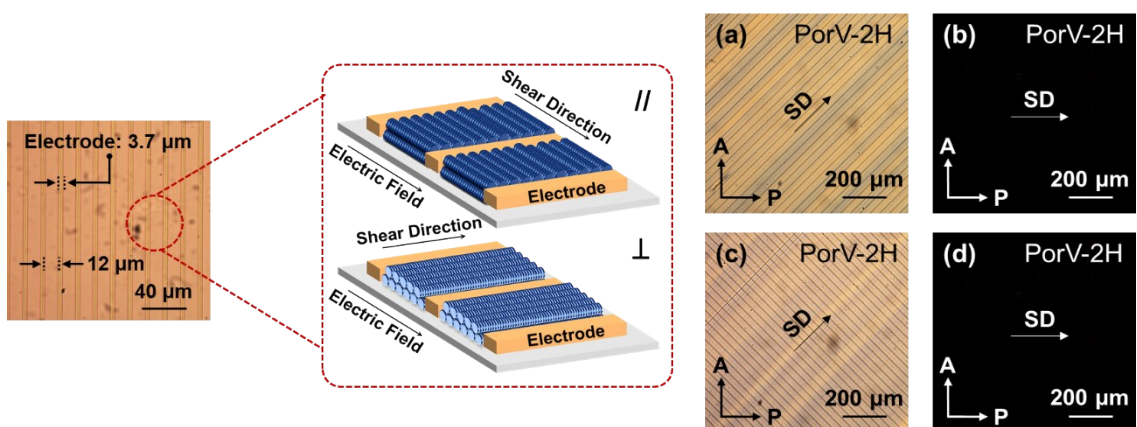


Figure S18. POM image of electrode-patterned glass substrate and schematic illustration of macroscopically oriented sample. POM images of the macroscopically oriented PorV-2H on the electrode-patterned glass substrate: when the SD is (a) parallel and (c) perpendicular to electrode at 45° to the polarization axes and when the SD in both cases is (b, e) parallel to the polarization axes.

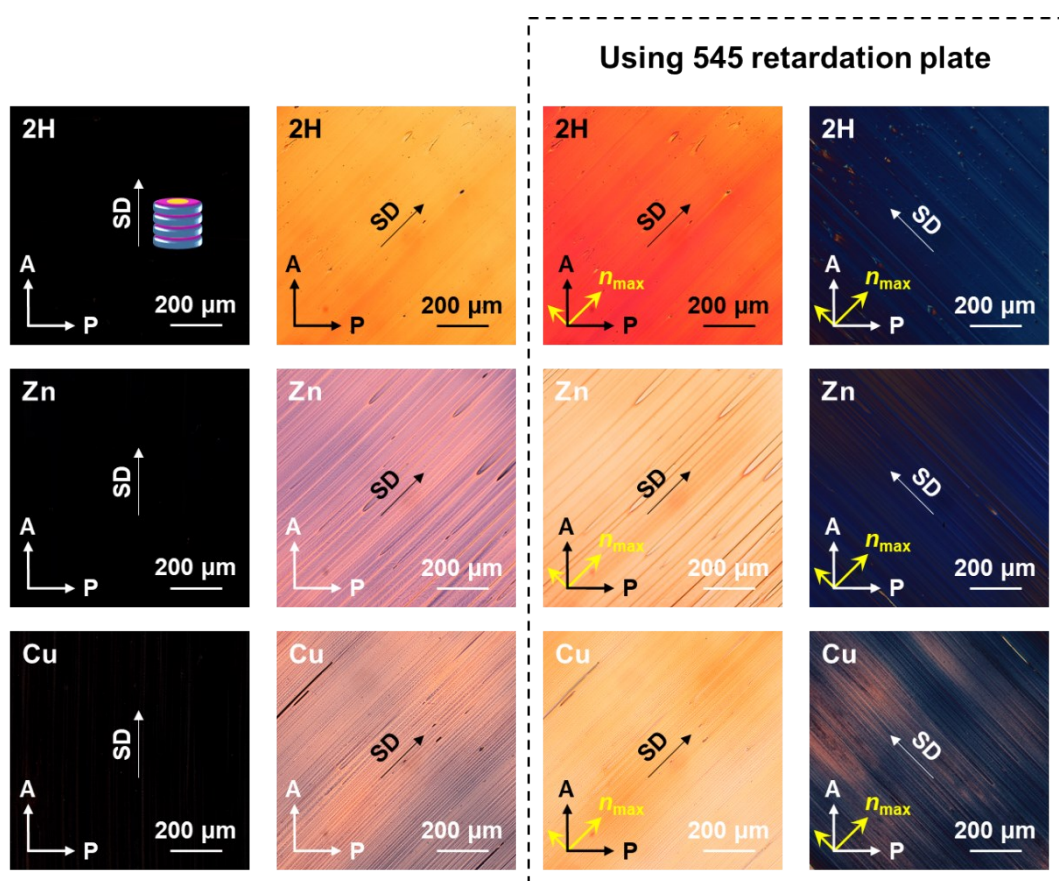


Figure S19. POM images of the macroscopically oriented PorV-x compounds with a 545 nm retardation plate. SD is the shear direction and n_{\max} is the slow axis of retardation plate.

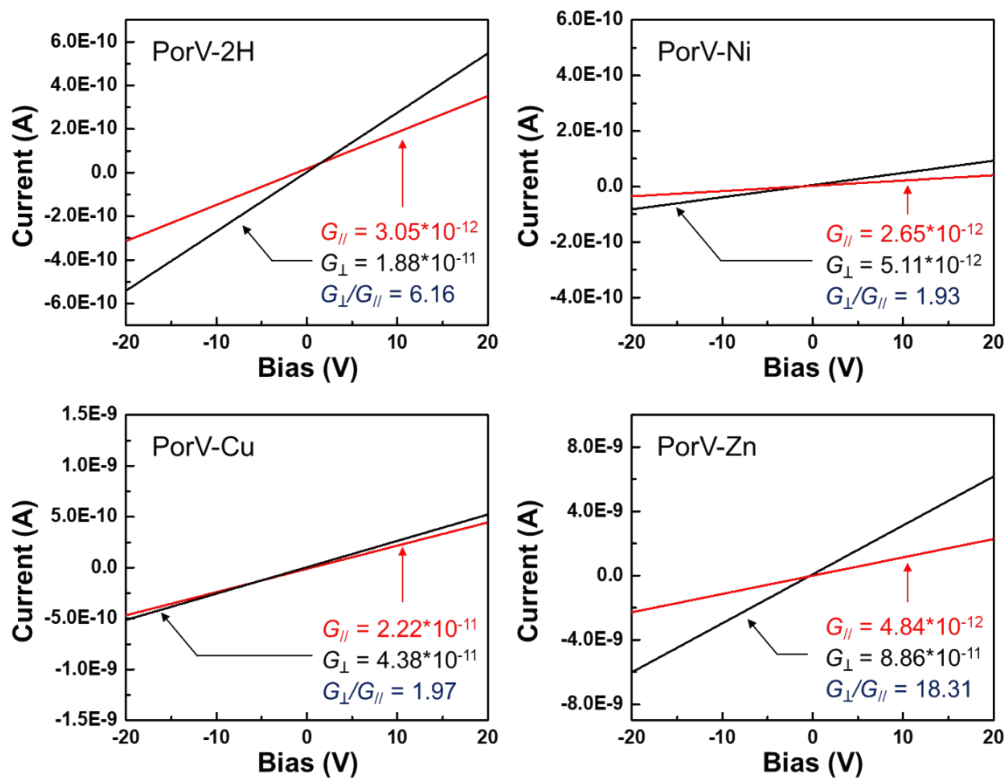


Figure S20. Ratio of conductance between the perpendicular and parallel directions.