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Supporting Information

$[C(NH_2)_3]_2S_2O_8$: Combining Delocalized and Localizes π-Conjugate Units Achieving Strong Optical Anisotropy

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Table S1. Atomic coordinates and U_{eq} for $[C(NH_2)_3]_2S_2O_8$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
S1	0.77780(15)	0.60300(15)	0.09383(8)	0.0305(4)
O1	0.7418(4)	0.7635(4)	0.04626(19)	0.0332(9)
O2	0.6758(5)	0.4956(4)	0.0585(2)	0.0411(11)
O3	0.9306(4)	0.5697(5)	0.0752(3)	0.0575(12)
O4	0.7469(4)	0.6482(4)	0.17975(19)	0.0463(11)
N1	0.5658(6)	0.8338(5)	0.3173(3)	0.0661(17)
H1A	0.616310	0.826952	0.270536	0.079
H1B	0.534323	0.919588	0.334508	0.079
N2	0.4576(6)	0.7249(6)	0.4340(3)	0.0609(15)
H2A	0.425744	0.810800	0.450772	0.073
H2B	0.438315	0.646164	0.463745	0.073
N3	0.5843(6)	0.5813(5)	0.3366(3)	0.0564(14)
H3A	0.634859	0.573238	0.289991	0.068
H3B	0.564587	0.502994	0.366635	0.068
C1	0.5368(7)	0.7136(7)	0.3622(4)	0.0425(15)

Table S2. Bond lengths [Å] and angles [deg] for $[C(NH_2)_3]_2S_2O_8$.

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
S1–O4	1.427(3)	O4–S1–O3	115.8(2)
S1–O3	1.427(4)	O4–S1–O2	115.3(2)
S1–O2	1.434(4)	O3–S1–O2	113.0(3)
S1–O1	1.647(3)	O4–S1–O1	98.01(18)
O1–O1[#1]	1.470(6)	O3–S1–O1	106.1(2)
N1–C1	1.308(7)	O2–S1–O1	106.60(19)
N1–H1A	0.8600	O1–O1–S1	107.6(3)
N1–H1B	0.8600	C1–N1–H1A	120.0
N2–C1	1.330(7)	C1–N1–H1B	120.0
N2–H2A	0.8600	H1A–N1–H1B	120.0
N2–H2B	0.8600	C1–N2–H2A	120.0
N3–C1	1.318(7)	C1–N2–H2B	120.0
N3–H3A	0.8600	H2A–N2–H2B	120.0
N3–H3B	0.8600	C1–N3–H3A	120.0
		C1–N3–H3B	120.0
		H3A–N3–H3B	120.0
		N1–C1–N3	120.7(5)
		N1–C1–N2	119.7(6)
		N3–C1–N2	119.6(6)

Symmetry transformations used to generate equivalent atoms: #1) x-1/2, y, -z+3/2; #2) x+1/2, y, -z+3/2.

Table S3. Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and ∠DHA > 110 deg for $[C(NH_2)_3]_2S_2O_8$ (D = Donor, A = Acceptor).

D-H	d(D-H)	d(H..A)	∠DHA	d(D..A)
N1–H1A···O4	0.86	2.43	3.159(6)	142.4
N1–H1B···O3$^{\#1}$	0.86	2.15	2.952(6)	154.1
N2–H2A···O3$^{\#1}$	0.86	2.35	3.093(6)	145.2
N2–H2A···O4$^{\#2}$	0.86	2.48	3.058(6)	125.0
N2–H2B···O2$^{\#3}$	0.86	2.20	3.013(6)	158.0
N3–H3A···O4	0.86	2.10	2.909(6)	156.6
N3–H3B···O2$^{\#4}$	0.86	2.05	2.910(6)	175.9

Symmetry transformations used to generate equivalent atoms:

#1: 1-Y, 2-X, 0.5-Z; #2: -0.5+X, 1.5-Y, 0.75-Z; #3: 1-X, 1-Y, 0.5+Z; #4: 1-Y, 1-X, 0.5-Z;

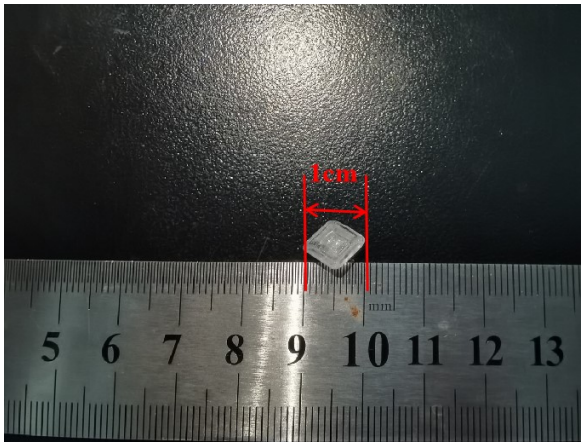

Figure S1. The photo of single crystals of $[C(NH_2)_3]_2S_2O_8$.

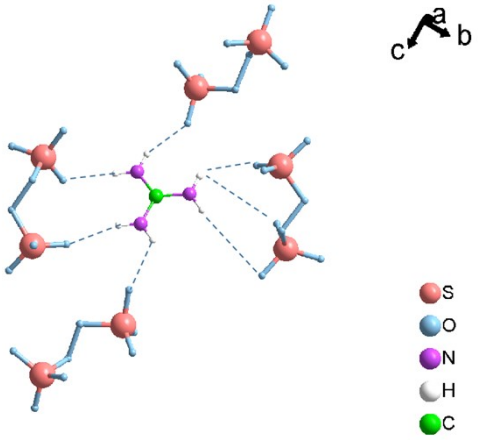

Figure S2. The hydrogen bonds between guanidine cation and $[S_2O_8]$ groups.

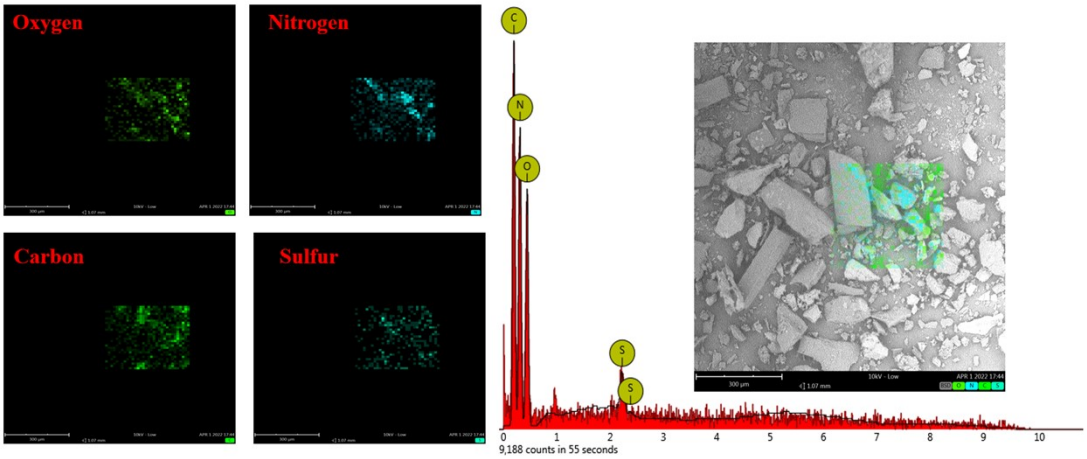

Figure S3. SEM images and EDX.microanalysis for $[C(NH_2)_3]_2S_2O_8$. The mole ratio of the elements is C: N: S: O=12.6 : 26.6 : 2.3 : 58.4. Noted that the EDX only provides semi-quantitative results.

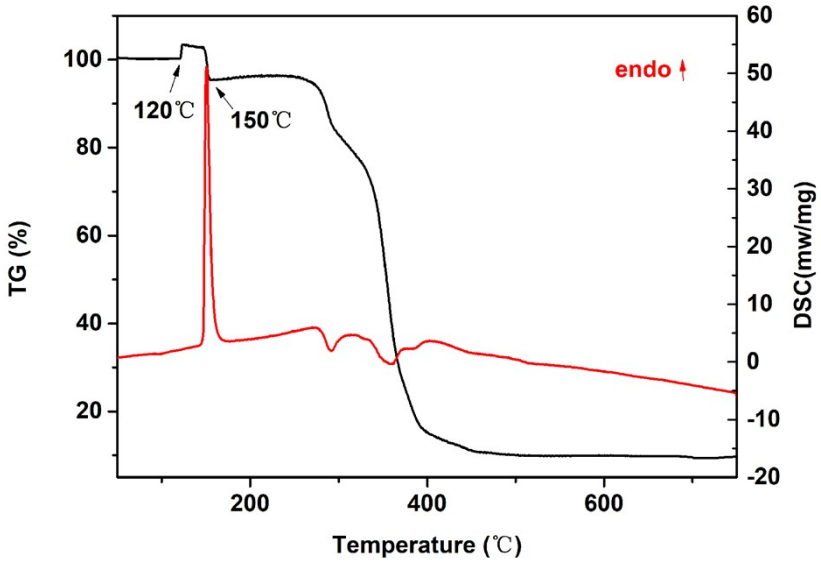

Figure S4. The TGA and DSC curves of $[C(NH_2)_3]_2S_2O_8$. The sudden change (120~150 °C) in TG curve may be attributed to the explosive decomposability of peroxides.

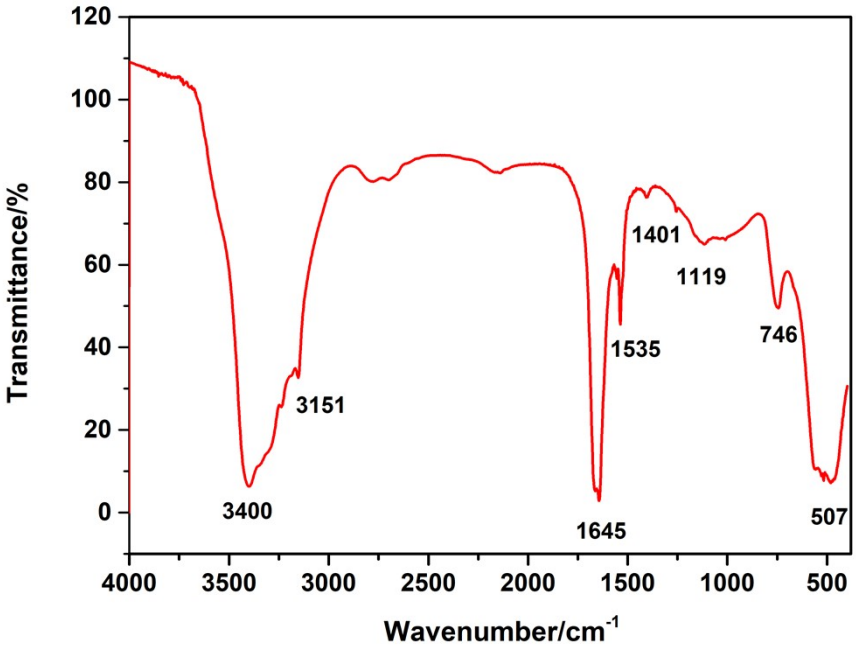

Figure S5. The IR spectrum for $[C(NH_2)_3]_2S_2O_8$.

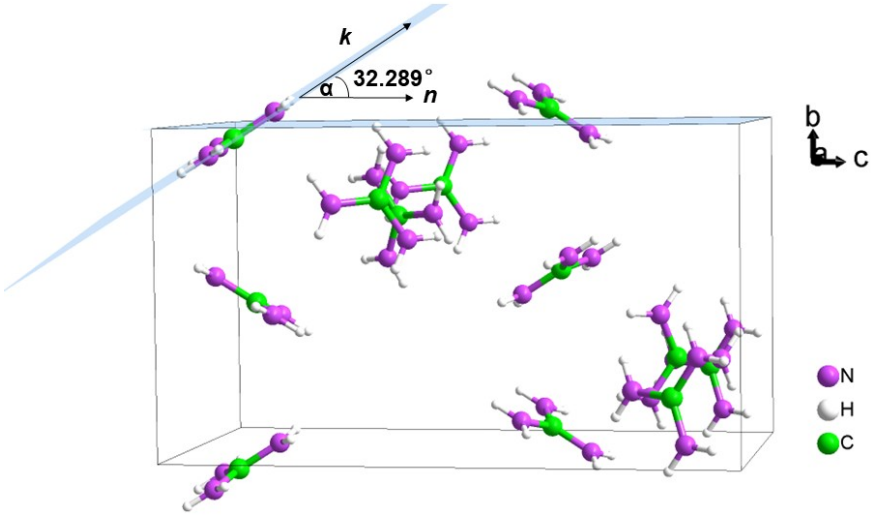

Figure S6. The arrangement of guanidine groups. *k* represents the direction of guanidine planes, *n* represents the optical axis direction, and *α* indicates the angle between guanidine plane and optical axis.

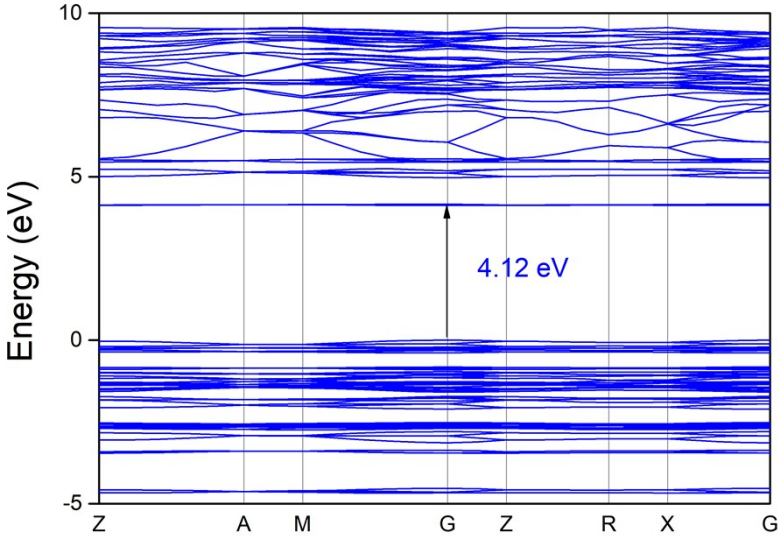

Figure S7. Band structure of $[C(NH_2)_3]_2S_2O_8$.

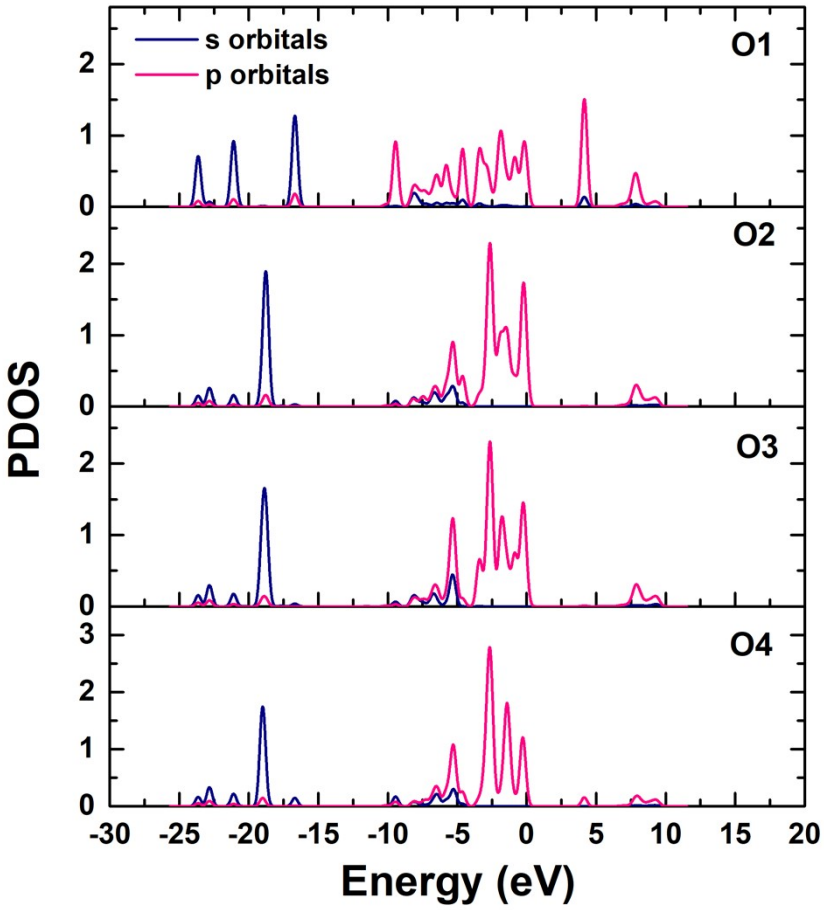

Figure S8. Partial density of states diagram of independent oxygen atoms.

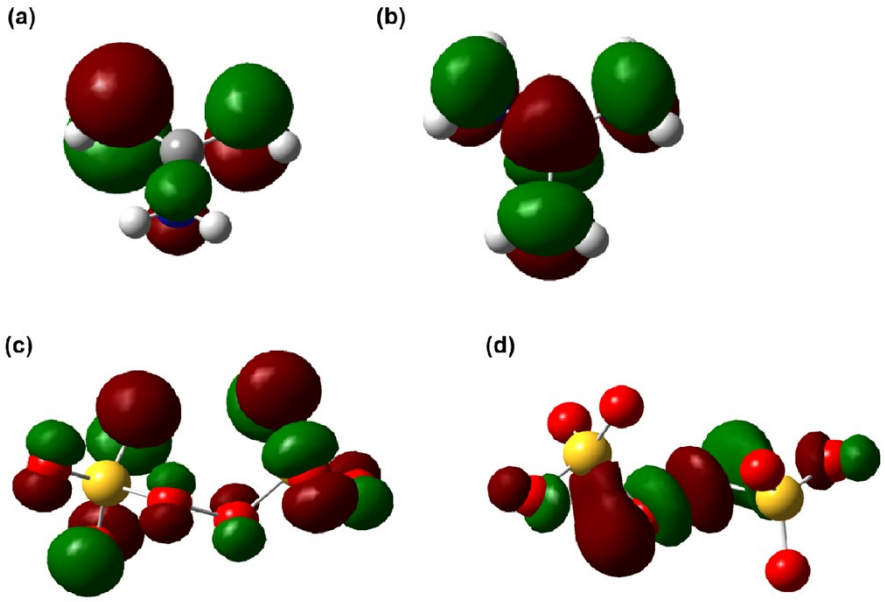

Figure S9. The frontier molecular orbitals of structural units in $[C(NH_2)_3]_2S_2O_8$. (a) HOMO and (b) LUMO diagrams of $[C(NH_2)_3]$ cations; (c) and (d) are HOMO and LUMO diagrams of $[S_2O_8]$ units.