

# Structure-property relationships in normal and mixed dithienylethenes – polyoxometalates supramolecular assemblies with fast solid-state photochromic properties

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## ELECTRONIC SUPPORTING INFORMATION

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## S1. Methods

**General:** All organic syntheses were performed using Schlenk techniques under argon atmosphere. All solvents were dried and purified by standard procedures. Precursor **A** and **B**,<sup>1,2</sup> **1**,<sup>3</sup> (NBu<sub>4</sub>)<sub>4</sub>[ $\alpha$ -Mo<sub>8</sub>O<sub>26</sub>],<sup>4</sup> (NBu<sub>4</sub>)<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>]<sup>5</sup> and (NBu<sub>4</sub>)<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>]<sup>6</sup> were synthesized according to the reported procedures. ((CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>(NH<sub>4</sub>)<sub>2</sub>[Mo<sub>8</sub>O<sub>26</sub>] which was used as an optical reference of the  $\beta$ -[Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> unit was synthesized as previously described.<sup>7</sup> NMR spectra were recorded on Bruker, AV 400 spectrometer. <sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C chemical shifts are determined by reference to residual solvent signals. High Resolution Mass Spectra were recorded on a Bruker maXis+ (ESI-QTOF). Elemental Analysis were performed at the CRMPO (Centre de Mesures Physiques de l'Ouest) in Rennes.

### UV-Vis absorption:

**Solution.** UV/Vis absorption spectra were recorded in pure dichloromethane using Specord 205 UV-Vis-NIR spectrophotometer in quartz cuvettes of 1 cm pathlength, against a reference of pure dichloromethane contained within a matched cuvette.

**Solid state.** Solid-state optical properties were investigated by Diffuse Reflectance Spectroscopy of microcrystalline powders. Diffuse reflectance spectra were collected at room temperature on a finely ground sample with a Perkin-Elmer Lambda 1050 spectrometer equipped with a 150 mm diameter integrating sphere coated with Spectralon®, a highly reflecting fluoropolymer. Diffuse reflectance was measured from 250 to 1000 nm with a 2 nm step using Spectralon® as reference (100% reflectance). The reflectance data were treated by a Kubelka-Munk transformation<sup>8</sup> to better determine the absorption thresholds. The photocoloration and fading kinetics were quantified by monitoring the temporal evolution of the photogenerated absorption  $Abs^{\lambda_{max}}(t)$  defined as  $Abs^{\lambda_{max}}(t) = -\log(R^{\lambda_{max}}(t)/R^{\lambda_{max}}(0))$ , where  $R^{\lambda_{max}}(t)$  and  $R^{\lambda_{max}}(0)$  are the reflectivities at the time  $t$  and at  $t = 0$ , respectively. For the coloration kinetics, the samples were irradiated with a Fisher Bioblock labosi UV lamp ( $\lambda_{ex} = 365$  nm,  $P = 6$ W) at a distance of 50 mm.  $Abs^{\lambda_{max}}(t)$  vs.  $t$  plots have been fitted according to a biexponential rate law  $Abs^{\lambda_{max}}(t) = (A_1 + A_2) - A_1 \exp(-k^c_1 t) - A_2 \exp(-k^c_2 t)$ , with  $k^c_1$  and  $k^c_2$  the extracted coloration rate constants, and  $A_1$  and  $A_2$  the associated amplitudes of absorption. For the bleaching processes, the samples were first irradiated under 365 nm-UV excitation until the photoinduced absorptions reach saturation. Then, the compounds were put under Thorlabs LED Array light sources (590 nm - 1.4 W/cm<sup>2</sup> or 630 nm - 2.4 W/cm<sup>2</sup>) at a distance of 100 mm. The bleaching kinetics were determined at room temperature by monitoring the temporal decays of

$Abs^{\lambda_{max}}(t)$  of samples once irradiated.  $Abs^{\lambda_{max}}(t)$  vs.  $t$  plots have been fitted according to a biexponential rate law  $Abs^{\lambda_{max}}(t) = (A_0 - A_1 - A_2) + A_1 \exp(-k'_1 t) + A_2 \exp(-k'_2 t)$ , with  $k'_1$  and  $k'_2$  the extracted fading rate constants,  $A_1$  and  $A_2$  the associated amplitudes of absorption, and  $A_0$  the amplitude of absorption at  $t = 0$ .

Photoisomerization experiments in solution have been made using a LS series Light Source of ABET technologies, Inc (150 W xenon lamp), with single wavelength light filters “350FS 10-25” or “450FS 40-25” for ring-closure and “650FS 10-25” for cycloreversion. Irradiations for  $^1H$  NMR experiments have been made using a Rayonet® with 350 nm light emitting lamps. Irradiation for  $^1H$  NMR experiments have been made using a Rayonet® with 350 nm emitting lamp.

**FT-IR:** FT-IR spectra were recorded in the 4000-400  $cm^{-1}$  range in KBr pellets on BRUKER Vertex equipped with a computer control using the OPUS software.

**Thermogravimetry:** Thermogravimetric analysis (TGA) were performed by flowing dry argon with a heating and cooling rate of 5  $^{\circ}C\ min^{-1}$  on a SETARAM TG-DSC 111 between 20 and 800  $^{\circ}C$ .

**X-ray crystallography:** For **2-Mo<sub>8</sub>**, X-ray diffraction measurements were performed on a Bruker Kappa CCD diffractometer, operating with a Mo-K $\alpha$  ( $\lambda = 0.71073\ \text{\AA}$ ) X-ray tube with a graphite monochromator. For the other compounds, X-ray single crystal diffraction data were collected on D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K $\alpha$  radiation ( $\lambda = 0.71073\ \text{\AA}$ , multilayer monochromator). The structures were solved by direct methods SHELXS-2016 and refined on F<sup>2</sup> by full matrix least-squares techniques using the SHELX-2016 program<sup>9</sup> within WINGX.<sup>10</sup> The hydrogen atoms were included in the geometrically calculated position and refined riding on the corresponding atom. The contribution of the disordered solvents to the calculated structure factors was estimated following the BYPASS algorithm, implemented as the SQUEEZE option in PLATON.<sup>11</sup> A new data set, free of solvent contribution, was then used in the final refinement. Crystallographic data for the reported structures can be obtained by quoting the deposition numbers CCDC 2057188 (**2**), 2057190 (**[2]OTf**), 2057191 (**2-Mo<sub>8</sub>**), 2057189 (**1-PMo<sub>12</sub>**), 2057192 (**2-PMo<sub>12</sub>**) and 2057193 (**2-PW<sub>12</sub>**). These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; email [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

## S2. Procedures for the synthesis of the DTEs and assemblies.

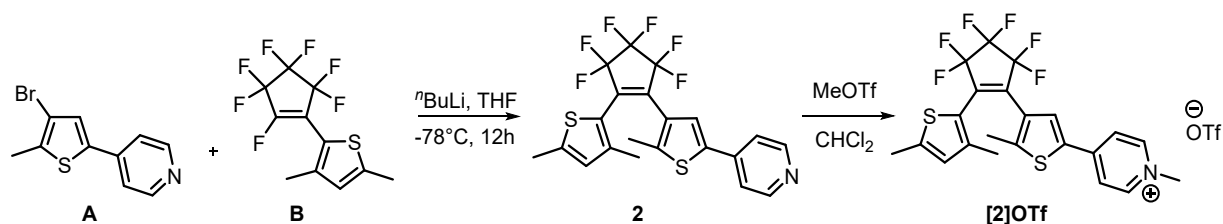


Fig. S1 Synthetic route for [2]OTf.

**Synthesis of 2.** To 100 mL freshly distilled THF solution containing compound **A** (1.17 g, 4.6 mmol) was added 2 mL  $n\text{BuLi}$  hexane solution (2.5 M, 5.0 mmol) under argon atmosphere at  $-78^\circ\text{C}$ , and the solution was stirred for 1h at low temperature. Precursor **B** (1.4 g, 4.6 mmol) in 10 mL of freshly distilled THF was slowly added to the reaction mixture at  $-78^\circ\text{C}$ , and the mixture was stirred for 3h at this temperature. The reaction temperature rose slowly ambient overnight. The product was extracted with two 100 mL portion of diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by column chromatography on silica gel with EtOAc/DMC, 3/1 as eluent to give the desired compound as dark green solid (0.85 g, 40 %). Single-crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the hexane solution of **2**.  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.60 (d,  $J = 4.7$  Hz, 2H), 7.44 (s, 1H), 7.41 (d,  $J = 5.9$  Hz, 2H), 6.53 (s, 1H), 2.44 (s, 3H), 2.02 (s, 3H), 1.73 (s, 3H).  **$^{19}\text{F NMR}$**  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -109.51 (m, 4F), -133.57 (m, 2F). **HRMS-ESI.** Calcd for  $\text{C}_{21}\text{H}_{16}\text{NS}_2\text{F}_6$  [ $\text{M}+\text{H}^+$ ],  $z=1$ ,  $m/z$ : 460.0623. Found: 460.0624 (<1 ppm). **E.A.** Anal. calc. for  $\text{C}_{21}\text{H}_{15}\text{NF}_6\text{S}_2$ : C 54.90, H 3.29, N 3.05, S 13.96 %; Found: C 55.45, H 3.59, N 3.15 %, S 13.76. The compound is soluble in most common organic solvents, insoluble in water.

**Synthesis of [2]OTf.** To 30 mL of dry DCM solution containing **2** (740 mg, 1.6 mmol) was added drop by drop methyl trifluoromethanesulfonate MeOTf (0.46 mL, 4 mmol) under argon atmosphere at room temperature, and the solution was stirred during 48 h. Brown precipitate formed during the reaction was filtered off, washed with pentane and dried in air (0.80 g, 81 %). Single-crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the methanol solution of [2]OTf.  **$^1\text{H NMR}$**  (400 MHz, MeOD)  $\delta$  8.74 (d,  $J = 6.8$  Hz, 2H), 8.24 (d,  $J = 7.0$  Hz, 2H) 8.11 (s, 1H), 6.66 (s, 1H), 4.32 (s, 3H), 2.45 (s, 3H), 2.12 (s, 3H), 1.78 (s, 3H).  **$^{19}\text{F NMR}$**  (376 MHz, MeOD)  $\delta$  -80.11 (s, 3F), -111.10 (m, 2F), -11.38 (m, 2F), -133.37

(m, 2F). **HRMS-ESI.** Calcd for  $C_{22}H_{18}NS_2F_6 [M^+]$ ,  $z=1$ ,  $m/z$ : 474.0779. Found: 474.0777 (<1 ppm). **FT-IR, KBr**,  $cm^{-1}$  3110 (w), 3050 (m), 1640 (s), 1550 (m), 1520 (m), 1474 (w), 1445 (m), 1336 (m), 1265 (s), 1194 (m), 1154 (m), 1121 (s), 1058 (m), 1030 (s), 985 (s), 897 (m), 874 (m), 840 (s), 787 (m), 756 (w), 637 (s), 517 (m), 478 (m). **ESI-HRMS.** Calcd for  $C_{22}H_{18}NS_2F_6$ ,  $z=1$ ,  $m/z$ : 474.07794. Found: 474.0777 (1 ppm). **E.A.** Anal. calc. for  $C_{23}H_{18}NO_3F_9S_3$ : C 44.30, H 2.91, N 2.25, S 15.43. Found: C 44.15, H 2.98, N 2.19, S 15.05 %. The compound is soluble in DMSO, DMF, ANC, sparingly soluble in DCM, insoluble in water.

**Synthesis of 1-PMo<sub>12</sub>.**  $(NBu_4)_3[PMo_{12}O_{40}]$  (0.054 g,  $2.1 \cdot 10^{-5}$  mol) was dissolved in 5 mL of acetonitrile. Then the solution of **[1]OTf** (0.04 g,  $6.4 \cdot 10^{-5}$  mol) in 4 mL of DMF was added and the mixture was stirred at room temperature for 1 h. Single-crystals suitable for X-ray diffraction analysis were obtained by vapor diffusion of diethyl ether into the solution in few days (0.035 g, 74 % in Mo). **FT-IR, KBr**,  $cm^{-1}$  3100 (w), 2969 (w), 1635 (s), 1555 (m), 1510 (m), 1475 (w), 1445 (m), 1336 (m), 1274 (s), 1223 (w), 1195 (s), 1144 (m), 1113 (m), 1088 (w), 1060 (s), 956 (s), 878 (s), 800 (s), 500 (w), 476 (w). **E.A.** Anal. calc. for  $C_{78}H_{69}F_{18}N_8O_{40}PS_6Mo_{12}$ : C 26.96, H 2.00, N 3.22, S 5.54 %; Found: C 26.90, H 2.30, N 3.02, S 5.10 %. The compound is soluble in DMSO, DMF, ACN, insoluble in water.

**Synthesis of 2-PMo<sub>12</sub>.** **2-PMo<sub>12</sub>** was prepared in a way similar to that of **1-PMo<sub>12</sub>**, but using **[2]OTf** (0.04 g,  $6.4 \cdot 10^{-5}$  mol). Single-crystals suitable for X-ray diffraction analysis were obtained by vapor diffusion of diethyl ether into the solution in few days (0.035 g, 74 % in Mo). **FT-IR, KBr**,  $cm^{-1}$  3100 (w), 2969 (w), 1637 (s), 1553 (m), 1513 (m), 1474 (w), 1443 (m), 1338 (m), 1274 (s), 1220 (w), 1194 (s), 1142 (m), 1113 (m), 1088 (w), 1060 (s), 956 (s), 878 (s), 800 (s), 500 (w), 476 (w). **E.A.** Anal. calc. for  $C_{78}H_{69}F_{18}N_8O_{40}PS_6Mo_{12}$ : C 26.96, H 2.00, N 3.22, S 5.54 %; Found: C 26.87, H 2.33, N 3.15, S 5.04 %. The compound is soluble in DMSO, DMF, ACN, insoluble in water.

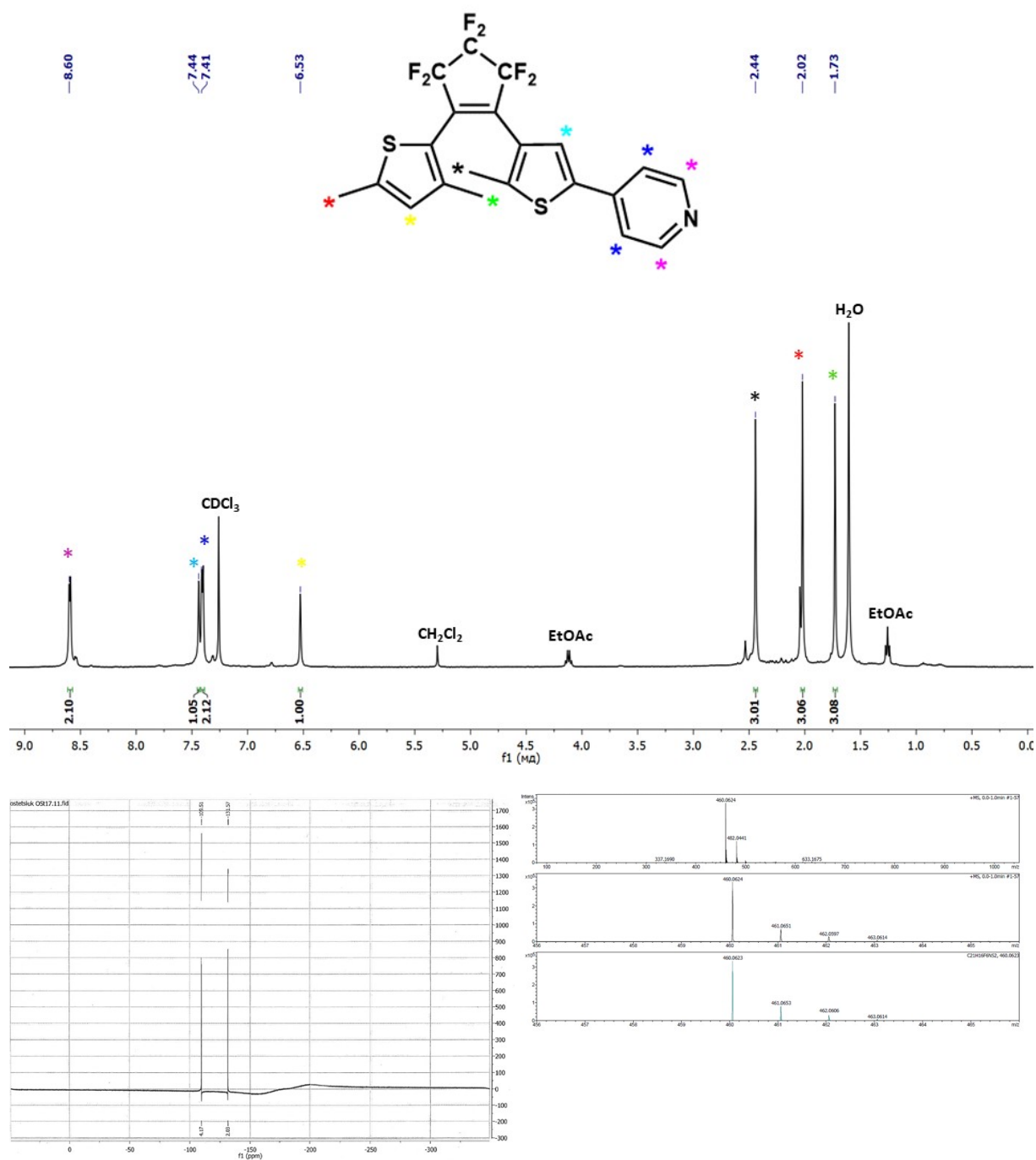
**Synthesis of 1-PW<sub>12</sub>.** **1-PW<sub>12</sub>** was prepared in a way similar to that of **1-PMo<sub>12</sub>**, but using  $(NBu_4)_3[PW_{12}O_{40}]$  (0.04 g,  $1.3 \cdot 10^{-5}$  mol) and **[1]OTf** (0.025 g,  $4.0 \cdot 10^{-5}$  mol). The polycrystalline powder was obtained by vapor diffusion of diethyl ether into the solution in few days (0.025 g, 42 % in W). **FT-IR, KBr**,  $cm^{-1}$  2970 (w), 1640 (m), 1556 (w), 1515 (w), 1475 (w), 1440 (w), 1337 (w), 1274 (m), 1195 (m), 1142 (w), 1113 (w), 1078 (s), 1049 (w), 979 (s), 895 (m), 812 (s), 517 (w). **E.A.** Anal. calc. for  $C_{78}H_{69}F_{18}N_8O_{40}PS_6W_{12}$ : C 20.68, H 1.54, N 2.47,

S 4.27 %. Found: C 20.55, H 1.77, N 2.35, S 4.15 %. The compound is soluble in DMSO, DMF, ACN, insoluble in water.

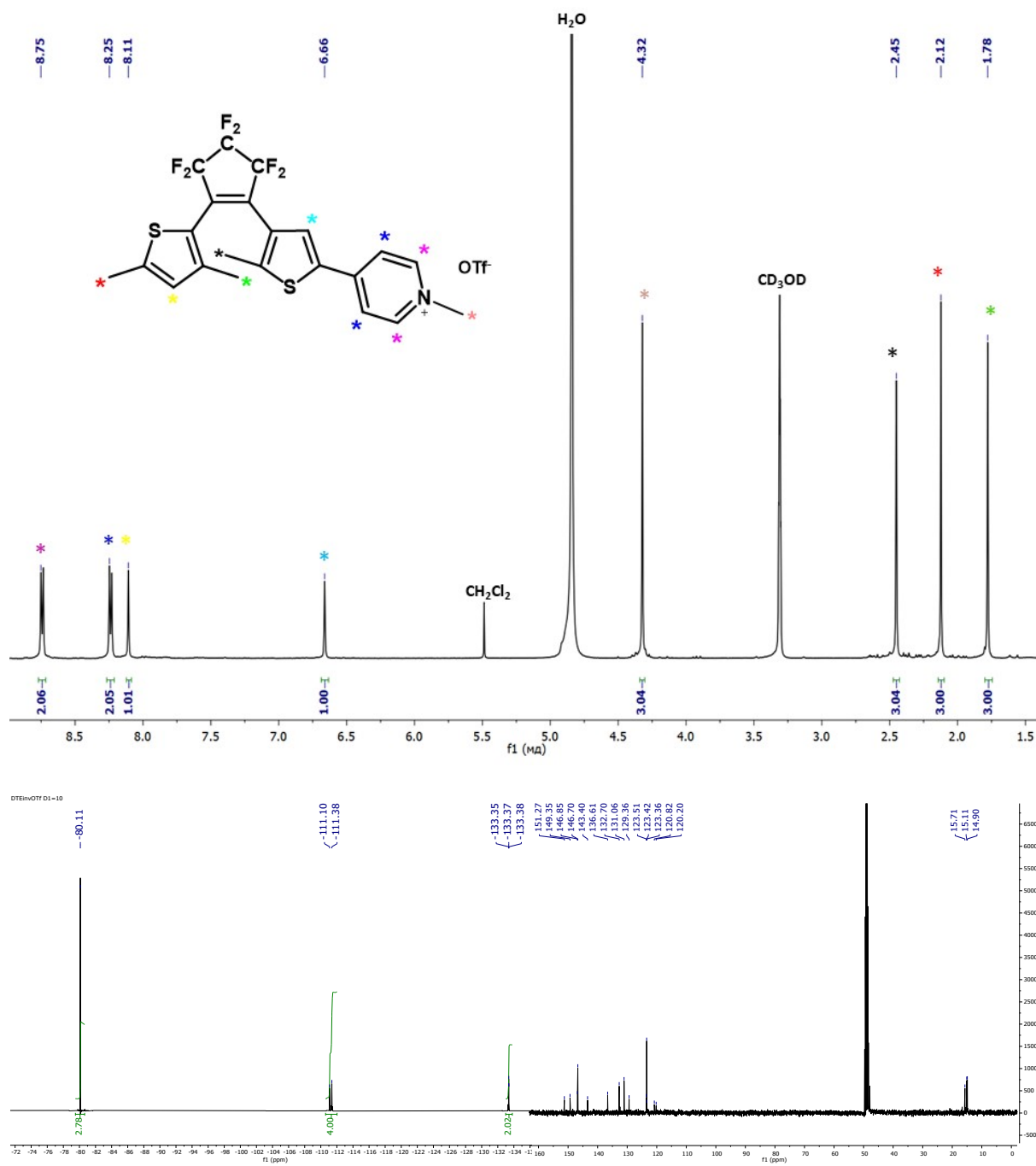
**Synthesis of 2-PW<sub>12</sub>.** 2-PW<sub>12</sub> was prepared in a way similar to that of 1-PW<sub>12</sub>, but using [2]OTf (0.025 g, 4.0·10<sup>-5</sup> mol). Single-crystals suitable for X-ray diffraction analysis were obtained by vapor diffusion of diethyl ether into the solution in few days (0.026 g, 44 % in W). **FT-IR**, KBr, cm<sup>-1</sup> 2969 (w), 1641 (m), 1555 (w), 1513 (w), 1472 (w), 1439 (w), 1338 (w), 1274 (m), 1196 (m), 1142 (w), 1113 (w), 1078 (s), 1049 (w), 979 (s), 895 (m), 812 (s), 517 (w). **E.A.** Anal. calc. for C<sub>78</sub>H<sub>69</sub>F<sub>18</sub>N<sub>8</sub>O<sub>40</sub>PS<sub>6</sub>W<sub>12</sub>: C 20.68, H 1.54, N 2.47, S 4.27 %. Found: C 20.44, H 1.83, N 2.85, S 4.35 %. The compound is soluble in DMSO, DMF, ACN, insoluble in water.

**Synthesis of 2-Mo<sub>8</sub>.** (NBu<sub>4</sub>)<sub>4</sub>[α-Mo<sub>8</sub>O<sub>26</sub>] (0.05 g, 2.3·10<sup>-5</sup> mol) was dissolved in 5 mL of DMF. Then the solution of [2]OTf (0.06 g, 9.5·10<sup>-5</sup> mol) in 3 mL of DMF was added and the mixture was stirred at room temperature for 1 h. Single-crystals suitable for X-ray diffraction analysis were obtained by the vapour diffusion of diethyl ether into the solution in few days (0.045 g, 58 % in Mo). **FT-IR**, KBr, cm<sup>-1</sup> 3120 (w), 3050 (m), 1672 (m), 1641 (s), 1550 (m), 1515 (w), 1475 (m), 1440 (m), 1384 (w), 1342 (m), 1274 (s), 1227 (w), 1192 (s), 1128 (s), 1058 (s), 989 (s), 946 (s), 911 (s), 845 (m), 713 (m), 666 (m), 556 (w), 480 (w). Anal. calc. for C<sub>100</sub>H<sub>96</sub>F<sub>24</sub>Mo<sub>8</sub>N<sub>8</sub>O<sub>30</sub>S<sub>8</sub>: C 35.64, H 2.87, N 3.33, S 7.61 %; Found: C 35.55, H 2.75, N 3.13, S 7.49 %. The compound is soluble in DMSO, DMF, insoluble in water.

### S3. NMR and mass spectra

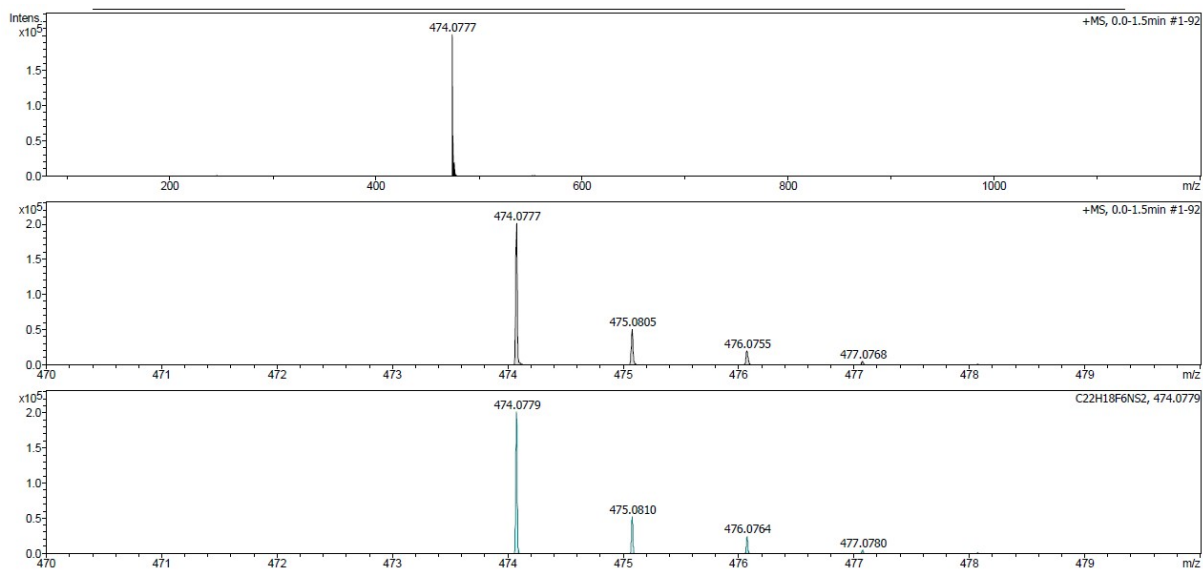


**Fig. S2** *top*: <sup>1</sup>H NMR and *bottom left*: <sup>19</sup>F NMR spectra of **2** in CDCl<sub>3</sub>. *bottom right*: ESI-HRMS spectra of **2**.



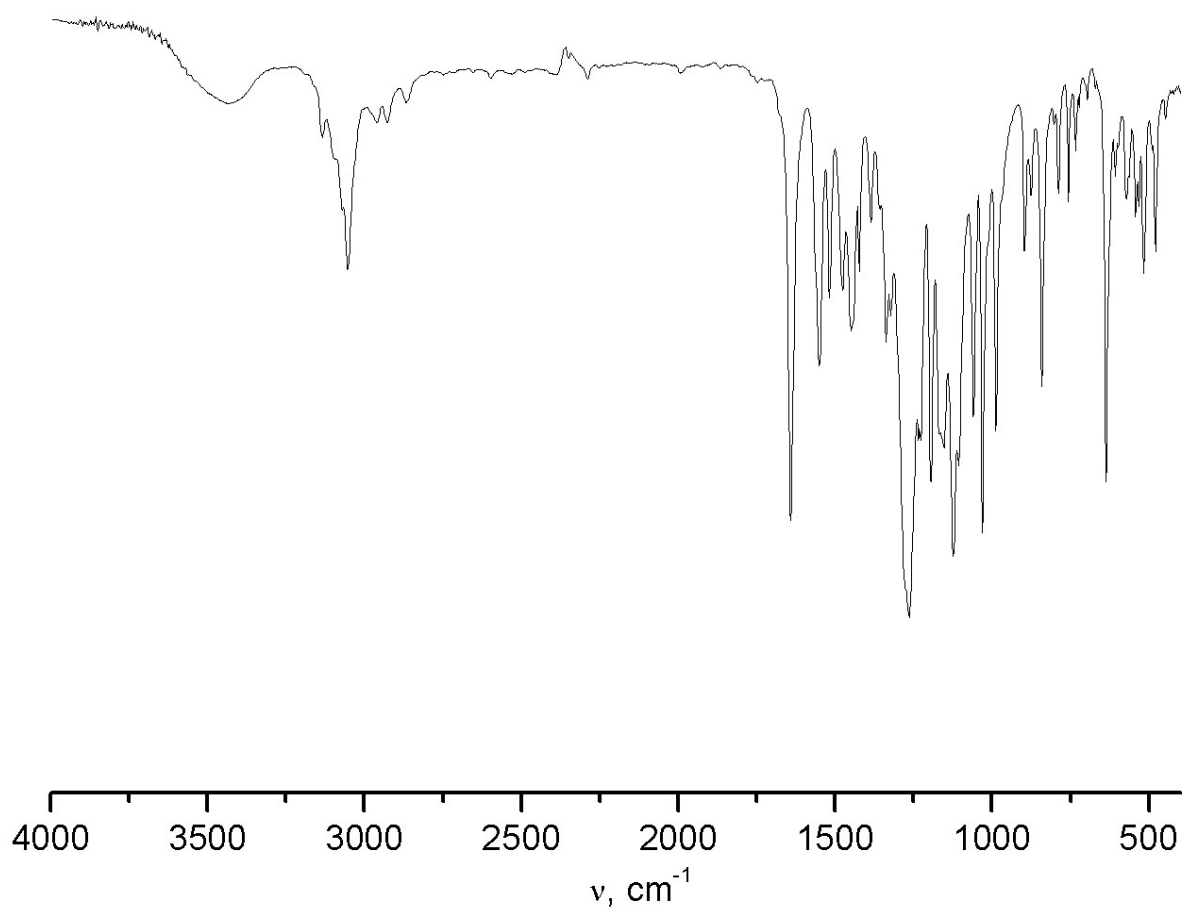
**Fig. S3** top: <sup>1</sup>H NMR, bottom left: <sup>19</sup>F NMR and bottom right: <sup>13</sup>C NMR spectra of [2]OTf in CD<sub>3</sub>OD.



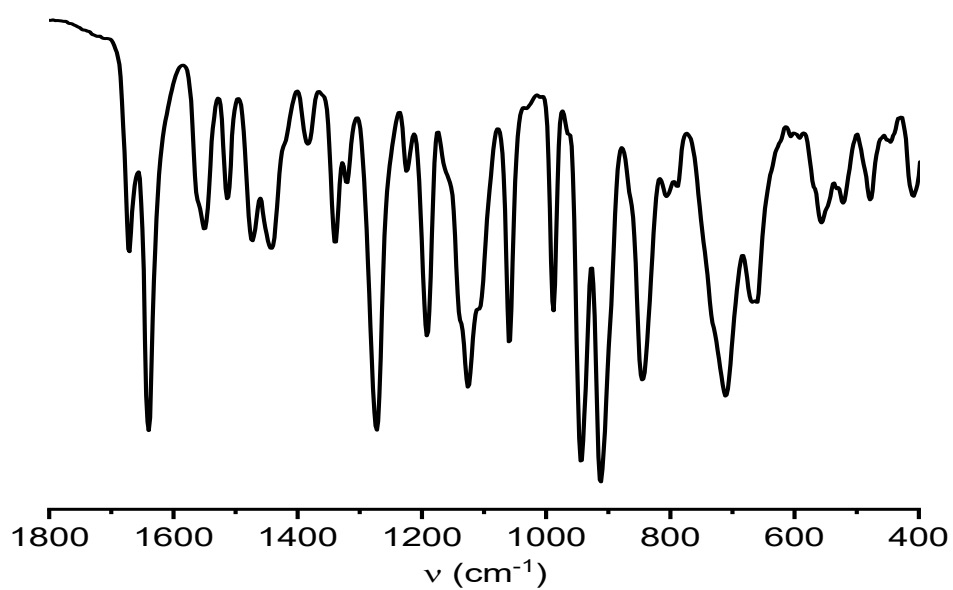


**Figure S4.** ESI-HRMS spectra of  $2^+$ .

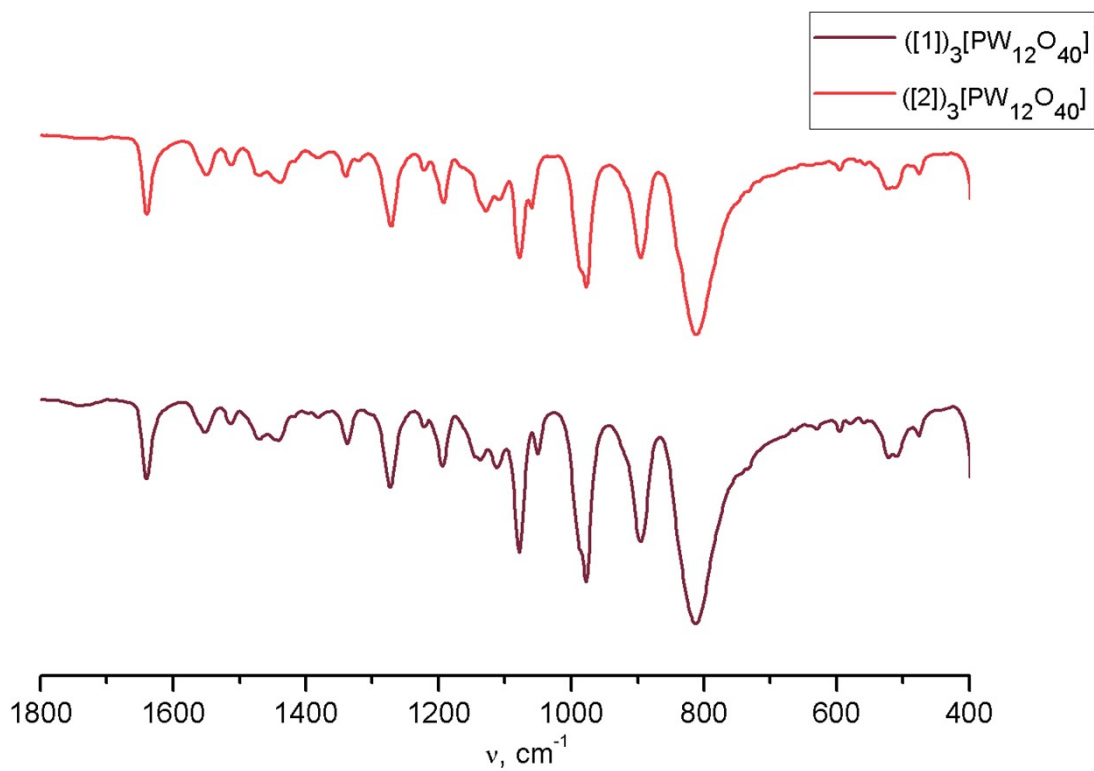
#### S4. FT-IR spectra



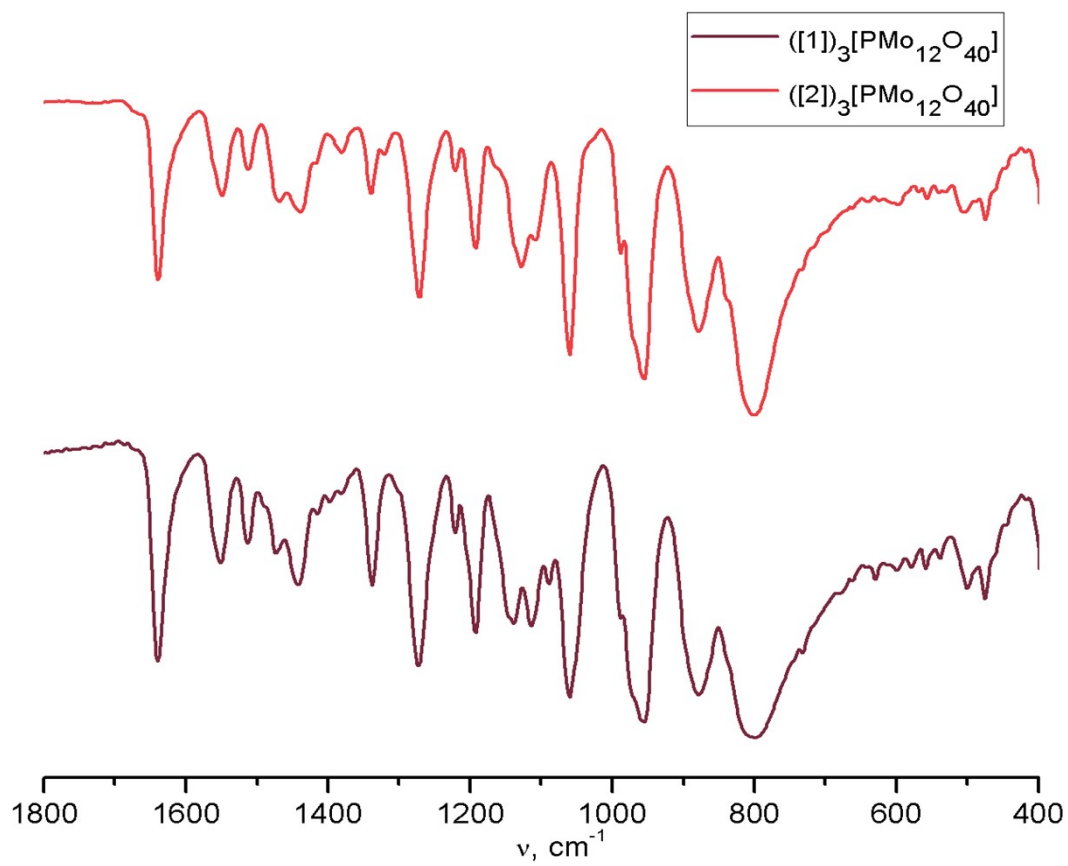
**Fig. S5** FT-IR spectrum of [2]OTf.



**Fig. S6** FT-IR spectrum of **2-Mo<sub>8</sub>**.

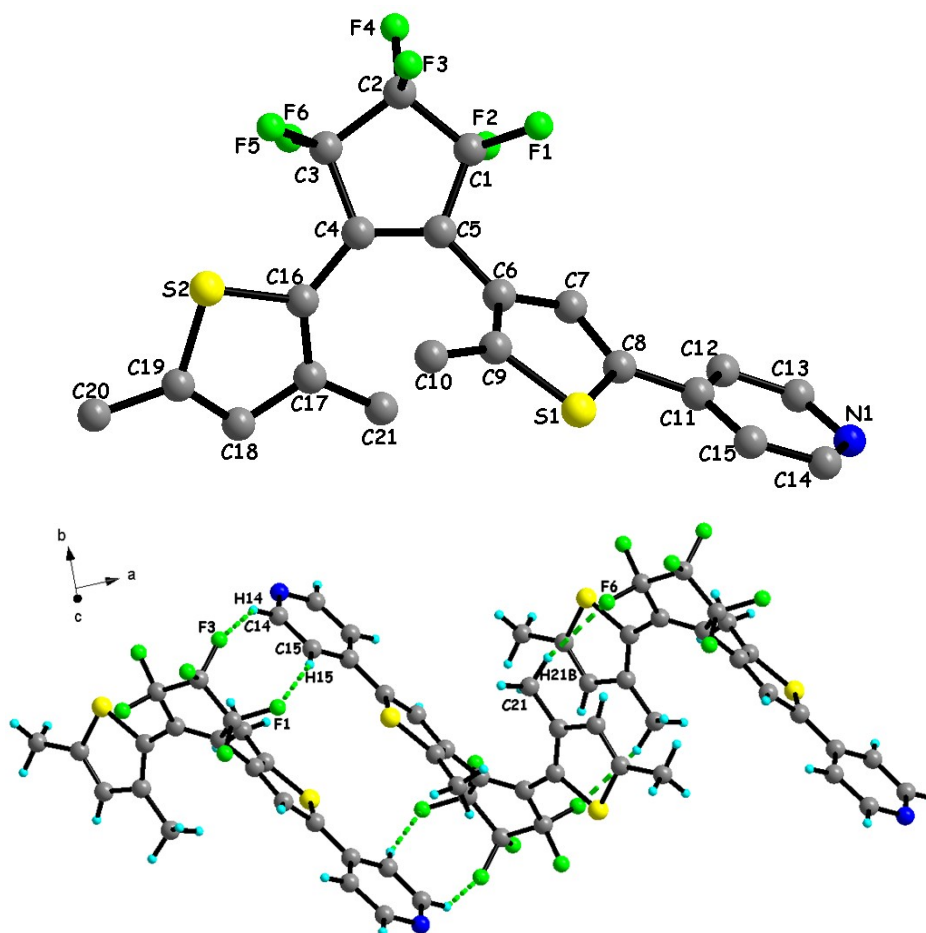


**Fig. S7** FT-IR spectra of **1-PW<sub>12</sub>** and **2-PW<sub>12</sub>**.



**Fig. S8** FT-IR spectra of **1-PMo<sub>12</sub>** and **2-PMo<sub>12</sub>**.

## S5. Crystallographic data



**Fig. S9** Crystal structure of **2** with atom labelling (top) and intermolecular H-bonds (bottom) displayed as green dotted lines.

**Table S1** Crystallographic data, details of data collection and structure refinement parameters.

Compound	<b>2</b>	<b>[2]OTf</b>	<b>1-PMo<sub>12</sub></b>	<b>2-PMo<sub>12</sub></b>	<b>2-PW<sub>12</sub></b>	<b>2-Mo<sub>8</sub></b>
Formula	C <sub>21</sub> H <sub>15</sub> F <sub>6</sub> NS <sub>2</sub>	C <sub>23</sub> H <sub>18</sub> F <sub>9</sub> NO <sub>3</sub> S <sub>3</sub>	C <sub>68</sub> H <sub>57</sub> F <sub>18</sub> Mo <sub>12</sub> N <sub>4</sub> O <sub>40</sub> PS <sub>6</sub>	C <sub>68</sub> H <sub>57</sub> F <sub>18</sub> Mo <sub>12</sub> N <sub>4</sub> O <sub>40</sub> PS <sub>6</sub>	C <sub>70</sub> H <sub>60</sub> F <sub>18</sub> N <sub>5</sub> O <sub>40</sub> PS <sub>6</sub> W <sub>12</sub>	C <sub>100</sub> H <sub>96</sub> F <sub>24</sub> Mo <sub>8</sub> N <sub>8</sub> O <sub>3</sub> OS <sub>8</sub>
M [g·mol <sup>-1</sup> ]	459.46	623.56	3286.78	3286.78	4382.76	3369.84
Crystal system	monoclinic	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> [Å]	14.2422(13)	8.7267(5)	11.733(4)	11.6948(9)	11.7500(12)	10.3229(11)
<i>b</i> [Å]	8.7585(9)	14.2672(9)	18.080(5)	18.4172(15)	18.4870(19)	11.421(2)
<i>c</i> [Å]	15.9650(18)	21.1854(14)	25.198(7)	25.2352(19)	25.300(2)	27.107(5)
$\alpha$ [°]	90	90	75.116(9)	75.004(3)	74.730(4)	89.39(2)
$\beta$ [°]	97.351(4)	94.306(3)	79.017(10)	80.190(3)	80.001(4)	84.551(12)
$\gamma$ [°]	90	90	84.375(13)	84.420(3)	84.034(4)	83.976(15)
V [Å <sup>3</sup> ]	1975.1(4)	2630.3(3)	5065(3)	5165.4(7)	5211.4(9)	3163.8(9)
<i>Z</i>	4	4	2	2	2	1
$\rho_{\text{calcd.}}$ [g/cm <sup>3</sup> ]	1.545	1.575	2.155	2.113	2.793	1.769
$\mu$ [mm <sup>-1</sup> ]	0.333	0.373	1.687	1.654	13.431	1.006
<i>F</i> (000)	936	1264	3180	3180	3992	1672
T [K]	150(2)	296.15	150	150	150	293(2)
2 $\Theta_{\text{max}}$	55	54	51	51	51	52
<i>R</i> <sub>int</sub>	0.0388	0.0363	0.0908	0.1223	0.0512	0.0666
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0385	0.0613	0.0606	0.0898	0.0601	0.0640
w <i>R</i> <sub>2</sub> (all data)	0.0960	0.1826	0.1765	0.2217	0.1493	0.1812
G.O.F.	1.064	1.031	0.997	1.075	1.083	1.004
Largest difference peak/hole (e Å <sup>-3</sup> )	0.353/-0.385	0.463/-0.457	2.691/-1.529	3.582/-2.304	5.152/-4.374	0.772/-0.642
CCDC number	2057188	2057190	2057189	2057192	2057193	2057191

**Table S2** Selected bond lengths for **2**.

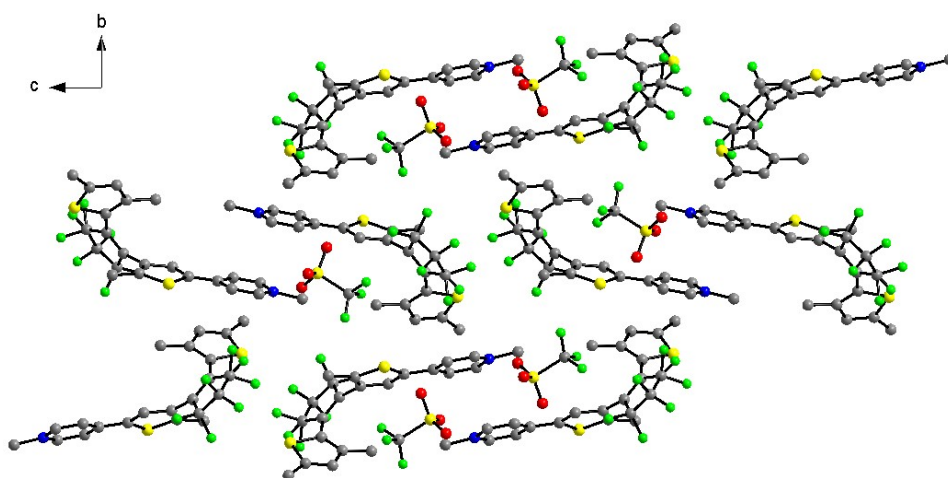
C1—F1	1.3532(17)	C8—S1	1.7337(15)
C1—F2	1.3644(18)	C9—C10	1.498(2)
C1—C5	1.505(2)	C9—S1	1.7200(15)
C1—C2	1.532(2)	C11—C15	1.395(2)
C2—F4	1.3369(18)	C11—C12	1.397(2)
C2—F3	1.3543(19)	C12—C13	1.383(2)
C2—C3	1.533(2)	C13—N1	1.338(2)
C3—F6	1.3550(19)	C14—N1	1.337(2)
C3—F5	1.3562(18)	C14—C15	1.391(2)
C3—C4	1.513(2)	C16—C17	1.384(2)
C4—C5	1.3575(19)	C16—S2	1.7456(15)
C4—C16	1.4547(19)	C17—C18	1.424(2)
C5—C6	1.4646(19)	C17—C21	1.500(2)
C6—C9	1.379(2)	C18—C19	1.361(2)
C6—C7	1.4324(19)	C19—C20	1.507(2)
C7—C8	1.367(2)	C19—S2	1.7179(17)
C8—C11	1.4691(19)		

**Table S3** Selected bond lengths for **[2]OTf**.

C1—C5	1.497(4)	C16—S2	1.734(3)
C1—C2	1.523(5)	C17—C18	1.425(5)
C2—C3	1.520(5)	C17—C21	1.490(5)
C3—C4	1.501(5)	C18—C19	1.353(6)
C4—C5	1.333(4)	C19—C20	1.502(5)
C4—C16	1.462(4)	C19—S2	1.715(4)
C5—C6	1.472(4)	C22—F8	1.271(6)
C6—C9	1.375(4)	C22—F7	1.306(5)
C6—C7	1.414(4)	C22—F9	1.308(6)
C7—C8	1.369(4)	C22—S3	1.836(5)
C8—C11	1.453(4)	C24—N1	1.471(4)
C8—S1	1.723(3)	F1—C1	1.342(4)
C9—S1	1.705(3)	F2—C1	1.363(4)
C10—C9	1.502(5)	F3—C2	1.339(4)
C11—C12	1.395(4)	F4—C2	1.326(4)
C11—C15	1.397(4)	F5A—C3	1.338(8)
C12—C13	1.362(5)	F6—C3	1.370(5)
C13—N1	1.347(4)	O1—S3	1.426(4)
C14—N1	1.336(4)	O2—S3	1.404(3)
C14—C15	1.362(5)	O3—S3	1.380(5)
C16—C17	1.371(5)		

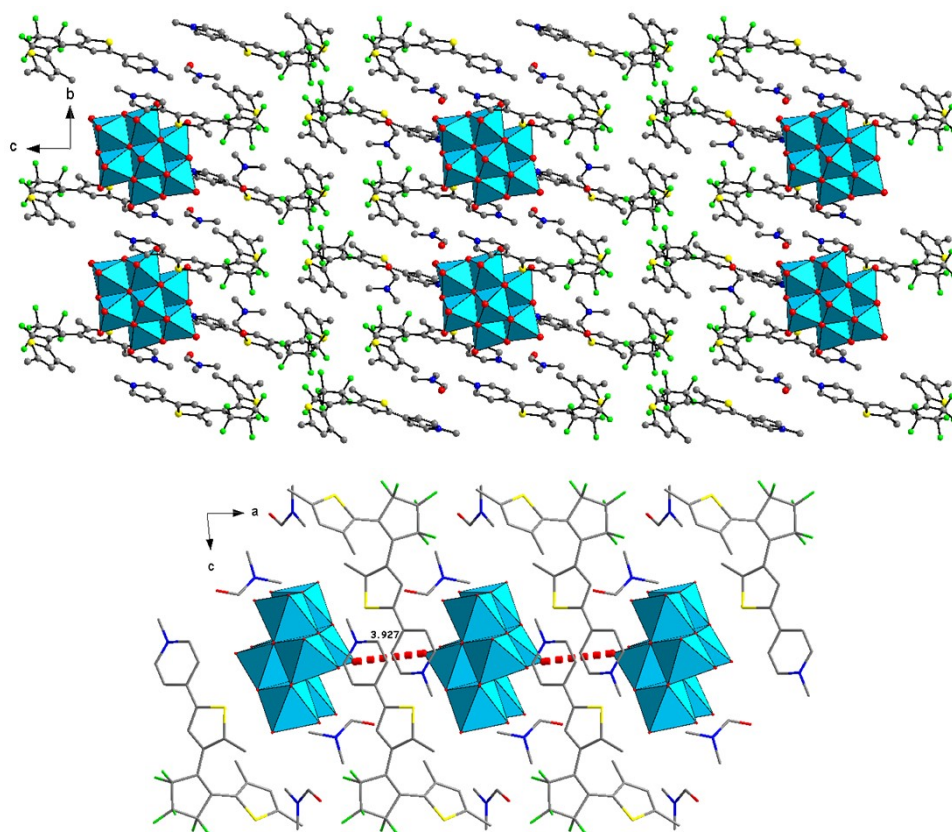
**Table S4** Intermolecular hydrogen bonds for **2**.

$d(\text{F}\cdots\text{H})$ [Å]	$d(\text{A}\cdots\text{D})$ [Å]	$\angle$ (AHD) [°]
F(3) $\cdots$ H(14) = 2.6268(12)	C(14) $\cdots$ F(3) = 3.4136(20)	140
F(1) $\cdots$ H(15) = 2.5579(10)	C(15) $\cdots$ F(1) = 3.4771(20)	163
F(6) $\cdots$ H(21B) = 2.5192(10)	C(21) $\cdots$ F(6) = 3.4540(18)	159

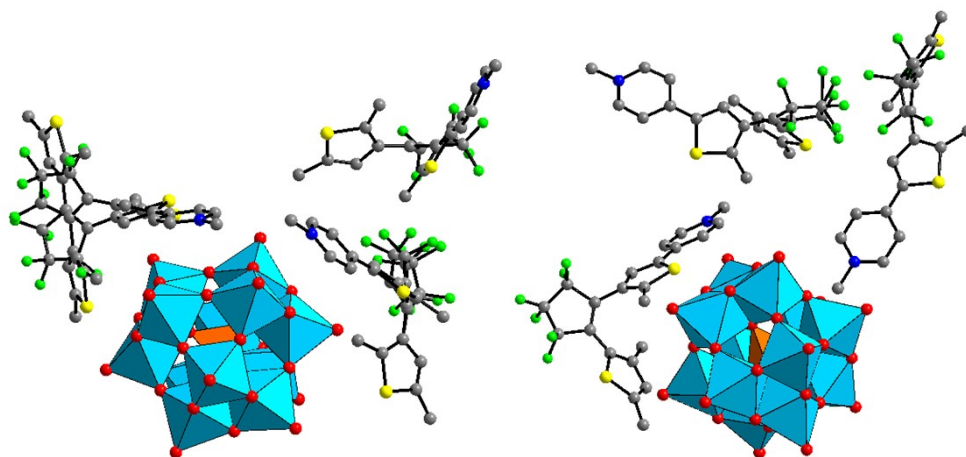


**Fig. S10** Crystal packing of **[2]OTf** representing the assembly of **2<sup>+</sup>** cations into supramolecular ribbons running along the *a*-axis. H atoms were omitted for clarity.

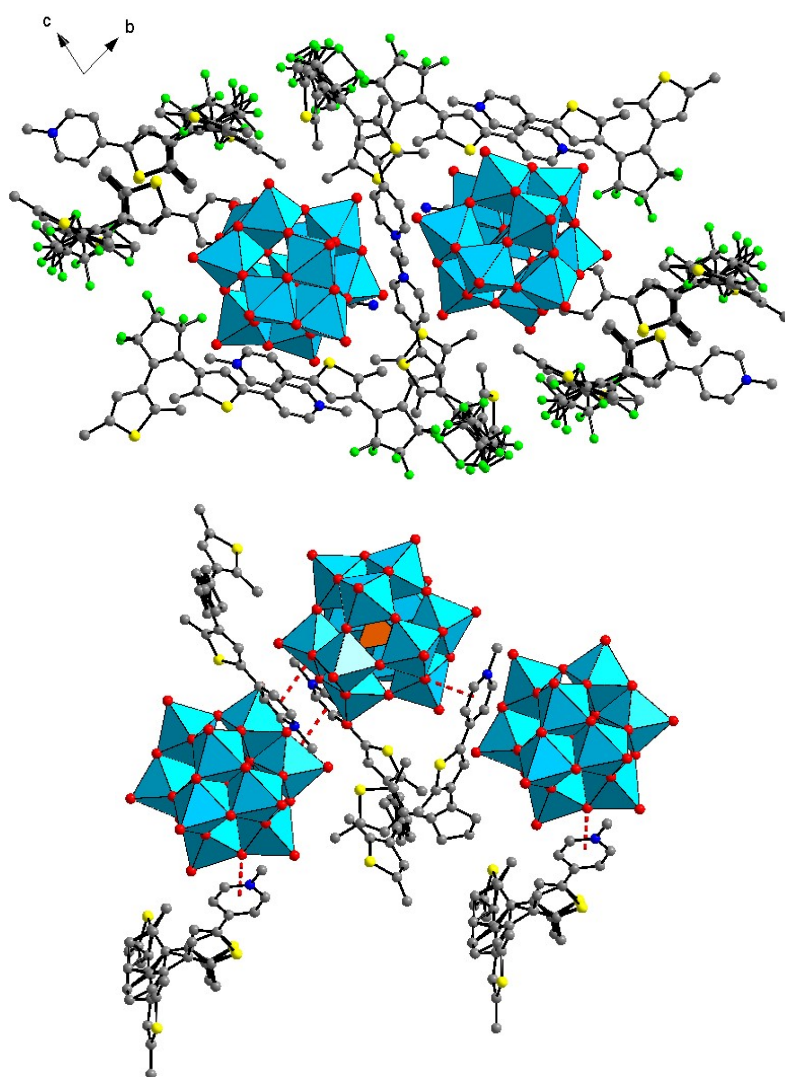




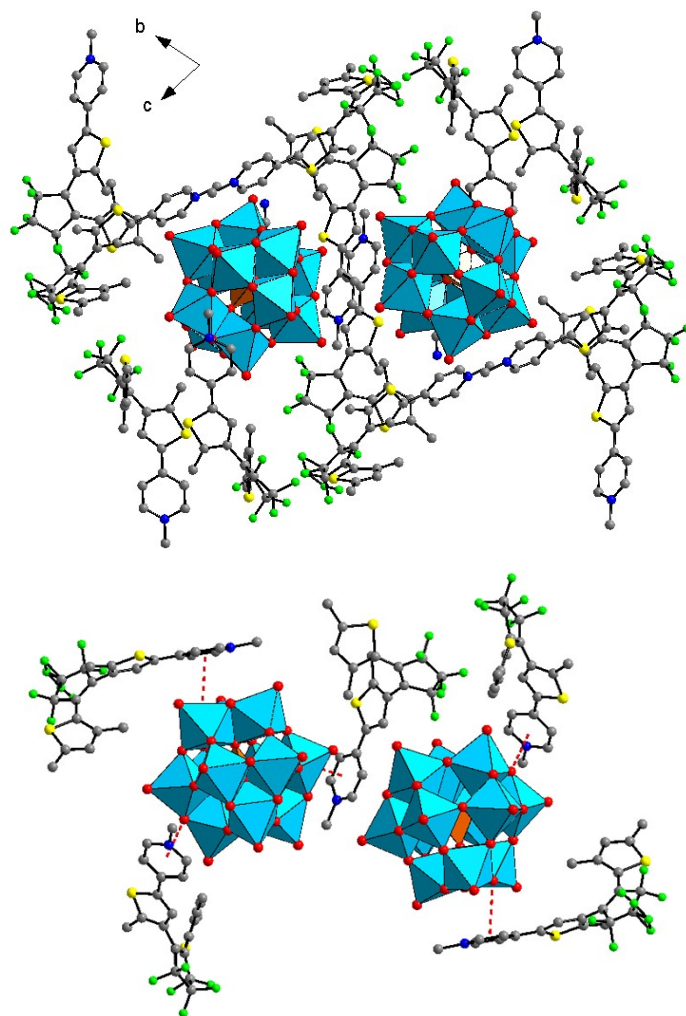
**Fig. S11** Crystal packing of **2-Mo<sub>8</sub>** (top) and the closest interanion contacts (red dotted lines) (bottom). (blue octahedra: MoO<sub>6</sub>, red sphere: oxygen, yellow sphere: sulfur, blue sphere: nitrogen, green sphere: fluorine, grey sphere: carbon). H atoms were omitted for clarity.



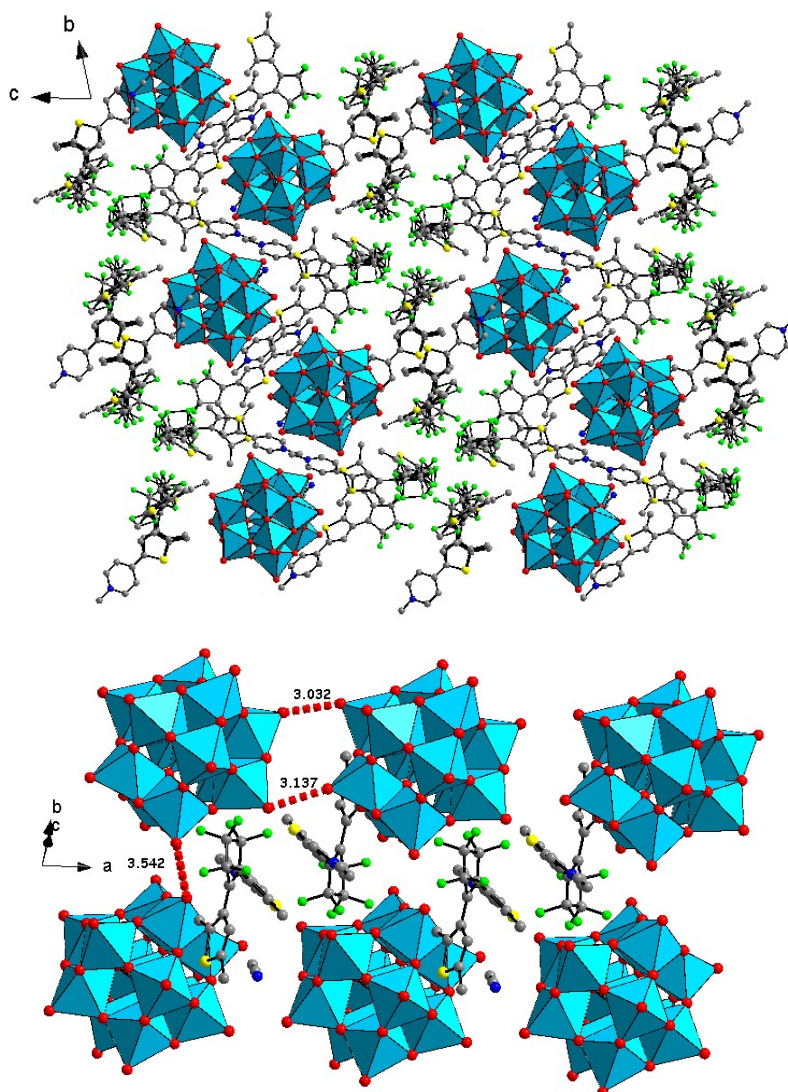
**Fig. S12** Crystal structures of **1-PMo<sub>12</sub>** (left) and **2-PMo<sub>12</sub>** (right), the POM anions are represented in polyhedral mode (blue octahedra: WO<sub>6</sub>, orange tetrahedron: PO<sub>4</sub>, red sphere: oxygen, yellow sphere: sulfur, blue sphere: nitrogen, green sphere: fluorine, grey sphere: carbon). H atoms and acetonitrile molecules were omitted for clarity.



**Fig. S13** Unit cell of **1-PMo<sub>12</sub>** along the *a*-axis (top) and crystal packing showing the  $\pi \cdots \pi$  interactions (red dotted lines) (bottom). H and F atoms were omitted for clarity.

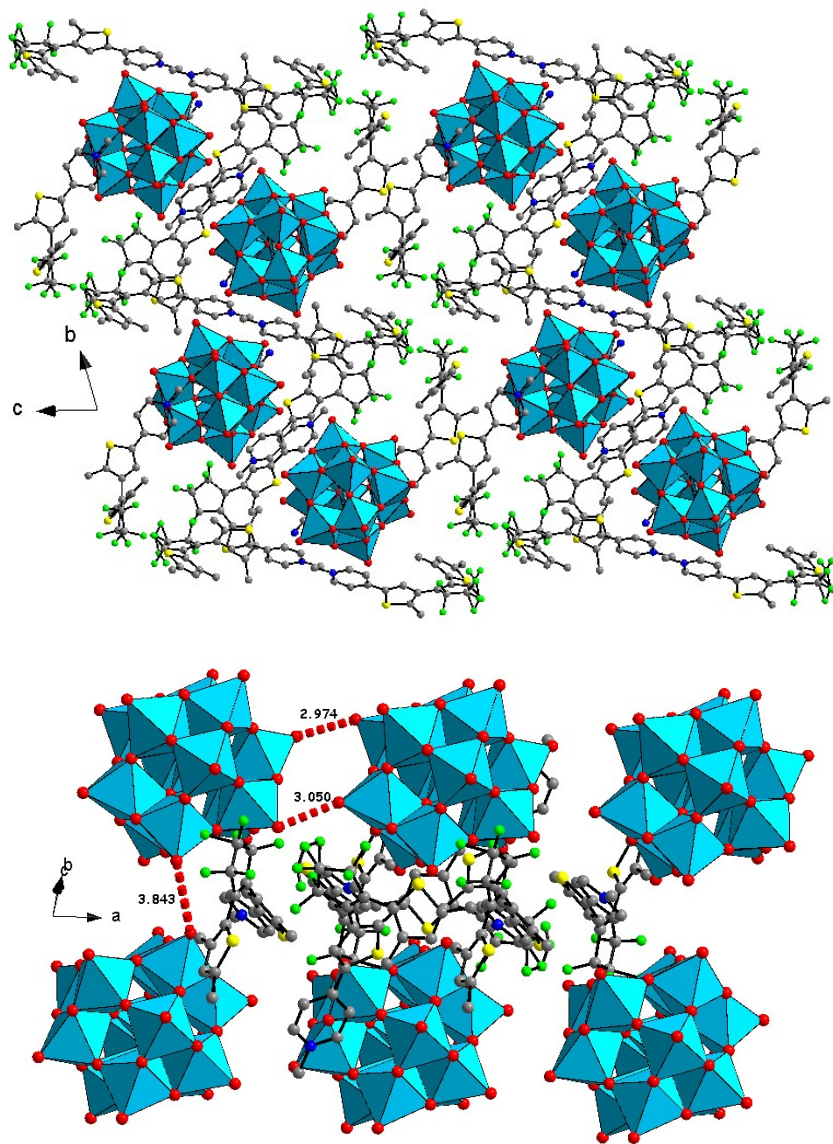


**Fig. S14** Unit cell of **2-PMo<sub>12</sub>** along the *a*-axis (top) and crystal packing showing the  $\pi \cdots \pi$  interactions (red dotted lines) (bottom). H atoms were omitted for clarity.

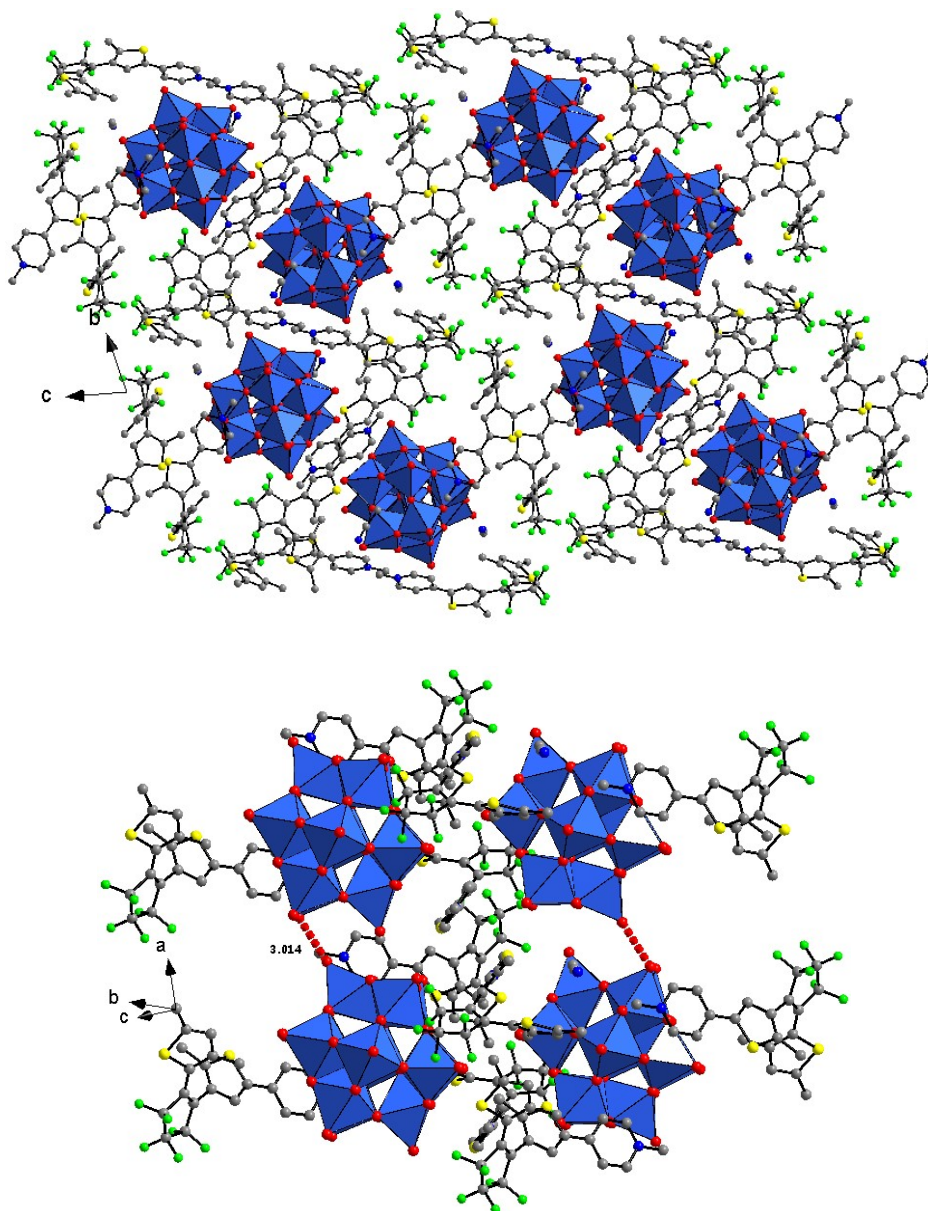


**Fig. S15** Crystal packing of **1-PMo<sub>12</sub>** (top) and the closest interanion contacts (red dotted lines) (bottom).



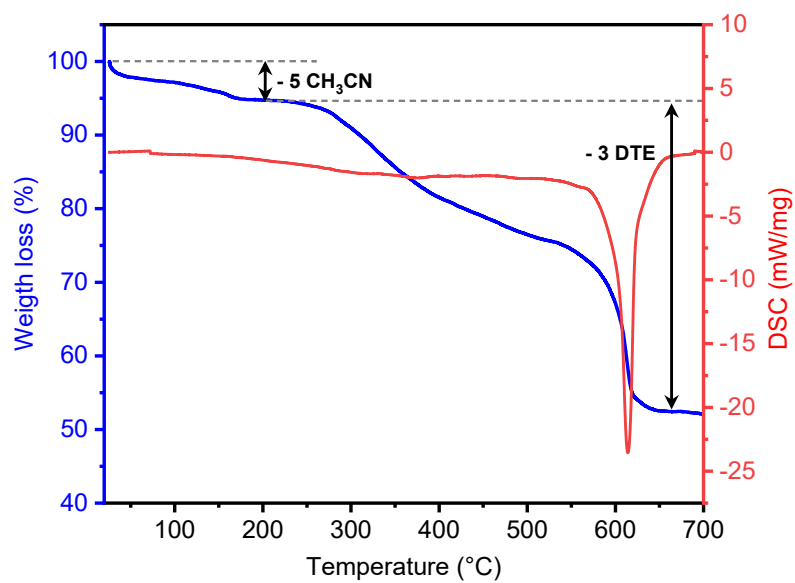


**Fig. S16** Crystal packing of 2-PMo<sub>12</sub> (top) and the closest interanion contacts (red dotted lines) (bottom).



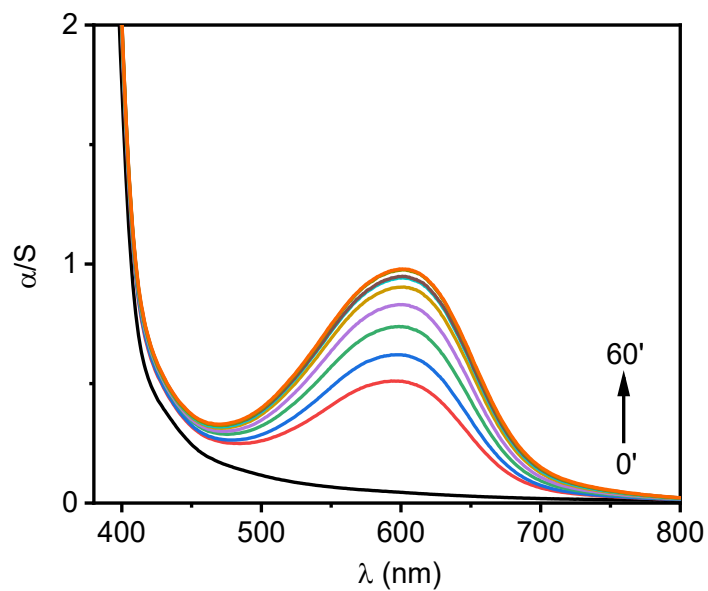
**Fig. S17** Crystal packing of 2-PW<sub>12</sub> (top) and the closest interanion contacts (red dotted lines) (bottom).

## S6. Thermogravimetry curves



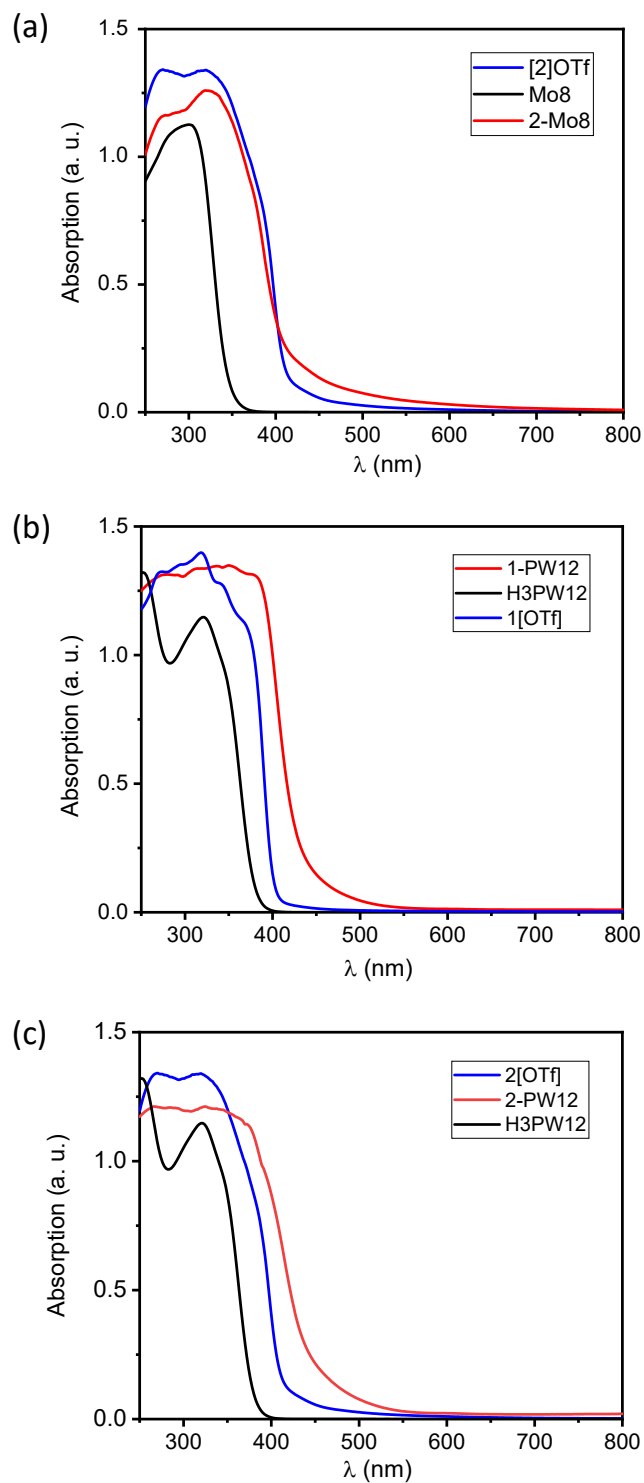
**Fig. S18** TGA (blue line) and DSC (red line) curves of **2-PMO<sub>12</sub>**.

## S7. K-M reflectivity spectra

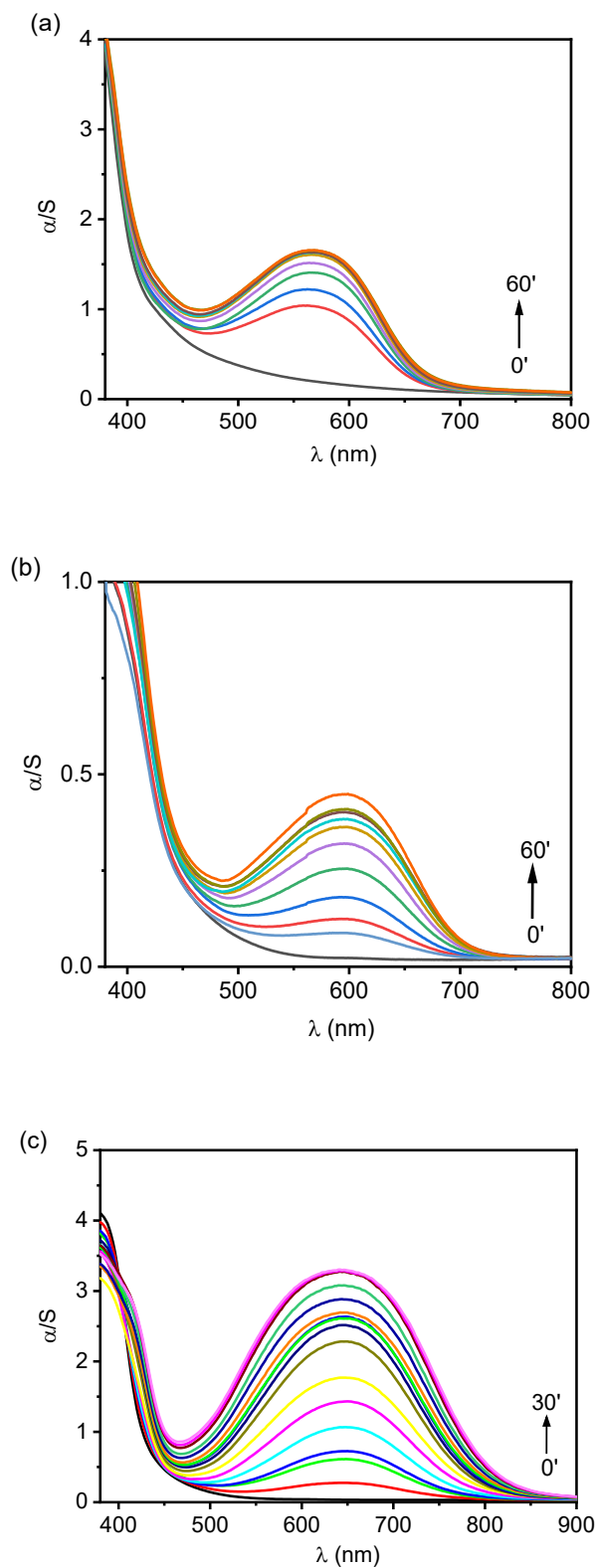


**Fig. S19** Kubelka-Munk transformed reflectivity spectra of [2]OTf at room temperature under UV irradiation ( $\lambda_{\text{ex}} = 365$  nm), over a period of 60 min.

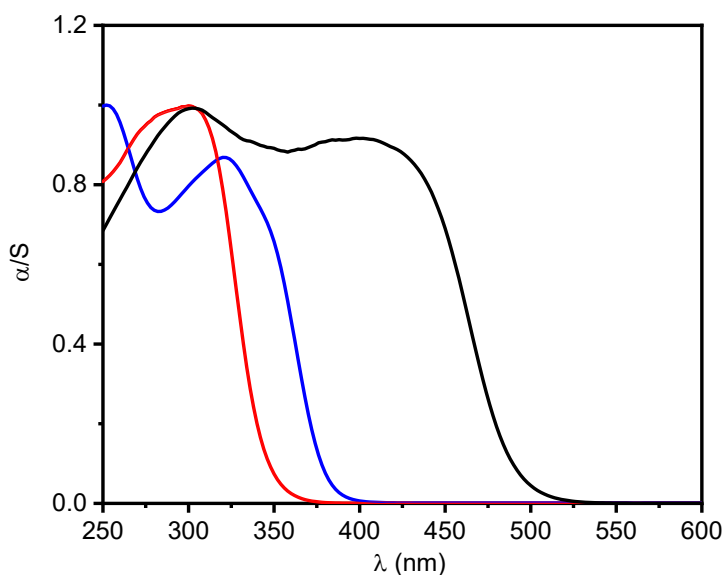




**Fig. S20** Kubelka-Munk transformed reflectivity spectra of (a) [2]OTf, 2-Mo<sub>8</sub> and ((CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>(NH<sub>4</sub>)<sub>2</sub>[Mo<sub>8</sub>O<sub>26</sub>] (Mo<sub>8</sub>), (b) [1]OTf, 1-PW<sub>12</sub> and H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] (H<sub>3</sub>PW<sub>12</sub>), and (c) [2]OTf, 2-PW<sub>12</sub> and H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] (H<sub>3</sub>PW<sub>12</sub>).



**Fig. S21** Kubelka-Munk transformed reflectivity spectra at room temperature under UV irradiation ( $\lambda_{\text{ex}} = 365$  nm) over a period of 60 min for (a) **2-Mo<sub>8</sub>** and (b) **2-PW<sub>12</sub>**, and 30 min for (c) **1-PW<sub>12</sub>**.



**Fig. S22** Normalized Kubelka-Munk transformed reflectivity spectra of  $((\text{CH}_3\text{CH}_2)_2\text{NH}_2)_2(\text{NH}_4)_2[\beta\text{-Mo}_8\text{O}_{26}]$  (red line),  $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$  (blue line) and  $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$  (black line).

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