In-situ Tailor-made Additives for Molecular Crystals: A Simple Route to Morphological Crystal Engineering

Seung-Heon Lee, [†] *Gyeong-Hui Lee,* [†] *Kang-Hyun Lee,* [†] *Mojca Jazbinsek,* [¶] *Bong Joo Kang,* [§] *Fabian Rotermund,* [§] *O-Pil Kwon** [*,†]

[†]Department of Molecular Science and Technology, Ajou University, Suwon 443-749, Korea

[¶]Institute of Computational Physics, Zurich University of Applied Sciences (ZHAW), 8401 Winterthur, Switzerland

[§]Department of Physics & Department of Energy Systems Research, Ajou University, Suwon 443-749, Korea

Crystal growth with *in-situ* tailor-made additive DDP

Single OH1 crystals are grown by slow evaporation with OH1 methanol solutions in the absence and presence of *in-situ* tailor-made additive DDP with various concentration. OH1/DDP solutions with different molar ratio of DDP (OH1 : DDP = 100 : 0, 99 : 1, 97 : 3, 95 : 5, 93 : 7, 90 : 10 mol/mol (i.e., 0, 1, 3, 5, 7 and 10 mol% of DDP)) are used.

For small-scale growth experiments (total amount of methanol = 10 mL), six OH1 solutions prepared by dissolving OH1 powder (0.1 g, 3.44×10^{-4} mol) in a different amount of methanol (10.00, 9.86, 9.58, 9.30, 9.02, and 8.60 mL) are mixed with the corresponding amount (0, 0.14, 0.42, 0.70, 0.98, and 1.40 mL) of NaOH solution (2.50×10^{-2} M in methanol). When an OH1/methanol solution is mixed with a NaOH/methanol solution, the color of the resulting solution immediately changes from orange to dark purple by the very fast acid-base neutralization reaction between the acidic -OH phenolic group on OH1 and the OH^- group from NaOH (see also the absorption spectrum in Figure 3). Note that in these solutions, the molar ratio of OH1 : NaOH = 1 : 0, 1 : 0.01, 1 : 0.03, 1 : 0.05, 1 : 0.07, and 1 : 0.10 mol/mol is practically identical to OH1 : DDP = 100 : 0, 99 : 1, 97 : 3, 95 : 5, 93 : 7, 90 : 10 mol/mol (i.e., 0, 1, 3, 5, 7 and 10 mol% of DDP). Notes that pH values of these solutions in the presence of DDP additives (i.e., by adding NaOH) are close to neutral, slightly basic condition: pH = 7.4, 7.8, 8.1, 8.2 and 8.4 for solutions with 1, 3, 5, 7 and 10 mol% of DDP, respectively. The mixed solutions are kept in an oven at a constant temperature of 30 ^{o}C for solvent evaporation during few days. During this time, OH1 crystals spontaneously nucleate and grow. The resulting OH1 crystals are obtained by filtering of the remaining solution.

In large-scale growth experiments (total amount of methanol = 100 mL), we use identical experimental conditions (i.e., identical concentration, molar ratio and growth temperature) with 10 times larger amounts of OH1 and NaOH.

As-grown OH1 crystals in the absence of additives (small-scale growth experiments) are shown in Figure 1b. In Figure 1c, the top two OH1 crystals and the bottom two OH1 crystals are grown in the presence of DDP (3 mol%) in small- and large-scale growth experiments, respectively. Figure S1 in SI shows photographs of as-grown OH1 crystals in the presence of DDP in small-scale growth experiments, excepting the last OH1 crystal on the right in Figure S1b, which is grown in a large-scale growth experiment.

Crystal growth with conventional tailor-made additive DDM

Single OH1 crystals were grown by slow evaporation with OH1 methanol solutions in the presence of conventional tailor-made additive DDM (OH1 : DDM = 97 : 3 mol/mol (i.e., 3 mol% of DDP). OH1 (0.1 g, 3.44×10^{-4} mol) and DDM (0.0033 g, 1.03×10^{-5} mol) powders are dissolved in methanol (15 mL). The mixed solutions were kept in an oven at a constant temperature of 30 ^{o}C for few days for evaporating the solvent. OH1 crystals spontaneously nucleate and the grown OH1 crystals are obtained by filtration. The resulting OH1 crystals are shown in Figure 1d and Figure S2 in SI.

UV-vis absorption and fluorescence measurements

To measure absorption and fluorescence spectra, OH1 solutions are prepared with various molar ratios of OH1 : NaOH (OH1 : DDP) and OH1 : DDM (see Figure 3). Compared to conventional chromophore concentration used for absorption and fluorescence spectroscopy (10^{-}

^{4}~10^{-5} M), the chromophore concentration in crystal growth conditions is much higher, about 2-3 orders of magnitude higher. In order to measure the absorption and fluorescence spectra of solutions with a similar concentration as in crystal growth conditions, the initial concentration of OH1 in methanol of 10^{-2} M is chosen, which is in the same order of magnitude as the OH1 solubility in methanol[R1] (e.g., 17 % of OH1 solubility in methanol at 25 ^{o}C (5.9×10^{-2} M)). Different OH1 solutions are prepared with various amounts of additives: OH1 : NaOH and OH1 : DDM = 1 : 0.01, 1 : 0.03, 1 : 0.06, 1 : 0.10, 1 : 0.30, 1 : 0.50, 1 : 0.80 and 1.00 : 1.00 mol/mol (i.e., 0, 1, 3, 6, 10, 30, 50, 80, and 100 mol% of DDP and 0, 1, 3, 6, 9, 23, 33, 44, 50 and 100 mol% of DDM). Absorption and fluorescence spectra are measured by using a cell of two slide glasses with a small gap and a 1 mm quartz cell, respectively. For comparison, pure OH1 and DDM solutions are also measured. The results are shown in Figure 3.

^{1}H NMR Measurements

For ^{1}H NMR spectra measurements as shown in Figure 4, the initial OH1 concentration of 4.7×10^{-2} M in CD_3OD solutions is used, which is about 80 % of the saturated concentration at 25 ^{o}C; the OH1 solubility in methanol at 25 ^{o}C is 5.9×10^{-2} M.[R1] All ^{1}H NMR spectra are measured by Varian 400 MHz. CD_3OD (100%, 99.96 atom %D, Aldrich) and NaOD (40 wt%, 99.5 atom %D, Aldrich) were used. After adding NaOD (40 wt%) aqueous solution with various molar ratios, ^{1}H NMR spectra are measured and the results are shown in Figure 4.

In order to investigate the influence of excess NaOD and water on intermolecular interactions in solutions, ^{1}H NMR spectra are also measured after adding excess amounts of NaOD and water; these results are shown in Figure S6 and S7 in SI, respectively. By adding

excess amounts of NaOD and water, no significant shift of the peaks in ^{1}H NMR spectra is observed.

Figure S1. Photographs of as-grown OH1 crystals in the presence of *in-situ* tailor-made additive DDP with a different molar ratio (scale bar: 0.5 mm). In the presence of DDP additives with up to 5 mol% (a-c), the as-grown OH1 crystals exhibit well-developed regular facets with clearly defined *b*-planes ((010) and (0-10) planes) with flat surfaces due to parallel-stereoselective inhibitions on the *b*-planes. However, in the presence of DDP additives of over 7 mol%, the as-grown OH1 crystals start to exhibit a slightly irregular morphology (d-e), which may be due to non-selective inhibition by the existence of relatively many DDP molecules around the growing OH1 crystal.

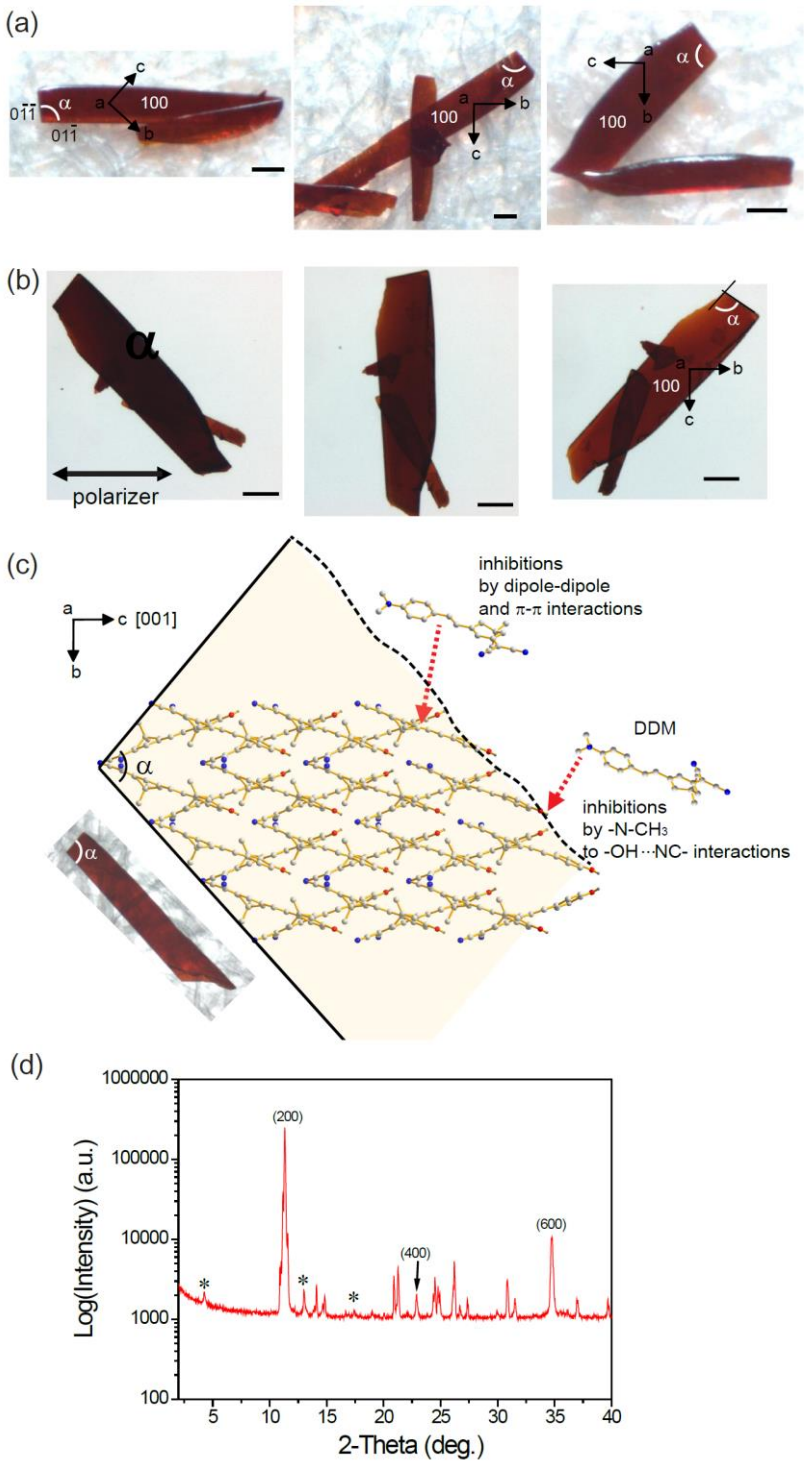

Figure S2. As-grown OH1 crystals in the presence of a conventional tailor-made additive DDM (3 mol%). (a) Photographs of OH1 crystals (scale bar: 0.1 mm) and (b) photographs of OH1 crystals on a plastic polarizer (scale bar: 0.1 mm). (c) Schematic illustration of rather non-

selective inhibitions by DDM additive on OH1 crystals. The inhibition by dipole-dipole and π-π interactions between OH1 molecules and the additives exhibit antiparallel dipole-dipole attachment, which is called here 'antiparallel-stereoselective inhibition'. (d) Powder X-ray diffraction patterns of OH1 crystals grown in the presence of DDM additives. The asterisks present the diffraction peaks from a small amount of tiny pure DDM crystals.

Figure S2c illustrates the rather non-selective inhibitions by DDM additive on OH1 crystals. The tendency of antiparallel dipole-dipole aggregations and π-π stacking interactions between DDM additive molecules and OH1 crystal faces are very similar with that of DDP additive molecules (see Figure S5 in SI). However, the weak hydrogen bond donor (i.e., hydrogen atoms on $–N-(CH_3)_2$ groups) with a relatively large size on the DDM additive may create weak and complicated hydrogen bonds with –OH groups of OH1 crystals, which results in rough growth surfaces and edges (presented by the dotted line in Figure S2c).

Figure S2d shows powder X-ray diffraction patterns of OH1 crystals grown in the presence of DDM additives and the peaks are determined by comparison with theoretical X-ray diffraction patterns from crystal structure of OH1 and DDM crystals, obtained from Ref. R2 and R3, respectively. OH1 crystals grown in the presence of DDM additive exhibit identical crystal structure to OH1 crystals grown in the absence of additives, which is confirmed by powder X-ray diffraction patterns, in which very small diffraction peaks from pure DDM crystals are observed – note that the solubility of DDM crystals in methanol is relatively low compared to OH1 and the amount of DDM used in the initial solution is also much lower.

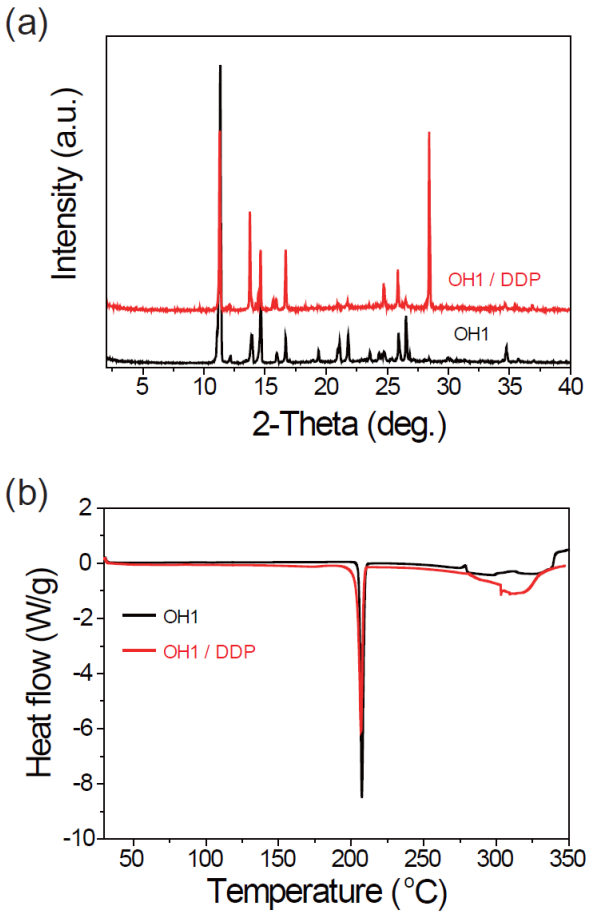

Figure S3. (a) Powder X-ray diffraction patterns and (b) differential scanning calorimetry (DSC) thermodiagrams of OH1 crystals grown in the absence and the presence of *in-situ* tailor-made additive DDP (3 mol%).

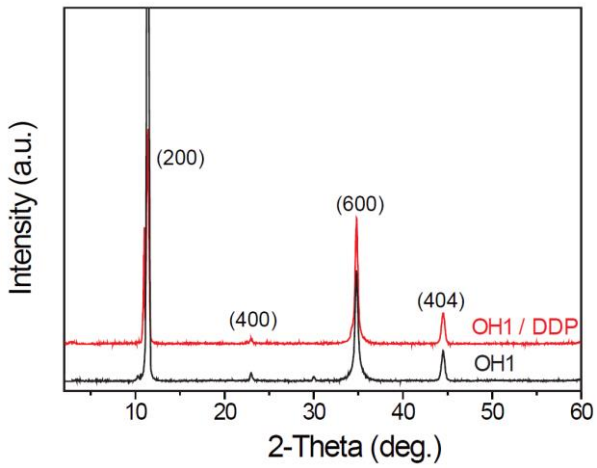

Figure S4. X-ray diffraction patterns obtained by X-ray reflection from (100) planes of OH1 crystals grown without additives (black curve) and grown in the presence of *in-situ* tailor-made additive DDP (3 mol%, red curve).

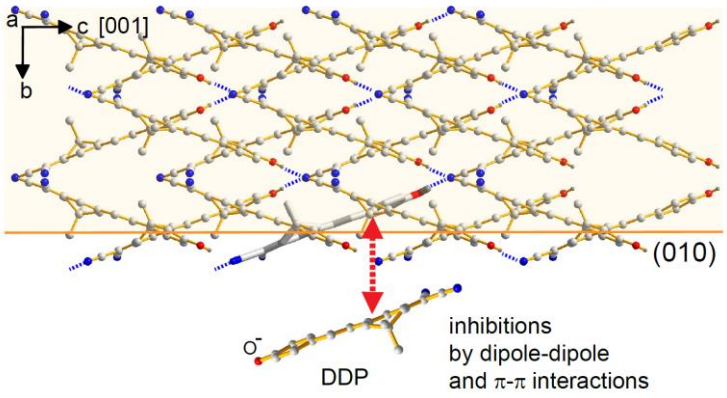

Figure S5. Schematic illustration of antiparallel-stereoselective inhibitions by DDP additives due to antiparallel dipole-dipole aggregation and π-π stacking interactions on the (010) *b*-plane of OH1 crystals.

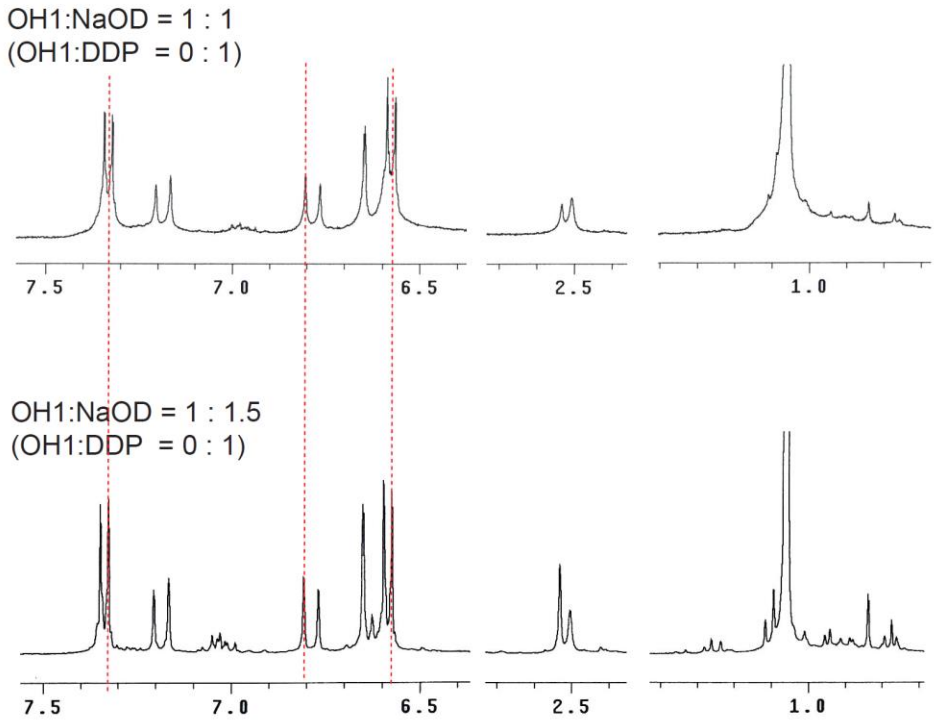

Figure S6. Influence of excess NaOH on ^{1}H NMR spectra of OH1: ^{1}H NMR spectra of OH1 with a different molar ratio of NaOD in CD_3OD solution: from top to bottom, OH1:NaOD (OH1:DDP) = 1:1 (0:1) and 1:1.5 (0:1). No influence of excess NaOH on ^{1}H NMR spectrum of OH1 is observed.

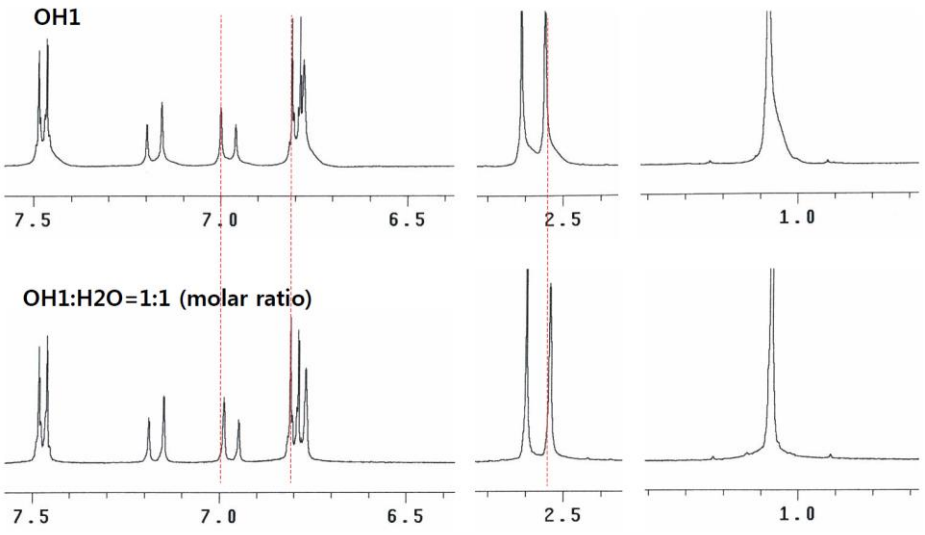

Figure S7. ^{1}H NMR spectra of OH1 and OH1:H_2O (1:1 mol/mol) in CD_3OD solution. No influence of H_2O molecules on ^{1}H NMR spectrum of OH1 is observed.

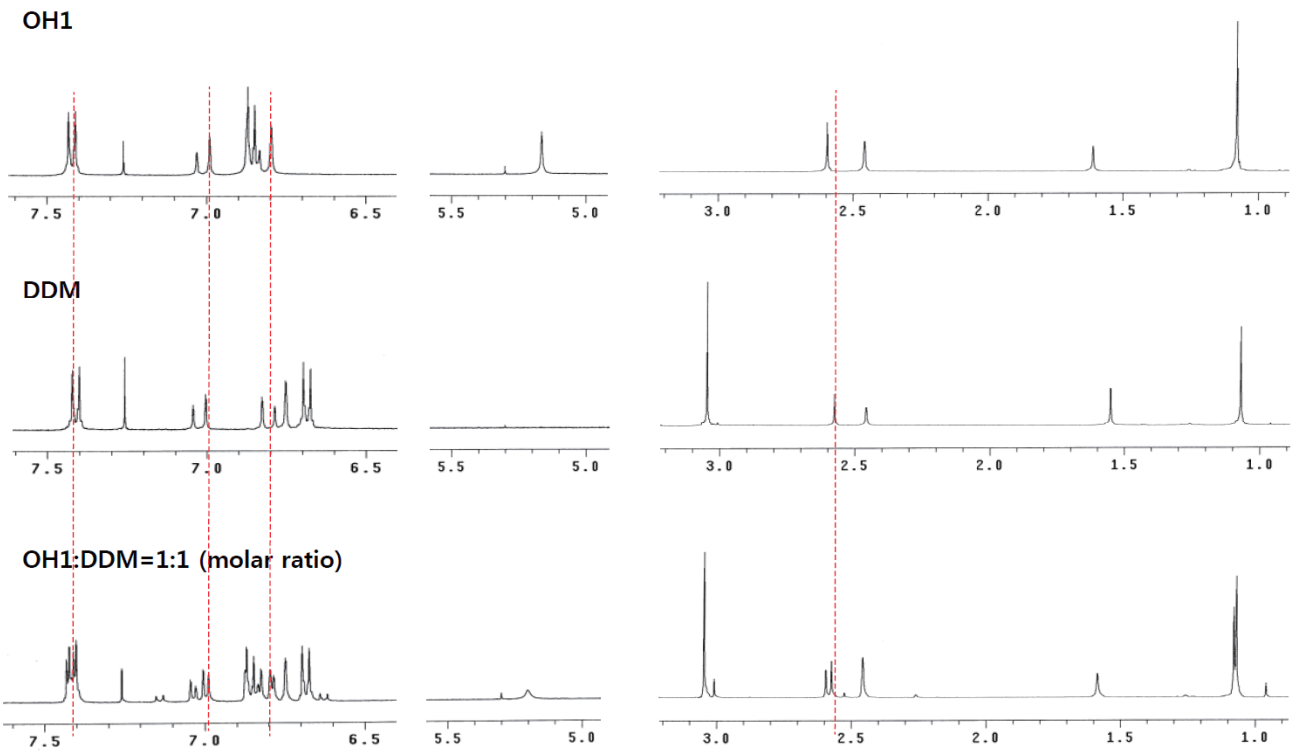

Figure S8. ^{1}H NMR spectra of OH1, DDM and OH1:DDM (1:1 mol/mol) in $CDCl_3$ solution. Due to weak interactions between OH1 and DDM molecules, ^{1}H NMR spectrum of OH1:DDM (1:1 mol/mol) exhibits no shift of the peak related to the π-conjugated bridge and is instead a simple mixture of single OH1 and DDM spectra.

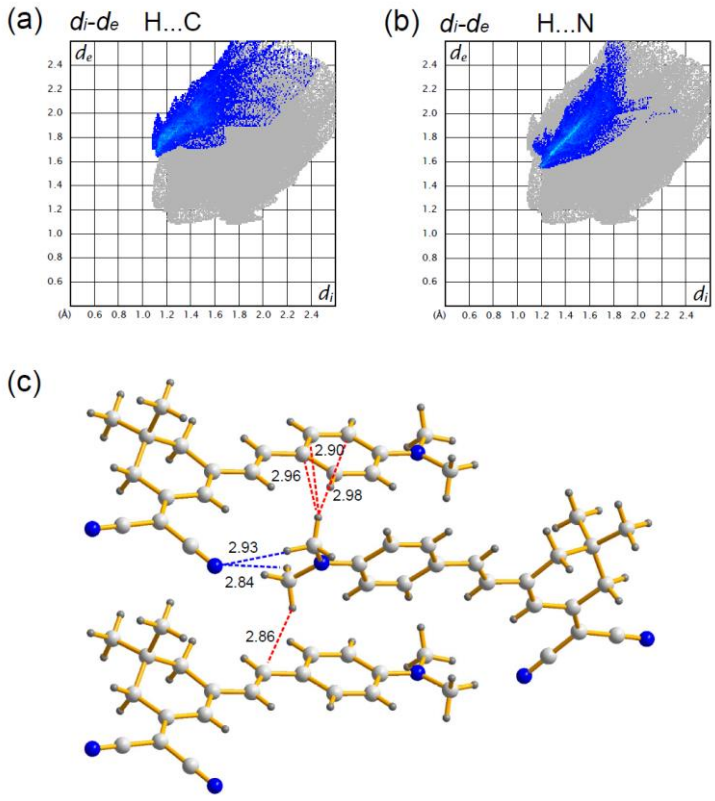

Figure S9. Hirshfeld surface analysis[R4-R6] of DDM crystals, for which the crystal structure of DDM is obtained from Ref. R3: Hirshfeld fingerprint of DDM resolved into (a) H···C and (b) H···N contacts. (c) Intermolecular interactions of two methyl groups on -$N(CH_3)_2$ with interatomic distance of less than 3 Å are H···C(π) and H···NC- interactions. Note that the two methyl groups on -$N(CH_3)_2$ of DDM are obviously involved in supramolecular interactions in DDM crystals.

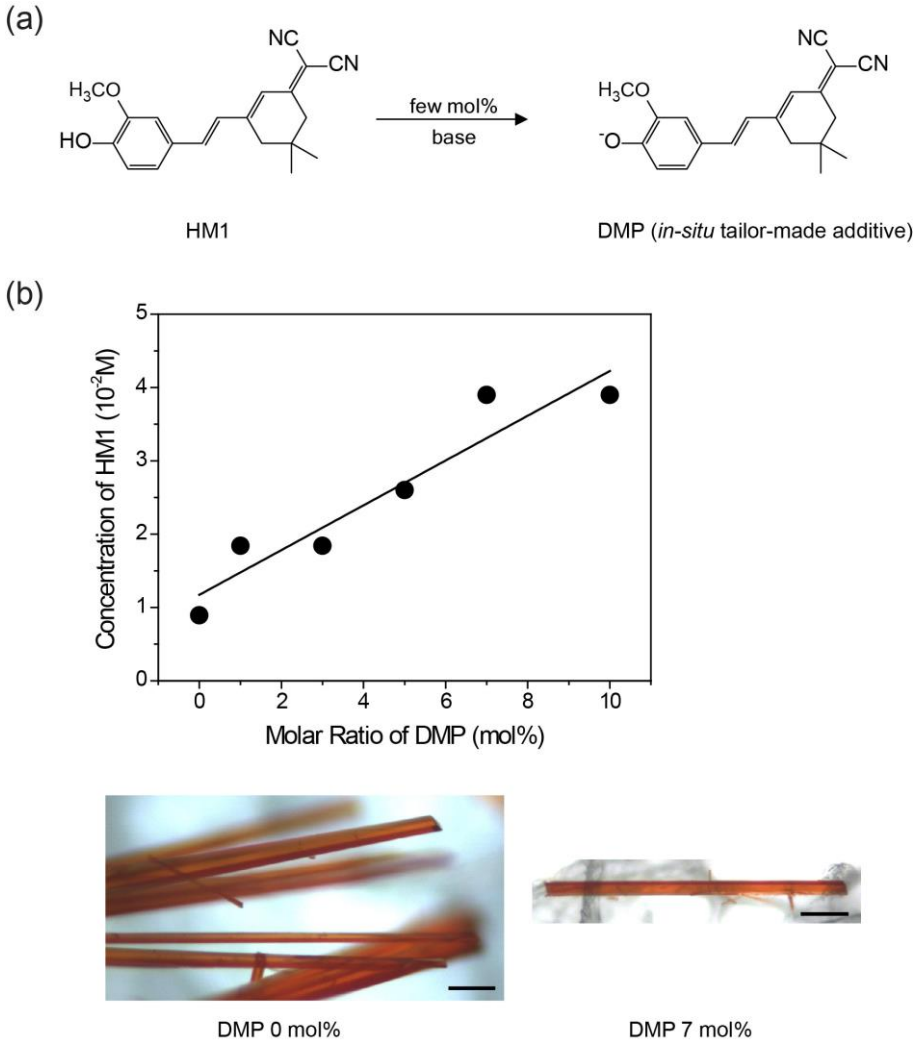

Figure S10. (a) Chemical structure of phenolic substrate molecule HM1 (2-(3-(4-hydroxy-3-methoxystyryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile) and *in-situ* tailor-made additive form DMP (4-(2-(3-(dicyanomethylene)-5,5-dimethylcyclohex-1-enyl)vinyl)-2-methoxyphenolate). (b) Nucleation point measurements and selected photographs of HM1 crystals grown by slow evaporation method in methanol solution at a constant temperature of 30 ^{o}C with various molar ratios of DMP (scale bar: 50 μm). The solutions with molar ratio of HM1 : DMP = 100 : 0, 99 : 1, 97 : 3, 95 : 5, 93 : 7, 90 : 10 mol/mol (i.e., 0, 1, 3, 5, 7 and 10 mol% of DMP) is prepared by adding NaOH (i.e., OH1 : NaOH = 1 : 0, 1 : 0.01, 1 : 0.03, 1 : 0.05, 1 : 0.07,

and 1 : 0.10 mol/mol). The initial concentration of HM1 in methanol solution (40 mL) is 7.8×10^{-3} M. When 5 mL of the solution remains by solvent evaporation, the resulting HM1 crystals are obtained by filtering of the remaining solution. Both HM1 crystals grown in the absence and the presence of DMP additives exhibit similar morphologies with needle shape. However, with increasing concentration of DMP additives, the concentration of HM1 solution at nucleation point remarkably increases and the size (i.e. length and width of needle) of HM1 crystals decreases. The solid line presents a linear fit function to the data.

THz Generation Experiments

For comparing the THz-wave generation characteristics using different faces of the rectangular rod-shaped OH1 crystals, THz waves are generated by optical rectification of 1600-nm pump pulses with pulse duration of 150 fs. The temporal time traces of the generated THz waves are recorded by electro-optic sampling technique using 800 nm probe pulses and a 1-mm-thick <110> ZnTe electro-optic crystal in dry air at room temperature in a similar setup reported in Ref. R7.

The generated THz spectral shape is affected by the phonon modes of the generation and detection crystals. The spectral center of mass f_c and the bandwidth of the generated THz wave are determined as follows: as shown in Figure S11 in SI, the spectral center of mass f_c of the generated THz wave is defined as the THz frequency at which the normalized integral THz amplitude reaches 0.5 and the bandwidth of THz spectra is defined as the difference of the THz frequencies whose normalized integral THz amplitude equals 0.75 and 0.25, respectively.

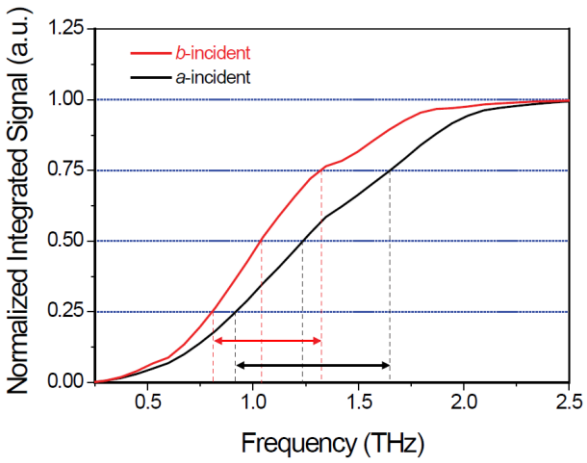

Figure S11. Normalized integrated THz amplitude as function of THz frequency, which is calculated from experimental frequency-domain amplitude spectra shown in Figure 2b.

References

(R1) Kwon, S. J.; Jazbinsek, M.; Kwon, O. P.; Günter, P. Crystal Growth and Morphology Control of OH1 Organic Electrooptic Crystals. *Cryst. Growth Des.* **2010**, *10*, 1552-1558.

(R2) Kwon, O. P.; Kwon, S. J.; Jazbinsek, M.; Brunner, F. D. J.; Seo, J.-I.; Hunziker, C.; Schneider, A.; Yun, H.; Lee, Y.-S.; Günter, P. Organic Phenolic Configurationally Locked Polyene Single Crystals for Electro-optic and Terahertz Wave Applications. *Adv. Funct. Mater*. **2008**, *18*, 3242-3250.

(R3) Kwon, O. P.; Ruiz, B.; Choubey, A.; Mutter, L.; Schneider, A.; Jazbinsek, M.; Gramlich, V.; Günter, P. Organic Nonlinear Optical Crystals Based on Configurationally Locked Polyene for Melt Growth. *Chem. Mater*. **2006**, *18*, 4049-4054.

(R4) Spackman, M. A.; Jayatilaka, D. Hirshfeld Surface Analysis. *CrystEngComm* **2009**, *11,* 19-32.

(R5) Spackman, M. A.; McKinnon, J. J. Fingerprinting Intermolecular Interactions in Molecular Crystals. *CrystEngComm* **2002**, *4*, 378–392.

(R6) McKinnon, J. J.; Jayatilaka, D.; Spackman, M. A. Towards Quantitative Analysis of Intermolecular Interactions with Hirshfeld Surfaces. *Chem. Commun*. **2007**, *37*, 3814–3816.

(R7) Lee, S.-H.; Kang, B.-J.; Kim, J.-S.; Yoo, B.-W.; Jeong, J.-H.; Lee, K.-H.; Jazbinsek, M.; Kim, J. W.; Yun, H.; Kim, J.; Lee, Y. S.; Rotermund, F.; Kwon, O. P. New Acentric Core Structure for Organic Electrooptic Crystals Optimal for Efficient Optical-to-THz Conversion. *Adv. Opt. Mater.* **2015**, *3*, 756-762.