Supporting Information

Two Metal-free Cyanurate Crystals with Large Optical Birefringence Resulting from the Combination of π-conjugated Units

Xiaomeng Liu,[†,§] Lei Kang,[†] Ruixin Guo[†,§] and Zheshuai Lin[†,‡,§]*

† Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

‡ Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

§ University of Chinese Academy of Sciences, Beijing 100190, China

*E-mail: zslin@mail.ipc.ac.cn (Z.L.)

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Synthesis of $GUH_2C_3N_3O_3$ and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$

Single crystals of $GUH_2C_3N_3O_3$ and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$ were synthesized by hydrothermal method at a temperature of 363 K. The experimental reagents used include $(CN_3H_6)_2CO_3$, $H_3C_3N_3O_3$ and H_3BO_3, all the reagents are analytical grade from commercial sources without further purification. For the synthesis of $GUH_2C_3N_3O_3$, the reaction mixture of $(CN_3H_6)_2CO_3$ (0.18 g, 1 mmol), $H_3C_3N_3O_3$ (0.13 g, 1 mmol), H_3BO_3 (0.1g, 1.6 mmol) and 8 ml deionized water were sealed in an autoclave with a Teflon linear (25 ml). After heating at 363 K for 3 h, the mixture was cooled to room temperature at a rate of 3 °C/h. Similarly, for the synthesis of $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$, the reaction mixture of $(CN_3H_6)_2CO_3$ (0.14 g, 0.78 mmol), $H_3C_3N_3O_3$ (0.19 g, 1.5 mmol) and 8 ml deionized water were sealed in an autoclave with a Teflon linear (25 ml). After heating at 363 K for 3 h, the mixture was cooled to room temperature at a rate of 3 °C/h. After that, the products were taken out and washed, and then colorless transparent $GUH_2C_3N_3O_3$ and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$ crystals were obtained.

$GUH_2C_3N_3O_3$ can also be obtained by the aqueous solution method. Weigh 1.35 g $(CN_3H_6)_2CO_3$ (7.5 mmol) and 0.65 g $H_3C_3N_3O_3$ (5 mmol) into a beaker, and add 10 ml deionized water, then stir with a magnet while heating. After a while, we can see that there are long flaky crystals in the solution. However, the quality of the crystals obtained by the aqueous solution method is not as good as the quality of the crystals obtained by the hydrothermal method.

Single-Crystal Structure Determination

The diffraction data of $GUH_2C_3N_3O_3$ and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$ were collected on a Rigaku AFC10 single-crystal diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 298(2) K. The crystal structures were solved by direct methods with the program SHELXS-97 and refined by full-matrix least squares on F^2 by SHELXTL programs.[1] The structures were verified using the ADDSYM algorithm from the program PLATON,[2] and no higher symmetry was found. The relevant crystallographic data, the atomic coordinates and equivalent isotropic displacement parameters, the anisotropic displacement parameters and the selected bond distances and angles are listed in Table S1-S5.

Powder X-ray Diffraction

Powder X-ray diffraction (XRD) of the polycrystalline materials were performed at room temperature using an automated Bruker D8 Focus X-ray diffractometer equipped with a diffracted monochromator set for Cu-Kα (λ=1.5418 Å) radiation. The scanning step width of 0.02° and the scanning rate of $0.4°s^{-1}$ were applied to record the patterns in the 2theta range of 5-70°.

Thermal Analysis

Thermogravimetric analysis (TGA) was performed on an NETZSCH STA 409C/CD thermogravimetric analyzer. The sample was placed in an alumina crucible, which was heated at a rate of 10 °C /min under N_2 flow from room temperature to 750 °C.

UV-vis-NIR Diffuse Reflectance Spectrum

The UV-vis-NIR diffuse reflectance spectrums of $GUH_2C_3N_3O_3$ and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$ were collected with a Cary 7000 UV−vis−NIR spectrometer equipped in the wavelength range from 200 to 800 nm.

Computational Methods

The first-principles calculations for $GUH_2C_3N_3O_3$ and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$ were performed by the plane-wave pseudopotential[3] method implemented in the CASTEP package[4] based on the density functional theory (DFT).[5] The Perdew-Burke-Ernzerhof (PBE) functionals of generalized gradient approximation (GGA) were adopted to describe the exchange-correlation (XC) functionals.[6] The plane-wave energy cutoff was set as 770 eV, self-consistent-field tolerance was set as 5.0×10^{-7} eV/atom and the *k*-point separation was set as 0.04 $Å^{-1}$ in the Brillouin zone.[7] The positions of H atoms in $GUH_2C_3N_3O_3$ and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$ were further optimized using the quasi-Newton method.[8] Based on optimized crystal structures, their electronic band structures were calculated. On the basis of the electronic structures, the linear optical properties were calculated by the scissors-corrected PBE method,[9] where the scissors operator is set as the difference between the experimental and first-principles band gaps in $GUH_2C_3N_3O_3$ and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$. After the imaginary part of the dielectric function ε_2 was calculated, its real part was determined by the Kramers-Kronig transform, from which the refractive indices (and the birefringence Δn) were obtained. Moreover, in order to analyze the contribution of an ion (or ionic group) to the birefringence, a real-space atom-cutting technique is adopted.[10]

Figure S1. Experimental and calculated XRD patterns of $GUH_2C_3N_3O_3$ (a) and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$ (b).

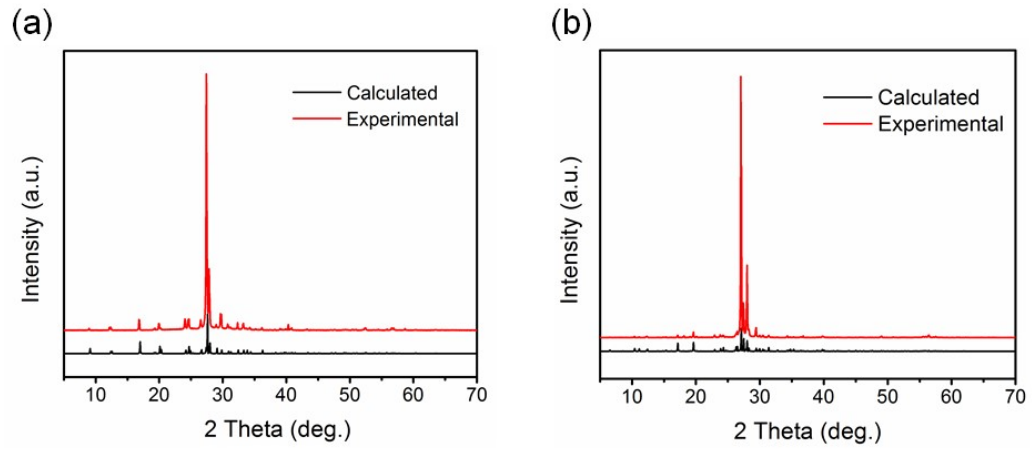

Figure S2. TG and DTA curves of $GUH_2C_3N_3O_3$ (a) and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$ (b).

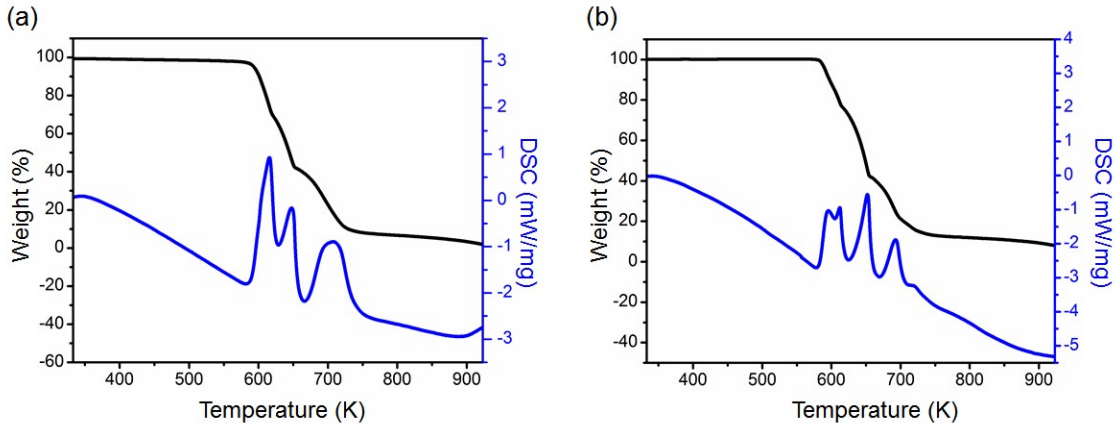

Table S1. Crystal data and structure refinement for $GUH_2C_3N_3O_3$ and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$.

Formula	$CN_3H_6(H_2C_3N_3O_3)$	$(CN_3H_6)_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$
Formula weight	188.16	693.57
Temperature (K)	293(2)	293(2)
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a (Å)	3.7706(2)	9.9296(5)
b (Å)	9.8381(6)	10.4028(4)
c (Å)	10.4914(5)	13.9056(6)
α (°)	87.925(4)	84.674(3)
β (°)	83.172(4)	76.702(4)
γ (°)	79.273(5)	83.421(4)
Volume ($Å^3$)	379.63(4)	1385.38(11)
Z	2	2
Calculated density (g/cm^3)	1.646	1.663
Absorption coefficient (mm^{-1})	0.140	0.143
F(000)	196.0	720.0
Theta range for data collection (°)	2.85 to 29.71	3.02 to 29.72
Index ranges	$-5 \le h \le 5$, $-13 \le k \le 12$, $-13 \le l \le 13$	$-13 \le h \le 13$, $-14 \le k \le 13$, $-18 \le l \le 18$
Reflections collected	5161	23250
Independent reflections	1863 [R_{int} = 0.0232, R_{sigma} = 0.0360]	7010 [R_{int} = 0.0266, R_{sigma} = 0.0265]
Data/restraints/parameters	1863/0/150	7010/0/541
Goodness-of-fit on F^2	1.061	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0375, wR_2 = 0.1067	R_1 = 0.0373, wR_2 = 0.1022
Final R indexes [all data]	R_1 = 0.0453, wR_2 = 0.1128	R_1 = 0.0520, wR_2 = 0.1100
Largest diff. peak/hole (e $Å^{-3}$)	0.20/-0.22	0.16/-0.28

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $GUH_2C_3N_3O_3$ and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$.

Compound	Atom	*x*	*y*	*z*	U(eq)
$GUH_2C_3N_3O_3$	O1	4219(3)	3307.2(10)	9166.8(8)	45.0(3)
	O2	11664(3)	-818.2(9)	8476.4(8)	39.3(3)
	O3	7172(3)	1675.0(10)	5115.2(8)	43.7(3)
	N1	9369(3)	415.9(10)	6782.5(8)	28.7(2)
	N2	7920(3)	1256.5(10)	8817.3(9)	30.5(2)
	N3	5546(3)	2604.5(10)	7096.9(9)	32.6(3)
	N4	-2820(3)	7270.3(11)	6932.1(11)	36.0(3)
	N5	1376(3)	5334.6(13)	6293.6(11)	38.5(3)
	N6	-554(4)	5696.5(13)	8421.6(10)	48.4(4)
	C1	-682(3)	6103.0(11)	7227.0(10)	28.4(2)
	C2	5807(3)	2445.9(11)	8364.6(10)	29.7(3)
	C3	9771(3)	217.5(11)	8050.9(10)	27.0(2)
	C4	7299(3)	1602.9(12)	6294.0(10)	29.0(3)
$GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$	O1	3805.5(9)	3563.5(8)	15434.6(6)	39.0(2)
	O2	5362.1(11)	7.0(7)	13724.5(6)	45.4(2)
	O3	5253.1(9)	3987.0(7)	12090.6(6)	37.0(2)
	O4	6142.0(10)	1002.1(8)	10919.0(6)	42.3(2)
	O5	6787.0(10)	5096.2(7)	9625.8(6)	42.6(2)
	O6	7580.7(11)	1787.7(8)	7595.5(6)	42.6(2)
	O7	8426.7(9)	5274.9(7)	7107.9(6)	35.5(2)
	O8	7157.3(10)	8689.5(7)	9025.7(6)	38.9(2)
	O9	8596.6(10)	9391.9(8)	5706.8(6)	42.1(2)
	O10	8517.1(10)	10881.7(8)	2619.5(6)	45.8(2)
	O11	10414.9(11)	11526.4(8)	-653.3(6)	46.5(2)
	O12	9332.0(11)	14934.7(8)	1282.6(6)	47.6(2)
	N1	6401.0(14)	8555.5(10)	12040.2(9)	45.8(3)
	N2	5817.2(13)	6501.1(10)	12593.1(8)	41.1(3)
	N3	6344.9(13)	7080.0(11)	10928.1(8)	43.1(3)
	N4	8796.4(14)	8498.9(10)	3783.2(9)	44.6(3)
	N5	9540.3(12)	6416.4(10)	4242.4(8)	38.4(2)
	N6	9378.2(12)	6967.9(11)	2630.3(8)	39.6(2)
	N7	7139.1(12)	13409.9(11)	5710.7(8)	41.7(3)
	N8	8141.1(12)	11843.3(10)	4631.6(9)	41.5(3)
	N9	7611.5(12)	13918.1(10)	4036.1(8)	39.1(2)
	N10	4449.7(10)	3888.3(8)	13760.5(7)	29.3(2)

Compund	Atom	*x*	*y*	*z*	U(eq)
$GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$	N11	4595.1(11)	1797.9(9)	14584.1(7)	32.6(2)
	N12	5245.3(11)	1997.6(9)	12900.9(7)	32.6(2)
	N13	6396.2(11)	3066.9(8)	10286.1(7)	32.0(2)
	N14	6882.8(11)	1368.6(9)	9257.1(7)	33.5(2)
	N15	7226.7(11)	3464.9(9)	8591.7(7)	32.8(2)
	N16	7729.7(10)	6981.8(8)	8052.2(7)	28.8(2)
	N17	7923.1(11)	9035.9(9)	7358.2(7)	31.4(2)
	N18	8582.3(10)	7288.2(8)	6320.5(7)	30.7(2)
	N19	8866.1(11)	12950.0(9)	2028.7(7)	34.0(2)
	N20	9456.3(11)	11201.8(9)	988.9(7)	33.6(2)
	N21	9874.7(11)	13244.9(9)	313.1(7)	32.7(2)
	C1	6193.7(12)	7375.0(10)	11863.7(8)	30.5(2)
	C2	9240.2(12)	7298.1(10)	3552.9(8)	30.2(2)
	C3	7633.2(11)	13057.6(10)	4793.8(8)	29.8(2)
	C4	4261.2(11)	3133.6(10)	14614.4(8)	28.0(2)
	C5	4978.6(11)	3342.9(10)	12908.7(8)	28.1(2)
	C6	5088.6(12)	1187.7(10)	13736.4(8)	30.5(2)
	C7	6802.5(12)	3946.1(10)	9508.5(8)	29.5(2)
	C8	6447.7(12)	1762.1(10)	10202.7(8)	29.5(2)
	C9	7250.3(12)	2183.0(10)	8426.1(8)	30.7(2)
	C10	7576.7(11)	8264.6(10)	8196.4(8)	26.9(2)
	C11	8386.9(12)	8575.2(10)	6415.0(8)	28.6(2)
	C12	8271.4(11)	6474.5(9)	7128.7(7)	26.4(2)
	C13	9339.5(12)	13750.6(10)	1236.1(8)	31.1(2)
	C14	8924.5(12)	11671.5(10)	1923.0(8)	30.3(2)
	C15	9950.0(12)	11964.4(10)	165.4(8)	30.7(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Anisotropic Displacement Parameters ($Å^2×10^3$) for $GUH_2C_3N_3O_3$ and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$.

Compound	Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$GUH_2C_3N_3O_3$	O1	61.0(6)	36.0(5)	27.0(4)	-5.4(3)	-2.4(4)	18.9(4)
	O2	55.1(6)	31.5(5)	22.9(4)	-1.0(3)	-9.4(4)	16.8(4)
	O3	54.9(6)	48.1(5)	18.2(4)	2.2(4)	-5.8(4)	16.6(4)
	N1	38.0(5)	26.3(5)	17.1(4)	-1.1(3)	-3.4(3)	6.6(4)
	N2	41.6(6)	27.5(5)	17.7(4)	-0.8(3)	-5.1(4)	7.2(4)
	N3	38.5(5)	30.0(5)	23.0(5)	1.9(4)	-3.6(4)	9.4(4)
	N4	43.0(6)	31.5(5)	28.5(5)	1.9(4)	-6.2(4)	7.0(4)
	N5	47.1(6)	37.9(6)	24.3(5)	-2.3(4)	-1.5(4)	7.0(5)
	N6	67.1(8)	41.2(6)	22.7(5)	2.8(4)	0.0(5)	22.8(6)
	C1	32.4(5)	27.1(5)	24.2(5)	-0.3(4)	-4.4(4)	-0.6(4)
	C2	34.6(6)	26.2(5)	23.7(5)	-0.6(4)	-2.5(4)	5.7(4)
	C3	32.9(5)	25.5(5)	19.7(5)	0.1(4)	-5.1(4)	3.1(4)
	C4	32.3(5)	30.6(5)	20.3(5)	3.6(4)	-3.6(4)	4.1(4)
$GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$	O1	57.8(5)	29.4(4)	25.2(4)	-7.6(3)	-2.6(4)	5.7(4)
	O2	82.3(7)	19.9(4)	25.5(4)	-0.9(3)	0.4(4)	4.6(4)
	O3	60.4(5)	22.9(4)	23.3(4)	1.5(3)	-1.5(4)	-3.6(3)
	O4	74.4(6)	22.1(4)	24.3(4)	3.2(3)	-0.1(4)	-4.8(4)
	O5	80.6(6)	18.5(4)	24.4(4)	-3.2(3)	0.3(4)	-9.4(4)
	O6	80.6(6)	21.9(4)	21.2(4)	-4.1(3)	-1.5(4)	-5.4(4)
	O7	57.2(5)	17.5(4)	26.3(4)	-1.8(3)	-0.4(3)	1.3(3)
	O8	69.3(6)	21.8(4)	21.0(4)	-3.8(3)	-0.1(4)	-3.3(4)
	O9	74.3(6)	22.4(4)	23.6(4)	3.3(3)	-1.1(4)	-4.0(4)
	O10	72.7(6)	27.5(4)	28.2(4)	6.4(3)	4.1(4)	-5.8(4)
	O11	85.1(7)	25.1(4)	23.8(4)	-5.6(3)	3.6(4)	-10.3(4)
	O12	91.6(7)	20.2(4)	26.9(4)	-3.0(3)	-2.7(4)	-8.9(4)
	N1	82.9(8)	21.5(5)	28.1(5)	-4.7(4)	0.1(5)	-7.9(5)
	N2	69.2(7)	27.0(5)	25.1(5)	1.9(4)	-4.7(5)	-10.8(5)
	N3	77.1(8)	26.6(5)	22.4(5)	-3.9(4)	-3.1(5)	-6.4(5)
	N4	79.9(8)	23.0(5)	28.2(5)	-3.7(4)	-10.1(5)	4.3(5)
	N5	56.2(6)	27.7(5)	27.7(5)	-2.9(4)	-6.9(4)	7.2(4)
	N6	63.7(7)	27.5(5)	27.6(5)	-5.6(4)	-12.0(5)	2.8(5)
	N7	60.0(7)	32.8(6)	28.2(5)	-2.1(4)	-6.1(5)	5.4(5)
	N8	59.3(7)	23.4(5)	35.2(6)	0.4(4)	-1.9(5)	4.1(4)
	N9	56.7(6)	24.9(5)	30.6(5)	-1.8(4)	-4.5(5)	6.8(4)
	N10	40.9(5)	19.9(4)	25.6(5)	-2.6(3)	-5.5(4)	0.9(3)

Compound	Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$	N11	51.4(6)	21.3(4)	20.3(4)	-0.2(3)	-1.3(4)	2.8(4)
	N12	52.6(6)	20.1(4)	20.2(4)	-1.9(3)	0.3(4)	0.6(4)
	N13	55.0(6)	18.4(4)	19.3(4)	-1.2(3)	-1.4(4)	-3.3(4)
	N14	59.2(6)	15.3(4)	22.5(5)	-1.9(3)	-1.9(4)	-3.5(4)
	N15	57.5(6)	18.2(4)	18.5(4)	-0.7(3)	0.8(4)	-5.4(4)
	N16	47.0(5)	16.1(4)	19.6(4)	0.6(3)	-0.6(4)	-2.9(4)
	N17	55.1(6)	14.0(4)	22.4(4)	-0.7(3)	-3.2(4)	-3.7(4)
	N18	47.5(5)	19.8(4)	21.3(4)	-1.8(3)	-1.3(4)	-1.6(4)
	N19	54.1(6)	23.4(5)	20.9(4)	-1.2(3)	-1.6(4)	-2.3(4)
	N20	54.1(6)	18.2(4)	24.8(5)	-1.0(3)	-0.4(4)	-5.8(4)
	N21	56.2(6)	19.0(4)	20.1(4)	-0.5(3)	-1.2(4)	-6.9(4)
	C1	44.5(6)	21.6(5)	22.2(5)	-2.3(4)	-2.6(4)	0.6(4)
	C2	38.6(6)	24.0(5)	25.9(5)	-3.4(4)	-2.9(4)	-2.0(4)
	C3	32.5(5)	25.8(5)	30.0(5)	-3.0(4)	-5.1(4)	-1.5(4)
	C4	34.2(5)	23.0(5)	25.0(5)	-3.9(4)	-4.4(4)	1.7(4)
	C5	36.7(5)	20.8(5)	25.5(5)	0.2(4)	-5.0(4)	-2.7(4)
	C6	43.1(6)	21.5(5)	23.1(5)	-1.5(4)	-1.6(4)	1.1(4)
	C7	47.3(6)	18.5(5)	20.4(5)	-1.3(4)	-2.9(4)	-2.9(4)
	C8	44.4(6)	20.4(5)	20.7(5)	-0.1(4)	-2.6(4)	-2.0(4)
	C9	49.2(6)	19.6(5)	20.8(5)	-1.7(4)	-2.7(4)	-2.8(4)
	C10	38.9(5)	19.2(5)	21.2(5)	-1.9(4)	-3.4(4)	-2.7(4)
	C11	40.7(6)	21.6(5)	21.5(5)	0.1(4)	-3.7(4)	-3.2(4)
	C12	36.8(5)	18.7(5)	21.5(5)	-2.3(4)	-3.1(4)	0.3(4)
	C13	50.3(6)	21.0(5)	20.7(5)	-2.0(4)	-4.8(4)	-3.8(4)
	C14	41.6(6)	23.7(5)	22.6(5)	1.6(4)	-2.8(4)	-2.1(4)
	C15	47.1(6)	20.9(5)	22.3(5)	-2.0(4)	-3.2(4)	-5.0(4)

[a] The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Table S4. Selected bond length (Å) for $GUH_2C_3N_3O_3$ and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$.

Compound	Bond	Length/Å	Bond	Length/Å
$GUH_2C_3N_3O_3$	O2-C3	1.2325(13)	N2-C2	1.3901(13)
	O1-C2	1.2360(14)	N4-C1	1.3242(15)
	O3-C4	1.2423(14)	N3-C4	1.3427(15)
	N1-C3	1.3602(13)	N3-C2	1.3465(14)
	N1-C4	1.3958(13)	N5-C1	1.3368(15)
	N2-C3	1.3560(13)	N6-C1	1.3053(15)
$GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$	O7-C12	1.2420(12)	N12-C6	1.3598(13)
	O8-C10	1.2369(13)	N14-C8	1.3716(13)
	O3-C5	1.2550(13)	N14-C9	1.3717(13)
	O5-C7	1.2203(13)	N15-C7	1.3698(13)
	O1-C4	1.2315(13)	N15-C9	1.3709(13)
	O9-C11	1.2353(13)	N21-C15	1.3576(14)
	O6-C9	1.2221(13)	N21-C13	1.3978(14)
	O4-C8	1.2161(13)	N19-C14	1.3448(14)
	O10-C14	1.2349(13)	N19-C13	1.3454(14)
	O2-C6	1.2280(13)	N11-C4	1.3933(13)
	O12-C13	1.2385(13)	N11-C6	1.3544(13)
	O11-C15	1.2342(13)	N20-C15	1.3576(14)
	N16-C10	1.3540(13)	N20-C14	1.3957(14)
	N16-C12	1.4000(13)	N5-C2	1.3247(15)
	N10-C5	1.3309(13)	N9-C3	1.3202(15)
	N10-C4	1.3489(14)	N6-C2	1.3315(14)
	N18-C11	1.3450(13)	N2-C1	1.3142(14)
	N18-C12	1.3411(13)	N8-C3	1.3250(14)
	N13-C8	1.3671(13)	N3-C1	1.3354(14)
	N13-C7	1.3670(13)	N7-C3	1.3260(15)
	N17-C10	1.3511(13)	N1-C1	1.3220(15)
	N17-C11	1.3965(14)	N4-C2	1.3192(14)
	N12-C5	1.3948(13)		

Table S5. Selected bond angles (deg.) for $GUH_2C_3N_3O_3$ and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$.

Compound	Bond	Angle/°	Bond	Angle/°
$GUH_2C_3N_3O_3$	C3-N1-C4	123.20(9)	N6-C1-N5	119.61(11)
	C3-N2-C2	123.72(9)	O3-C4-N1	117.38(10)
	C4-N3-C2	119.38(9)	O3-C4-N3	122.96(10)
	O2-C3-N1	123.08(10)	N3-C4-N1	119.66(9)
	O2-C3-N2	122.36(10)	O1-C2-N2	117.29(10)
	N2-C3-N1	114.56(9)	O1-C2-N3	123.25(10)
	N4-C1-N5	119.75(11)	N3-C2-N2	119.46(9)
	N6-C1-N4	120.64(11)		
$GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$	C10-N16-C12	123.68(9)	N21-C15-N20	114.67(9)
	C5-N10-C4	119.21(9)	N9-C3-N8	119.66(11)
	C12-N18-C11	119.36(9)	N9-C3-N7	119.92(10)
	C7-N13-C8	124.18(9)	N8-C3-N7	120.42(11)
	C10-N17-C11	123.92(9)	O7-C12-N16	117.15(9)
	C6-N12-C5	123.46(9)	O7-C12-N18	123.50(9)
	C8-N14-C9	124.68(9)	N18-C12-N16	119.34(9)
	C7-N15-C9	123.80(9)	O4-C8-N13	122.26(10)
	C15-N21-C13	123.23(9)	O4-C8-N14	122.35(10)
	C14-N19-C13	119.48(9)	N13-C8-N14	115.38(9)
	C6-N11-C4	123.87(9)	O5-C7-N13	121.76(10)
	C15-N20-C14	123.65(9)	O5-C7-N15	121.91(10)
	O3-C5-N10	122.92(9)	N13-C7-N15	116.33(9)
	O3-C5-N12	117.17(10)	N2-C1-N3	119.77(11)
	N10-C5-N12	119.90(9)	N2-C1-N1	121.08(11)
	O8-C10-N16	122.68(10)	N1-C1-N3	119.14(11)
	O8-C10-N17	123.10(9)	O6-C9-N14	122.06(9)
	N17-C10-N16	114.22(9)	O6-C9-N15	122.45(10)
	N5-C2-N6	119.90(10)	N15-C9-N14	115.49(9)
	N4-C2-N5	119.95(11)	O2-C6-N12	123.06(10)
	N4-C2-N6	120.15(11)	O2-C6-N11	122.90(10)
	O9-C11-N18	123.58(10)	N11-C6-N12	114.04(9)
	O9-C11-N17	117.15(9)	O10-C14-N19	122.87(10)
	N18-C11-N17	119.27(9)	O10-C14-N20	117.79(10)
	O1-C4-N10	123.32(9)	N19-C14-N20	119.34(10)
	O1-C4-N11	117.34(10)	O12-C13-N21	117.50(10)
	N10-C4-N11	119.35(9)	O12-C13-N19	122.87(10)
	O11-C15-N21	122.86(10)	N19-C13-N21	119.63(9)
	O11-C15-N20	122.46(10)		

Table S6. The real-space atomic cutting analysis for the birefringence of $GU(H_2C_3N_3O_3)$ and $GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)$.

	Δn at 400 nm $[GU(H_2C_3N_3O_3)]$	(Δn at 400 nm) $[GU_3(H_2C_3N_3O_3)_3(H_3C_3N_3O_3)]$
Total	0.419	0.402
GU cations	0.178 (32%)	0.148 (29.5%)
$(H_xC_3N_3O_3)^{x-3}$ (x = 0 ~ 3)	0.379 (68%)	0.354 (70.5%)

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