$Hg[CS(NH_2)_2]_4(SiF_6)$: A Fluorosilicate Crystal with Large Birefringence Achieved via Multi-Functional Group Modification

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Supporting Information

S1. Experimental Section

Materials and Instrumentations.

All the chemicals were obtained from commercial sources and used without further purification: $CS(NH_2)_2$ (Adamas-beta, 99%), $Hg(CF_3SO_3)_2$ (Adamas-beta, 98%), and H_2SiF_6 (Adamas-beta, 30% in water).

Powder X-ray diffraction (PXRD) patterns of $Hg[CS(NH_2)_2]_4(SiF_6)$ was collected on the Miniflex 600 powder X-ray diffractometer using Cu Kα radiation (λ = 1.54186 Å) at room temperature in the angular range of 2θ = 5-70° with a scan step size of 0.02°.

Microprobe elemental analysis was carried out with the aid of a field-emission scanning electron microscope (JSM6700F) outfitted with an energy-dispersive X-ray spectroscope (Oxford INCA).

IR spectra were carried out on a Magna 750 FT-IR spectrometer using air as background in the range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1} at room temperature.

The UV-vis-NIR spectra were obtained at 2000-200 nm by a PerkinElmer Lambda 900 spectrophotometer using $BaSO_4$ as the reference, and the reflection spectra were converted into an absorption spectrum using the Kubelka-Munk function. Absorption data was calculated from the diffuse reflection data by the Kubelka-Munk function: $\alpha/S = (1-R)^2/2R$, where α and S represent the absorption coefficient and the scattering coefficient, respectively. The band gap value can be given by extrapolating the absorption edge to the baseline in the α/S vs. energy graph.

Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were measured by Netzsch STA 499C installation. The samples about 3.0-5.0 mg were placed in alumina crucibles and heated in 20-700 °C at a rate of 15 °C/min under N_2 atmosphere.

Single-crystal X-ray diffraction data was obtained on Agilent Technologies SuperNova dual-wavelength CCD diffractometer with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. Data reduction and cell refinement and were performed with *CrysAlisPro*. The structure was solved by the direct methods and refined by full-matrix leastsquares fitting on F^2 using *OLEX2-1.5* crystallographic software package. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structural data were also checked by PLATON and no higher symmetry was found. The detailed crystallographic data for $Hg[CS(NH_2)_2]_4(SiF_6)$ was given in Table S1. The bond lengths and bond angles were listed in Table S2 and S4.

S2. Computational Method

Single-crystal structural data of $Hg[CS(NH_2)_2]_4(SiF_6)$ was used for the theoretical calculations. The electronic structures were performed using a plane-wave basis set and pseudo-potentials within density functional theory (DFT) implemented in the total-energy code CASTEP[1]. For the exchange and correlation functional, we chose Perdew-Burke-Ernzerhof (PBE) in the generalized gradient approximation (GGA)[2]. The interactions between the ionic cores and the electrons were described by the Nom-conserving pseudopotential in reciprocal space[3]. The following valence-electron configurations were considered in the computation: Hg-$5d^{10}5p^26s^2$, C-$2s^22p^2$, S-$3s^23p^4$, N-$2s^22p^3$, H-$1s^2$, Si-$3s^23p^2$ and F-$2s^22p^5$. The numbers of plane waves included in the basics sets were determined by cutoff energy of 850 eV for $Hg[CS(NH_2)_2]_4(SiF_6)$. The Brillouin zone integration was performed using a 2×2×2 Monkhorst-Pack k-point mesh, whose convergence was verified against denser k-point samplings. All other calculation parameters and convergence criteria were set to the CASTEP code defaults.

The calculations of linear optical properties in terms of the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ were made. The imaginary part of the dielectric function ε2 was given in the following equation:

$$\varepsilon^{ij}_2(\omega) = \frac{8\pi^2 h^2 e^2}{(m^2 V)} \sum_k \sum_{cv} (f_c - f_v) \frac{p^i_{cv}(k) p^j_{cv}(k)}{E^2_{vc}} \delta[E_c(k) - E_v(k) - h\omega]$$

The f_c and f_v represent the Fermi distribution functions of the conduction and valence band. The term $p^i_{cv}(k)$ denotes the momentum matrix element transition from the energy level c of the conduction band to the level v of the valence band at the *k*th point in the Brillouin zone (BZ), and V is the volume of the unit cell.

The real part $\varepsilon_1(\omega)$ of the dielectric function $\varepsilon(\omega)$ follows from the Kramer-Kronig relationship. All the other optical constants may be derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. For example, the refractive index $n(\omega)$ can be calculated using the following expression[4]:

$$n(\omega)=\left(\frac{1}{\sqrt{2}}\right)\left[\sqrt{\varepsilon_1^2(\omega)+\varepsilon_2^2(\omega)}+\varepsilon_1(\omega)\right]^{1/2}$$

Furthermore, a sensitivity analysis of the scissor operator was conducted. The calculated birefringence values were 0.120 @1064 nm and 0.139 @546 nm with a 0.3 eV scissor operator, and 0.130 @1064 nm and 0.115 @546 nm with a 0.6 eV operator.

Table S1. Summary of crystal data and structural refinements for $Hg[CS(NH_2)_2]_4(SiF_6)$.

Molecular formula	**$Hg[CS(NH_2)_2]_4(SiF_6)$**
Formula Weight	647.17
Crystal system	monoclinic
Space group	$P2_1/c$
Temperature (K)	296.15
F(000)	1232.0
a/Å	11.9952(8)
b/Å	13.2312(8)
c/Å	11.8979(10)
α/deg	90
β/deg	104.765(7)
γ/deg	90
$V/Å^3$	1826.0(2)
Z	4
$D_{calc}/g\cdot cm^{-3}$	2.354
GOF on F^2	1.028
R_1, $wR_2[I > 2\sigma(I)]^{\alpha}$	$R_1 = 0.0344$, $wR_2 = 0.0753$
R_1, wR_2 (all data)$^{\alpha}$	$R_1 = 0.0433$, $wR_2 = 0.0812$

$^{a}R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$

Table S2. Selected bond distances (Å) for Hg[CS(NH$_2$)$_2$]$_4$(SiF$_6$).

Bond	**Bond lengths**
Hg(1)-S(1)	2.545(2)
Hg(1)-S(2)	2.594(18)
Hg(1)-S(3)	2.555(18)
Hg(1)-S(4)	2.493(17)
Si(1)-F(1)	1.691(4)
Si(1)-F(2)	1.659(5)
Si(1)-F(3)	1.665(5)
Si(1)-F(4)	1.686(4)
Si(1)-F(5)	1.669(5)
Si(1)-F(6)	1.682(5)
C(1)-N(1)	1.308(9)
C(1)-N(2)	1.307(9)
C(1)-S(1)	1.733(7)
C(2)-N(3)	1.303(9)
C(2)-N(4)	1.309(9)
C(2)-S(2)	1.735(7)
C(3)-N(5)	1.310(8)
C(3)-N(6)	1.304(9)
C(3)-S(3)	1.750(7)
C(4)-N(7)	1.321(9)
C(4)-N(8)	1.308(9)
C(4)-S(4)	1.720(7)

Table S3. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters ($Å^2$×10^3) for $Hg[CS(NH_2)_2]_4(SiF_6)$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Hg1	5272.2(2)	4786.6(2)	12420.9(2)	33.91(12)
S4	3238.6(14)	4207.3(12)	11685.3(16)	31.0(4)
S3	5577.3(16)	6682.3(13)	12777.9(16)	34.0(4)
S2	6072.3(16)	3849.7(13)	14375.0(15)	33.8(4)
S1	6200.4(17)	4162.5(15)	10849.7(17)	39.2(4)
Si1	345.8(15)	2282.1(14)	9460.1(17)	28.3(4)
F1	-1108(3)	2201(3)	9043(4)	40.4(10)
F4	1798(3)	2343(3)	9859(4)	45.3(11)
F2	310(4)	3220(4)	8525(5)	72.3(17)
F3	246(4)	3106(4)	10487(5)	67.0(15)
F5	403(4)	1337(4)	10402(5)	64.2(15)
N5	7687(5)	6839(4)	12496(5)	36.8(14)
N4	6806(6)	5570(5)	15485(5)	39.8(15)
F6	459(4)	1426(4)	8449(5)	68.3(16)
N6	6238(5)	6974(5)	10840(5)	38.3(15)
N7	2680(5)	6170(5)	11772(6)	45.3(17)
C3	6588(6)	6843(5)	11960(6)	26.5(14)
C2	7095(6)	4739(5)	15031(6)	29.3(15)
N3	8182(6)	4576(5)	15102(7)	54(2)
N2	8327(5)	4446(5)	12185(6)	48.5(17)
N1	8001(6)	2970(5)	11199(6)	52.9(19)
N8	1217(5)	5045(5)	11291(7)	57(2)
C4	2326(6)	5226(5)	11576(6)	31.1(15)
C1	7620(6)	3835(5)	11483(6)	32.9(16)

Table S4. Selected bond angles for $Hg[CS(NH_2)_2]_4(SiF_6)$.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
S4	Hg1	S3	116.49(6)	F3	Si1	F6	178.5(3)
S4	Hg1	S2	105.85(6)	F5	Si1	F1	90.7(2)
S4	Hg1	S1	102.38(6)	F5	Si1	F4	89.1(2)
S3	Hg1	S2	108.40(6)	F5	Si1	F6	88.8(3)
S1	Hg1	S3	111.70(6)	F6	Si1	F1	90.7(2)
S1	Hg1	S2	111.85(6)	F6	Si1	F4	88.2(2)
C4	S4	Hg1	109.4(2)	N5	C3	S3	118.9(5)
C3	S3	Hg1	96.7(2)	N6	C3	S3	119.8(5)
C2	S2	Hg1	97.8(2)	N6	C3	N5	121.4(6)
C1	S1	Hg1	109.1(2)	N4	C2	S2	121.6(6)
F4	Si1	F1	178.9(3)	N3	C2	S2	119.8(6)
F2	Si1	F1	90.1(2)	N3	C2	N4	118.5(7)
F2	Si1	F4	90.1(3)	N7	C4	S4	123.9(5)
F2	Si1	F3	90.5(3)	N8	C4	S4	117.5(5)
F2	Si1	F5	179.2(3)	N8	C4	N7	118.6(7)
F2	Si1	F6	91.0(3)	N2	C1	S1	122.0(6)
F3	Si1	F1	89.7(2)	N2	C1	N1	119.6(7)
F3	Si1	F4	91.4(2)	N1	C1	S1	118.4(6)
F3	Si1	F5	89.8(3)				

Table S5. State energies (eV) of the lowest conduction band (L-CB) and the highest valence band (H-VB) of Hg[CS(NH_2)$_2$]$_4$(SiF_6).

Compound	**k-point**	**L-CB**	**H-VB**
Hg[CS(NH_2)$_2$]$_4$(SiF_6)	Z (0.000, 0.000, 0.500)	3.036249	-0.00655
	G (0.000, 0.000, 0.000)	2.979945	-0.0194
	Y (0.000, 0.500, 0.000)	3.018859	-0.04572
	A (-0.500, 0.500, 0.000)	3.018254	-0.05825
	B (-0.500, 0.000, 0.000)	2.979949	-0.03092
	D (-0.500, 0.000, 0.500)	3.031659	-0.01947
	E (-0.500, 0.500, 0.500)	3.05326	-0.01361
	C (0.000, 0.500, 0.500)	3.052199	0

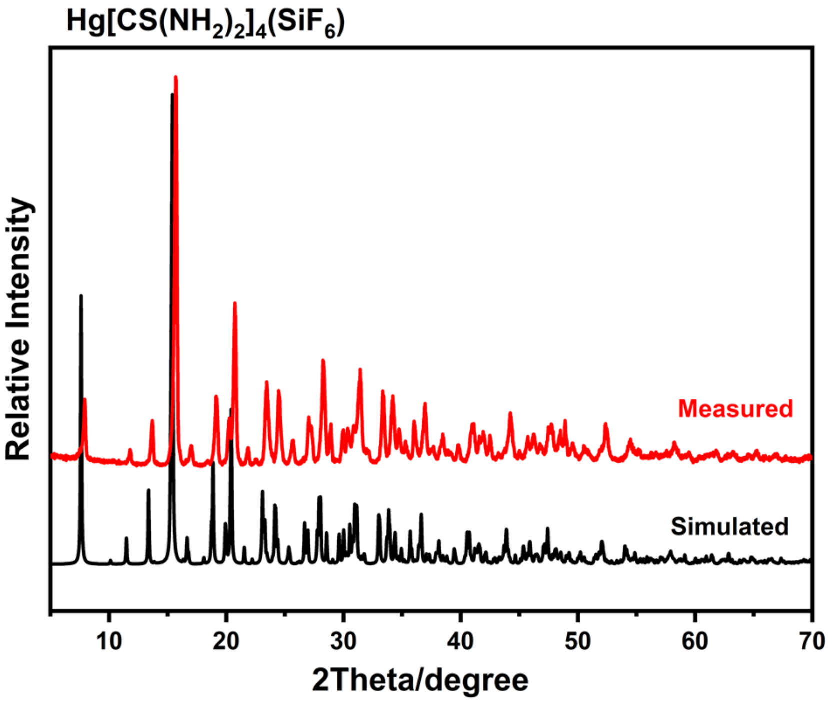

Figure S1. Simulated and experimental powder X-ray diffractometer patterns of $Hg[CS(NH_2)_2]_4(SiF_6)$.

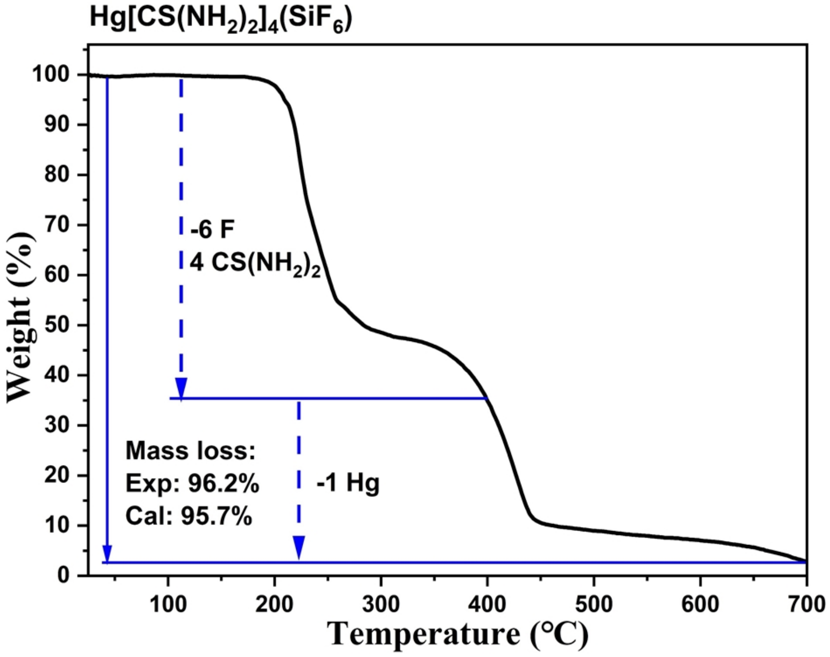

Figure S2. The thermal stability curves of $Hg[CS(NH_2)_2]_4(SiF_6)$.

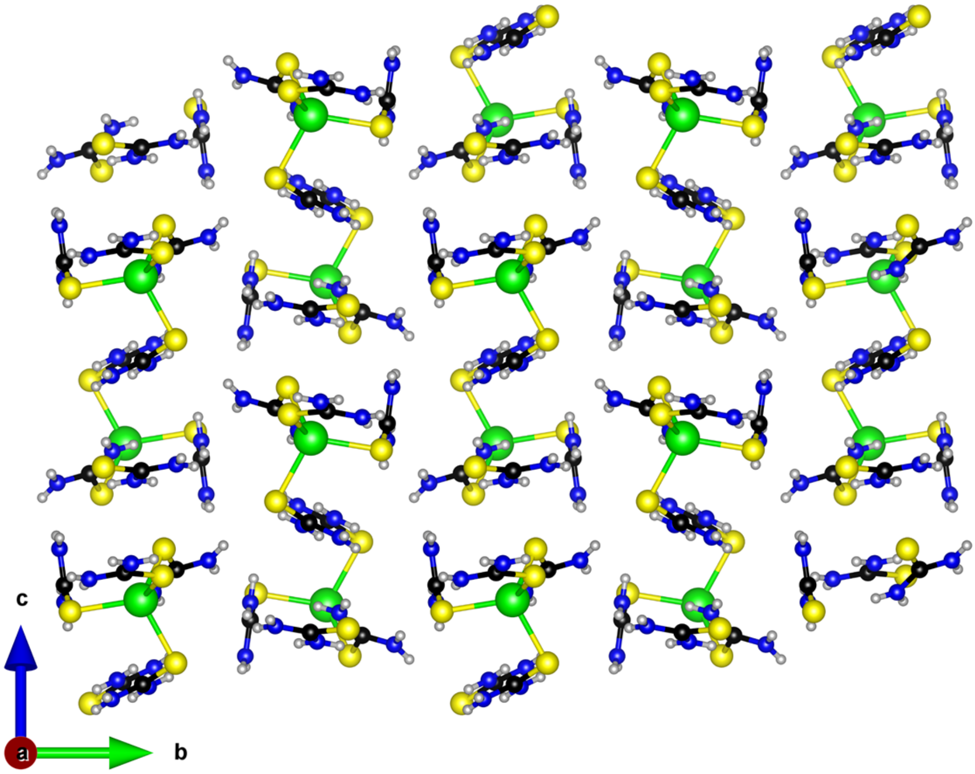

Figure S3. Arrangement of the $CS(NH_2)_2$ groups in $Hg[CS(NH_2)_2]_4(SiF_6)$.

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