A rare case of a dye co-crystal showing better dyeing performance

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Supporting Information

Experimental details

Materials and measurements. All melting points were measured without corrections. The reagents of analytical grade were purchased from commercial sources and used without any further purification. Infrared (IR) spectra (4000–400 cm⁻¹) were recorded using a Nicolet FT–IR 170X spectrophotometer on KBr disks. Electrospray ionization mass spectra (ESI–TOF–MS) were recorded on a Finnigan MAT SSQ 710 mass spectrometer in a scan range of 200–2000 amu. ¹H NMR spectra were measured with a Bruker dmx500 MHz NMR spectrometer at room temperature in CDC13 with tetramethylsilane as the internal reference. UV–vis spectra were recorded with a Shimadzu UV–3150 double–beam spectrophotometer using a quartz glass cell with a path length of 10 mm. Powder X–ray diffraction (PXRD) measurements were performed on a Philips X'pert MPD Pro X–ray diffractometer using Cu Ka radiation ($\lambda = 0.15418$ nm), in which the X–ray tube was operated at 40 kV and 40 mA at room temperature. TGA-DSC (thermogravimetry analysis-differential scanning calorimeter) experiments were carried out by a NETZSCH STA449C thermogravimetric analyzer instrument in the nitrogen flow from 10 to 500 °C at a heating rate of 5.0 °C/min.

Synthesis of *N***-Me dye 1.** 2,3-Dimethylaniline (1.21 g, 10.0 mmol) was dissolved in a mixture of concentrated sulfuric acid (2 mL) and glacial acetic acid (10 mL) at ~5

°C in an ice bath. Sodium nitrite (0.76 g, 11.0 mmol) was dissolved in cold water and added dropwise to the reaction mixture for 0.5 h under stirring. The diazonium salt was obtained and used for the next coupling reaction. 1,4-Dimethyl-3-cyano-6hydroxypyrid-2-one (1.64 g, 10.0 mmol) was added to a methanol/water (2:1, v/v) solution (60 mL) in a three-necked flask immersed in an ice bath. Freshly prepared diazonium salt was added dropwise for 1 h to the reaction mixture under vigorous mechanical stirring (0~5 $^{\circ}$ C). After additional stirring for 1.5 h, the mixture was neutralized with ammonia water to pH 5~6, and the precipitate was filtered and dried after thorough washing with acetone and ethanol. The crude product was recrystallized by ethanol and water (v:v = 5:1) and the microcrystals of N-Et dye 1 were finally obtained. Yield, 1.85 g (62 %). Characterizations of co-crystal dye 1: m.p., 264~266 °C. ¹H NMR (500 MHz, CDCl₃, ppm): δ 15.33 (s, 1H, hydrazone), 7.64 (d, 1H, benzo), 7.24 (q, 1H, benzo), 7.13 (d, 1H, benzo), 3.40 (s, 3H, N-CH₃), 2.65 (s, 3H, pyridone-CH₃), 2.38 (s, 6H, benzo-CH₃). Main FT-IR absorptions (KBr pellets, v, cm⁻¹): 3446 (w), 2220 (s), 1681 (s), 1632 (s), 1505 (s), 1391 (s), 1291 (s), and 781 (m). ESI-TOF-MS (negative): m/z 295.17 [M-H]⁻. Elemental analysis: calcd (%) for C₁₆H₁₆N₄O₂: C, 64.85; H, 5.44; N, 18.91; found: C, 64.97; H, 5.33; N, 18.72.

Synthesis of *N***-Et dye 2.** The procedure for the synthesis of *N*-Me dye **2** was repeated except that 3-cyano-4-methyl-6-hydroxy-*N*-ethyl-2-pyridone (1.78 g, 10.0 mmol) was used instead of *N*-Et dye **1**. Yield, 2.16 g (69 %). Characterizations of co-crystal dye **2**: m.p., 244~246 °C. ¹H NMR (500 MHz, CDCl₃, ppm): δ 15.34 (s, 1H, hydrazone), 7.64 (d, 1H, benzo), 7.22 (t, 1H, benzo), 7.13 (d, 1H, benzo), 4.07 (dd, 2H, *N*-CH₂), 2.63 (s, 3H, pyridone-CH₃), 2.38 (s, 6H, benzo-CH₃), 1.26 (t, 3H, *N*-CH₃). Main FT–IR absorptions (KBr pellets, *v*, cm⁻¹): 3444 (w), 2225 (s), 1666 (s), 1623 (s), 1510 (s), 1396 (s), 1292 (s), and 782 (m). ESI–TOF–MS (negative): *m/z* 309.25 [M–H]⁻. Elemental analysis: calcd (%) for C₁₇H₁₈N₄O₂: C, 65.79; H, 5.85; N, 18.05; found: C, 65.68; H, 5.70; N, 17.97.

Synthesis of co-crystal dye 3. There are two methods to prepare co-crystal dye 3. One follows the same method of 1 and 2 but only a mixture of half molar amounts of 1,4-dimethyl-3-cyano-6-hydroxypyrid-2-one and 3-cyano-4-methyl-6-hydroxy-*N*-ethyl-2-pyridone is used (Method A). The other is just mixing equal molar ratio of dyes 1 and 2 and undergoing the following co-sublimation under reduced pressure (Method B). Characterizations of co-crystal dye 3: m.p., 228~230 °C. ¹H NMR (500 MHz, CDCl₃, ppm): δ 15.36 (s, 2H, hydrazone), 7.67 (d, 2H, benzo), 7.26 (t, 2H, benzo), 7.15 (d, 2H, benzo), 4.10 (q, 2H, *N*-CH₂), 3.42 (s, 3H, *N*-CH₃ of Me), 2.67 (d, 6H, pyridone-CH₃), 2.40 (s, 12H, benzene-CH₃), 1.29 (t, 3H, *N*-CH₃ of Et). Main FT–IR absorptions (KBr pellets, *v*, cm⁻¹): 3442 (w), 2227 (s), 1676 (s), 1632 (s), 1452 (s), 1398 (s), 1294 (s), and 782 (m). ESI–TOF–MS (negative): *m/z* 309.25 [M–H]⁻. Elemental analysis: calcd (%) for C₁₇H₁₈N₄O₂: C, 65.33; H, 5.65; N, 18.47; found: C, 65.25; H, 5.59; N, 18.33. Single-crystal samples of dyes **1-3** suitable for X-ray diffraction measurement were all grown from chloroform by slow evaporation in air at room temperature for 4 days.

X-ray data collection and solution. Single-crystal samples of dyes 1-3 were covered in glue and mounted on glass fibers for data collection on a Bruker SMART 1K CCD area detector at 291(2) K, respectively, using graphite mono-chromated Mo K*a* radiation ($\lambda = 0.71073$ Å). The collected data were reduced by using the program SAINT and empirical absorption corrections were done by SADABS program. The crystal systems were determined by Laue symmetry and the space groups were assigned on the basis of systematic absences by using XPREP. The structures were solved by direct method and refined by least-squares method. All non-hydrogen atoms were refined on F^2 by full-matrix least-squares procedure using anisotropic displacement parameters. The hydrazone protons in dyes 1-3 were located in the difference synthesis and were refined isotropically in order to examine exactly the hydrogen bonding interactions. All the other hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters at 1.2 times of the equivalent isotropic U of the atoms to which they are attached (1.5 times for the methyl groups) and allowed to ride on their respective parent atoms. All calculations were carried out on a PC with the SHELXTL PC program package and molecular graphics were drawn by using XSHELL, Diamond and ChemBioDraw softwares. The summary of the crystal data, experimental details and refinement results for dyes **1-3** is listed in Table SI11. Selected bond distances and bond angles of dye **1-3** are given in Table SI2, while hydrogen bonding interactions are listed in Table SI3.

Tables

compound	1	2	3
Empirical formula	$C_{16}H_{16}N_4O_2$	$C_{17}H_{18}N_4O_2$	$C_{33}H_{34}N_8O_4$
Formula weight	296.33	310.35	606.68
Temperature / K	291(2)	291(2)	291(2)
Crystal Size (mm)	0.10×0.10×0.10	0.12×0.10×0.06	0.10×0.12×0.12
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\overline{1}$	$P\bar{1}$	$P\bar{1}$
<i>a</i> / Å	7.3985(5)	8.0716(9)	7.811(2)
b / Å	7.5160(5)	9.9236(12)	12.550(4)
<i>c</i> / Å	13.5827(9)	11.1322(13)	16.146(5)
α / °	100.737(1)	65.872(1)	94.579(5)
$\beta / ^{\circ}$	93.491(1)	80.149(2)	91.539(5)
γ/°	103.171(1)	74.023(2)	98.774(5)
$V/Å^3$	718.32(8)	780.60(16)	1558.0(8)
$Z / D_{\text{calcd}} (\text{g} / \text{cm}^3)$	2 / 1.370	2 / 1.320	2 / 1.293
<i>F</i> (000)	312	328	640
μ / mm ⁻¹	0.094	0.090	0.088
h_{\min} / h_{\max}	-8 / 7	-6 / 9	-8 / 9
k_{\min} / k_{\max}	-8 / 8	-11 / 11	-14 / 14
l_{\min} / l_{\max}	-16 / 16	-13 / 13	-19 / 16
Data / parameters	2501 / 207	2699 / 216	5454 / 421
Einel Dindiese[$I > 2/(D)$]	$R_1 = 0.0437$	$R_1 = 0.0575$	$R_1 = 0.0645$
Final <i>K</i> indices[$I > 20(I)$]	$wR_2 = 0.1327$	$wR_2 = 0.1665$	$wR_2 = 0.1692$
Dindiaga(all data)	$R_1 = 0.0520$	$R_1 = 0.0645$	$R_1 = 0.0970$
K indices(all data)	$wR_2 = 0.1384$	$wR_2 = 0.1754$	$wR_2 = 0.1986$
S	1.07	1.09	0.90

Table SI1Crystal data and structural refinements for compounds 1-3.

Max. / min. $\Delta \rho / e^{-3}$	0.19 / -0.20	0.23 / -0.34	0.56 / -0.32
$R_1 = \Sigma Fo - Fc / \Sigma Fo , \eta$	$wR_2 = [\Sigma[w(Fo^2 - Fc^2)]$	$(2)^{2}]/\Sigma w(Fo^{2})^{2}]^{1/2}$	

Bond distances		Bond angles	
1			
O1–C10	1.234(2)	N2-N1-C1	121.6(1)
O2–C11	1.216(2)	N1-N2-C9	119.0(1)
N1-N2	1.302(2)	C10-N3-C11	123.9(1)
N1-C1	1.407(2)	C10-N3-C14	118.7(1)
N2-C9	1.331(2)	C11-N3-C14	117.3(1)
N3-C10	1.377(2)	N1-C1-C6	120.8(1)
N3-C11	1.394(2)	N1-C1-C2	117.4(1)
N3-C14	1.463(2)	N2-C9-C10	123.0(1)
N4-C15	1.140(2)	N2-C9-C13	116.5(1)
C1–C6	1.388(2)	O1-C10-C9	122.4(1)
C1–C2	1.402(2)	N3-C10-C9	117.7(1)
		O1-C10-N3	120.0(1)
		N3-C11-C12	116.6(1)
		O2-C11-N3	120.7(1)
		O2-C11-C12	122.8(1)
		N4-C15-C12	178.6(2)
2			
O1–C11	1.207(2)	N2-N1-C1	121.5(1)
O2–C10	1.239(2)	N1-N2-C9	118.8(1)
N1-N2	1.306(2)	C10-N3-C11	123.8(2)
N1-C1	1.408(2)	C10-N3-C14	118.2(1)
N2-C9	1.328(2)	C11-N3-C14	118.1(1)
N3-C10	1.370(2)	N1-C1-C6	121.1(1)
N3-C11	1.401(2)	N1-C1-C2	117.0(2)
N3-C14	1.481(2)	O1-C11-N3	120.9(2)
N4-C16	1.141(2)	N3-C10-C9	118.4(1)
C1–C6	1.386(3)	O1-C11-C12	123.0(2)
C1–C2	1.403(2)	O2-C10-C9	122.1(2)
		O2-C10-N3	119.5(2)
		N3-C11-C12	116.1(1)
		N4-C16-C12	178.9(2)
		N3-C14-C15	112.5(2)
3			
O1–C10	1.237(4)	N2-N1-C1	120.2(2)
O2–C11	1.226(4)	N1-N2-C9	120.0(2)
O3–C27	1.235(4)	C10-N3-C11	123.7(3)
O4–C28	1.220(4)	N6-N5-C18	120.9(3)
N1-C1	1.413(3)	N5-N6-C26	120.0(3)
N1N2	1.305(3)	N1C1C6	120.2(2)
N2-C9	1.326(3)	N1-C1-C2	117.2(2)

Table SI2Selected bond distances (Å) and angles (°) for compounds 1-3.

N3-C11	1.395(4)	N2-C9-C10	123.3(2)
N3-C14	1.465(4)	N2-C9-C13	116.2(2)
N3-C10	1.378(4)	O2C11C12	122.9(3)
N4-C16	1.146(4)	O2C11N3	120.1(3)
N5-N6	1.298(4)	O1C10N3	120.1(2)
N5-C18	1.412(4)	O1-C10-C9	122.5(2)
N6-C26	1.331(4)	N3-C11-C12	117.0(3)
N7–C28	1.393(5)	N3-C10-C9	117.5(2)
N7-C27	1.377(4)	N4-C16-C12	179.5(3)
N8-C32	1.138(5)	N3-C14-C15	110.8(4)
C1–C6	1.385(4)	C9-C13-C12	118.0(2)

Table SI3Hydrogen bonding parameters (Å, °) in compounds 1-3.

D–H···A	D–H	H···A	D···A	∠DHA	Symmetry code
1					
N1-H1…O1	0.92(2)	1.75(2)	2.554(2)	144(2)	
2					
N1-H1…O2	0.96(2)	1.74(2)	2.553(2)	141(2)	
<u>C8–H8A</u> …O1	0.96	2.39	3.305(3)	159	1+x, 1+y, 1+z
3					
N1-H1…O1	0.95(3)	1.84(4)	2.580(3)	132(3)	
N5−H5A…O3	0.92(3)	1.79(3)	2.582(4)	144(3)	
С7–Н7С…О4	0.96	2.58	3.473(4)	154	- <i>x</i> , 1- <i>y</i> , 1- <i>z</i>
C15–H15B…O2	0.96	2.54	3.350(6)	142	1- <i>x</i> , 1- <i>y</i> , - <i>z</i>
C24–H24C…N4	0.96	2.61	3.554(5)	167	x, y, 1+z

Table SI 4 Standard determination of dye-uptake for disperse yellow dyes 1, 2, mixture of equal molar amounts of 1 and 2, and 3 at high temperature dyeing on the standard acrylic fibers with the percentage of weight of fabric (OWF %) as 0.5 and 2.0 %, together with C.I. Disperse Red 60 and C.I. Disperse Blue 56 for comparison.

Temperature / °C	55 °C	100 °C	110 °C	120 °C	130 °C	130°C+20min	130°C+40min
Time / min	0	15	25	35	45	65	85
1 / 0.5 %	0	20.6	37.6	89.9	98.8	100.8	100.8
2 / 0.5 %	0	9.3	27.6	59.6	99.5	100.0	100.0 <i>a</i>
(1 + 2) / 0.5 %	0	23.4	49.5	91.6	99.1	100.3	100.3
3 / 0.5 %	0	20.0	61.0	93.2	96.7	100.0	100.0
C.I. Disperse Red 60 / 0.5 %	0	17.3	77.7	100.2	102.0	100.0	100.0
C.I. Disperse Blue 56 / 0.5 %	0	39.3	84.5	95.2	98.2	100.0	100.0
1 / 2.0 %	0	21.3	44.3	126.9	244.2	291.7	291.7
2 / 2.0 %	0	10.5	29.3	66.3	196.5	250.3	250.3
(1+2)/2.0%	0	23.6	48.6	177.7	273.8	291.2	291.2
3 / 2.0 %	0	20.7	97.3	238.8	289.8	291.2	291.2
C.I. Disperse Red 60 / 2.0 %	0	16.1	70.1	240.3	291.6	291.7	291.7
C.I. Disperse Blue 56 / 2.0 %	0	43.7	176.8	264.3	282.8	291.7	291.7

^{*a*} dye-uptake of disperse yellow dye **2** at 130 $^{\circ}$ C for 40 minutes was set as 100 %.

Figures



Fig. SI1. FT–IR spectrum of dye 1.



Fig. SI2. FT–IR spectrum of dye **2**.



Fig. SI3. FT–IR spectrum of dye co-crystal 3.



Fig. SI4. ESI-MS spectrum (negative mode) of compound 1.



Fig. SI5. ESI-MS spectrum (negative mode) of compound 2.



Fig. SI6. ESI-MS spectrum (negative mode) of compound 3.



Fig. SI7. UV–vis spectra of dyes 1-3 in their methanol solutions with the same concentration of 3.0×10^{-5} mol·L⁻¹



Fig. SI8. ¹H NMR spectrum of compound 1.



Fig. SI9. ¹H NMR spectrum of compound **2**.



Fig. SI10. ¹H NMR spectrum of compound 3.



Fig. SI11. TGA-DSC curves for dye 1.



Fig. SI12. TGA-DSC curves for dye 2.





Fig. SI13. TGA-DSC curves for dye co-crystal 3.