Electronic Supporting information

All-in-one Type ESIPT-Active Multi-Stimuli Responsive *7*-Diethylamino-*4*-hydroxycoumarin-Rhodamine B Hydrazone as Molecular Switches and Reversible Photochromic Features of Its Zinc Ensemble

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Materials and methods

Rhodamine B dye was purchased from Avra synthesis. 3-*N,N*-diethylaminophenol, $POCl_3$ and malonic acid were purchased from Sigma Aldrich. Trichloro phenol was obtained from Alfa Aesar. All the solvents used for synthesis were purchased from Thomas Baker and were used after purification by standard methods. All the nitrate, chloride and acetate metal salts were purchased from Loba chemicals and used for the reaction without further purification. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance-II 400 MHz instrument in DMSO-d_6 solvent and $CDCl_3$, TMS was utilized as an internal standard. The chemical shift values were expressed in ppm and the coupling constant values were represented in Hz (hertz). The following abbreviations such as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m) were used to denote the multiplicities. HR ESI-MS (Q-TOF) mass analyzer was used to get accurate mass spectrometric data of the compounds. Bruker Tensor 27 with KBr pellets in the solid-state was used to record FT-IR spectra of the compounds. The UV-vis absorption spectral data of the compounds were recorded using JASCO V-630 UV-visible spectrometer in the range of 200-800 nm wavelength. JASCO FP-8300 spectrofluorometer in the range of 400-800 nm wavelengths was utilized to determine the emission spectral data. 1.0 cm path length quartz cuvette was used to record the UV-vis absorption and emission spectral data. Solid-state emission data was recorded using a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. Fluorescence lifetime was measured with a Horiba DeltaFlex TCSPC system equipped with a NanoLED laser (371 nm, Pulse width <200 ps) excitation source and a PPD-850 photon detection module. The Gaussian 09W program was used for DFT calculations. 6-31G* basis set and B3LYP hybrid density functional was used to optimize the geometries. DLS (dynamic light scattering)

measurements were performed on a Malvern Zetasizer Nano ZS instrument equipped with a 4.0 mW helium–neon laser at a wavelength of 633 nm. FE-SEM images of the compounds were taken on a JEOL JSM6480LV system coupled with an energy-dispersive X-ray spectrometer.

Stock solution preparation for absorption and emission measurements

1×10^{-5} M stock solution of **DHCRH** and **CDCRH** were prepared and used for the solvent effect and acidochromism studies. For aggregation measurements, 1×10^{-3} M stock solutions was prepared in THF solvent then 500 μL of this solution transferred to separate vials and make up to 5 mL (1×10^{-4} M) by adding different water fraction from 0-99 %. The double distilled ultrapure water and THF solvents were used for aggregation studies. The same procedure was used to get the DLS data.

Stock solution preparation for photochromic studies

1×10^{-5} stock solutions of **DHCRH** and **CDCRH** were prepared in THF solvent and the same concentrations of chloride, nitrate and acetate metal salts were prepared. 10 equivalents of metal solutions were added to the bare **DHCRH** solution in separate vials and utilized for take photographic images in day light as well as UV light. For UV-visible absorption and emission measurements same procedure was followed.

Quantum yield Calculation

The fluorescence quantum yield experiment was performed by using following formula. Quinine sulfate[1] was used as a standard at 367 nm with a known ϕ value of 0.546 in 0.5 M H_2SO_4.

$$\Phi_s = \left(\frac{A_s}{A_r}\right)\left(\frac{f_s}{f_r}\right)\left(\frac{\eta_r^2}{\eta_r^2}\right)\Phi_r$$

Where, Φ_s and Φ_r are fluorescence quantum yield of sample and reference respectively. A_s and A_r are the area under the curve of sample and reference emission spectrum. The terms f_s and f_r represent the absorption optical density value for sample and reference while η is the refractive index of the solvent

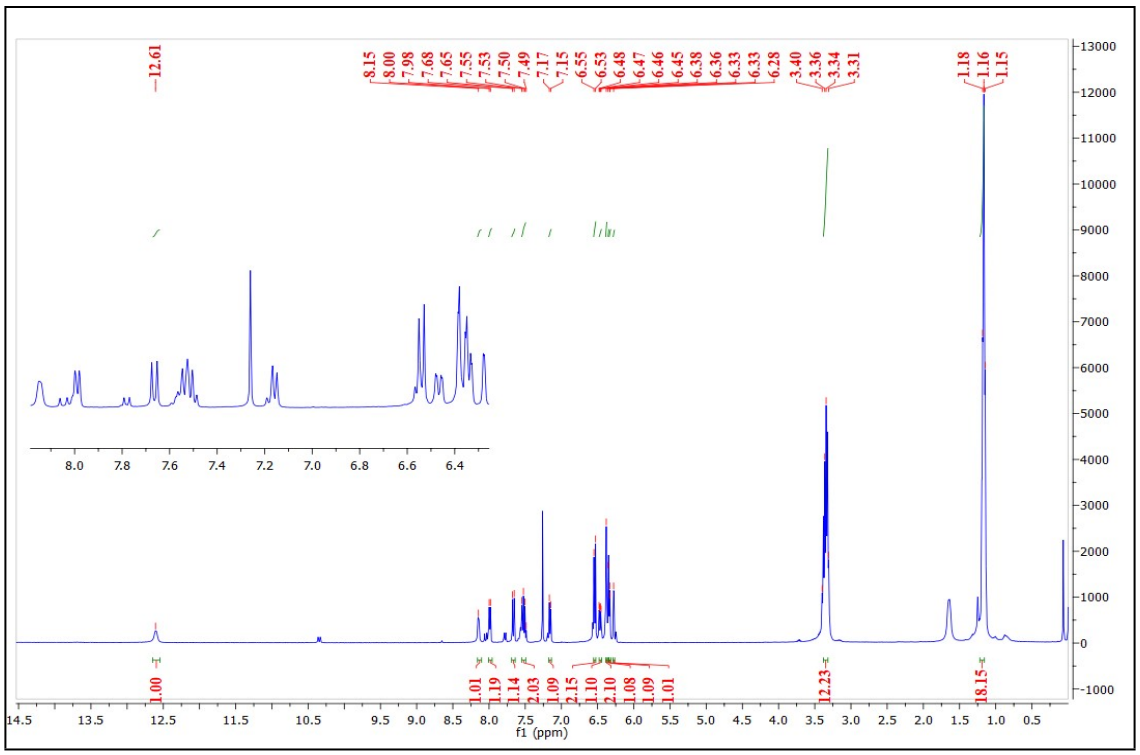

Figure S1. ^{1}H NMR spectra of **DHCRH**.

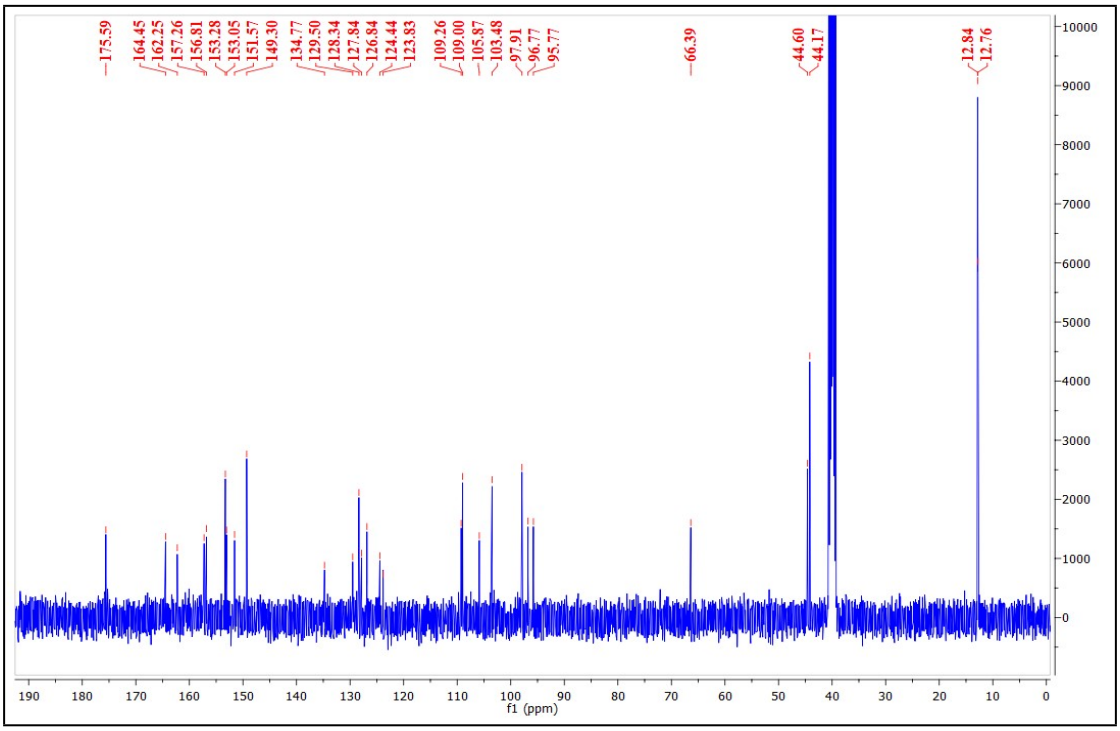

Figure S2. ^{13}C NMR spectra of **DHCRH**.

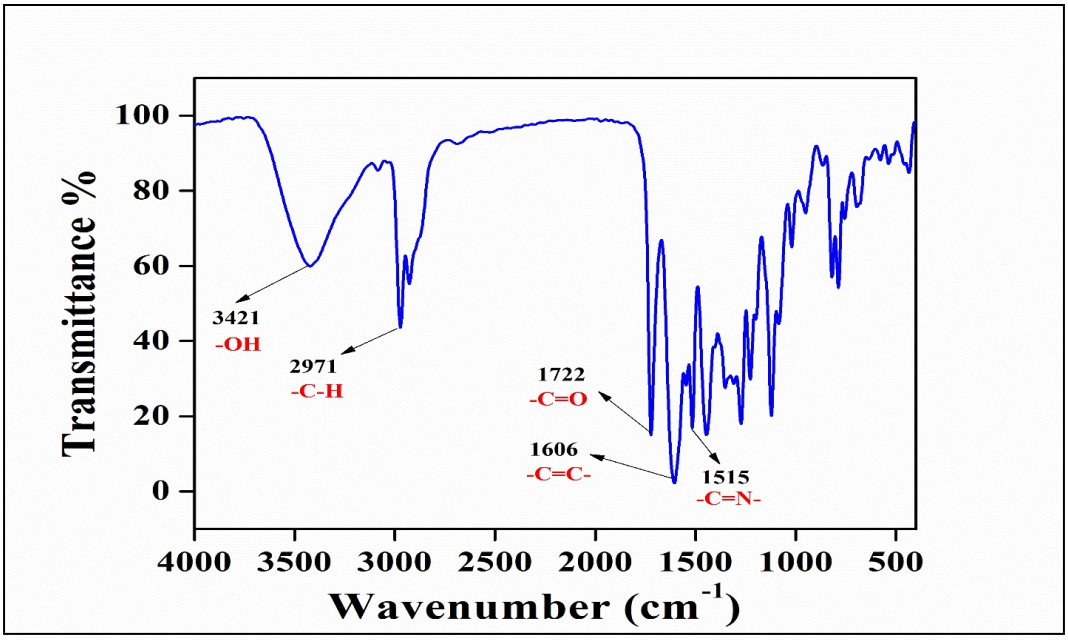

Figure S3. FT-IR spectra of **DHCRH**.

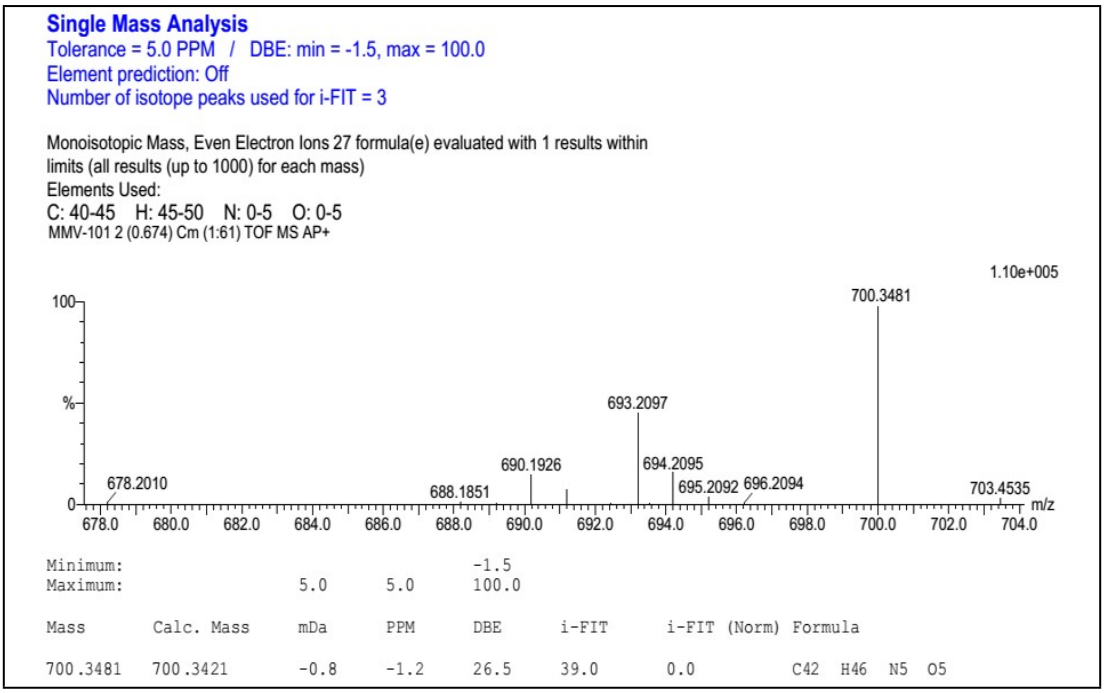

Figure S4. Mass spectra of **DHCRH**.

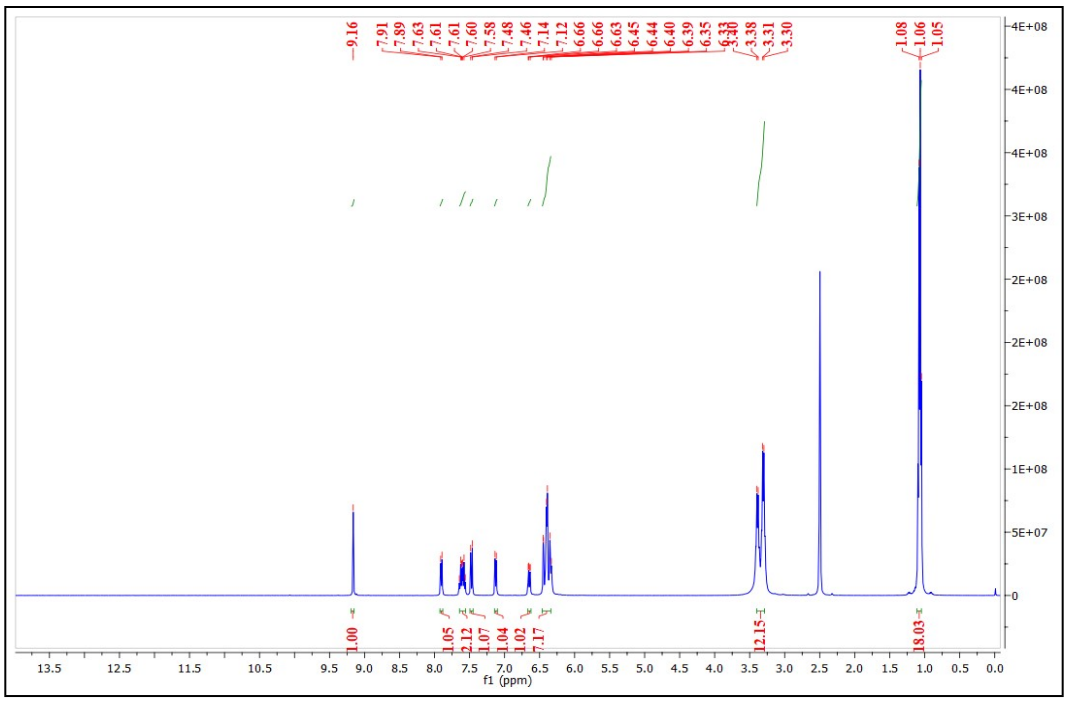

Figure S5. ^{1}H NMR spectra of **CDCRH**.

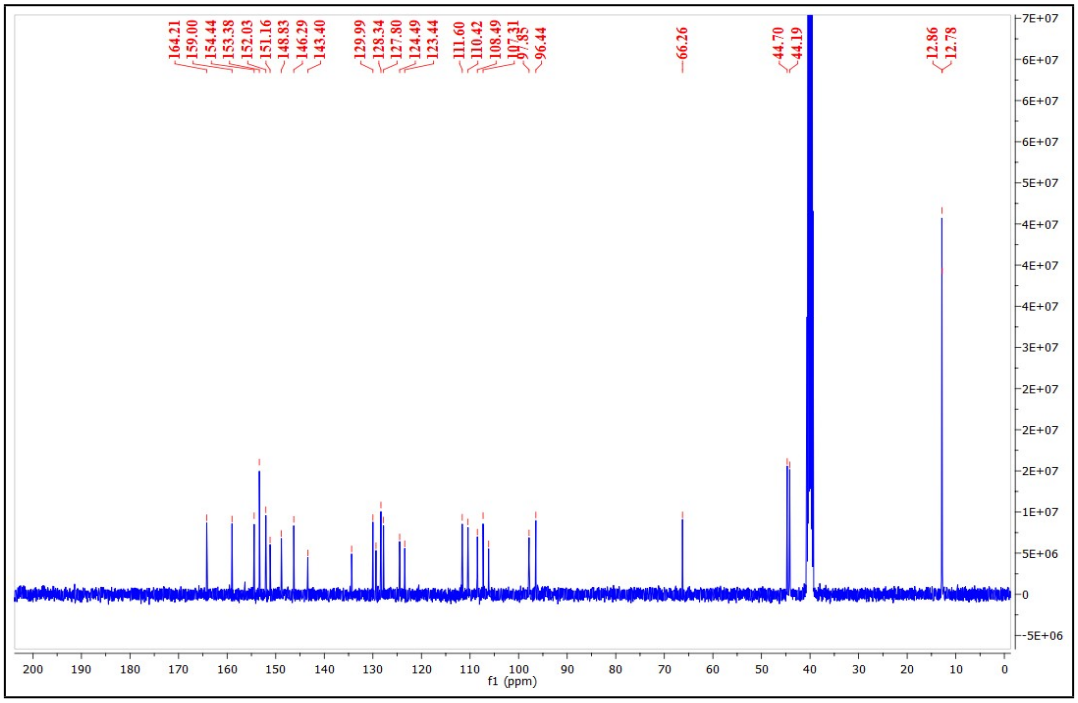

Figure S6. ^{13}C NMR spectra of **CDCRH**.

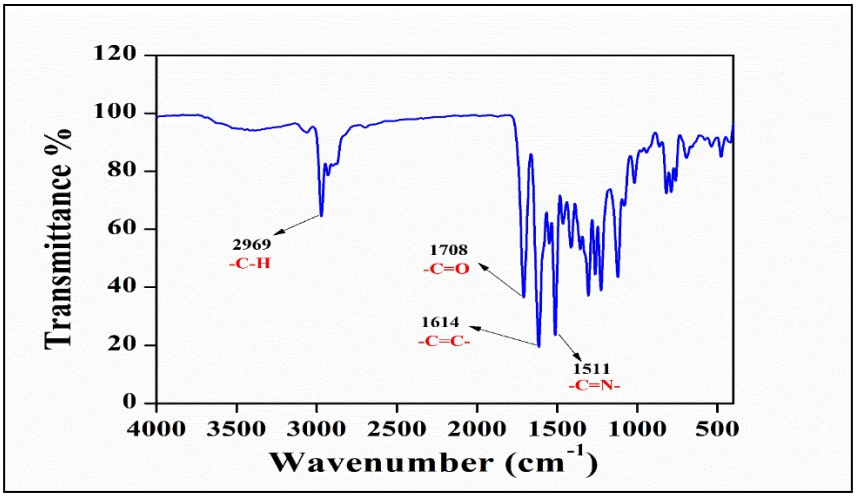

Figure S7. FT-IR spectra of **CDCRH**.

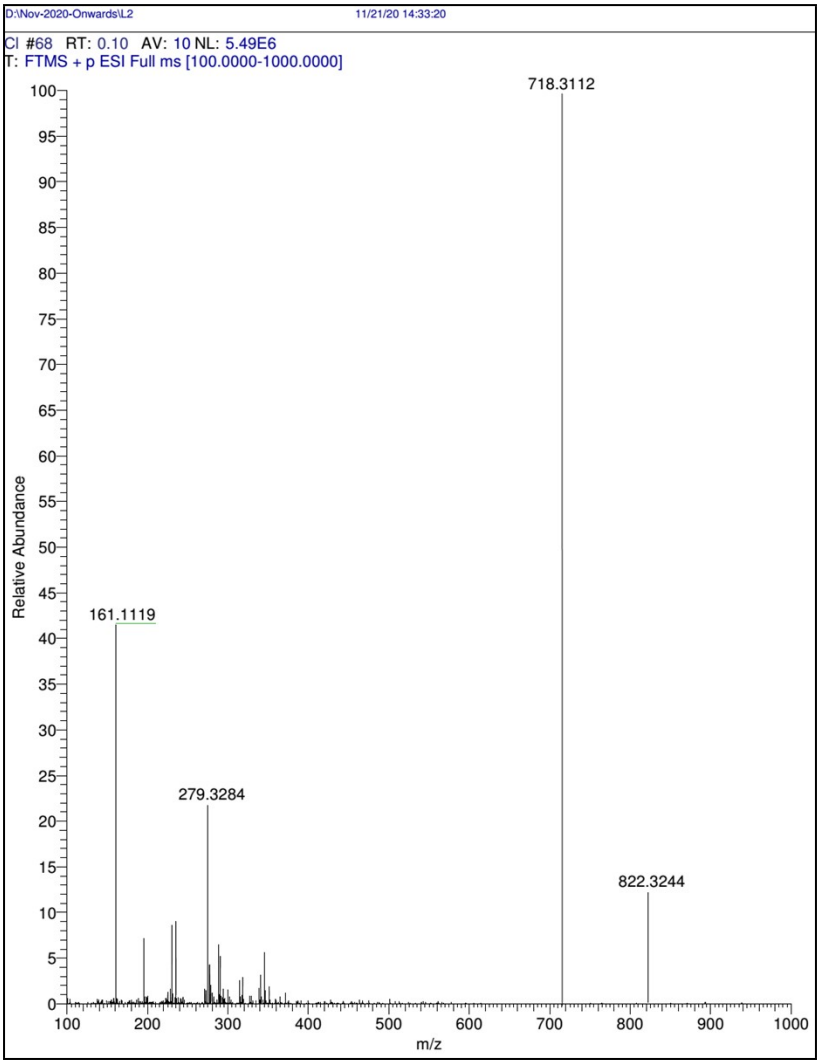

Figure S8. Mass spectra of **CDCRH**.

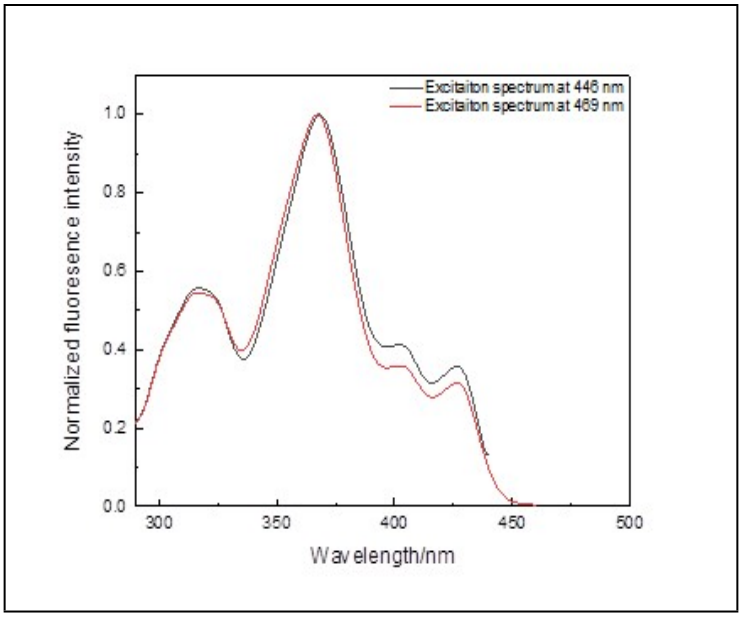

Figure S9. Excitation spectrum of **DHCRH** in toluene.

Table S1. Photophysical data of **DHCRH** in different solvents.

Solvent	**λ_{abs} (nm)**	**λ_{em} (nm)**	**Life time (ns)**	**Quantum yield (Φ_F)**
Toluene	272(s), 311(s), 380, 424 (s)	444, 469	0.14 (90.47%) 4.29 (9.53%)	0.0417
$CHCl_3$	278(s), 316(s), 389, 428 (s)	424	0.93 (50.57) 1.44 (49.43)	0.0212
THF	271(s), 310(s), 392	448, 472	0.22 (91.83) 1.45 (2.87)	0.0771
Dioxane	274(s), 312(s), 380, 423 (s)	445, 467	-	0.1201
DMF	276(s), 314(s), 385	490	0.96 (40.86) 2.43 (59.14)	0.2110
DMSO	273(s), 309(s), 393	475	0.50 (32.38) 1.61 (67.62)	0.0162
CH_3CN	276(s), 313(s), 390, 427(s)	484	0.10 (60.79) 0.74 (39.21)	0.0450
EtOH	273(s), 309(s), 393	476	-	0.0824
MeOH	396, 558	473, 584	0.17 (47.13) 0.99 (52.87)	0.0119

Abbreviations: λ_{ab}= absorption maximum, λ_{em}= emission maximum,
Φ_F= fluorescence quantum yield, s=shoulder.

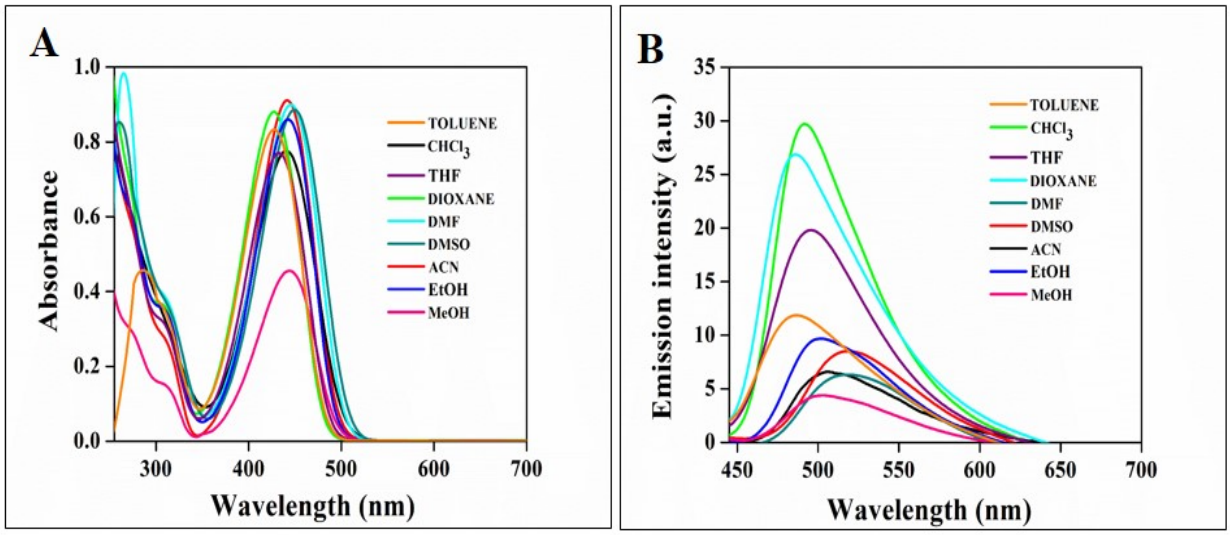

Figure S10. A) Absorption and B) emission spectra of **CDCRH** in different organic solvents.

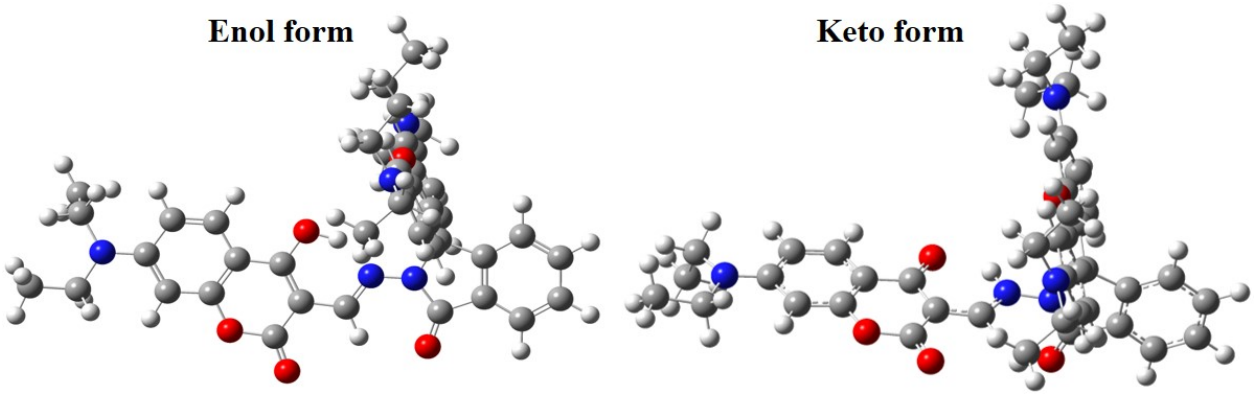

Figure S11. Optimized structure of enol and keto form of **DHCRH**.

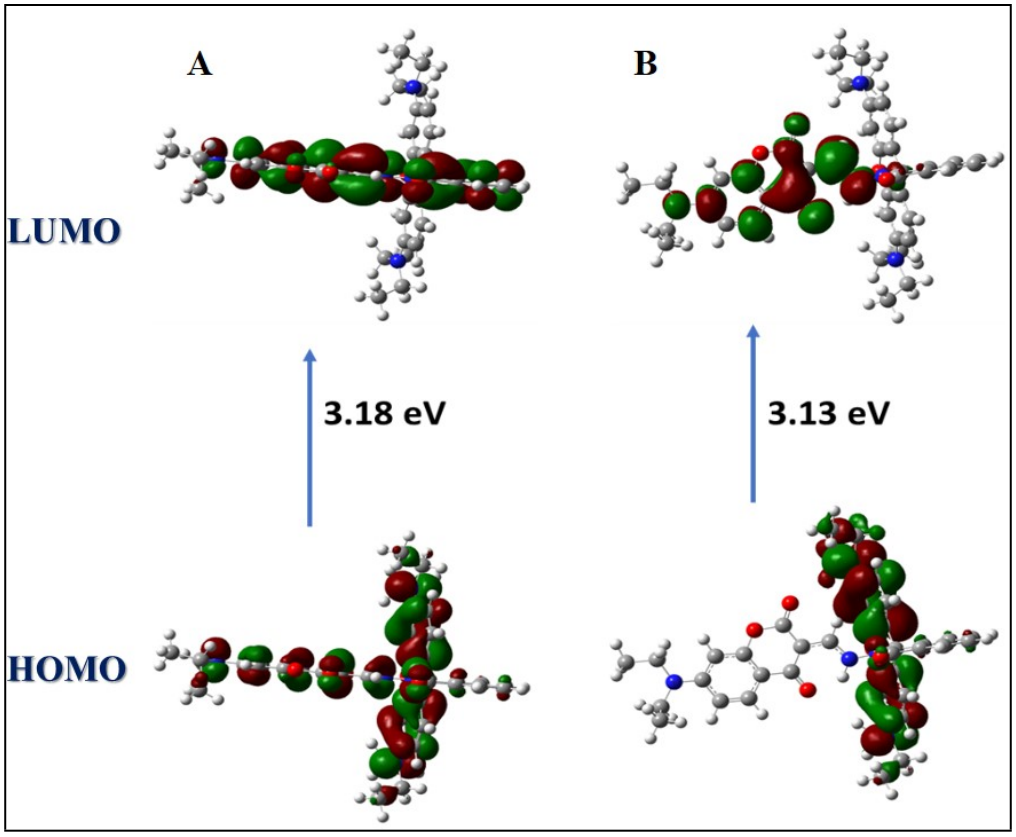

Figure S12. Molecular orbital electron density plot of (A) Enol and (B) Keto forms of **DHCRH**.

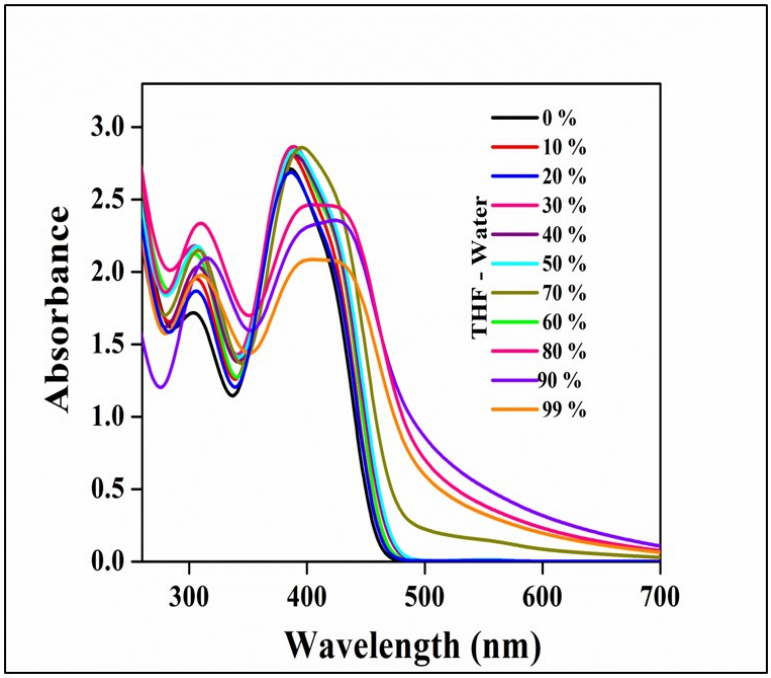

Figure S13. Absorption spectra of **DHCRH** in THF-water mixture (0-99%).

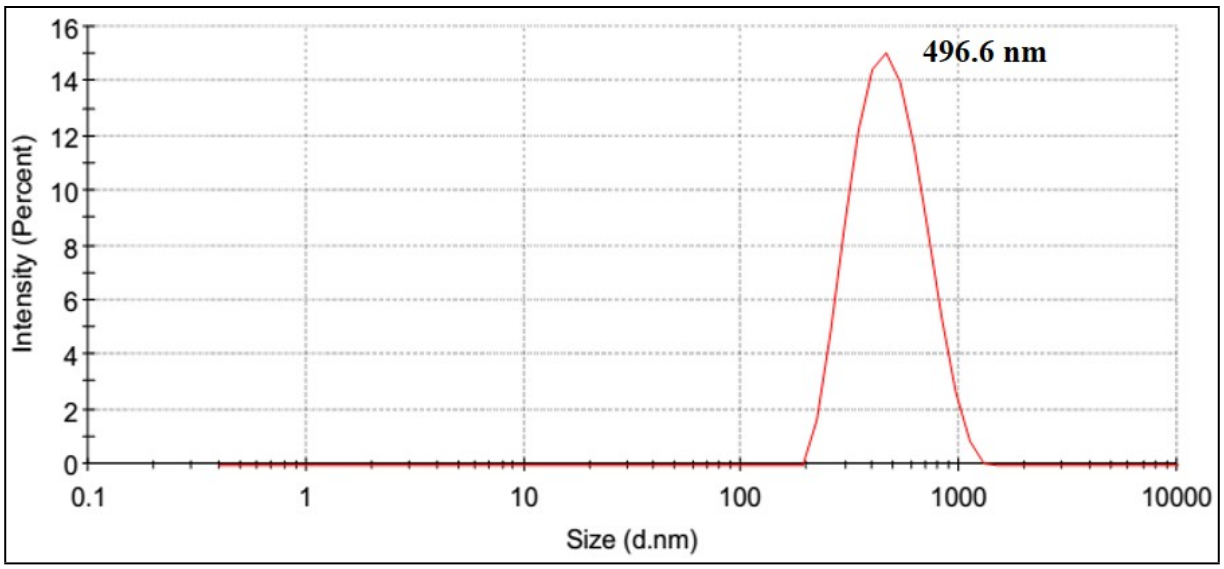

Figure S14. Dynamic light scattering measurement of **DHCRH** with particle size distribution at THF-water, 10:90 %.

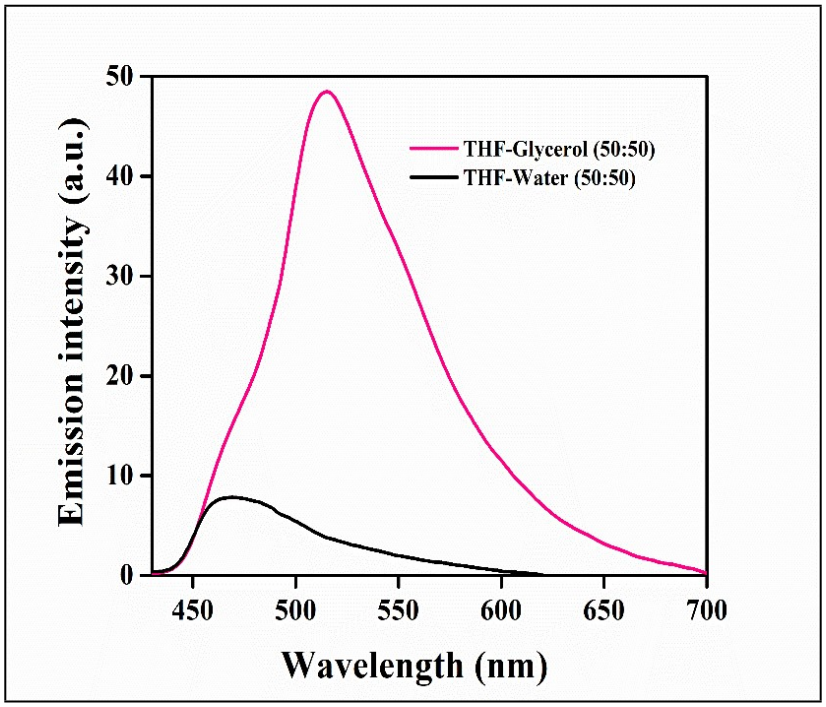

Figure S15. Emission spectra of **DHCRH** in THF-water and THF-glycerol mixture (50:50).

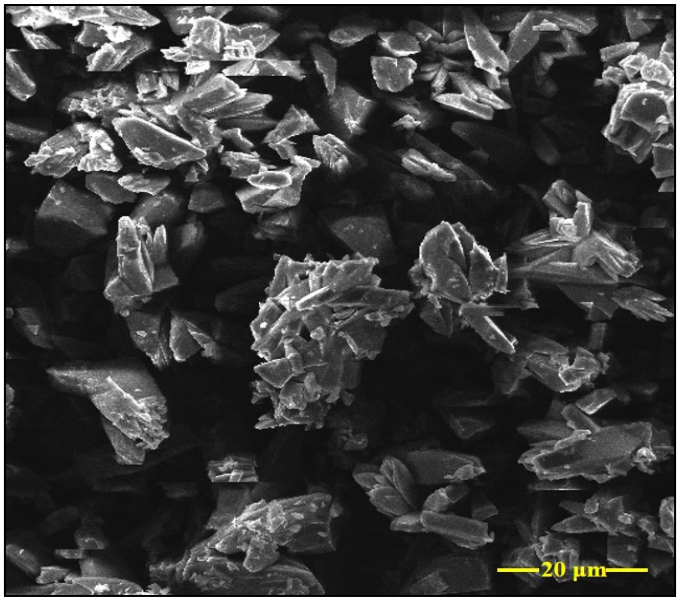

Figure S16. FESEM image of **DHCRH** in aggregated state.

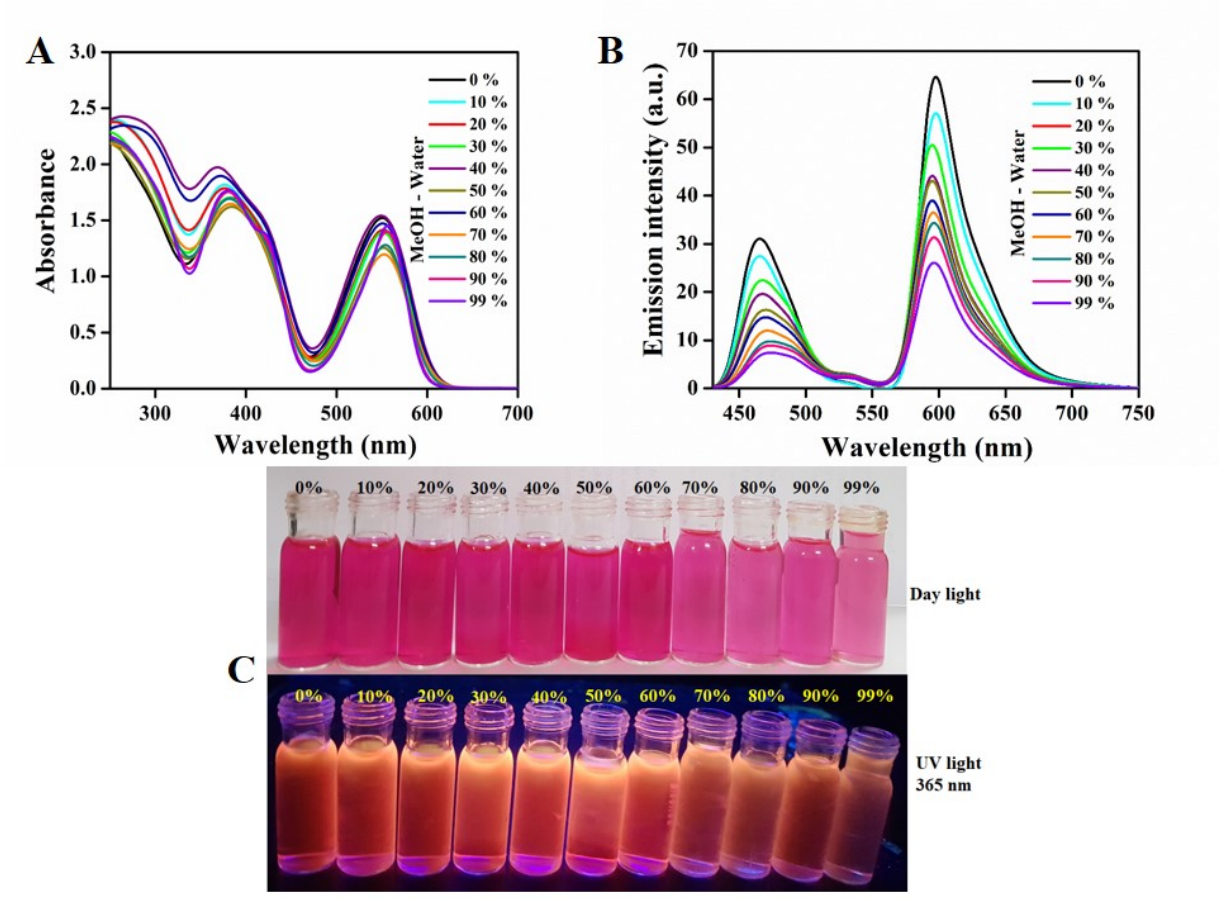

Figure S17. A) Absorption spectra of **DHCRH** in MeOH-water mixture (0-99%). B) Emission spectra of **DHCRH** (100 µM) in mixture (0-99%). C) Photographic image of **DHCRH** in various MeOH-water mixtures in day light and UV light (365 nm).

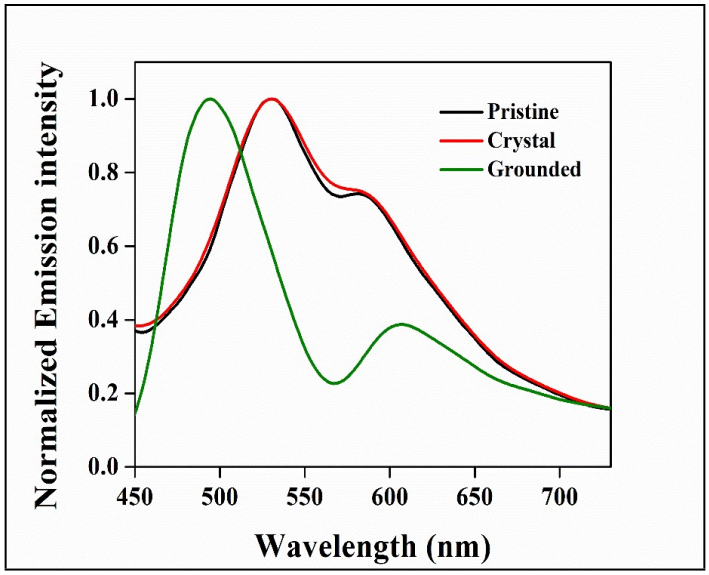

Figure S18. Normalized solid state emission spectra of pristine, crystal and ground form of **DHCRH**.

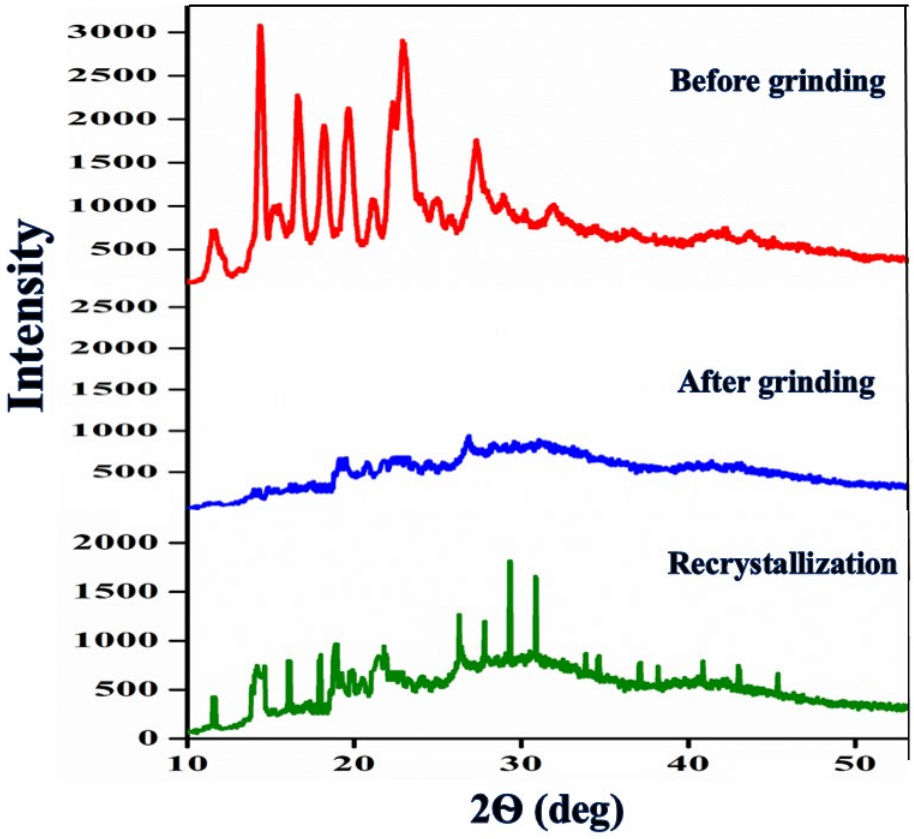

Figure S19. PXRD pattern of **DHCRH** before grinding, after grinding and after recrystallization of ground sample.

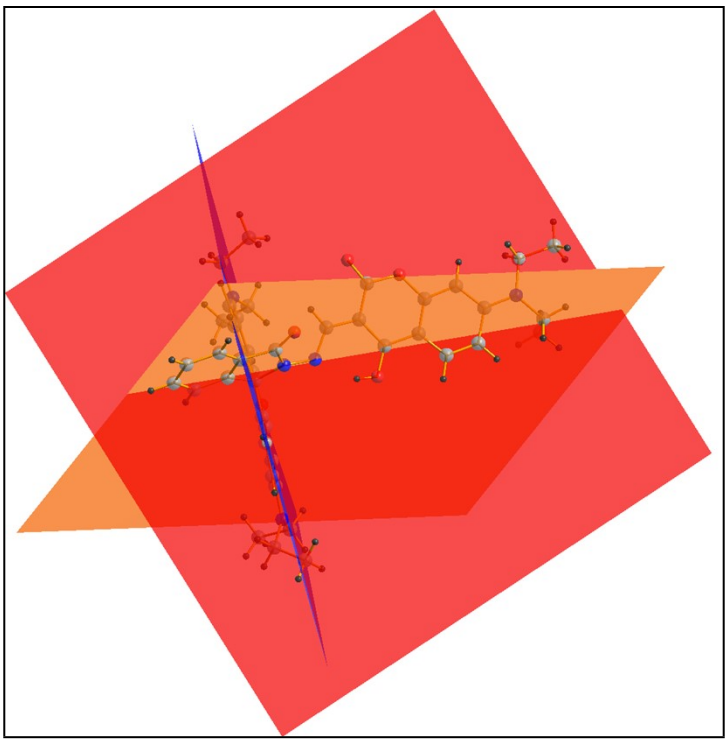

Figure S20. Illustration of non-planar and twisted conformation of **DHCRH**.

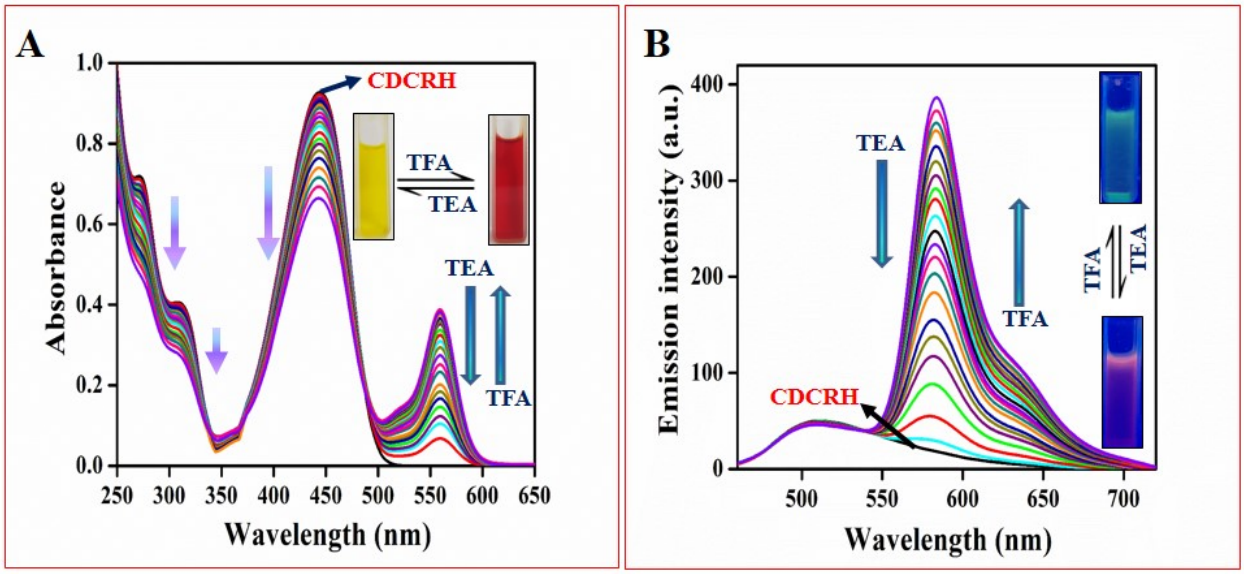

Figure S21. A) Absorption titration of **CDCRH** with incremental addition of TFA and TEA in CH_3CN. B) Emission titration of **CDCRH** with incremental addition of TFA and TEA in CH_3CN (λ_{ex}= 440 nm).

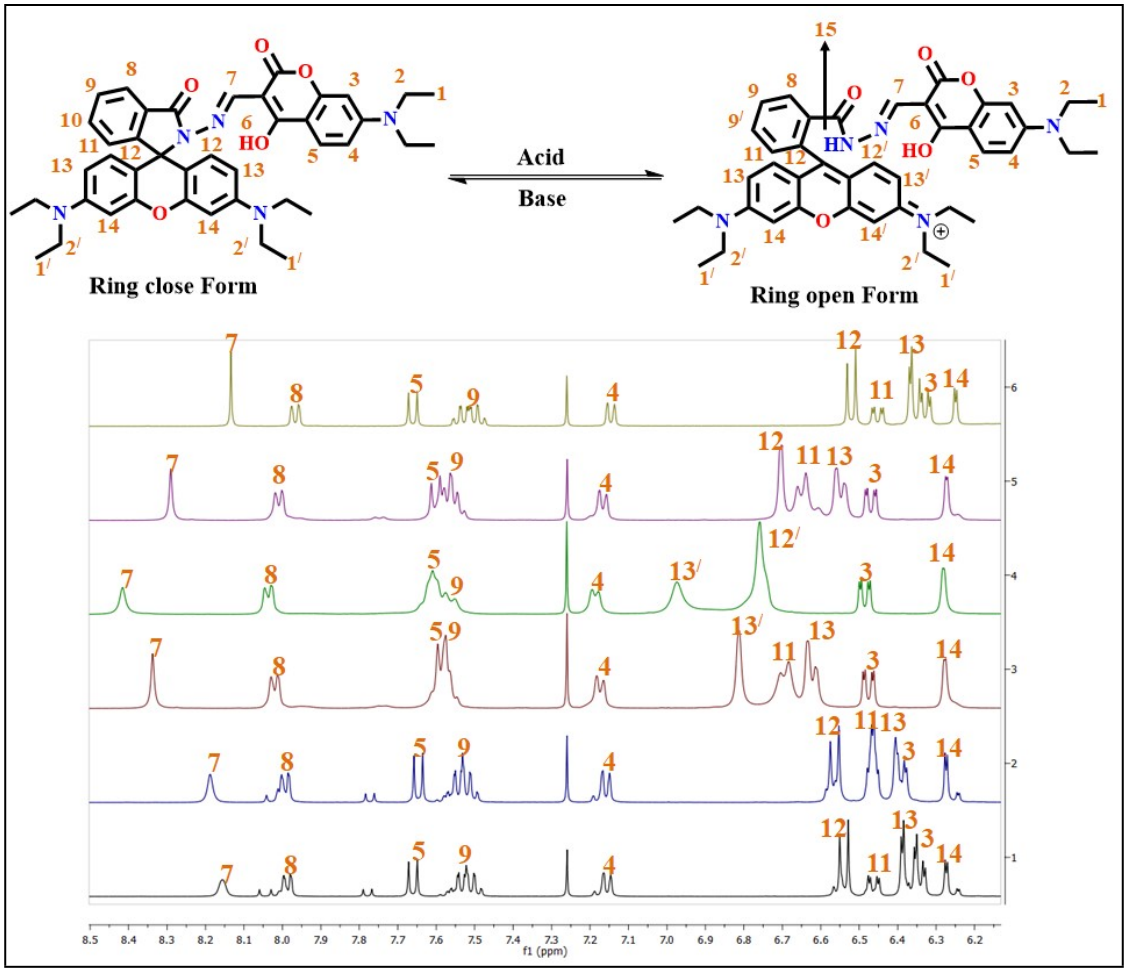

Figure S22. Expanded ^{1}H NMR spectra of **DHCRH** before and after addition of TFA/TEA.

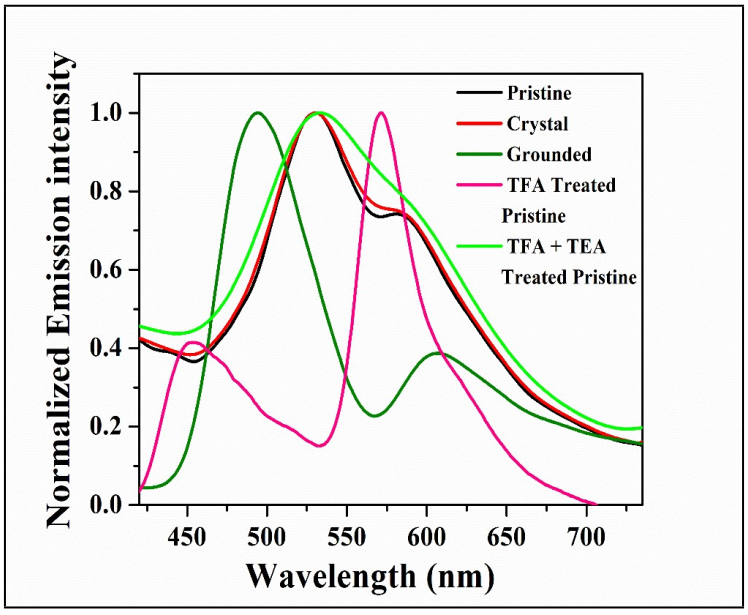

Figure S23. Normalized solid state emission spectra of **DHCRH** upon exposure to various external stimuli.

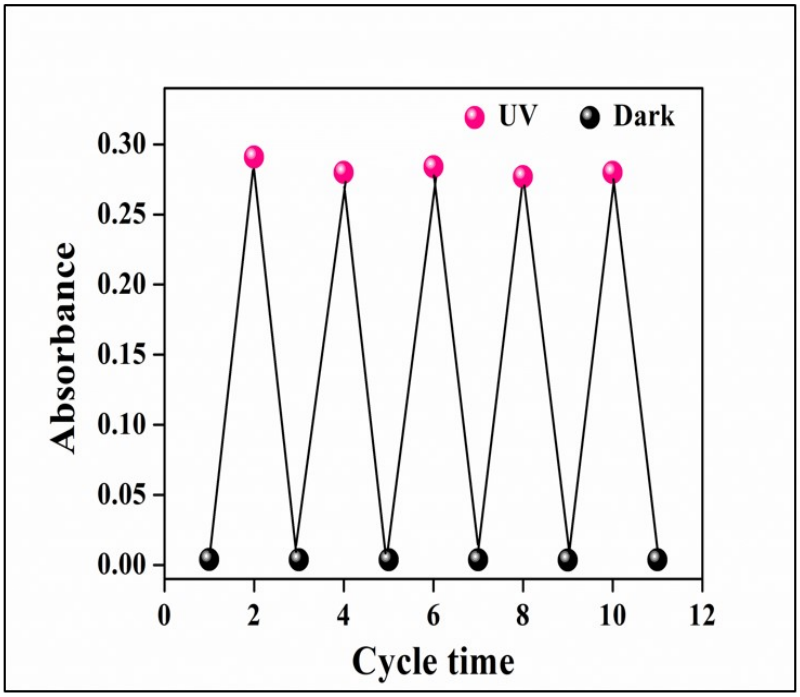

Figure S24. Fatigue resistance of **DHCRH**-Zn upon irradiation with a light source of λ=365 nm as well as keeping in dark alternatively in THF, [**DHCRH**] =10μM, [Zn(II)] = 100μM, and corresponding absorbance are recorded at λmax= 558 nm.

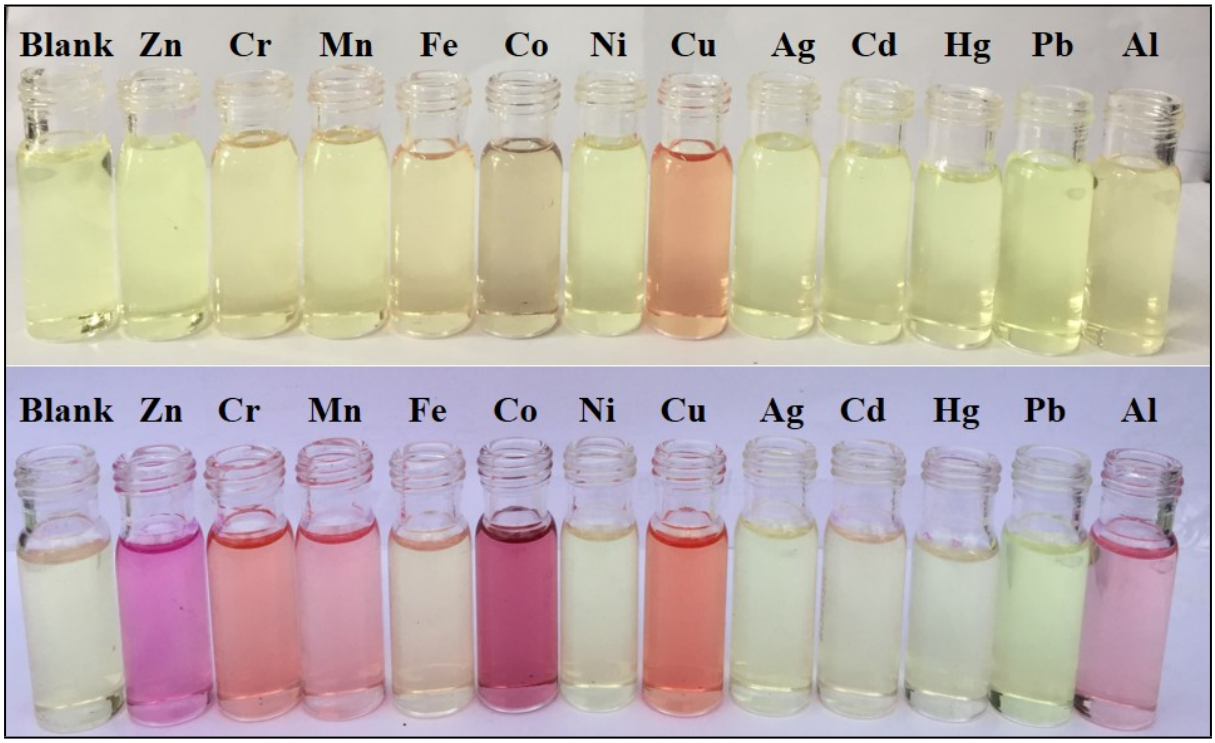

Figure S25. Photographic images of **DHCRH** in the presence of various metal ions in THF solution before (upper) and after (lower) UV/sunlight irradiation.

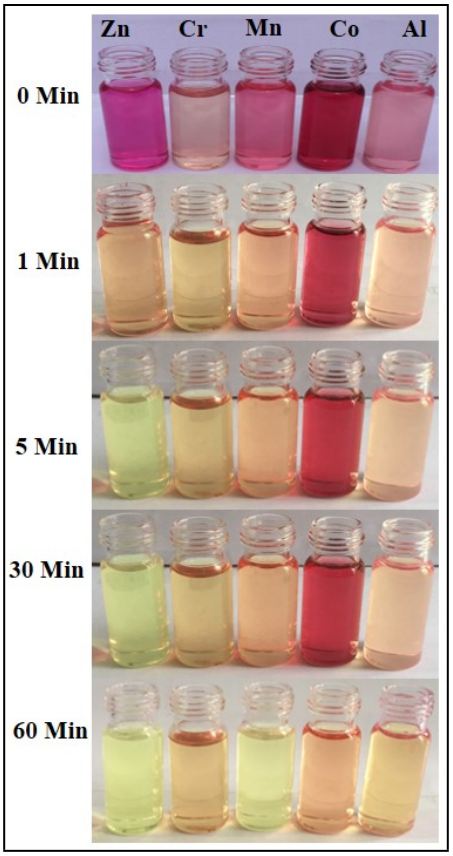

Figure S26. Photographic images for recovery rate (0 min to 60 min) of photochromic responses of **DHCRH-M** ensembles (M = Zn^{2+}, Cr^{3+}, Mn^{2+}, Co^{2+} and Al^{3+}) in THF solutions after sunlight exposure for 5 min.

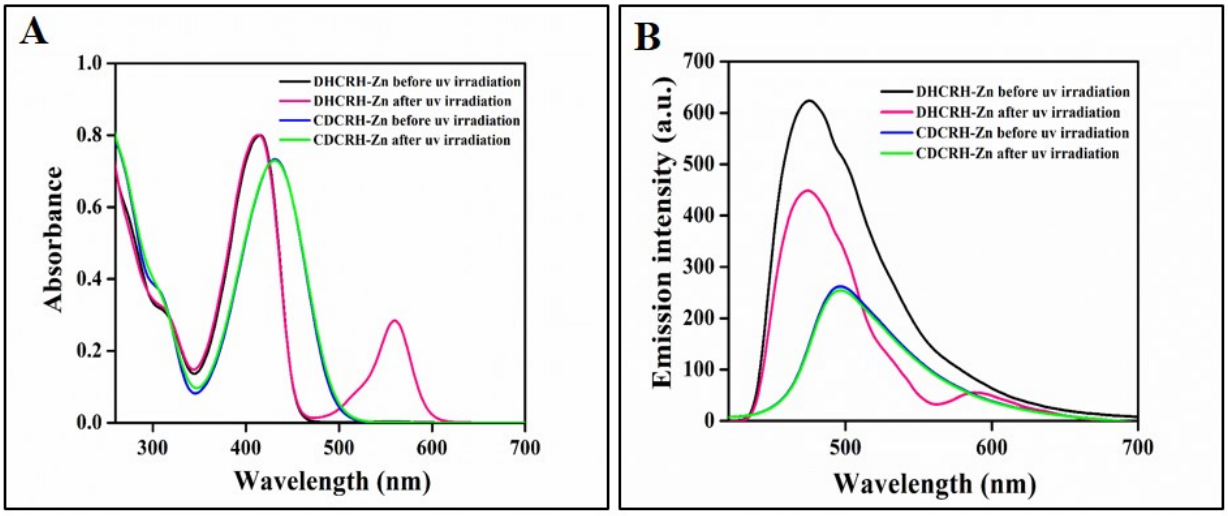

Figure S27. Absorption (A) and emission spectra (B) of *in-situ* prepared **DHCRH-Zn** and **CDCRH-Zn** ensembles in THF solution before and after UV irradiation.

Table S2. Crystallographic data for **DHCRH**.

Empirical formula	$C_{42}H_{45}N_5O_5$
Formula weight	699.83
Temperature	100(2) K
Crystal system	Monoclinic
Wavelength	0.71073 Å
Space group	$P2_1/c$
Unit cell dimensions a [Å] b [Å] c [Å] α [°] β [°] γ [°]	 16.0255(7) 12.3417(5) 19.1839(8) 90 111.830(2) 90
Volume	3522.1(3) $Å^3$
Z	4
Calculated density	1.320 Mg/m^3
Absorption coefficient	0.088 mm^{-1}
F(000)	1488
Crystal dimensions	0.3 x 0.2 x 0.15 mm^3
θ range for data collection	2.008 to 28.387°
Index ranges	-21<=h<=21, -16<=k<=15, -25<=l<=25
Reflections collected	28958
Independent reflections	8788 [R(int) = 0.0549]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6575
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8788 / 0 / 469
Goodness-of-fit on F^2	1.056
Final R indices [I>2σ(I)]	R_1 = 0.0696, wR_2 = 0.1773
R indices (all data)[a]	R_1 = 0.1212, wR_2 = 0.2052
Largest diff. Peak and hole	0.577 and -0.436 $e.Å^{-3}$

References

(1) Lakowicz, J. R. *Principles of fluorescence spectroscopy*, Springer science & business media: 2013.