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Supplementary information

Polymorphism of Vanillin Revisited: The Discovery and Selective Crystallization of a Rare Crystal Structure

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X-ray Crystallography information

The X-ray diffraction data were measured on a Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu Kα INCOATEC Imus micro-focus source (λ = 1.54178 Å). The crystal was kept at 100(2) K during data collection. Indexing was performed using APEX2.[1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01.[2] Absorption correction was performed by multi-scan method implemented in SADABS.[3] Space groups were determined using XPREP implemented in APEX2.[1] The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-2013[7] (full-matrix least-squares on F2) contained in APEX2[1,7], WinGX v1.70.01[4-7] and OLEX2.[7,8] All non-hydrogen atoms were refined anisotropically. H9 Hydrogen atom of hydroxyl group has been found from difference Fourier map and was freely refined with Uiso(H) = 1.5Ueq(-OH). The remaining hydrogen atoms of -OH groups as well as –CHO groups have been found from difference Fourier map and were freely refined. All other hydrogen atoms (of -CH, -CH2 and -CH3 groups) were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH,-CH2) and Uiso(H) = 1.5Ueq(-CH3).

Table S1. Hydrogen Bonds for vanillin Form II.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/°	D-H-A/°
O9	H9	O7^{i}	1.07 (4)	1.69 (4)	2.681 (3)	151 (3)
O6	H6	O3^{ii}	1.03 (5)	1.81 (5)	2.712 (3)	144 (4)
O8	H8	O9^{iii}	0.97 (6)	1.96 (6)	2.806 (3)	144 (5)
O10	H10	O6^{iv}	0.85 (5)	2.10 (5)	2.794 (3)	139 (4)

Symmetry operations: (i) -1/2+X,1/2-Y,+Z; (ii) 1/2+X,3/2-Y,+Z; (iii) 1/2-X,1/2+Y,1/2+Z; (iv) +X,-1+Y,+Z

Table S2. Crystal data and structure refinement for vanillin Form II

Empirical formula	$C_8H_8O_3$
Formula weight	152.14
Temperature/K	100 (2)
Crystal system	Orthorhombic
Space group	*Pna2₁*
a/Å	16.397 (7)
b/Å	3.810 (1)
c/Å	45.645 (2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2851.61 (19)
Z	16
Z’	4
ρ calc mg/mm^3	1.418
μ/mm^{-1}	0.918
F(000)	1280.0
Crystal size/mm^3	0.11 × 0.04 × 0.02
Radiation	CuKα (λ = 1.54178)
2θ range for data collection	7.748 to 144.68°
Index ranges	$-20 \leq h \leq 20$, $-4 \leq k \leq 4$, $-56 \leq l \leq 54$
Reflections collected	14594
Independent reflections	5340 [Rint = 0.0521, Rsigma = 0.0485]
Data/restraints/parameters	5340/1/432
Goodness-of-fit on F2	1.028
Final R indexes [I>=2σ (I)]	R1 = 0.0387, wR2 = 0.0887
Final R indexes [all data]	R1 = 0.0465, wR2 = 0.0925
Largest diff. peak/hole / e Å^{-3}	0.18/-0.23
Flack parameter 0.12 (10)	Flack parameter 0.12 (10)

Fig. S1: Comparison of calculated PXRD patterns of vanillin Form I crystal structures reported by Natarajan et al. (YUHTEA) and Nieger (YUHTEA01).

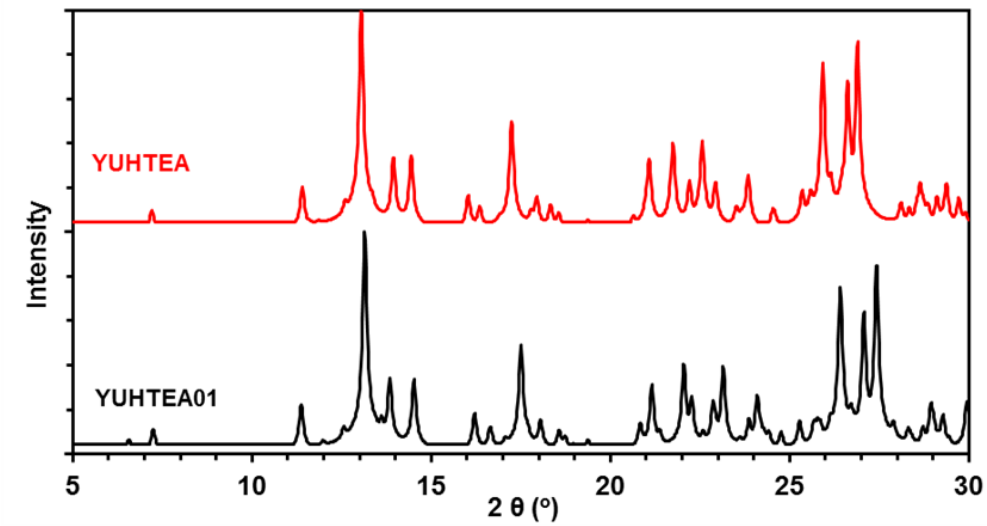


Fig. S2: PXRD patterns of calculated FI and FII of vanillin and it comparision to the PXRD patterns of vanillin crystals obtained from Isopropy alcohol, water, ethanol, acetonitrile, acetone.

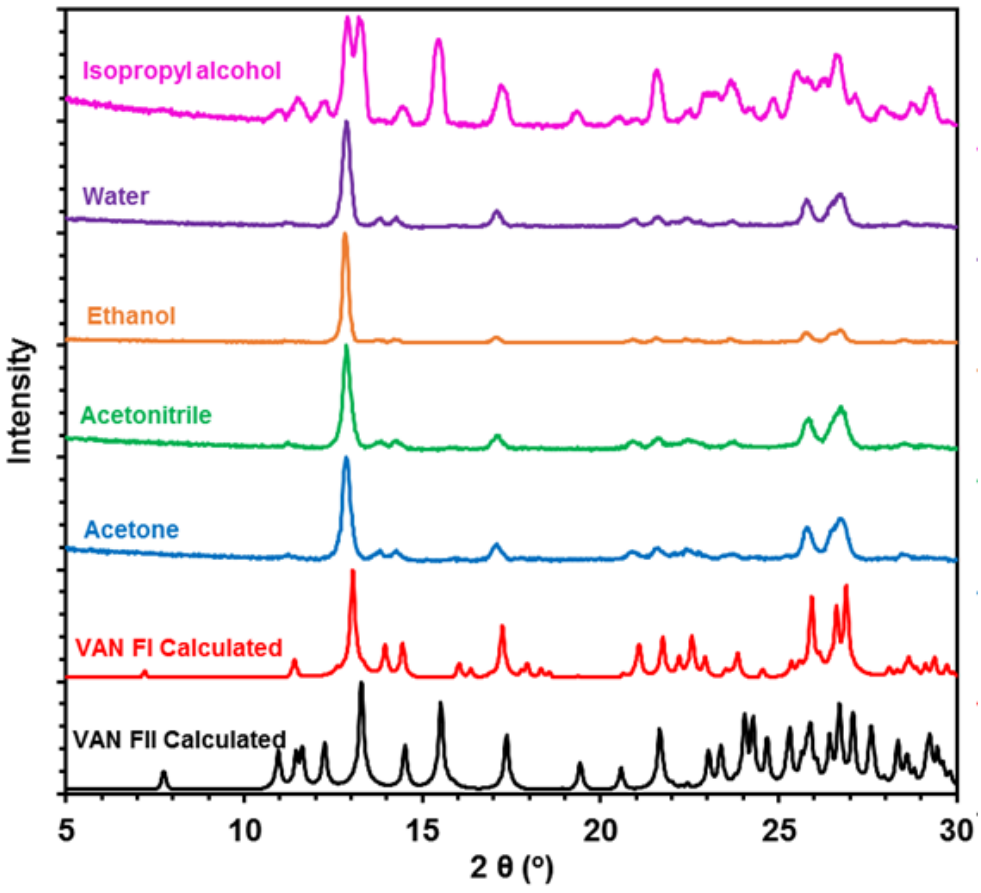


Fig. S3: Illustration of (a) hydrogen bonding in vanillin Form I; (b) lateral interactions in vanillin tapes in Form I (CSD ref code: YUHTEA).

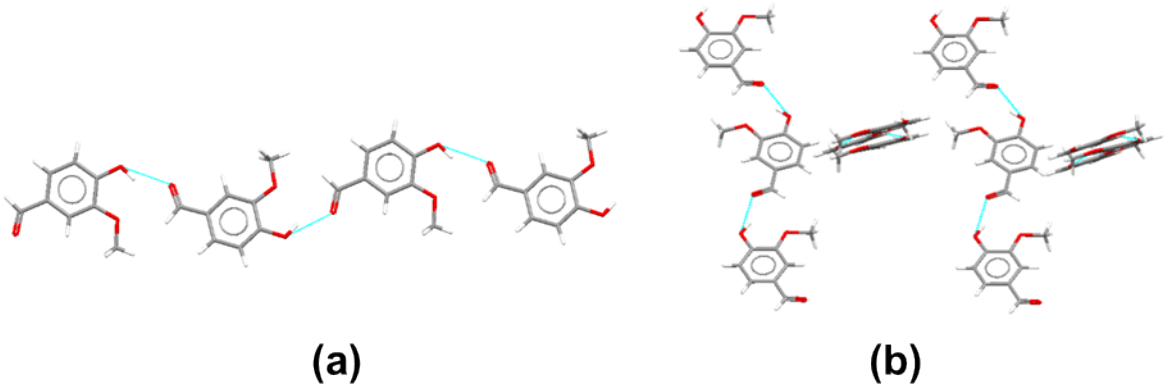


Fig. S4: DSC traces showing melting points of vanillin Forms I (red) and Form II (green).

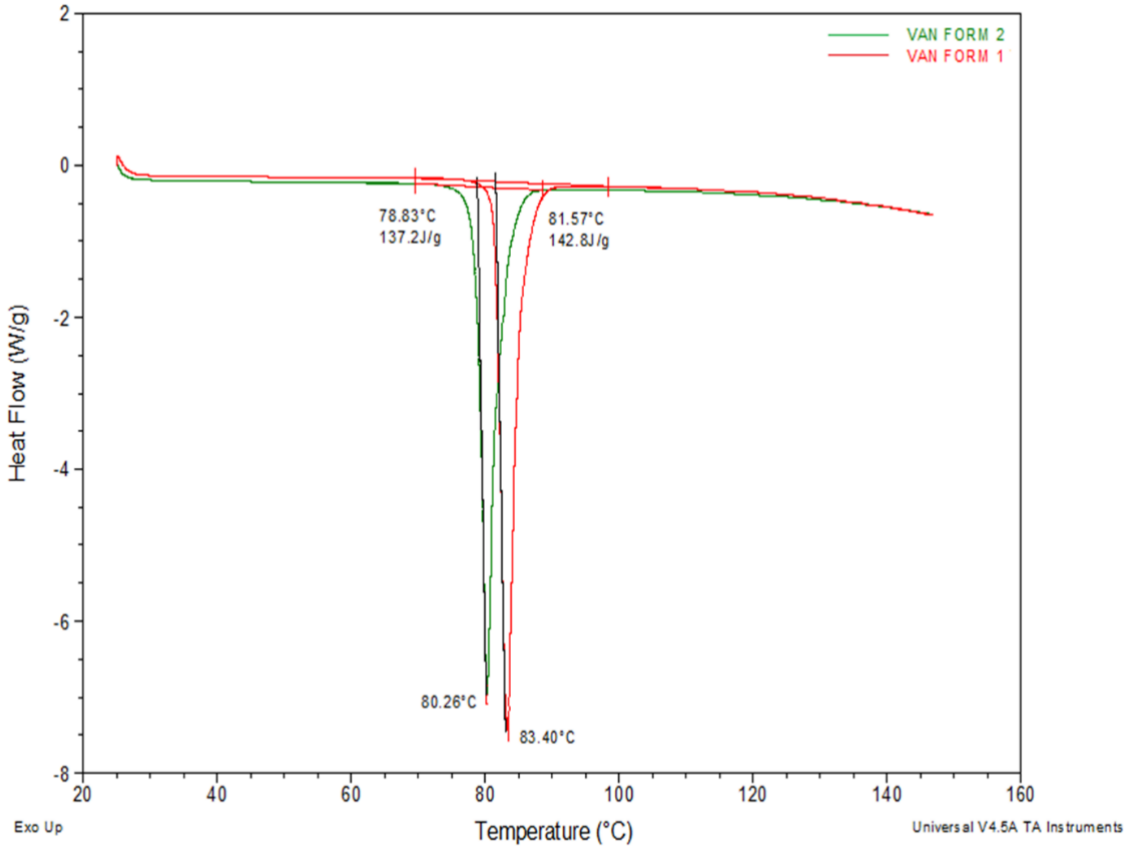


Fig. S5: PXRD patterns of vanillin crystals obtained from slow evaporation of Isopropy alcohol in presence of PAA, PMMA, and PEG.

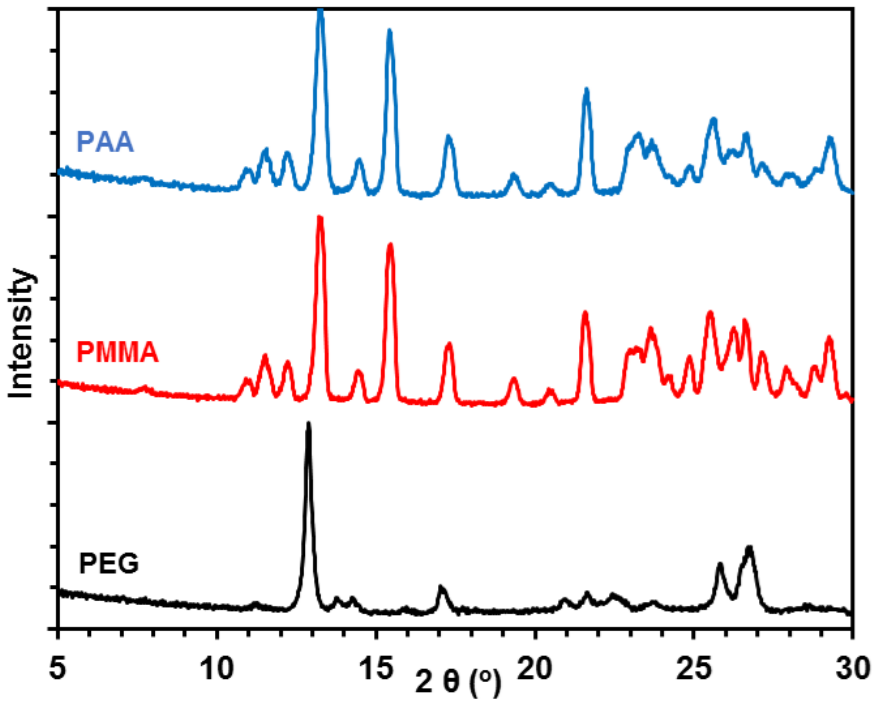


Fig. S6: SEM image of vanillin Form I crystallized in presence of PEG by slow evaporation

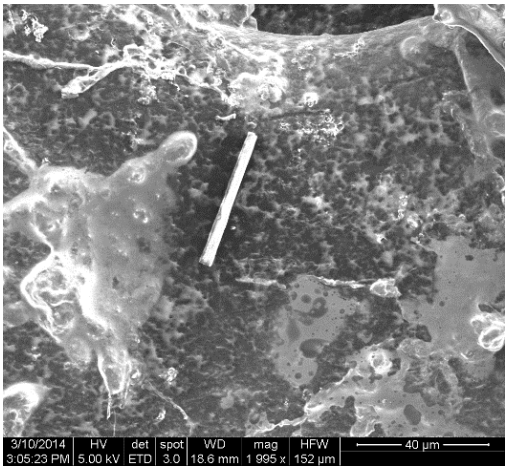
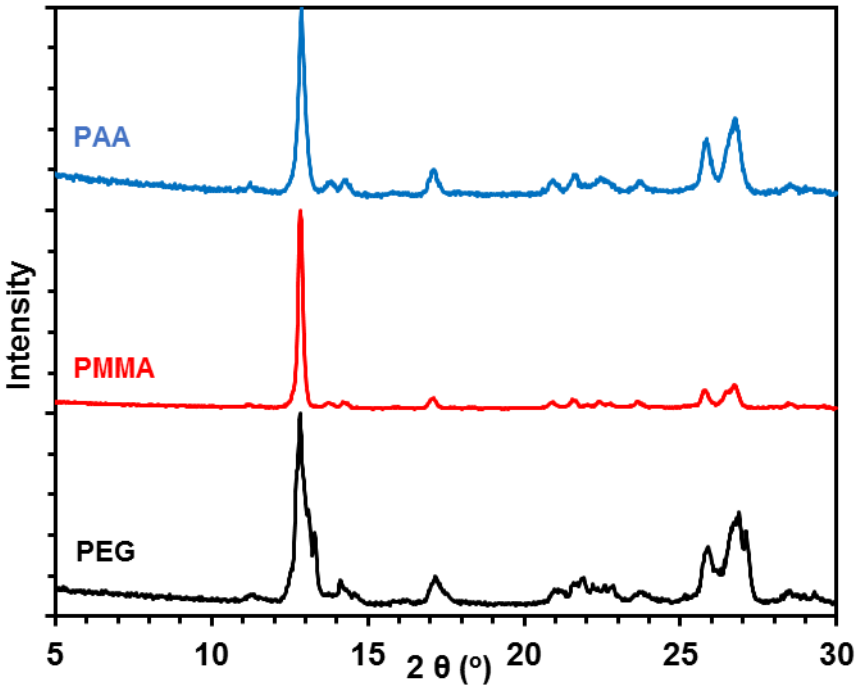


Fig. S7: PXRD patterns of vanillin crystals obtained by cooling crystallization from Isopropy alcohol in presence of PAA, PMMA, and PEG.



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