Electronic Supplementary Information
For

Hierarchical Construction of SHG-active Polar Crystals by Using Multi-component

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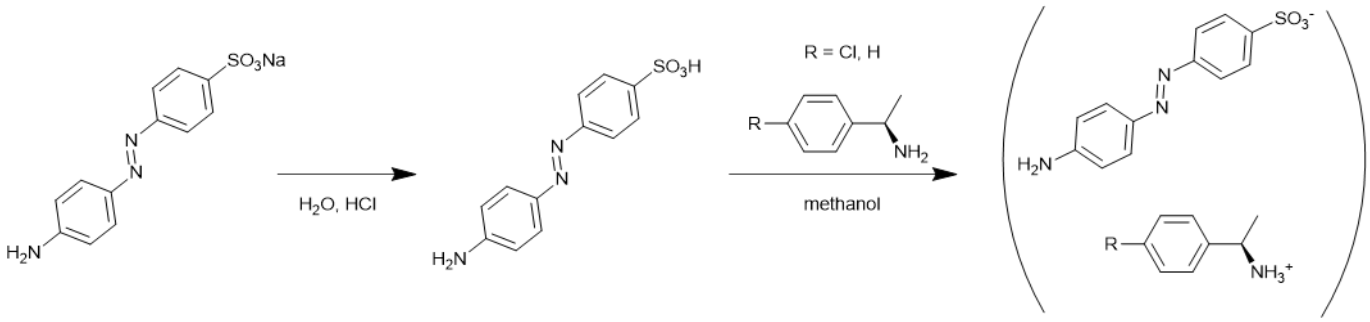
Experimental section



Preparation of 4-aminoazobenzene-4-sulfonic acid (AAS): Sodium (E)-4-((4-aminophenyl)diazenyl) benzenesulfonate (0.898g, 3.00 mmol) was dissolved into water and 0.5 M aqueous solution of HCl was added to yield precipitates. The precipitates were dried in vaco to yield AAS (0.730g, 2.63 mmol, 88 %) as a pale orange powder.

Preparation of salt 1 and salt 2: AAS and (R)-1-(4-Chlorophenyl) ethylamine or (R)-1-Phenylethylamine were mixed in methanol in a 1:1 molar ratio. The solution was evaporated to yield orange powder of the crude salt.

Preparation of single crystals: AAS single crystals were prepared by recrystallization from water. The crude salts 1 and 2 were dissolved in methanol and then various guest solvents were added to the solution. Slow evaporation of the solvent gave each single crystals.

Crystallographic analysis of single crystals: X-ray diffraction data except for AAS crystal were collected on a Rigaku R-AXIS RAPID diffractometer with a 2D area detector by using graphite-monochromatized Cu Kα radiation (λ = 1.54178 Å). Diffraction data of AAS crystal collected on a two-dimensional X-ray detector (PILATUS 200K/R) equipped in Rigaku XtaLAB PRO diffractometer using thin multi-layer mirror monochromated Cu-Kα radiation (λ =1.54187 Å). The cell refinements were performed with a software CrysAlisPro 1.171.39.5a.[S1] A direct method of SHELXT[S2] was used for the structure solution of the crystals. All calculations were performed with the observed reflections [$I > 2\sigma(I)$] with the program CrystalStructure crystallographic software packages[S3], except for refinement which was performed by SHELXL[S4]. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters.

Powder SHG measurement: The powder SHG measured by the Kurtz−Perry method.[S5] The samples were placed in a quartz cell and measured SHG signals at 1.4, 1.5, 1.6 μm by using an optical parametric amplifier and a Nd: YAG solid-state laser (1064 nm, 1 kHz). We measured the intensity of the frequency-doubled output emitted from the sample using a photomultiplier tube. The second harmonic efficiency of the sample was compared to that of a standard powder sample of Urea.

S1. Rigaku Oxford Diffraction (2015), Software CrysAlisPro 1.171.39.5a Rigaku Corporation, Tokyo, Japan.

S2. SHELXT Version 2014/5. Sheldrick, G. M. Acta Cryst. 2014. A70, C1437.

S3. Rigaku (2015). CrystalStructure. Versions 4.2. Rigaku Corporation, Tokyo, Japan.

S4. SHELXL Version 2014/7. Sheldrick, G.M. Acta Cryst. 2008, A64, 112-122.

S5. Kurtz, S. K.; Perry, T. T. J. Appl. Phys. 1968, 39, 3798−3792.

Table S1. X-ray crystallographic parameters for the crystals.

crystal	**AAS**	**1-GF**	**1-DMSO**
Formula	$C_{12}H_{11}N_3O_3S$	$(C_{12}H_{11}N_3O_3S)\bullet(C_8H_{10}ClN)$	$(C_{12}H_{11}N_3O_3S)\bullet(C_8H_{10}ClN) \bullet (C_2H_6OS)$
Fw	432.92	432.92	511.05
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1$	$P2_1$
Temperature (K)	213	213	213
a (Å)	5.8245(3)	7.3493(2)	5.99452(11)
b (Å)	7.5038(4)	6.04446(19)	23.7139(4)
c (Å)	13.8162(4)	23.3114(6)	9.33438(17)
α	94.785(3)	90	90
β	94.970(3)	94.6950(17)	108.5280(11)
γ	95.755(4)	90	90
V ($Å^3$)	595.96(5)	1032.07(5)	1258.14(4)
Z	2	2	2
reflections observed	5827	11000	12525
reflections unique	2411	3640	4386
R1 [I > 2.0σ(I)]	0.0560	0.0724	0.0789
Rw (all data)	0.1506	0.1559	0.1667
CCDC no.	1504254	1504262	1504257

Table S1. X-ray crystallographic parameters for the crystals.

crystal	**1**-**Dioxane**	**1**-**DMF**	**1**-**DMA**
Formula	$(C_{12}H_{11}N_3O_3S)\bullet(C_8H_{10}ClN) \bullet (C_4H_8O_2)$	$(C_{12}H_{11}N_3O_3S)\bullet(C_8H_{10}ClN) \bullet (C_3H_7NO)$	$(C_{12}H_{11}N_3O_3S)\bullet(C_8H_{10}ClN) \bullet (C_4H_9NO)$
Fw	521.03	506.02	520.05
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1$	$P1$	$P2_1$
Temperature (K)	213	213	213
a (Å)	6.00155(11)	5.94757(14)	6.11235(13)
b (Å)	26.1427(5)	9.5911(2)	28.1898(6)
c (Å)	8.40735(15)	11.4509(3)	7.71338(17)
α	90	83.8975(16)	90
β	105.2470(9)	82.0150(15)	92.9285(13)
γ	90	71.9997(15)	90
V ($Å^3$)	1272.66(4)	613.82(3)	1327.33(5)
Z	2	1	2
reflections observed	13914	6470	13867
reflections unique	4492	3604	4695
R1 [I > 2.0σ(I)]	0.0499	0.0851	0.1118
Rw (all data)	0.1047	0.2281	0.2752
CCDC no.	1504260	1504255	1504256

Table S1. X-ray crystallographic parameters for the crystals.

crystal	**1-DEF**	**2-Dioxane**	**2-DMA**
Formula	$(C_{12}H_{11}N_3O_3S)•(C_8H_{10}ClN) • (C_5H_{11}NO)$	$(C_{12}H_{11}N_3O_3S)•(C_8H_{11}N) • (C_4H_8O_2)$	$(C_{12}H_{11}N_3O_3S)•(C_8H_{11}N) • (C_4H_9NO)$
Mw	534.07	486.58	485.60
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$
Temperature (K)	213	213	213
a (Å)	6.26161(11)	6.06973(12)	6.19100(11)
b (Å)	25.9240(5)	23.5497(5)	26.0113(5)
c (Å)	8.62429(16)	9.2011(2)	8.06978(15)
α	90	90	90
β	102.2264(7)	108.6090(12)	102.6890(10)
γ	90	90	90
V ($Å^3$)	1368.19(4)	1246.44(5)	1267.79(4)
Z	2	2	2
reflections observed	14234	13460	14197
reflections unique	4864	4359	4506
R1 [I > 2.0σ(I)]	0.0739	0.0814	0.0764
Rw (all data)	0.1847	0.1545	0.1583
CCDC no.	1504253	1504259	1504258

Table S1. X-ray crystallographic parameters for the crystals.

crystal	**2-DEF**
Formula	$(C_{12}H_{11}N_3O_3S)\bullet(C_8H_{11}N) \bullet (C_5H_{11}NO)$
Fw	499.63
Crystal system	Monoclinic
Space group	$P2_1$
Temperature (K)	213
a (Å)	6.21672(11)
b (Å)	26.5810(5)
c (Å)	7.98985(14)
α	90
β	99.5040(7)
γ	90
V (Å^3)	1302.17(4)
Z	2
reflections observed	13515
reflections unique	4617
R1 [I > 2.0σ(I)]	0.0513
Rw (all data)	0.1175
CCDC no.	1504261