

Electronic Supplementary Information for:

**Role of flexible bulky groups and weak interactions involving halogens in the vapoluminescence of a metal-free dye**

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## Experimental

### 1. General

All solvents were purchased from commercial sources and were used without further purification. The synthesis of **1** is described in our previous study [1]. Thermogravimetric analysis (TGA) of **1O** was carried out using a Rigaku Thermo plus TG8120 instrument at a heating rate of 10 K/min. Differential thermal analysis (DTA) was performed simultaneously with TGA measurements.

### 2. X-Ray analysis

A crystal of **1O** having X-ray diffraction quality was obtained by slowly evaporating a solution of **1** in benzene. The diffraction data for **1O** were collected at 93 K on a Rigaku R-AXIS Rapid diffractometer using graphite-monochromated Cu- $K\alpha$  radiation ( $\lambda = 1.54187 \text{ \AA}$ ). The absorption correction for **1O** was performed by multi-scan using RAPID-AUTO [2]. The structures of **1O** were solved and refined using SHELXS [3] and SHELXL [4], respectively. All non-hydrogen atoms were anisotropically refined by a full-matrix least-squares refinement based on  $F^2$ . Hydrogen atoms were located at the calculated positions and refined using the riding model. The publication materials were generated by CrystalStructure 4.2 [5] and Mercury 3.8 [6].

Powder X-ray diffraction was performed using the same equipment as for the single crystal X-ray diffraction at room temperature. The measurement was conducted in a  $2\theta$  range from  $5^\circ$  to  $40^\circ$ .

### 3. Optical measurements

Absorption and emission spectra of **1** in  $\text{CHCl}_3$  were recorded on a Lambda 20 spectrometer (Perkin Elmer) and an LS-45 fluorometer (Perkin Elmer), respectively.

The absorption spectra of **1O** and **1Y** were corrected using a SIS-50 surface and interface spectrometer based on optical waveguide spectroscopy (System Instruments). The fluorescence spectra of **1O** and **1Y** were recorded on a FP-8500 fluorometer (JASCO), and the quantum yield was determined using an integrating sphere unit.

### 4. Vapoluminescence

The powder of **1Y** was placed on a filter paper and exposed to the vapours of several solvents at room temperature. The vapour exposure was performed in a sealed bottle containing a small amount of solvent. The paper was not in contact with the solvent, and the experiment was carried out for three days.

### 5. Calculation of absorption spectra and exciton interactions

The UV-vis spectra of **1O** and **1Y** were calculated by TD-DFT (Gaussian 09 [7]) using the B3LYP functional [8] and a 6-31G(d) basis set for all atoms with the exception of chlorine, where LanL2DZ

[9] was used. The positions of non-hydrogen atoms were based on the atomic coordinates obtained by X-ray analysis, and the positions of hydrogen atoms were normalized.

Exciton interaction was evaluated using the expanded dipole model [10]:

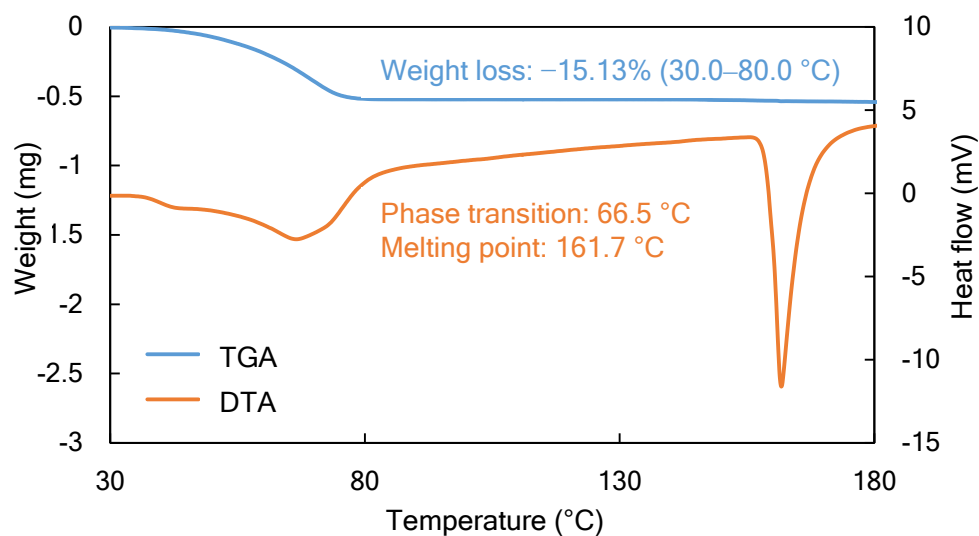
$$\Delta E_{exciton} = \frac{\mu^2}{4\pi\epsilon_0\epsilon l^2} \left( \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{r_3} - \frac{1}{r_4} \right)$$

where  $\mu$  is the transition dipole moment and  $l$  is the dipole length. These two values were calculated using the results of TD-DFT. The dielectric constant of the medium,  $\epsilon$ , was set to 2.5 [11]. The distance between the charges ( $r_i$ , for details see Fig. 7 in [11]) was estimated by applying the calculated dipole moment to the molecules in the crystal structure, with 14 molecules in the vicinity of the reference molecule examined.

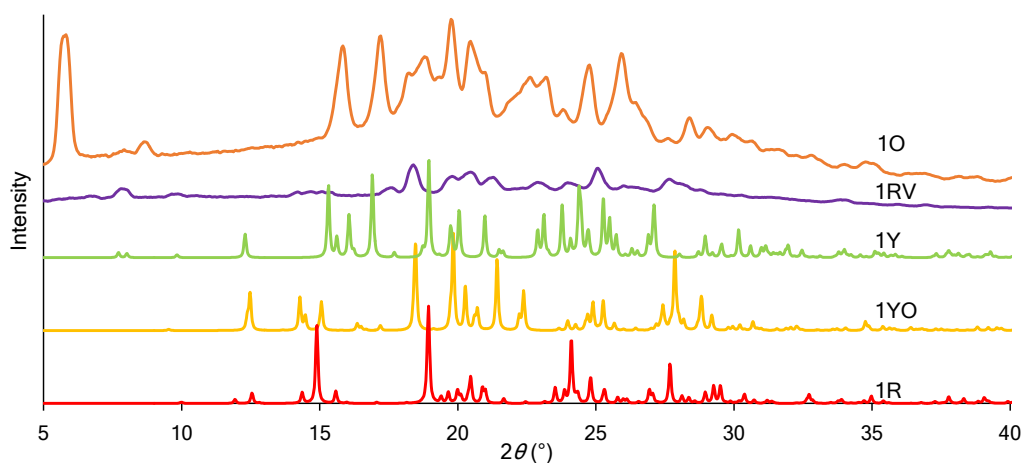
## 6. Calculation of conformational energy and lattice energy

Conformational energy was calculated by density functional theory using Gaussian 09 at the B3LYP/6-31G\* level of theory. Single-point energy calculation was carried out using the atomic coordinates obtained by X-ray analysis. The hydrogen atom positions were normalised in all calculations.

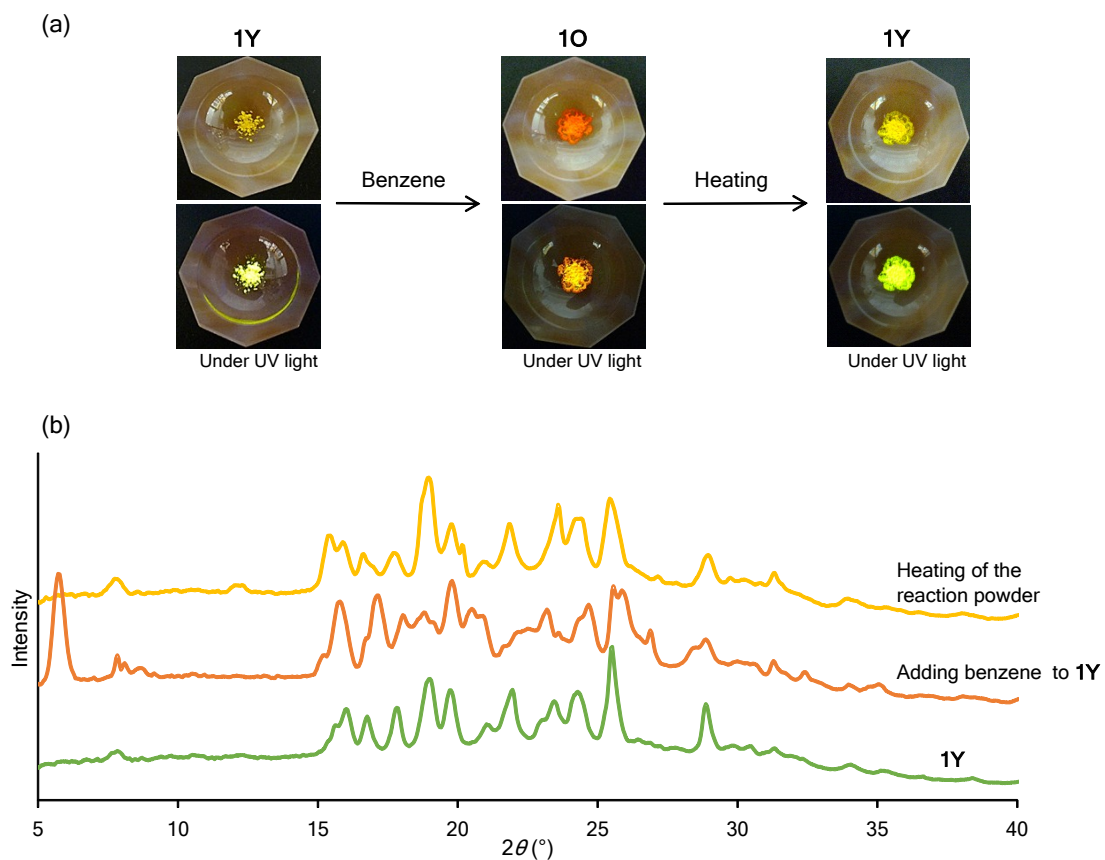
The lattice energy and the energy of the molecular pairs in the crystal structure were calculated using the atom-atom Coulomb-London-Pauli (AA-CLP) model, a computer program package for the empirical calculation of intermolecular interactions and crystal energy developed by Gavezzotti [12]. The AA-CLP calculation was performed using the atomic coordinates in the crystal structure. The proportion of the Coulombic term of an intermolecular interactions was estimated using the calculated results of the AA-CLP calculation.



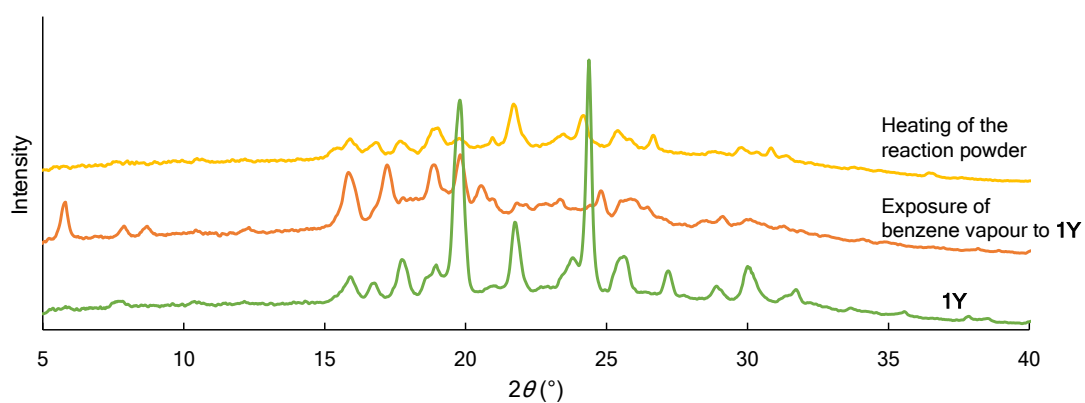
**Figure S1.** TGA-DTA curves of **10**.



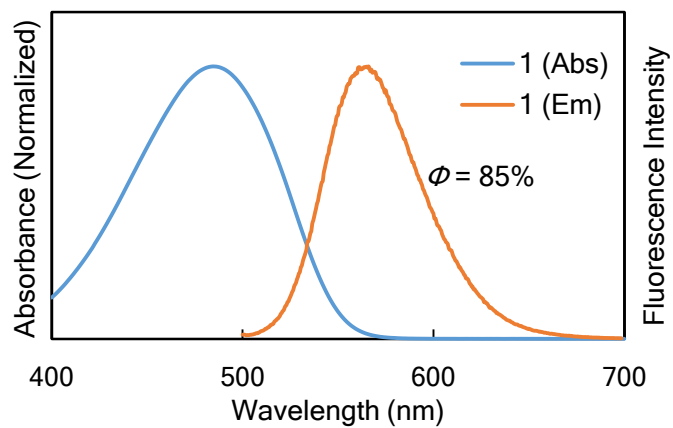
**Figure S2.** XRD patterns of the five crystal forms of **1**. The crystal structures of three forms, **1Y**, **1YO**, and **1R** were solved by single-crystal X-ray analysis, and thus those patterns were simulated using the atomic coordinates obtained by X-ray analysis. The powder of **1O** was obtained by slow evaporation of its solution in benzene. **1RV** was characterized using powder X-ray diffraction pattern because the crystal of X-ray diffraction quality of **1RV** could not be obtained despite an effort of many crystallizations. The powder of **1RV** was obtained using a combination of  $\text{CHCl}_3$  and *n*-hexane solvents.



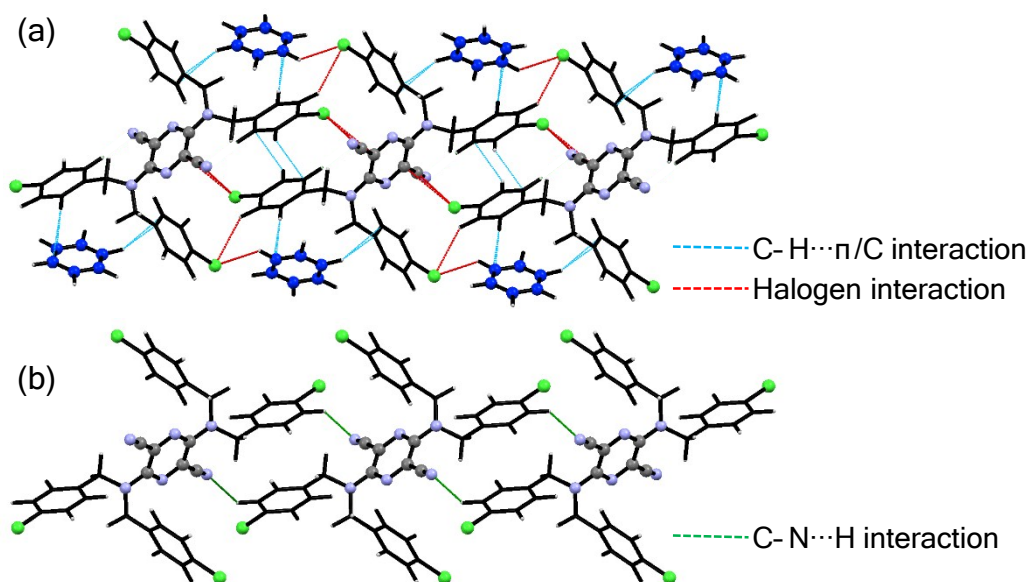
**Figure S3.** (a) Result of benzene addition to the powder of **1Y** and subsequent heating. (b) Changes in the XRD pattern of the powder during the reversible reaction.



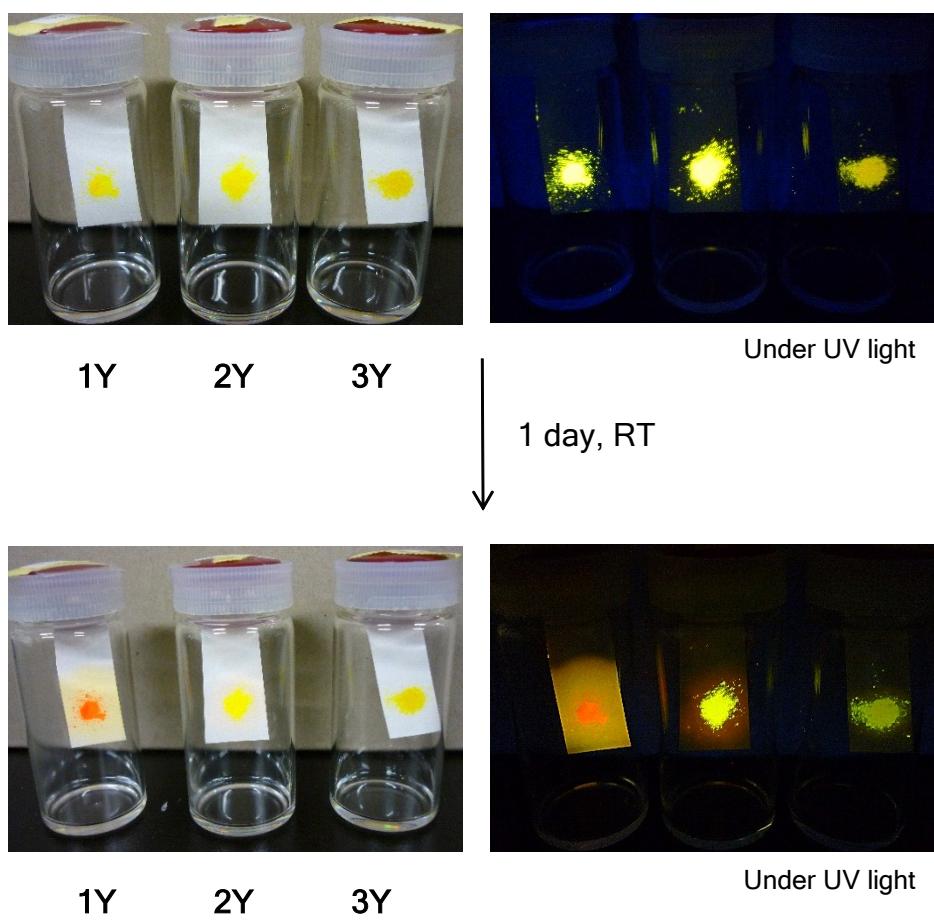
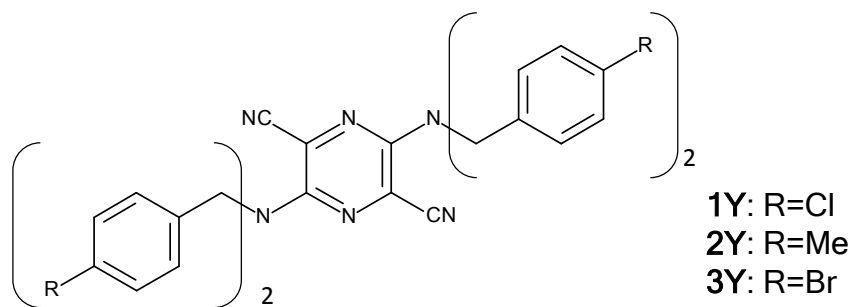
**Figure S4.** Changes in the XRD pattern during the exposure of **1Y** to benzene vapour and subsequent heating of the powder.



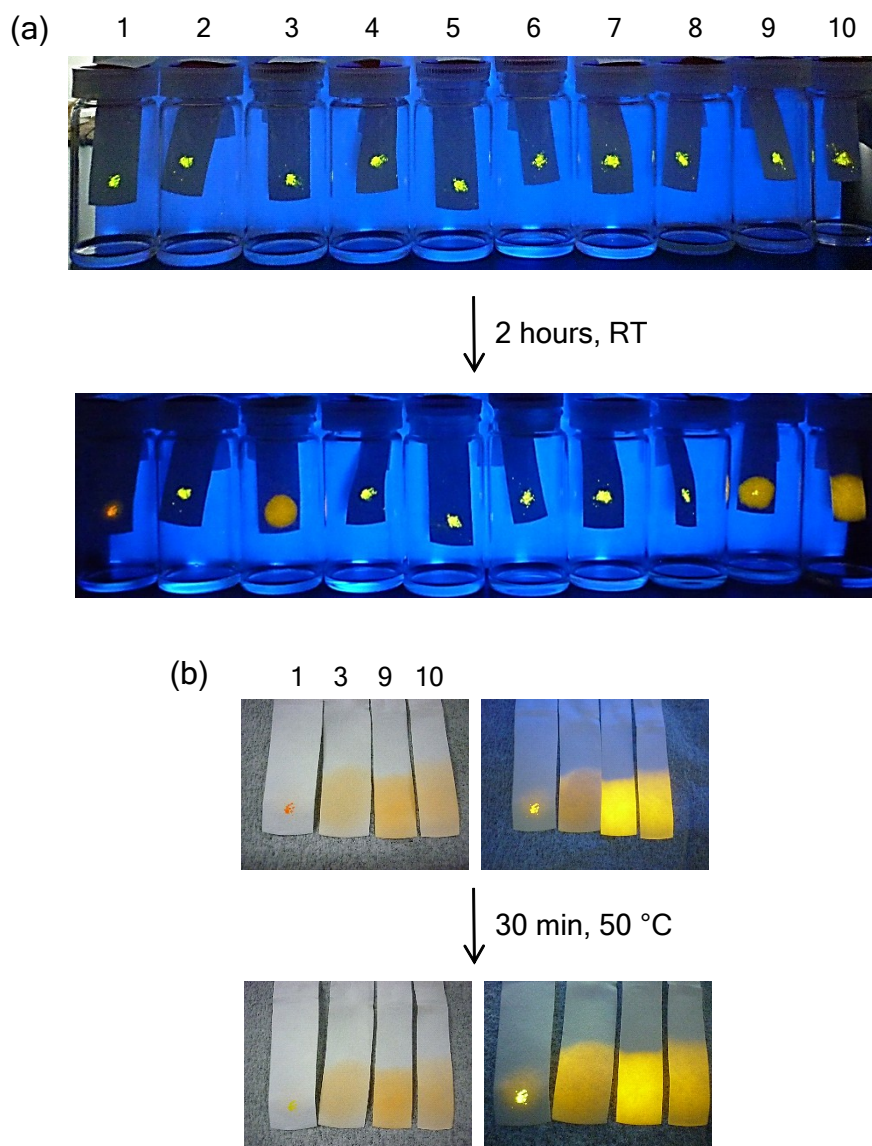
**Figure S5.** Absorption and emission spectra of **1** in  $\text{CHCl}_3$ .



**Figure S6.** Arrangement between 1-D chromophore stacking columns in the crystal structure of (a) **1O** and (b) **1Y**.



**Figure S7.** The result of exposure to benzene vapour for **1Y**, **2Y**, and **3Y**.



**Figure S8.** (a) The result of exposing **1Y** to vapours of different solvents (1: benzene, 2: toluene, 3: pyridine, 4: *o*-xylene, 5: *m*-xylene, 6: *p*-xylene, 7: chlorobenzene, 8: nitrobenzene, 9: cyclohexane, 10: chloroform). (b) The result of heating the samples exhibiting a colour change upon vapour exposure at 50 °C. The colour of sample **1**, resulting from benzene vapour exposure, changed, whereas no colour change was observed for samples **3**, **9**, and **10**.



**Table S1.** Crystallographic data for **1O** and **1Y**.

Crystal forms	<b>1O</b>	<b>1Y</b> <sup>[1]</sup>
Formula	C <sub>34</sub> H <sub>24</sub> N <sub>6</sub> Cl <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	C <sub>34</sub> H <sub>24</sub> N <sub>6</sub> Cl <sub>4</sub>
Formula weight	814.64	658.42
Space group	<i>P2<sub>1</sub>/n</i>	<i>C2/c</i>
<i>T</i> (K)	93	296
<i>a</i> (Å)	15.9806 (19)	23.485(5)
<i>b</i> (Å)	5.8569(7)	5.974(1)
<i>c</i> (Å)	22.172(3)	22.593(7)
<i>α</i> (°)	90	90
<i>β</i> (°)	109.263(8)	102.69(1)
<i>γ</i> (°)	90	90
<i>Z</i>	2	4
<i>V</i> (Å <sup>3</sup> )	1959.0(4)	3092.3(1)
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.381	1.414
<i>F</i> (000)	844	1352
<i>μ</i> (mm <sup>-1</sup> )	3.079	3.760
No. of reflns collection	3490	13712
No. of unique reflns /parameters	3490/253	2618/211
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub>	0.0535/0.1500	0.0470/0.0620
GOF	1.019	1.279

**Table S2.** Assignments of the absorption spectra of **1O** and **1Y** calculated by TD-DFT.

	<b>1O</b>	<b>1Y</b>
1 <sup>st</sup> transition	516.54 nm (2.4003 eV)	454.17 nm (2.7299 eV)
Oscillator strength	0.0383	0.0411
Configuration interaction	HOMO to LUMO: 98.5%	HOMO to LUMO: 97.2%
2 <sup>nd</sup> transition	389.01 nm (3.1872 eV)	396.27 nm (3.1288 eV)
Oscillator strength	0.0136	0.023
Configuration interaction	HOMO-2 to LUMO: 99.5%	HOMO-1 to LUMO: 92.5%

**Table S3.** Intermolecular interactions between 1-D chromophore stacking columns (shown in Fig. S6) based on short contacts in the crystal structures of **1O** and **1Y**.

	Interaction	Distance ( $d/D$ ) <sup>a</sup>	$\theta$ <sup>b</sup>	Symmetry operation
<b>1O</b>	Dye···Dye interaction			
	C–H <sub>Ph3</sub> ···Cl	2.934/3.820(4)	138.6	1/2–x, ±1.5+y, 1/2–z, 1.5–x, ±1.5+y, 1.5–z,
	C–Cl···C <sub>py</sub>	-/3.435(3)	114.5(1)	1/2–x, ±1.5+y, 1/2–z, 1.5–x, ±1.5+y, 1.5–z,
	C–Cl···C <sub>CN</sub>	-/3.305(3)	92.5(1)	1/2–x, ±1.5+y, 1/2–z, 1.5–x, ±1.5+y, 1.5–z,
	C–H <sub>Ph3</sub> ···C <sub>Ph2</sub>	2.788/3.615(5)	132.6	1/2–x, ±1.5+y, 1/2–z, 1.5–x, ±1.5+y, 1.5–z,
	C–H <sub>Ph2</sub> ···N <sub>CN</sub>	2.386/3.445(5)	163.7	x, ±1+y, z
	N–C <sub>CN</sub> ···C <sub>CN</sub> –N	-/3.397(4)	93.5(2)/ 93.5(2)	x, ±1+y, z
	C–H <sub>CH2</sub> ···C <sub>Ph3</sub>	2.883/3.849(5)	147.8	x, ±1+y, z
	Dye···Benzene interaction			
	C–H <sub>Ph2</sub> ···C <sub>Bz</sub>	2.743/3.758(6)	154.9	x, y, z, x, -1+y, z
C–H <sub>CH2</sub> ···C <sub>Bz</sub>	2.874/3.741(6)	136.6	x, y, z, x, -1+y, z	
C–H <sub>Bz</sub> ···Cl	2.774/3.710(4)	144.0	1/2–x, 1/2+y, 1/2–z, 1.5–x, -1.5+y, 1.5–z,	
<b>1Y</b>	C–H <sub>Ph3</sub> ···N <sub>CN</sub>	2.478/3.419(3)	143.9	x, 1–y, ±1/2+z

<sup>a</sup>  $d$  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.

<sup>b</sup>  $\theta$  represents the X–H···A angle (°).

H<sub>Ph $n$</sub>  is a hydrogen atom in the phenyl ring of the dye molecule and  $n$  is its position in the ring. For example, H<sub>Ph4</sub> represents the hydrogen in the 4-position of the phenyl ring. H<sub>CH2</sub> is the hydrogen atoms of the methylene group.

C<sub>py</sub> and C<sub>CN</sub> are the carbon atoms of the pyrazine ring and the cyano group of the dye molecule, respectively. N<sub>CN</sub> is the nitrogen atom of a cyano group.

C<sub>Bz</sub> and H<sub>Bz</sub> are the carbon and hydrogen atoms of the benzene molecule, respectively.

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