

Supplementary Information for

**A novel approach towards white photoluminescence and
electroluminescence by controllably protonating a blue fluorophore**

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Experimental section

General information

All solvents and materials were used as received from commercial suppliers without further purification. ^1H NMR spectra were measured on Varian Mercury 300 MHz spectrometer with tetramethylsilane as the internal standard. Mass spectra were recorded on a Shimadzu AXIMA-CFR MALDITOF mass spectrometer. Elemental analyses were performed on a flash EA 1112 spectrometer. UV-vis absorption spectra were recorded by a Shimadzu UV-2550 spectrophotometer. The emission spectra were recorded by a Shimadzu RF-5301 PC spectrometer. The absolute fluorescence quantum yields of films were measured on Edinburgh FLS920 steady state fluorimeter. The single crystal of **1** (CCDC: 937726) suitable for X-ray structural analysis was obtained by vacuum sublimation. Diffraction data were collected on a Rigaku RAXIS-PRID diffractometer using the ω -scan mode with graphite-monochromator Mo-K α radiation. The structure was solved with direct methods using the SHELXTL programs and refined with full-matrix least-squares on F^2 .^{s1} Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. [s1]. SHELXTL, Version 5.1; Siemens Industrial Automation, Inc. 1997; G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution; University of Göttingen: Göttingen, 1997.

Device fabrication and measurement

Before device fabrication, the ITO glass substrates were pre-cleaned carefully and treated by UV/O₃ for 2 min. Then the sample was transferred to the deposition system. The devices were prepared in vacuum at a pressure of 5×10^{-6} Torr. The hole-transporting material NPB and exciton blocking material TCTA were commercially available and thermally evaporated at a rate of $1.0 \text{ \AA s}^{-1}$. Before device fabrication, compounds **1** and **2** are purified by the train sublimation method. After the organic film deposition, 1 nm of LiF and 100 nm of aluminum were thermally evaporated onto the organic surface. The thicknesses of

the organic materials and the cathode layers were controlled using a quartz crystal thickness monitor. The electrical characteristics of the devices were measured with a Keithley 2400 source meter. The EL spectra and luminance of the devices were obtained on a PR650 spectrometer. All measurements were carried out at room temperature under ambient conditions.

Synthesis of 2-(4-bromophenyl)-4-phenylquinazoline

A 500 mL three neck flask was charged with 2.4 g (100 mmol) of magnesium and 100 mL of dried tetrahydrofuran, and 100 mL of a tetrahydrofuran solution of 17.2 g (110 mmol) of 1-bromobenzene was added thereto to prepare a Grignard reagent. A dried tetrahydrofuran 50 mL solution of 5.91 g (50 mmol) of 2-cyanoaniline was dropwise added in 30 minutes to the above solution heated on an oil bath of 45 °C. The solution was further heated for 1.5 hour to carry out reaction and then cooled down to 0 °C in an ice and water bath. Next, a dried ether 100 mL solution of 13.2 g (60 mmol) of 4-bromobenzoic chloride was dropwise added thereto in 10 minutes, and the solution was heated on an oil bath of 45 °C for another 2 hours. After finishing the reaction, the solution was cooled down to 0 °C in an ice and water bath, and a saturated ammonium chloride aqueous solution was added thereto. The deposit was filtered, washed with a small amount of methanol and then dried under vacuum to obtain 2-(4-bromophenyl)-4-phenylquinazoline (yield: 50 %).

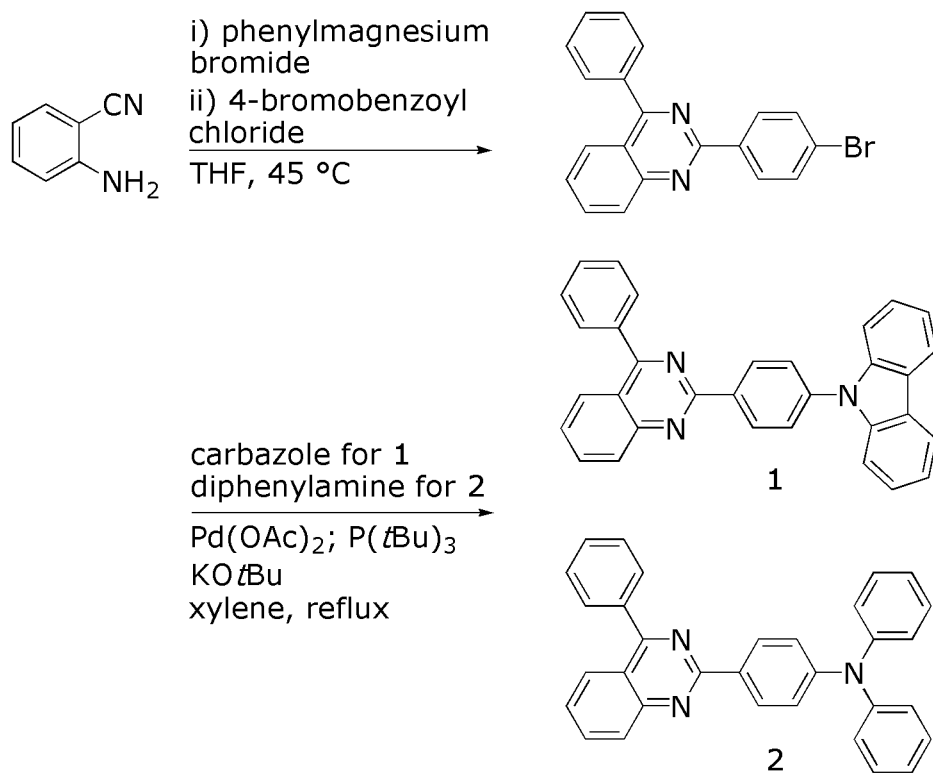
Synthesis of 9-(4-(4-phenylquinazolin-2-yl)phenyl)-9H-carbazole (**1**)

Under the nitrogen atmosphere, Pd(OAc)₂ (25 mg) and P(*t*Bu)₃ (0.1 mL) was added to the mixture of 2-(4-bromophenyl)-4-phenylquinazoline (180 mg, 0.5 mmol), carbazole (100 mg, 0.6 mmol), KO^{*t*}Bu (168 mg, 1.5 mmol), and xylene (25 mL), then refluxed for 4 h. After cooling and removal of the solvent, the residue was purified by column chromatography on silica gel using dichloromethane as the eluent to give the product 9-(4-(4-phenylquinazolin-2-yl)phenyl)-9H-carbazole (**1**). Yield: 156 mg, 70%. ¹H NMR

(300MHz; CDCl₃): δ 8.93 (d, J = 8.4 Hz, 2 H), 8.27 (d, J = 8.7 Hz, 1 H), 8.18 (m, 3 H), 7.91–7.98 (m, 3 H), 7.74–7.78 (m, 2 H), 7.59–7.66 (m, 4H), 7.54 (d, J = 8.4 Hz, 2 H), 7.41–7.47 (m, 2H), 7.28–7.34 (m, 2 H). **1** + TFA: δ 8.90 (d, J = 8.1 Hz, 2 H), 8.58 (d, J = 8.4 Hz, 1 H), 8.33 (d, J = 8.1 Hz, 1 H), 8.14–8.17 (m, 3 H), 7.97–8.02 (d, J = 7.2 Hz, 2 H), 7.88 (d, J = 7.5 Hz, 2H), 7.82 (t, J = 7.5 Hz, 1 H) 7.67–7.75 (m, 3 H), 7.58 (d, J = 8.1Hz, 2 H), 7.46 (t, J = 7.5 Hz, 2 H), 7.34 (t, J = 6.9 Hz, 2 H). Ms m/z: 447.43 [M]⁺ (calcd: 447.53). Anal.Calcd (%) for C₃₂H₂₁N₃: C, 85.88; H, 4.73; N, 9.39. Found: C, 85.99; H, 4.61; N, 9.33.

Synthesis of 9-(4-(4-phenylquinazolin-2-yl)phenyl)-9H-diphenylamine (**2**)

The compound **2** was prepared according to the same procedure as the compound **1** but using diphenylamine instead of carbazole. Yield: 167 mg, 75%. ¹H NMR (300 MHz; CDCl₃): δ 8.54 (d, J = 7.8 Hz, 2 H), 8.12 (d, J = 8.7 Hz, 2 H), 7.85–7.89 (m, 3 H), 7.57–7.60 (m, 3 H), 7.50–7.55 (m, 1 H), 7.25–7.31 (m, 4 H), 7.18 (d, J = 8.7 Hz, 6 H), 7.05–7.10 (m, 2 H). **2** + TFA: δ 8.33 (d, J = 8.1 Hz, 2 H), 8.28 (d, J = 8.4 Hz, 1 H), 8.12–8.18 (m, 2 H), 7.94 (d, J = 8.4 Hz, 2 H), 7.73–7.81 (m, 2 H), 7.65–7.70 (m, 2 H), 7.39–7.44 (t, J = 7.5 Hz, 4 H), 7.24–7.29 (t, J = 7.5 Hz, 6 H), 7.06 (d, J = 8.7 Hz, 2 H). Ms m/z: 449.10 [M]⁺ (calcd: 449.19). Anal.Calcd (%) for C₃₂H₂₃N₃: C, 85.50; H, 5.16; N, 9.35. Found: C, 85.67; H, 5.02; N, 9.25.



Scheme S1. The synthetic route for compounds of **1** and **2**.

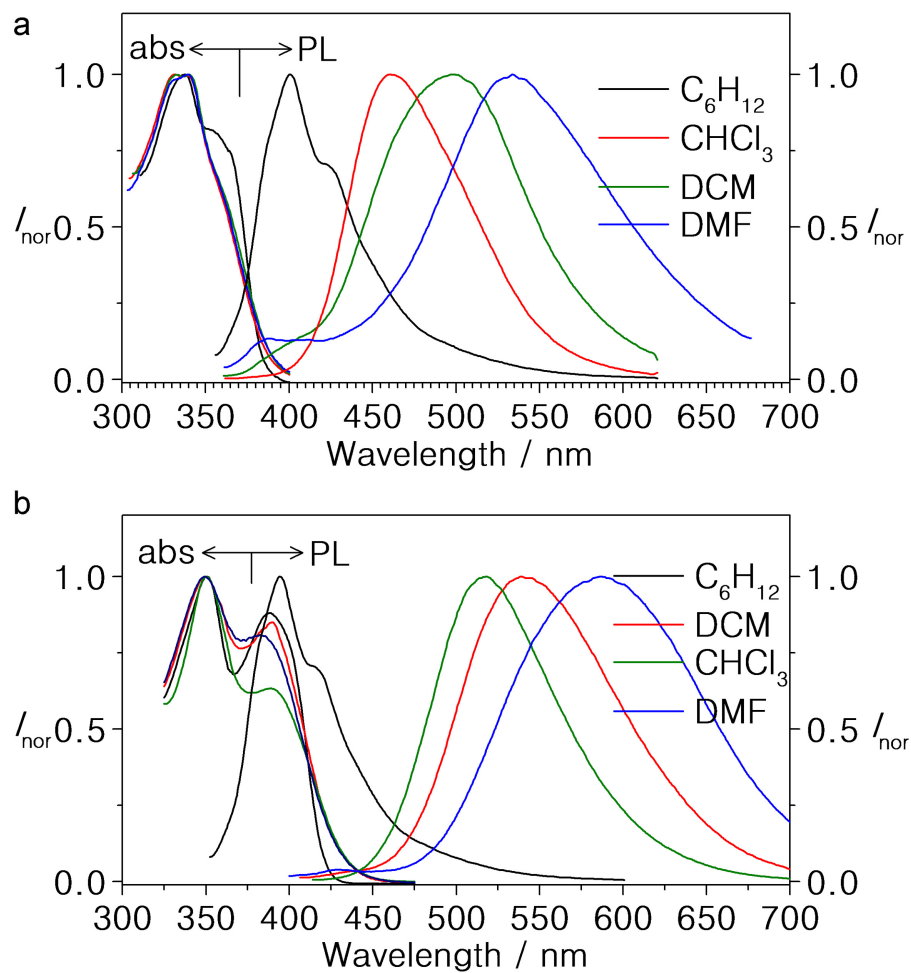


Fig. S1 Absorption and fluorescence spectra of **1** (a) and **2** (b) in different solutions

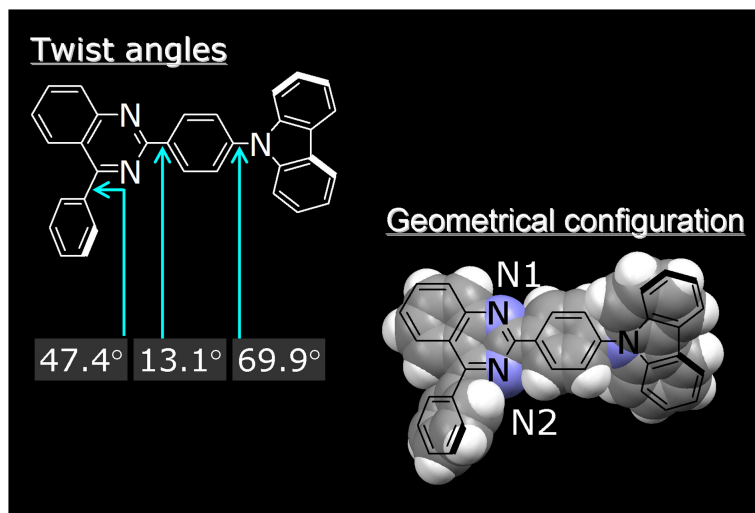


Fig. S2 Twist angles between aromatic units and a spacefill image of geometrical configuration showing the free space of N1 and N2 atoms.

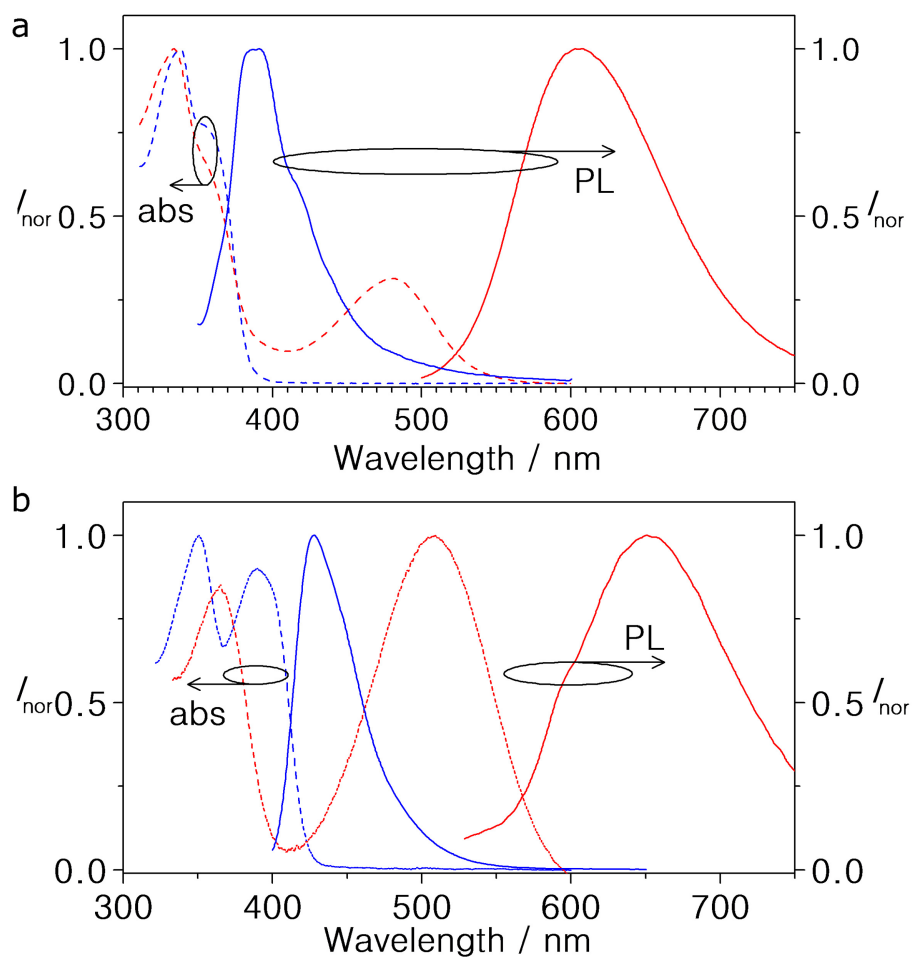


Fig. S3 Abs and PL spectra of **1** (a) and **2** (b) before and after adding TFA.

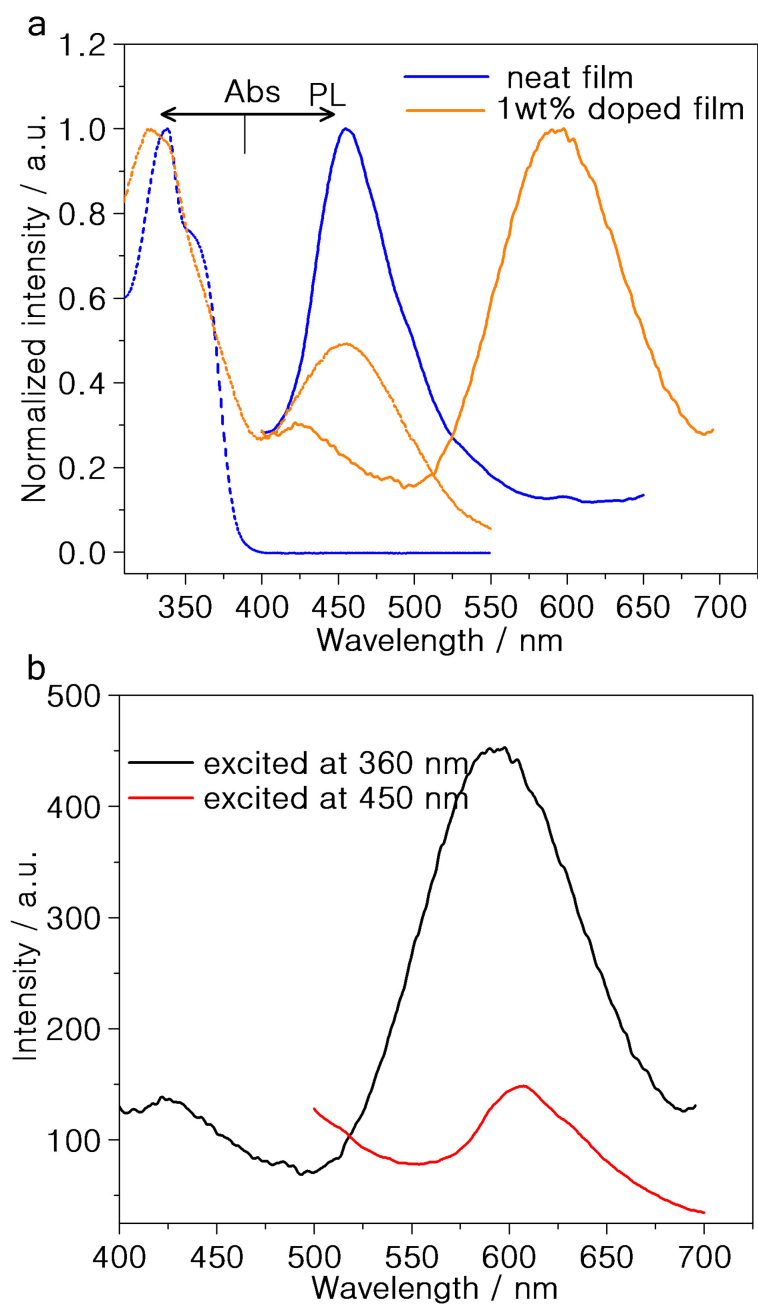


Fig. S4 Absorption and emission spectra of neat and doped (1wt%) films (a) and emission spectra of 1wt% doped film excited at different wavelength (b).

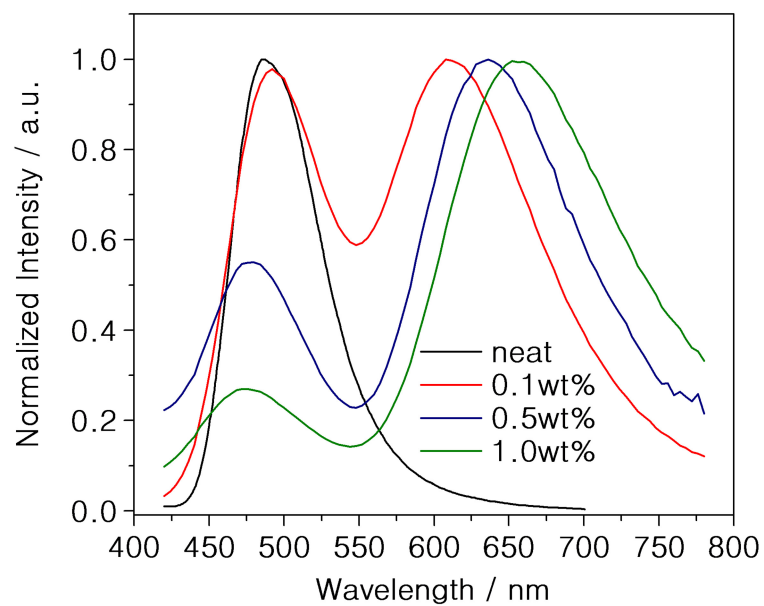


Fig. S5 PL spectra of **2** with different CSA concentrations in thin films.

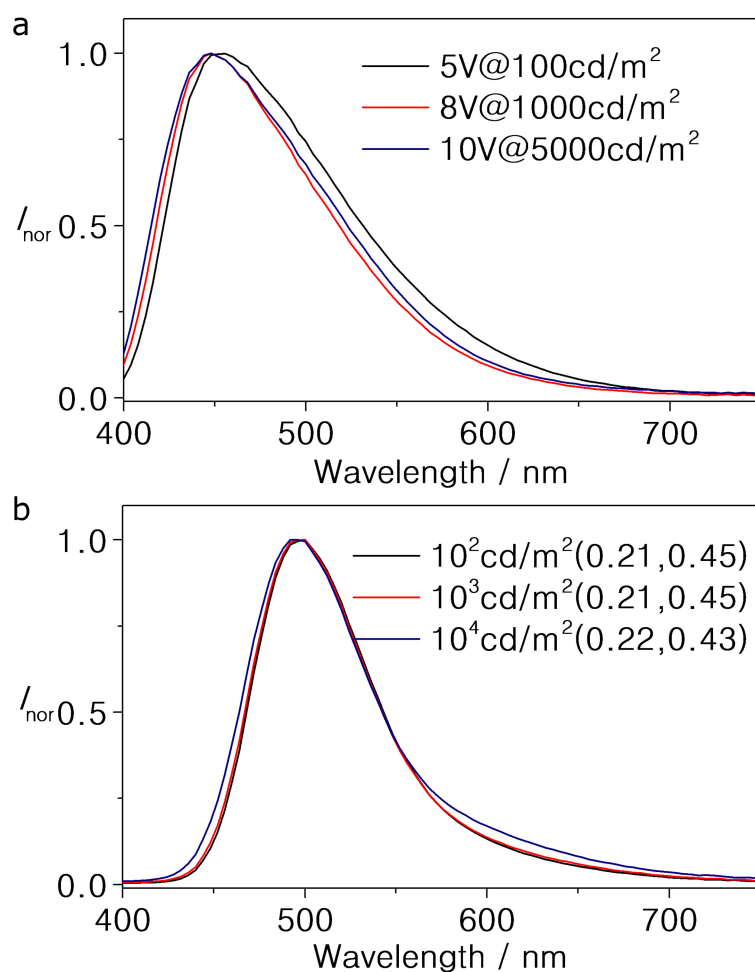


Fig. S6 EL spectra of devices employing **1** (a) or **2** (b) as an emitting material.

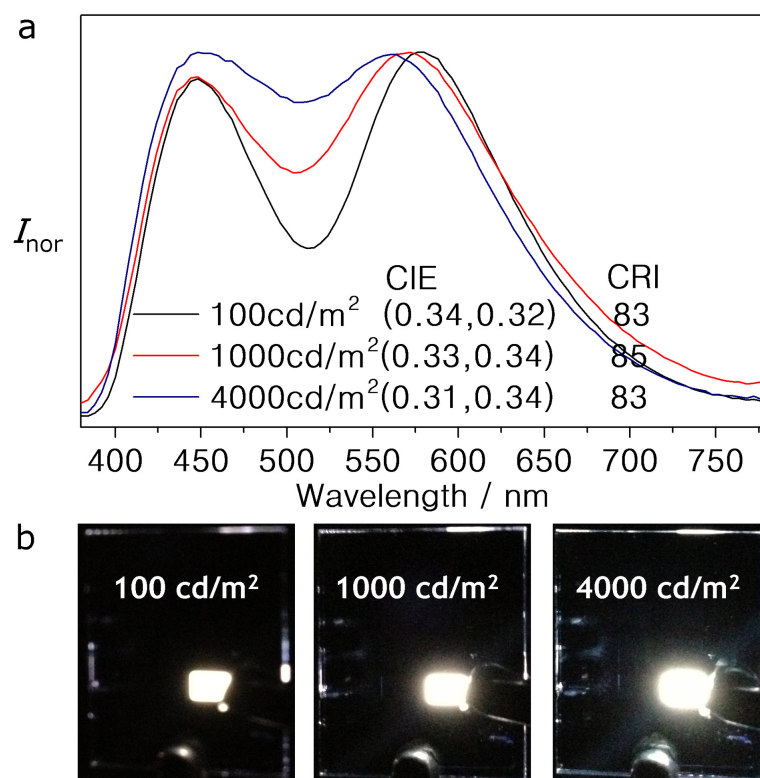


Fig. S7 EL spectra (a) and photographic images (b) of WOLEDs based on **1** under different driving voltages.

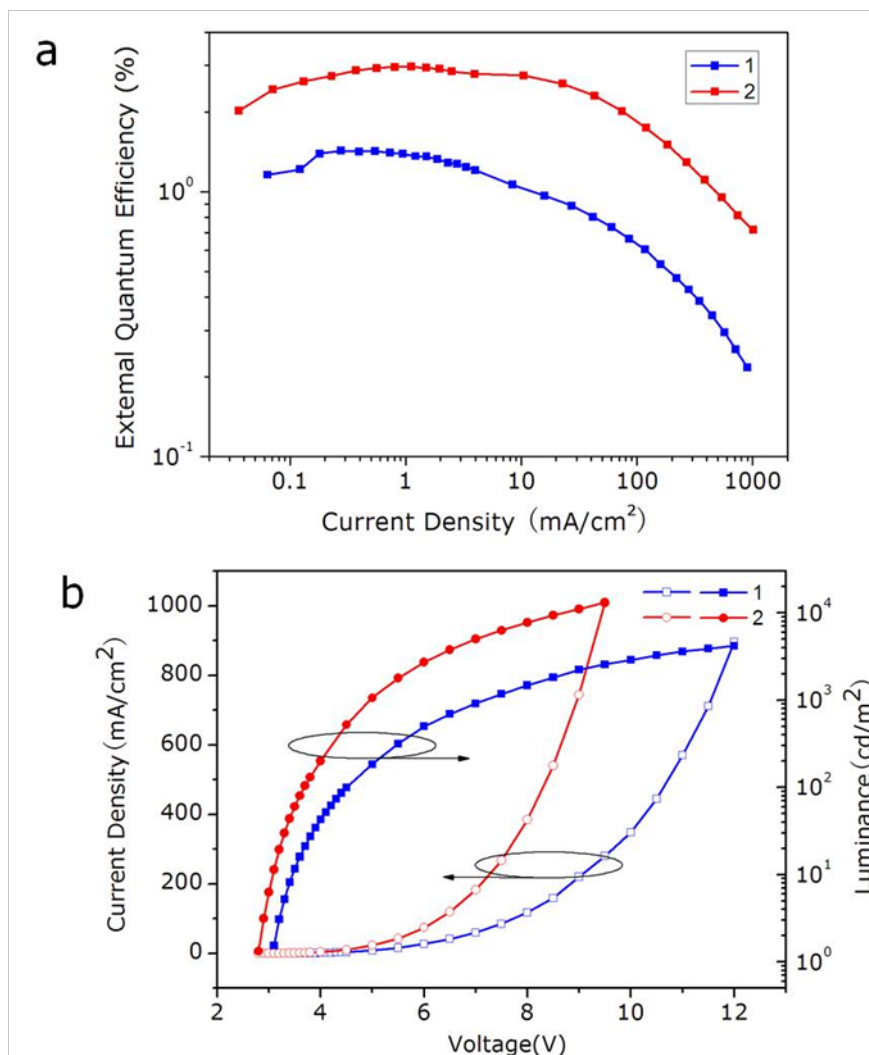


Fig. S8 External electroluminescence quantum efficiency as a function of current density (a) and the current density – voltage – luminance characteristics (b) of the white OLEDs based on **1** and **2**.

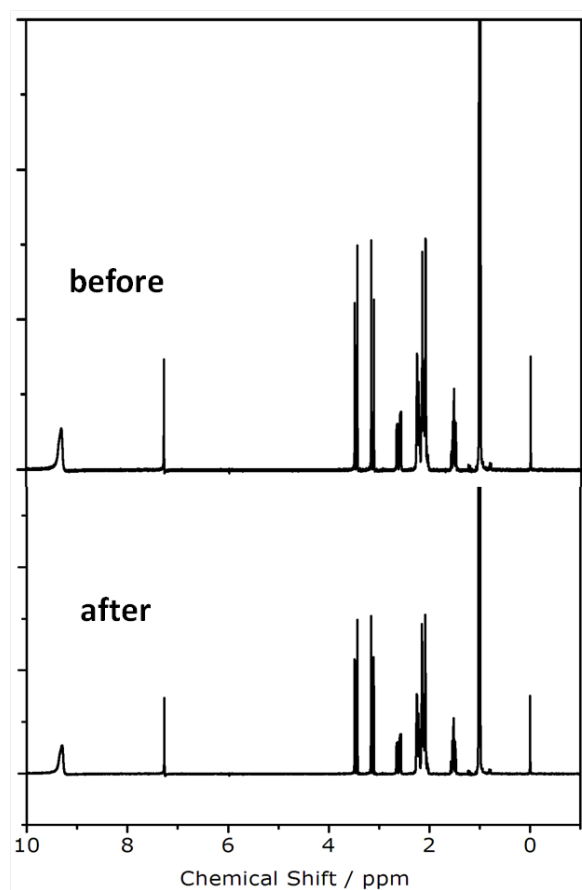


Fig. S9 NMR chart of CSA before and after vacuum sublimation.