Electronic supplementary information (ESI)

Quinolinium single crystals with high optical nonlinearity and unusual out-of-plane polar axis

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A. Polar Axis of Benchmark Nonlinear Optical Organic Crystals

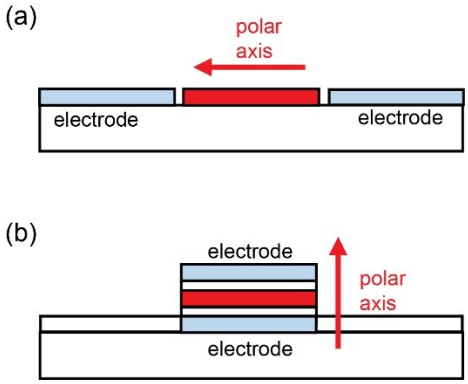

Figure S1. Various photonic configurations employing materials with second-order optical nonlinearity depend on the direction of the polar axis (red arrow) of these materials: (a) in-plane polar axis with in-plane electrodes and (b) out-of-plane polar axis with vertical electrodes.

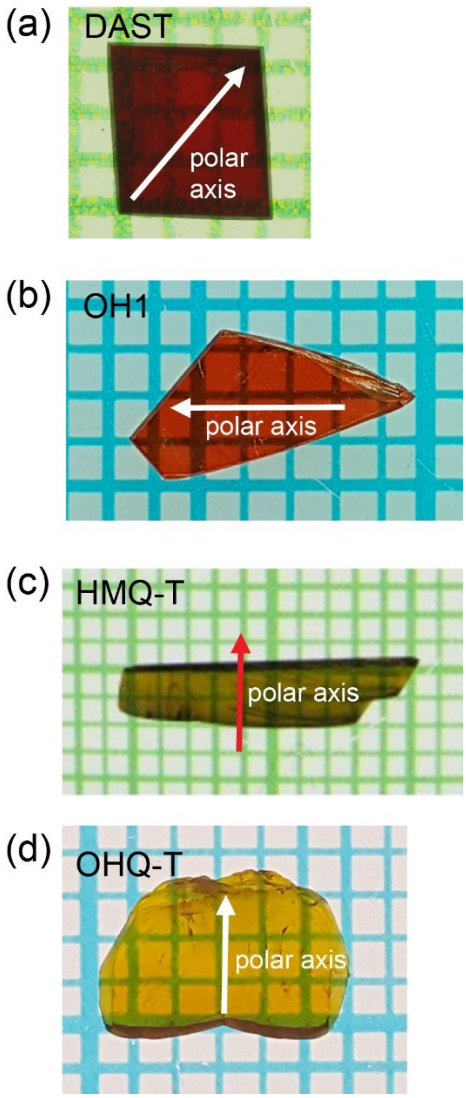

Figure S2. Photographs of benchmark nonlinear optical organic crystals possessing an in-plane polar axis: (a) DAST (*N,N*-dimethylamino-*N*'-methylstilbazolium 4-methylbenzenesulfonate), (b) OH1 (2-(3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile), (c) HMQ-T (2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium 4-methylbenzenesulfonate)crystals, and (d) OHQ-T (2-(4-hydroxystyryl)-1-methylquinolinium 4-methylbenzenesulfonate), which are grown in solution.

B. Powder Second Harmonic Generation (SHG) Test

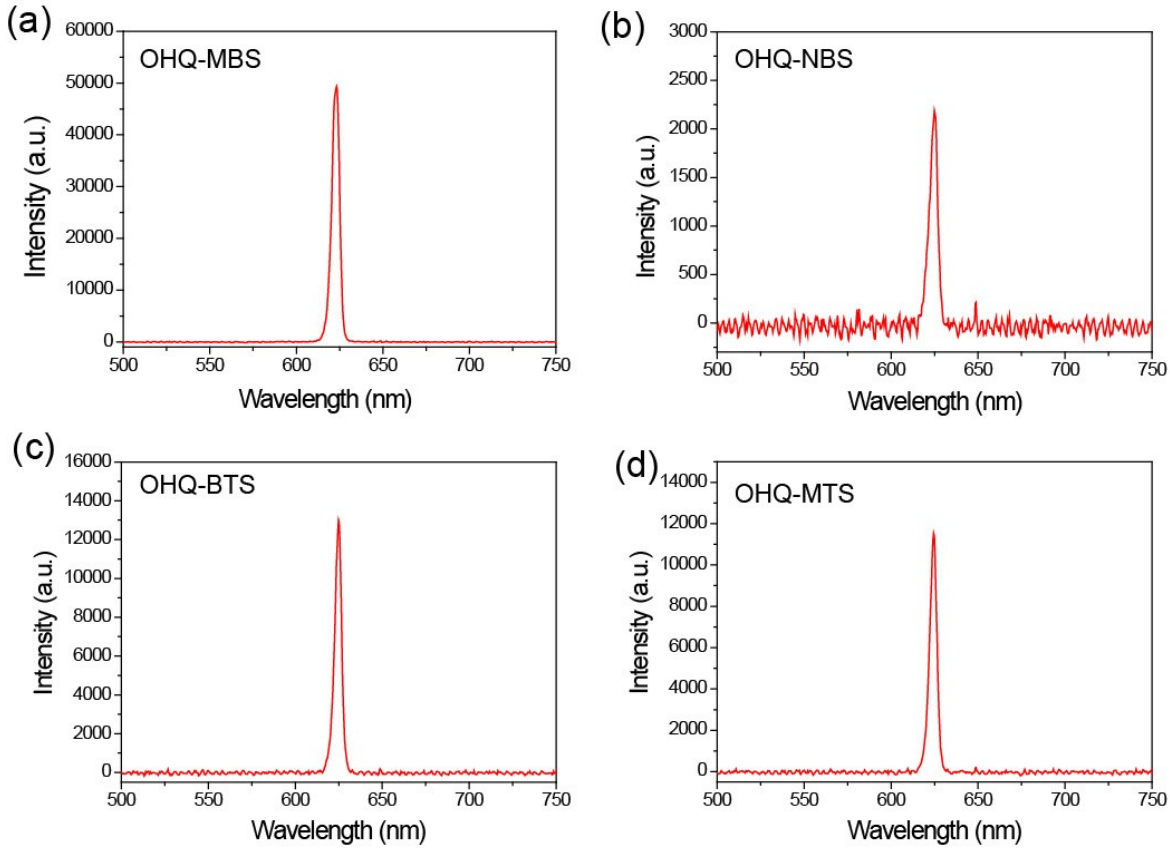

Figure S3. Qualitative powder second harmonic generation (SHG) test of OHQ analogous crystalline powders. The fundamental wavelength is 1250 nm with a pulse duration of 150-200 fs. For qualitatively screening whether four OHQ crystals exhibits noncentrosymmetric or centrosymmetric crystal structures, the magnitude of the generated SHG signals of OHQ-based crystalline powders are compared to that of DAST crystalline powders by the naked eye and the spectra of SHG signals with the central wavelength of 625 nm are recorded by a spectrometer. [SR1] Note that the SHG intensity (i.e., *y*-axis) of Figure S3 is in arbitrary units and the absolute values cannot be directly compared to each other. The quantitative macroscopic optical nonlinearity of OHQ-MBS crystals is evaluated by quantum chemical calculations and considering the crystal structure (see section D in ESI).

C. Single-crystal X-ray Structure Analysis

OHQ-MBS single crystals for X-ray structure analysis are grown by slow evaporation method in methanol. $C_{25}H_{23}NO_5S$, M_r = 449.50, monoclinic, space group *Pn*, *a* = 11.6942(4) Å, *b* = 7.0690(2) Å, *c* = 13.1573(5) Å, β = 101.210(1) °, *V* = 1066.91(6) Å^3, *Z* = 2, *T* = 290(1) K, μ(MoKα)= 0.19 mm^{-1}. Of 9319 reflections collected in the θ range 3.2°-27.5° using ω scans on a Rigaku R-axis Rapid S diffractometer, 4786 were unique reflections (R_{int} = 0.0136). The structure was solved and refined against F^2 using SHELX97, [SR2] 292 variables, wR_2 = 0.0894, R_1 = 0.0322 (Fo^2 > 2σ(Fo^2)), GOF = 1.087, Flack absolute structure parameter x=0.009(14), and max/min residual electron density 0.267/-0.172 eÅ^{-3}. CCDC-1525019.

D. Macroscopic Optical Nonlinearity

For the evaluation of microscopic and macroscopic optical nonlinearities of OHQ-MBS crystals we considered only the highly nonlinear OHQ cations and exclude MBS anions having comparably a very small nonlinearity. [SR3] The crystal structure of OHQ-MBS crystals is isomorphic with previously studied OHQ-T crystals. [SR1] The molecular conformation of OHQ cations in OHQ-MBS crystals is also very similar to that of OHQ-T crystals as shown in Figure S4. In addition, the dihedral angle between the quinolinium ring and the phenolic ring in OHQ cations is very similar; 21 and 24 degree for OHQ-MBS and OHQ-T crystals, respectively.

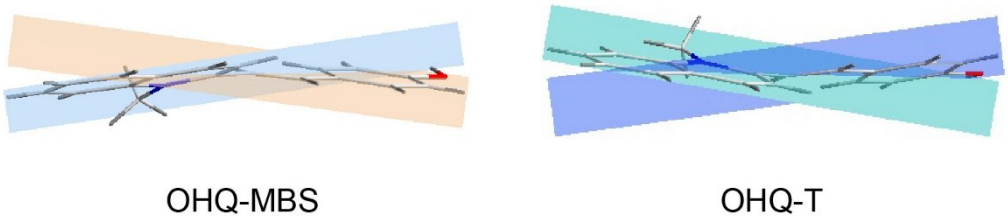

Figure S4. Molecular conformation of OHQ cations in OHQ-MBS and OHQ-T crystals. The dihedral angle between the quinolinium ring and the phenolic ring is 21 and 24 degree for OHQ-MBS and OHQ-T crystals, respectively.

Consequently, the amplitude and the direction of the maximum first-order hyperpolarizability β_{max} of OHQ cations in OHQ-MBS and in OHQ-T crystals may be considered identical. Therefore, the maximum first-order hyperpolarizability β_{max} of OHQ cations of OHQ-MBS crystals is 121×10^{-30} esu as-like in OHQ-T crystals, which has been previously evaluated using quantum chemical calculations. [SR1] The direction of the maximum first-order hyperpolarizability β_{max} is presented in Figure 2. The directions of polar axis and maximum first-order hyperpolarizability β_{max} are superimposed as shown in Figure 2; i.e., the angle θ_p between the polar axis and the directions of maximum first-order

hyperpolarizability β_{max} of OHQ chromophores is practically zero, resulting in maximal order parameter $\cos^3\theta_p$ = 1.0 for OHQ-MBS crystals. Therefore, OHQ-MBS crystals exhibit a large macroscopic optical nonlinearity with the largest diagonal component of the effective hyperpolarizability tensor $\beta_{iii}^{eff} = \beta_{max} \cdot \cos^3\theta_p = 121\times10^{-30}$ esu.

E. Cleaving Method for Samples with an In-Plane Polar Axis

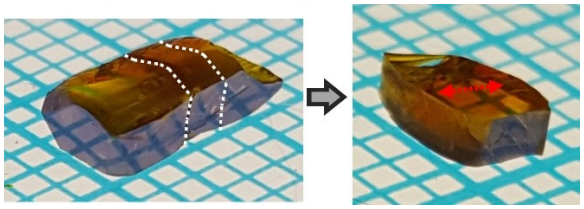

Figure S5. Photograph of a cleaved OHQ-MBS crystal possessing an in-plane polar axis (right), which is prepared using a simple cleaving method [SR4] from an as-grown OHQ-MBS crystal (left) with a relatively large thickness. The dotted lines illustrate the orientation of cleavage planes.

References in ESI

[SR1] S. H. Lee, B. J. Kang, J. S. Kim, B. W. Yoo, J. H. Jeong, K. H. Lee, M. Jazbinsek, J. W. Kim, H. Yun, J. Kim, Y. S. Lee, F. Rotermund and O. P. Kwon, *Adv. Opt. Mater.*, 2015, **3**, 756−762.

[SR2] G. M. Sheldrick, *SHELXL 2014/7*, University of Göttingen, Germany, 2014.

[SR3] S. J. Kwon, O. P. Kwon, J. I. Seo, M. Jazbinsek, L. Mutter, V. Gramlich, Y. S. Lee, H. Yun and P. Günter, *J. Phys. Chem. C*, 2008, **112**, 7846–7852.

[SR4] J. H. Jeong, B. J. Kang, J. S. Kim, M. Jazbinsek, S. H. Lee, S. C. Lee, I. H. Baek, H. Yun, J. Kim, Y. S. Lee, J. H. Lee, J. H. Kim, F. Rotermund and O. P. Kwon, *Sci. Rep.*, 2013, **3**, 3200.