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Morphology-dependent Fluorescence ON/OFF of a Beryllium Complex: ACQ in Amorphous Solids, AIEE in Crystalline Powders and the Dark/Bright Fluorescence Switch

Xiao Cheng, Houyu Zhang, Kaiqi Ye, Hongyu Zhang, and Yue Wang*

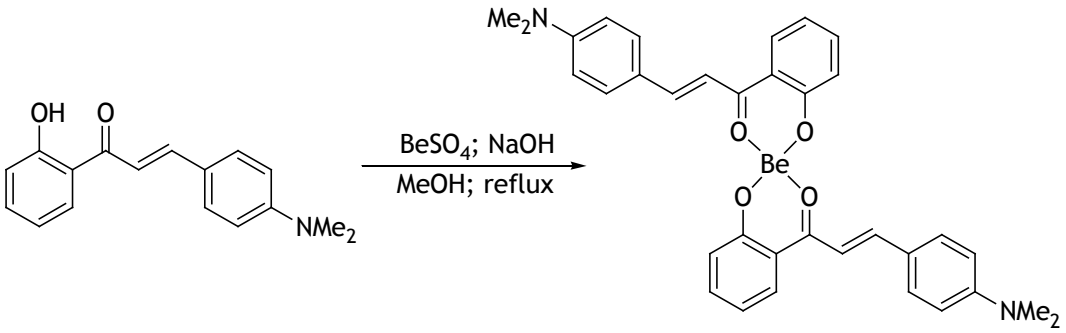
Materials. All starting materials were purchased from Aldrich Chemical Co. and used without further purification. The solvents for syntheses were common commercial grade and were used as received.

Instrumentation. NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer with tetramethylsilane as the internal standard. Mass spectrum was recorded on a GC/MS mass spectrometer. Element analyses were performed on a FlashEA1112 spectrometer. UV−vis absorption spectra were recorded by a Shimadzu UV-2550 spectrophotometer. The emission spectra of solutions were recorded by a Shimadzu RF-5301 PC spectrometer. The emission spectra of crystals/powders were recorded using a Maya2000 Pro CCD spectrometer. The absolute fluorescence quantum yields were measured on Edinburgh FLS920 in an integrating sphere. Thin film/Powder X-ray diffraction data were collected at 298K on a Bruker SMART-CCD diffractometer.

Computational details. Ab initio calculations were carried out with the Gaussian 09 program. Geometry at ground state was optimized with the density functional theory (DFT) using the B3LYP functional and 6–31G** basis set. The geometry optimization at excited state was carried out with the time–dependent density functional theory (TDDFT) at the same level of theory.

Single Crystal Structure. Single crystal X-ray diffraction data were collected on a Rigaku RAXIS-PRID diffractometer using the ω-scan mode with graphite-monochromator Mo Kα radiation. The structures were solved with direct methods using the SHELXTL programs and refined with full-matrix leastsquares on F^2. Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. CCDC 949486 and 949487 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.

Scheme S1 Synthesis of the beryllium complex $Be(HC)_2$.



Synthetic procedure. In a 100 mL round-bottomed flask, 2'-hydroxychalcone was dissolved in MeOH. Subsequently, a solution of sodium hydroxide (2 mol equiv) in water (1 mL) was added to the solution and the mixture was heated to reflux. Then a solution of beryllium sulfate (0.5 mol equiv) in water (1 mL) was added and the mixture was refluxed for 16 h. After cooling, the produced precipitates were filtered. The solid was recrystallized twice from CH_2Cl_2/MeOH or CH_2Cl_2/petroleum ether 1:2 to yield the pure beryllium complex $Be(HC)_2$.Yield was 88%. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.10 (d, J = 15 Hz, 1 H), 7.93 (dd, J = 8.5 Hz, 1.5 Hz, 1 H), 7.55 (m, 3 H), 7.47 (m, 1 H), 7.01 (d, J = 8.0 Hz, 1 H), 6.69 (m, 3 H), 3.05 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.45, 170.32, 152.59, 148.84, 138.04, 131.40, 130.14, 123.91, 122.64, 120.71, 115.46, 113.65, 111.88, 40.17. MS m/z: 541.79 $[M]^+$ (calcd: 541.25). Anal. Calcd (%) for $C_{34}H_{32}BeN_2O_4$: C,75.39; H, 5.95; N, 5.17; Found: C,74.93; H,5.902; N,5.13.

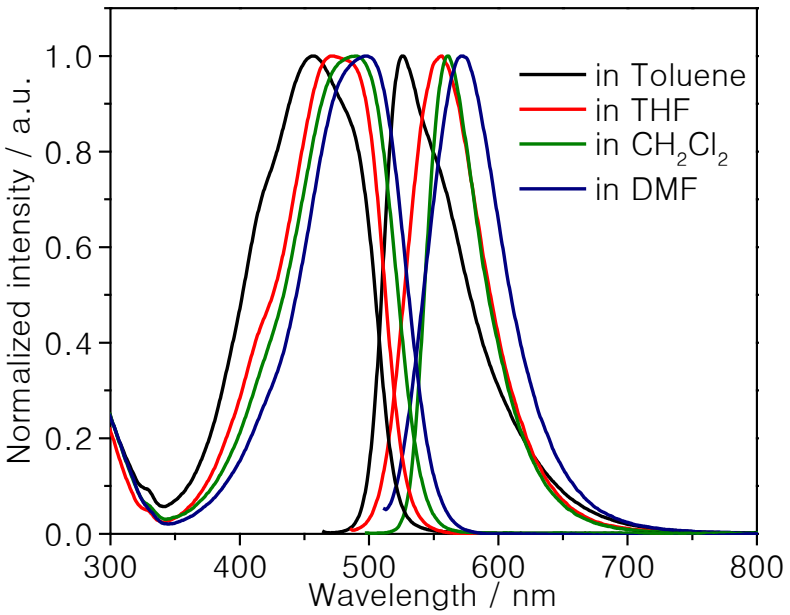


Fig. S1 Solvatochromic behaviours of $Be(HC)_2$ in different solutions.

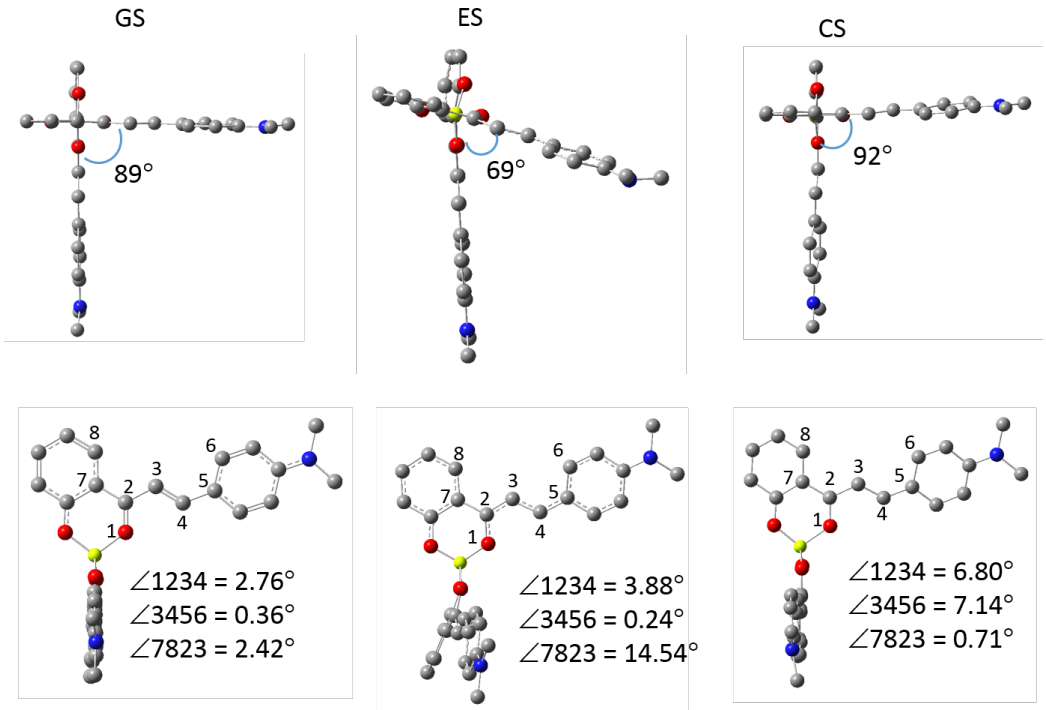


Fig. S2 The optimized ground state (GS) and excited state (ES) structures, with comparison with the crystal state (CS) structures from the top view (upper panel) and side view (lower panel). The H atoms are omitted for clarification.

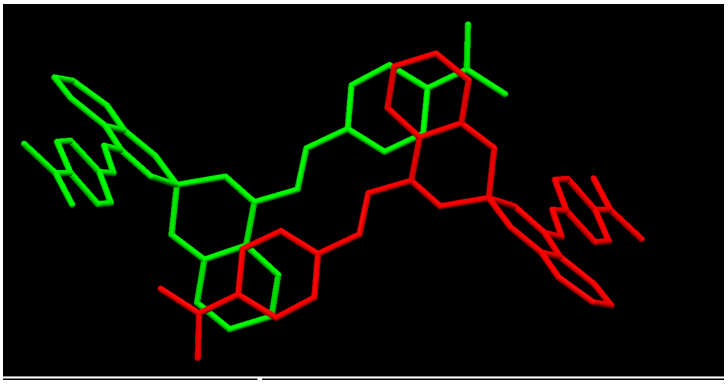


Fig. S3 Intermolecular π–π interaction in crystals **I** and **II**.

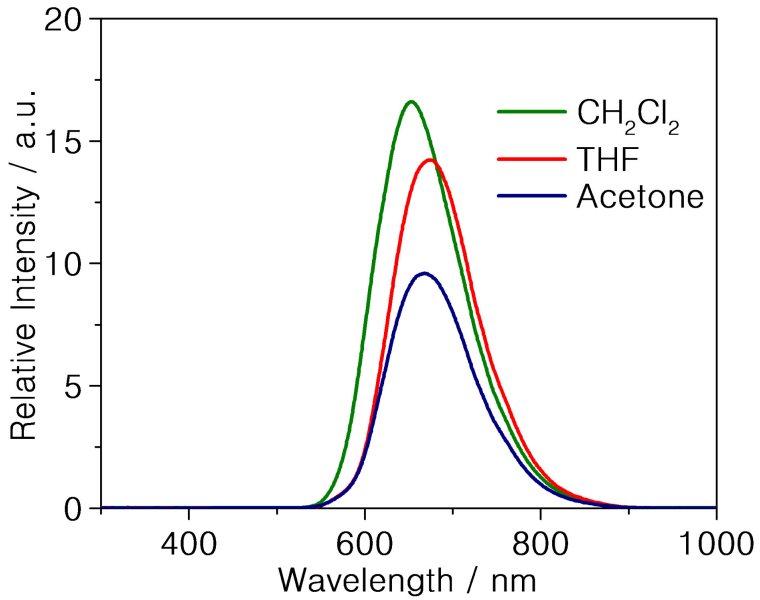


Fig. S4 PL spectra of ground sample after fuming by different VOCs.

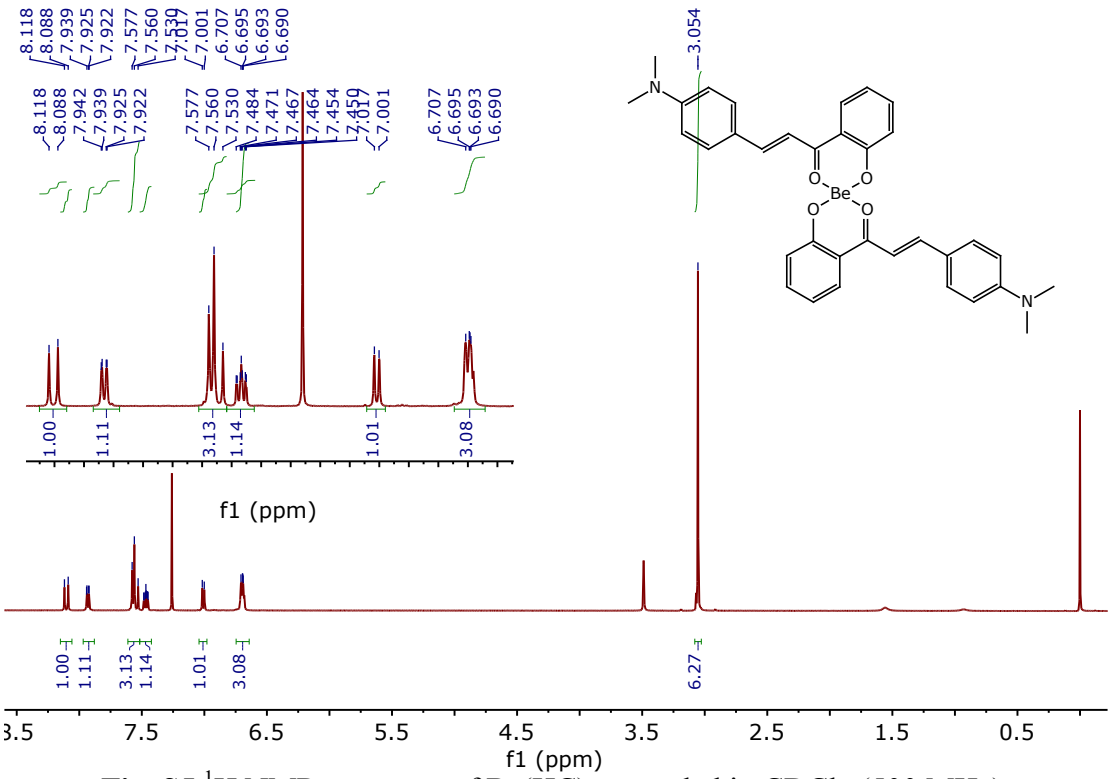


Fig. S5 ^{1}H NMR spectrum of $Be(HC)_2$ recorded in $CDCl_3$ (500 MHz).

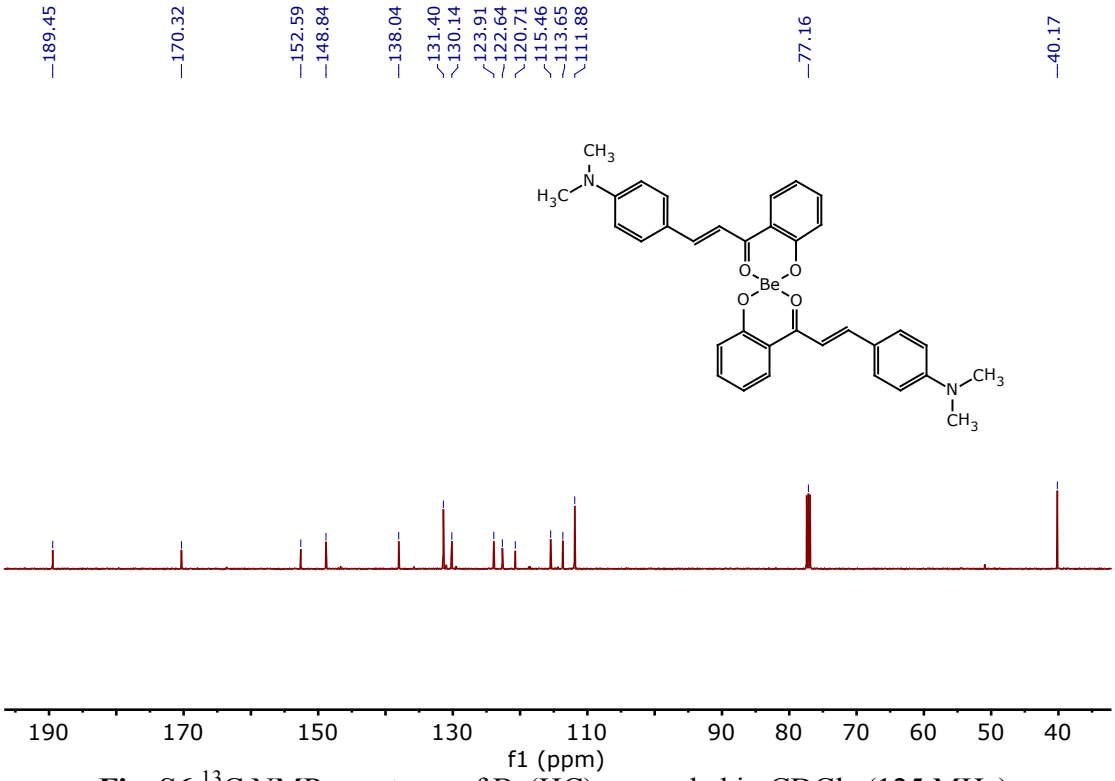


Fig. S6 ^{13}C NMR spectrum of $Be(HC)_2$ recorded in $CDCl_3$ (125 MHz).