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Supporting Information

Crystalline Transformations of Dinaphthyridinylamine Derivatives with Alteration of Solid-state Emission in Response to External Stimuli

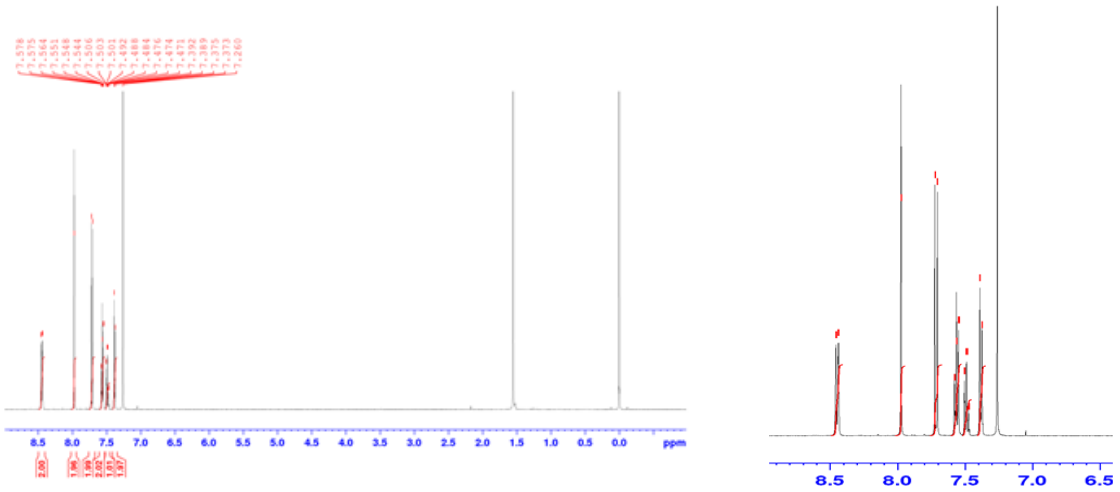
Ryusuke Hagihara,[1] Naomi Harada, [1] Satoru Karasawa*,[1, 2] and Noboru Koga*[1]

[1]. Graduate School of Pharmaceutical Sciences, Kyushu University, 3-1-1 Maidashi, Higashi-ku, Fukuoka, 812-8582 Japan

[2]. PRESTO, Japan Science and Technology Agency, Kawaguchi, 332-0012 Japan

Contents

(a)



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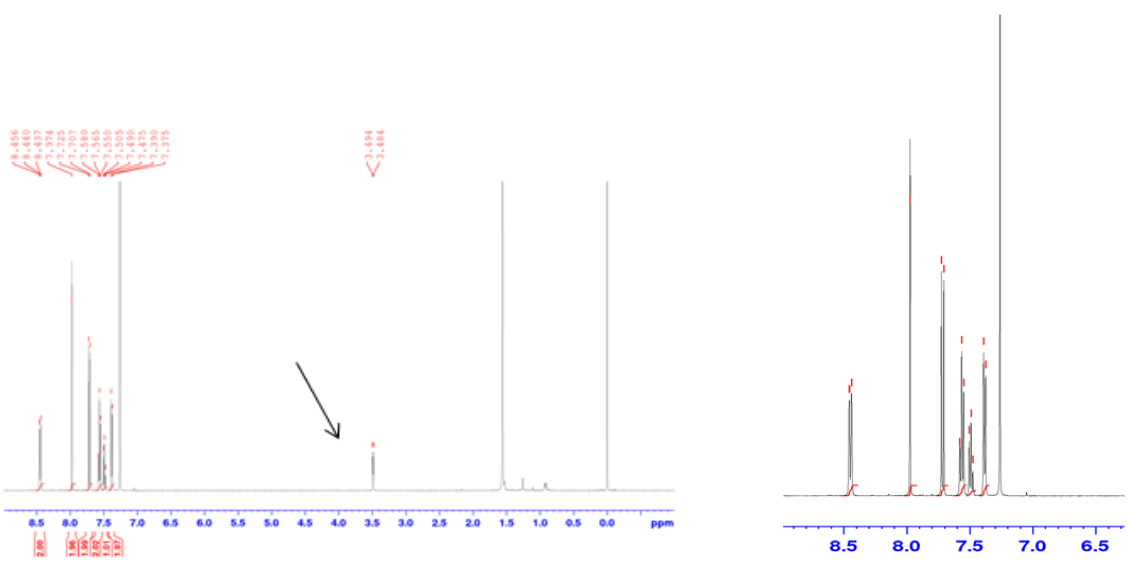
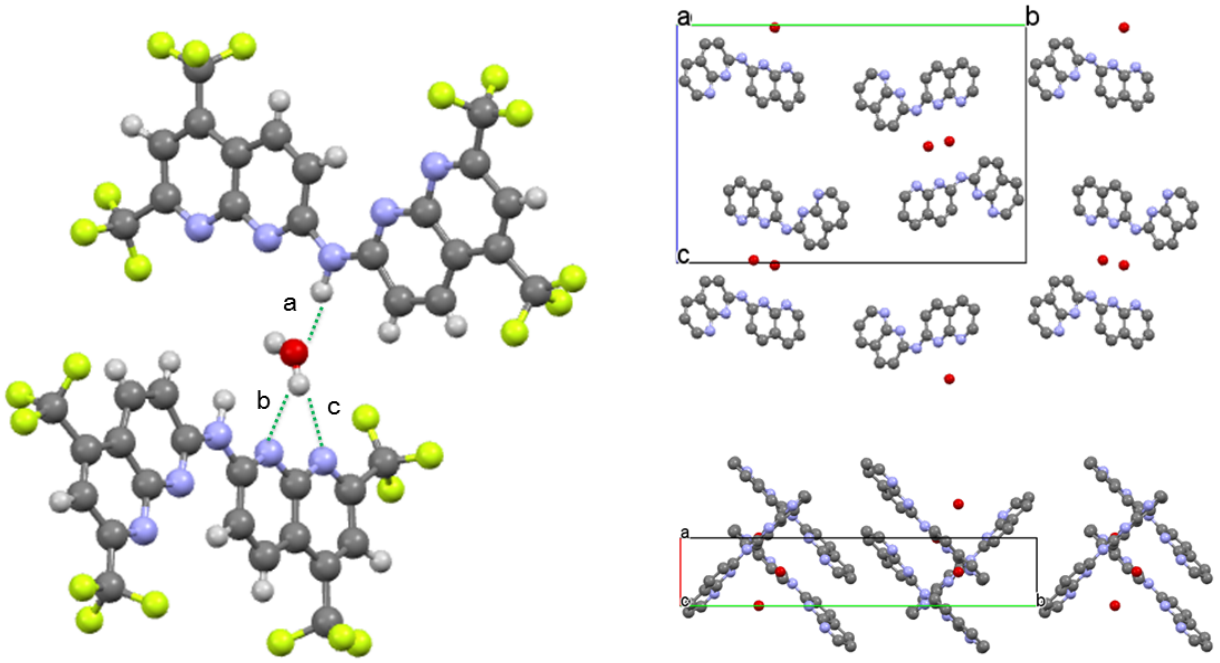


Figure S1. ^{1}H NMR spectra of the crystals for **3-α** (a) and **3-β** (b) dissolved in $CDCl_3$. Arrow in (b) indicates methyl group of MeOH molecules. Right figures are the expansion in the aromatic region.

S2.

(a) (b)



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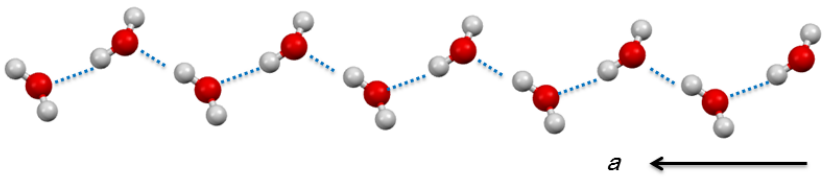
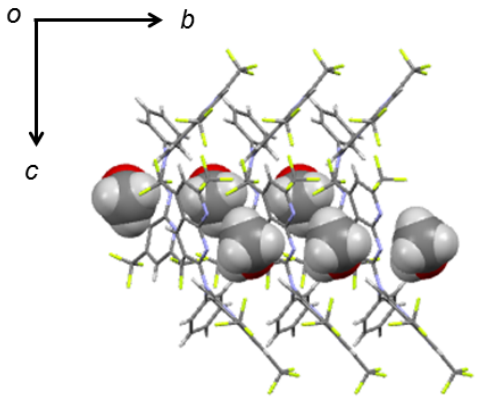


Figure S2. Molecular structures (a) and packings (b) of **1** and water molecules forming 2-fold helical structure (c). Green dotted line in (a) indicate hydrogen bonds between N atoms and a water molecule by 1.80 Å (a; $r_{H\text{-}O(H2O)}$), 2.495 Å (b; $r_{N\text{-}H(H2O)}$), and 2.135 Å (c; $r_{N\text{-}H(H2O)}$), respectively. Top and bottom in (b) represent views projecting along *a* and *c* axes, respectively and trifluoromethyl groups and H atoms are omitted for a sake of clarity. Sky blue dotted lines in (c) indicate hydrogen bonds by 2.034 Å within helical 1D structure of water molecules.

(a)



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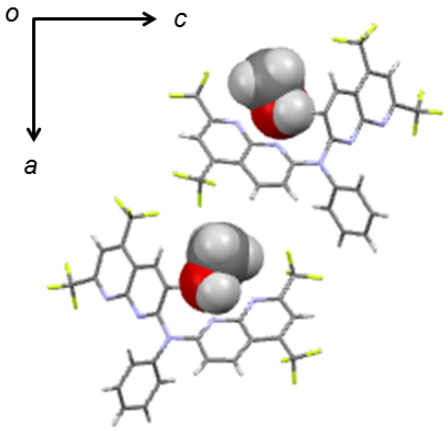

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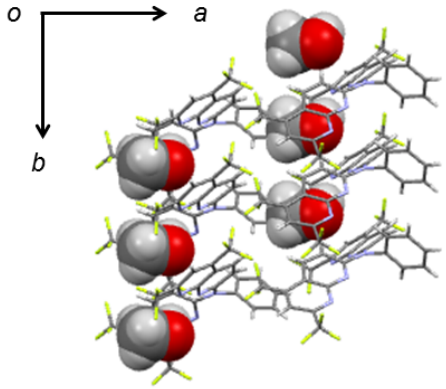


Figure S3. Molecular packing of **3-β'** projection of *a* (a), *b* (b), and *c* (c) axes, respectively. MeOH molecules are shown as space filling model.

S4.

(a) (b)

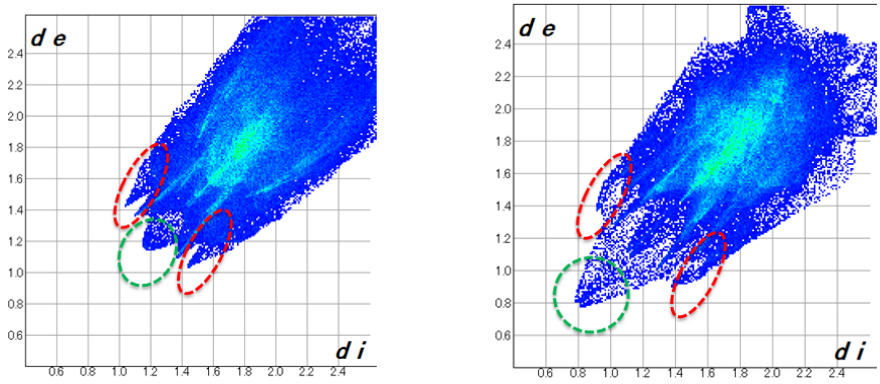
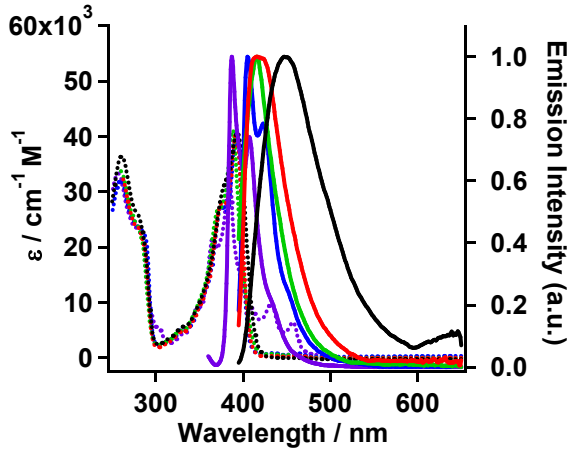


Figure S4. Fingerprint plots by Harshfeld surface calculations of **3-α** (a) and **3-β** (b). The red and green circles indicate the intermolecular short contact of CH-N and H-H, respectively.

Table S1. Photophysical properties of **1**, **2**, and **3** in various solvents.

	n-hexane	Bu_2O	$CHCl_3$	AcOEt	MeOH
			$\lambda_{max}{}^{abs}$ / nm (logε / cm^{-1} M^{-1})		
1	384 (4.53)	392 (4.61)	388 (4.61)	392 (4.61)	393 (4.61)
2	396 (4.46)	398 (4.46)	399 (4.46)	396 (4.46)	395 (4.46)
3	390 (4.43)	390 (4.40)	393 (4.40)	391 (4.40)	392 (4.41)
			$\lambda_{max}{}^{f}$ / nm (ϕ)		
1	387 (0.09)	405 (0.26)	416 (0.21)	416 (0.38)	447 (0.09)
2	414 (0.08)	427 (0.12)	428 (0.25)	446 (0.17)	440 (0.01)
3	510 (0.25)	545 (0.08)	558 (0.04)	- (0.01 >)	- (0.01 >)
			$\Delta^{f\text{-}ab}$ / nm (cm^{-1})		
1	3 (3.3 x 10^6)	13 (7.7 x 10^5)	28 (3.6 x 10^5)	24 (4.2 x 10^5)	54 (1.9 x 10^5)
2	18 (5.6 x 10^5)	29 (3.4 x 10^5)	29 (3.4 x 10^5)	50 (2.0 x 10^5)	45 (2.2 x 10^5)
3	120 (8.3 x 10^4)	155 (6.5 x 10^4)	165 (6.1 x 10^4)	-	-

(a)



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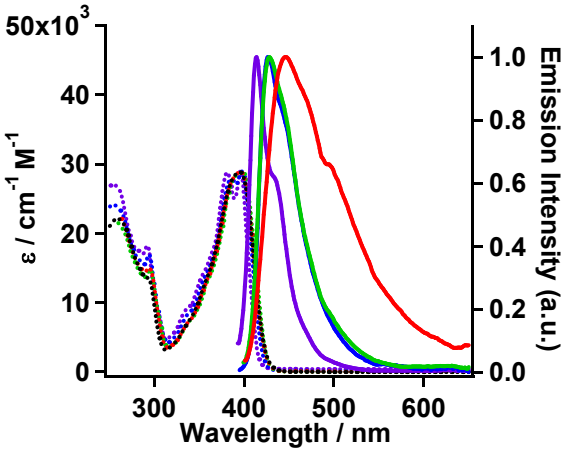


(c)

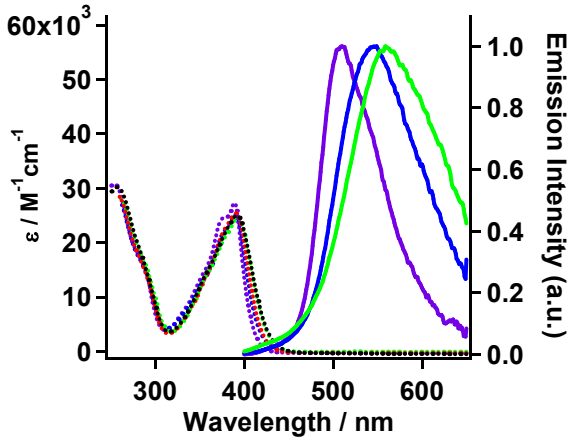


Figure S5. Absorption (dotted line) and emission (solid line) spectra of **1** (a), **2** (b), and **3** (c) in *n*-hexane (violet), Bu_2O (blue), $CHCl_3$ (green), AcOEt (black), and MeOH (red), respectively.

S7. (a) (b)

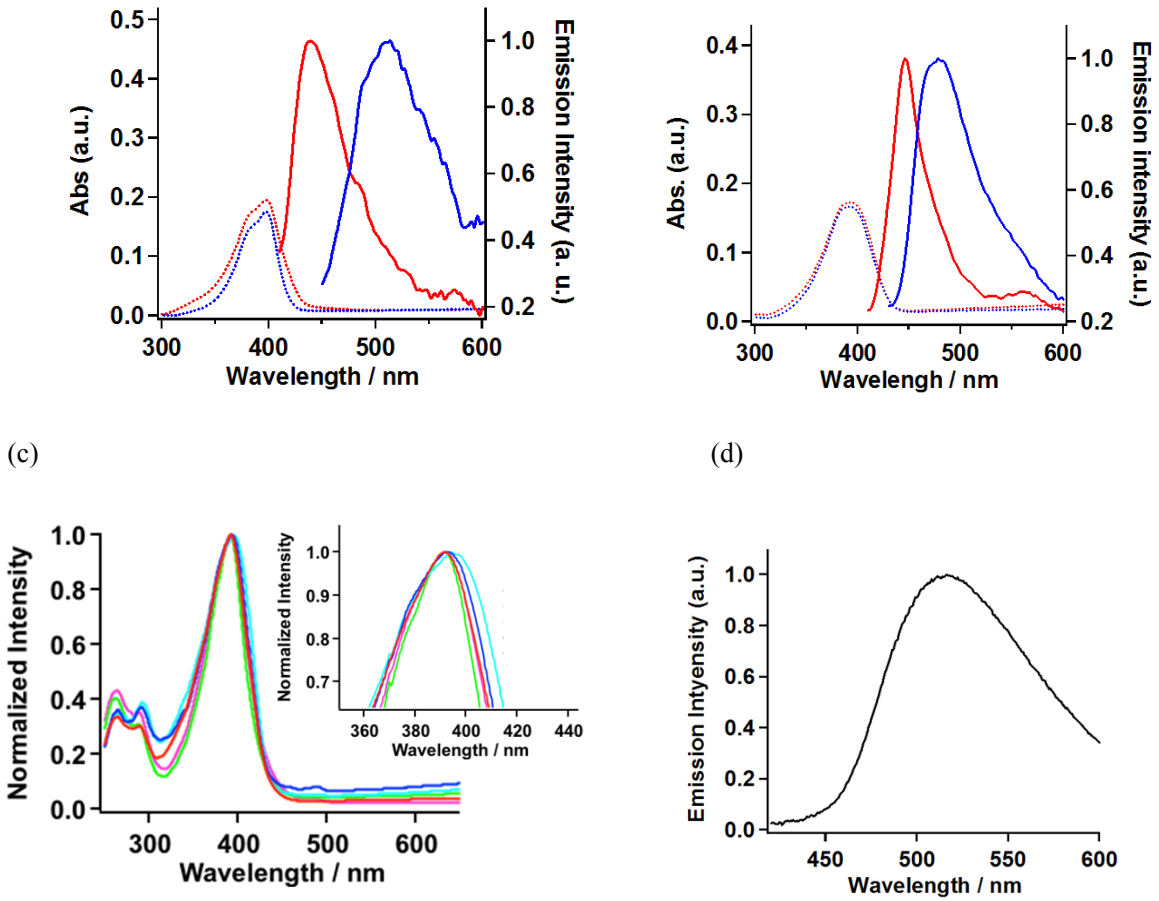


Figure S6. Absorption (dotted lines) and emission (solid lines) spectra of **1** (a) and **2** (b) in crystalline (red) and ground powder sample (blue). (c) Absorption spectra of **3** in **3-α** (light blue), **3-β** (red), **3-β'** (blue), glass (purple), and ground powder sample (green). Emission spectra of the glass sample for **3** (d).

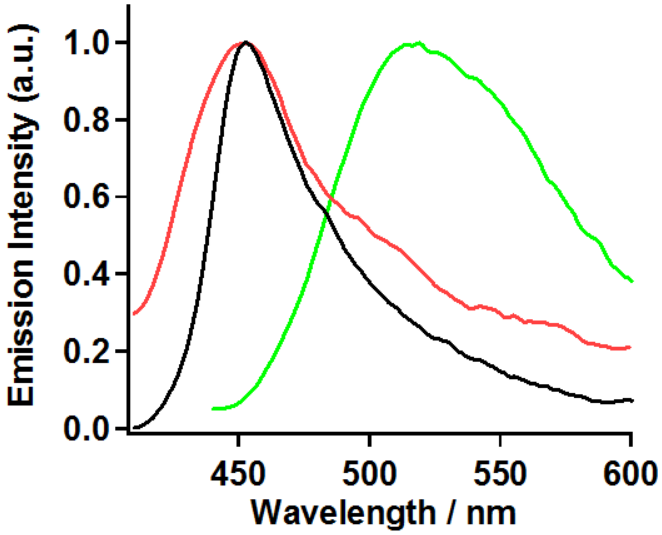


Figure S7a. Emission spectra of **3-α** (black), the ground powder of **3- α** (light green), and the ground powder left under MeOH vapor for 2 day (red).

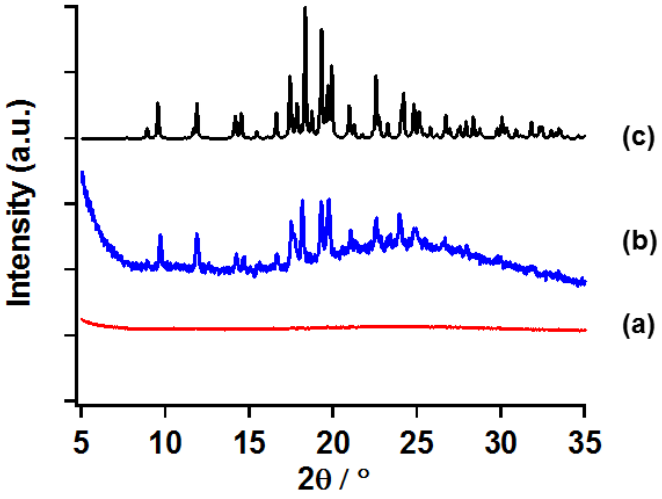


Figure S7b. Alteration of XRD patterns of the ground sample (red) of **3-α**, subsequently exposed to MeOH vapor for 5 day (blue), and the simulation pattern (black) of **3-α** obtained by SXRD.

(a) (b)

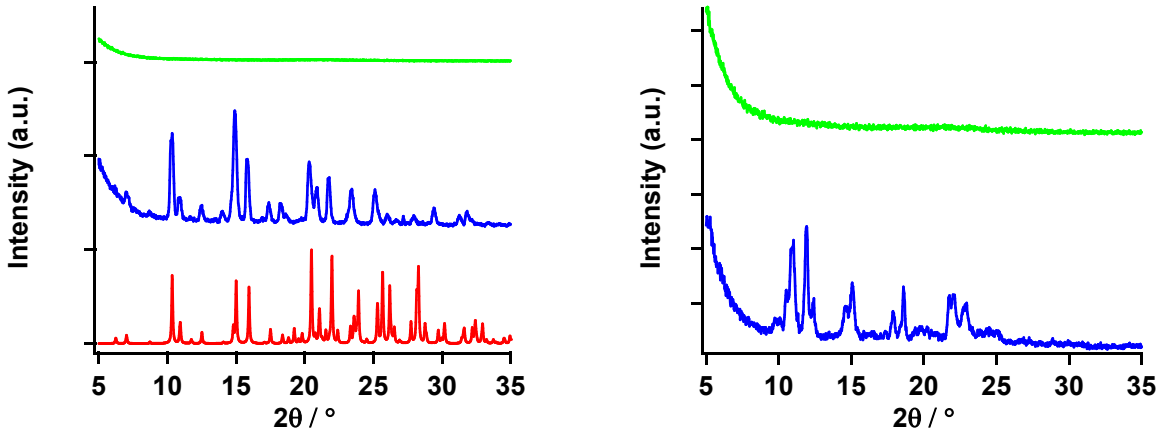


Figure S8. XRD patterns of the crystal (blue) and its ground samples (light green) for **1** (a) and **2**(b) with the simulation pattern (red).

S10.

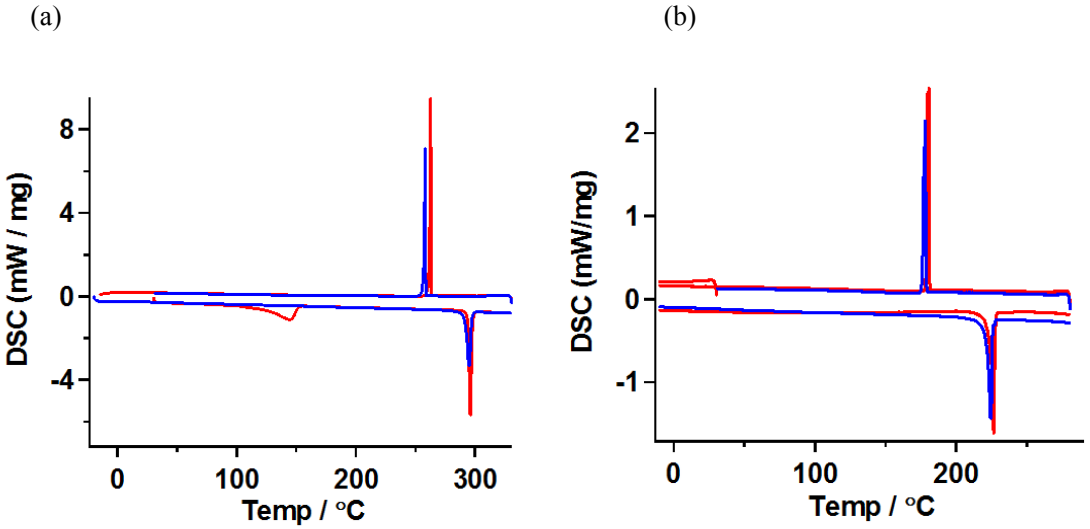


Figure S9. DSC profiles in the first (red line) and second (blue line) cycle of **1** (a) and **2**(b).

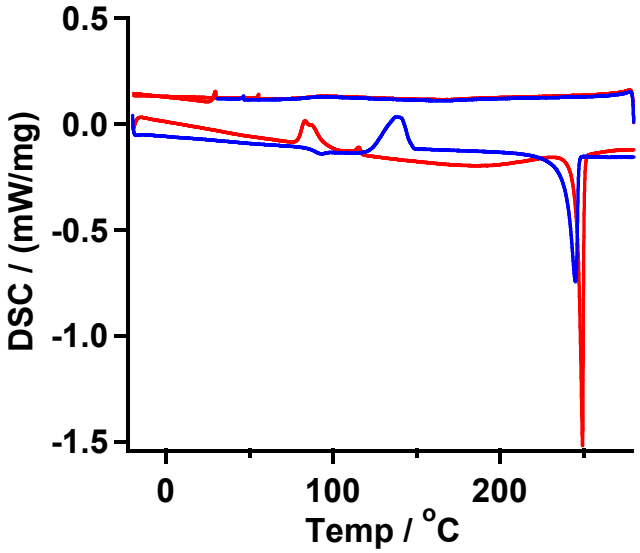


Figure S10. DSC profile of the powder sample obtained from **3-β'** by grinding in first (red) and second (blue) cycle.

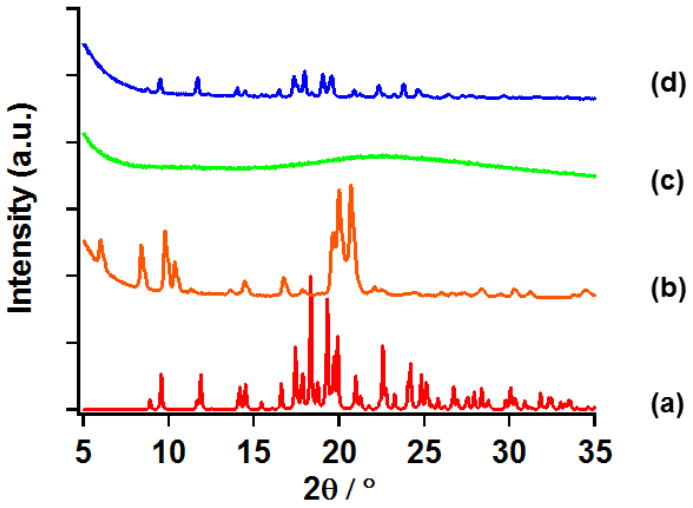
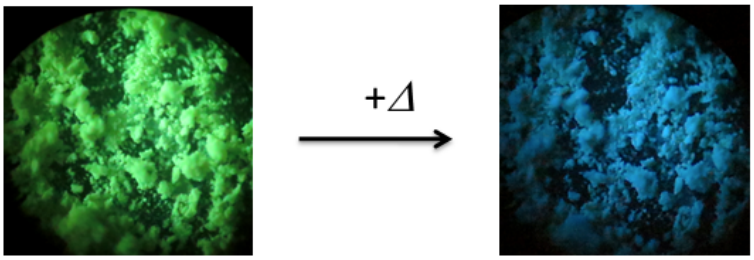


Figure S11. XRD pattern of **3-β'** (b), the powder obtained from **3-β'** by grinding (c), and the resulting powder by heating at 100 °C together with the simulation obtained from the result of **3-α** by SXRD (a).

S13.

(a)



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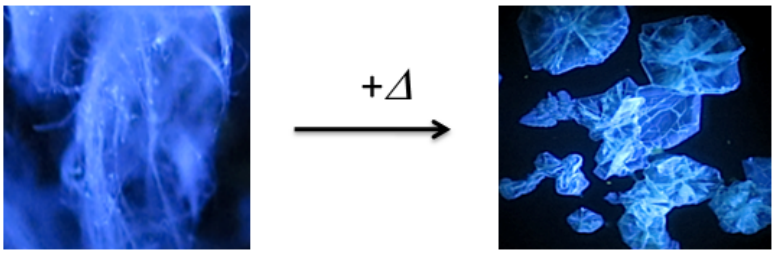

Figure S12. Photographs taken under irradiation at 365 nm for thermal transformation (a) from powders (amorphous) (left) to **3-α** (right) and (b) from **3-β'** (left) to **3-α** (right).

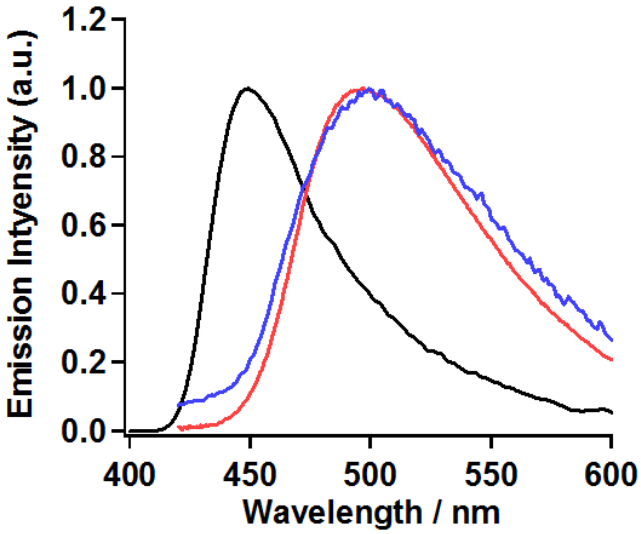

Figure S13. Emission spectra of **3-β** (red), **3- β'** (black), and **3- β'** left under MeOH vapor for 1 day (blue)