Supporting Information

Self-Assembly Solid-State Enhanced Red Emission of Quinolinemalononitrile: Optical Waveguides and Stimuli-Response

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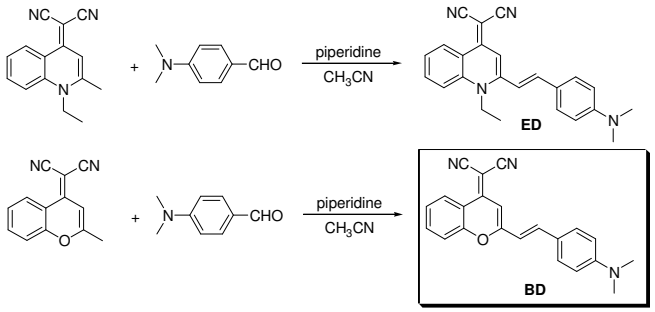
1. Synthesis of ED and BD



Scheme S1 Synthetic route of **ED and BD**

The intermediate of 1-ethyl-2-methy-4-(dicyanomethylene)-1,4-dihydroquinoline was prepared by the literature procedure (Horwitz, L., *J. Am. Chem. Soc.*, 1955, 77, 1687). Another intermediate of 2-(2-methyl-*4H*-chromen-4-ylidene)malononitrile was prepared by the established literature procedure (G. G. Badcock, F. M. Dean, A. Robertson and W. B. Whalley, *J. Chem. Soc.*, 1950, 903).

2. Absorption, photoluminescence spectra, and SEM image of ED

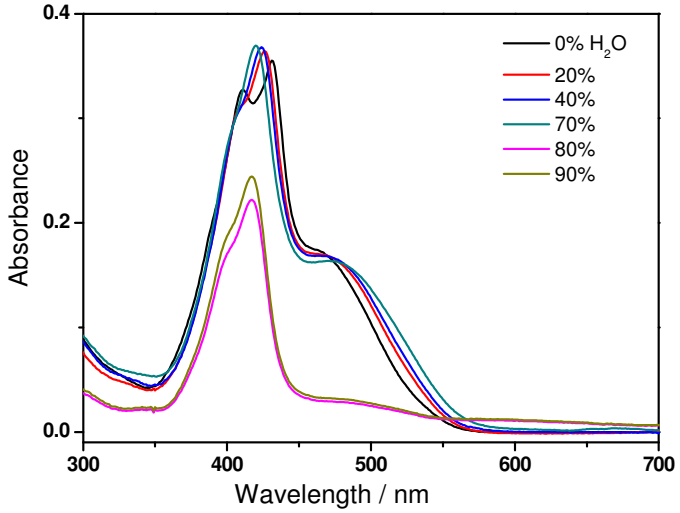


Figure S1. UV/visible absorption spectra of **ED** (10^{-5} M) in H_2O/THF mixtures with different volume fractions of water. Note: the absorption of the resultant solution was determined after 12 h.

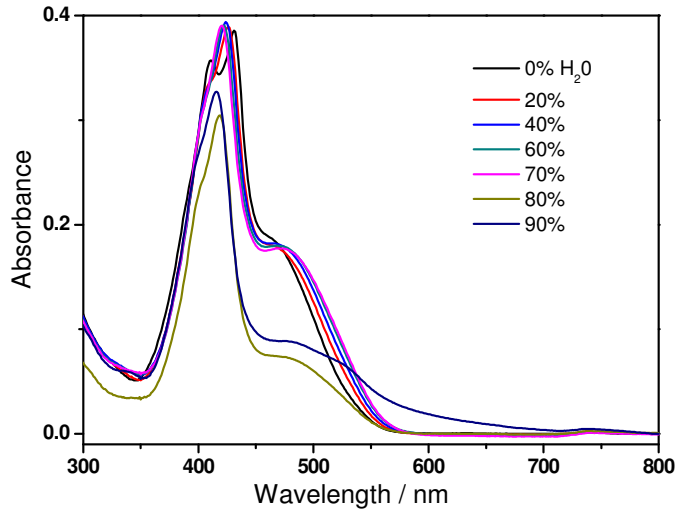


Figure S2. UV/visible absorption spectra of freshly prepared **ED** (10^{-5} M) in H_2O/THF mixtures with different volume fractions of water. Note: the absorption of the resultant solution was determined immediately.

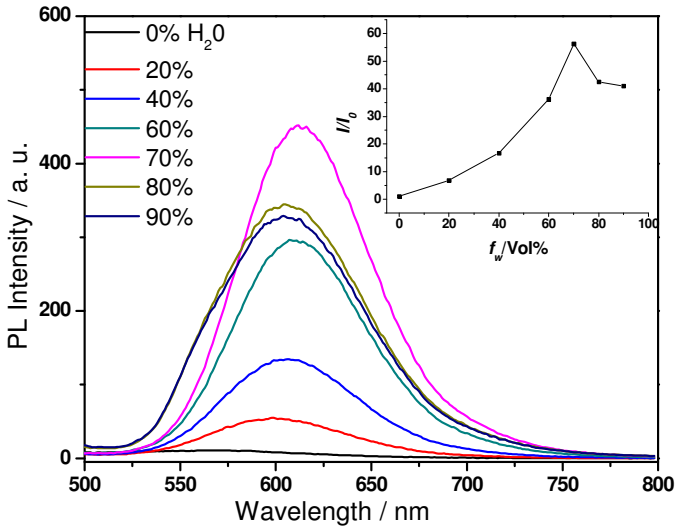


Figure S3. Emission spectra of freshly prepared **ED** (10^{-5} M) in H_2O/THF mixtures with different volume fractions of water. λ_{ex} = 430 nm. Insets: plot of relative PL intensity against water content (f_w). Note: the emission spectra of the resultant solution was determined immediately.

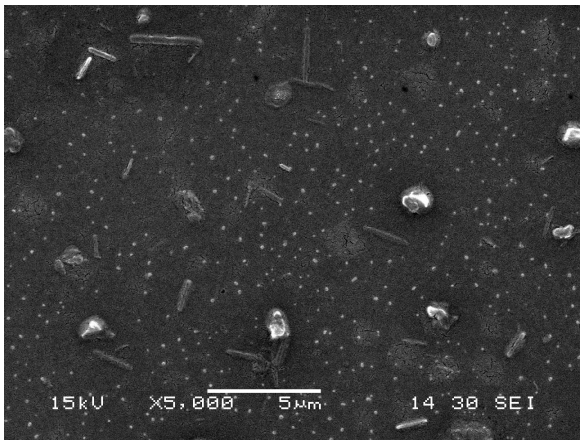


Figure S4. SEM image of random agglomerates obtained from **ED** suspension (80% H_2O).

3. Photographic images, absorption and photoluminescence spectra of BD

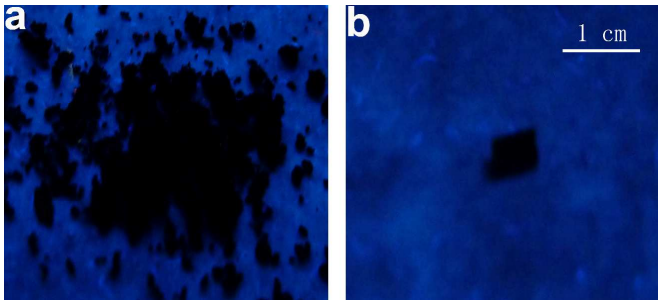


Figure S5. Photographic images of powder and crystal for compound **BD** under 365 nm UV light illumination, showing severe ACQ effect with little fluorescence. Scale bar: 1 cm.

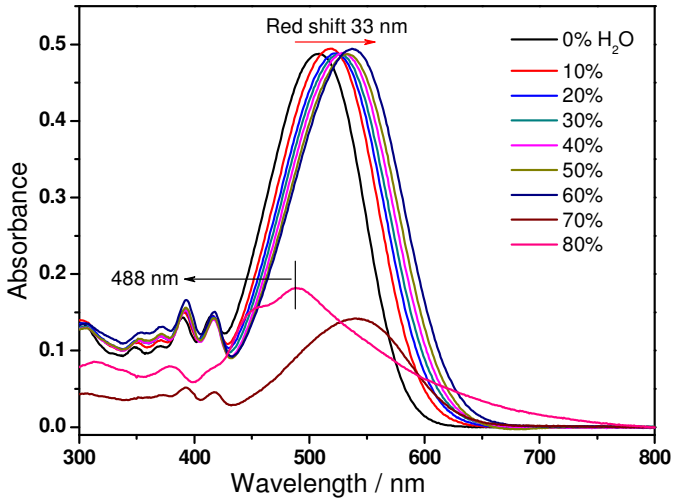


Figure S6. UV/visible absorption spectra of **BD** (10^{-5} M) in H_2O/THF mixtures with different volume fractions of water.

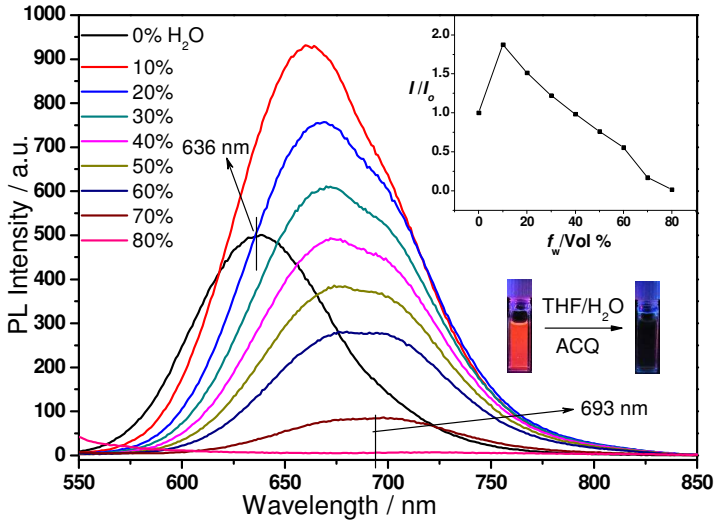


Figure S7. Emission spectra of **BD** (10^{-5} M) in H_2O/THF mixtures with different volume fractions of water. λ_{ex} = 510 nm. Insets: plot of relative PL intensity against water content (f_w). Inset: Fluorescence image of BD (0 and 80% H_2O) under 365 nm illumination.

4. Solvent effect

Table S1. Optical properties of **ED** and **BD** in different solvents [a]

Solvent		hexane	toluene	chloroform	tetrahydrofuran	ethanol
ED	λ_{ab}[nm]	436	436	432	431	423
	λ_{em}[nm]	NA	NA	NA	594	594
BD	λ_{ab}[nm]	475	493	507	505	513
	λ_{em}[nm]	NA	584	611	636	660

[a] Abbreviations: λ_{ab} = absorption maximum, λ_{em} = emission maximum, Solvent polarity parameter = $\{(\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)\}$, where ε is the dielectric constant and n is the refractive index. The solvent used and the corresponding polarity parameters are: hexane (~0), toluene (0.014), chloroform (0.149), tetrahydrofuran (0.207), ethanol (0.288). Note: NA = not available (signal too weak to be accurately detected).

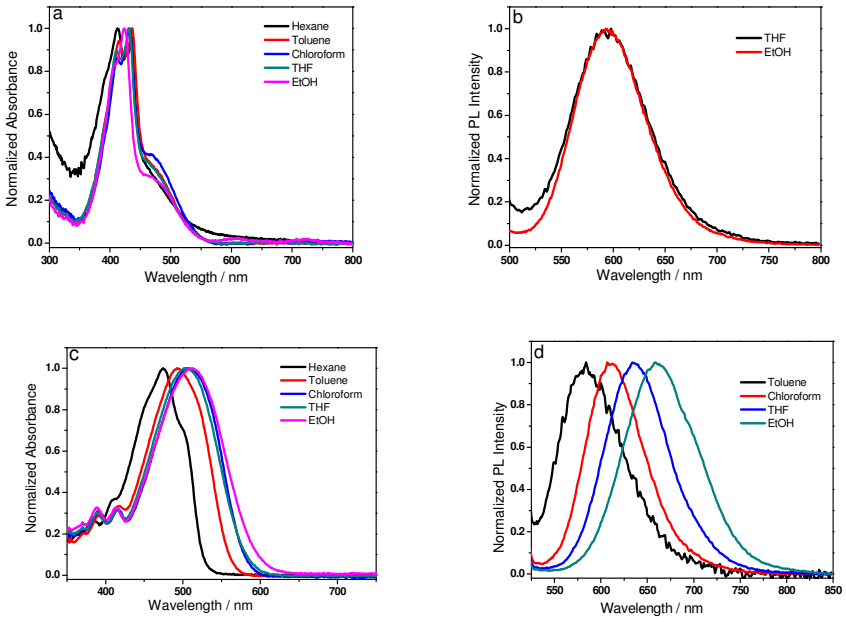


Figure S8. Normalized Absorption and emission spectra of **ED** (a, b) and **BD** (c, d) in dilute solvent with different polarities. The solvent used and the corresponding polarity parameters are: hexane (0), toluene (0.014), chloroform (0.149) , tetrahydrofuran (0.207), ethanol (0.288).

5. The DFT calculation for BD and ED

The ground-state geometries of **ED** and **BD** have been optimized in the gas phase by DFT with the Gaussian09 package,[1] using the hybrid B3LYP functional and the standard 6-31G* basis set.[2]

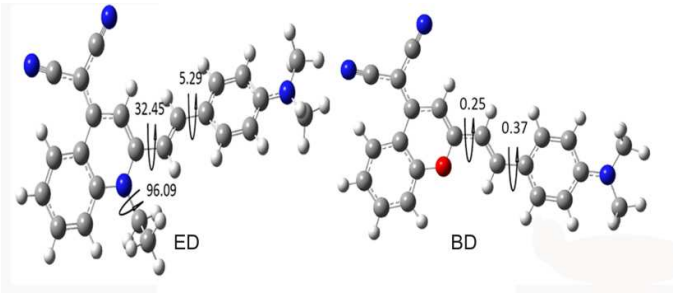
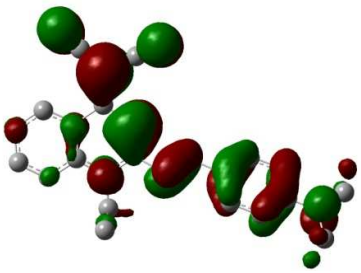
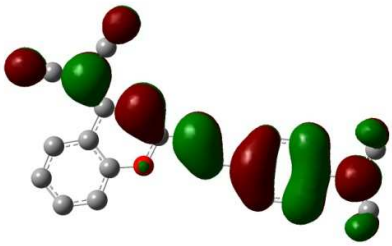
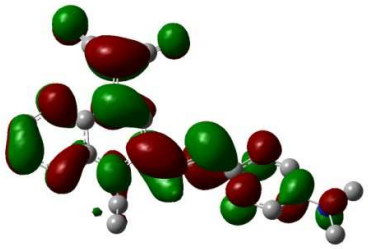
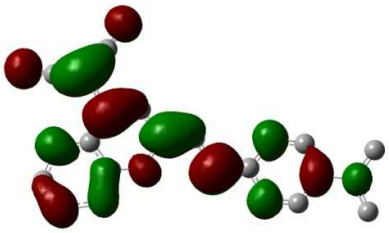


Figure S9. The optimized geometries of **BD** and **ED** for isolated state in gas phase at the B3LYP/6-31G* level.

Table S2. The frontier orbitals of compounds **ED** and **BD** (isodensity=0.020 a.u.).

ED	BD
	
HOMO (-5.40 eV)	HOMO(-5.32 eV)
	
LUMO(-2.07 eV)	LUMO(-2.51 eV)

[1] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[2] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372–1377.

6. Crystallographic data

CCDC 881659 (**ED**) and CCDC 881660 (**BD**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S3. Crystal Data and Structure Refinements of **ED** and **BD**.

Crystal	**ED**	**BD**
Empirical formula	$C_{24}H_{22}N_4$	$C_{22}H_{17}N_3O$
Formula weight	366.46	339.39
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	*P2(1)/c*	*P2(1)/c*
Unit cell dimensions	a = 15.856(2) Å $\alpha = 90^o$	a = 14.7186(12) Å $\alpha = 90^o$
	b = 16.169(2) Å $\beta = 96.660(3)^o$	b = 15.3159(11) Å $\beta = 93.723(2)^o$
	c = 7.8214(11) Å $\gamma = 90^o$	c = 7.8609(6) Å $\gamma = 90^o$
Volume	1991.7(5) $Å^3$	1768.3(2) $Å^3$
Z	4	4
Calculated density	1.222 g/cm^3	1.275 g/cm^3
Absorption coefficient	0.074 mm^{-1}	0.080 mm^{-1}
F(000)	776	712
Crystal size	0.361 x 0.270 x 0.121 mm^3	0.356 x 0.228 x 0.200 mm^3
Theta range for data collection	1.81 to 25.50 ^{o}	1.92 to 26.00 ^{o}
Index ranges	-19≤h≤18	-16≤h≤18
	-15≤k≤19	-16≤k≤18
	-9≤l≤9	-9≤l≤9
Reflections collected / Unique	10408 / 3705 [R(int) = 0.0816]	10687 / 3469 [R(int) = 0.1209]
Completeness to theta = 25.50	99.6 %	100.0 %
Absorption correction	Empirical	Empirical
Max. and min. transmission	1.00000 and 0.79776	1.0000 and 0.6948
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3705 / 0 / 257	3469 / 0 / 238
Goodness-of-fit on F^2	0.846	0.917
Final R indices [I>2σ (I)]	R_1 = 0.0445, wR_2 = 0.0771	R_1 = 0.0583, wR_2 = 0.1486
R indices (all data)	R_1 = 0.1068, wR_2 = 0.0918	R_1 = 0.0839, wR_2 = 0.1593
Extinction coefficient	0.0035(3)	0.0053(11)
Largest diff. peak and hole	0.105 and -0.121 e. $Å^{-3}$	0.214 and -0.265 e. $Å^{-3}$

7. Stimuli-responsive section

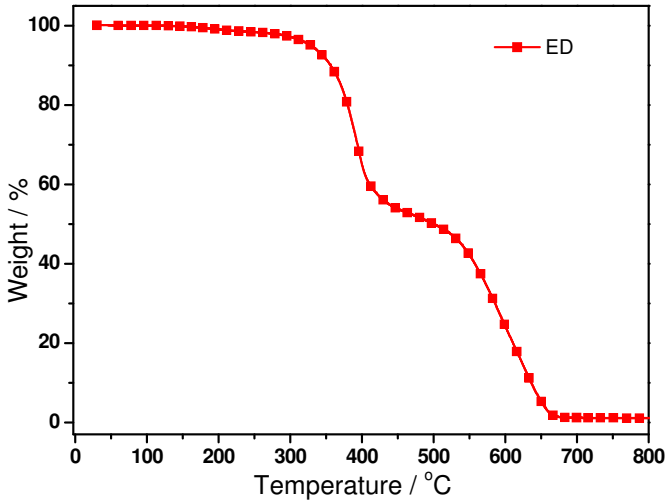


Figure S10. The TGA curves of pristine powder of **ED** under nitrogen (Scan rate: 10 °C min^{-1})

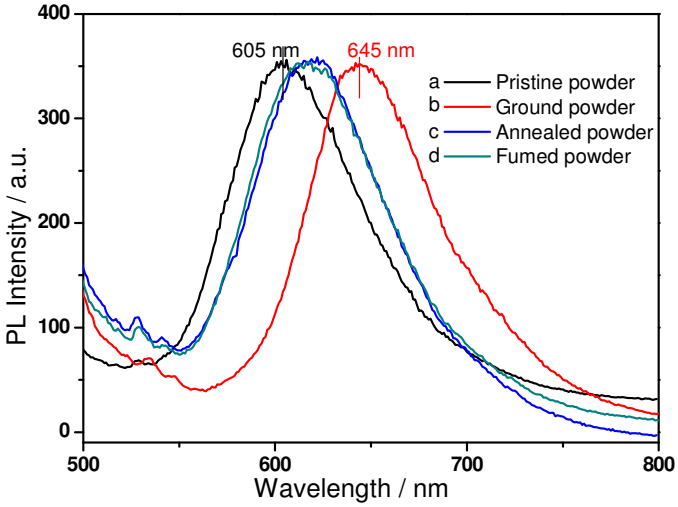


Figure S11. PL spectra of **ED**: (a) pristine powder, (b) ground powder (grinding pristine powder with pestle), (c) annealed powder (ground powder annealed at 100 °C for 5 min), (d) fumed powder (reground powder in dichloromethane vapor for 5 min).

8. Cell imaging

Cell culture: A human nasopharyngeal epidermal carcinoma cell line (KB cell) was provided by the Institute of Biochemistry and Cell Biology, SIBS, CAS (China). Cells were grown at 37 °C and with 5% CO_2 in Roswell Park Memorial Institute medium (RPMI) 1640 supplemented with 10% fetal bovine serum (FBS). Cells (5×10^8 L^{-1}) were plated on 18 mm glass cover slips, and allowed to adhere for 24 h. The cells were washed three times with PBS buffer, and the medium was replaced with PBS buffer before imaging.

Microscopy and imaging methods: Confocal luminescence imaging of cells was performed with a modified Olympus FV1000 laser-scanning microscope. A 60 × oil-immersion objective lens was used. Excitation was carried out with a semiconductor laser at λ = 405 nm, and emission was collected in the range λ = 565 – 665 nm, including the maximum emission wavelength of **ED**. KB cells were incubated with a PBS solution of **ED** (10 μM) for dye loading for 0.5 h at 37°C. The stained cells were washed three times with PBS buffer. Then the treated cells were imaged by fluorescence microscopy.

9. Characterization of compounds ED and BD

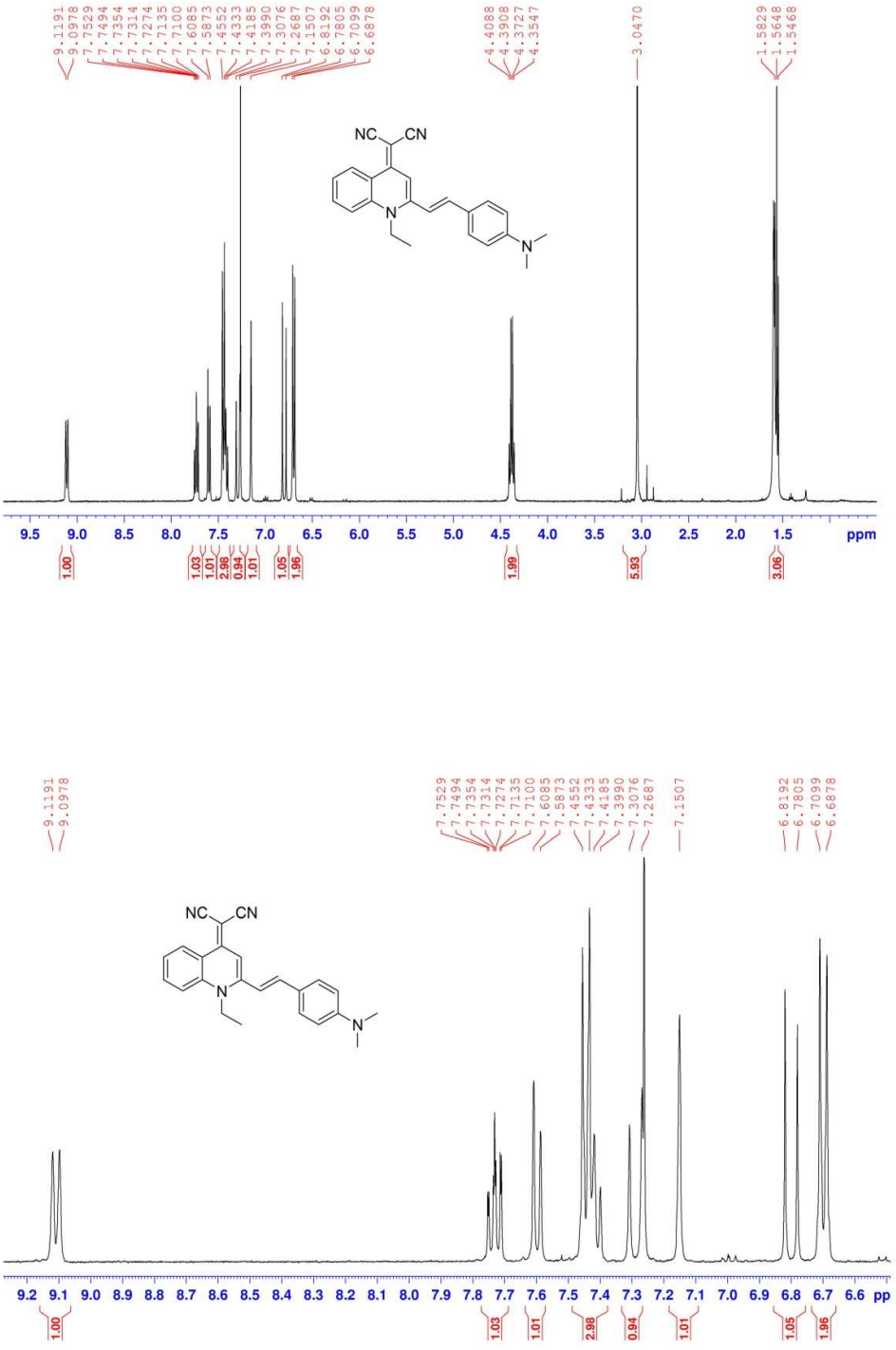


Figure S12. ^{1}H NMR spectra of compound **ED** in $CDCl_3$

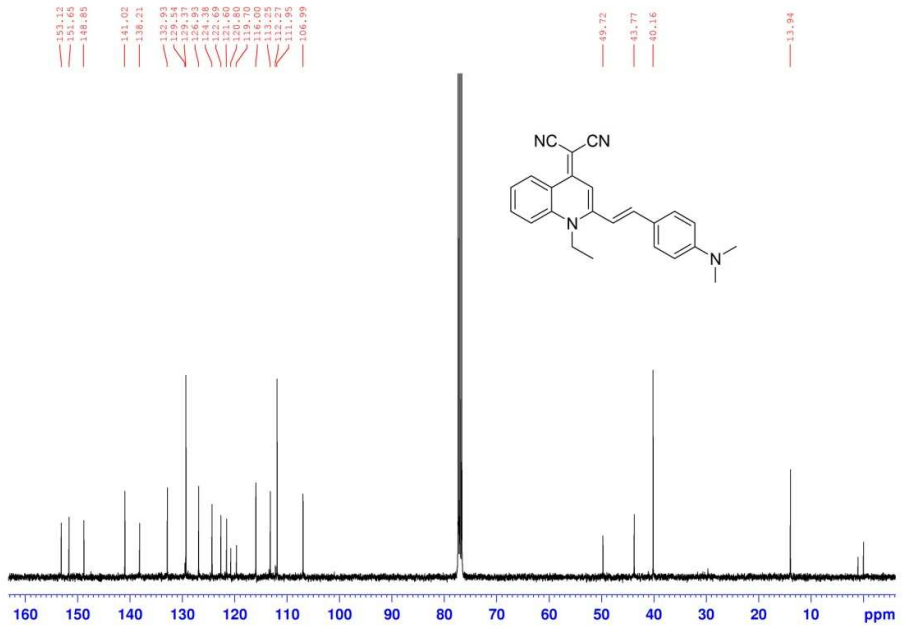


Figure S13. ^{13}C NMR spectra of compound **ED** in $CDCl_3$

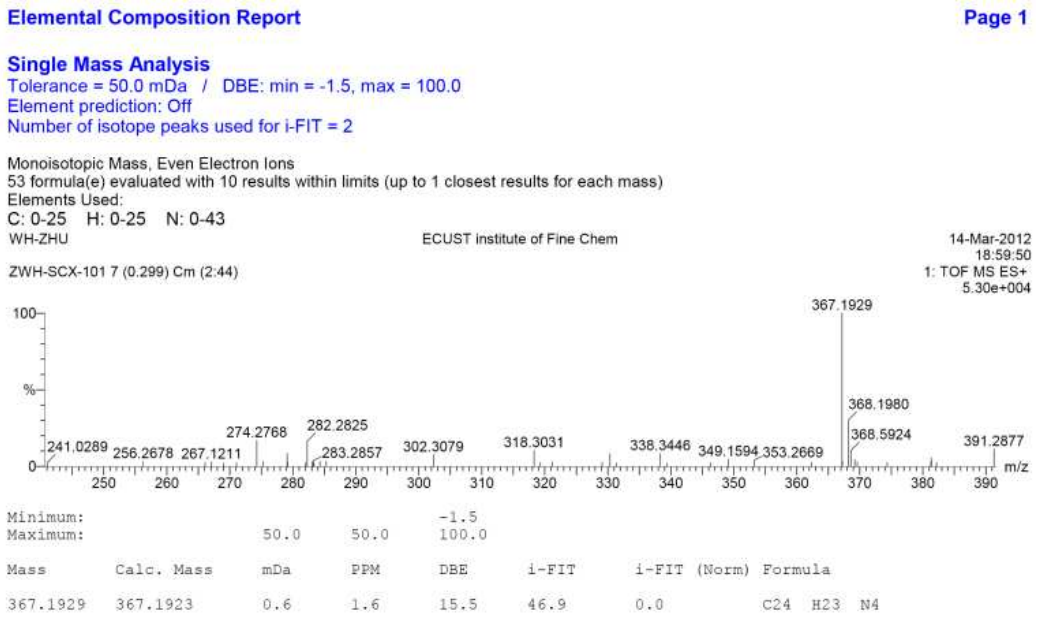


Figure S14. HR mass spectra of **ED**

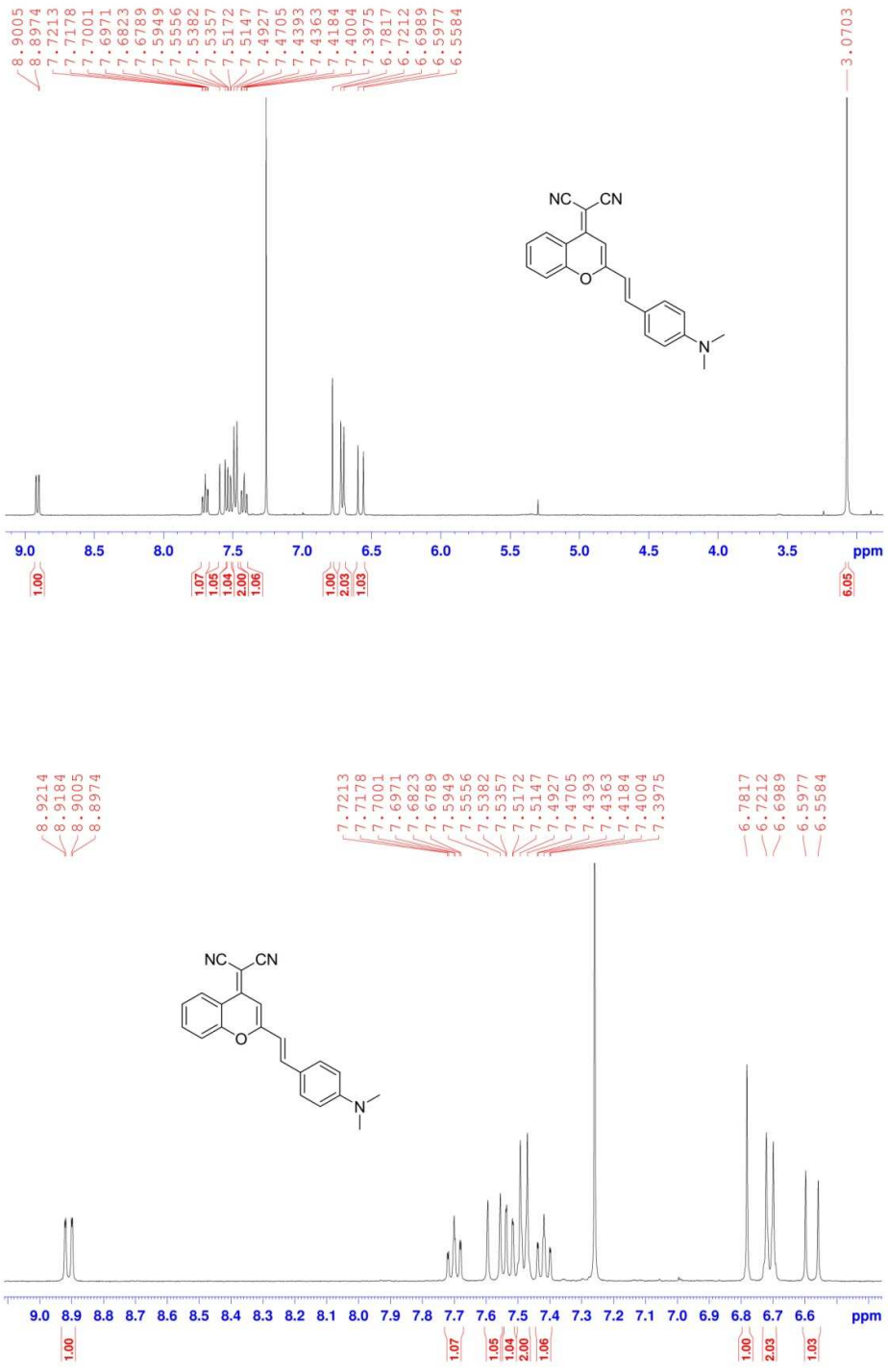


Figure S15. ^{1}H NMR spectra of compound **BD** in $CDCl_3$

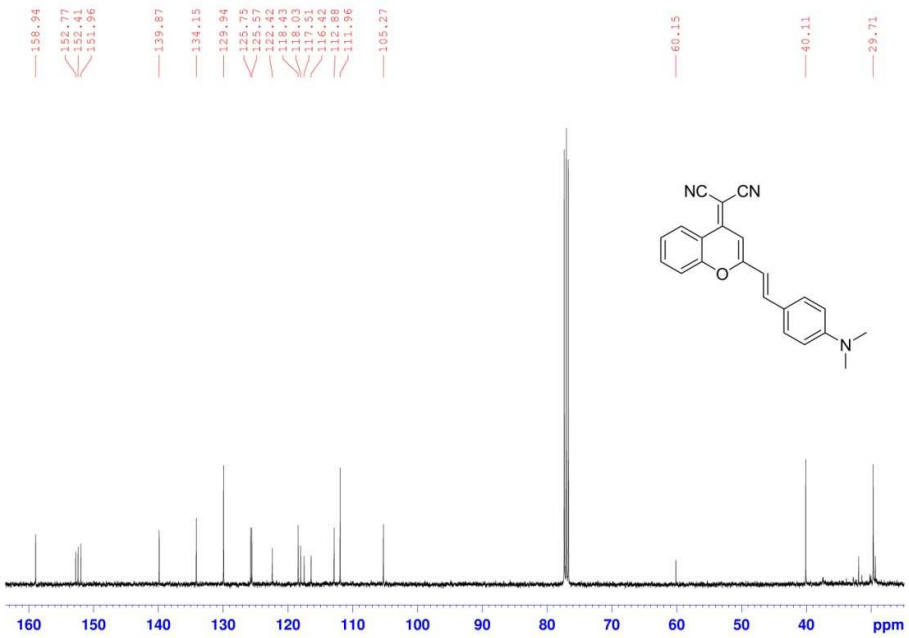


Figure S16. ^{13}C NMR spectra of compound **BD** in $CDCl_3$

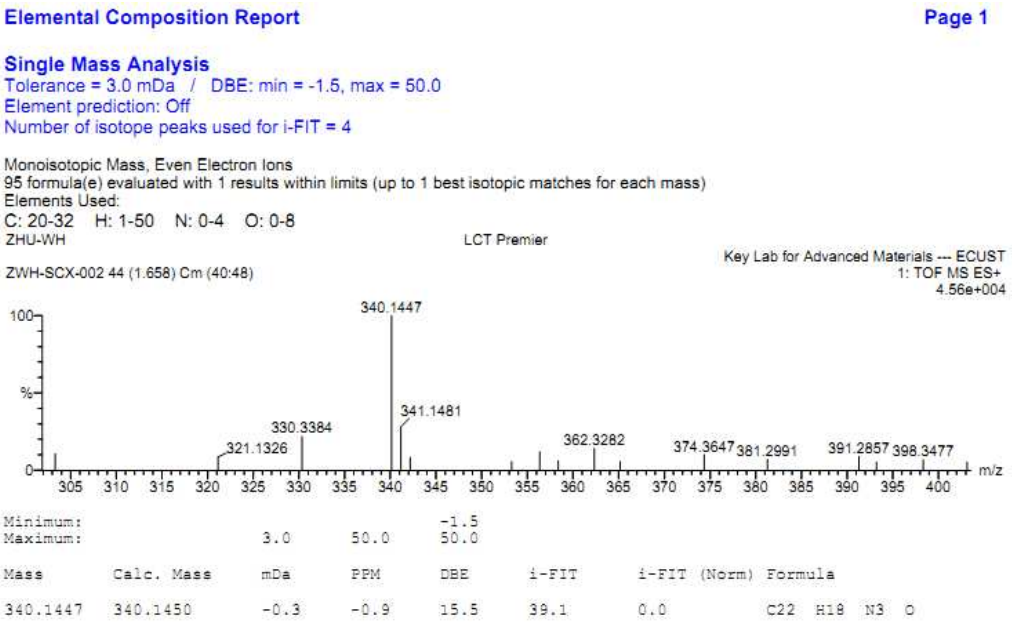


Figure S17. HR mass spectra of **BD**