

Supporting Informations

Self-Assembled Pd^{II}₆ Molecular Spheroids and their Proton Conduction Property

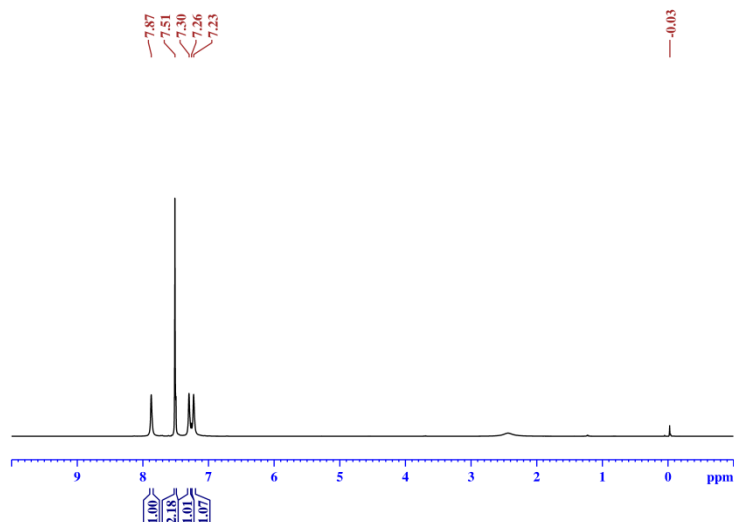
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Table S1. Crystallographic Data and Refinement Parameters of **SP1** and **SP3**.

Identification code	SP1	SP3
Empirical formula	C ₁₄₄ H ₁₂₀ N ₆₀ O ₃₆ Pd ₆	C ₂₁₆ H ₁₆₈ N ₅₀ O ₂₀ Pd ₆
Formula weight	3905.39	4422.39
Temperature (k)	100 (2)	100 (2)
Wavelength	0.70000	0.71073
Crystal system	monoclinic	monoclinic
Space group	P21/ <i>n</i>	C 2/ <i>m</i>
Unit cell dimension	a = 18.524 (4) b = 34.021 (7) c = 23.246 (5) α = 90 β = 108.71 (3) γ = 90	a= 32.038 (3) b= 30.653 (3) c= 26.205 (3) α = 90 β = 110.896 (3) γ = 90
Volume (Å ³)	13876 (5)	24043 (4)
Z	2	2
δ (g/cm ⁻³)	0.935	0.611
Mu (mm ⁻¹)	0.436	0.253
F(000)	3936.0	4500.0
GooF	1.081	1.017
R	0.0894	0.1010
wR2	0.2920	0.3156
CCDC no.	1813498	1813499

**Figure S1.** ¹H NMR spectra of the **L1** in CDCl₃ at room temperature.

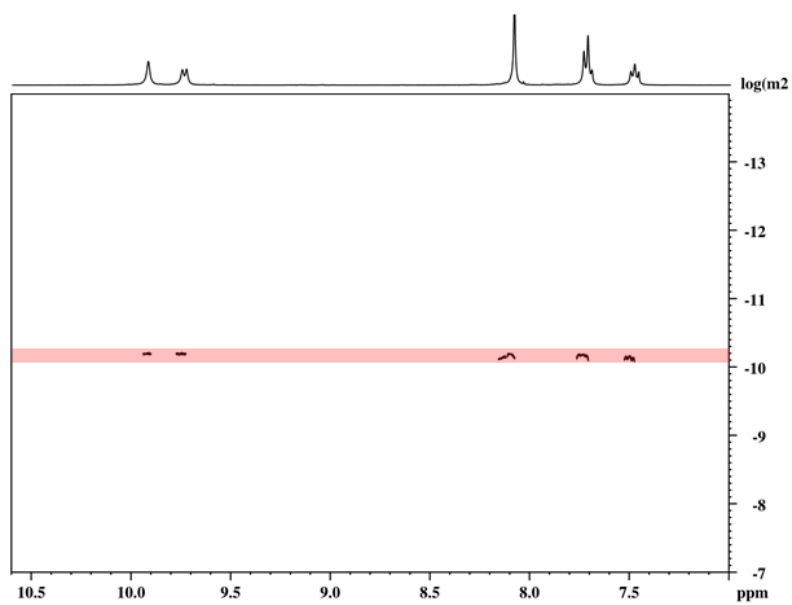


Figure S5. DOSY NMR spectra of **SP2** in DMSO- d_6 at room temperature.

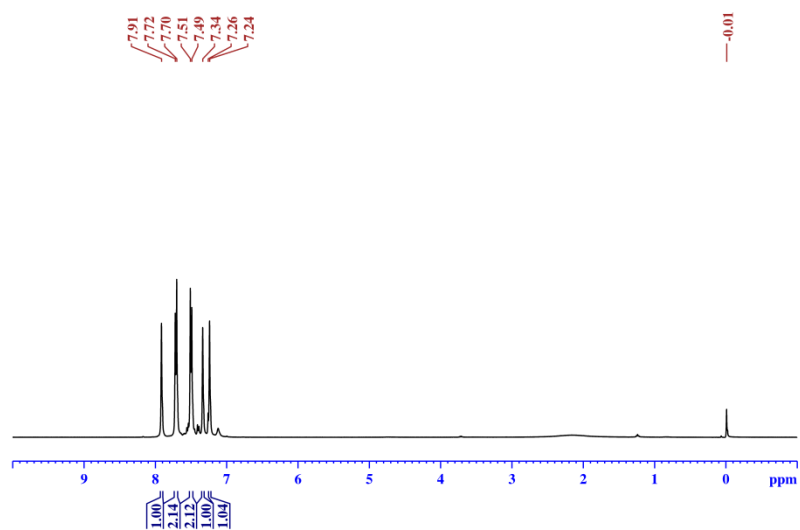


Figure S6. ^1H NMR spectra of the **L3** in CDCl_3 at room temperature.

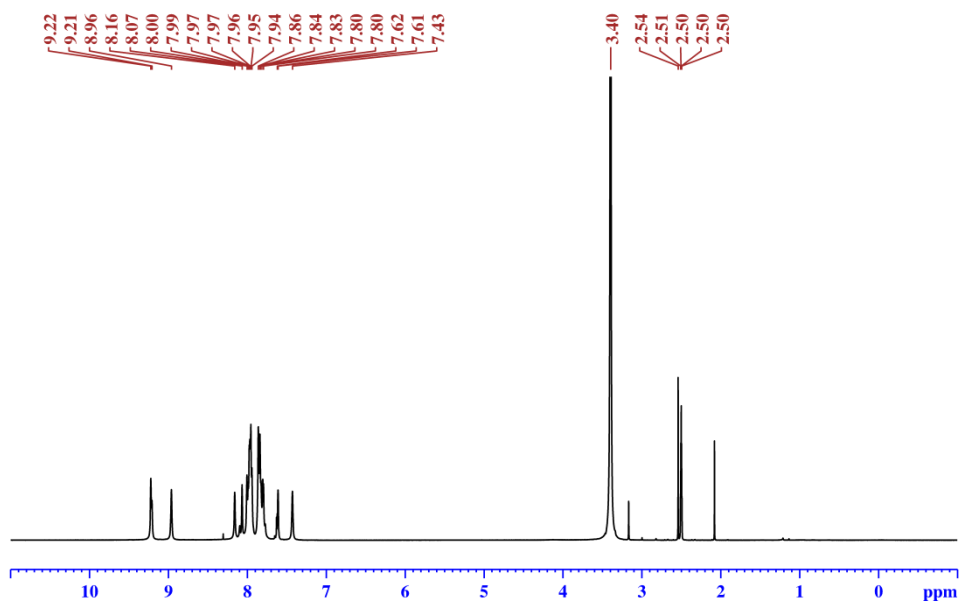


Figure S7. ^1H NMR spectra of the **SP3** in DMSO-d_6 at $20\text{ }^\circ\text{C}$.

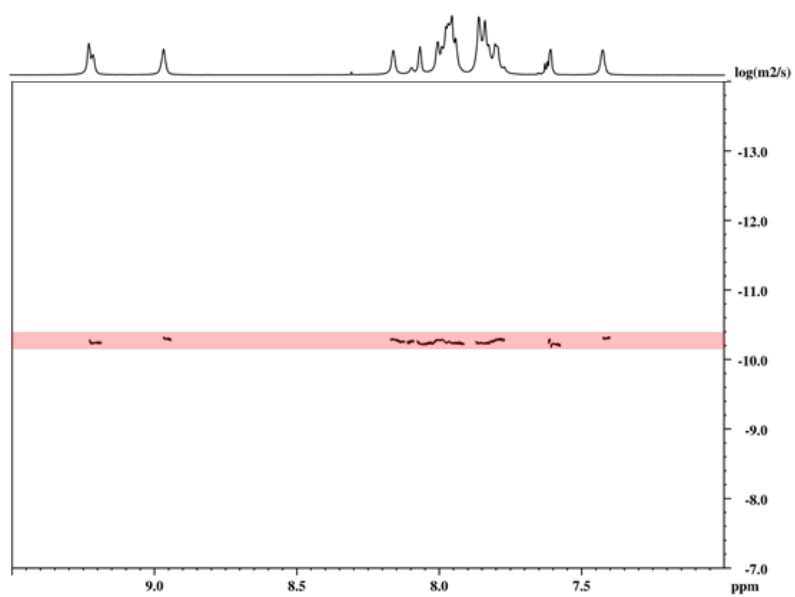


Figure S8. DOSY NMR spectra of **SP3** in DMSO-d_6 at $20\text{ }^\circ\text{C}$.

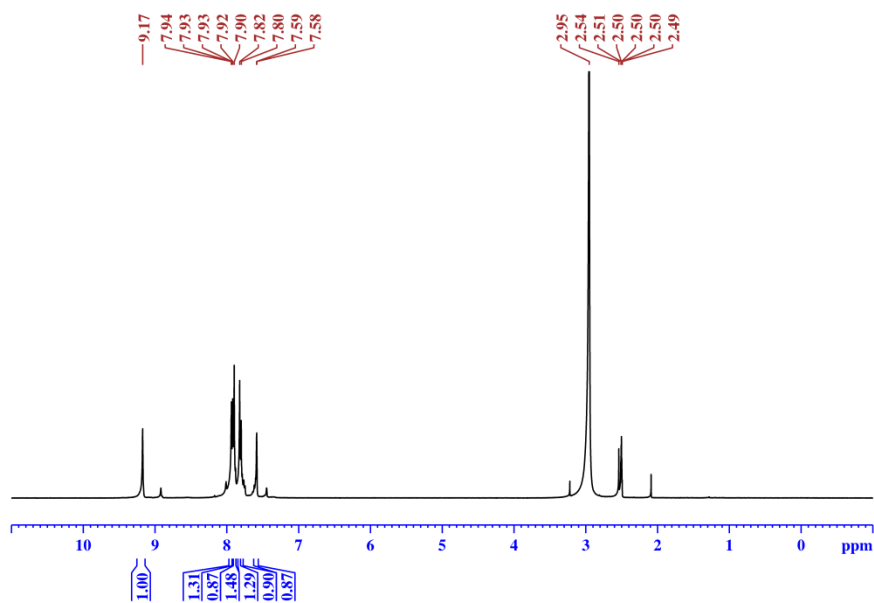


Figure S9. ¹H NMR spectra of **SP3** in DMSO-d₆ at 100 °C.

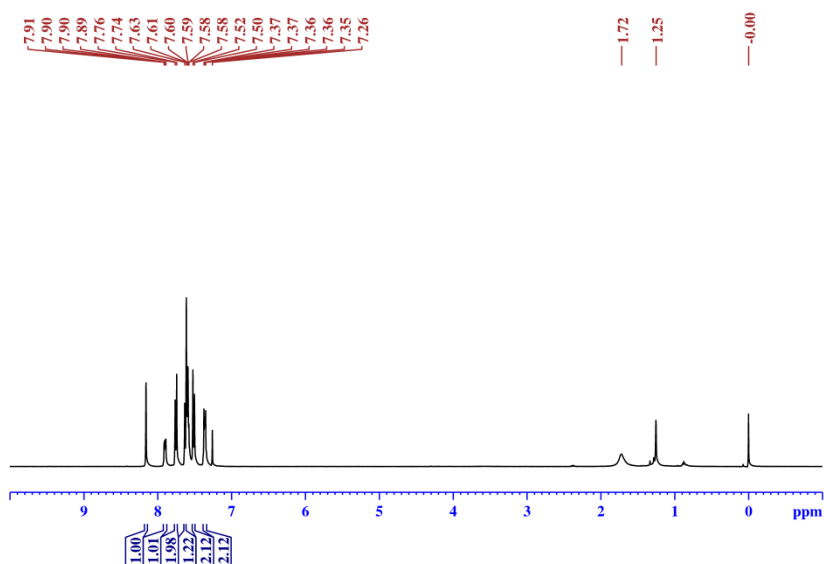


Figure S10. ¹H NMR spectra of the **L4** in CDCl₃ at room temperature.

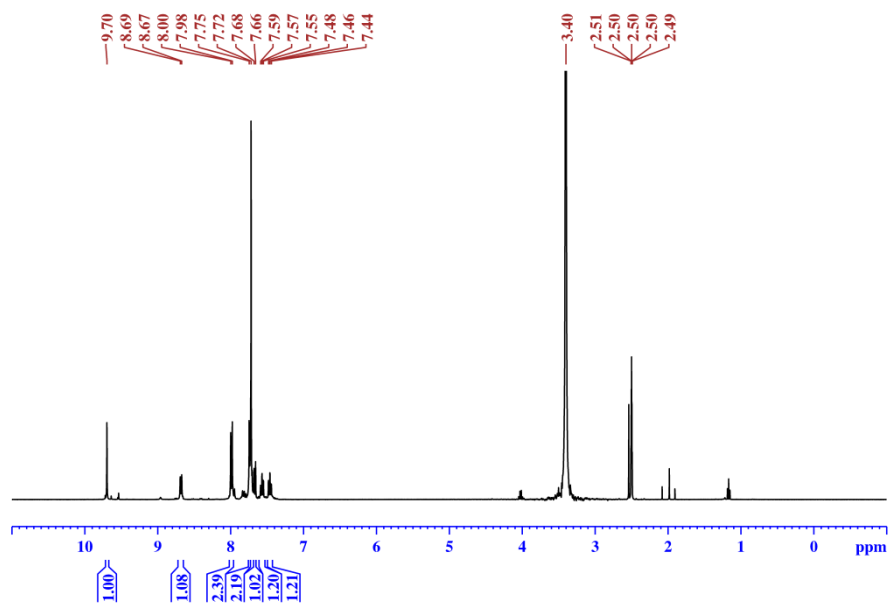


Figure S11. ^1H NMR spectra of **SP4** in DMSO-d_6 at room temperature.

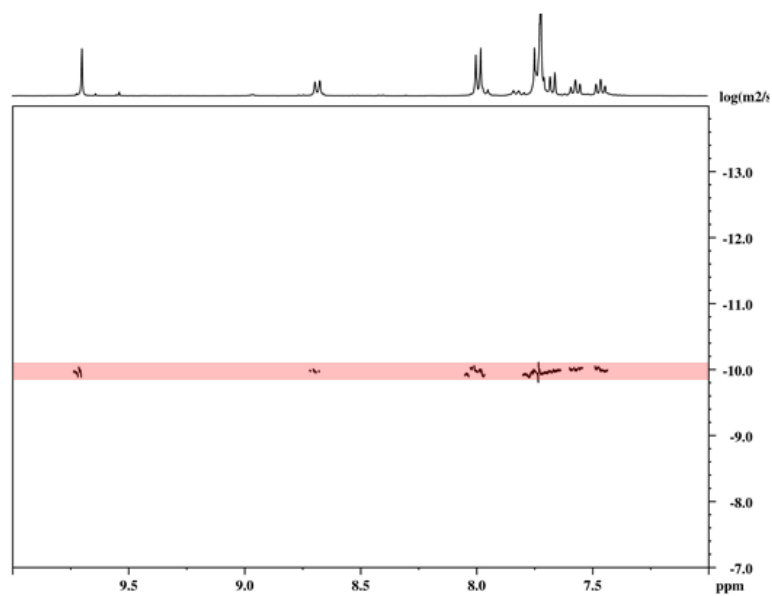


Figure S12. DOSY NMR spectra of **SP4** in DMSO-d_6 at room temperature.

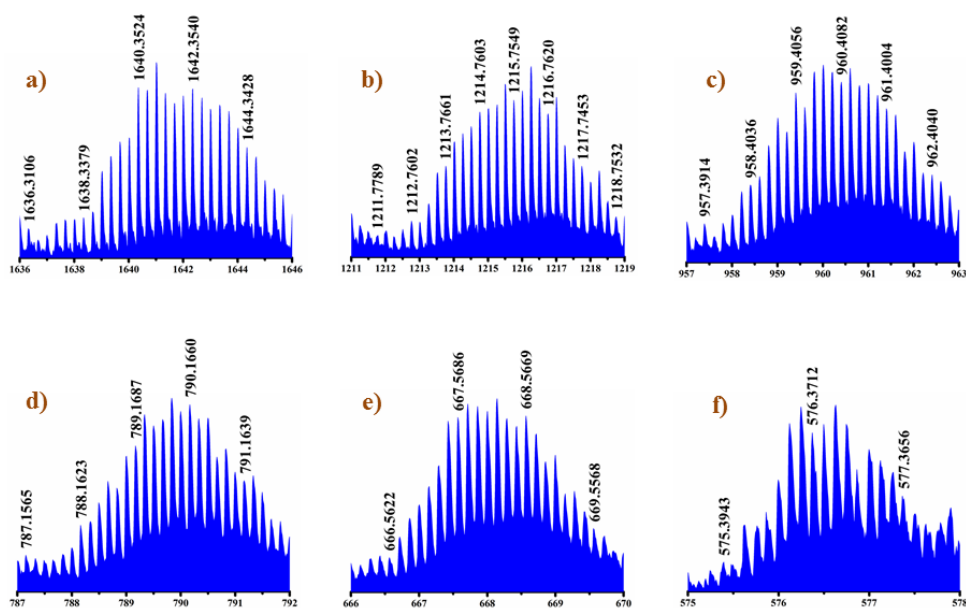


Figure S13. Experimental isotopic distribution patterns of the peaks corresponding to $[\text{SP2-3NO}_3]^{3+}$ (a); $[\text{SP2-4NO}_3]^{4+}$ (b); $[\text{SP2-5NO}_3]^{5+}$ (c); $[\text{SP2-6NO}_3]^{6+}$ (d); $[\text{SP2-7NO}_3]^{7+}$ (e) and $[\text{SP2-8NO}_3]^{8+}$ (f).

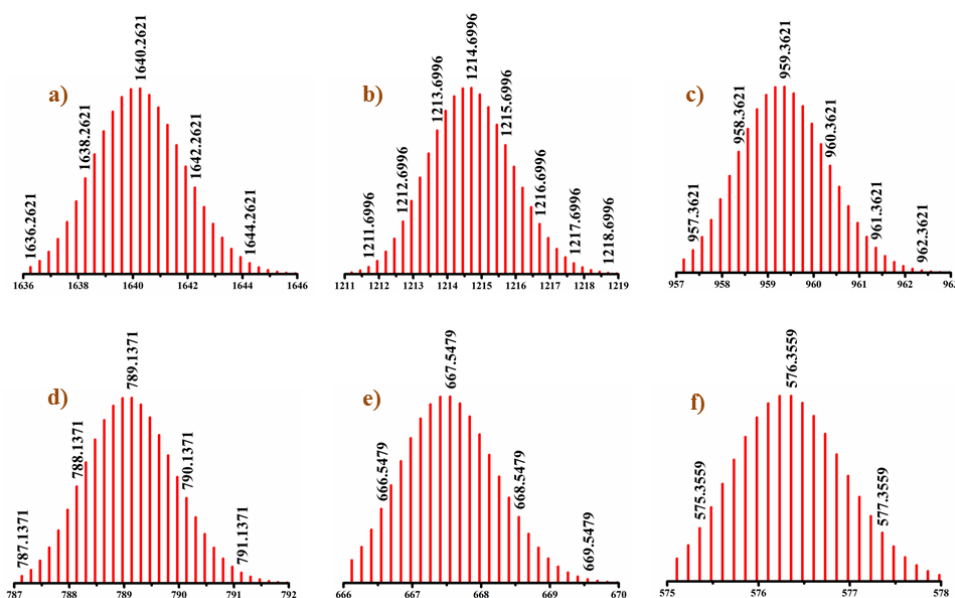


Figure S14. Calculated isotopic distribution patterns of the peaks corresponding to $[\text{SP2-3NO}_3]^{3+}$ (a); $[\text{SP2-4NO}_3]^{4+}$ (b); $[\text{SP2-5NO}_3]^{5+}$ (c); $[\text{SP2-6NO}_3]^{6+}$ (d); $[\text{SP2-7NO}_3]^{7+}$ (e) and $[\text{SP2-8NO}_3]^{8+}$ (f).

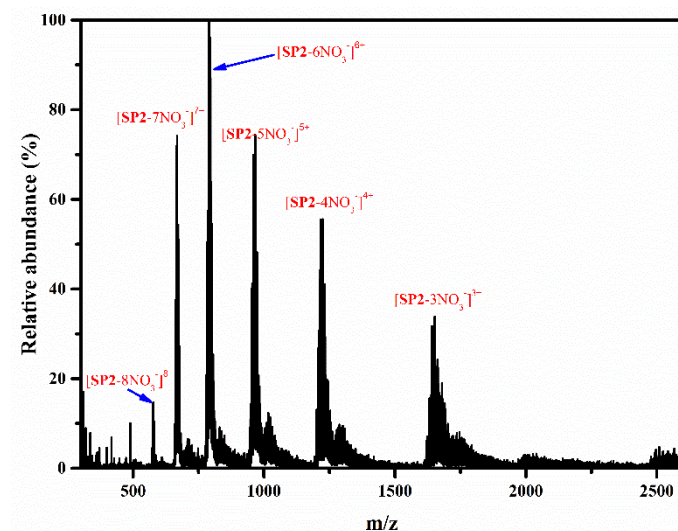


Figure S15. Full mass spectra of SP2.

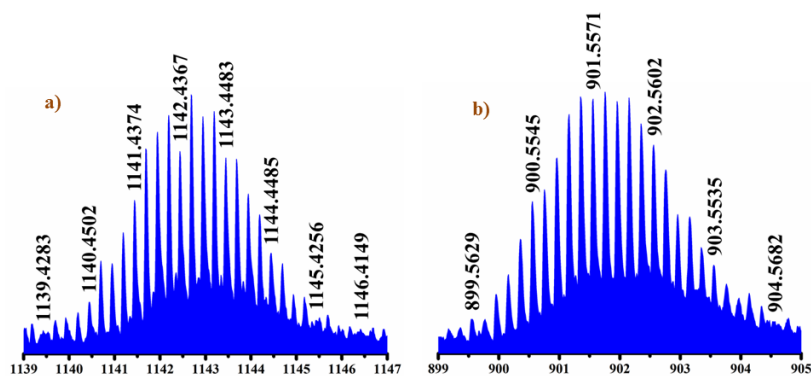


Figure S16. Experimental isotopic distribution patterns of the peaks corresponding to [SP3-4NO₃]⁴⁺ (a) and [SP3-5NO₃]⁵⁺ (c).

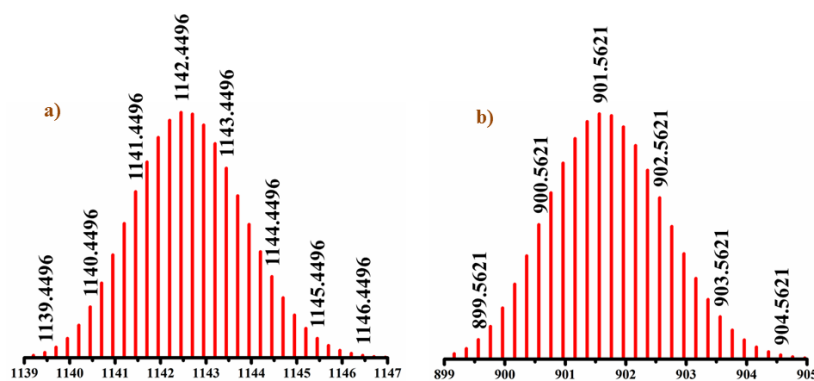


Figure S17. Calculated isotopic distribution patterns of the peaks corresponding to [SP3-4NO₃]⁴⁺ (a) and [SP3-5NO₃]⁵⁺ (b).

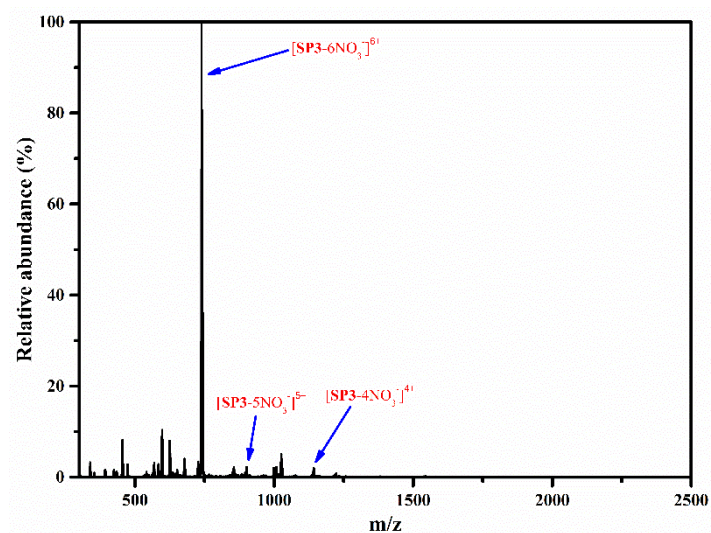


Figure S18. Full mass spectra of SP3.

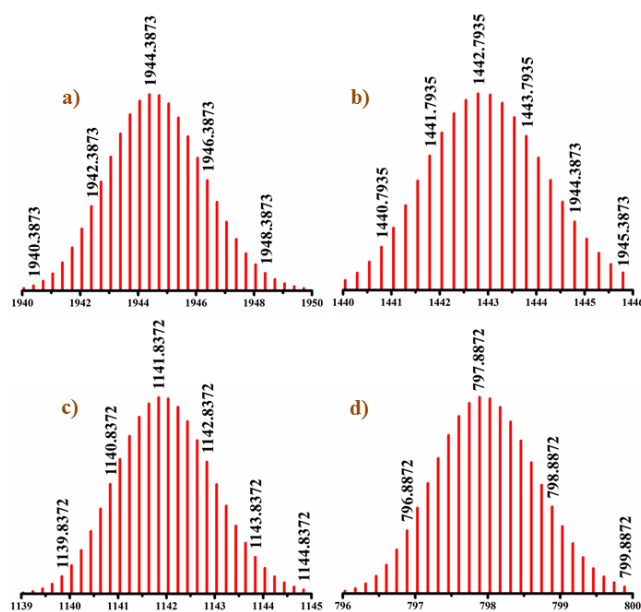


Figure S19. Calculated isotopic distribution patterns of the peaks corresponding to $[\text{SP4-3NO}_3]^{3+}$ (a); $[\text{SP4-4NO}_3]^{4+}$ (b); $[\text{SP4-5NO}_3]^{5+}$ (c) and $[\text{SP4-7NO}_3]^{7+}$ (d).

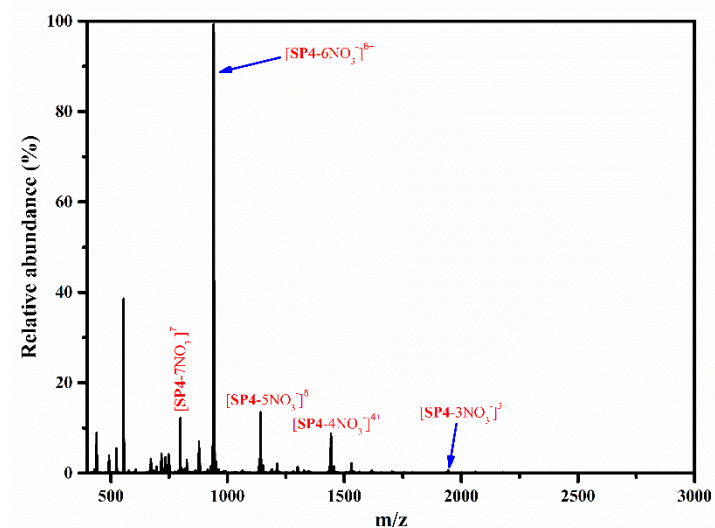


Figure S20. Full mass spectra of SP4.

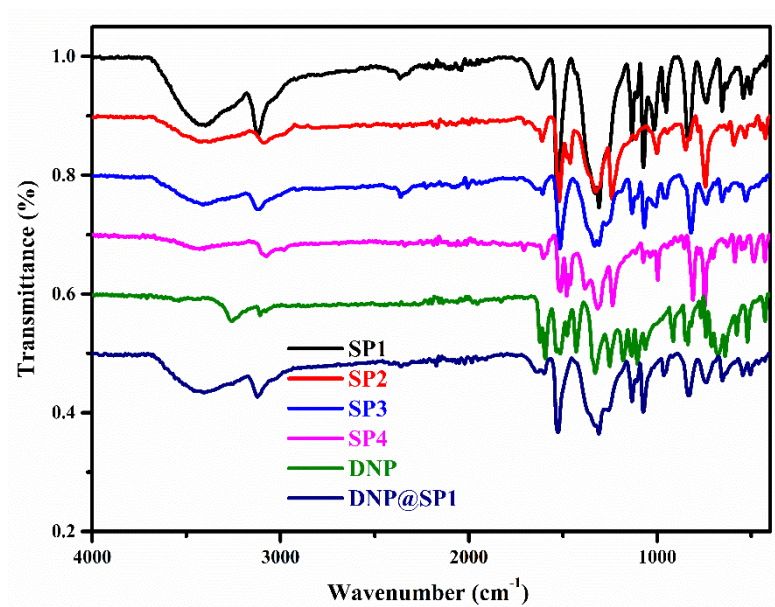


Figure S21. IR spectra of molecular spheroids SP1, SP2, SP3, SP4, DNP and adsorbed DNP in spheroid SP1 (DNP@SP1).

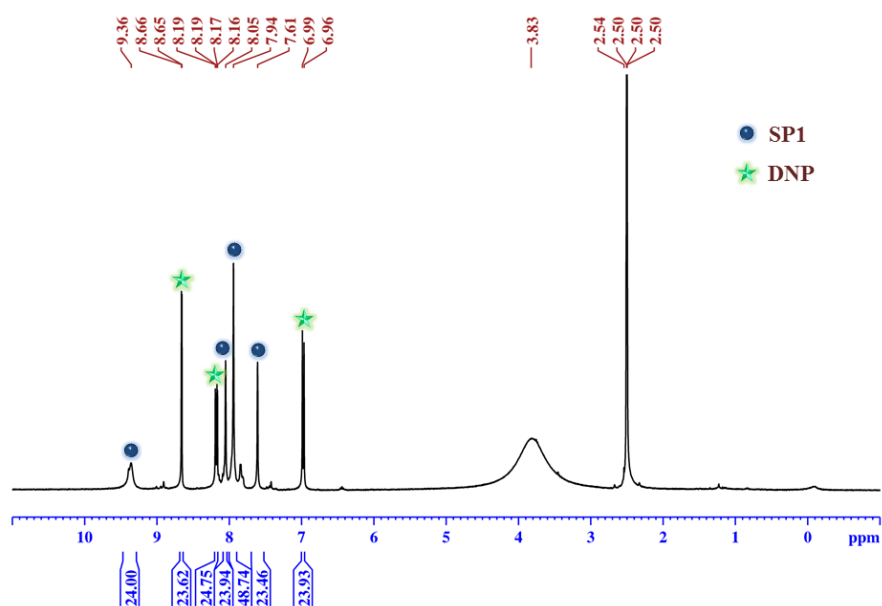


Figure S22. ^1H NMR spectra of **DNP@SP1** in DMSO-d_6 at room temperature containing 24 **DNP** molecules.

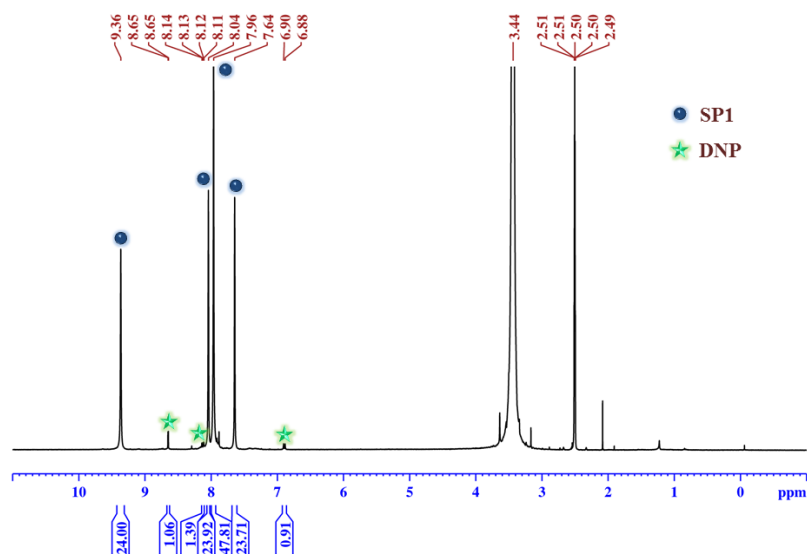


Figure S23. ^1H NMR spectra of **DNP@SP1** in DMSO-d_6 at room temperature containing one **DNP** molecule.

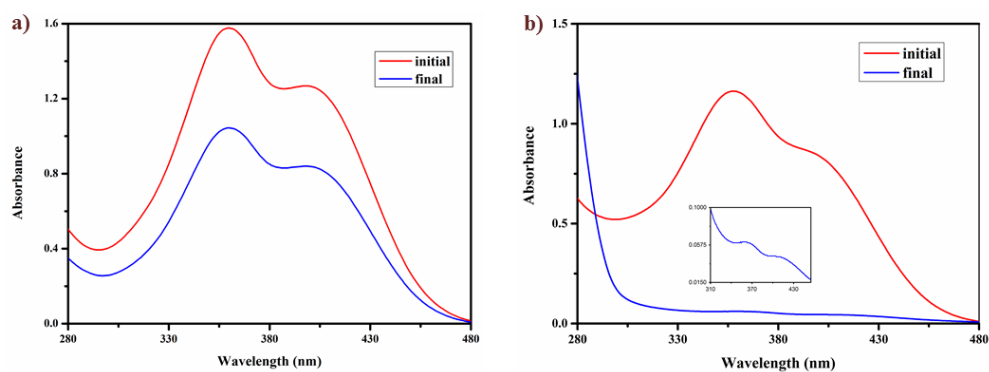


Figure S24. UV-Vis Spectra of EtOH:H₂O (1:9) 2,4-DNP solution starting with 0.5 mmol **DNP** molecule (a) and 0.01 mmol **DNP** molecule (b).

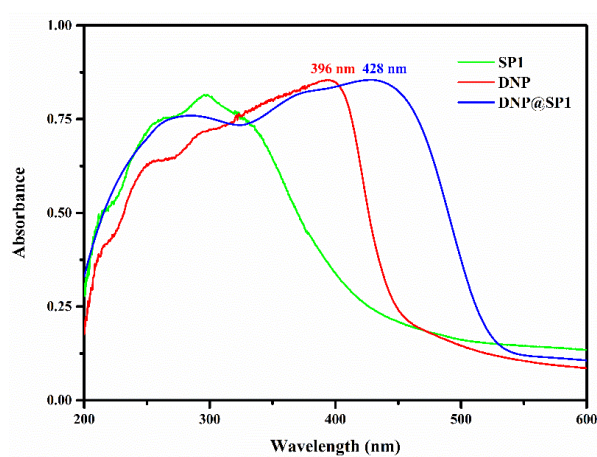


Figure S25. Solid state UV-Vis spectra of **SP1**, **DNP** and adsorped **DNP** in spheroid **SP1** (**DNP@SP1**).

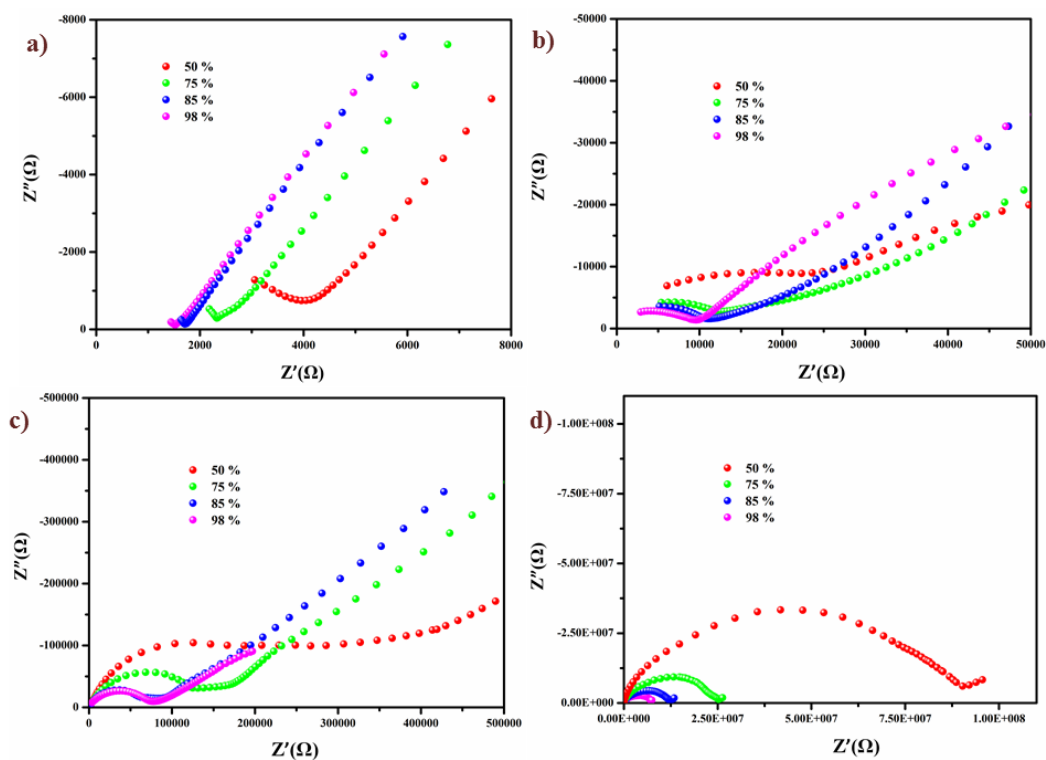


Figure S26. Nyquist plots of SP1 (a), SP2 (b), SP3 (c) and SP4 (d) at 20 °C and different relative humidity.

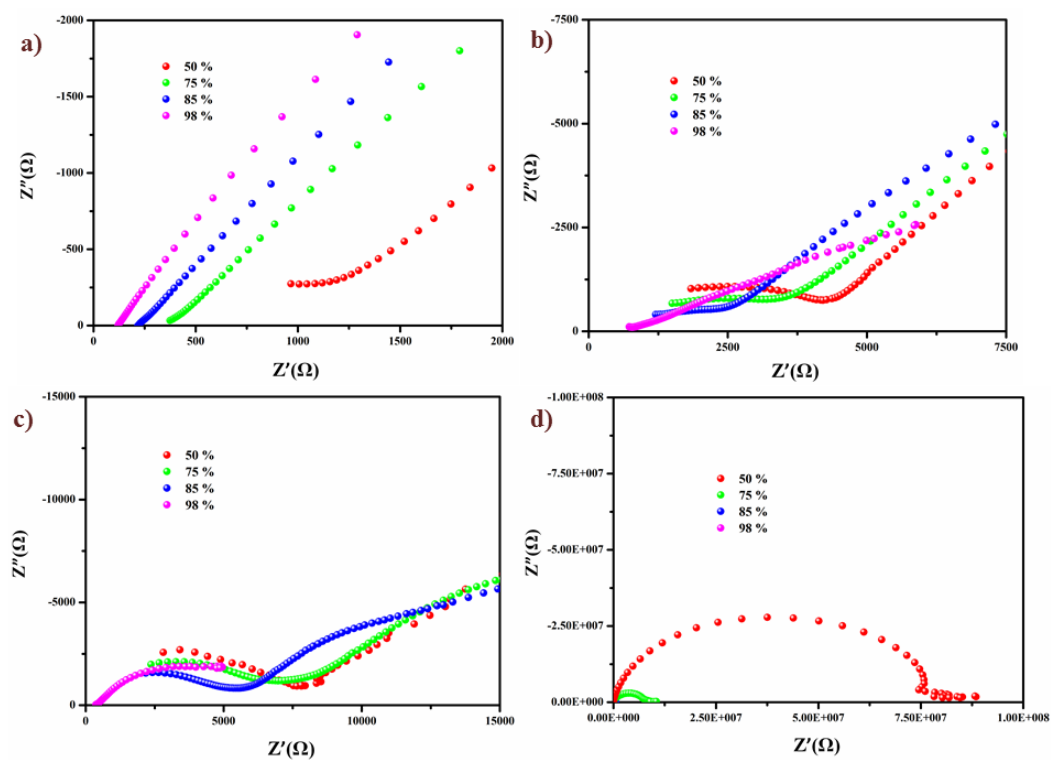


Figure S27. Nyquist plots of SP1 (a), SP2 (b), SP3 (c) and SP4 (d) at 70 °C and different relative humidity.

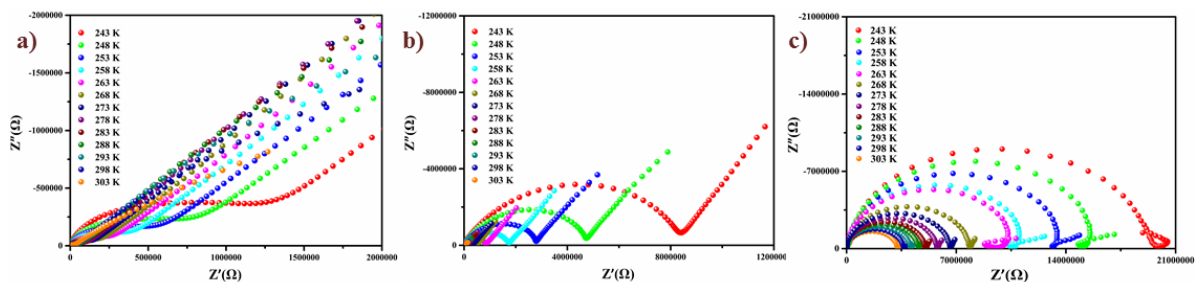


Figure S28. Nyquist plots of **SP1** (a), **DNP** (b) and **DNP@SP1** (c) between 243 K to 303 K.

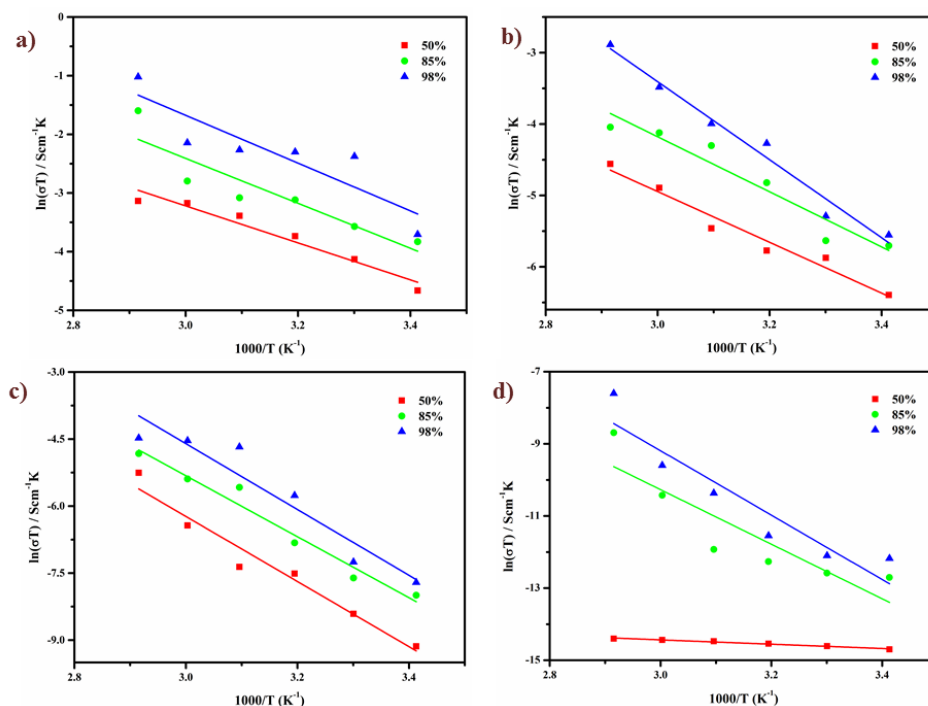


Figure S29. Arrhenius plot of proton conductivity for **SP1** (a), **SP2** (b), **SP3** (c) and **SP4** (d) at 50%, 85% and 98% relative humidity.

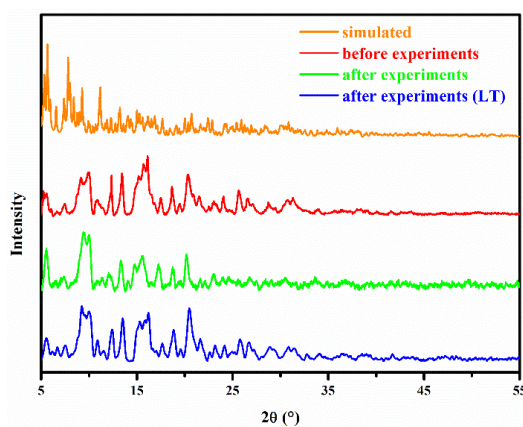


Figure S30. PXRD patterns of **SP1**. **LT** means the sample after proton conduction measurement in the temperature range -30°C to $+30^{\circ}\text{C}$.

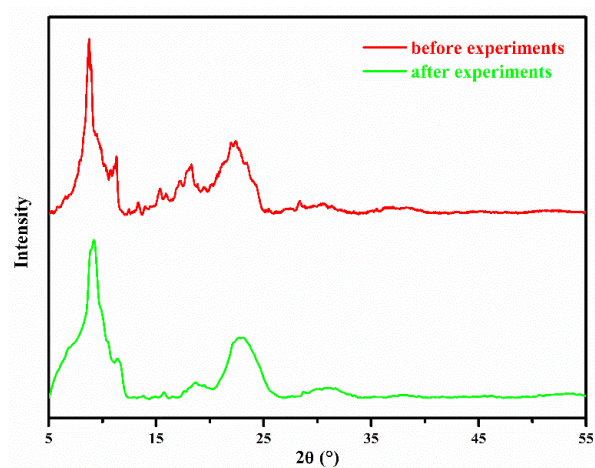


Figure S31. PXRD patterns of SP2.

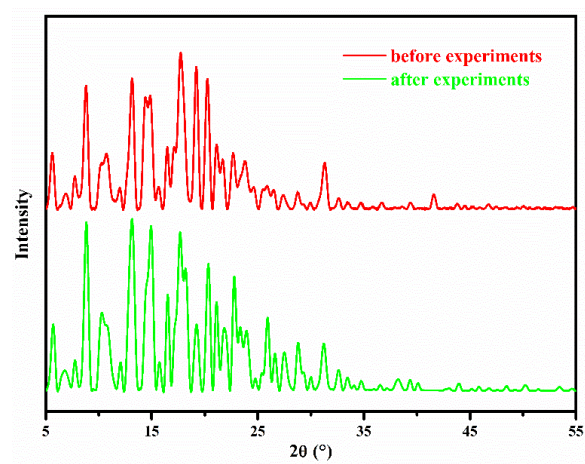


Figure S32. PXRD patterns of SP3.

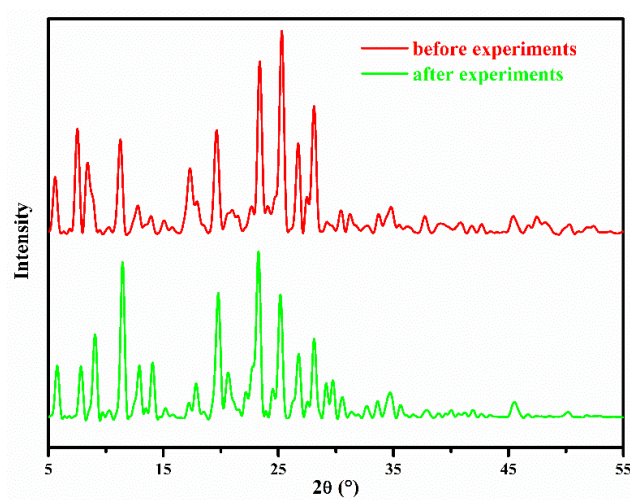


Figure S33. PXRD patterns of SP4.

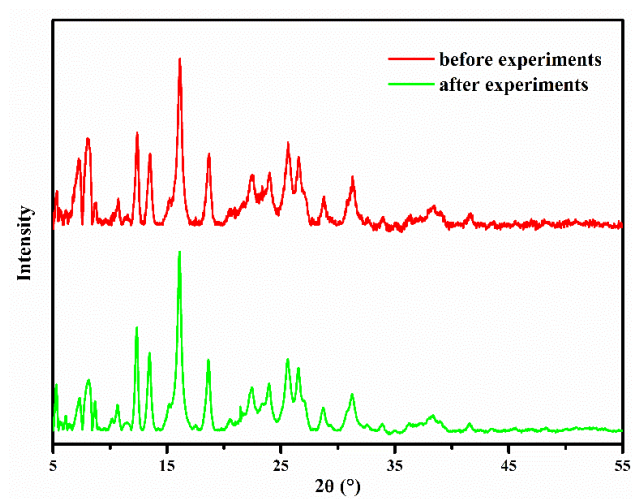


Figure S34. PXRD patterns of DNP@SP1.