Electronic Supplementary Information for:

Tuning of fluorescence efficiency via local modification of the crystal structure by benzyl groups in polymorphism of a pyrazine dye

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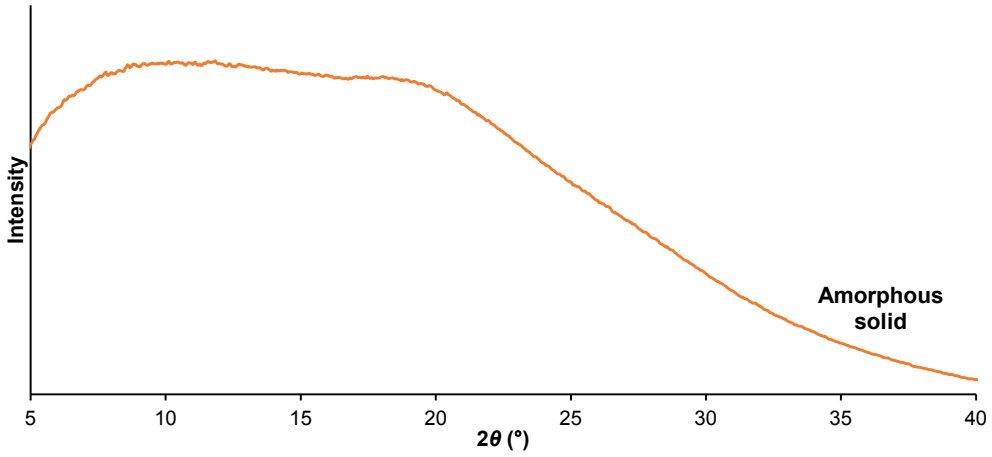

Figure S1. XRD patterns of an amorphous solid of **1**, for which no diffraction peak was observed.

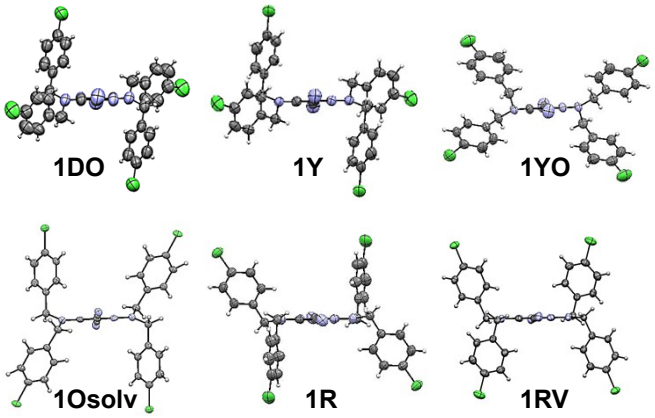

Figure S2. Molecular conformations of the six crystal forms of **1**.

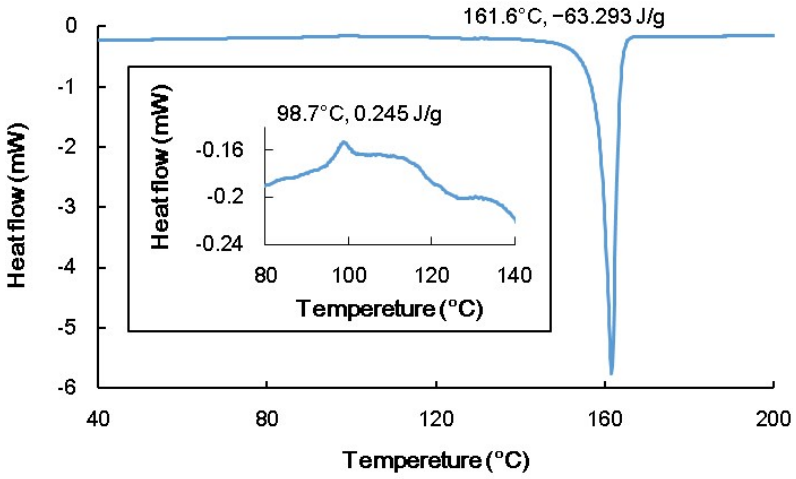

Figure S3. DSC curves of **1DO**. After the exothermic peak at 98.7 °C, the melting point was found at 161.6 °C. The melting point was consistent with that of **1Y**;[1] therefore, **1DO** presumably transformed into **1Y** upon heating. The broad endothermic peak around 120 °C probably resulted from the distribution of the baseline due to sample heterogeneity.

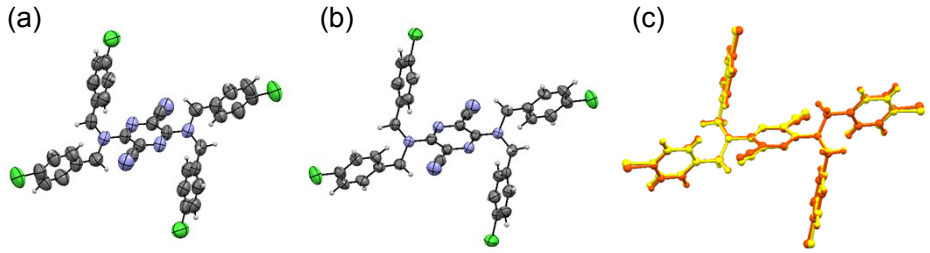

Figure S4. Molecular conformation of (a) **1DO** and (b) **1Y**. ORTEP diagrams were drawn with 50% ellipsoid probability by Mercury 3.8. (c) Overlap of the conformations of **1DO** (solid orange line) and **1Y** (solid yellow line) using the Molecule Overlay module of Mercury 3.8.

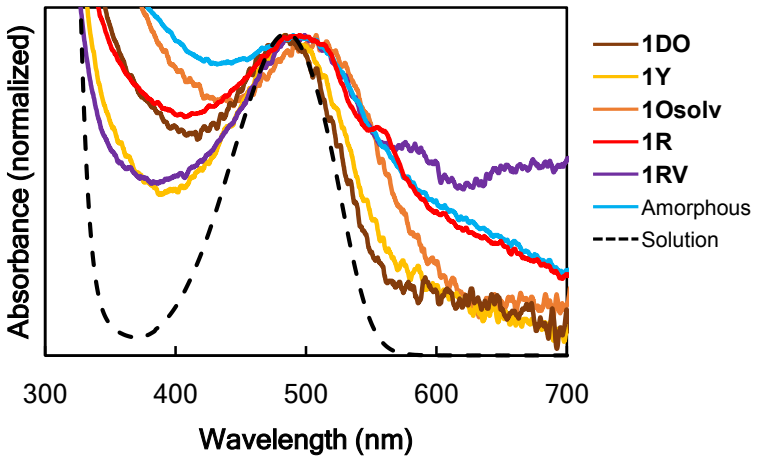

Figure S5. Absorption spectra of **1DO** (λ_{max} = 484 nm), **1Y** (λ_{max} = 484 nm),[2] **1Osolv** (λ_{max} = 508 nm)[2], **1R** (λ_{max} = 554 nm), **1RV** (λ_{max} = 593 nm), an amorphous solid of **1** (λ_{max} = 490 nm), and a chloroform solution of **1** (λ_{max} = 485 nm).[2]

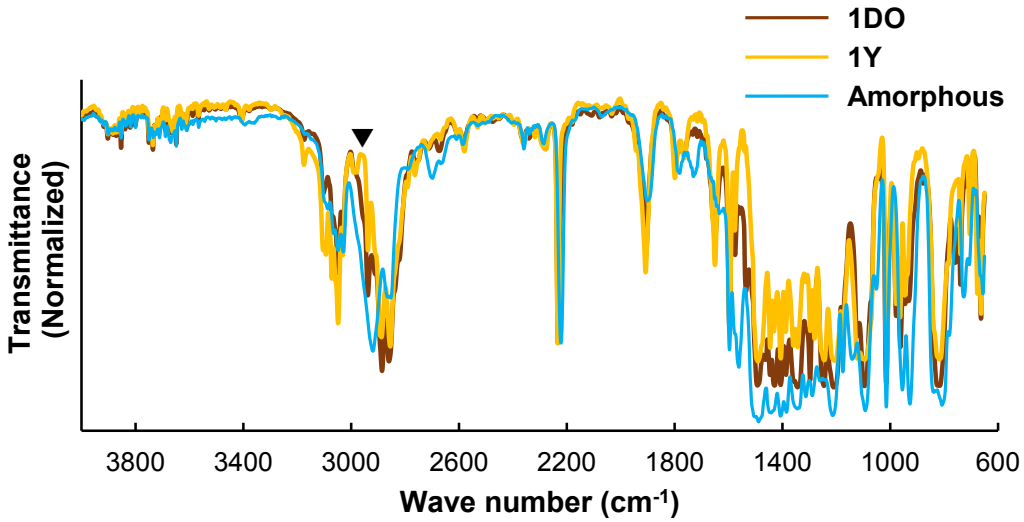

Figure S6. FTIR spectra of **1DO**, **1Y**, and the amorphous solid. The black triangle represents the difference between **1DO** and **1Y** at 2953 cm^{-1}.

Table S1. Conformational similarities of the six crystal forms of **1**. The similarity was determined by RMSD, which is the root mean square deviation of distance between two molecular structure, calculated using the Molecule Overlay module of Mercury 3.8. The values of the RMSD among **1Y**, **1YO**, and **1R** were the previously values.[1] When the RMSD value between two conformations was less than 1 Å, the conformations are considered to be similar, i.e. conformational adjustment.[3]

RSMD/Å	1Y	1YO	1Osolv	1R	1RV
1DO	0.135	1.518	1.358	1.397	1.524
1Y	-	1.485[1]	1.424	1.415[1]	1.556
1YO	-	-	1.652	1.414[1]	1.303
1Osolv	-	-	-	1.048	0.967
1R	-	-	-	-	0.562

Table S2. Intermolecular interactions based on short contacts in the crystal structures of **1DO** and **1Y**.

	Interaction	Distance (d/D)[a]	θ[b]	Symmetry operation
1DO	$C–H_{Ph3}\cdots N_{CN}$	2.381/3.324(9)	144.0	2.5−x, ±1/2+y, 1.5−z
	$C–H_{CH2}\cdots Cl$	2.943/3.915(6)	148.7	1.5−x, ±1/2+y, 1.5−z,
	$C–H_{Ph3}\cdots Cl$	2.888/3.801(7)	141.5	1.5−x, ±1/2+y, 1.5−z,
	$C–H_{Ph2}\cdots \pi_{ph}$	2.857/3.665	131.0	1.5−x, ±1/2+y, 1.5−z,
1Y [1]	$C–H_{Ph3}\cdots N_{CN}$	2.478/3.419(3)	143.9	x, 1−y, ±1/2+z
	$C–H_{CH2}\cdots Cl$	2.8791/3.921(3)	160.2	−x, −y, 1−z

[a] d represents the H···A distance (Å), and D represents the X···A distance (Å). H is the hydrogen atom, X is the donor atom, and A is the acceptor atom in a hydrogen bond.

[b] θ represents the X–H···A angle (°).

H_{Phn} is a hydrogen atom in the phenyl ring of the dye molecule and n is its position in the ring. For example, H_{Ph4} represents the hydrogen in the 4-position of the phenyl ring. H_{CH2} is a hydrogen atom of the methylene group, N_{CN} is the nitrogen atom of a cyano group, and π_{ph} represents the center of the phenyl ring.

References

[1] Y. Akune, H. Gontani, R. Hirosawa, A. Koseki and S. Matsumoto, *CrystEngComm*, 2015, **17**, 5789-5800.

[2] Y. Akune, R. Hirosawa, H. Takahashi, M. Shiro and S. Matsumoto, *RSC Adv*., 2016, **6**, 74506-74509.

[3] A. J. Cruz-Cabeza and J. Bernstein, *Chem*. *Rev*., 2014, **114**, 2170–2191.