

Post-functionalization through covalent modification of organic counter ions: a stepwise and controlled approach for novel hybrid polyoxometalate materials

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Materials and methods

(4-Methylthio)benzaldehyde was purchased from Alfa Aesar. Silver trifluoromethane sulfonate, iodomethane, silicotungstic acid and silicomolybdic acid were purchased from Sigma Aldrich. The compound FPDST was synthesized and characterized by following procedures reported for similar compounds.¹ All the solvents used were of spectroscopic grade. Acetonitrile was distilled over CaH₂ and stored over 4 Å molecular sieves prior to the use.

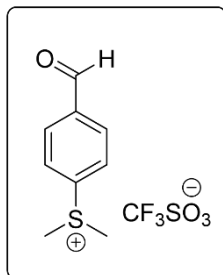
Instruments

FT-IR spectra were recorded on Agilent Technology's Cary 600 Series instrument. ¹H, ¹³C, ¹⁹F and ²⁹Si NMR spectra were recorded on Jeol-JNM 500 MHz NMR spectrometer using DMSO-d₆ solvent and TMS as internal standard. Data are presented as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, m = multiplet), coupling constant J (Hz), integration, and interpretation. ESI-MS spectra were recorded on Bruker HD compact instrument and the data were processed using Bruker Data Analysis software. DRS spectra were recorded on PerkinElmer UV/Vis/NIR Lambda 750 spectrophotometer. A homemade photo reactor with lamp LZC-UVA ($\lambda_{exc} = 350$ nm, P = 8 W) was used for the photo-irradiation of the POM hybrids. The X-Ray Photoelectron Spectroscopy (XPS) of the hybrids were recorded on a Thermo Scientific NEXSA photo-emission spectrometer using Al-K α (1486.6 eV) X-ray radiation. The raw data obtained from the instrument were processed using Avantage software. CHNS(O) elemental analysis was carried out in a Thermo finnigan FLSH EA 1112 elemental analyzer.

X-ray crystallography

Single crystal X-ray diffraction data of hybrids 1 and 2 were collected on an Agilent Super Nova diffractometer, equipped with multilayer optics, monochromatic dual source (Cu and Mo) and Eos CCD detector, using Mo-K α (0.71073 Å) and Cu-K α (1.54184 Å) radiations at 150 K. Data acquisition, reduction and analytical face-index based absorption correction were performed by using CrysAlisPRO program.² The structures were solved with ShelXS³ and refined on F^2 by full matrix least-squares technique using ShelXL³ program provided in Olex² (v.1.2) program package.⁴ Anisotropic displacement parameters were applied for all the atoms, except hydrogen atoms. CCDC 1977039-1977040 contain the supplementary crystallographic data for this paper. These data can be obtained at free of charge via www.ccdc.cam.ac.uk/data_request/cif

Synthesis and characterization of FPDST



To an ice-cooled and stirred solution of (4-methylthio)benzaldehyde (0.50 g, 3.28 mmol) and AgOTf (1.26 g, 4.92 mmol) in anhydrous acetonitrile was added methyl iodide (0.34 ml, 4.92 mmol) under N₂ atmosphere. The stirring was continued at 0 °C for 2 h. After that, the stirring was stopped for 30 min. to settle down the silver iodide (AgI). The AgI was filtered-off and the solvent was removed under reduced pressure to afford FPDST as a viscous liquid. Yield: 0.82 g, 80%. Anal. Calc. for C₁₀H₁₁F₃O₄S₂: C, 37.97%, H, 3.51%, S, 20.27%; found: C, 37.5%, H, 3.2%, S, 19.8%. ¹H NMR (500 MHz, DMSO-d₆): δ_{ppm} 10.13 (s, 1H), 8.26 (d, 2H, *J* = 8.9 Hz, ArH), 8.19 (d, 2H, *J* = 8.95 Hz, ArH), 3.30 (s, 6H, -S(CH₃)₂). ¹³C NMR (125 MHz, DMSO-d₆): δ_{ppm} 193.04, 139.60, 133.36, 131.10, 118.65, 28.47. ¹⁹F NMR (470 MHz, DMSO-d₆): δ_{ppm} -77.67 (3F, s, -CF₃). ESI-MS: Calcd. for C₉H₁₁OS⁺ [M]⁺: 167.05, found: 167.0530. FT-IR (cm⁻¹): 3490 (m), 3031 (sh), 2934 (m), 2851 (w), 1699 (vs), 1594 (vs), 1422 (sh), 1242 (sh), 1159 (vs), 1025 (vs), 812 (sh).

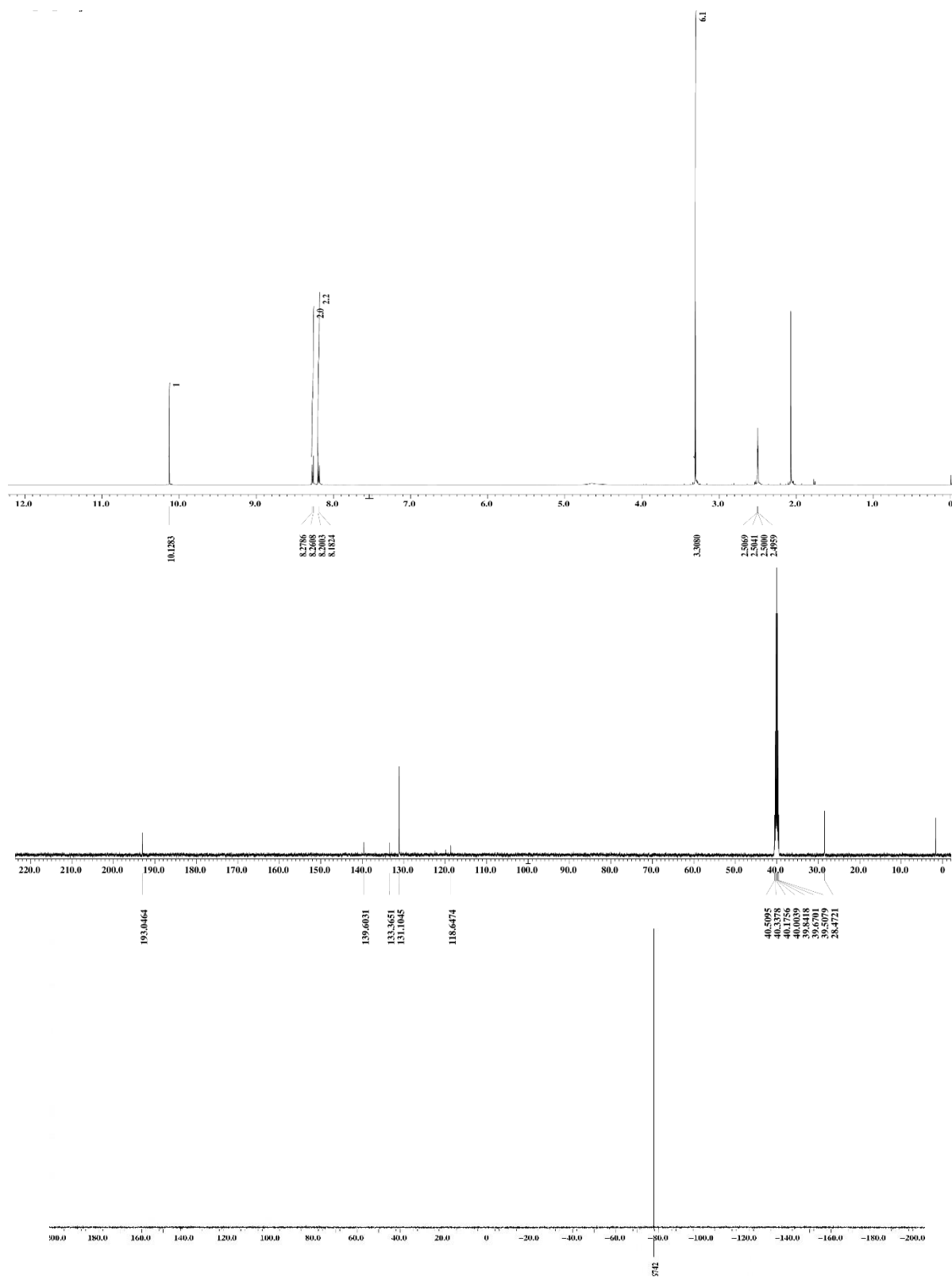


Fig. S1 ¹H, ¹³C and ¹⁹F NMR of FPDST in DMSO-d₆.

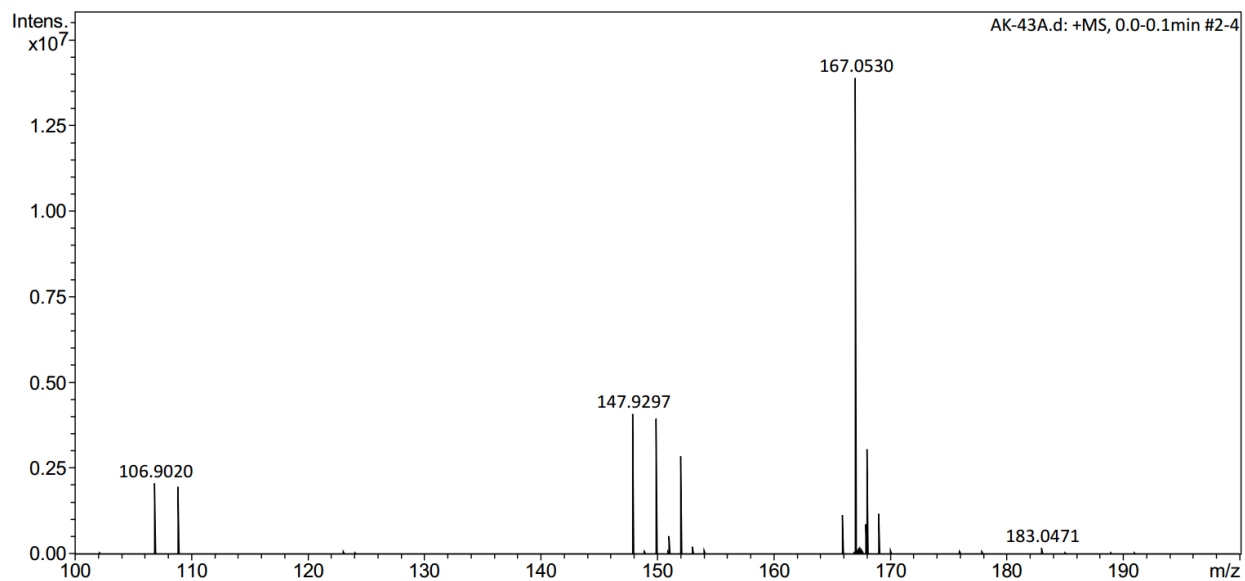


Fig. S2 ESI-MS of FPDST.

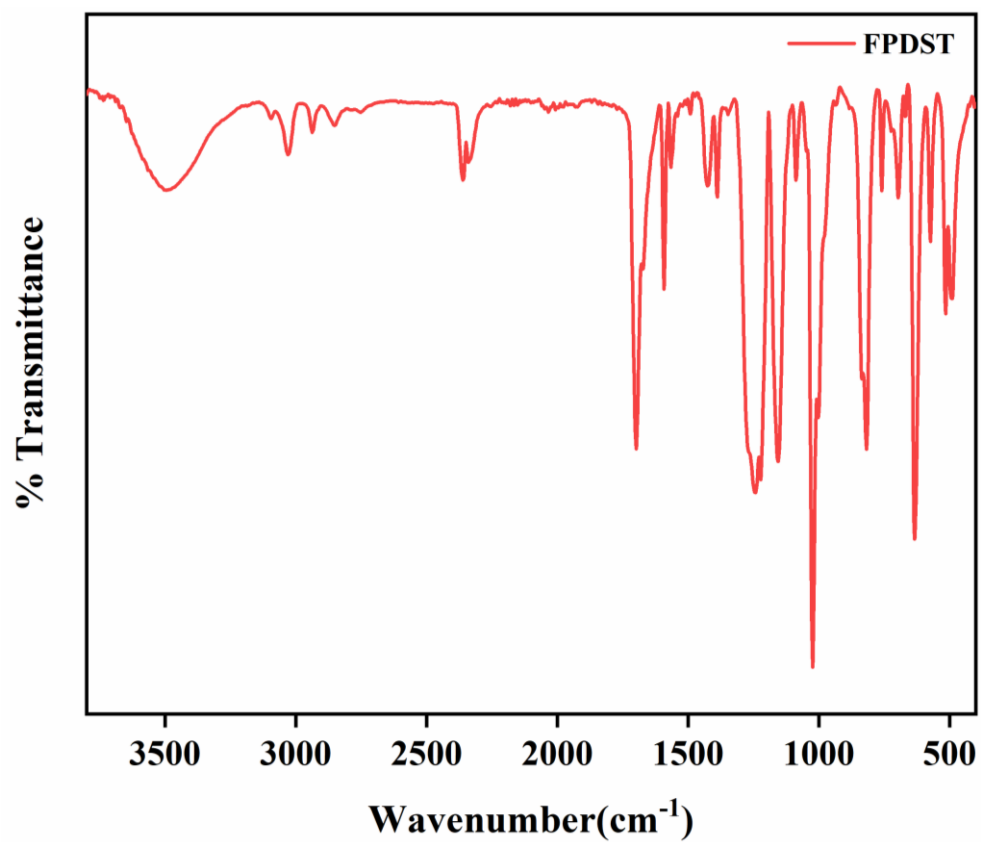


Fig. S3 FT-IR spectrum of FPDST.

1. Synthesis and characterization data of hybrids 1-4

Synthetic procedure for hybrid 1.

In a typical reaction, Keggin type POM, $H_4[SiW_{12}O_{40}]$ (1 g, 0.35 mmol, 1 equiv.) was taken in a mortar and ground to a fine powder. To this powdered POM, FPDST (1.75 mmol, 5 equiv.) was added, and the mixture was ground for 30 minutes at room temperature, until a fine white paste like material is obtained. This material was washed with DI-water, EtOH and Et₂O respectively, followed by centrifugation at 8000 rpm for 10 min. each time. The solid compound thus collected was dried at 40 °C for 12 h. Single crystals of hybrid **1** were grown from DMF solution, by ether diffusion method. Yield: 1.07 g (86%). Anal. Calc. for $(C_9H_{11}OS)_4(SiW_{12}O_{40})$: C, 12.2%, H, 1.25%, S, 3.62%; found: C, 11.9%, H, 1.5%, S, 3.8%. ¹H NMR (500 MHz, DMSO-d₆): δ_{ppm} 10.13 (s, 1H), 8.28 (d, 2H, *J* = 8.25 Hz, ArH), 8.20 (d, 2H, *J* = 8.25 Hz, ArH), 3.31 (s, 6H, -S(CH₃)₂). ²⁹Si NMR (100 MHz, DMSO-d₆): δ_{ppm} -79.58. FT-IR (cm⁻¹) 3087, 3017, 2929 (C-H), 1702 (C=O), 1594, 1576, 1424 (ArC=C), 969 (W=O), 918 (Si-O) 880, 789 (W-O-W).

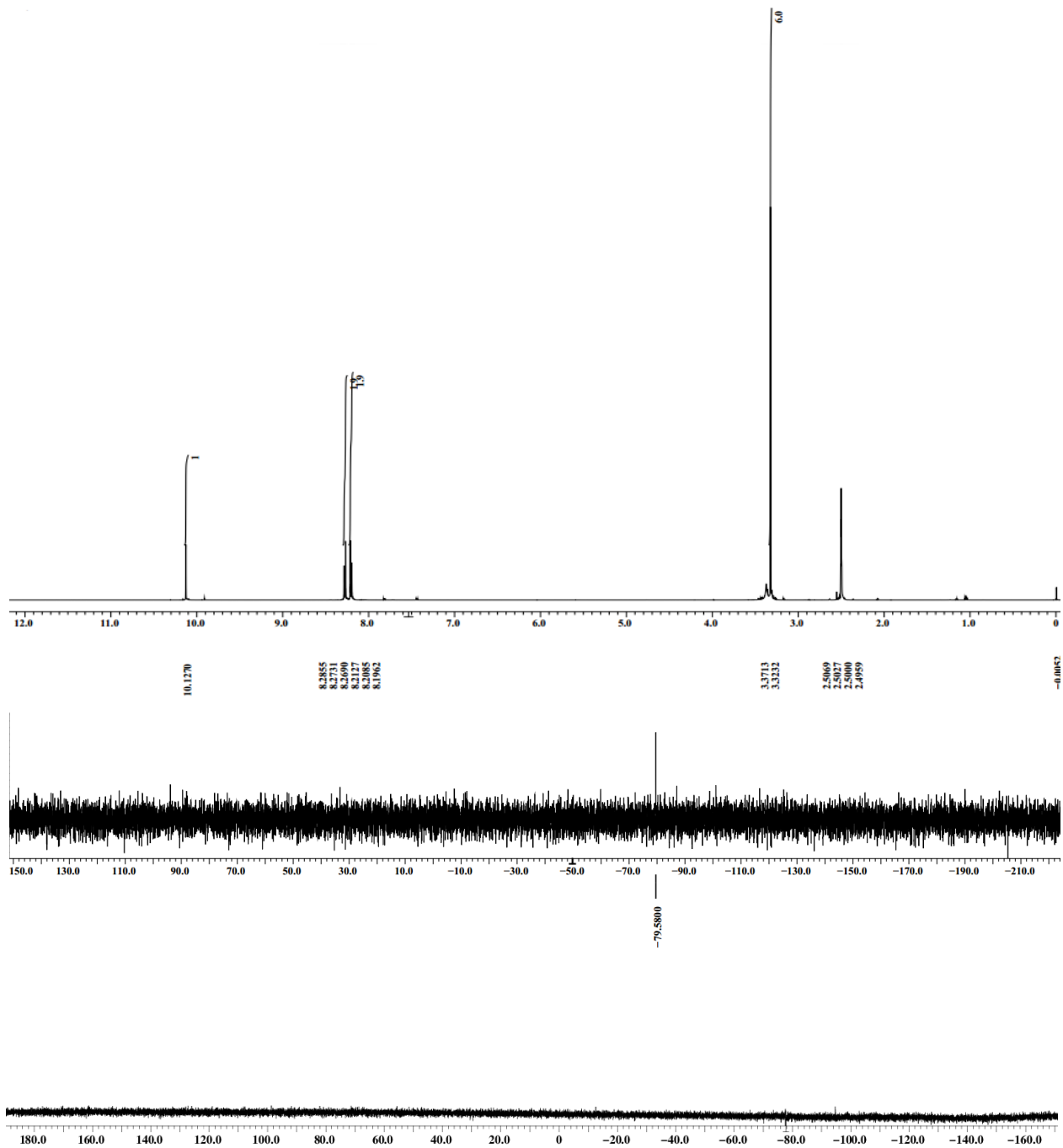


Fig. S4 ¹H, ²⁹Si and ¹⁹F NMR of hybrid **1** in DMSO-d₆.

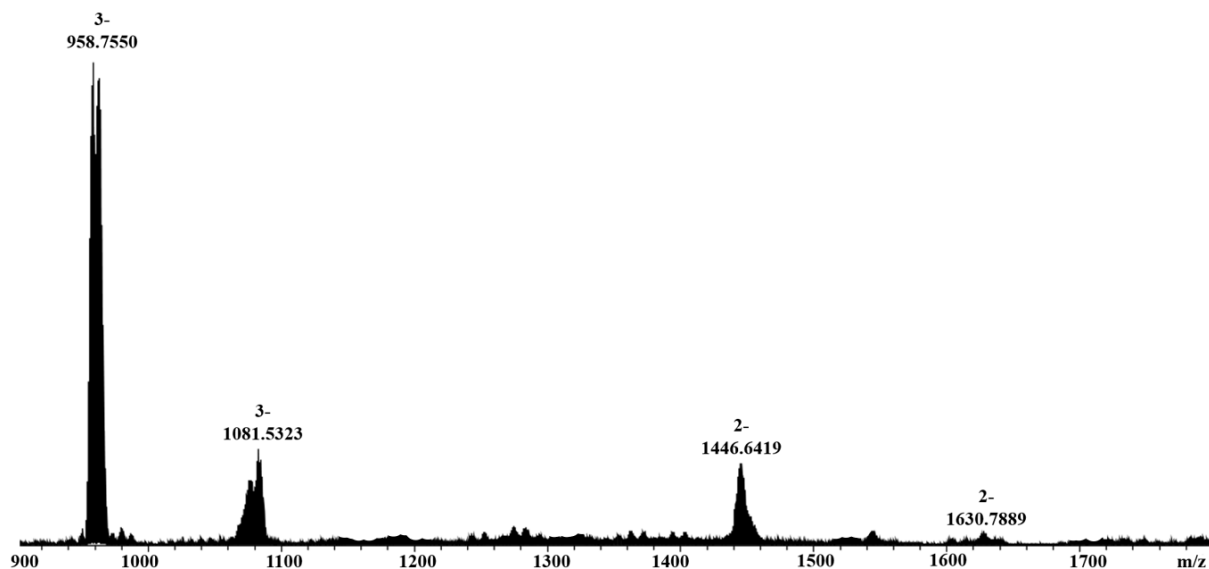


Fig S5 Negative mode ESI-MS data of hybrid 1 using MeCN as solvent.

Table S1. Detailed assignment of mass spectral data for hybrid 1.

Sr. No.	Ion (Hybrid 1)	m/z calculated	m/z observed
1.	$\text{H}[\text{SiW}_{12}\text{O}_{40}]^{3-}$	958.38	958.7550
2.	$[\text{SiW}_{12}\text{O}_{40}]^{3-}(\text{C}_9\text{H}_{11}\text{OS})_2 \cdot 2\text{H}_2\text{O}$	1081.56	1081.5323
3.	$[\text{H}_2\text{SiW}_{12}\text{O}_{40}]^{2-}(\text{H}_2\text{O})$	1447.085	1446.6419
4.	$[\text{SiW}_{12}\text{O}_{40}]^{2-}(\text{C}_9\text{H}_{11}\text{OS})_2 \cdot 3\text{H}_2\text{O}$	1631.34	1630.7889

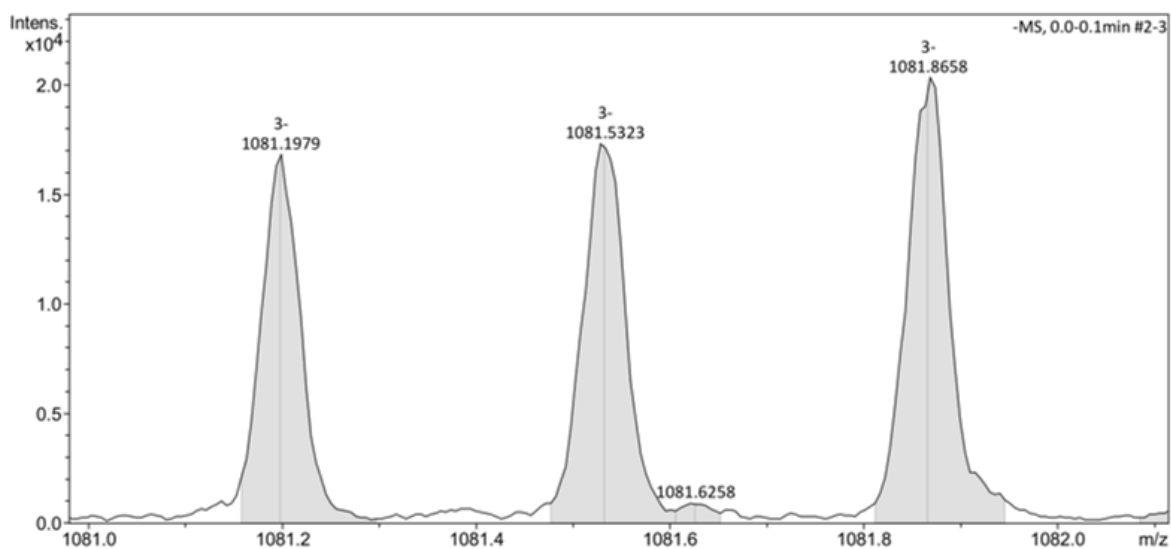


Fig. S6 Zoom-in of the peak centered at m/z 1081.5323 in the ESI-MS spectrum of hybrid 1 to show its -3 charge.

Synthetic procedure for hybrid 2.

For hybrid **2**, Keggin type POM, $H_4[SiMo_{12}O_{40}]$ (865 μ L, 0.55 mmol, 1 equiv.) was taken in a mortar and FPDST (2.75 mmol, 5 equiv.) was added to it. The mixture was ground for 30 min. at room temperature, until a fine yellow paste like material is obtained. This paste like material was subjected to the same kind of treatment like that used in the case of hybrid **1**. Single crystals of hybrid **2** were also grown from its DMF solution, by ether diffusion method. Yield: 981 mg (72 %). Anal. Calc. for $(C_9H_{11}OS)_4(SiMo_{12}O_{40})$: C, 17.37%, H, 1.78%, S, 5.15%; found: C, 17.0%, H, 2.1%, S, 5.3%. 1H NMR (500 MHz, DMSO- d_6): δ_{ppm} 10.13 (s, 1H), 8.27 (d, 2H, $J = 8.25$ Hz, ArH), 8.20 (d, 2H, $J = 8.25$ Hz, ArH), 3.32 (s, 6H, $-S(CH_3)_2$). ^{29}Si NMR (100 MHz, DMSO- d_6): δ_{ppm} -79.79. FT-IR (cm^{-1}) 3085, 3015, 2927 (C-H), 1702 (C=O), 1592, 1575, 1419 (ArC=C), 946 (Si-O), 897 (Mo=O), 787,533 (Mo-O-Mo).

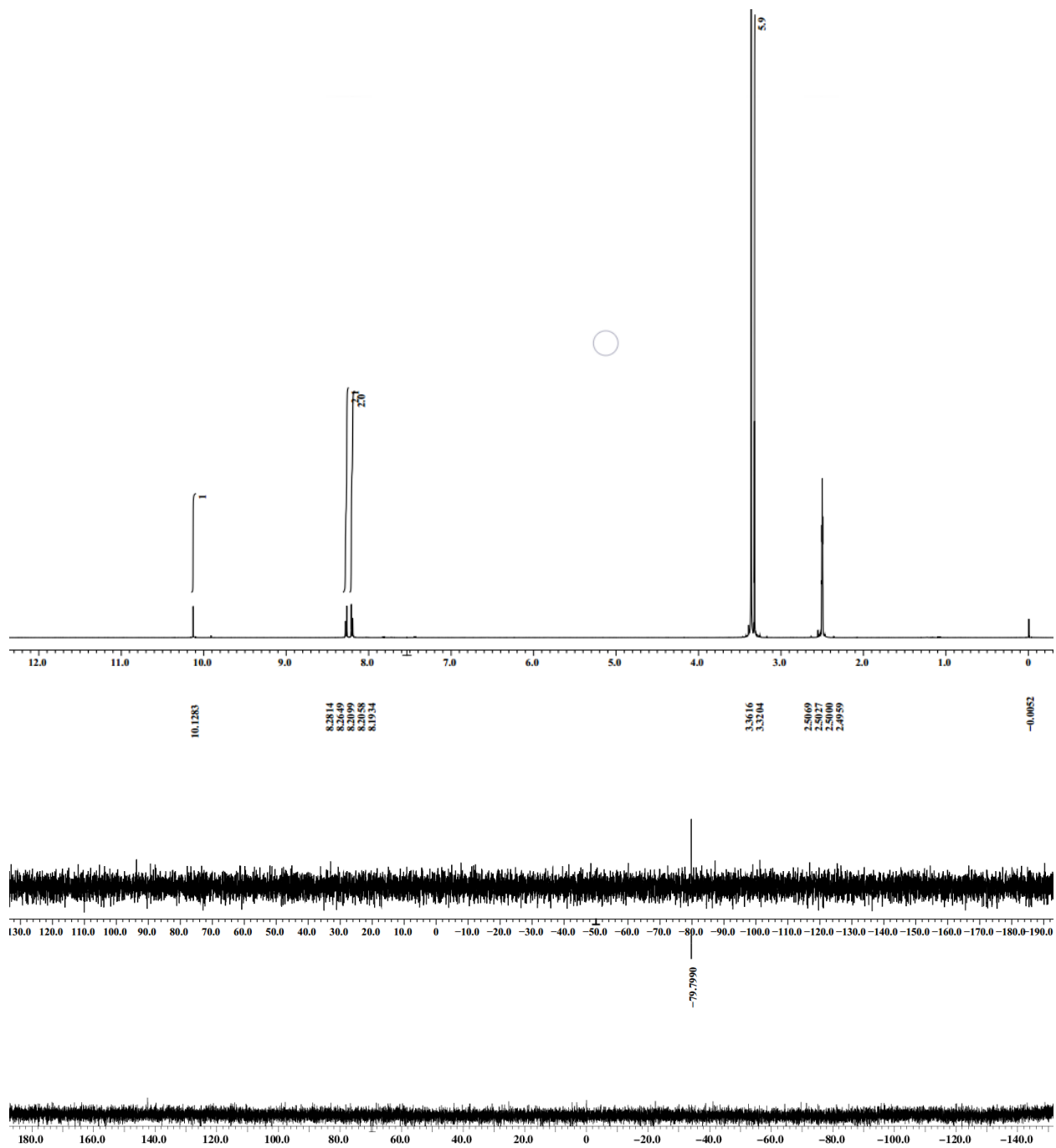


Fig. S7 ¹H, ²⁹Si and ¹⁹F NMR of hybrid 2 in DMSO-d₆.

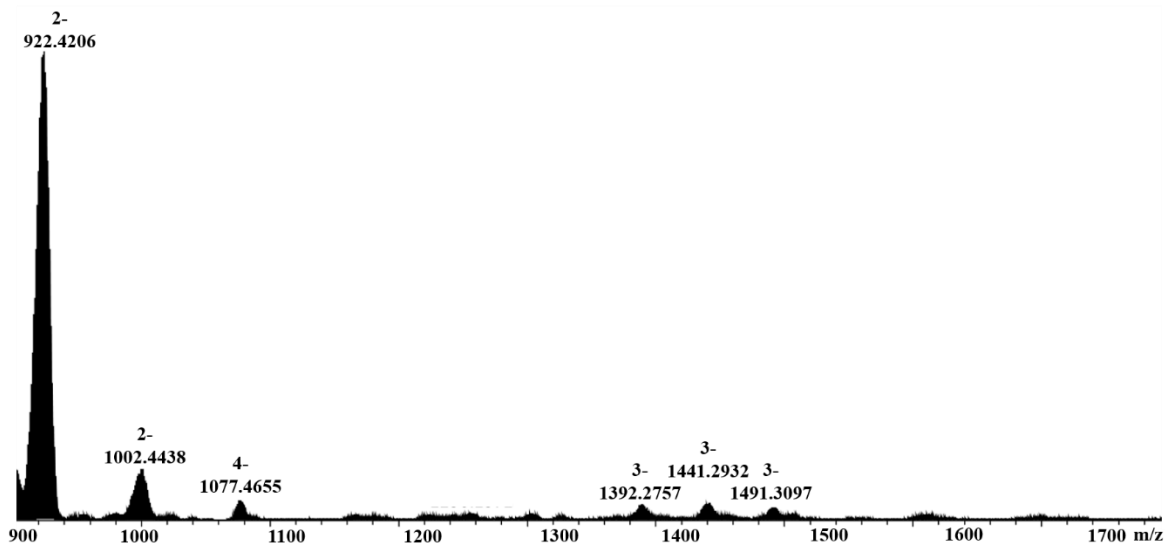


Fig. S8 Negative mode ESI-MS data of hybrid **2** using MeCN as solvent.

Table S2. Detailed assignment of mass spectral data for hybrid **2**.

Sr. No.	Ion (Hybrid 2)	m/z calculated	m/z observed
1.	$[\text{NaHSiMo}_{12}\text{O}_{40}]^{2-}$	921.67	922.4206
2.	$[\text{HSiMo}_{12}\text{O}_{40}]^{2-}(\text{C}_9\text{H}_{11}\text{OS})(\text{H}_2\text{O})$	1002.805	1002.4438
3.	$[\text{SiMo}_{12}\text{O}_{40}]_2^{4-}(\text{C}_9\text{H}_{11}\text{OS})_4$	1076.91	1077.4655
4.	$[\text{HSiMo}_{12}\text{O}_{40}]_2^{3-}(\text{C}_9\text{H}_{11}\text{OS})_3 \cdot 2\text{H}_2\text{O}$	1392.82	1392.2757
5.	$\text{H}[\text{SiMo}_{12}\text{O}_{40}]_2^{3-}(\text{C}_9\text{H}_{11}\text{OS})_4(\text{H}_2\text{O})$	1442.23	1441.2932
6.	$[\text{SiMo}_{12}\text{O}_{40}]_2^{3-}(\text{C}_9\text{H}_{11}\text{OS})_5$	1491.64	1491.3097

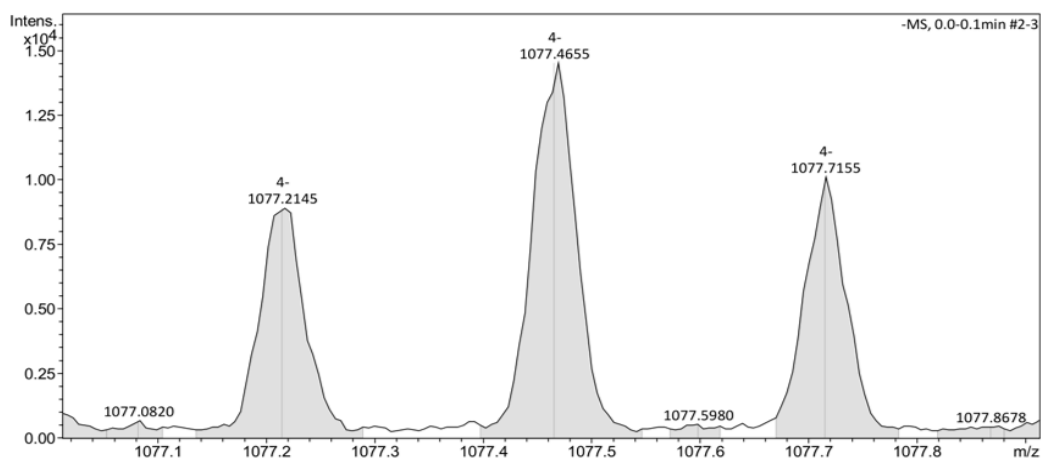


Fig. S9 Zoom-in of the peak centered at m/z 1077.2145 in the ESI-MS spectrum of hybrid **2** to show its -4 charge.

Synthetic procedure for hybrid 3.

Hybrid **1** (700 mg, 0.197 mmol, 1 equiv.), was taken in a mortar and ground into fine powder. To this powdered hybrid **1**, p-anisidine (1.182 mmol, 6 equiv.) was added and ground together until the material showed visible color change from white to brown and started sticking to the mortar walls. Methanol was added in small quantity to moist the material and the paste thus formed was ground again for 30 min. at room temperature. Finally, the material formed was washed with MeOH and Et₂O respectively, followed by centrifugation at 8000 rpm for 10 min. each time. The solid product thus collected was dried at 40 °C for 12 h. Yield: 713 mg (91.31%). Anal. Calc. for (C₁₆H₁₈NOS)₄(SiW₁₂O₄₀): C, 19.4%, H, 1.83%, N, 1.41%, S, 3.24%; found: C, 19.2%; H, 2.2%; N, 1.5%, S, 2.9%. ¹H NMR (500 MHz, DMSO-d₆): δ_{ppm} 8.80 (s, 1H), 8.19 (q, 4H, ArH), 7.39 (d, 2H, *J* = 8.95 Hz), 7.02 (d, 2H, *J* = 8.90 Hz, ArH), 3.79 (s, 3H, -OCH₃), 3.32 (s, 6H, -S(CH₃)₂). ²⁹Si NMR (100 MHz, DMSO-d₆): δ_{ppm} -78.52. FT-IR (cm⁻¹) 3075, 3016, 2927 (C-H), 1650 (C=N), 1585, 1509, 1431, 1419 (ArC=C), 1464, 1440 (C-H bending), 1336 (C-N), 1304 (C-O-C), 1027, 920 (Si-O), 971 (W=O), 883, 793 (W-O-W).

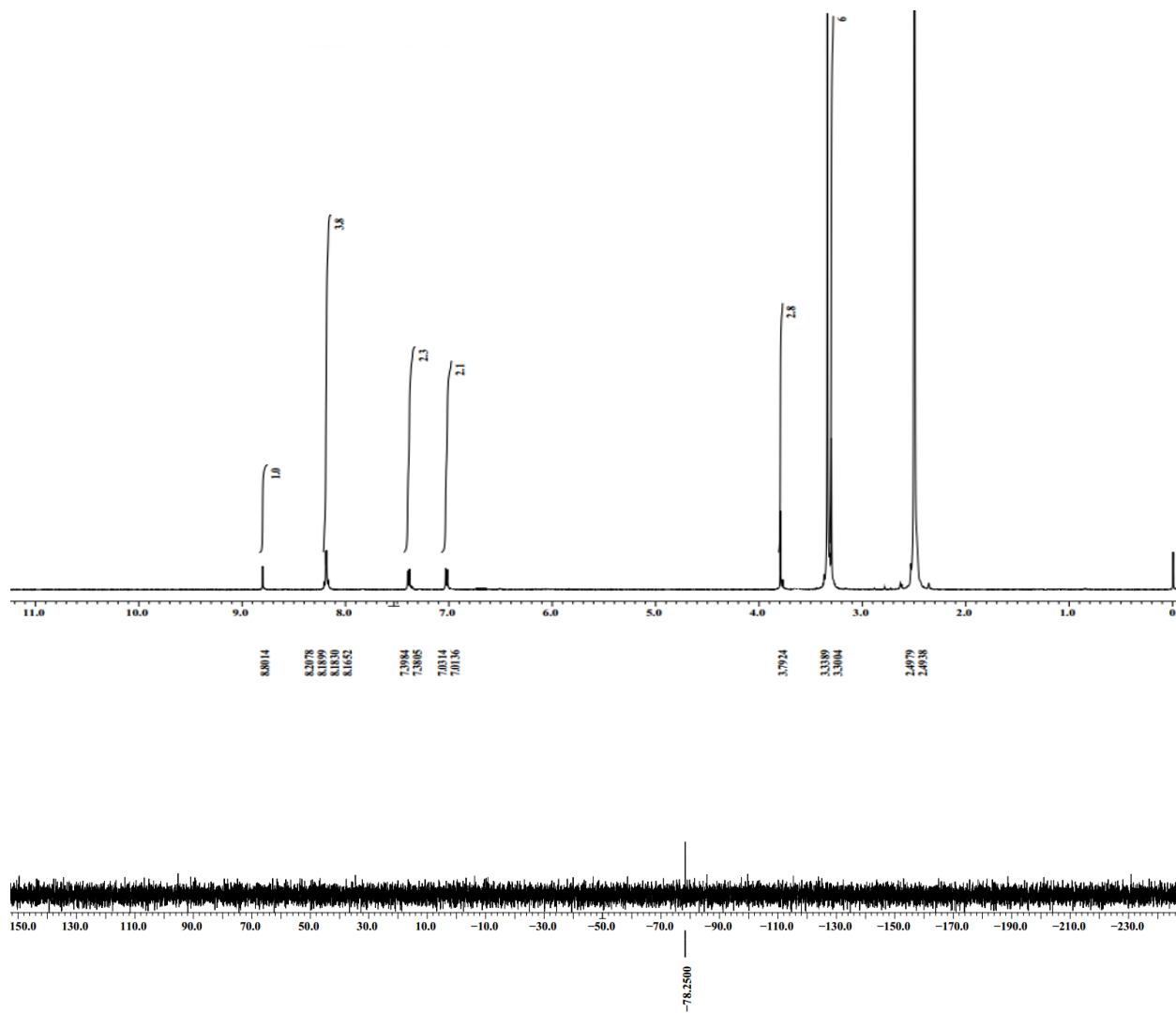


Fig. S10 ¹H and ²⁹Si NMR of hybrid **3** in DMSO-d₆.

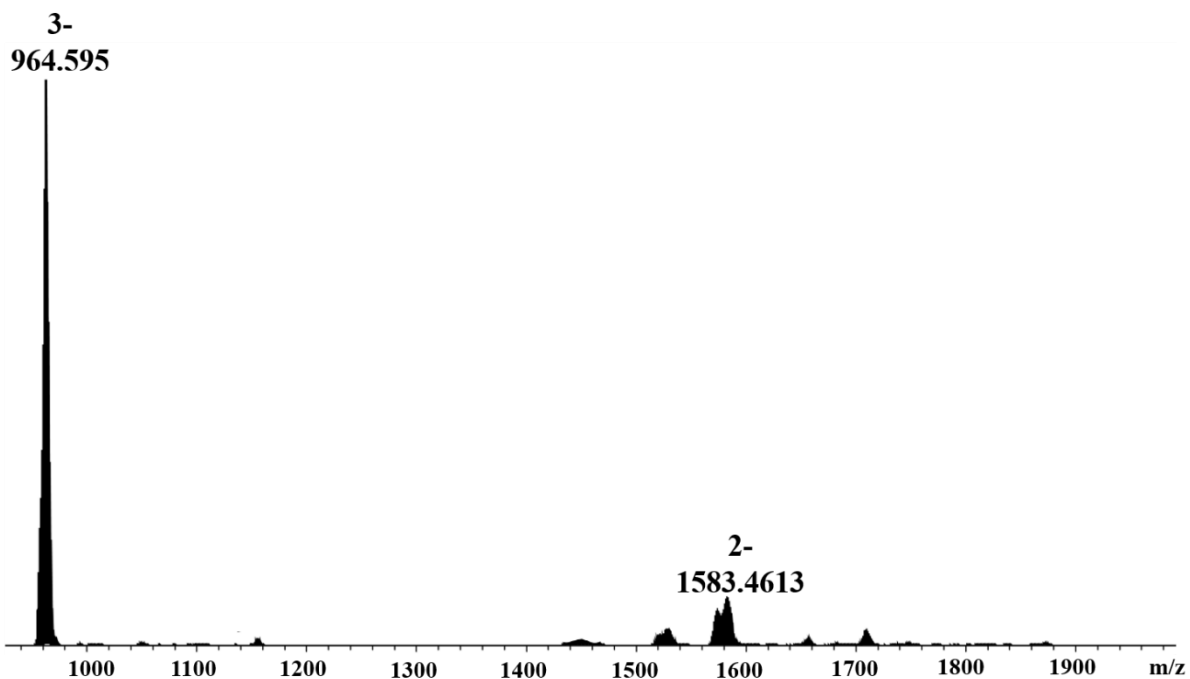


Fig. S11 Negative ion mode ESI-MS data for hybrid **3** using MeCN as solvent.

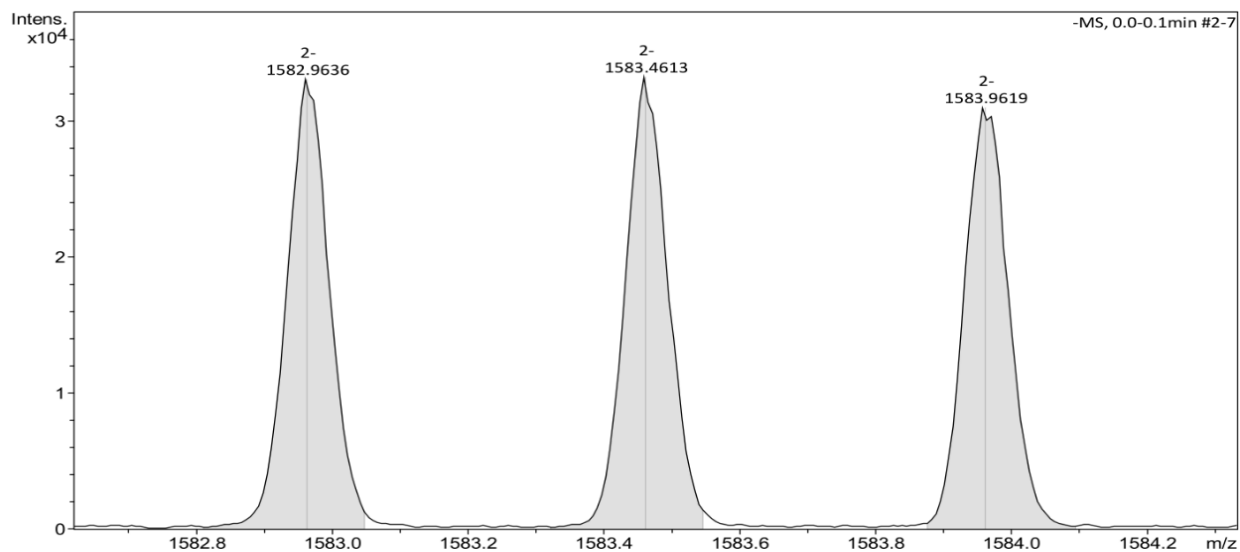


Fig. S12 Zoom-in of the peak centered at m/z 1583.4613 in the ESI-MS spectrum of hybrid **3** to show its -2 charge.

Table S3. Detailed assignment of mass spectral data for hybrid **3**.

Sr.No.	Ion (Hybrid 3)	m/z calculated	m/z observed
1.	$[\text{HSiW}_{12}\text{O}_{40}]^{3-}(\text{H}_2\text{O})$	964.38	964.595
2.	$[\text{HSiW}_{12}\text{O}_{40}]^{2-}(\text{C}_{16}\text{H}_{18}\text{NOS})(\text{H}_2\text{O})$	1582.775	1583.4813

Synthetic procedure for hybrid 4.

Hybrid **2** (700 mg, 0.281 mmol), was taken in a mortar and ground into a fine powder. To this powdered hybrid **2**, p-anisidine (1.686 mmol, 6 equiv.) was added and ground together until the material showed visible color change from yellow to green, and started sticking to the mortar walls. Methanol was added in small quantity to moist the material and the paste thus formed was again ground for 30 min at room temperature. Finally, the material formed was washed with MeOH and Et₂O respectively, followed by centrifugation at 8000 rpm for 10 min. each time. The solid product thus collected was dried at 40 °C for 12 h. Yield: 739 mg (90.2 %). Anal. Calc. for (C₁₆H₁₈NOS)₄(SiMo₁₂O₄₀): C, 26.42%, H, 2.5%, N, 1.93%, S, 4.41%; found: C, 26.6%, H, 2.8%, N, 2.2%, S, 4.1%. ¹H NMR (500 MHz, DMSO-d₆): δ_{ppm} 8.89 (s, 1H), 8.27 (s, 3H, ArH), 7.47 (s, 3H, ArH), 7.11 (s, 2H, ArH), 3.88 (s, 3H, -OCH₃), 3.36 (s, 6H, -S(CH₃)₂). ²⁹Si NMR (100 MHz, DMSO-d₆): δ_{ppm} -79.48. FT-IR (ν_{max} in cm⁻¹) 3063, 3006, 2958, 2838 (C-H), 1651 (C=N), 1585, 1510, 1409 (ArC=C), 1460, 1440 (C-H bending), 1335 (C-N), 1260 (C-O-C), 1026, 946 (Si-O), 895 (Mo=O), 791, 532 (Mo-O-Mo).

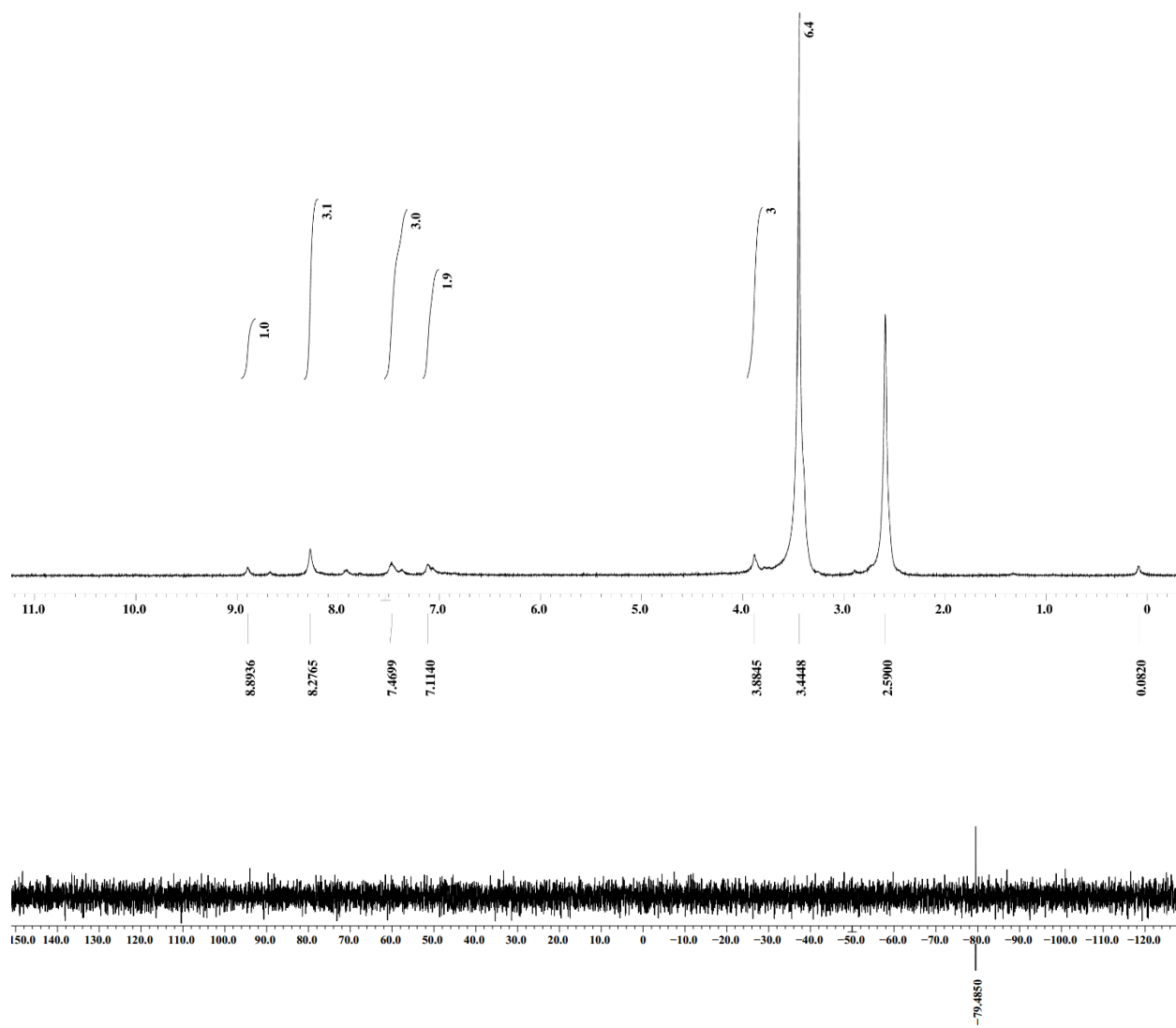


Fig. S13 ¹H and ²⁹Si NMR of hybrid 4 in DMSO-d₆.

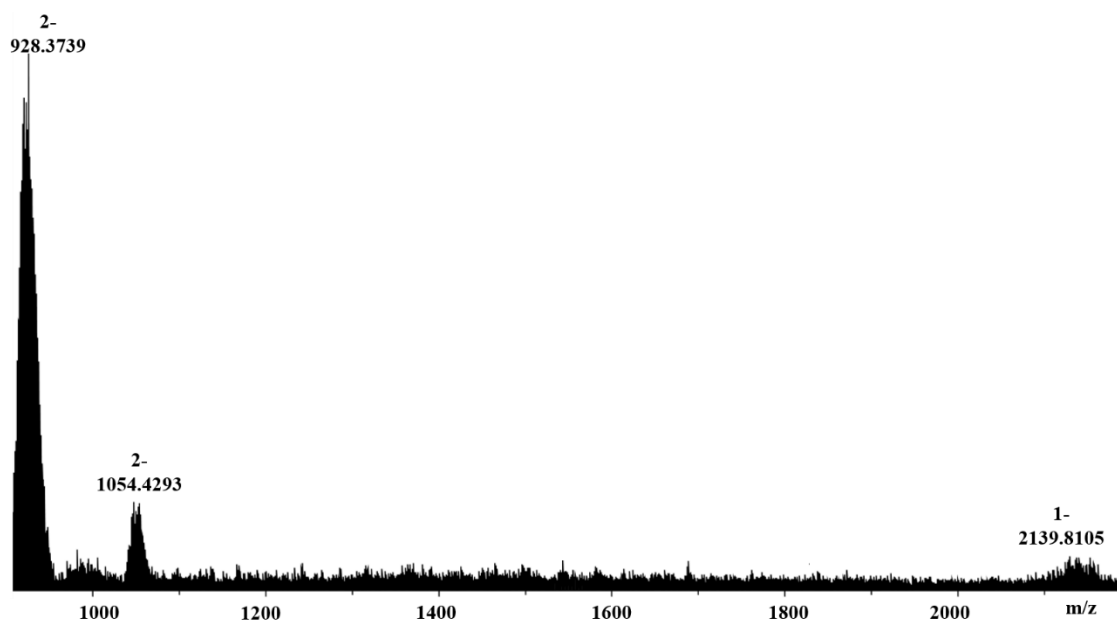


Fig. S14 Negative mode ESI-MS data for hybrid **4** using MeCN as solvent.

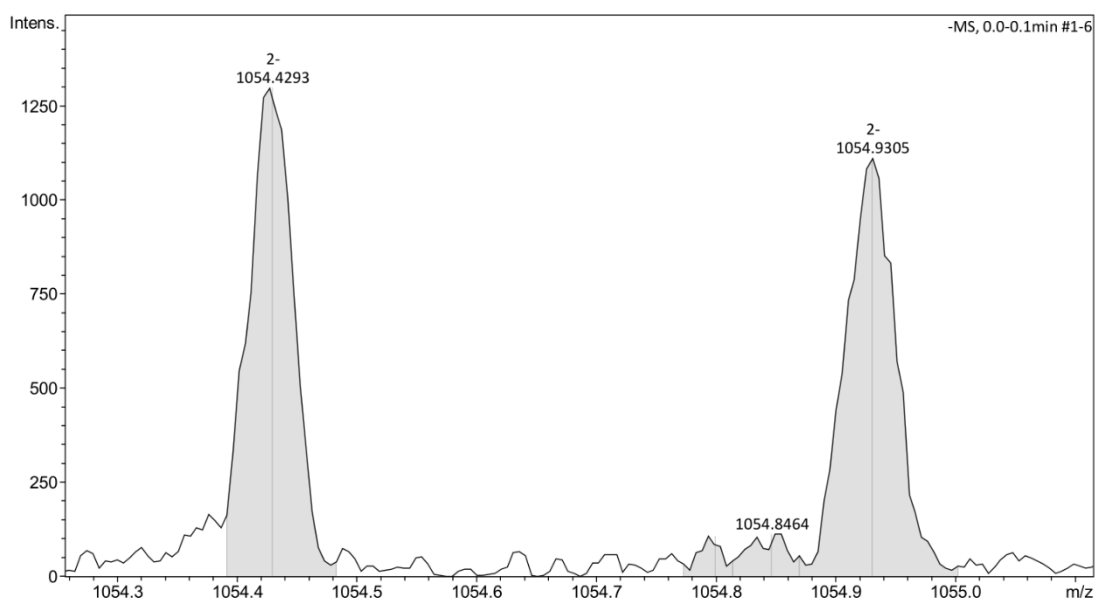


Fig. S15 Zoom-in of the peak centered at m/z 1054.4293 in the ESI-MS spectrum of hybrid **4** to show its -2 charge.

Table S4. Detailed assignment of mass spectral data for hybrid **4**.

Sr. No.	Ion (Hybrid 4)	m/z calculated	m/z observed
1.	$[\text{H}_2\text{SiMo}_{12}\text{O}_{40}]^{2-} \cdot 2\text{H}_2\text{O}$	928.695	928.3739
2.	$[\text{HSiMo}_{12}\text{O}_{40}]^{2-} (\text{C}_{16}\text{H}_{18}\text{NOS}) (\text{H}_2\text{O})$	1055.9301	1054.4293
3.	$[\text{Na}_2\text{HSiMo}_{12}\text{O}_{40}]^{1-} (\text{C}_{16}\text{H}_{18}\text{NOS})$	2138.8155	2139.8105

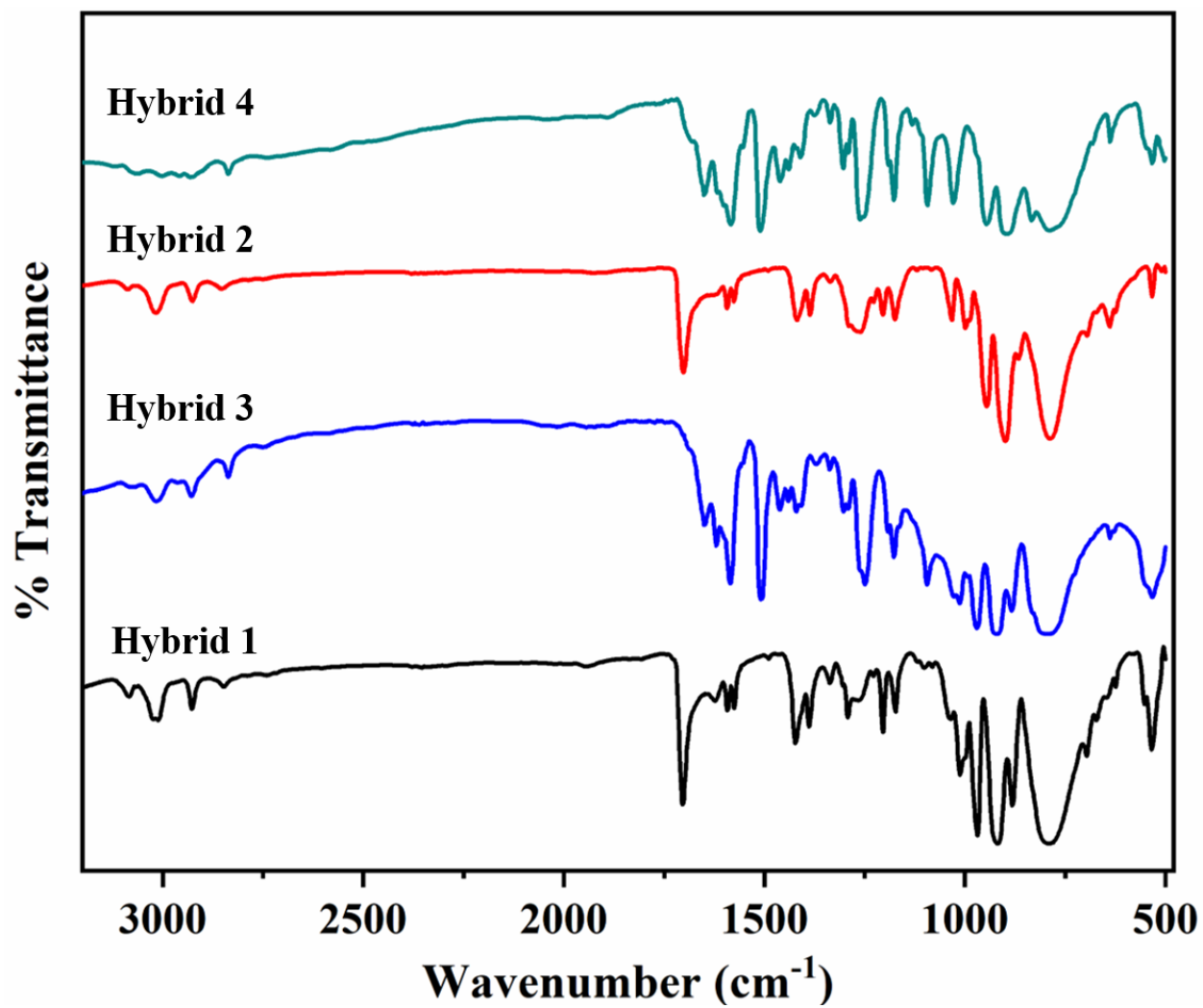
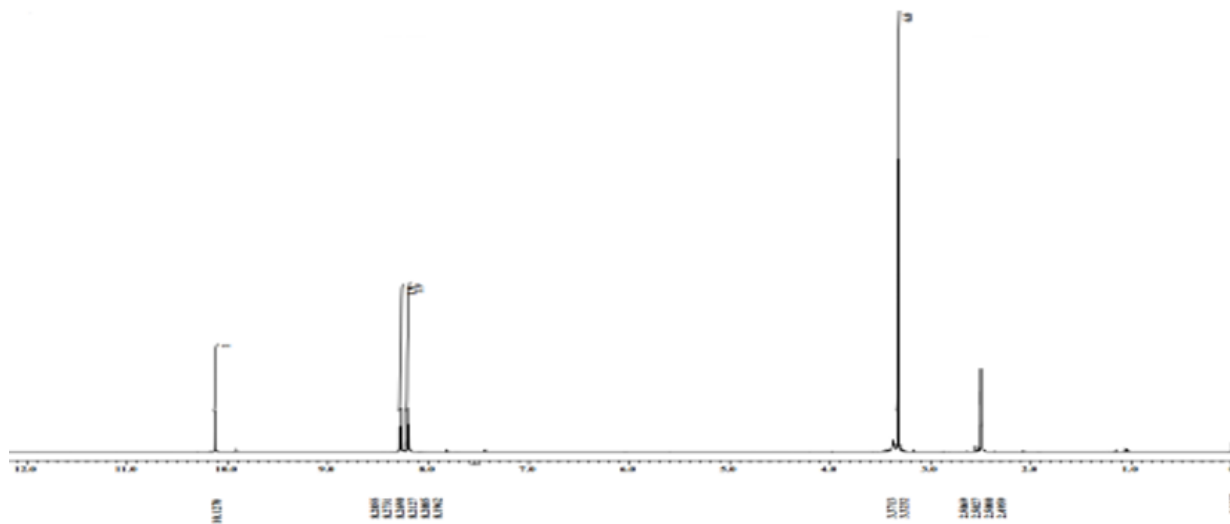
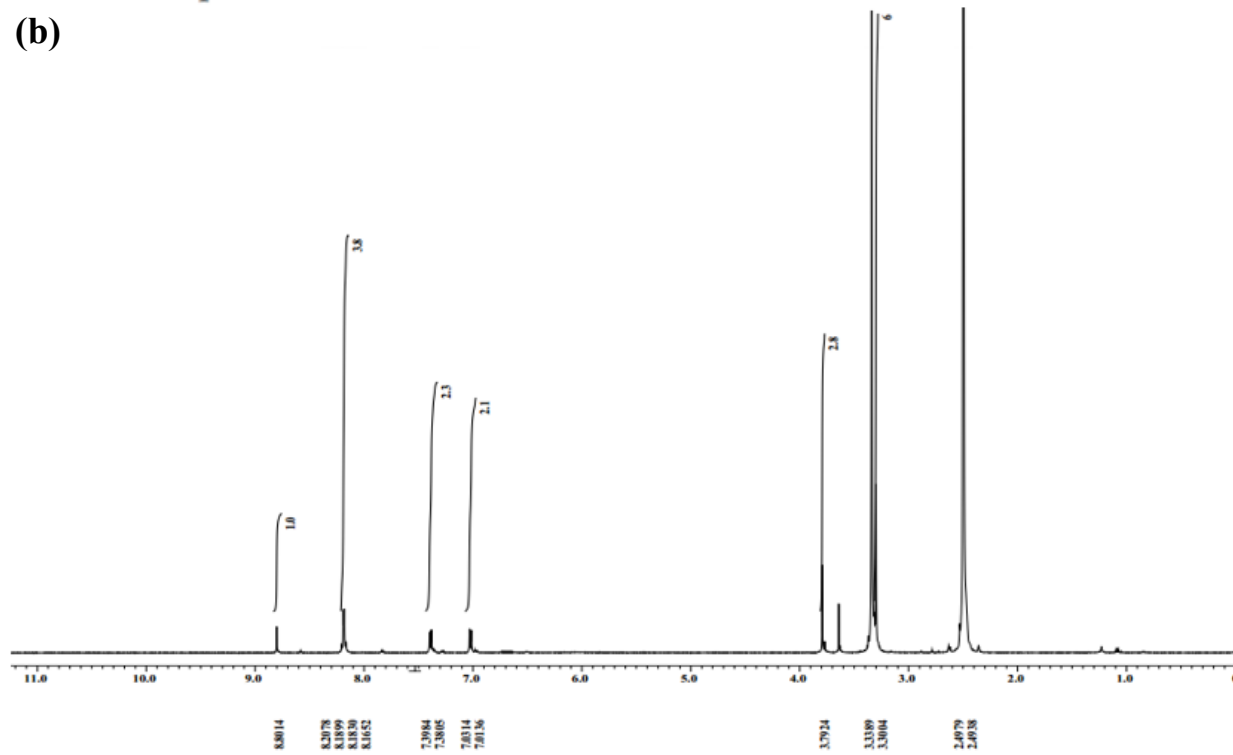


Fig. S16 FT-IR spectra of hybrids 1-4.

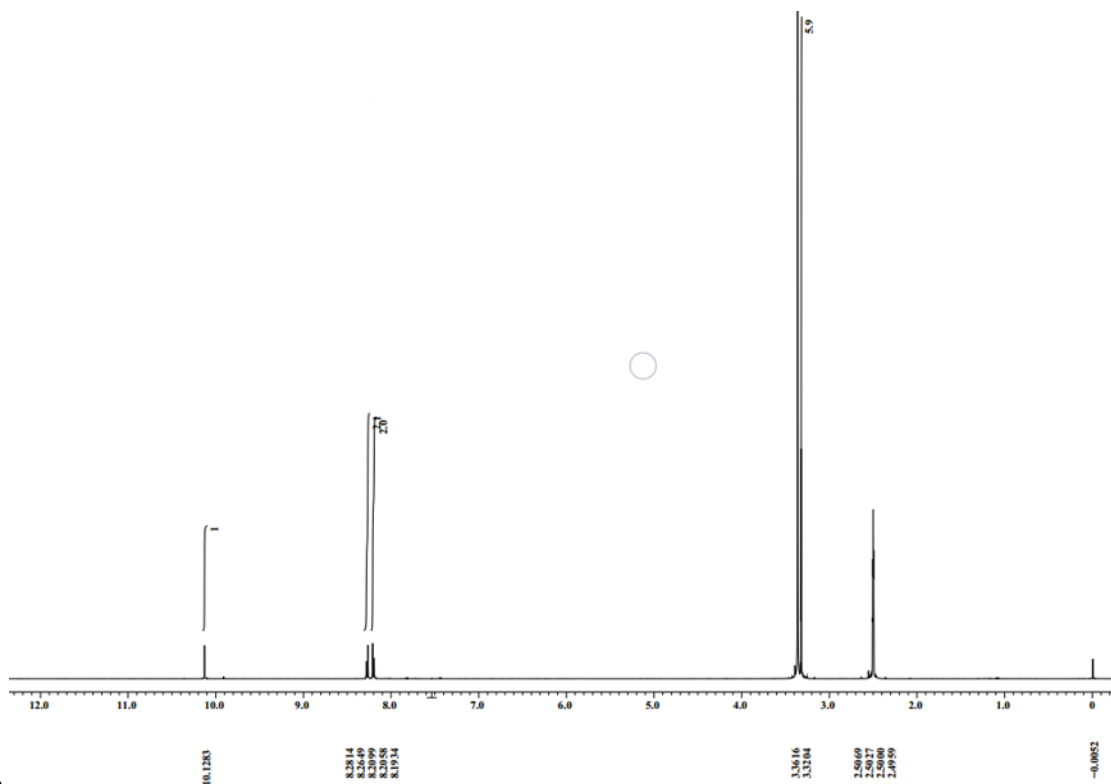
(a)



(b)



(c)



(d)

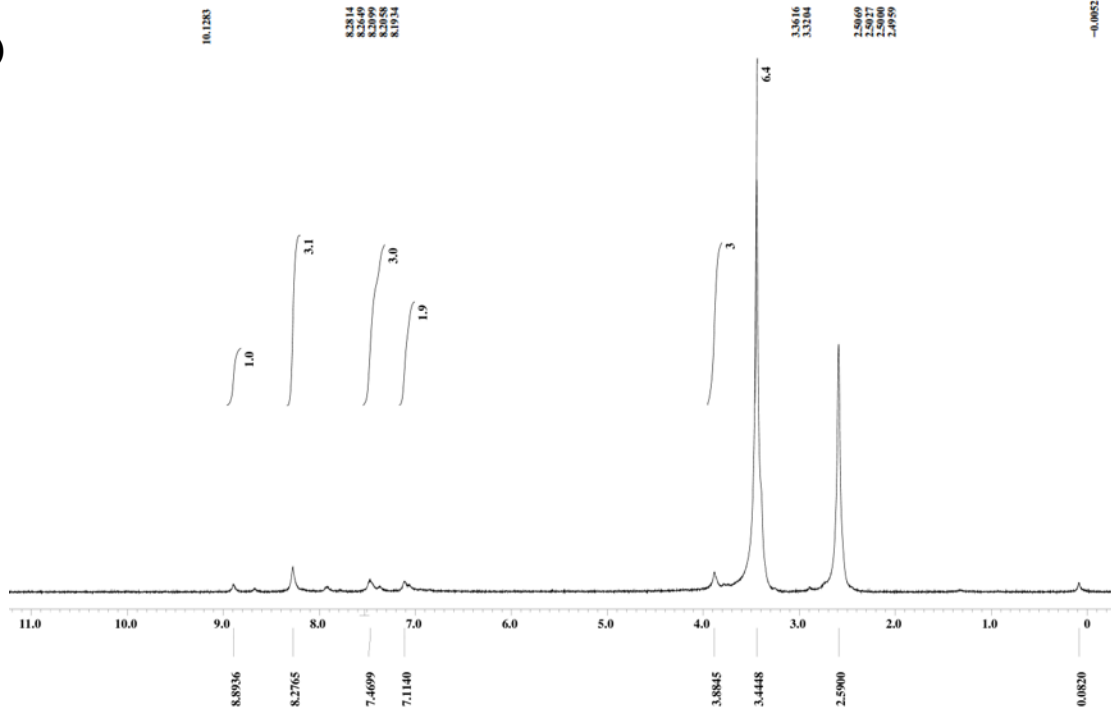


Fig. S17 ¹H NMR spectra of (a) hybrid 1, (b) hybrid 3, (c) hybrid 2 and (d) hybrid 4.

Table S5. Crystallographic data and structure refinement parameters of hybrid **1** and **2**.

	1	2
Empirical Formula	C ₄₂ H ₅₈ N ₂ O ₄₆ S ₄ SiW ₁₂	C ₄₂ H ₅₈ Mo ₁₂ N ₂ O ₄₆ S ₄ Si
Formula Weight	3689.43	2634.51
T/K	150.00(10)	150.00(10)
Wavelength/ Å	0.71073	0.71073
Crystal System	triclinic	triclinic
Space group	P-1	P-1
a (Å)	13.3509(8)	13.3411(13)
b (Å)	14.4698(7)	14.4694(9)
c (Å)	19.8148(11)	19.6679(17)
α (°)	92.730(4)	93.167(6)
β (°)	101.278(5)	100.730(8)
γ (°)	104.065(5)	104.086(7)
V(Å ³)	3623.2(3)	3597.9(5)
Z	2	2
D _c (Mg mm ⁻³)		
μ (mm ⁻¹)	19.193	2.251
F (000)	2764.0	2764.0
Crystal Size (mm ³)	0.237x 0.088x 0.068	0.237 × 0.088 × 0.068
2θ (°)	3.44 to 56.92	3.42 to 56.94°
Reflections collected	19311	19936
Independent reflections	14724[R(int) = 0.0360]	15426[R(int) = 0.0480]
Data/restraints/parameters	14724/0/966	15426/0/976
Goodness-of-fit on F ²	1.026	1.074
Final R Indices[I > 2σ(I)]	R ₁ = 0.0602, wR ₂ = 0.1408	R ₁ = 0.0812, wR ₂ = 0.2030
R indices (all data)	R ₁ = 0.0846, wR ₂ = 0.1625	R ₁ = 0.1049, wR ₂ = 0.2349
Largest diff. peak and hole (e.Å ⁻³)	4.02/-4.12	6.13/-3.51

Details of photochromism studies

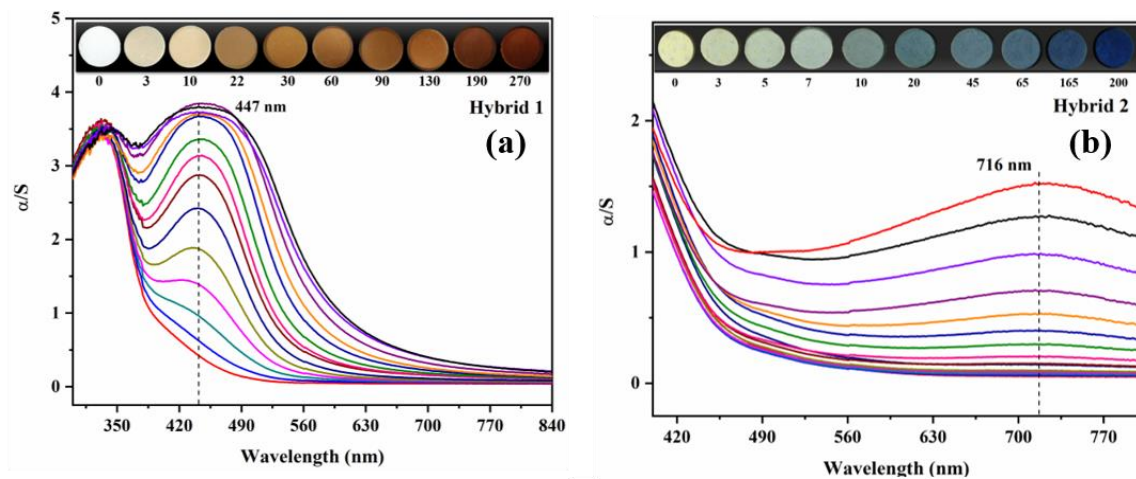


Fig. S18 Kubelka-Munk transformed reflectivity of (a) hybrid 1 and (b) hybrid 2 after irradiation with 365 nm UV. Inset: Color change of hybrids with time.

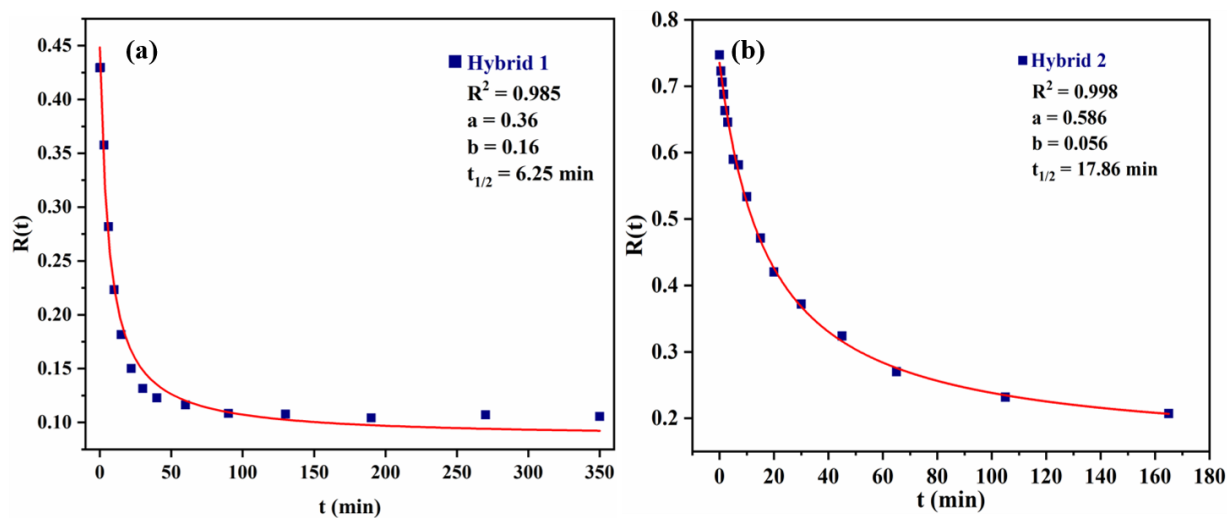


Fig. S19 Reflectivity $R(t)$ vs time (t) plots for (a) hybrid **1** and (b) hybrid **2**.

Table S6. Optical characteristics and coloration kinetics parameters of hybrids **1** and **2**.

	Hybrid 1	Hybrid 2
λ_{\max} (nm) ^p	447	716
$R^{\lambda_{\max}}$ (0) ^q	0.429	0.746
a^r	0.36	0.586
b^r	0.16	0.056
R^{2s}	0.985	0.998
$t_{1/2}^t$	6.25	17.86

^pPhoto-induced absorption band wavelength.

^qReflectance value before UV irradiation ($t = 0$) at λ_{\max} .

^rSalient coloration kinetic parameter.

^sRegression coefficient.

^tHalf-life time (min.) of photochromic process.

XPS spectra of hybrids 1-4.

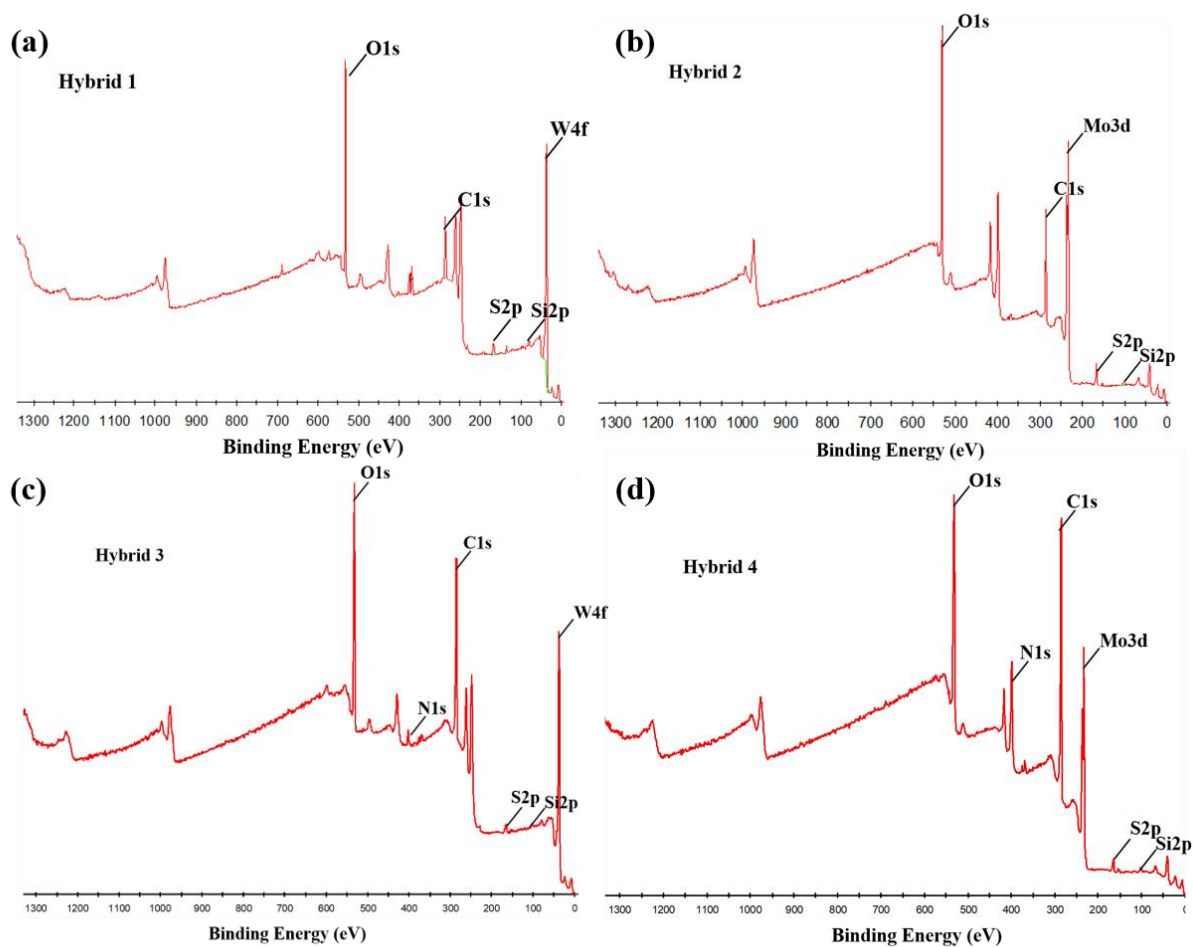


Fig. S20 XPS survey scan for (a) hybrid 1 (b) hybrid 2 (c) hybrid 3 and (d) hybrid 4.

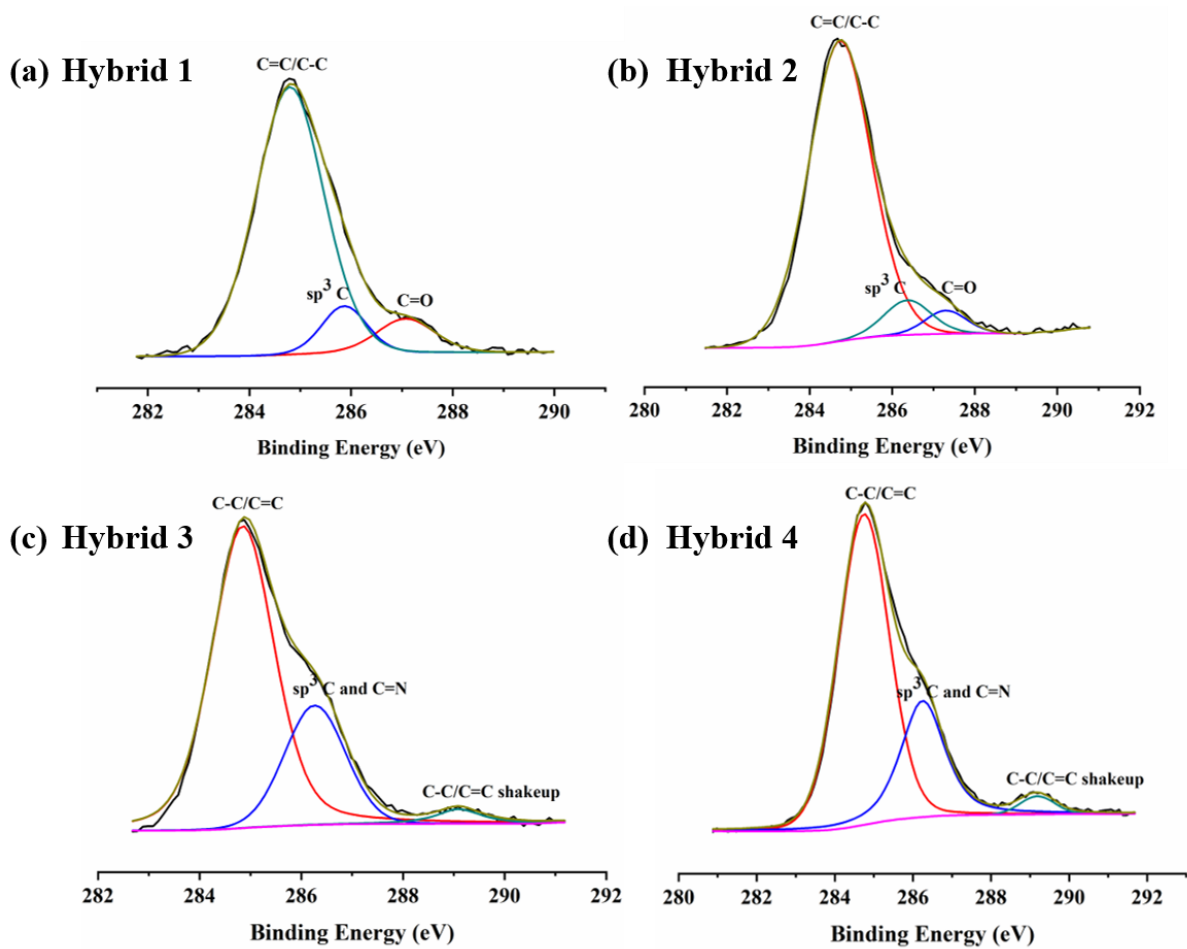


Fig. S21 C1s scan for (a) hybrid 1; (b) hybrid 2; (c) hybrid 3 and (d) hybrid 4.

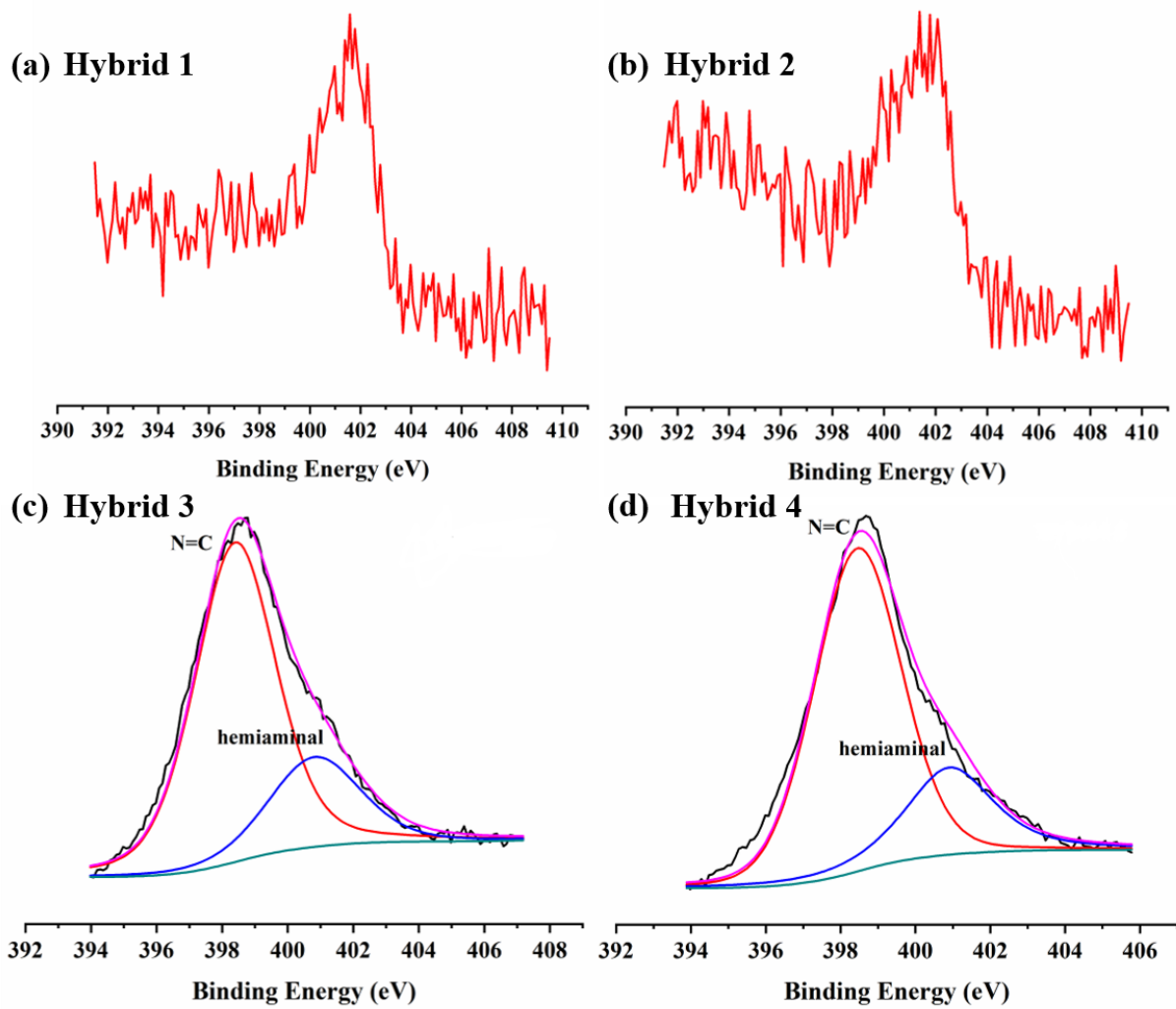


Fig. S22 N1s scan for (a) hybrid 1; (b) hybrid 2; (c) hybrid 3 and (d) hybrid 4.

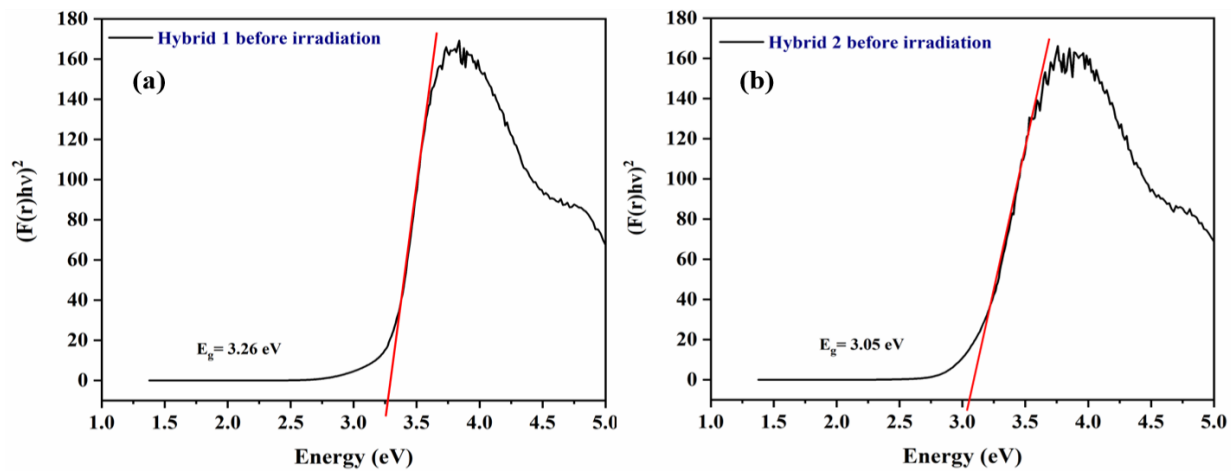


Fig. S23 UV-vis diffuse reflectance spectra: K-M function vs energy (eV) for (a) hybrid 1 and (b) hybrid 2.

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