Electronic Supplementary Information

Solvatochromic, Thermochromic and pH-Sensory DCDHF-Hydrazone Molecular Switch: Response to Alkaline Analytes

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Synthesis of 2-(dicyanomethylene)-2,5-dihydro-4,5,5-trimethylfuran-3-carbonitrile 7: [1, 2]
In a 2-neck 250 ml round bottom flask in a room temperature water bath, sodium metal (300 mg, 13 mmol) was dissolved in 10 mL of absolute ethanol. Next, 3-hydroxy-3-methyl-2-butanone (9.0 gm, 88.0 mmol) and malononitrile (12.0 g, 181 mmol) were added to the sodium ethoxide solution with stirring. After 1hr an additional 30 mL of absolute ethanol was added and the resulting mixture was heated at reflux for 1 additional hr. The resulting mixture was cooled in a refrigerator and the solid was filtered off, washed with a minimal amount of cold ethanol, and then air dried giving a first crop of 8.52 g of off-white crystalline solid. Concentration of the filtrate and cooling gave a second crop of 1.49 g product (total yield 57%). mp 201ºC–203ºC. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 2.36 (s, 3H), 1.64 (s, 6H).

General synthetic procedure for DCDHF-based aryl-hydrazone chromophores 1-6:
A mixture of arylamine (5.0 mmol), hydrochloric acid (3.0 mL) and water (1.0 mL) in a 25 ml Erlenmeyer flask was stirred and cooled in an ice bath at 0-5ºC. The aniline diazonium salt was prepared by slow addition of a solution of sodium nitrite (5.0 mmol) in 2.0 mL of water at 0-5ºC and the resulting mixture was stirred for an additional 30 minutes at 0-5ºC. In a separate round bottom flask, 2-(dicyanomethylene)-2,5-dihydro-4,5,5-trimethylfuran-3-carbonitrile **7** (5.0 mmol) was dissolved in acetonitrile (5.0 mL), cooled to 0-5ºC and acetic acid (2.0 mL) and sodium acetate (1.5 g) were added. This mixture was vigorously stirred in the ice bath at 0-5ºC as the cold diazonium salt solution was added dropwise. After stirring the resulting mixture for two more hours, the crude solid product was filtered off with a Buchner funnel, washed with distilled water (3 x 10 mL), crystallized and air dried to afford the solid product.

Synthesis of 2-(dicyanomethylene)-2,5-dihydro-4-(methyl-(phenylazo))-5,5-trimethylfuran-3-carbonitrile 1:
Prepared from aniline (500 mg, 5.0 mmol) and 2-(dicyanomethylene)-2,5-dihydro-4,5,5-trimethylfuran-3-carbonitrile (1.0 g, 5.0 mmol). The crude product was isolated by filtration of the reaction mixture with a Buchner funnel, crystallization from chloroform and air drying to afford an orange solid (1.10 g; yield 73%). DSC: decomposition at 217°C; ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 12.66 (s-broad, 1H, N-H), 7.83 (s, 1H, =C-H), 7.43 (t, 2H, *J* = 7.8 Hz), 7.29 (d, 2H, *J* = 8 Hz), 7.15 (t, 1H, *J* = 7.2 Hz), 1.80 (s, 6H); ^{13}C NMR (400 MHz, DMSO-d_6), δ (ppm): 177.69, 172.63, 142.45, 137.69, 130.36, 128.78, 126.68, 125.09, 115.63, 114.88, 113.58, 112.82, 111.39, 98.84, 26.63; IR (neat, v/cm^{-1}) 3301 (NH), 2223 (CN), 1624 (C=N); MS *m/z* (%): 302 [*M*-H]$^{+}$; Elemental analysis calculated for $C_{17}H_{13}N_5O$ (303.11): C 67.32, H 4.32, N 23.09; Found: C 67.48, H 4.41, N 23.21.

Synthesis of 2-(dicyanomethylene)-2,5-dihydro-4-(methyl-(4-nitro-phenylazo))-5,5-trimethylfuran-3-carbonitrile 2:
Prepared from 4-nitroaniline (300 mg, 2.2 mmol), and 2-(dicyanomethylene)-2,5-dihydro-4,5,5-trimethylfuran-3-carbonitrile (400 mg, 2.0 mmol). The crude product was isolated by filtration of the reaction mixture with a Buchner funnel, crystallization from ethanol/chloroform, and air drying to afford a brick red solid (590 mg; yield 79%). DSC: decomposition at 226ºC; ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 12.80 (s-broad, 1H, N-H), 8.27 (d, 2H, *J* = 9.2 Hz), 8.00 (s, 1H, =C-H), 7.39 (d, 2H, *J* = 8.8 Hz), 1.82 (s, 6H); ^{13}C NMR (400 MHz, DMSO-d_6), δ (ppm): 177.36, 171.89, 147.80, 142.84, 129.17, 126.51, 115.17, 113.12, 112.36, 110.85, 99.42, 99.28, 26.34; IR (neat, v/cm^{-1}) 3274 (NH), 2225 (CN), 1578 (C=N), 1512 and 1312 (NO_2); MS *m/z* (%): 347 [*M*-H]$^{+}$;

Elemental analysis calculated for $C_{17}H_{12}N_6O_3$ (348.10): C 58.62, H 3.47, N 24.13; Found: C 58.78, H 3.53, N 24.28.

Synthesis of 2-(dicyanomethylene)-2,5-dihydro-4-(methyl-(2,4-dinitro-phenylazo))-5,5-trimethylfuran-3-carbonitrile 3:

Prepared from 2,4-dinitroaniline (400 mg, 2.2 mmol), and 2-(dicyanomethylene)-2,5-dihydro-4,5,5-trimethylfuran-3-carbonitrile (400 mg, 2.0 mmol). The crude product was isolated by filtration of the reaction mixture with a Buchner funnel, crystallization from *n*-propanol/chloroform and air drying to afford a dark red solid (570 mg; yield 66%); DSC: decomposition at 236ºC; ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 12.11 (s-broad, 1H, N-H), 8.59 (s, 1H, =C-H), 8.38 (d, 1H, *J* = 2.4 Hz), 8.24 (dd, 1H, *J* = 11.6, 2.4 Hz), 7.66 (d, 1H, *J* = 8.8 Hz), 1.82 (s, 6H); ^{13}C NMR (400 MHz, DMSO-d_6), δ (ppm): 176.82, 171.14, 142.04, 132.26, 125.96, 124.54, 115.46, 112.58, 111.82, 110.70, 25.81; IR (neat, ν/cm^{-1}) 3256 (NH), 2226 (CN), 1577 (C=N), 1509 and 1324 (NO_2); MS *m/z* (%): 392 [*M*-H]$^+$; Elemental analysis calculated for $C_{17}H_{11}N_7O_5$ (393.08): C 51.91, H 2.82, N 24.93; Found: C 51.89, H 2.71, N 24.79.

Synthesis of 2-(dicyanomethylene)-2,5-dihydro-4-(methyl-(4-methyl-phenylazo))-5,5-trimethylfuran-3-carbonitrile 4:

Prepared from 4-methylaniline (430 mg, 4.0 mmol), and 2-(dicyanomethylene)-2,5-dihydro-4,5,5-trimethylfuran-3-carbonitrile (80 mg, 4.0 mmol). The crude product was isolated by filtration of the reaction mixture with a Buchner funnel, crystallization from chloroform/methanol and air drying to afford a red solid (850 mg; yield 59%); DSC: decomposition at 215ºC; ^{1}H NMR (400 MHz, DMSO-d_6): ppm 12.64 (s-broad, 1H, N-H), 7.78 (s, 1H, =C-H), 7.211 (d, 2H, *J* = 10.4 Hz), 7.189 (d, 2H, *J* = 27.6 Hz), 2.30 (s, 3H), 1.79 (s, 6H); ^{13}C NMR (400 MHz, DMSO-d_6), δ (ppm): 177.69, 172.28, 140.20, 134.84, 130.79, 124.44, 115.85, 113.77, 113.01, 111.59, 98.56, 26.72, 21.03; IR (neat, ν/cm^{-1}) 3391 (NH), 2902 (CH aliphatic), 2852 (CH aromatic), 2207 (CN), 1579 (C=N); MS *m/z* (%): 316 [*M*-H]$^+$; Elemental analysis calculated for $C_{18}H_{15}N_5O$ (317.13): C 68.13, H 4.76, N 22.07; Found: C 68.21, H 4.89, N 22.13.

Synthesis of 2-(dicyanomethylene)-2,5-dihydro-4-(methyl-(4-methoxy-phenylazo))-5,5-trimethylfuran-3-carbonitrile 5:

Prepared from 4-anisidine (0.50 gm, 4.0 mmol), and 2-(dicyanomethylene)-2,5-dihydro-4,5,5-trimethylfuran-3-carbonitrile (0.80 gm, 4.0 mmol); The crude product was isolated by filtration of the reaction mixture with a Buchner funnel, crystallization from chloroform and air drying to afford a blue solid (0.88 gm; yield 66 %); DSC: decomposition at 216ºC; ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 12.75 (s-broad, 1H, N-H), 7.74 (s, 1H, =C-H), 7.27 (d, 2H, *J* = 9.2 Hz), 7.04 (d, 2H, *J* = 9.2 Hz), 3.77 (s, 3H), 1.79 (s, 6H); ^{13}C NMR (400 MHz, DMSO-d_6), δ (ppm): 177.71, 172.25, 157.53, 135.82, 123.75, 117.35, 115.84, 113.09, 113.08, 111.69, 98.41, 55.91, 26.77, 23.68; IR (neat, ν/cm^{-1}) 3241 (NH), 2225 (CN), 1571 (C=N), 1274 (OCH_3), 1164 (C-O); MS *m/z* (%): 332 [*M*-H]$^+$; Elemental analysis calculated for $C_{18}H_{15}N_5O_2$ (333.12): C 64.86, H 4.54, N 21.01; Found: C 64.92, H 4.71, N 21.18.

Synthesis of 2-(dicyanomethylene)-2,5-dihydro-4-(methyl-(2-hydroxy-4-nitro-phenylazo))-5,5-trimethylfuran-3-carbonitrile 6:

Prepared from 2-amino-5-nitrophenol (340 mg, 2.2 mmol), and 2-(dicyanomethylene)-2,5-dihydro-4,5,5-trimethylfuran-3-carbonitrile (400 mg, 2.0 mmol). The crude product was isolated by filtration of the reaction mixture with a Buchner funnel, crystallization from ethanol/chloroform and air drying to afford an orange solid (750 mg; yield 94%); DSC:

decomposition at 229ºC; ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 12.27 (s-broad, 1H, N-H), 11.29 (s, 1H, O-H), 8.45 (s, 1H, =C-H), 7.81 (dd, 1H, *J* = 11.6, 2.4 Hz), 7.70 (d, 1H, *J* = 2.8 Hz), 7.47 (d, 1H, *J* = 9.2 Hz), 1.81 (s, 6H); ^{13}C NMR (400 MHz, DMSO-d_6), δ (ppm): 177.51, 172.18, 145.68, 142.96, 137.04, 130.00, 117.15, 114.20, 113.29, 112.50, 110.91, 110.56, 99.78, 99.28, 26.44, 23.67; IR (neat, ν/cm^{-1}) 3378 (OH), 3262 (NH), 2210 (CN), 1587 (C=N), 1509 and 1328 (NO_2); MS *m/z* (%): 363 [*M*-H]$^{+}$; Elemental analysis calculated for $C_{17}H_{12}N_6O_4$ (364.09): C 56.05, H 3.32, N 23.07; Found: C 56.17, H 3.22, N 23.19**.**

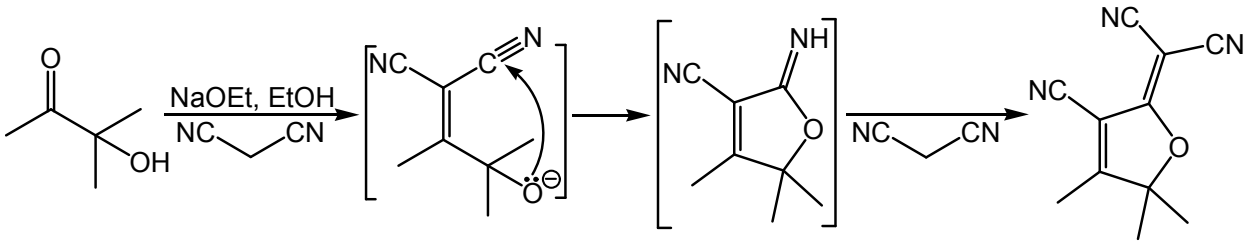

Figure 1S. Two step Knoevenagel condensation reaction to build up the DCDHF heterocycle head. [1, 2]

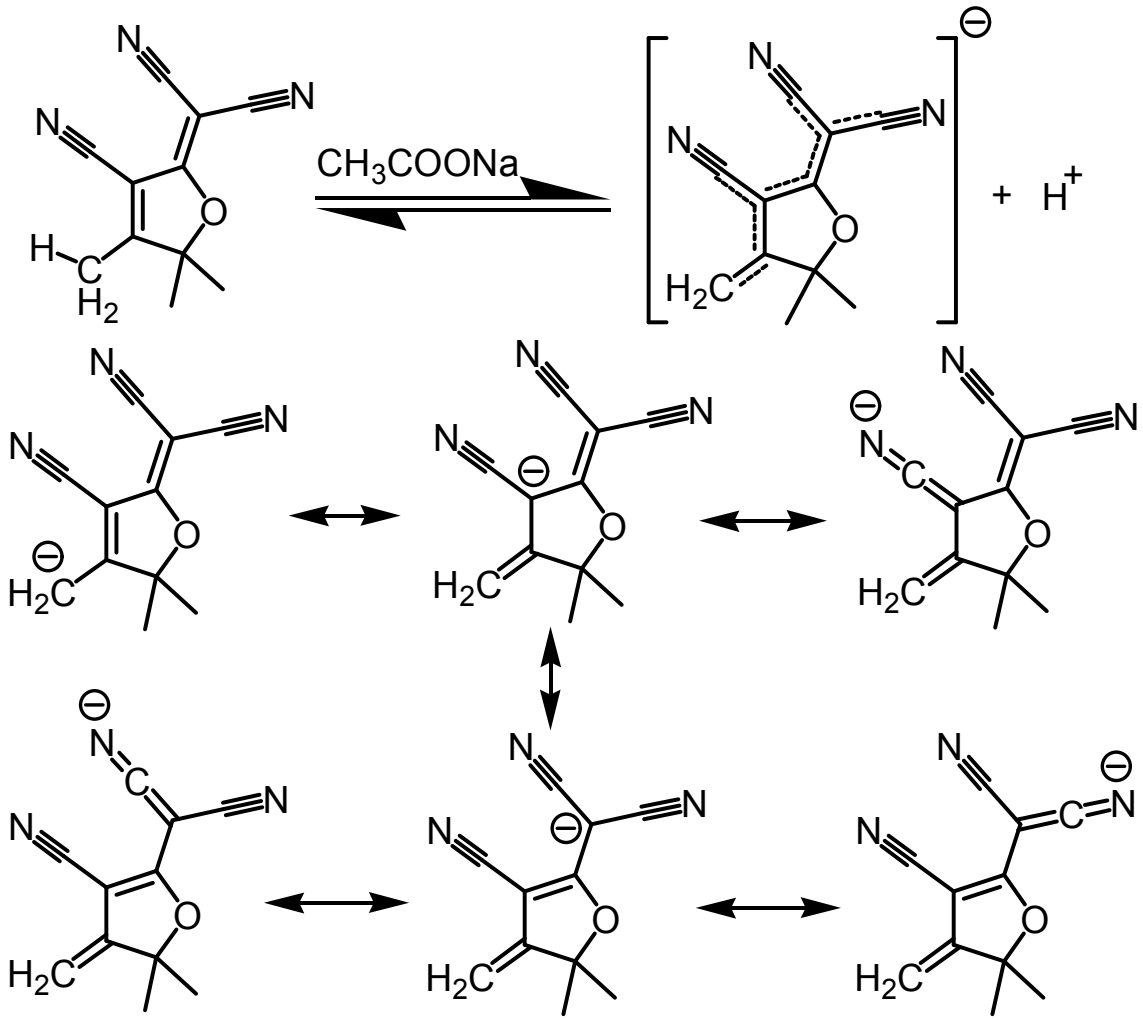

Figure 2S. Proposed DCDHF's conjugate anion resonance structures. [2-4]

Table 1S. Spectroscopic data and fluorescence quantum yields (Φ) of DCDHF-Hs **1-6** in various solvents at a fixed neutral pH value. Rhodamine 101 in ethanol (Φ_r = 0.96) and rhodamine 6G in ethanol (Φ_r = 0.95) were used as fluorescence quantum yield references. [5, 6]

Solvent	E_T(30) (kcal mol^{-1}) [7]	λ_{max} (nm)											
		Chromophore **1** R = H		Chromophore **2** R = 4-NO_2		Chromophore **3** R = 2,4-diNO_2		Chromophore **4** R = 4-CH_3		Chromophore **5** R = 4-OCH_3		Chromophore **6** R = 2-OH, 4-NO_2	
		Abs.	Em. (Φ)	Abs.	Em. (Φ)	Abs.	Em. (Φ)	Abs.	Em. (Φ)	Abs.	Em. (Φ)	Abs.	Em. (Φ)
Methanol	55.4	476	555 (0.37)	465	540 (0.22)	455	-	486	569 (0.38)	502	606 (0.40)	494	-
Formic acid	54.3	481	552 (0.31)	467	544 (0.26)	458	542 (0.27)	498	577 (0.23)	513	604 (0.39)	493	547 (0.18)
Ethanol	51.9	476	553 (0.41)	466	535 (0.20)	456	534 (0.23)	488	572 (0.42)	508	607 (0.21)	503	602 (0.12)
n-Propanol	50.7	479	-	467	536 (0.31)	456	528 (0.26)	500	-	506	-	-	-
DMSO	45.1	485	564 (0.43)	490	557 (0.29)	594	668 (0.34)	492	584 (0.40)	495	615 (0.46)	517	605 (0.21)
DMF	43.2	478	-	562	-	590	-	478	-	478	-	592	-
Acetone	42.2	469	554 (0.38)	461	537 (0.32)	450	532 (0.30)	481	572 (0.37)	498	613 (0.26)	484	594 (0.15)
Benzonitrile	41.5	485	568 (0.28)	569	564 (0.17)	606	672 (0.21)	485	569 (0.32)	489	598 (0.30)	592	667 (0.13)
Dichloromethane	40.7	465	553 (0.30)	454	532 (0.23)	453	535 (0.17)	478	570 (0.31)	498	606 (0.18)	477	544 (0.22)
Chloroform	39.1	461	550 (0.35)	452	548 (0.28)	451	528 (0.19)	474	564 (0.22)	494	601 (0.19)	-	-
Tetrahydrofuran	37.4	472	551 (0.38)	460	535 (0.31)	454	533 (0.22)	483	568 (0.29)	503	612 (0.23)	485	533 (0.11)
1,4-Dioxane	36.0	465	541 (0.24)	458	528 (0.27)	451	520 (0.20)	475	557 (0.15)	490	588 (0.27)	473	520 (0.19)
Toluene	33.9	465	541 (0.21)	457	531 (0.16)	453	529 (0.14)	475	556 (0.18)	494	593 (0.32)	-	-

" – " No fluorescence detected

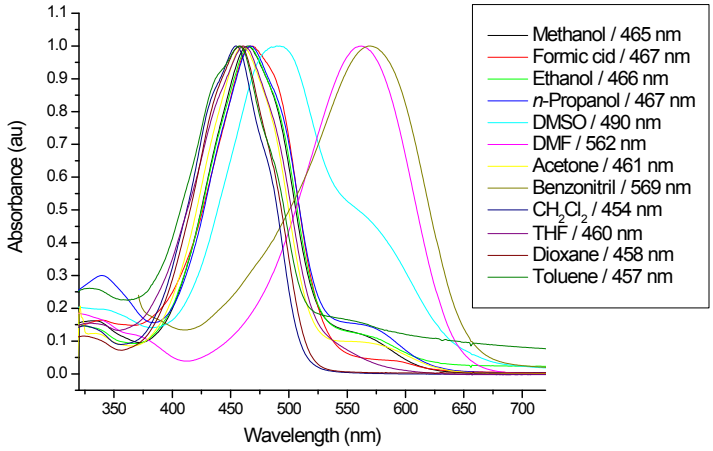

Figure 3aS

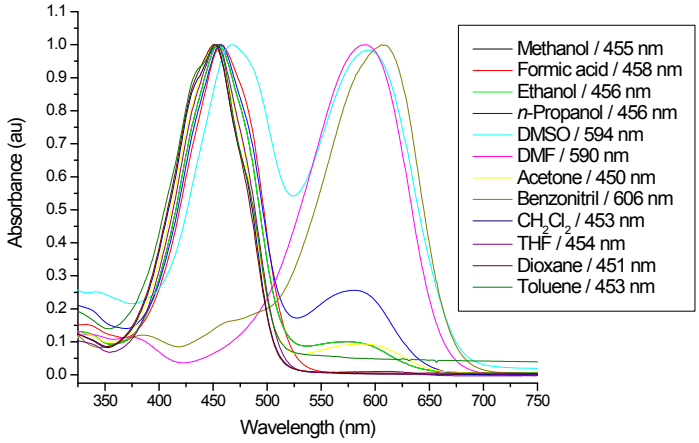

Figure 3bS

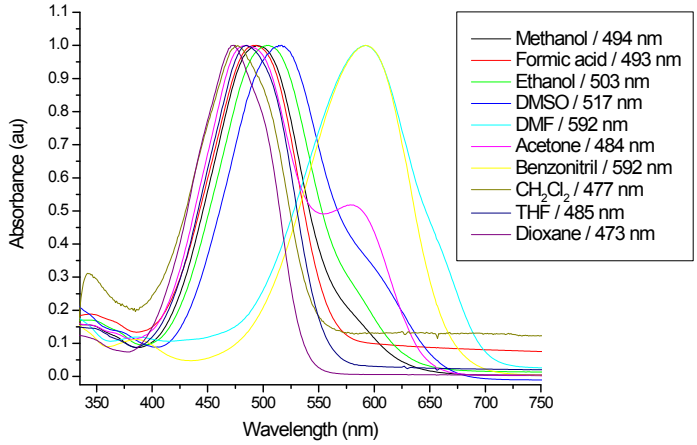

Figure 3cS

Figure 3S. Normalized UV-Vis absorption spectra of (a) S-1-H (R= 4-NO_2), (b) S-2-H (R= 2,4-NO_2), and (c) S-3-H (R= 2-OH, 4-NO_2); in different solvents

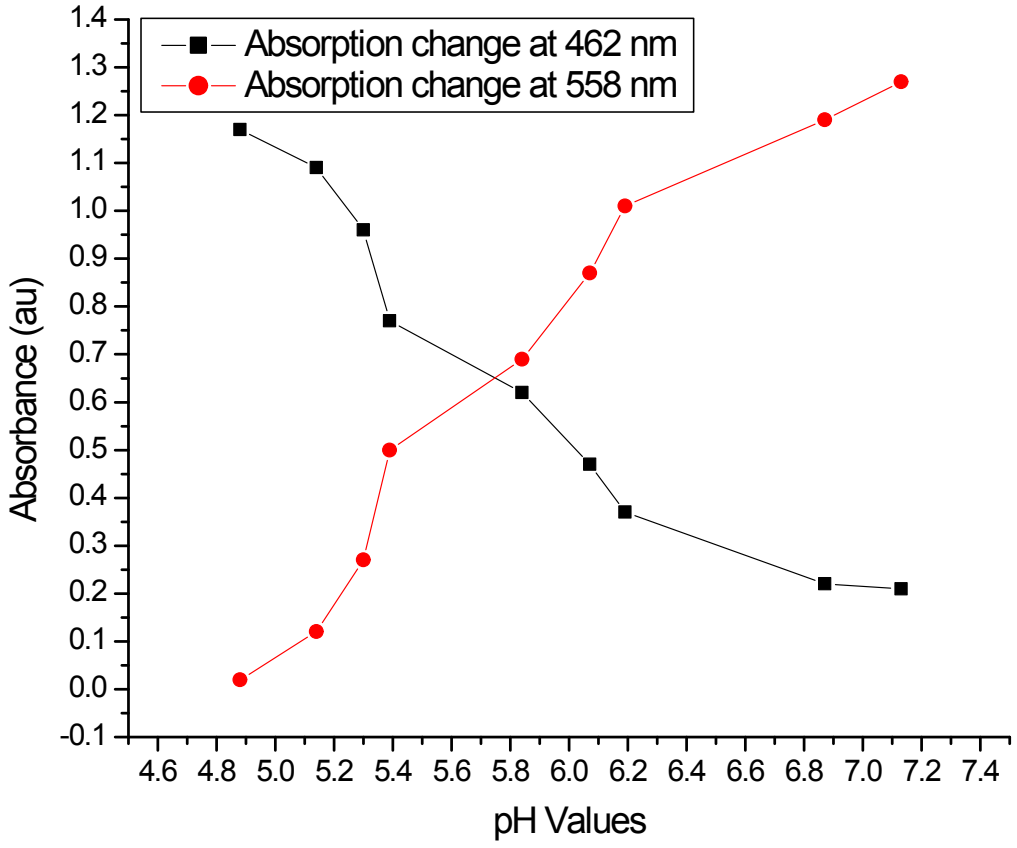

Figure 4S. Absorbance intensity plotted against pH for DCDHF-H (**2**; R= 4-NO_2) at maximal absorption wavelengths λ_{max} 462 and 558 nm; in acetone solution (conc. 2.2 x 10^{-5} mol L^{-1}) at ambient temperature.

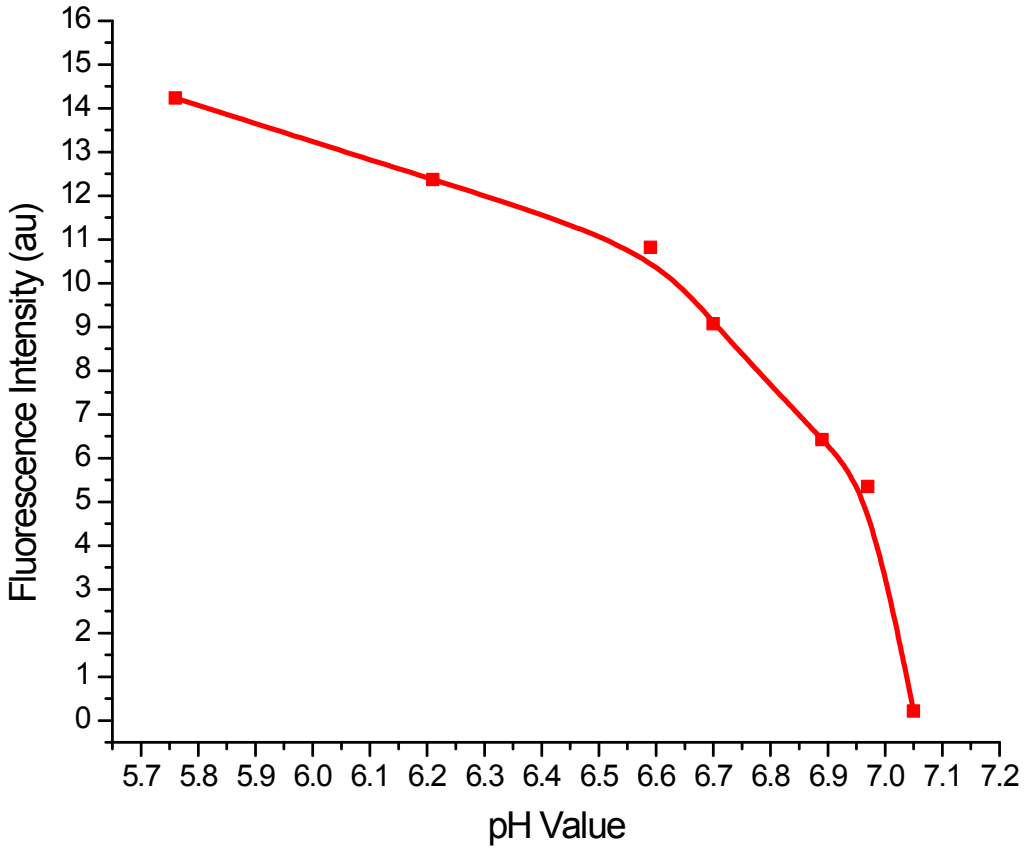

Figure 5S. Fluorescence emission intensity plotted against pH for DCDHF-H (**2**; R=4-NO_2; excitation wavelength at 488 nm) in dimethylsulfoxide solution (conc. $2.5x10^{-5}$ mol L^{-1}) at ambient temperature.

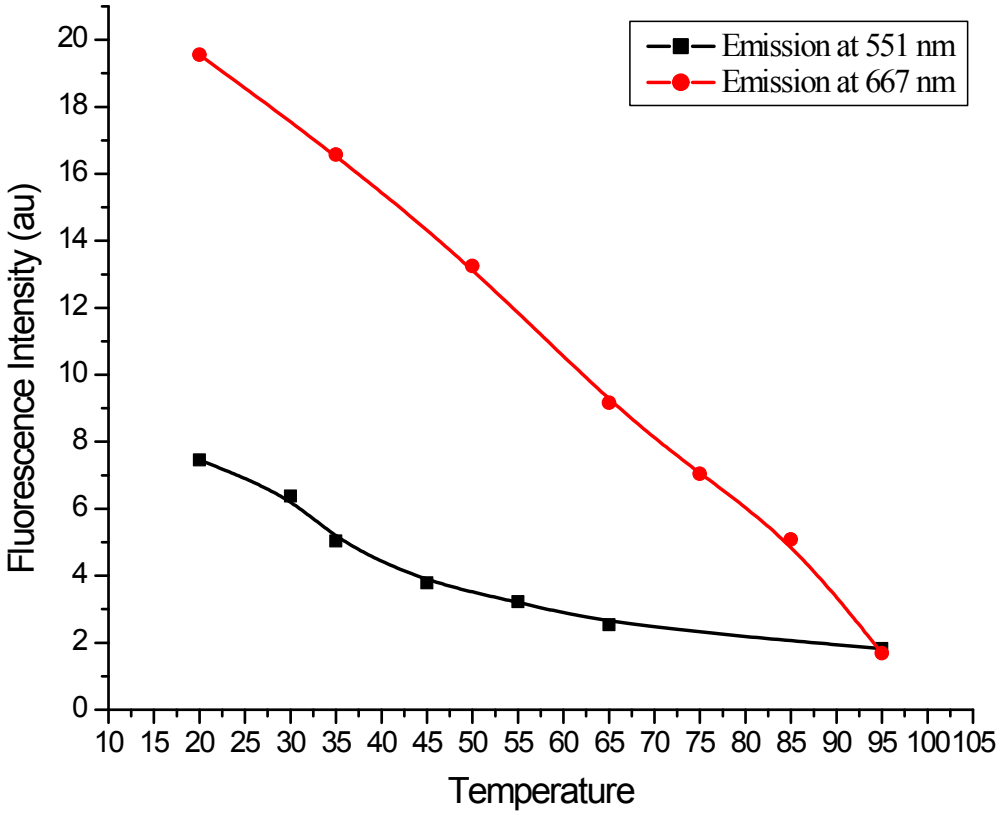

Figure 6S. Changes of the fluorescence emission spectra of **3** at two distinct excitation wavelengths (467 and 594 nm) in dimethylsulfoxide solution (conc. 2.9×10^{-5} mol L^{-1}) at various temperatures (20-95°C).

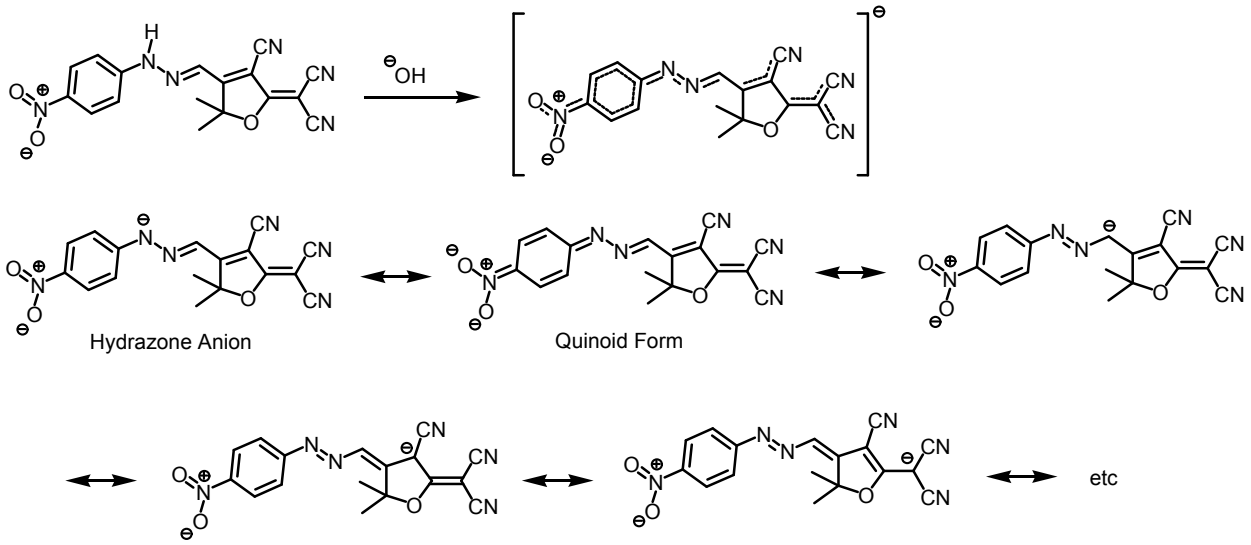

Figure 7S. The 4-nitro-substituted DCDHF-H chromophore and the various resonance structures of its hydrazone anion.

Table 2S. The UV-Vis absorption spectra of sensors **2** at 559 nm in acetone (4a), **3** at 592 nm in acetone (4b), and **6** at 544 nm in ethanol (4c); upon addition of increasing concentrations of ammonium hydroxide aqueous solution.

Sensor **2** (S-1-H)	Conc. of aqueous NH_3 (μM)	UV-Vis absorption intensity in acetone	Sensor **3** (S-2-H)	Conc. of aqueous NH_3 (μM)	UV-Vis absorption intensity in acetone	Sensor **6** (S-3-H)	Conc. of aqueous NH_3 (μM)	UV-Vis absorption intensity in ethanol
S-1-H 4	0.7	0.23	S-2-H 8	0.7	0.17	S-3-H 4	0.7	0.34
S-1-H 8	1.1	0.67	S-2-H 4	1.1	0.51	S-3-H 5	1.1	0.79
S-1-H 3	1.8	0.94	S-2-H 3	1.8	0.83	S-3-H 3	1.8	1.03
S-1-H 2	3.5	1.22	S-2-H 7	3.5	1.01	S-3-H 9	3.5	1.39
S-1-H 7	3.9	1.48	S-2-H 2	3.9	1.23	S-3-H 10	3.9	1.60
S-1-H 6	4.8	1.71	S-2-H 6	4.8	1.63	S-3-H 6	4.8	1.94
S-1-H 5	5.6	1.96	S-2-H 5	5.6	1.70	S-3-H 2	5.6	2.06
S-1-H 1	6.3	2.27	S-2-H 1	6.3	1.98	S-3-H 7	6.3	2.44
						S-3-H 8	6.7	2.57
						S-3-H 11	6.9	2.88
						S-3-H 1	7.8	3.32

Table 3S. Optical properties of the hydrazone dyes (S-1-H, S-2-H, and S-3-H) and its corresponding hydrazone anions (S-1-HA, S-2-HA, and S-3-HA) resulting from the reaction with ammonium hydroxide aqueous solution (Conc. ca. 1.0×10^{-6}) in some selected solvents

Solvent	Hydrazone (H) form	$\lambda_{max,\ abs.}$ (nm); ε (molar absorptivity) L mol^{-1} cm^{-1}	$\lambda_{max,\ em.}$ (nm)	Hydrazone Anion (HA) form	$\lambda_{max,\ abs.}$ (nm); ε (molar absorptivity) L mol^{-1} cm^{-1}	$\lambda_{max,\ em.}$ (nm)
Ethanol	S-1-H	466 (59793)	535	S-1-HA	551 (54436)	-
DMSO		490 (40574)	557		562 (73678)	-
Acetone		461 (55509)	537		559 (66124)	-
Ethanol	S-2-H	456 (53500)	534	S-2-HA	581 (49652)	-
DMSO		467 (30753)	551		594 (81241)	668
Acetone		450 (58420)	532		592 (71472)	-
Ethanol	S-3-H	503 (38714)	602	S-3-HA	544 (36122)	-
DMSO		517 (44361)	605		592 (56470)	-
Acetone		484 (41745)	594		580 (51034)	-

(-) No fluorescence determined

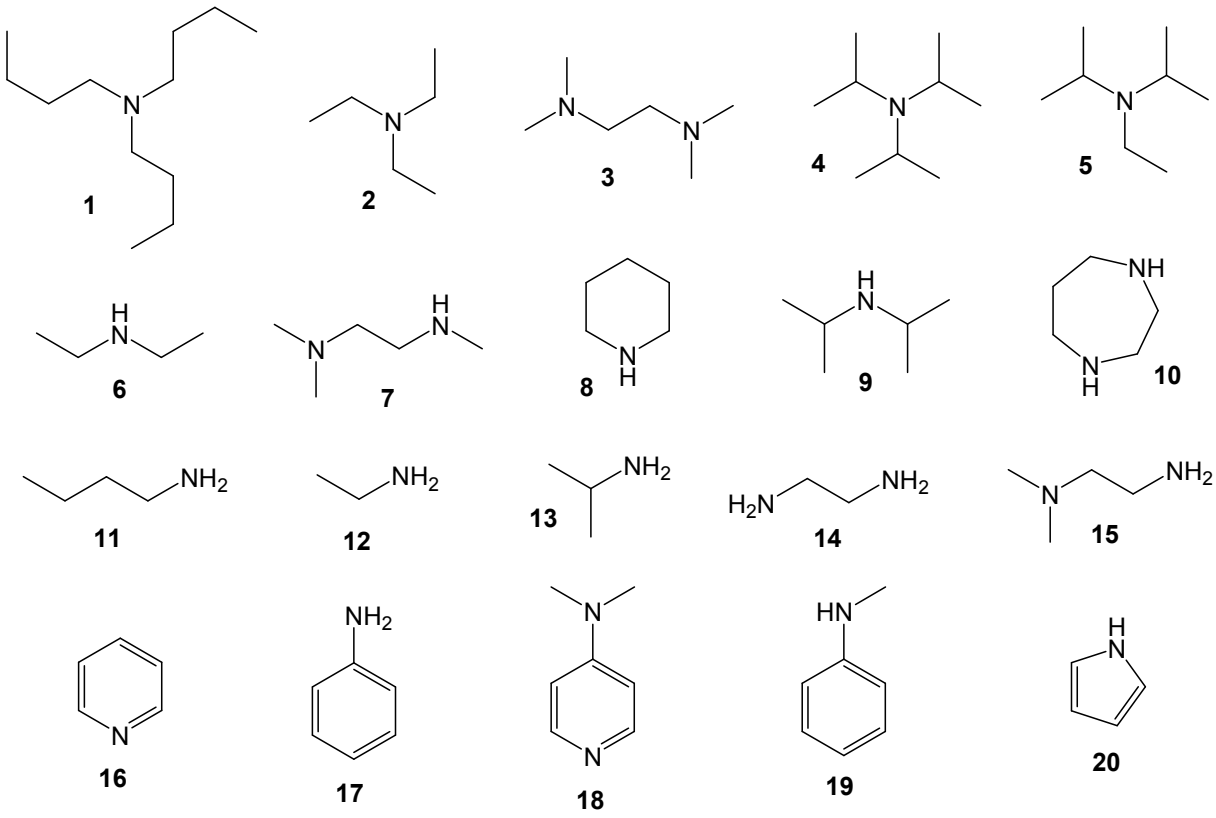

Figure 8S. Structures of the amines utilized in this study.

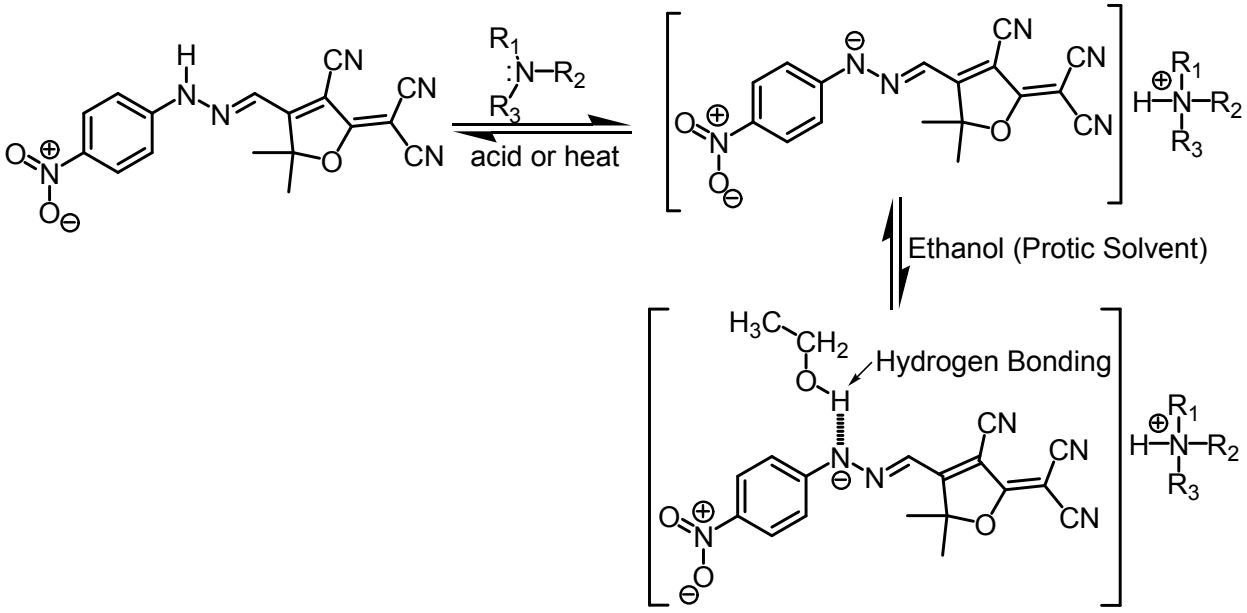

Figure 9S. Hydrogen bonding between the hydrazone anion and ethanol leads to a new species in equilibrium with other two species; the hydrazone dye and its corresponding hydrazone anion.

Table 4S. Changes in absorption maxima (at 580 nm) of acetone solutions containing the molecular probe S-3-H at ~4.0 μM different types of amines.

No.	Amine name	Amine category	UV-Vis absorption intensity	pK_b values* [8-13]
1	tributylamine	Tertiary aliphatic	0.79	3.11
2	triethylamine	Tertiary aliphatic	0.88	3.25
3	tetramethyl ethylene diamine	Tertiary aliphatic	0.94	5.85
4	triisopropylamine	Tertiary aliphatic	0.53	5.94
5	diisopropylethylamine	Tertiary aliphatic	0.67	3.02
6	diethylamine	Secondary aliphatic	1.50	3.16
7	*N,N,N*'-trimethylethylenediamine	Secondary aliphatic	1.82	3.46
8	Piperidine	Secondary aliphatic	1.69	2.89
9	Diisopropylamine	Secondary aliphatic	1.51	3.43
10	1,4-diazepane	Secondary aliphatic	1.97	2.97
11	*n*- butylamine	Primary aliphatic	1.28	3.40
12	ethylamine	Primary aliphatic	1.12	3.35
13	isopropylamine	Primary aliphatic	1.22	3.37
14	ethylenediamine	Primary aliphatic	1.46	4.07
15	*N,N*-dimethylethylenediamine	Primary aliphatic	1.34	3.46
16	pyridine	Aromatic	0.12	8.77
17	Aniline	Aromatic	0.08	9.13
18	4-Dimethylaminopyridine	Aromatic	0.18	9.7
19	*N*-methylaniline	Aromatic	0.14	9.3
20	pyrrole	Aromatic	0.03	13.6

* Base Ionization Constants in Water at 25 °C

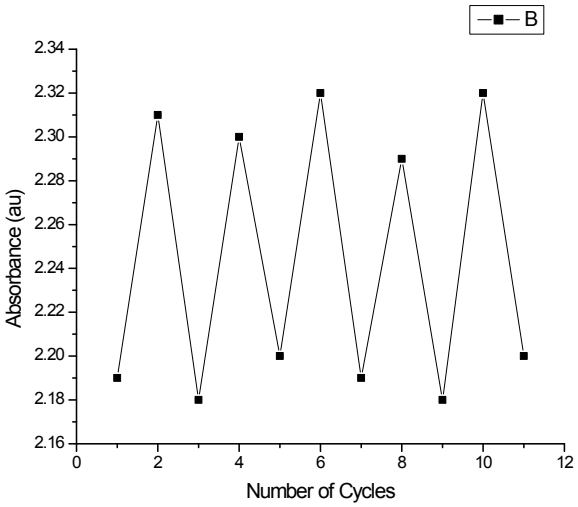

Figure 10S. Changes in the ratio of the absorbance at 517 nm and 592 nm of S-3-H in dimethyl sulfoxide solution (conc. 2.2 x 10^{-5} mol L^{-1}) at ambient temperature. The absorbance values were switched back and forth between 2.19 and 2.31 respectively using aqueous solution of ammonium hydroxide (conc. 2.6 x 10^{-3} mol L^{-1}) and heating.

Table 5S. Fluorescence emission intensity of the dinitro-substituted DCDHF-H chromophore **3** at 551 nm (excitation wavelength 467 nm) and at 667 nm (excitation wavelength 594 nm); in dimethylsulfoxide solution (conc. 2.9 x 10^{-5} mol L^{-1}) at various temperatures.

Fluorescence intensity at 551 nm (excitation wavelength 467 nm)	Temperature °C	Fluorescence intensity at 667 nm (excitation wavelength 594 nm)	Temperature °C
7.56	20	19.68	20
6.68	30	16.77	35
5.21	35	13.20	50
3.89	45	9.33	65
3.23	55	7.54	75
2.62	65	5.19	85
1.82	95	1.87	95

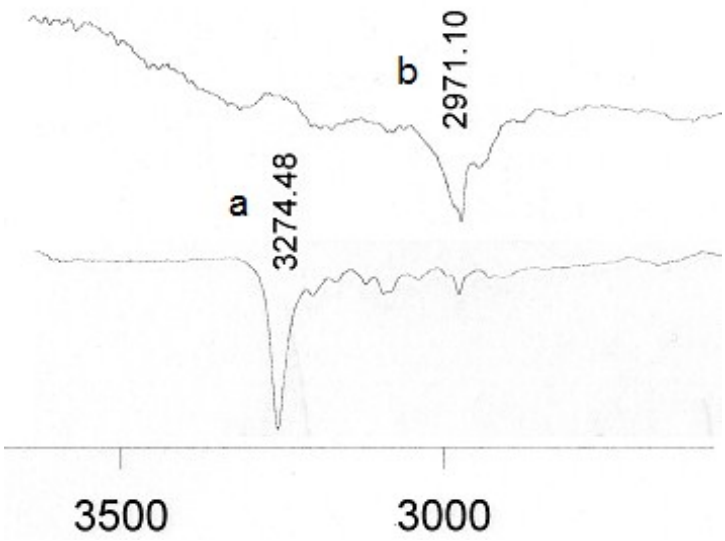

Figure 11S. NH peak appear in IR spectra of the hydrazone form **2** (DCDHF-H; a) and disappear in hydrazone anion form (DCDHF-HA; b).

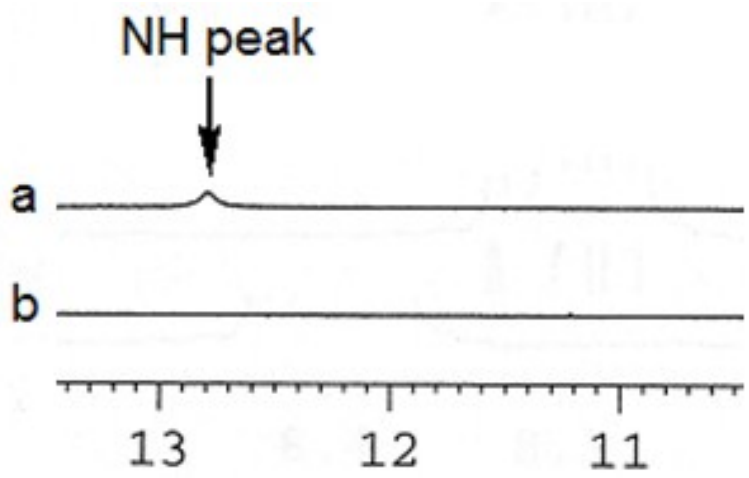

Figure 12S. NH peak appear in ^{1}H NMR spectra of both the hydrazone form **2** (DCDHF-H; a) and disappear hydrazone anion form (DCDHF-HA; b).

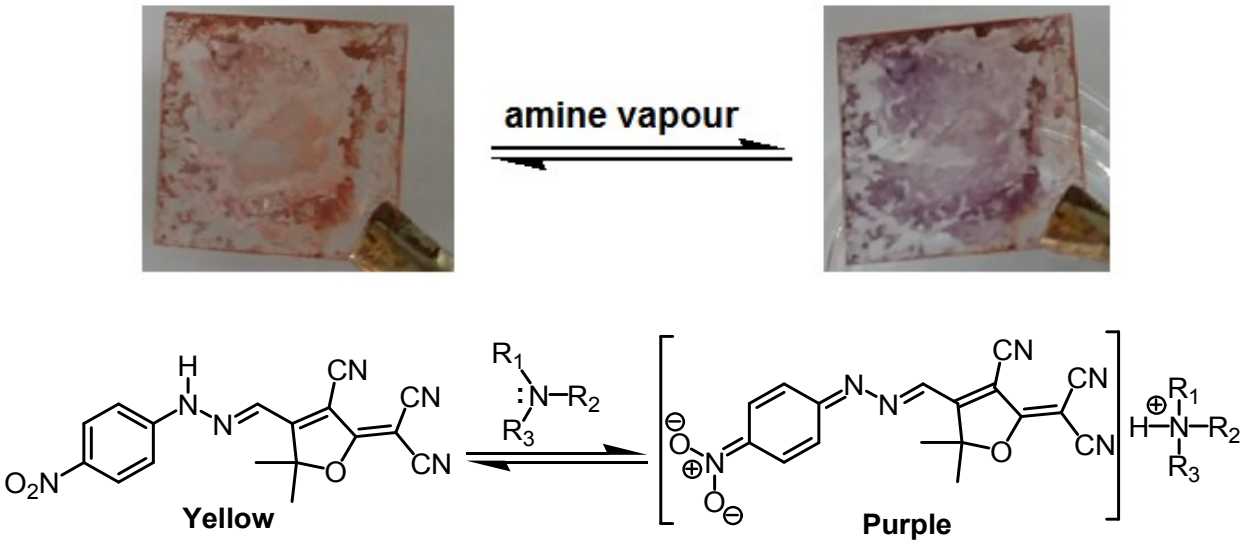

Figure 13S Solid-state reversible optical sensing nano-device changes colour from orange to purple upon exposure to amine vapour.

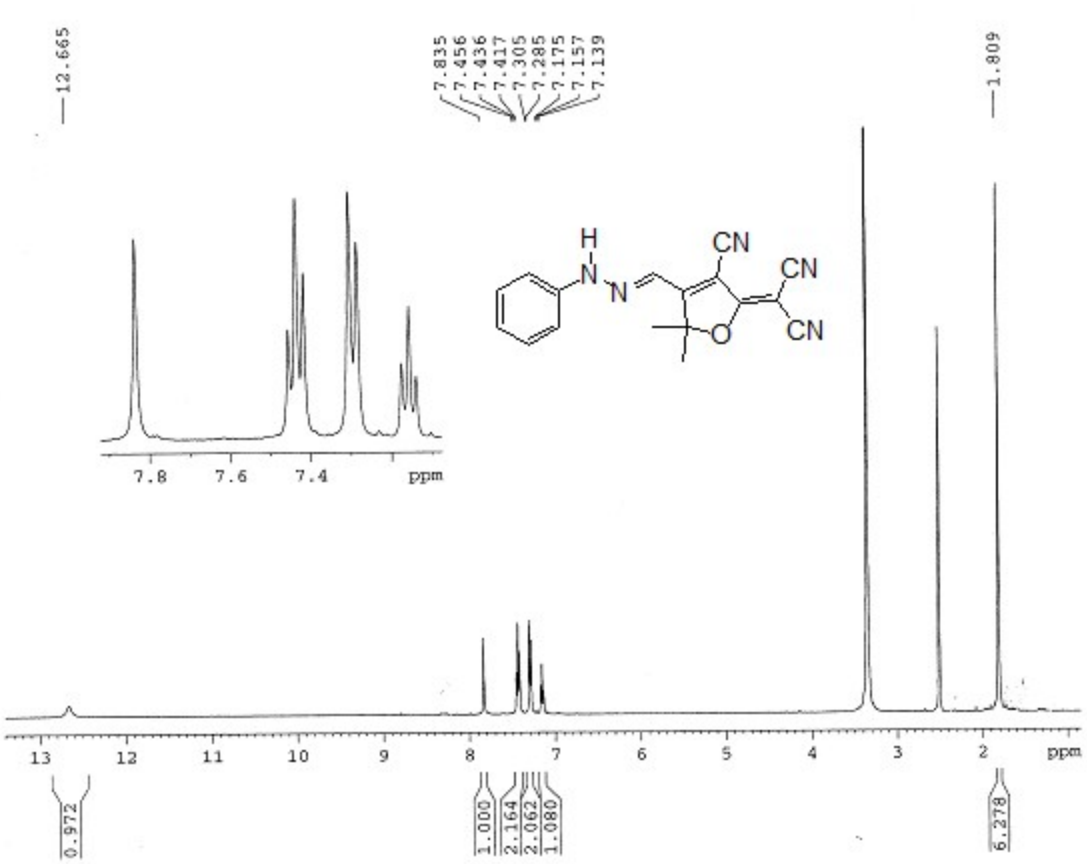

Figure 14S. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): Chromophore **1**

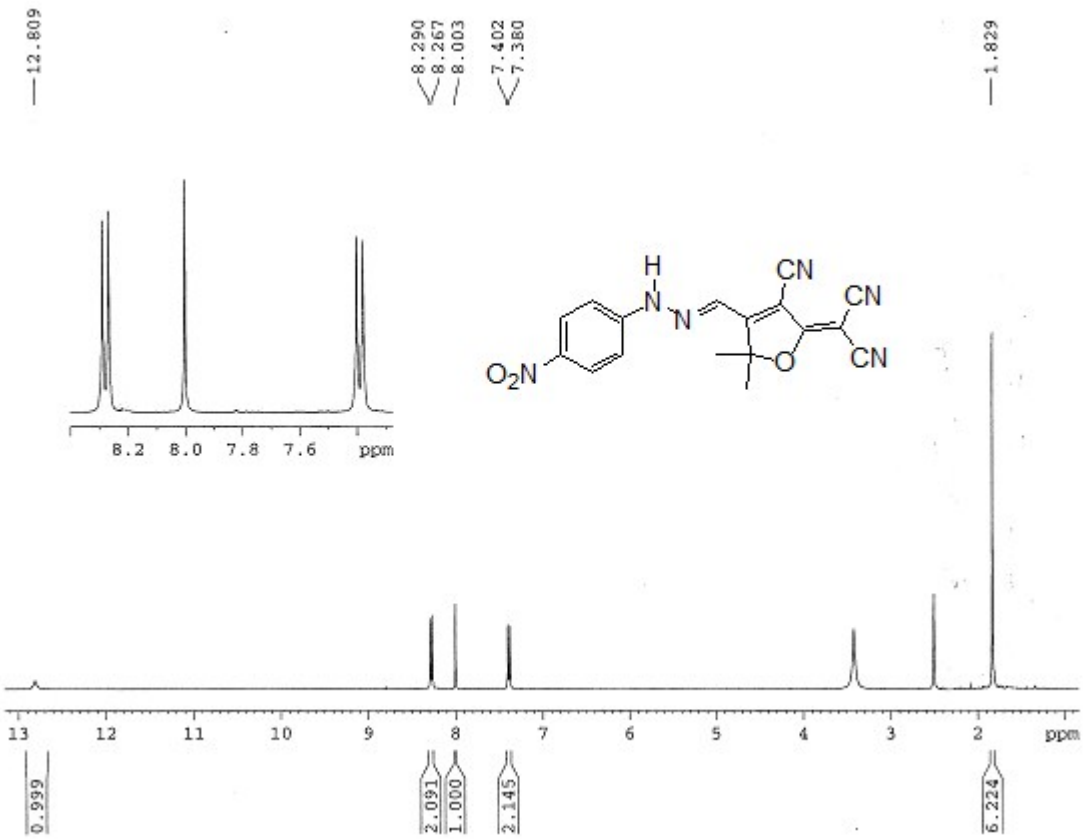

Figure 15S. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): Chromophore **2**

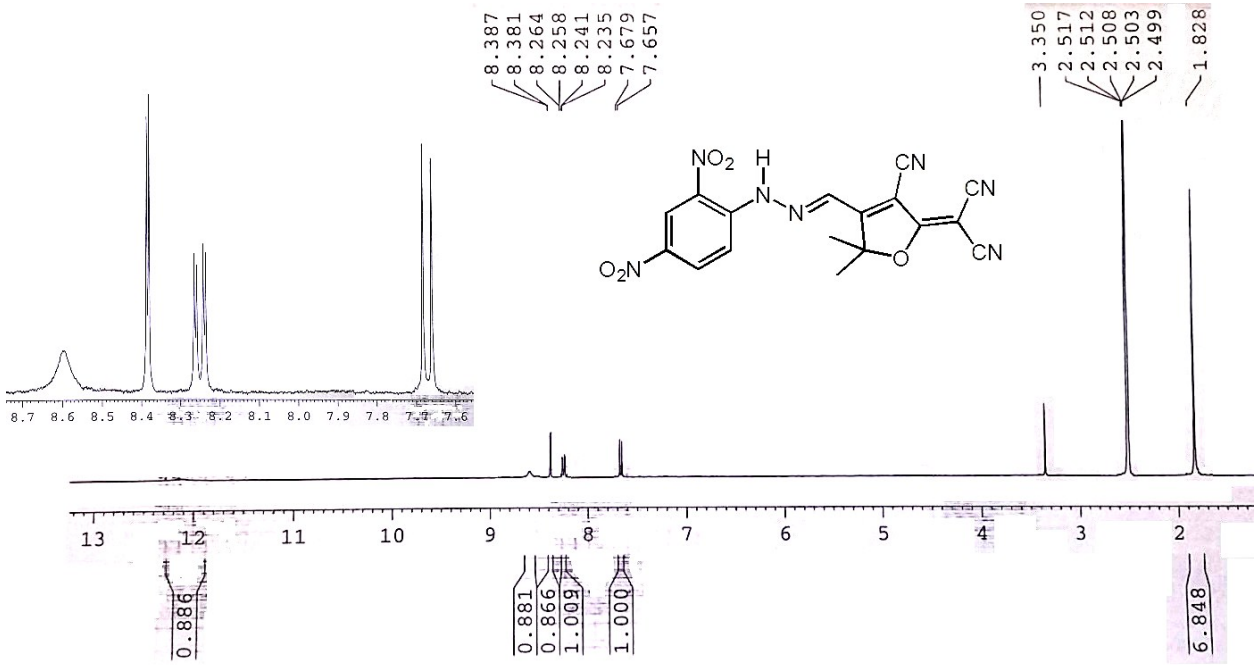

Figure 16S. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): Chromophore **3**

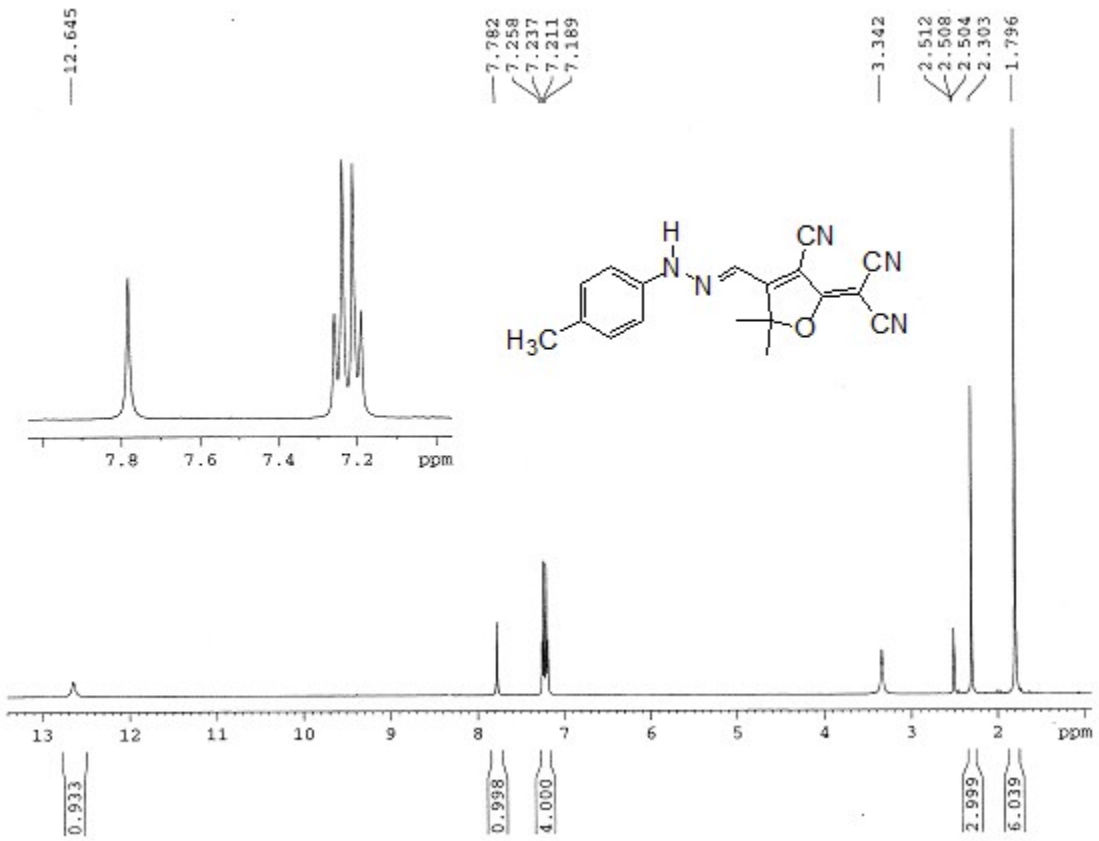

Figure 17S. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): Chromophore **4**

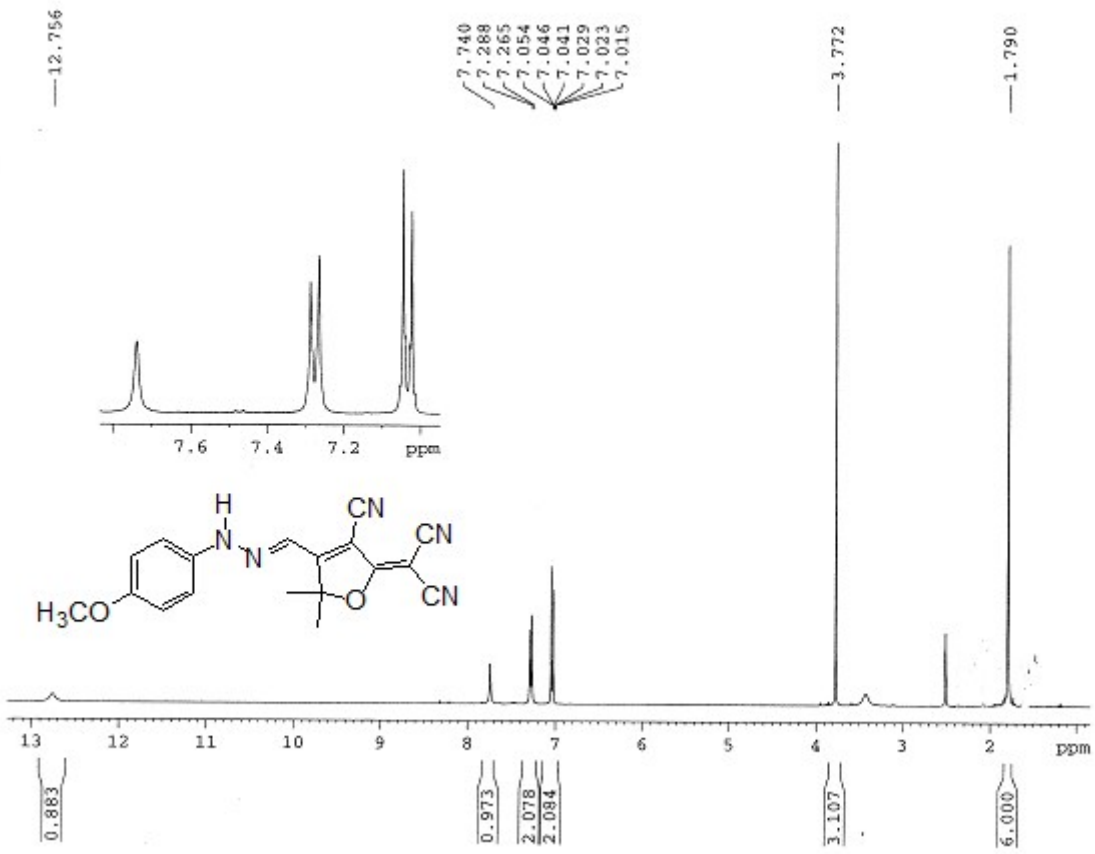

Figure 18S. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): Chromophore **5**

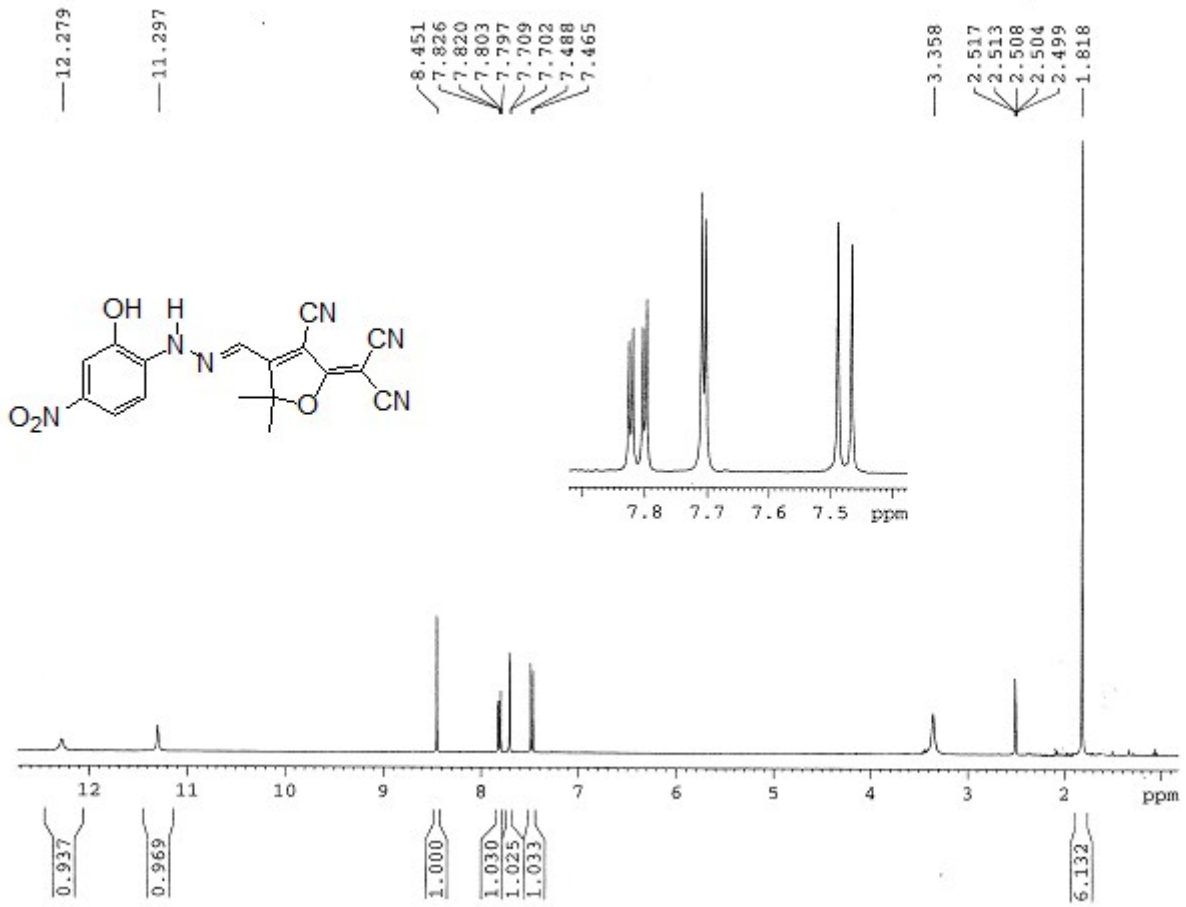

Figure 19S. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): Chromophore **6**

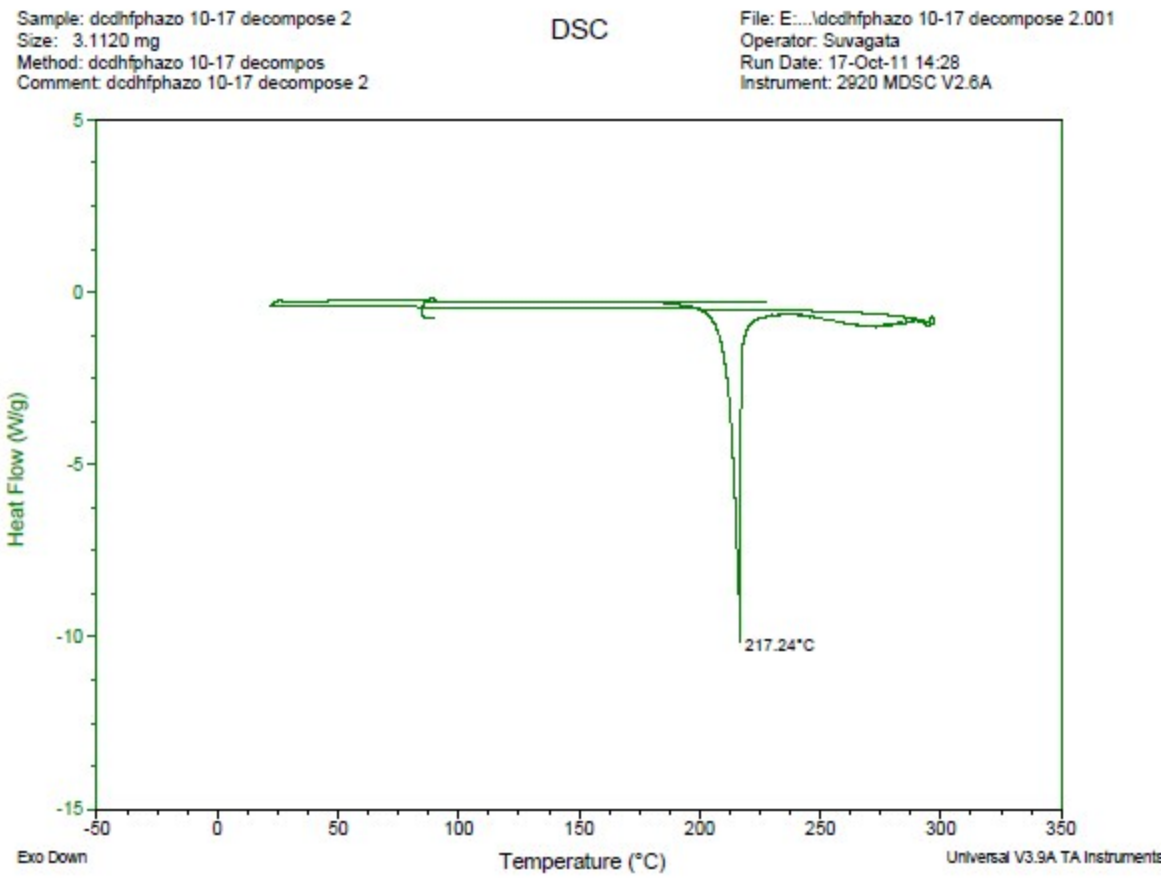

Figure 20S. DSC data for chromophore **1**.

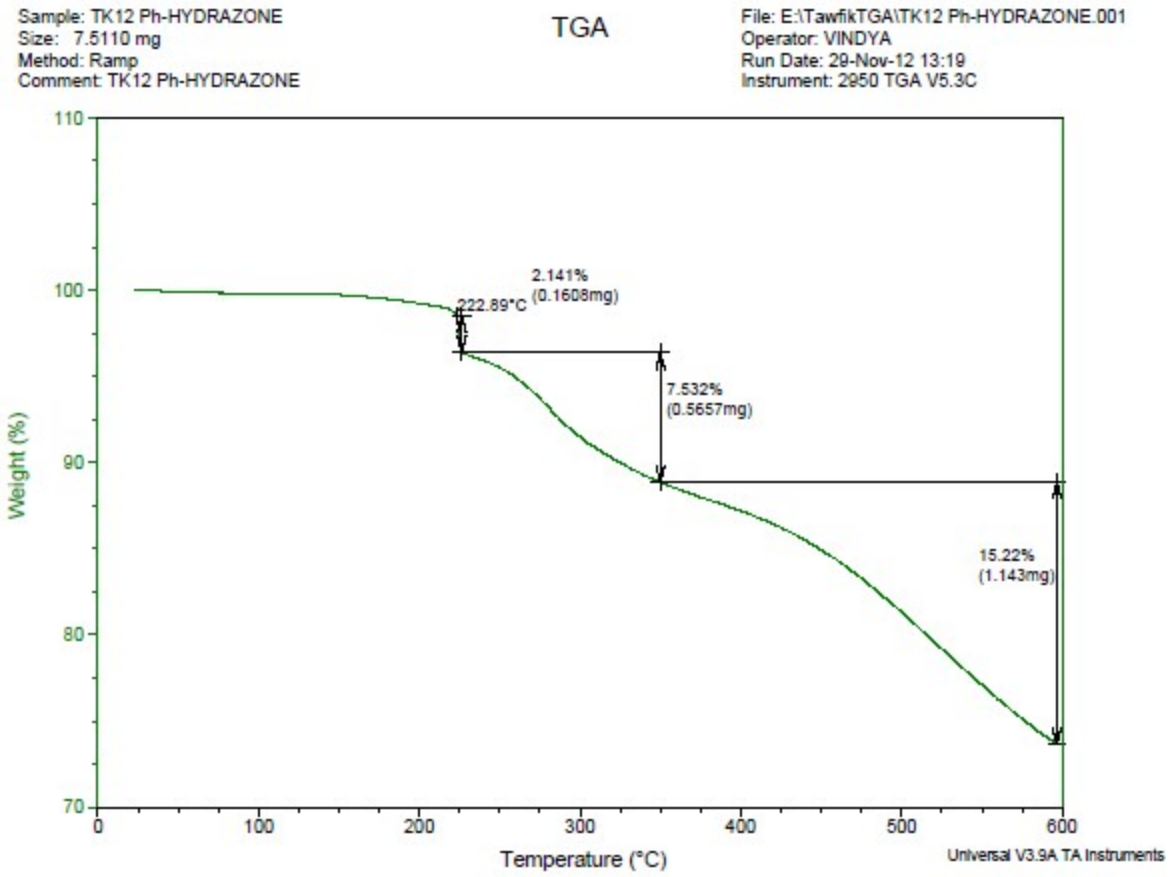

Figure 21S. TGA data for chromophore **1**.

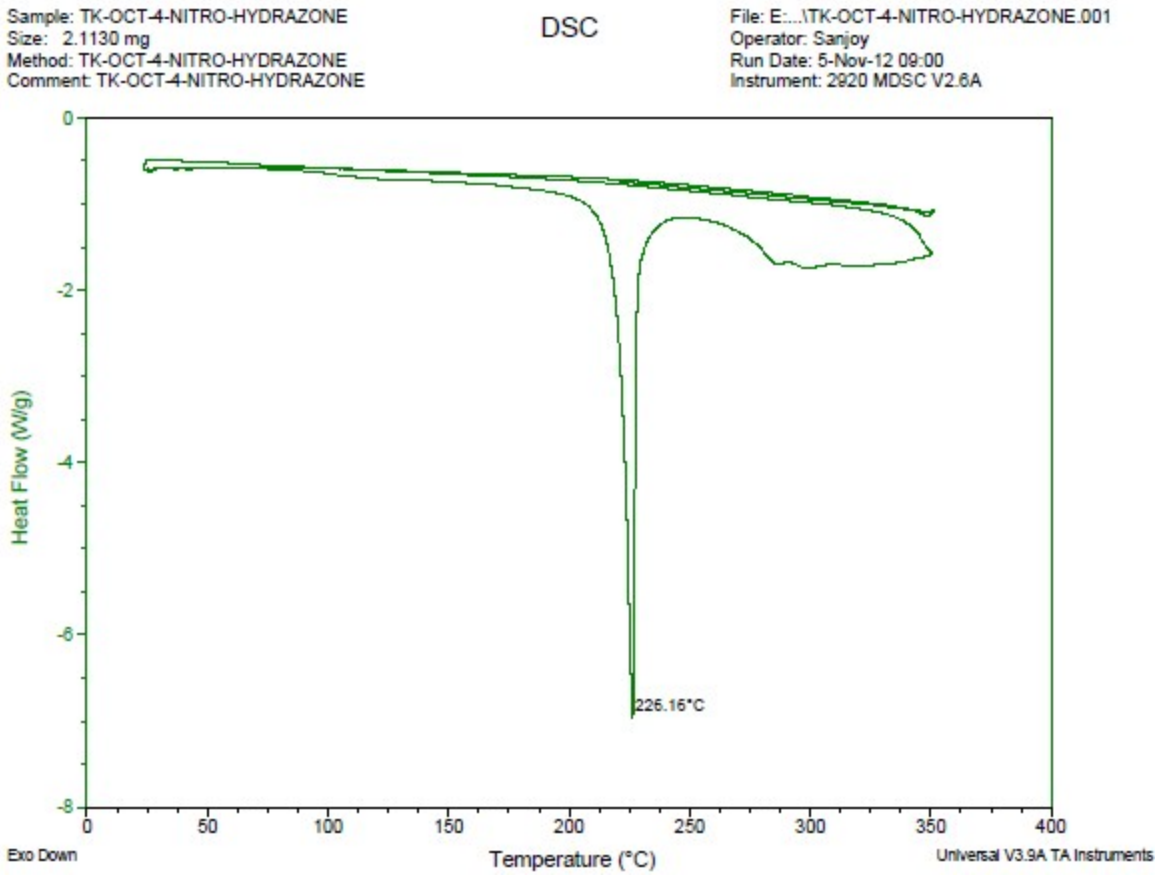

Figure 22S. DSC data for chromophore **2**.

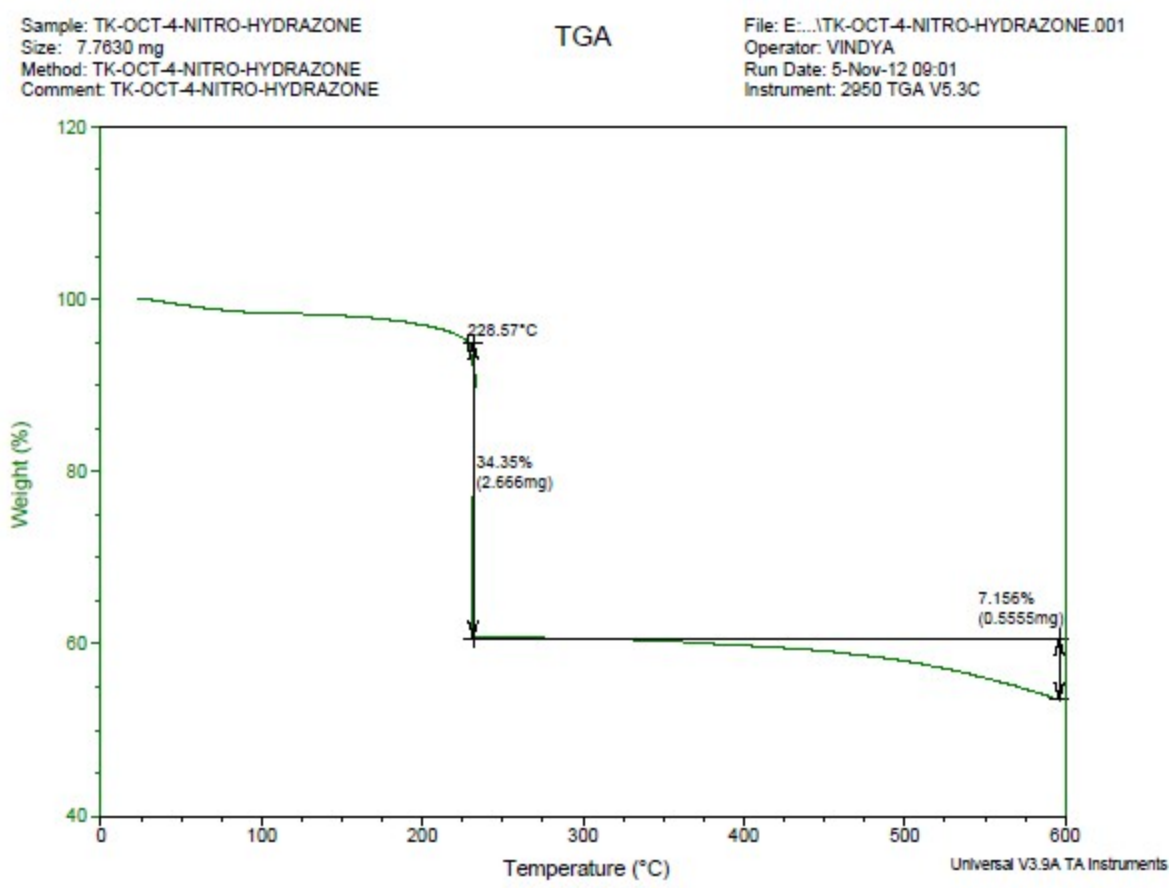

Figure 23S. TGA data for chromophore **2**.

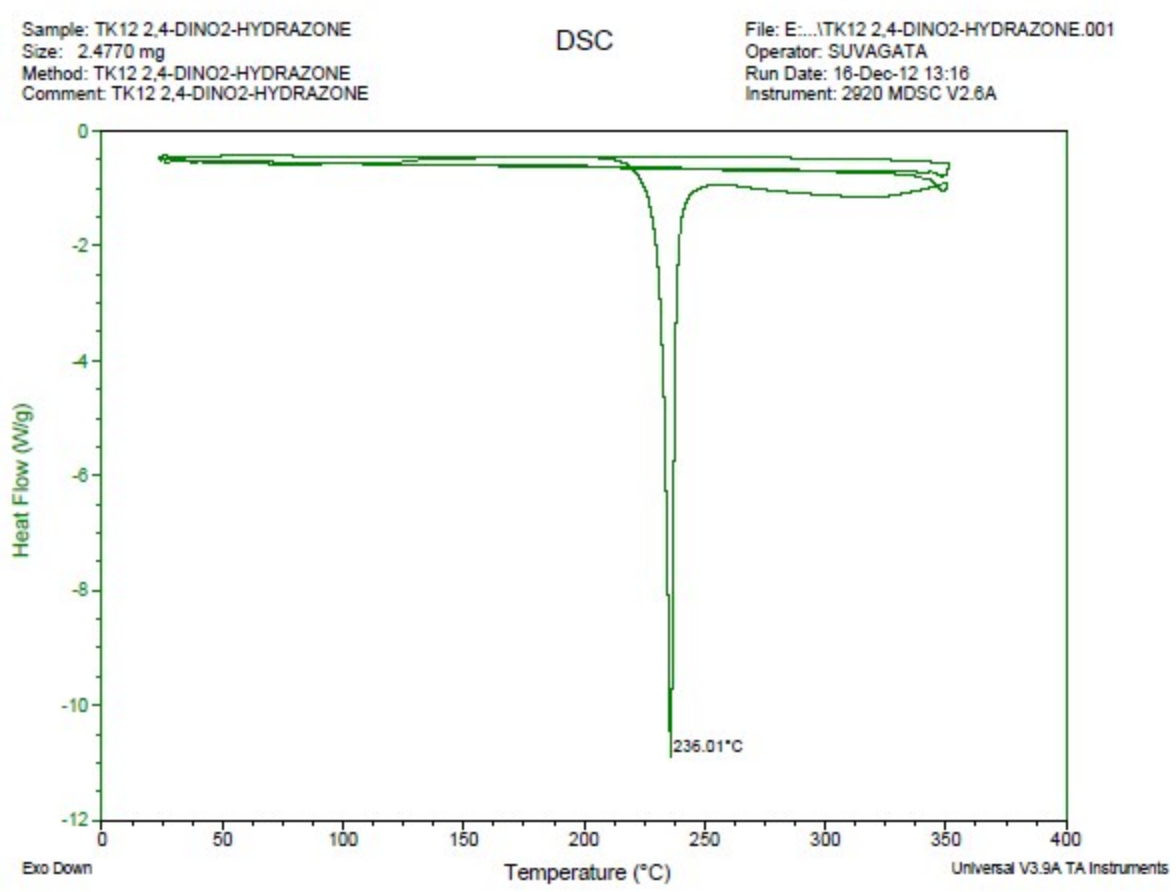

Figure 24S. DSC data for chromophore **3**.

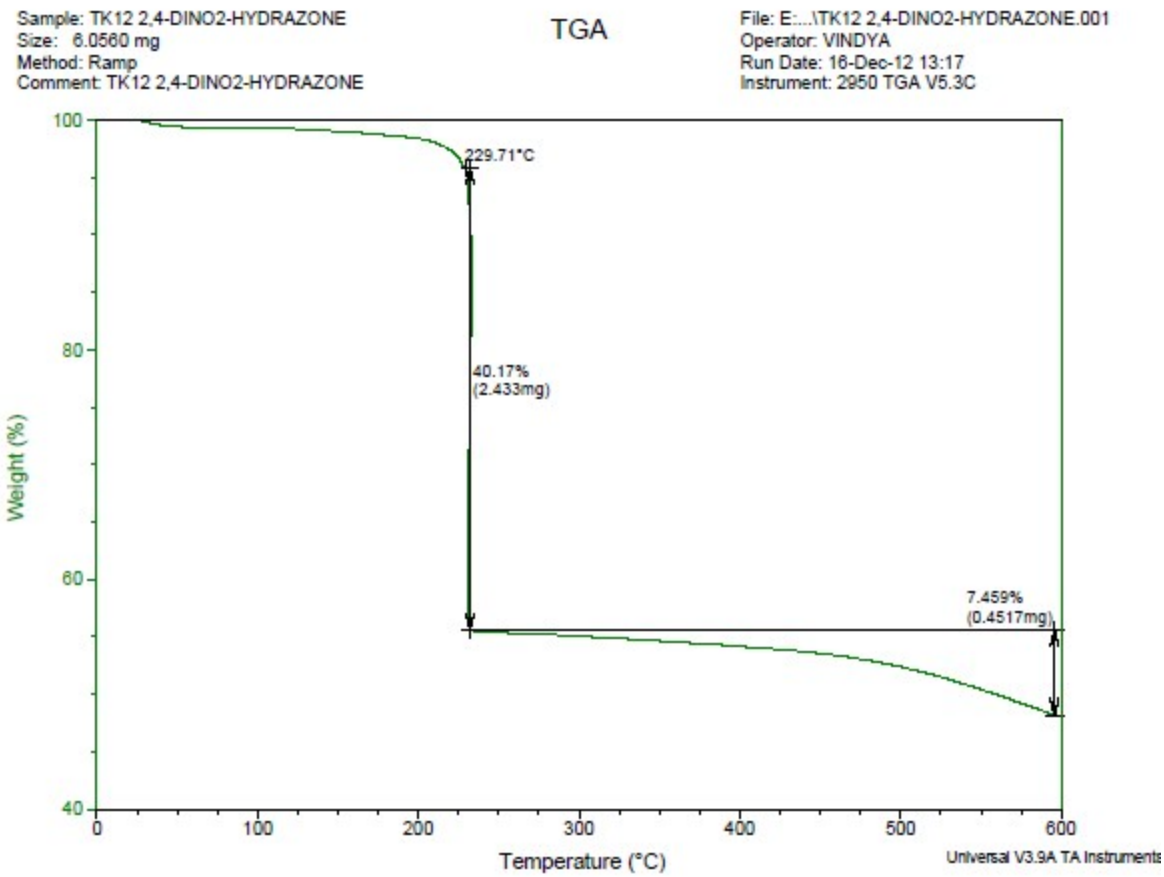

Figure 25S. TGA data for chromophore **3**.

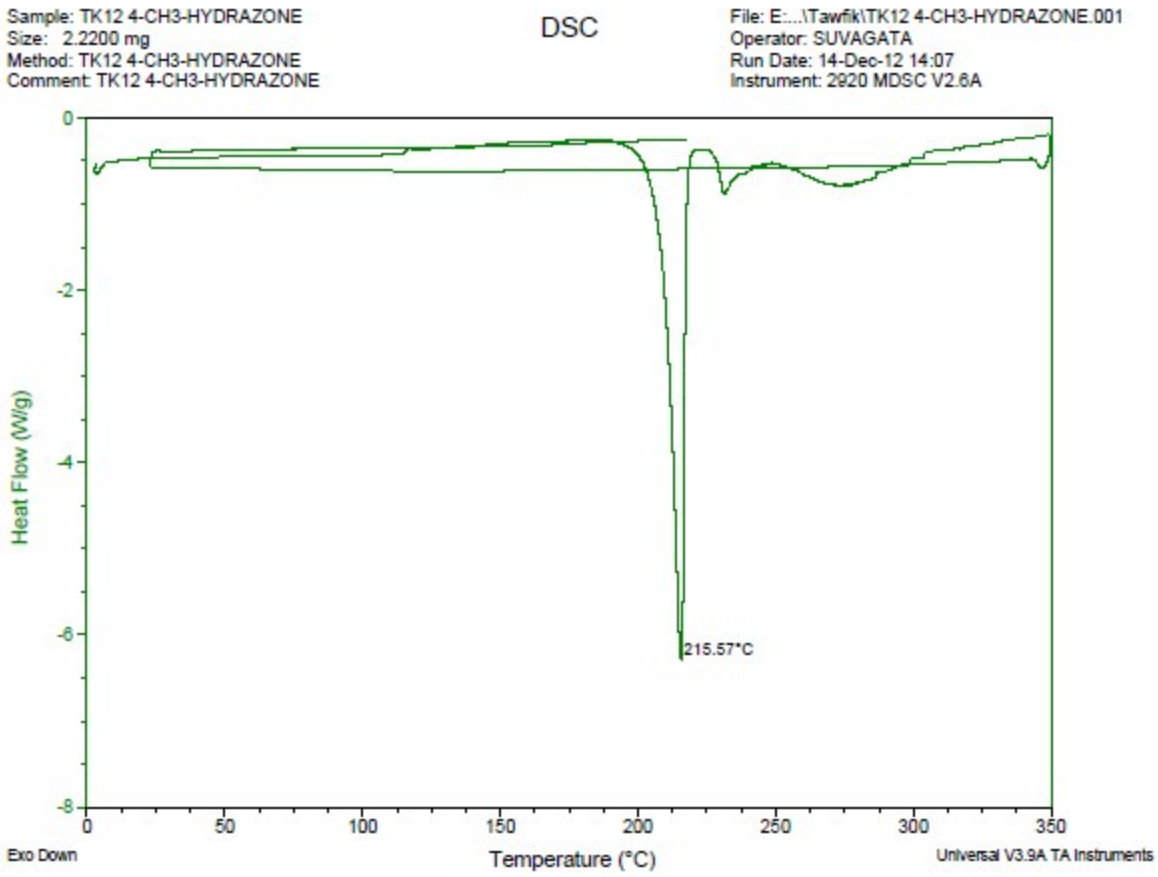

Figure 26S. DSC data for chromophore **4**.

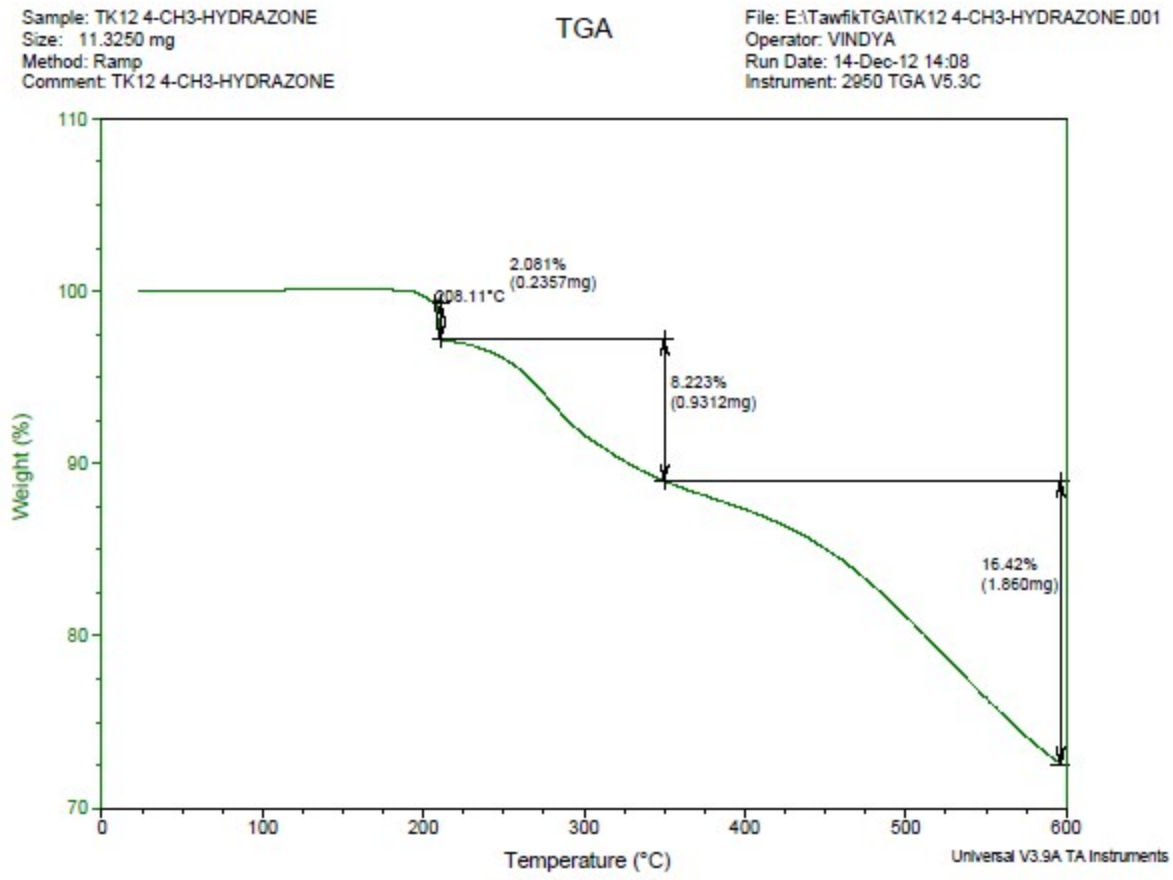

Figure 27S. TGA data for chromophore **4**.

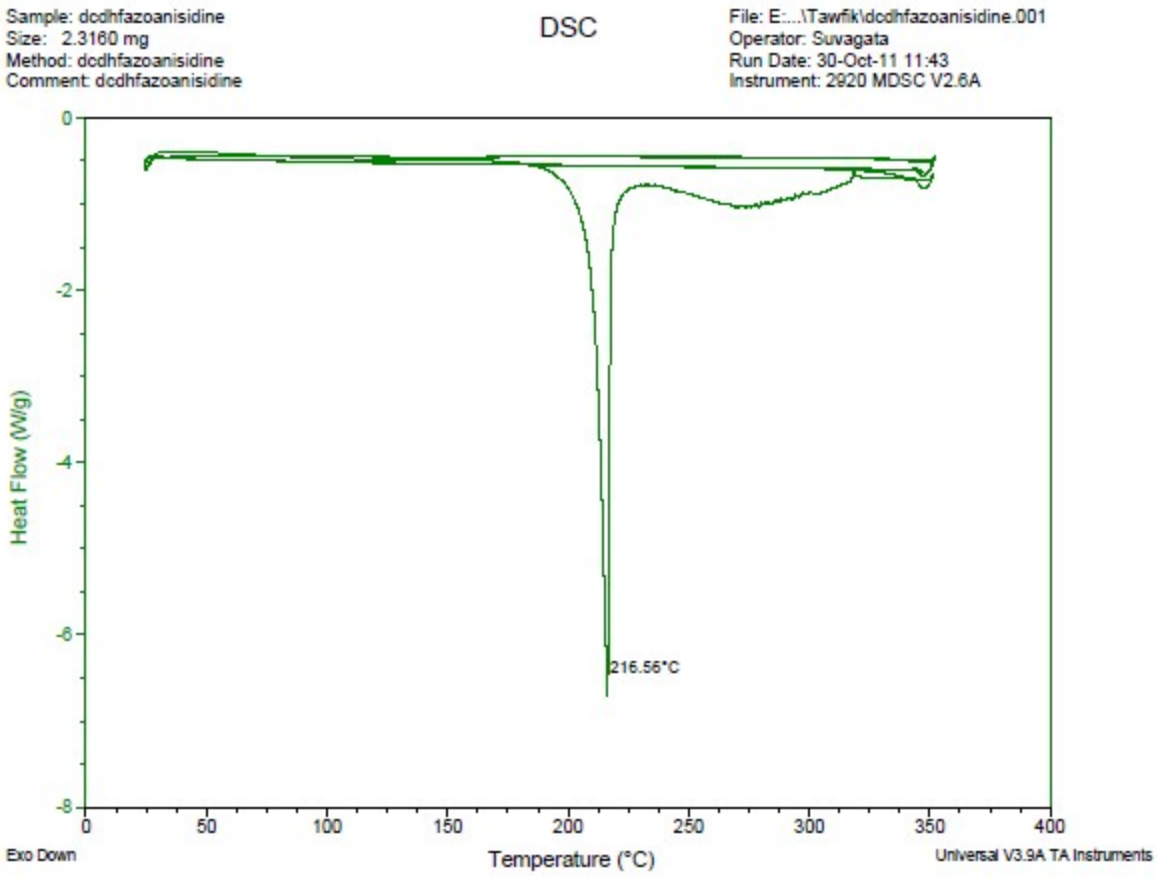

Figure 28S. DSC data for chromophore **5**.

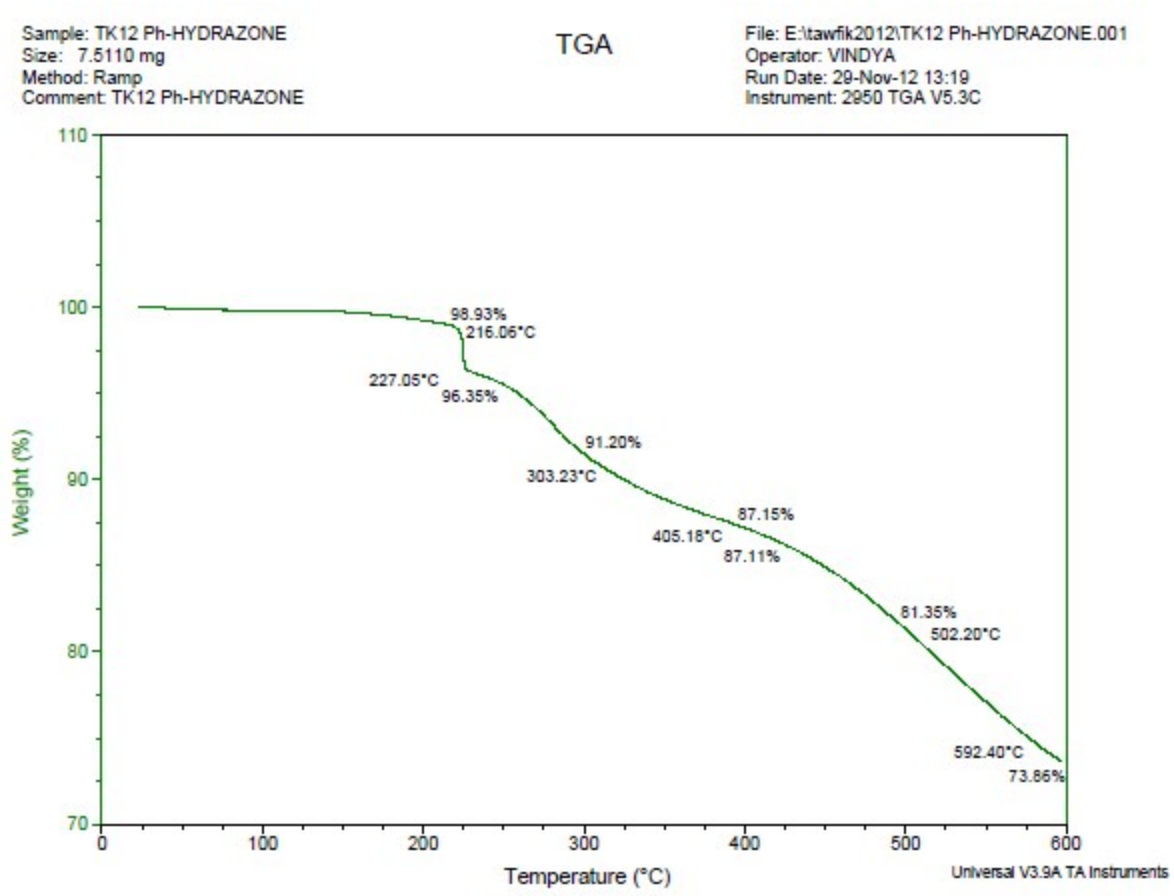

Figure 29S. TGA data for chromophore **5**.

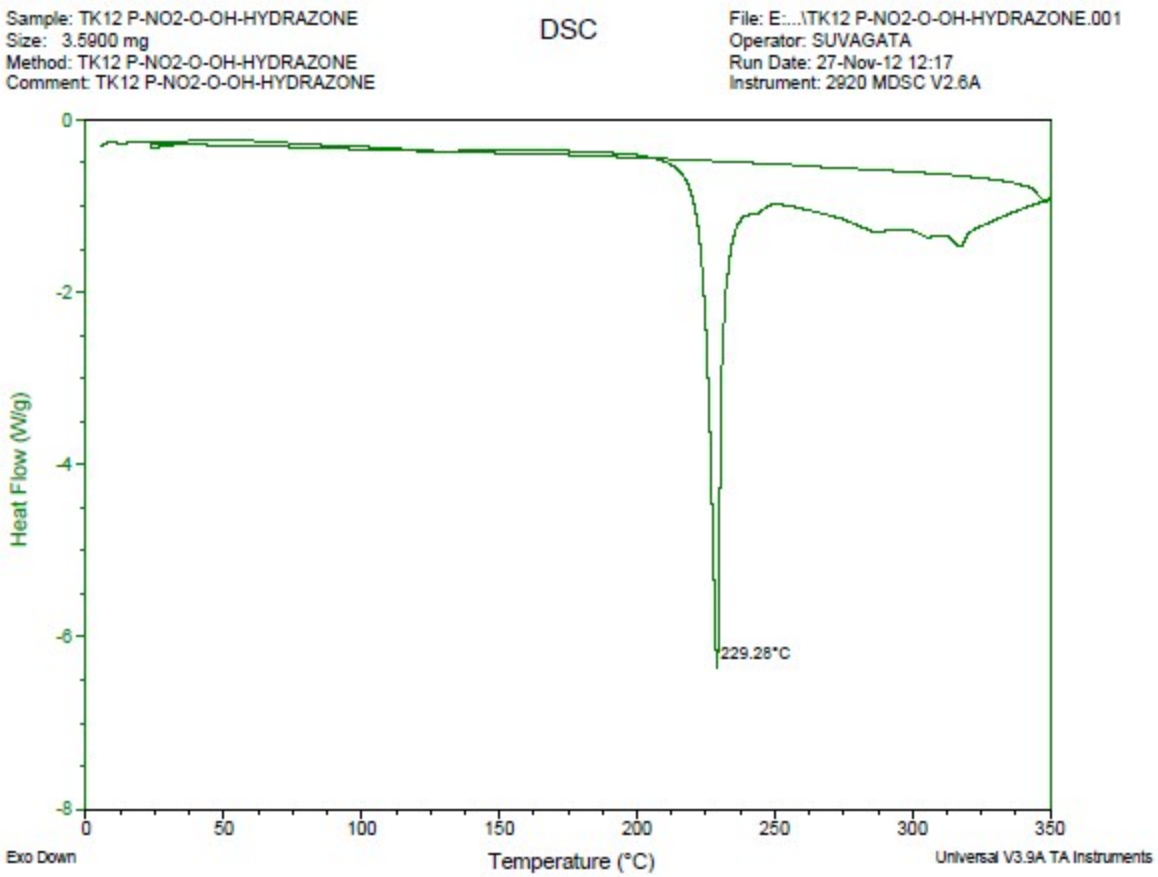

Figure 30S. DSC data for chromophore **6**.

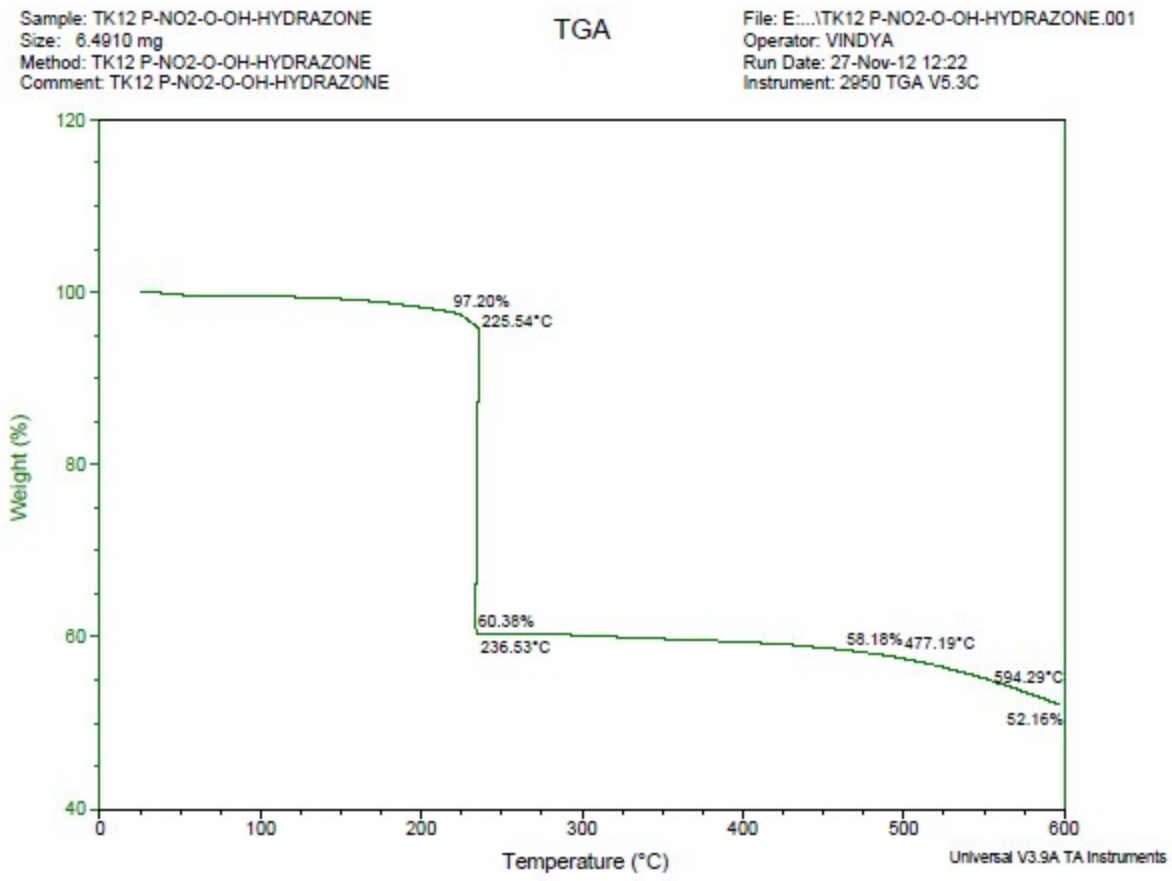

Figure 31S. TGA data for chromophore **6**.

X-ray crystal structure information:

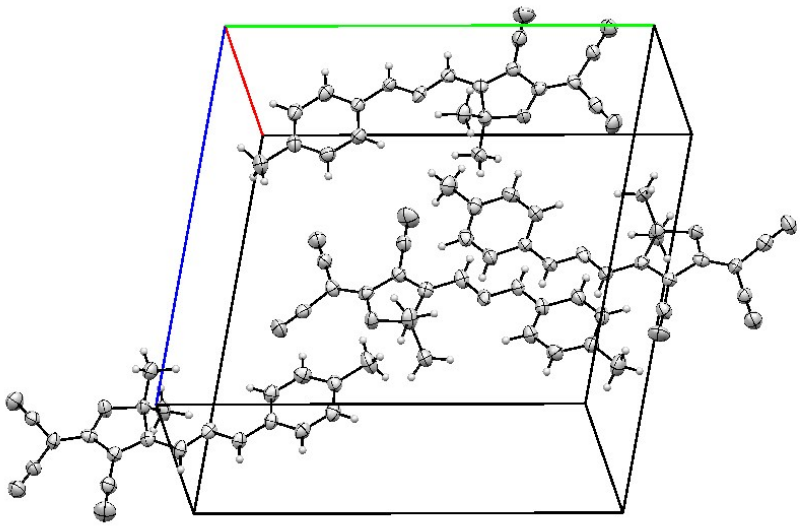

Figure 32S. Crystal packing diagram of DCDHF-H **4**.

Table 6S. Crystal data and structure refinement for DCDHF-H **4**.

Empirical formula	C_{18} H_{15} N_5 O
Formula weight	317.13
Temperature	188(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 6.8827(10) A alpha = 90 deg.
	b = 16.544(2) A beta = 90 deg.
	c = 17.510(2) A gamma = 90 deg.
Volume	1993.9(5) A^3
Z, Calculated density	4, 1.257 Mg/m^3
Absorption coefficient	0.084 mm^-1
F(000)	800
Crystal size	0.10 x 0.10 x 0.10 mm
Theta range for data collection	1.69 to 25.04 deg.
Limiting indices	-8<=h<=8, -19<=k<=19, -20<=l<=20
Reflections collected / unique	16132 / 3535 [R(int) = 0.0671]
Completeness to theta = 25.04	100.0 %
Absorption correction	None
Max. and min. transmission	0.9916 and 0.9916
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3535 / 0 / 220
Goodness-of-fit on F^2	0.947
Final R indices [I>2sigma(I)]	R1 = 0.0603, wR2 = 0.1529
R indices (all data)	R1 = 0.0870, wR2 = 0.1681
Absolute structure parameter	-2(3)
Largest diff. peak and hole	0.209 and -0.164 e.A^-3

Table 7S. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for DCDHF-H **4**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	6837(4)	6429(1)	428(1)	40(1)
N(1)	6857(4)	3161(1)	-420(1)	33(1)
N(2)	6851(4)	3903(2)	-160(2)	36(1)
N(3)	6827(6)	8558(2)	629(2)	53(1)
N(4)	6487(5)	8088(2)	-1794(2)	52(1)
N(5)	6902(6)	6000(2)	-2266(2)	64(1)
C(1)	6919(7)	479(2)	1654(2)	59(1)
C(2)	6933(6)	1184(2)	1105(2)	41(1)
C(3)	6802(6)	1083(2)	311(2)	43(1)
C(4)	6784(6)	1720(2)	-184(2)	42(1)
C(5)	7073(6)	1987(2)	1365(2)	43(1)
C(6)	7066(6)	2638(2)	876(2)	40(1)
C(7)	6890(6)	2506(2)	99(2)	34(1)
C(8)	6841(5)	4500(2)	-654(2)	38(1)
C(9)	6839(5)	5295(2)	-367(2)	34(1)
C(10)	6833(6)	5535(2)	470(2)	37(1)
C(11)	4983(5)	5278(2)	888(2)	47(1)
C(12)	8681(5)	5303(2)	907(2)	46(1)
C(13)	6767(5)	5998(2)	-797(2)	35(1)
C(14)	6827(6)	6674(2)	-293(2)	34(1)
C(15)	6757(6)	7483(2)	-445(2)	37(1)
C(16)	6770(6)	8072(2)	164(2)	38(1)
C(17)	6632(6)	7806(2)	-1192(2)	39(1)
C(18)	6790(6)	6008(2)	-1616(2)	42(1)

Table 8S. Bond lengths [A] and angles [deg] for DCDHF-H **4**.

O(1)-C(14)	1.324(3)
O(1)-C(10)	1.481(3)
N(1)-N(2)	1.311(3)
N(1)-C(7)	1.414(4)
N(1)-H(1)	0.8800
N(2)-C(8)	1.312(4)
N(3)-C(16)	1.146(4)
N(4)-C(17)	1.158(4)
N(5)-C(18)	1.139(4)
C(1)-C(2)	1.512(5)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.403(5)
C(2)-C(5)	1.408(4)
C(3)-C(4)	1.364(4)
C(3)-H(3)	0.9500
C(4)-C(7)	1.394(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.376(5)
C(5)-H(5)	0.9500
C(6)-C(7)	1.383(4)
C(6)-H(6)	0.9500
C(8)-C(9)	1.407(4)
C(8)-H(8)	0.9500
C(9)-C(13)	1.388(4)
C(9)-C(10)	1.519(4)
C(10)-C(11)	1.529(5)
C(10)-C(12)	1.533(5)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.425(4)
C(13)-C(18)	1.436(4)
C(14)-C(15)	1.366(4)
C(15)-C(17)	1.414(5)
C(15)-C(16)	1.444(5)
C(14)-O(1)-C(10)	110.8(2)
N(2)-N(1)-C(7)	119.6(2)
N(2)-N(1)-H(1)	120.2
C(7)-N(1)-H(1)	120.2
N(1)-N(2)-C(8)	118.4(3)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5

C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-C(5)	115.9(3)
C(3)-C(2)-C(1)	122.5(3)
C(5)-C(2)-C(1)	121.6(3)
C(4)-C(3)-C(2)	122.6(3)
C(4)-C(3)-H(3)	118.7
C(2)-C(3)-H(3)	118.7
C(3)-C(4)-C(7)	119.6(3)
C(3)-C(4)-H(4)	120.2
C(7)-C(4)-H(4)	120.2
C(6)-C(5)-C(2)	122.5(3)
C(6)-C(5)-H(5)	118.8
C(2)-C(5)-H(5)	118.8
C(5)-C(6)-C(7)	119.3(3)
C(5)-C(6)-H(6)	120.4
C(7)-C(6)-H(6)	120.4
C(6)-C(7)-C(4)	120.1(3)
C(6)-C(7)-N(1)	120.8(3)
C(4)-C(7)-N(1)	119.1(3)
N(2)-C(8)-C(9)	117.9(3)
N(2)-C(8)-H(8)	121.1
C(9)-C(8)-H(8)	121.1
C(13)-C(9)-C(8)	126.2(3)
C(13)-C(9)-C(10)	107.7(3)
C(8)-C(9)-C(10)	126.1(3)
O(1)-C(10)-C(9)	102.2(2)
O(1)-C(10)-C(11)	107.7(3)
C(9)-C(10)-C(11)	113.1(3)
O(1)-C(10)-C(12)	105.8(3)
C(9)-C(10)-C(12)	114.5(3)
C(11)-C(10)-C(12)	112.5(3)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(9)-C(13)-C(14)	108.7(3)
C(9)-C(13)-C(18)	123.5(3)
C(14)-C(13)-C(18)	127.6(3)
O(1)-C(14)-C(15)	119.1(3)
O(1)-C(14)-C(13)	110.5(3)
C(15)-C(14)-C(13)	130.3(3)
C(14)-C(15)-C(17)	123.6(3)
C(14)-C(15)-C(16)	121.0(3)
C(17)-C(15)-C(16)	115.4(3)

N(3)-C(16)-C(15)	177.2(4)
N(4)-C(17)-C(15)	177.8(4)
N(5)-C(18)-C(13)	176.5(5)

Symmetry transformations used to generate equivalent atoms:

Table 9S. Anisotropic displacement parameters (A^2 x 10^3) for DCDHF-H **4**.

The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	58(2)	29(1)	33(1)	1(1)	-10(1)	-2(1)
N(1)	36(1)	30(1)	34(1)	-6(1)	-6(2)	-2(2)
N(2)	28(1)	33(2)	48(2)	-10(1)	0(2)	-6(2)
N(3)	68(2)	42(2)	48(2)	-14(2)	2(2)	-5(2)
N(4)	68(2)	47(2)	42(2)	3(2)	3(2)	-3(2)
N(5)	84(3)	74(2)	35(2)	-4(2)	-13(2)	2(3)
C(1)	74(3)	40(2)	63(3)	13(2)	-6(3)	-10(2)
C(2)	42(2)	33(2)	48(2)	3(2)	2(2)	-2(2)
C(3)	38(2)	35(2)	56(2)	-5(2)	-4(2)	-3(2)
C(4)	46(2)	36(2)	43(2)	-10(2)	0(2)	0(2)
C(5)	47(2)	48(2)	34(2)	-5(2)	-5(2)	-5(2)
C(6)	45(2)	35(2)	40(2)	-6(2)	-5(2)	0(2)
C(7)	33(2)	30(2)	39(2)	-3(1)	-6(2)	1(2)
C(8)	37(2)	33(2)	44(2)	-4(2)	-11(2)	6(2)
C(9)	28(2)	35(2)	37(2)	1(1)	-4(2)	1(2)
C(10)	49(2)	26(2)	36(2)	0(1)	3(2)	-1(2)
C(11)	55(2)	36(2)	51(2)	-7(2)	8(2)	1(2)
C(12)	57(3)	38(2)	44(2)	8(2)	-16(2)	5(2)
C(13)	35(2)	36(2)	33(2)	-2(1)	-3(2)	1(2)
C(14)	31(2)	42(2)	31(2)	0(1)	0(2)	-7(2)
C(15)	39(2)	32(2)	39(2)	0(1)	-5(2)	8(2)
C(16)	36(2)	39(2)	39(2)	7(2)	6(2)	0(2)
C(17)	47(2)	34(2)	35(2)	3(2)	2(2)	2(2)
C(18)	50(2)	36(2)	42(2)	-4(2)	1(2)	-7(2)

Table 10S. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for DCDHF-H **4**.

	x	y	z	U(eq)
H(1)	6841	3070	-916	40
H(1A)	8175	200	1632	88
H(1B)	5882	102	1511	88
H(1C)	6693	677	2174	88
H(3)	6722	551	110	51
H(4)	6699	1627	-719	50
H(5)	7176	2084	1898	52
H(6)	7181	3172	1069	48
H(8)	6836	4399	-1188	45
H(11A)	4977	5512	1403	71
H(11B)	4941	4687	925	71
H(11C)	3845	5470	605	71
H(12A)	9789	5603	698	70
H(12B)	8915	4722	854	70
H(12C)	8522	5438	1449	70

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