Electronic supplementary information (ESI)

Multi-functional Supramolecular Building Blocks with Hydroxy Piperidino Groups: New Opportunities for Developing Nonlinear Optical Ionic Crystals

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Non-centrosymmetric Cation Core Structure

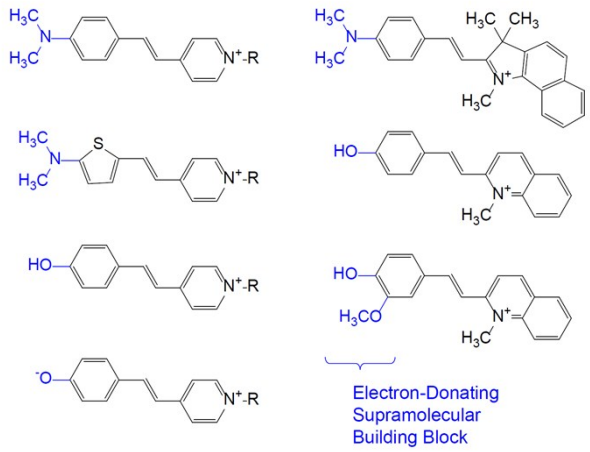
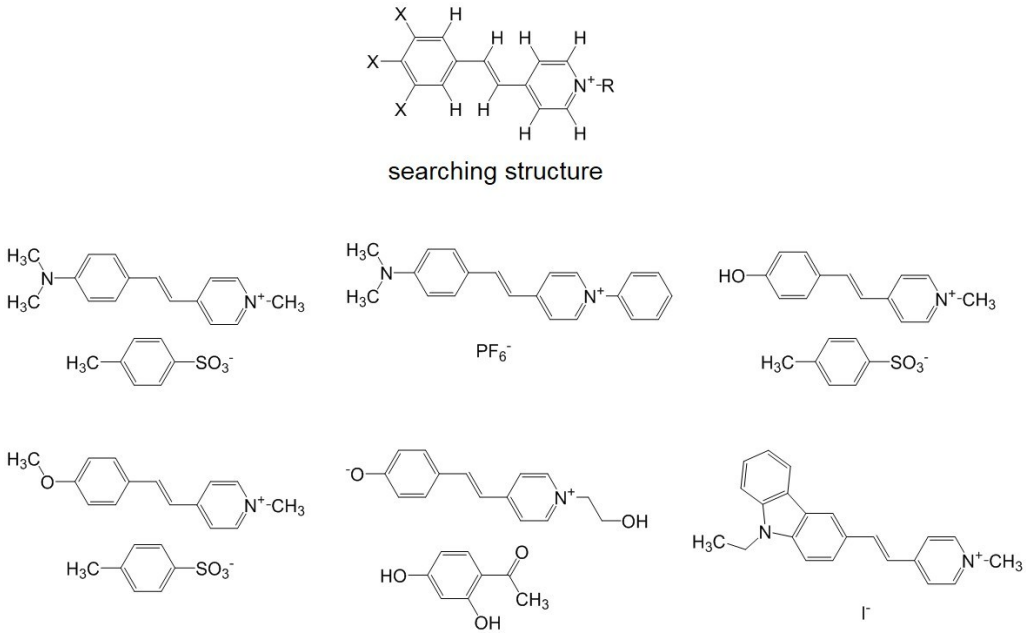


Fig. S1 Non-centrosymmetric cation core structures in nonlinear optical ionic crystals with large nonlinear optical properties.[11-26]

Search of Crystal Structures in Cambridge Structural Database

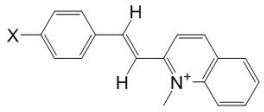
The crystal structures possessing heteroaromatic cations (styryl pyridinium (i.e., stilbazolium), styryl quinolinium and ((thiophen-2-yl)vinyl)-pyridinium), which are part of chemical structure of non-centrosymmetric cation core structures in Fig. S1 (ESI†), have been searched in the Cambridge Structural Database (updated Nov. 2014, version 5.36). The details are described below. Only four electron-donating building blocks (*N,N*-dimethylamino group, (di)alkoxy groups, phenolic and/or phenolate groups with/without methoxy groups and carbazole groups) result in acentric crystal structures.

A. Crystal Structures with styryl pyridinium (i.e., stilbazolium)

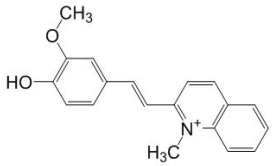


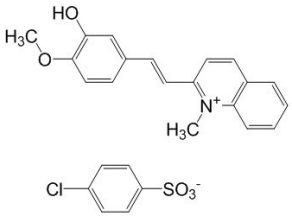
The number of crystal structures possessing styryl pyridinium is 231 (see above the structure searched). Among them, the number of acentric crystal structures is 49. Among these acentric structures, 4 classes of electron-donating building blocks have been identified for 28 structures: 16 structures have *N,N*-dimethylamino group, 4 structures have (di)alkoxy group, 5 structures phenolic and/or phenolate groups, and 3 structures carbazole group. The remaining 22 acentric structures have not been classified in these groups because: 1) 14 of crystal structures are hydrate and/or solvent-inclusion phases due to low stability, 2) 5 of crystal structures introduce a very weak electron donor (typically hydrogen atom), electron acceptor (cyano group and ionic tertiary amine group), or organometallic donor on electron-donating building blocks, and 3) 2 structures have counter anions including a metal ion cluster. The structure searched and some selected examples of molecules exhibiting an acentric crystal structure are shown above.

B. Crystal Structures with styryl quinolinium



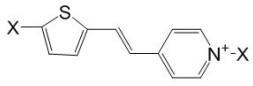
searching structure



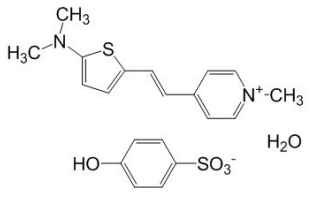


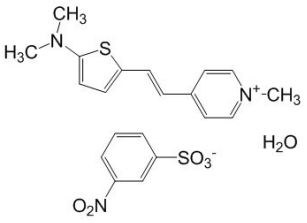
The number of crystal structures possessing styryl quinolinium is 51 (see above the structure searched). Among them, the number of acentric crystal structures is 11. Among the acentric structures, 7 structures contain an identical electron-donating building block (hydroxy-methoxyphenyl group). The remaining 4 acentric crystal structures are hydrate phases and are therefore not classified. The structure searched and selected examples of molecules exhibiting an acentric crystal structure are shown above.

C. Crystal Structures with ((thiophen-2-yl)vinyl)-pyridinium



searching structure





The number of crystal structures possessing ((thiophen-2-yl)vinyl)-pyridinium is 2 (see below the structure searched). All crystal structures possess the *N,N*-dimethylamino electron-donating building block and exhibit an acentric crystal structure, but are also all hydrate phases. The structure searched and the two compounds found are shown above.

Microscopic Optical Nonlinearity

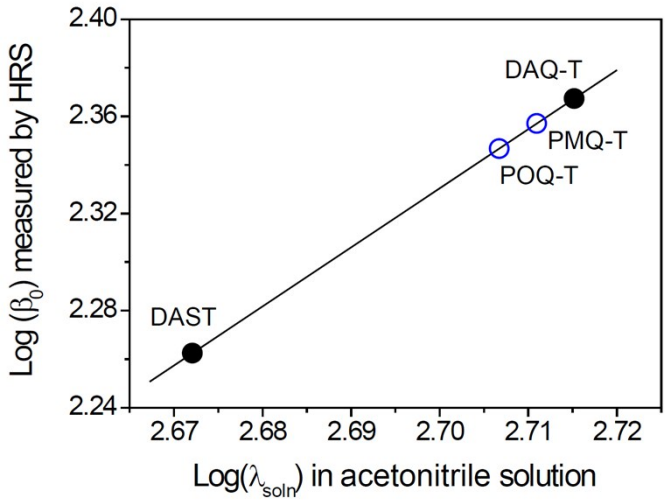


Fig. S2 Microscopic optical nonlinearity of PMQ-T and POQ-T cations is estimated by the nonlinearity-transparency trade-off. The molecular first hyperpolarizability β_o of DAQ-T and DAST were measured by hyper-Rayleigh scattering (HRS) technique in acetonitrile solution as previously reported Ref. 33: $\beta_o = 233 \times 10^{-30}$ esu for DAQ-T and 183×10^{-30} esu for DAST (closed circles). The wavelength of maximum absorption λ_{soln} of compounds is measured in acetonitrile solution with a concentration of 10^{-5} M. The open circles are estimated values of β_o for PMQ-T and POQ-T, in which the relation between $\log(\beta_o)$ and $\log(\lambda_{soln})$ is assumed to be linear.

Powder Second Harmonic Generation (SHG) Test

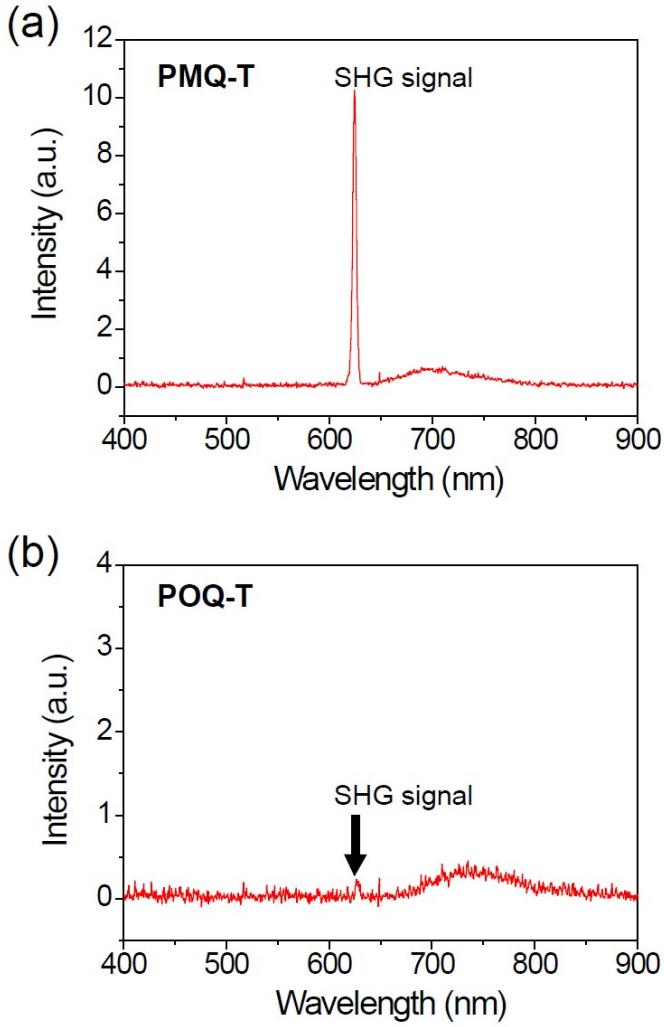


Fig. S3 The spectrally resolved powder SHG signal of PMQ-T and POQ-T crystals grown in methanol. The wavelength of the fundamental beam is 1250 nm.

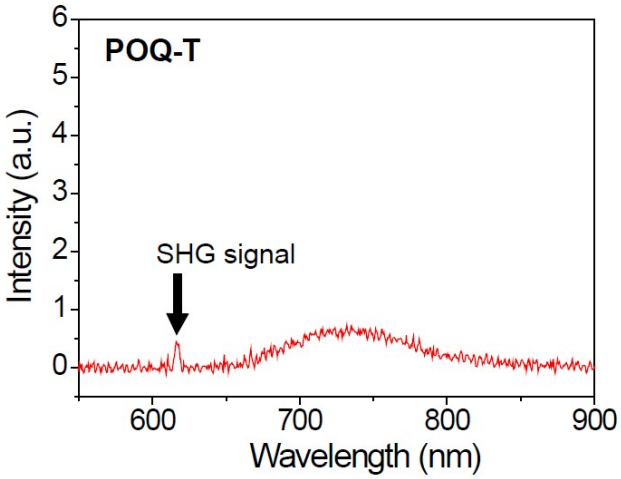


Fig. S4 The spectrally resolved powder SHG signal of POQ-T crystals, which are prepared by a heat treatment of POQ-T crystals grown in methanol at 105 ^{o}C in vacuum oven for about 12 h. POQ-T crystals before and after heat treatment exhibit identical powder X-ray diffraction pattern and DSC and TGA thermodiagrams. .

Non-Hydrate Phase of DAQ-T

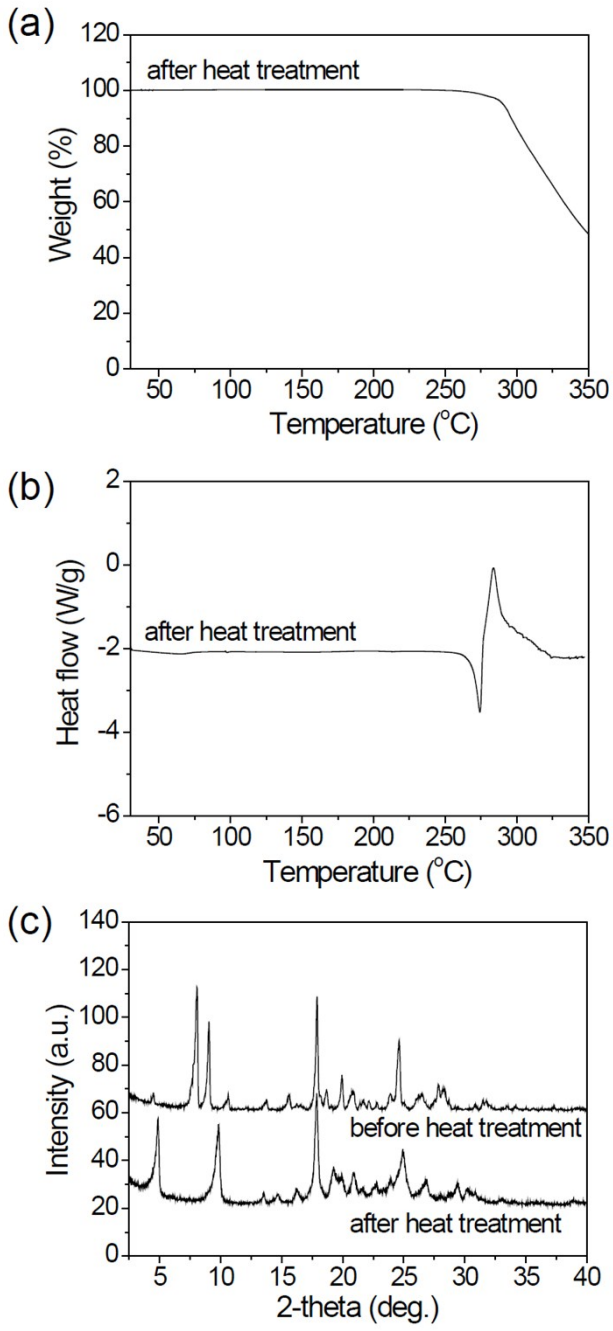


Fig. S5 TGA, DSC and powder X-ray diffraction patterns of non-hydrate DAQ-T crystals, which are prepared from DAQ-T crystals crystallized in methanol (hydrate phase) by heat treatment at 105 °C in vacuum oven for about 12 h