Supporting Information

**CHCl3-Dependent Emission Color and Jumping Behavior of Cyclic Chalcone Single Crystals: the** **Halogen Bond Network Effect**

*Zeqing Tan, Jian Zhao, Jing Zhi Sun, Jiaxin Zhao, Xinrui He, Zhe Liu, Lin Zhu, Xiao Cheng\* and Chuanjian Zhou\**

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**General Information**

**Materials and Instruments:** Chemicals of the highest purity level available were obtained from Acros, Sigma-Aldrich, or J&K Scientific, and were used without further purification. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer with tetramethylsilane as the internal standard, while mass spectra were recorded on a Thermo Fisher ITQ1100 mass spectrometer. Elemental analyses were performed on a FlashEA1112 spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer, emission spectra were recorded using a Shimadzu RF-5301 PC spectrometer. Absolute fluorescence quantum yields and lifetimes were measured on an Edinburgh FLS920 with or without an integrating sphere. All measurements were carried out at room temperature under ambient conditions.

(2*E*)​-5-​chloro-​2-​[[4-​(diphenylamino)​phenyl]​methylene]​-​2,​3-​dihydro-​1*H*-​inden-​1-​one (**1**). Yield: 79%. 1H NMR (400 MHz, CDCl3): *δ* 7.76 (d, *J* = 8.4 Hz, 1H), 7.56 (s, 1H), 7.44 (m, 3H), 7.40 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.25 (m, 4H), 7.07 (m, 6H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 2H). 13C NMR (100 MHz, CDCl3): *δ* 191.8, 149.8, 148.5, 145.6, 139.3, 135.8, 133.5, 131.1, 130.3, 128.5, 127.2, 126.8, 125.2, 124.6, 124.3, 123.3, 120.2, 31.3. MS m/z: 422.13 [M]+ (calcd: 421.92). Anal. Calcd (%) for C28H20ClNO: C, 79.71; H, 4.78; N, 3.32. Found: C, 78.05; H, 4.65; N, 3.27.

**Single-crystal X-ray Diffraction:** Single-crystal X-ray diffraction data were collected on a Rigaku RAXIS-PRID diffractometer in ω-scan mode using graphite-monochromated Mo-Kα radiation. Structures were solved with direct methods using the SHELXTL program and refined with full-matrix least squares on *F*2. Non-hydrogen atoms were refined anisotropically, while the positions of hydrogen atoms were calculated and refined isotropically.

[CCDC 1975830 for **1** and 1975831 for **1•2CHCl3** 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.]

**Computational Details:** All the geometries came from the single crystal data, and the calculations were performed by ORCA 4.1.0[1,2] at RI-B3LYP/def2-TZVP level of theory with fine integration grid for both B3LYP and RICOSX, containing the atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ)[3]. The Multiwfn 3.6 package[4] was utilized to extract the cube file of the value of orbital wavefunction and reduced density gradient (RDG)[5] by using the molden file generated from the ORCA calculation. The cube files were regarded as the input file for VMD 1.9.3[6], which was used to visualize the graphs of HOMO and LUMO as well as the RDG at the isosurface at 0.01 and 0.50, respectively.

**References**

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[4] T. Lu, F. Chen, *Journal of computational chemistry* **2012**, *33*, 580.

[5] Johnson, E. R.; Keinan, S.; Mori-Sanchez, P.; Contreras-Garcia, J.; Cohen, A. J.; Yang, W. Revealing noncovalent interactions. J. Am. Chem. Soc. 2010, 132, 6498−6506.

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Figure S1. Transient PL decay curve of compound **1** in crystal phase **1** state.

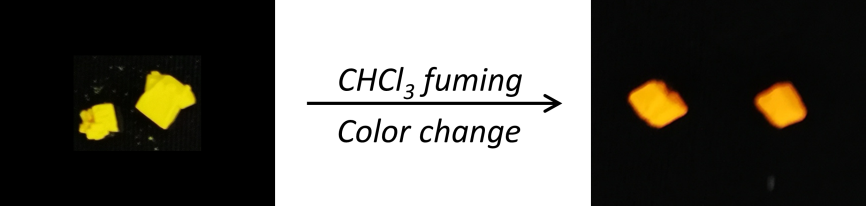


Figure S2. The change of the desolvated yellow block (**1•2CHCl3** when losed CHCl3) when fuming with CHCl3.



Figure S3. 1H-NMR spectra (400 MHz, CD2Cl2) of crystal **1** after UV irridiation (the red curve) and the untreated sample (the black curve).

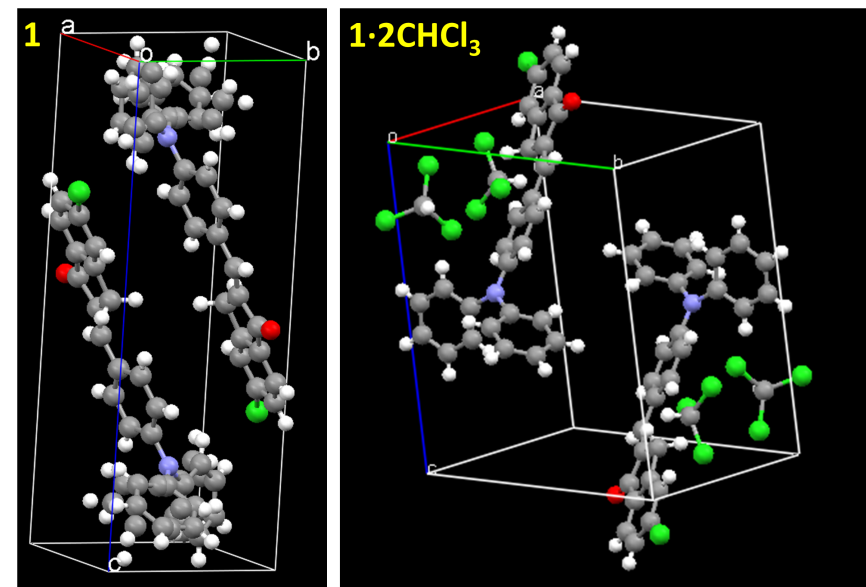


Figure S4. Unit cells of crystal **1** and **1•2CHCl3**.

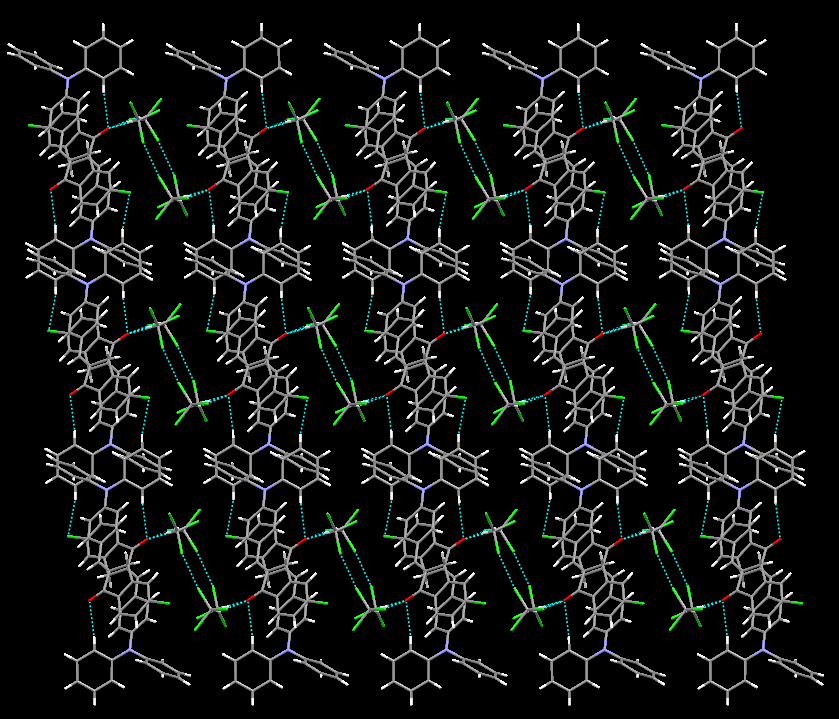


Figure S5. Infinite halogen bond network packing structure in crystal **1•2CHCl3**.



Figure S6. Absorption and emission spectra of compounds **1** in various solvents (THF: tetrahydrofuran; EA: ethyl acetate; DMSO: dimethylsulfoxide) with different polarity.

Table S1. The maximum absorption wavelength λabs and maximum emission wavelength λem of compound 1 in different solvents.

|  |  |  |
| --- | --- | --- |
| solvent | λabs | λem |
| toluene | 428 | 493 |
| CH2Cl2 | 432 | 559 |
| THF | 424 | 535 |
| EA | 422 | 541 |
| CHCl3 | 436 | 550 |
| CH3CN | 424 | 564 |
| EtOH | 432 | 558 |
| DMSO | 430 | 575 |

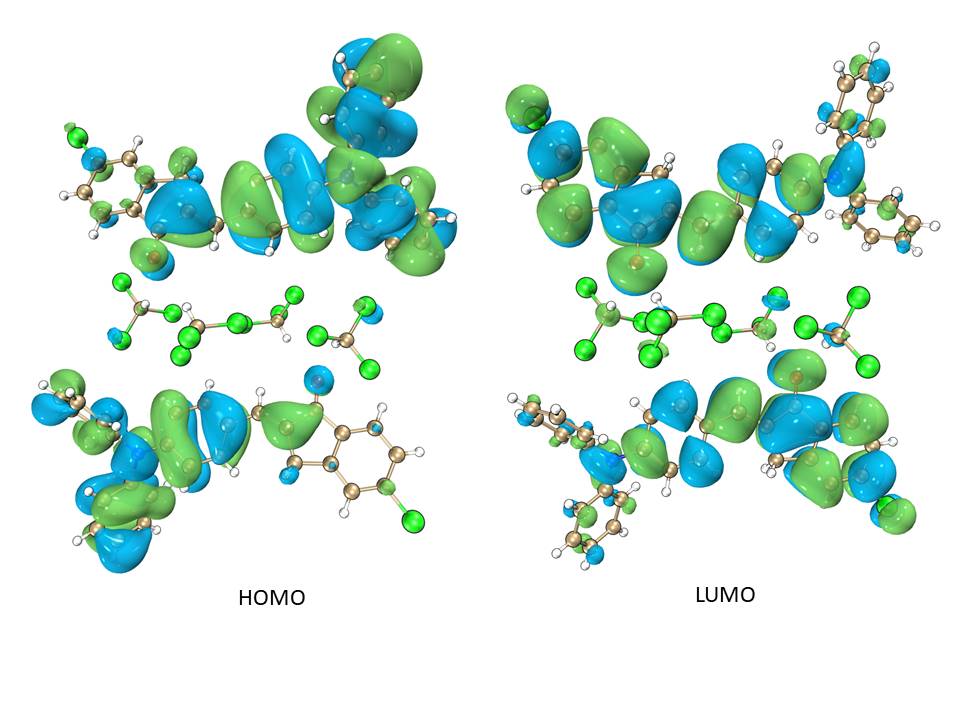


Figure S7. The calculated HOMO and LUMO molecular orbitals of the muti-molecule “complex” (containing two chaccone molecules and four CHCl3 molecules) where the two chalcone molecules are connected via abuntant weak interactions.

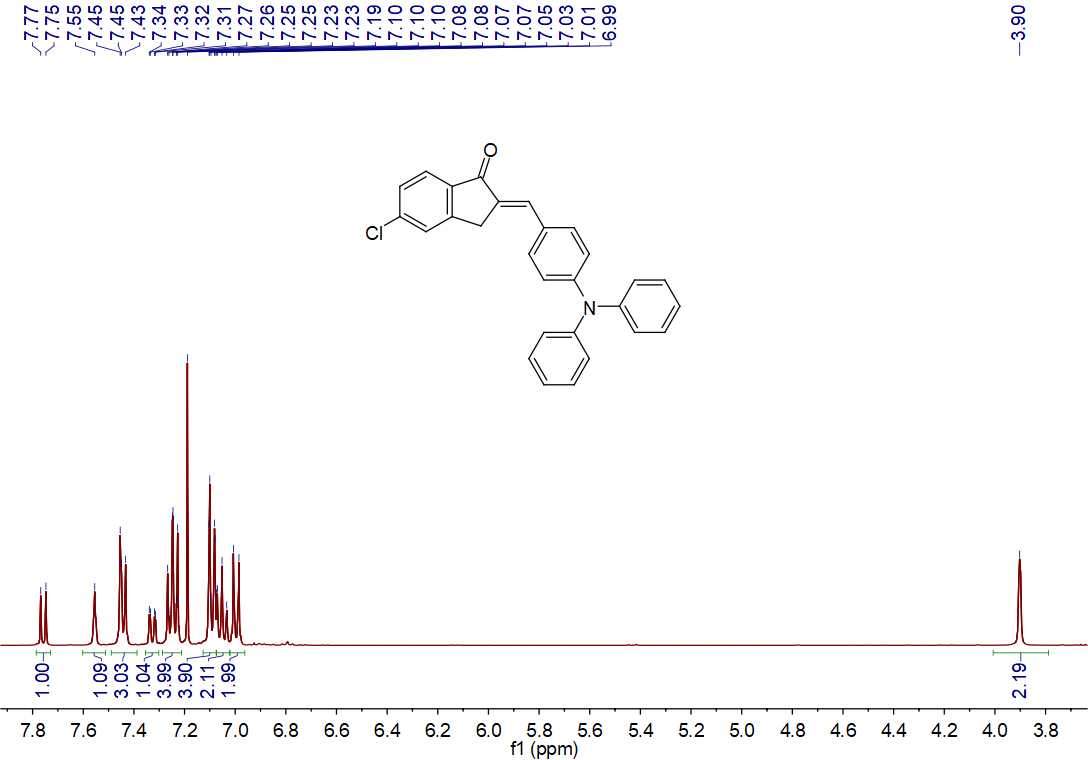


Figure S8. 1H-NMR spectrum of compound **1** (400 MHz, in CDCl3).

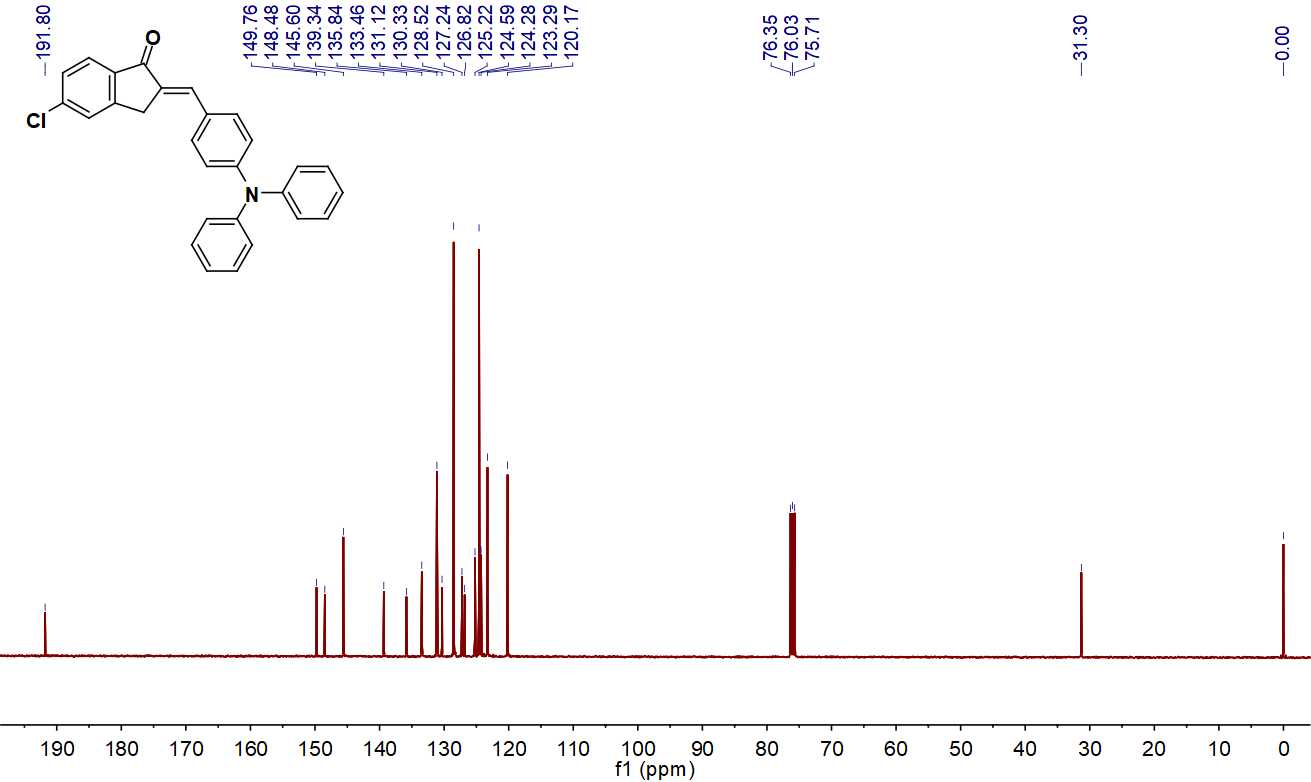


Figure S9. 13C-NMR spectrum of compound **1** (100 MHz, in CDCl3).