Supporting Information

Competing Hydrogen-Bonding Interactions in a High-T_c Organic Molecular-Ionic Crystal with Evident Nonlinear Optical Response

Wen-Tao Xu, Jun-Chao Liu, Yu-Ling Zeng, Hua Zhang and Zhong-Xia Wang*

Ordered Matter Science Research Center, Nanchang University, Nanchang 330031, People's Republic of China

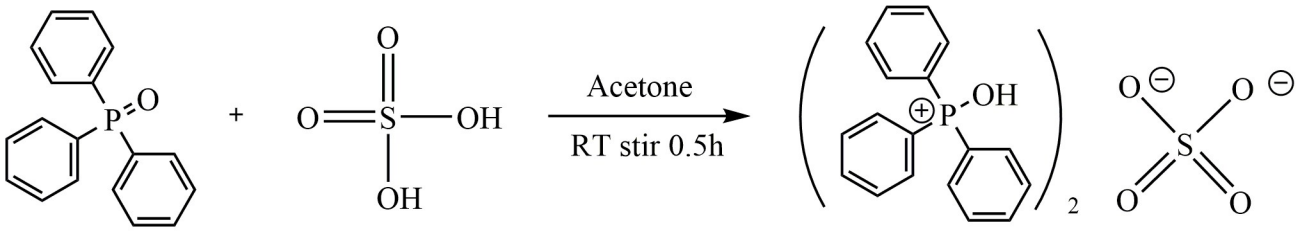
Experimental section

Materials.

Triphenylphosphine Oxide (Adamas-beta, 99%), sulfuric acid-d_2 (D, 99.5%) (Aladdin, 96% in D_2O). Sulfuric acid and acetone were used as received.

Synthesis.

As shown in Scheme 1, triphenylphosphine Oxide (0.556 g, 2 mmol) and sulfuric acid (0.103 g, 1 mmol) in 15 ml acetone were placed into a 100 mL flask with stirring for 30 min at room temperature. A large number of white crystals precipitated, which were subsequently filtrated and washed with acetone. The crystals of $(TPPO–H)_2SO_4$ (0.560 g, yield 85%) was collected and was further characterized by X-ray diffraction.



Scheme 1. Synthesis of $(TPPO–H)_2SO_4$.

Methods.

IR spectra of $(TPPO–H)_2SO_4$ in KBr pellets were recorded on a Shimadzu IR Prestige-21 instrument at room temperature. Thermogravimetric analyses (TGA) were carried out on a TA Q50 system with a heating rate of 10 K min^{-1} under a nitrogen atmosphere. PXRD measurements were taken on a Rigaku D/MAX 2000 PC X-ray diffraction instrument in the 2θ range of 5-50° with a step size of 0.02°. Differential scanning calorimeter (DSC) measurements for $(TPPO–H)_2SO_4$ were carried out on a PerkinElmer Diamond DSC instrument in the temperature range from 293 K to 450 K with a heating rate of 5 K min^{-1} under nitrogen atmosphere. Variable-temperature X-ray single-crystal diffractions were performed on Rigaku Oxford Diffraction 2018 with Mo-Kα radiation (λ = 0.71073 Å) and the

crystal data were collected at 293 K and 423 K, respectively. The Crystalclear software package (Rigaku, 2018) was used to process crystal data. The variable-temperature crystal structures were solved using a direct method, and the SHELXLTL software package (SHELXLTL-2014) was used for the refinement of crystal structures on F^2 using full-matrix least-squares refinement. The anisotropically of non-hydrogen atoms were refined for all reflections with $I > 2\sigma(I)$ and the positions of the hydrogen atoms were generated geometrically. The DIAMOND software (Brandenburg and Putz, 2005) was used to draw asymmetric units and package views. For complex dielectric measurements, the polycrystalline samples were ground into powder and then pressed into a thin plate. The complex dielectric constants ($\varepsilon = \varepsilon' - i\varepsilon''$, where ε' is the real parts, and ε'' represents the imaginary parts) were measured by TongHui TH2828A instrument in the frequency range of 10 kHz to 1 MHz with a temperature range of 293 K to 450 K. For SHG measurements, an unexpanded laser beam with low divergence (pulsed Nd:YAG at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power, 10 Hz repetition rate) was used. The instrument model is Ins 1210058, INSTEC Instruments, while the laser is Vibrant 355 II, OPOTEK. $(TPPO–H)_2SO_4$ samples were ground and sifted into different particle size ranges: 15–30, 35–50, 60–90, 130–170, and 260–300 μm. The numerical values of the nonlinear optical coefficients for SHG were determined by comparison with a KDP reference. For Hirshfeld surfaces analysis, molecular Hirshfeld surface and the related 2D-fingerprint plot calculations were performed by using the CrystalExplorer17.5 program with inputting structure file in CIF format. All bond lengths to hydrogen were automatically modified to typical standard neutron values. In this work, all the Hirshfeld surfaces were generated using a standard (high) surface resolution. The intensity of molecular interaction is mapped onto the Hirshfeld surface by using a red–blue–white color scheme: where the white regions exactly correspond to the distance of van der Waals contact, the blue regions correspond to longer contacts, and the red regions represent closer contacts. In 2D fingerprint plots, each point represents an individual pair (di, de), reflecting the distances to the nearest atom inside (di) and outside (de) of the Hirshfeld surface, and the frequency of occurrence for these points corresponds to the colors from blue (low), through green, to red (highest).

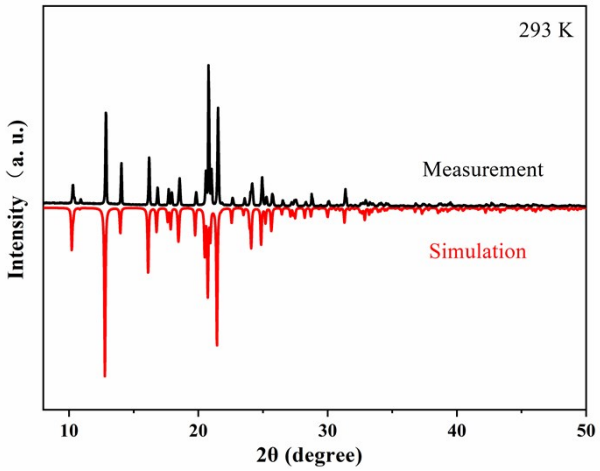


Fig. S1 The pattern of powder X-ray diffraction of $(TPPO–H)_2SO_4$ at 293 K.

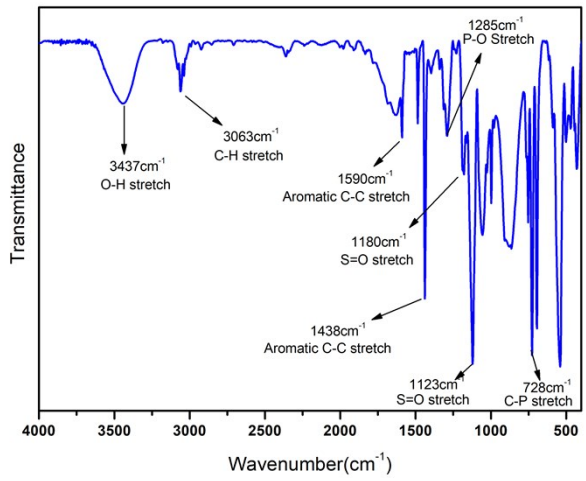


Fig. S2 IR spectra of $(TPPO–H)_2SO_4$ at room temperature.

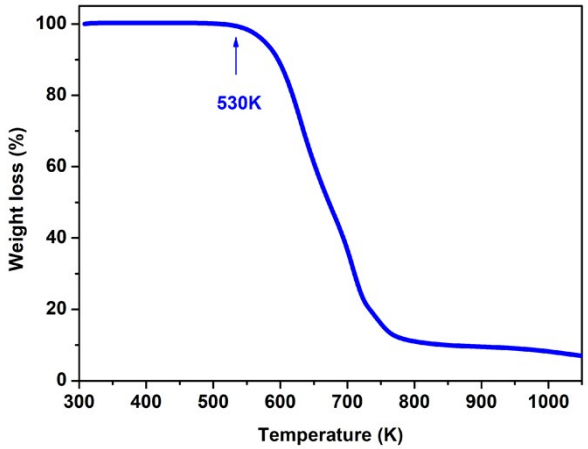


Fig. S3 TG analysis of $(TPPO–H)_2SO_4$, stable up to 530 K.

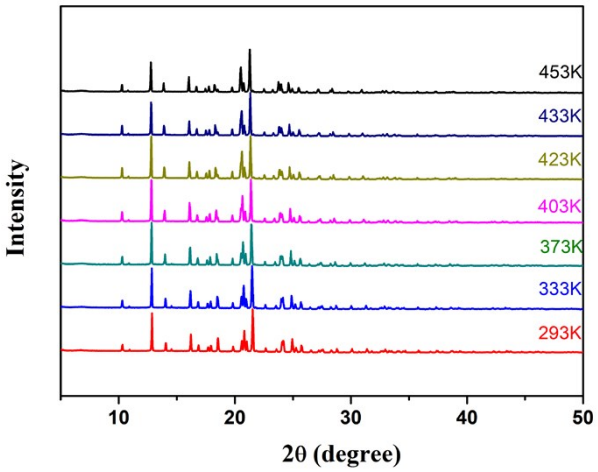


Fig. S4 Various-temperature PXRD measured for $(TPPO–H)_2SO_4$.

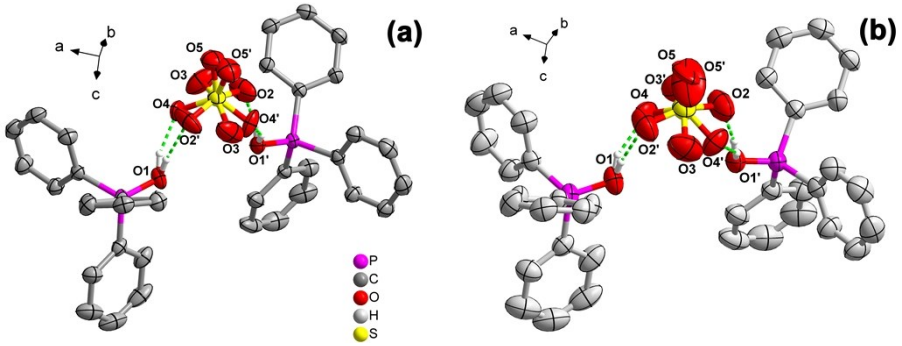


Fig. S5 Crystal structures plotted in ellipsoid view (30%) for $(TPPO–H)_2SO_4$ at 293 K and 423 K. Hydrogen-bonding interactions (green dashed lines) between the TPPO cations and sulfate anion. The hydrogen atoms of the benzene rings were omitted for clarity.

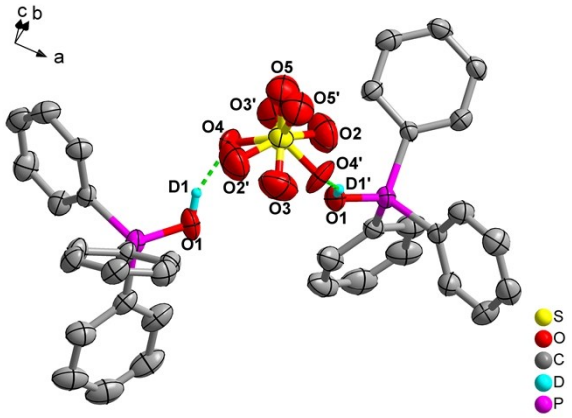


Fig. S6 Crystal structure in ellipsoid view (30%) for $(TPPO–D)_2SO_4$ at 293 K. Hydrogen-bonding interactions (green dashed lines) between the TPPO cations and sulfate anion. The hydrogen atoms of the benzene rings were omitted for clarity.

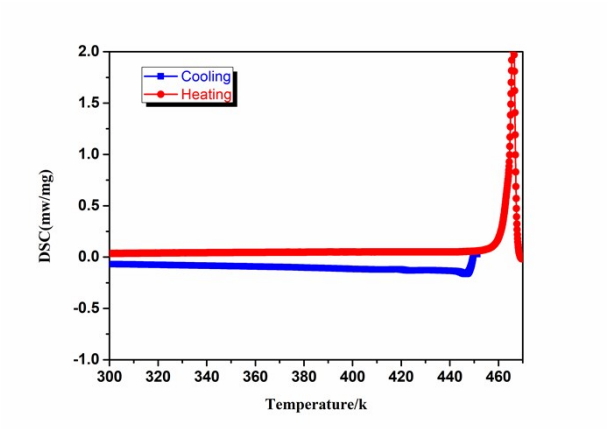


Fig. S7 The DSC curve of $(TPPO–D)_2SO_4$ in the heating and cooling process. (m.p. = 192 °C)

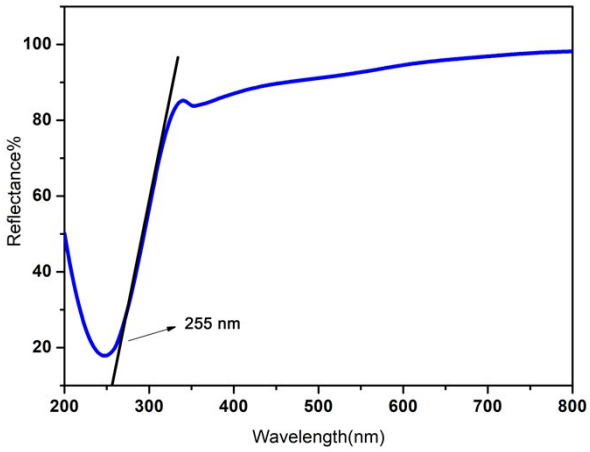


Fig. S8 UV-vis spectrum of $(TPPO–H)_2SO_4$.

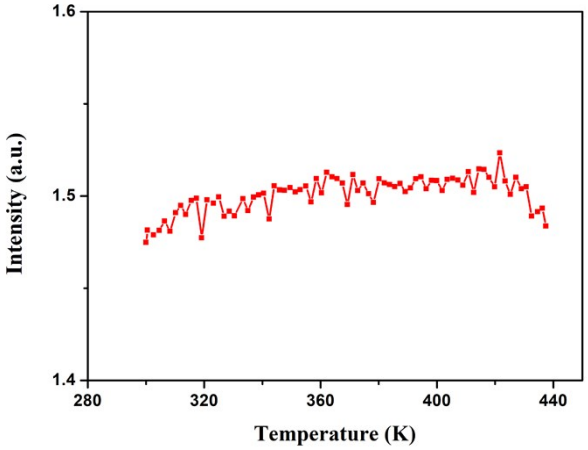


Fig. S9 Various-temperature SHG intensity measured for $(TPPO–H)_2SO_4$.

Table S1. Crystal data and structure refinements.

Compound	$(TPPO–H)_2SO_4$	$(TPPO–H)_2SO_4$	$(TPPO–D)_2SO_4$
Empirical formula	$C_{36}H_{32}O_6P_2S$	$C_{36}H_{32}O_6P_2S$	$C_{36}H_{30}D_2O_6P_2S$
Formula weight	654.62	654.62	656.62
Temperature/K	293	423	293
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Fdd*2	*Fdd*2	*Fdd*2
a/Å	20.1201(18)	20.3657(15)	20.087(3)
b/Å	32.676(3)	33.018(3)	32.633(5)
c/Å	10.0411(8)	10.0713(8)	10.0097(18)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
Volume/Å^3	6601.4(9)	6772.4(10)	6561.5(18)
Z	8	8	8
ρ_{calc} g/cm^3	1.317	1.284	1.329
Reflections collected	7299	7688	10172
Goodness-of-fit on F^2	1.004	1.001	1.001
Final R indexes [I >= 2σ (I)]	R_1 = 0.0379, wR_2 = 0.1046	R_1 = 0.0440, wR_2 = 0.1261	R_1 = 0.0785, wR_2 = 0.1566
Flack	0.05(5)	0.06(14)	0.3(2)

Table S2. Bond Lengths for Crystal data of $(TPPO\text{-}H)_2SO_4$ at 293K.

Atom-Atom	Length/Å	Atom-Atom	Length/Å
P1-O1	1.500(2)	C14-C15	1.408(7)
P1-C13	1.796(3)	C15-C16	1.362(8)
P1-C1	1.796(3)	C17-C16	1.350(8)
P1-C7	1.801(3)	S1-O2	1.392(6)
C1-C2	1.388(4)	S1-O2[1]	1.392(6)
C1-C6	1.390(4)	S1-O5	1.434(8)
C13-C14	1.376(5)	S1-O5[1]	1.434(8)
C13-C18	1.396(5)	S1-O3[1]	1.464(7)
C7-C12	1.379(5)	S1-O3	1.464(7)
C7-C8	1.388(5)	S1-O4[1]	1.511(6)
C11-C10	1.377(6)	S1-O4	1.511(6)
C11-C12	1.388(5)	O2-O4[1]	1.297(11)
C2-C3	1.380(5)	O2-O3[1]	1.466(13)
C6-C5	1.389(5)	O3-O4[1]	1.434(12)
C3-C4	1.373(5)	O3-O2[1]	1.466(14)
C8-C9	1.383(5)	O4-O2[1]	1.297(11)
C18-C17	1.371(6)	O4-O3[1]	1.434(12)
C4-C5	1.370(5)	O5-O5[1]	0.71(2)
C9-C10	1.360(6)		

[1]1/2-X, 1/2-Y, +Z

Table S3. Bond Angles for Crystal data of $(TPPO\text{-}H)_2SO_4$ at 293K.

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
O1-P1-C13	108.52(15)	O2[1]-S1-O5[1]	103.6(8)
O1-P1-C1	111.40(14)	O5-S1-O5[1]	28.6(8)
C13-P1-C1	109.30(15)	O2-S1-O3[1]	61.7(6)
O1-P1-C7	112.59(14)	O2[1]-S1-O3[1]	109.9(6)
C13-P1-C7	106.79(14)	O5-S1-O3[1]	118.0(7)
C1-P1-C7	108.12(13)	O5[1]-S1-O3[1]	92.8(7)
C2-C1-C6	118.7(3)	O2-S1-O3	109.9(6)
C2-C1-P1	118.7(2)	O2[1]-S1-O3	61.7(6)
C6-C1-P1	122.6(2)	O5-S1-O3	92.8(7)
C14-C13-C18	119.0(4)	O5[1]-S1-O3	118.0(7)
C14-C13-P1	119.2(3)	O3[1]-S1-O3	149.0(8)
C18-C13-P1	121.7(2)	O2-S1-O4[1]	52.9(5)
C12-C7-C8	119.3(3)	O2[1]-S1-O4[1]	108.9(5)
C12-C7-P1	120.9(2)	O5-S1-O4[1]	111.7(5)
C8-C7-P1	119.5(2)	O5[1]-S1-O4[1]	135.4(6)
C10-C11-C12	119.5(4)	O3[1]-S1-O4[1]	103.7(4)

C3-C2-C1	120.4(3)	O3-S1-O4[1]	57.6(5)
C5-C6-C1	120.5(3)	O2-S1-O4	108.9(5)
C7-C12-C11	120.5(3)	O2[1]-S1-O4	52.9(5)
C4-C3-C2	120.4(3)	O5-S1-O4	135.4(6)
C9-C8-C7	119.5(3)	O5[1]-S1-O4	111.7(5)
C17-C18-C13	120.4(4)	O3[1]-S1-O4	57.6(5)
C5-C4-C3	120.3(3)	O3-S1-O4	103.7(4)
C10-C9-C8	121.0(4)	O4[1]-S1-O4	112.2(6)
C13-C14-C15	119.1(4)	O4[1]-O2-S1	68.3(4)
C4-C5-C6	119.8(3)	O4[1]-O2-O3[1]	115.7(7)
C16-C15-C14	120.5(4)	S1-O2-O3[1]	61.6(5)
C16-C17-C18	120.8(5)	O4[1]-O3-O2[1]	109.1(6)
C9-C10-C11	120.1(3)	O4[1]-O3-S1	62.8(4)
C17-C16-C15	120.2(5)	O2[1]-O3-S1	56.7(4)
O2-S1-O2[1]	150.9(7)	O2[1]-O4-O3[1]	117.6(6)
O2-S1-O5	103.6(8)	O2[1]-O4-S1	58.8(4)
O2[1]-S1-O5	104.6(8)	O3[1]-O4-S1	59.5(4)
O2-S1-O5[1]	104.6(8)	O5[1]-O5-S1	75.7(4)

[1]1/2-X, 1/2-Y, +Z

Table S4. Hydrogen Bonds for Crystal data of (TPPO-H)2SO4 at 293K.

D-H...A	d(D-H)/Å	d(H...A)/Å	d(D...A)/Å	D-H...A/°
O1-H1A-O4[1]	0.85	1.58	2.379(7)	156.5
O1-H1A-O2[2]	0.85	1.70	2.541(8)	169.0

[1]3/4-X, -1/4+Y, -3/4+Z; [2]1/4+X, 1/4-Y, -3/4+Z

Table S5. Bond Lengths for Crystal data of $(TPPO\text{-}H)_2SO_4$ at 423K.

Atom-Atom	Length/Å	Atom-Atom	Length/Å
S1-O5[1]	1.325(10)	C1-C2	1.376(5)
S1-O5	1.325(10)	C1-C6	1.386(5)
S1-O2[1]	1.395(8)	C2-C3	1.373(7)
S1-O2	1.395(8)	C3-C4	1.372(7)
S1-O3	1.469(10)	C4-C5	1.341(7)
S1-O3[1]	1.469(10)	C5-C6	1.377(6)
S1-O4[1]	1.515(7)	C7-C8	1.363(6)
S1-O4	1.515(7)	C7-C12	1.373(6)
P1-O1	1.494(3)	C8-C9	1.365(8)
P1-C1	1.787(4)	C9-C10	1.346(9)
P1-C13	1.799(4)	C10-C11	1.372(9)
P1-C7	1.804(4)	C11-C12	1.381(7)
O2-O4[1]	1.267(13)	C13-C14	1.367(6)

O2-O3[1]	1.538(16)	C13-C18	1.378(7)
O3-O4[1]	1.427(15)	C14-C15	1.420(9)
O3-O2[1]	1.538(16)	C15-C16	1.334(11)
O4-O2[1]	1.267(13)	C16-C17	1.340(11)
O4-O3[1]	1.427(15)	C17-C18	1.355(8)
O5-O5[1]	0.44(6)		

[1]1/2-X, 1/2-Y, +Z

Table S6. Bond Angles for Crystal data of $(TPPO\text{-}H)_2SO_4$ at 423K.

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
O5[1]-S1-O5	19(3)	O4[1]-O2-S1	69.2(6)
O5[1]-S1-O2[1]	107.1(12)	O4[1]-O2-O3[1]	111.4(8)
O5-S1-O2[1]	99.0(12)	S1-O2-O3[1]	59.9(6)
O5[1]-S1-O2	99.0(12)	O4[1]-O3-S1	63.1(5)
O5-S1-O2	107.1(12)	O4[1]-O3-O2[1]	107.8(8)
O2[1]-S1-O2	153.6(9)	S1-O3-O2[1]	55.2(5)
O5[1]-S1-O3	115.9(15)	O2[1]-O4-O3[1]	117.5(9)
O5-S1-O3	97.0(15)	O2[1]-O4-S1	59.4(5)
O2[1]-S1-O3	64.9(7)	O3[1]-O4-S1	59.8(6)
O2-S1-O3	107.1(7)	O5[1]-O5-S1	80.5(14)
O5[1]-S1-O3[1]	97.0(15)	C2-C1-C6	118.1(4)
O5-S1-O3[1]	115.9(15)	C2-C1-P1	118.8(3)
O2[1]-S1-O3[1]	107.1(7)	C6-C1-P1	123.1(3)
O2-S1-O3[1]	64.9(7)	C3-C2-C1	120.2(4)
O3-S1-O3[1]	147.1(11)	C4-C3-C2	120.8(4)
O5[1]-S1-O4[1]	129.5(14)	C5-C4-C3	119.7(4)
O5-S1-O4[1]	121.2(14)	C4-C5-C6	120.6(4)
O2[1]-S1-O4[1]	110.9(6)	C5-C6-C1	120.7(4)
O2-S1-O4[1]	51.4(6)	C8-C7-C12	118.7(4)
O3-S1-O4[1]	57.1(7)	C8-C7-P1	120.2(3)
O3[1]-S1-O4[1]	102.2(6)	C12-C7-P1	120.9(3)
O5[1]-S1-O4	121.2(14)	C7-C8-C9	120.4(5)
O5-S1-O4	129.5(14)	C10-C9-C8	121.2(5)
O2[1]-S1-O4	51.4(6)	C9-C10-C11	119.9(5)
O2-S1-O4	110.9(6)	C10-C11-C12	119.0(5)
O3-S1-O4	102.2(6)	C7-C12-C11	120.9(5)
O3[1]-S1-O4	57.1(7)	C14-C13-C18	118.2(5)
O4[1]-S1-O4	108.4(7)	C14-C13-P1	119.1(4)
O1-P1-C1	111.67(18)	C18-C13-P1	122.7(3)
O1-P1-C13	108.3(2)	C13-C14-C15	119.0(6)
C1-P1-C13	108.99(19)	C16-C15-C14	119.6(7)

O1-P1-C7	112.75(19)	C15-C16-C17	121.7(7)
C1-P1-C7	107.84(17)	C16-C17-C18	119.4(8)
C13-P1-C7	107.10(17)	C17-C18-C13	122.0(6)

[1]1/2-X, 1/2-Y, +Z

Table S7. Hydrogen Bonds for Crystal data of $(TPPO\text{-}H)_2SO_4$ at 423K.

D-H...A	d(D-H)/Å	d(H...A)/Å	d(D...A)/Å	D-H...A/°
O1-H1B-O2[1]	0.85	1.70	2.539(11)	168.1
O1-H1A-O4[2]	0.85	1.60	2.387(10)	152.6

[1]1/4+X, 1/4-Y, -3/4+Z; [2]3/4-X, -1/4+Y, -3/4+Z

Table S8. Bond Lengths for Crystal data of (TPPO-D)2SO4 at 293K.

Atom-Atom	Length/Å	Atom-Atom	Length/Å
S1-O3	1.353(9)	C6-C16	1.372(7)
S1-O3[1]	1.353(9)	C7-C15	1.362(7)
S1-O2	1.383(9)	C8-C12	1.361(7)
S1-O2[1]	1.383(9)	C9-C14	1.366(7)
S1-O5	1.451(8)	C9-C17	1.374(7)
S1-O5[1]	1.451(8)	C10-C16	1.410(7)
S1-O4[1]	1.496(7)	C11-C18	1.372(6)
S1-O4	1.496(7)	C11-C12	1.384(7)
O4-O2[1]	1.194(12)	C13-C18	1.400(6)
O4-O3[1]	1.516(12)	C15-C17	1.382(7)
O5-O5[1]	0.69(2)	C16-P1	1.781(5)
C1-C2	1.330(9)	C17-P1	1.807(4)
C1-C6	1.391(8)	C18-P1	1.801(4)
C2-C4	1.371(9)	O1-P1	1.507(3)
C3-C8	1.357(7)	O2-O4[1]	1.194(12)
C3-C13	1.366(7)	O2-O3[1]	1.292(15)
C4-C10	1.369(9)	O3-O2[1]	1.292(15)
C5-C7	1.345(8)	O3-O4[1]	1.516(12)
C5-C14	1.376(9)		

[1]1/2-X, 3/2-Y, +Z

Table S9. Bond Angles for Crystal data of $(TPPO\text{-}D)_2SO_4$ at 293K.

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
O3-S1-O3[1]	143.0(10)	C8-C3-C13	121.4(5)
O3-S1-O2	112.7(6)	C10-C4-C2	117.7(6)
O3[1]-S1-O2	56.3(6)	C7-C5-C14	120.3(5)
O3-S1-O2[1]	56.3(6)	C16-C6-C1	120.7(5)
O3[1]-S1-O2[1]	112.7(6)	C5-C7-C15	121.4(6)

O2-S1-O2[1]	149.2(10)	C3-C8-C12	120.3(5)
O3-S1-O5	96.9(7)	C14-C9-C17	121.1(6)
O3[1]-S1-O5	119.7(7)	C4-C10-C16	122.4(5)
O2-S1-O5	104.3(7)	C18-C11-C12	120.8(5)
O2[1]-S1-O5	105.6(7)	C8-C12-C11	119.5(4)
O3-S1-O5[1]	119.7(7)	C3-C13-C18	119.1(4)
O3[1]-S1-O5[1]	96.9(7)	C9-C14-C5	118.9(6)
O2-S1-O5[1]	105.6(7)	C7-C15-C17	119.3(5)
O2[1]-S1-O5[1]	104.3(7)	C6-C16-C10	116.8(5)
O5-S1-O5[1]	27.5(8)	C6-C16-P1	121.5(4)
O3-S1-O4[1]	64.1(6)	C10-C16-P1	121.5(4)
O3[1]-S1-O4[1]	94.3(6)	C9-C17-C15	119.0(4)
O2-S1-O4[1]	48.8(5)	C9-C17-P1	121.1(4)
O2[1]-S1-O4[1]	110.8(6)	C15-C17-P1	119.6(4)
O5-S1-O4[1]	113.5(5)	C11-C18-C13	118.9(4)
O5[1]-S1-O4[1]	135.2(6)	C11-C18-P1	122.9(4)
O3-S1-O4	94.3(6)	C13-C18-P1	118.2(3)
O3[1]-S1-O4	64.1(6)	O1-P1-C16	107.3(2)
O2-S1-O4	110.8(6)	O1-P1-C18	111.8(2)
O2[1]-S1-O4	48.8(5)	C16-P1-C18	109.5(2)
O5-S1-O4	135.2(6)	O1-P1-C17	112.29(19)
O5[1]-S1-O4	113.5(5)	C16-P1-C17	107.7(2)
O4[1]-S1-O4	110.4(7)	C18-P1-C17	108.2(2)
O2[1]-O4-S1	60.7(6)	O4[1]-O2-O3[1]	114.5(9)
O2[1]-O4-O3[1]	113.8(8)	O4[1]-O2-S1	70.6(6)
S1-O4-O3[1]	53.3(5)	O3[1]-O2-S1	60.6(6)
O5[1]-O5-S1	76.3(4)	O2[1]-O3-S1	63.0(6)
C2-C1-C6	120.3(6)	O2[1]-O3-O4[1]	115.0(8)
C1-C2-C4	122.2(7)	S1-O3-O4[1]	62.6(5)

[1]1/2-X, 3/2-Y, +Z

Table S10. Hydrogen Bonds for Crystal data of $(TPPO\text{-}D)_2SO_4$ at 293K.

D-H...A	d(D-H)/Å	d(H...A)/Å	d(D...A)/Å	D-H...A/°
O1-D1-O2[2]	0.85	1.82	2.510(13)	136.7
O1-D1-O4[1]	0.85	1.55	2.346(9)	155.1

[1]3/4-X, 1/4+Y, 3/4+Z; [2]1/4+X, 7/4-Y, 3/4+Z