Supporting Information

A New Polar Glass-Ceramic Built from Monovalent Perrhenate Anions and Large Methyltriphenylphosphonium Cations

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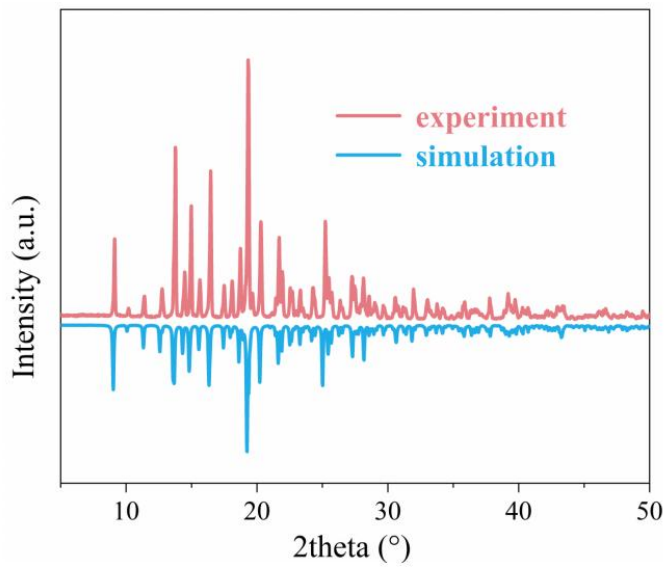

Fig. S1. The experimental X-ray diffraction pattern of **1** and the theoretical pattern simulated from its single-crystal structure.

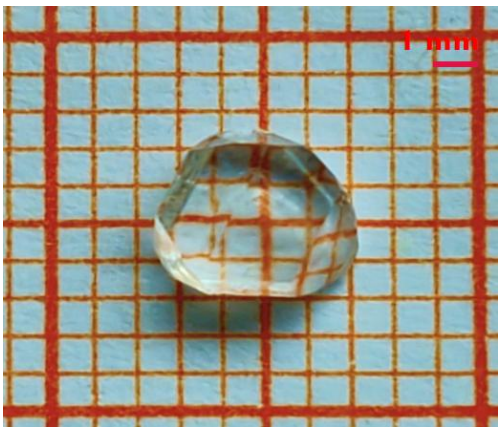

Fig. S2 Photograph of block-like crystals of compound **1** obtained by the solvent evaporation method.

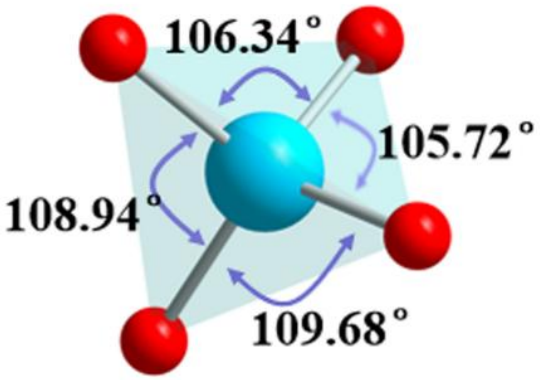

Fig. S3 The structure of **1** contains severely distorted tetrahedra.

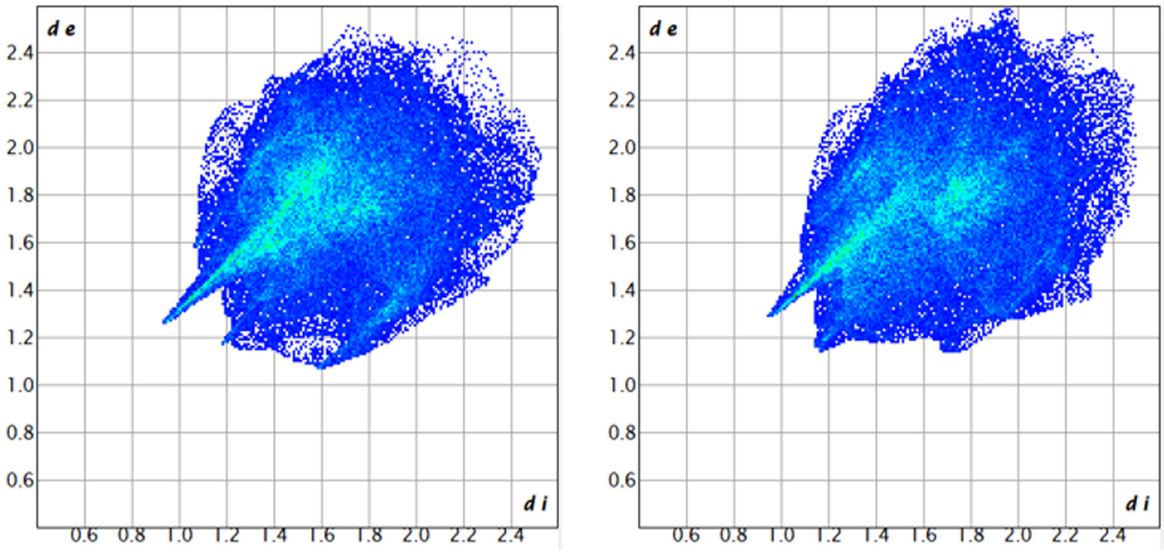

Fig. S4 Two-dimensional fingerprint plots for the two independent organic cations in **1**.

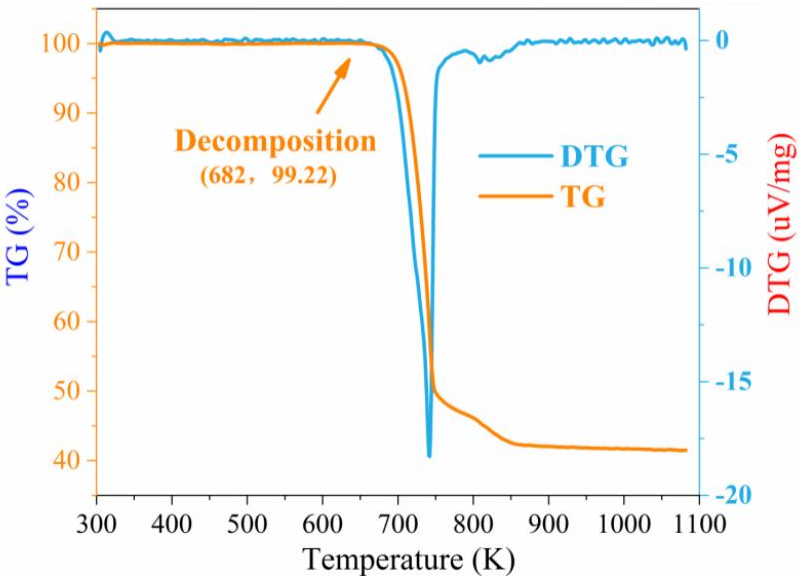

Fig. S5 Thermogravimetric analysis (TGA) of **1**.

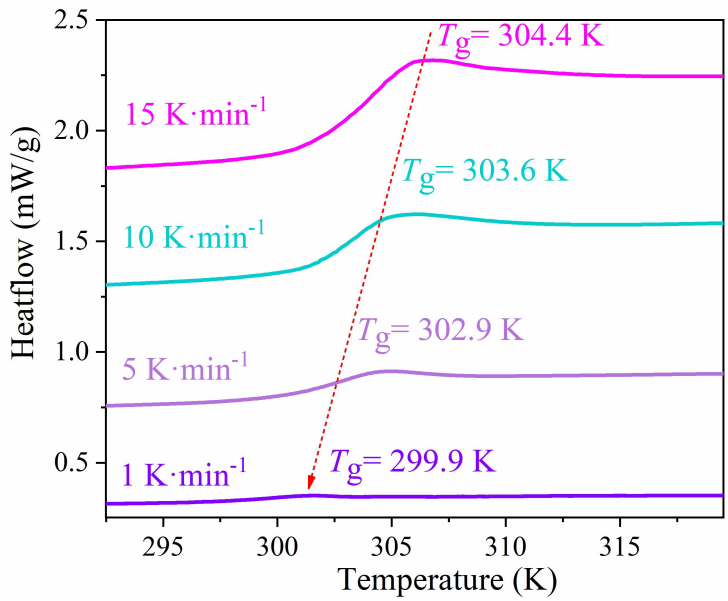

Fig. S6 Glass transition temperature as a function of heating rate.

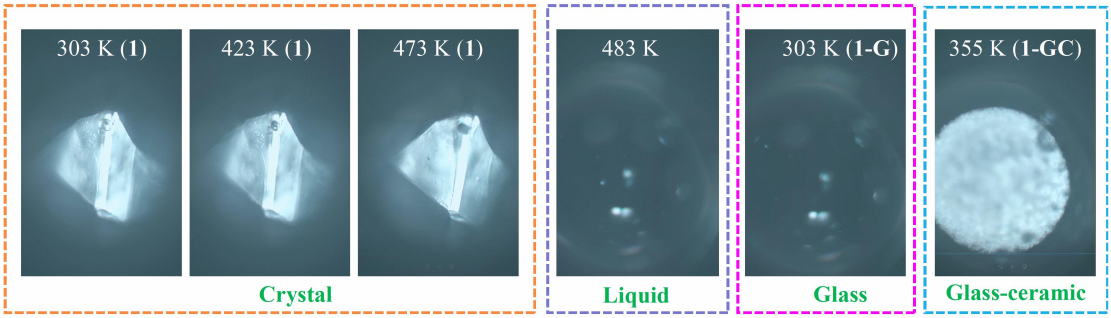

Fig. S7 Polarizing optical microscopy images of **1**, liquid, **1-G**, and **1-GC**.

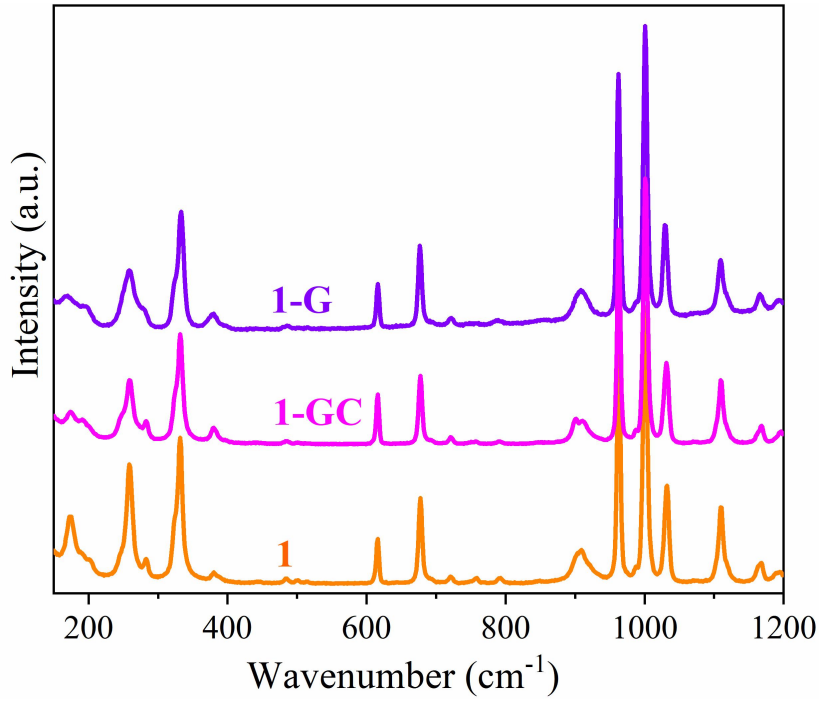

Fig. S8 Raman spectra at different states.

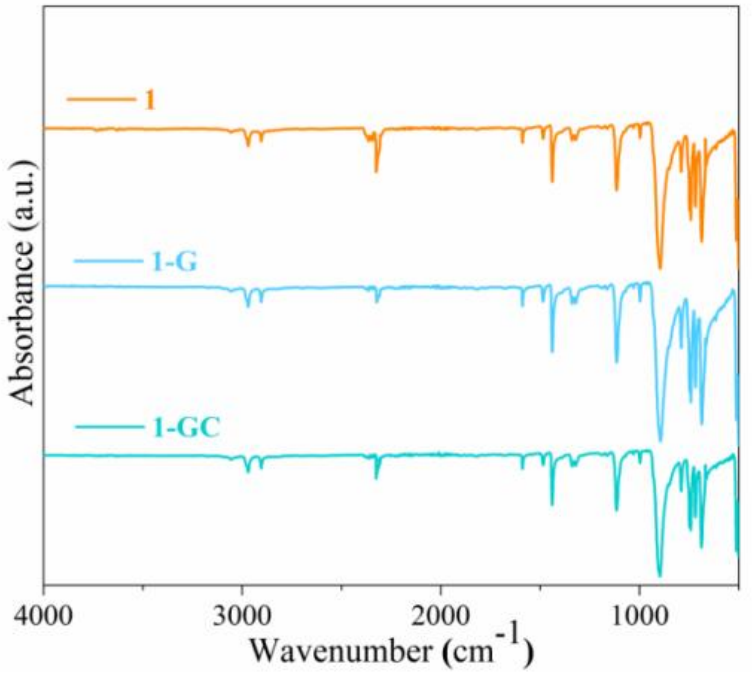

Fig. S9 IR spectra of **1**, **1-G**, **1-GC**.

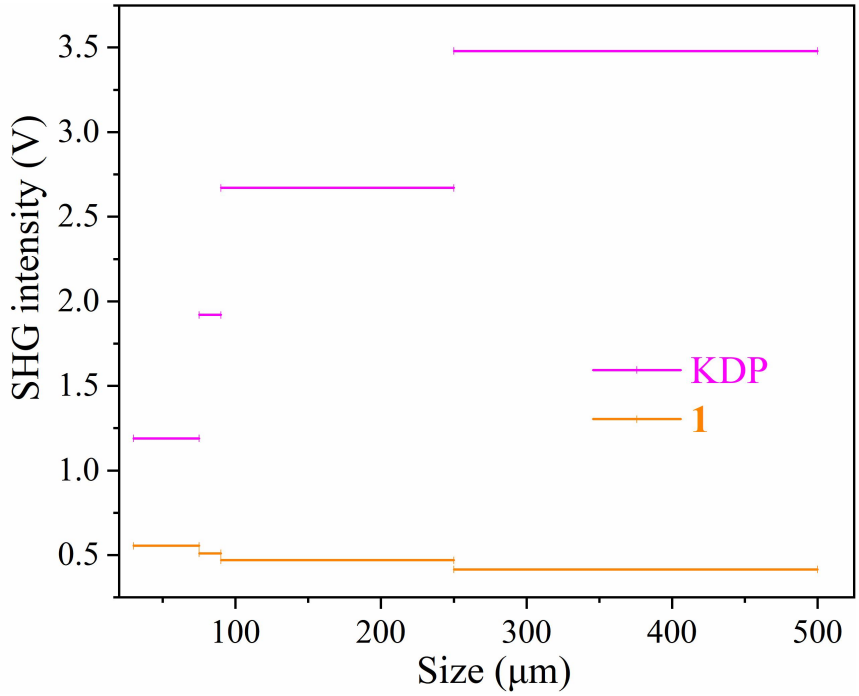

Fig. S10 Variation of nonlinear signal intensity with particle size for KDP and **1-GC**.

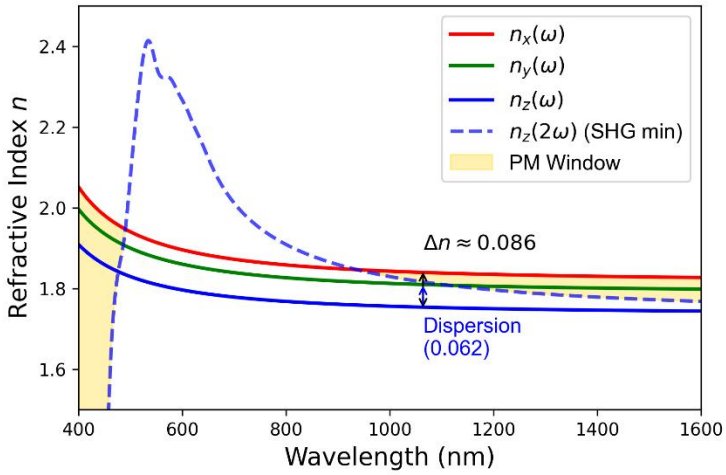

Fig. S11 Refractive index and phase-matching calculations of **1**.

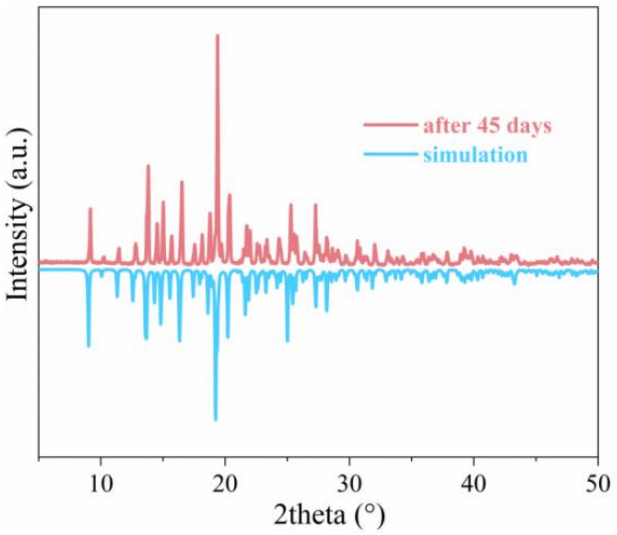

Fig. S12 The X-ray powder diffraction pattern of **1-GC** after being stored at ambient temperature for 45 days.

Table S1. X-Ray crystallographic data for **1**.

Compound	**1**
Empirical formula	$C_{19}H_{18}O_4PRe$
Formula weight	527.50
Temperature/K	250.01(10)
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	15.0665(3)
b/Å	12.9576(3)
c/Å	19.5981(5)
Volume/Å^3	3826.05(15)
Z	8
ρ_{calc}g/cm^3	1.832
μ/mm^{-1}	13.385
F(000)	2032.0
Radiation	Cu Kα (λ = 1.54184 Å)
Reflections collected	26419
Independent reflections	7101 [R_{int} = 0.0949, R_{sigma} = 0.0897]
Goodness-of-fit on F^2	1.108
Final R indexes [I>=2σ (I)]	R_1 = 0.0367(7174), wR_2 = 0.1096(7193)
Final R indexes [all data]	R_1 = 0.0514, wR_2 = 0.1453
Largest diff. peak/hole / e Å^{-3}	1.05/-1.61

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

Table S2. Bond lengths of **1** at 250 K.

Atom	Atom	Bond length / Å
Re2	O7	1.729(17)
Re2	O6	1.694(13)
Re2	O8	1.709(19)
Re2	O5	1.66(2)
Re1	O1	1.71(2)
Re1	O4	1.641(18)
Re1	O3	1.68(3)
Re1	O2	1.60(2)
P1	C1	1.785(7)
P1	C7	1.785(9)
P1	C19	1.774(14)
P1	C13	1.788(8)
P2	C21	1.783(7)
P2	C27	1.780(8)
P2	C33	1.794(8)
P2	C20	1.786(13)

[1]-X, -Y, -Z; [2]Y, -X+Y, -Z; [3]-Y, X-Y, Z; [4]X-Y, X, -1/2+Z, [5]-X+Y, -X, 1/2-Z; [6]1-Y, X-Y, Z; [7]1-X+Y, 1-X, 1/2-Z, [8]1-X+Y, 1-X, -1/2-Z, [9]X, Y, 1/2-Z

Table S3. A comparison of the O-Re-O bond angles (°) in the $[ReO_4]^-$ tetrahedra of (BET)$[ReO_4]$ and compound **1**.

	1		(BET)$[ReO_4]$
O6-Re2-O7	109.5(10)	O1-Re-O4	110.8(8)
O6-Re2-O8	109.7(12)	O1-Re-O2	107.7(7)
O8-Re2-O7	109.3(10)	O4-Re-O2	109.1(8)
O5-Re2-O7	116.4(13)	O1-Re-O3	109.8(8)
O5-Re2-O6	105.5(12)	O4-Re-O3	110.6(9)
O5-Re2-O8	106.2(16)	O2-Re-O3	108.9(7)
O2-Re1-O1	111(2)		
O2-Re1-O4	104(2)		
O2-Re1-O3	113(3)		
O4-Re1-O1	112.5(13)		
O4-Re1-O3	108.6(15)		
O3-Re1-O1	108.1(19)		