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Electronic Supporting Information

Touch-sensitive yellow organic mechanophosphorescence and the versatile strategy for white organic mechanoluminescence

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General method

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC500 spectrometer at 500 MHz and 125 MHz, respectively, using deuterated chloroform or deuterated dimethyl sulfoxide as the solvent and tetramethylsilane (TMS) as the internal standard. High performance liquid chromatography (HPLC) was performed on an Essentia LC-16. The running rate was 1 ml/min. Photofluorescence and phosphorescence emission spectra were recorded on Hitachi F-4600 spectrophotometers. Fluorescence and phosphorescence decay curves were recorded by a Hamamatsu compact fluorescence lifetime spectrometer (FLS-1000). The lifetimes (τ) of the luminescence were obtained by fitting the decay curve with a multi-exponential decay function of

$$R(t) = \sum_i B_i e^{-\frac{t}{\tau}} \quad \text{(S1)}$$

where B_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.

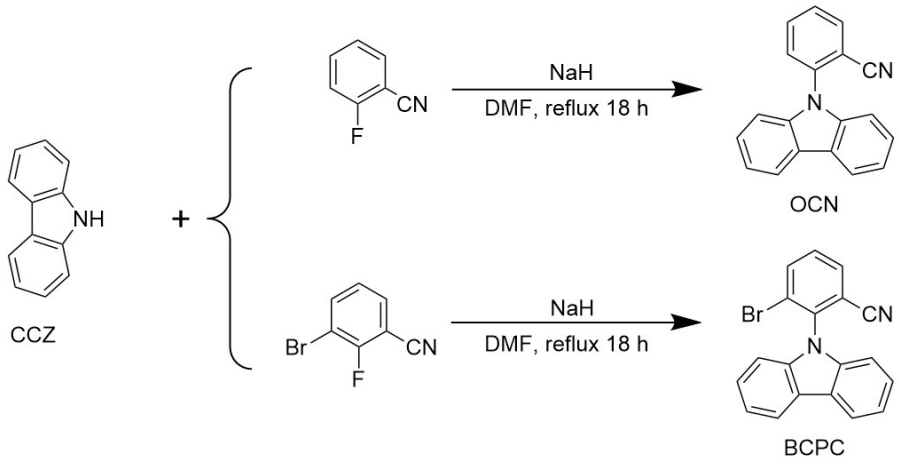
The digital photographs were captured by the FDR-AX700 4K HDR digital cameras (SONY, Japan). Elemental analysis was characterized using a Flash EA 1112 instrument. Absolute PL quantum yields (PLQY) were determined with a spectrometer C11347 (Hamamatsu, Japan). The RTP yields were generally obtained by peak-differentiation-imitating analysis from the delay PL spectrum, the transient PL spectra and the absolute total quantum yield (Φ). By peak-differentiation-imitating analysis, the RTP ratio can be identified, and from Φ, both fluorescent and RTP yields can be figured out. As illustrated in Equation S2, Φ is obtained by photon counting from the excitation source into an integration sphere with the ratio of photons emitted:

(S2)

In this equation, N^{em} is the number of emitted photons and N^{abs} is the number of absorbed photons.

Synthesis and Characterization

Scheme S1. The synthetic route of OCN and BCPC.

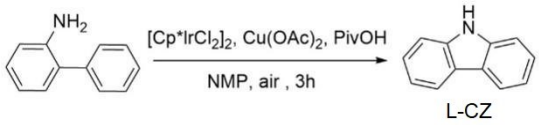


N-(2-cyanpphenyl)carbazole (OCN). In a 100 ml bottom commercial 9H-carbazole (CCZ, 1.50 g, 8.97 mmol) and NaH (0.43 g, 17.94 mmol) in DMF (50 ml) was stirred at 0 °C for 1 h. 2-fluorobenzonitrile (1.73 g, 9.87 mmol) was added in the mixture and stirred at 150 °C for 18 h. After cooling, the reaction mixture was extracted with ethyl acetate, the combined organic layer dried with anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by silica-gel column chromatography using petroleum ether/ dichloromethane (5:2 v/v), yielding a white solid (1.93 g, Yield 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15

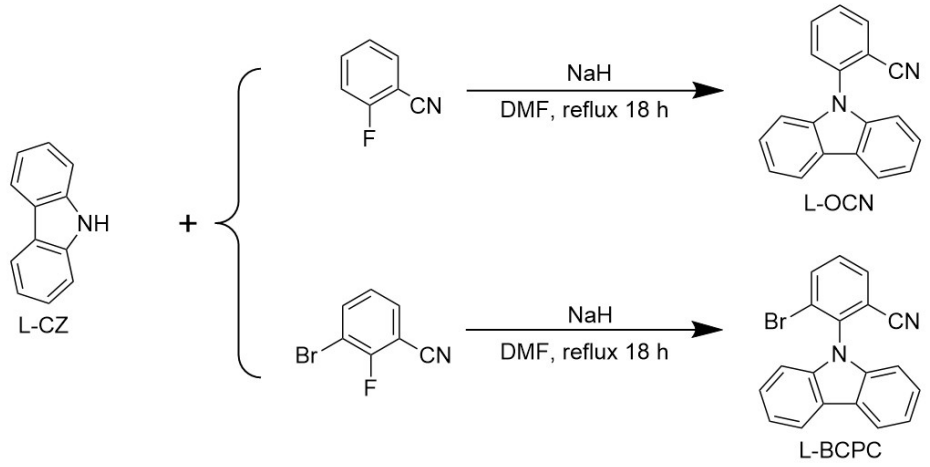
(dt, *J* = 7.7, 1.0 Hz, 2H), 7.96 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.84 (td, *J* = 7.8, 1.6 Hz, 1H), 7.67–7.59 (m, 2H), 7.43 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 2H), 7.33 (td, *J* = 7.5, 1.0 Hz, 2H), 7.21 (dd, *J* = 8.1, 0.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.70, 140.60, 134.49, 134.26, 129.67, 128.43, 126.17, 123.87, 120.76, 120.52, 115.98, 112.85, 109.65. Anal. Calcd. For $C_{19}H_{12}N_2$: C, 85.05; H, 4.51; N, 10.44. Found: C, 85.08; H, 4.52; N, 10.42.

N-(2-bromo-5-cyano)phenyl-carbazole (BCPC). The BCPC was prepared following the same procedure of OCN by using 3-bromo-2-fluorobenzonitrile. The eluent is petroleum ether/ dichloromethane (4:1 v/v), yielding a white solid (2.59 g, Yield 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.7 Hz, 2H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.04, 139.44, 138.65, 133.20, 130.44, 126.32, 126.01, 123.87, 120.89, 120.73, 116.53, 114.84, 109.55. Anal. Calcd. For $C_{19}H_{11}BrN_2$: C, 65.73; H, 3.19; Br, 23.01; N, 8.07. Found: C, 65.74; H, 3.20; N, 8.06.

Scheme S2. The synthetic route of L-CZ, L-OCN and L-BCPC.



Lab-carbazole (L-CZ). In a 100 ml two-necked flask 2-Aminobiphenyl (2.50 g, 14.77 mmol), $[Cp^*IrCl_2]_2$ (0.25 g, 0.31 mmol), $Cu(OAc)_2$ (0.54 g, 2.97 mmol),and PivOH (3.05 g, 29.86 mmol) in NMP (50 ml) was stirred under air at 120 °C for 3 h. After cooling, the reaction mixture was extracted with ethyl acetate, the combined organic layer dried with anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by silica-gel column chromatography using petroleum ether/ dichloromethane (5:1 v/v), yielding a white solid (1.31 g, Yield 53 %). ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.27 (s, 1H), 8.13 (d, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 139.66, 125.44, 122.34, 120.08, 118.42, 110.87. Anal. Calcd. For $C_{12}H_9N$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.24; H, 5.40; N, 8.35.



Lab-N-(2-cyanpphenyl)carbazole (L-OCN). In a 100 ml bottom commercial 9H-carbazole (L-CZ, 1.50 g, 8.97 mmol) and NaH (0.43 g, 17.94 mmol) in DMF (50 ml) was stirred at 0 °C for 1 h. 2-fluorobenzonitrile (1.73 g, 9.87 mmol) was added in the mixture and stirred at 150 °C for 18 h. After cooling, the reaction mixture was extracted with ethyl acetate, the combined organic layer dried with anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by silica-gel column chromatography using petroleum ether/ dichloromethane (5:2 v/v), yielding a white solid (1.95 g, Yield 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (dt, *J* = 7.8 Hz, 2H), 7.98–7.94 (m, 1H), 7.84 (td, *J* = 7.8, 1.5 Hz, 1H), 7.65–7.61 (m, 2H), 7.46–7.41 (m, 2H), 7.35–7.31 (m, 2H), 7.21 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.70, 140.60, 134.50, 134.26, 129.67, 128.43, 126.17, 123.87, 120.76, 120.52, 115.98, 112.85, 109.65. Anal. Calcd. For $C_{19}H_{12}N_2$: C, 85.05; H, 4.51; N, 10.44. Found: C, 85.06; H, 4.51; N, 10.43.

Lab-N-(2-bromo-5-cyano)phenyl-carbazole (L-BCPC). The L-BCPC was prepared following the same procedure of L-OCN by using 3-bromo-2-fluorobenzonitrile. The eluent is petroleum ether/ dichloromethane (4:1 v/v), yielding a white solid (2.56 g, Yield 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.7 Hz, 2H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.04, 139.44, 138.65, 133.20, 130.44, 126.32, 126.01, 123.87, 120.89, 120.73, 116.53, 114.84, 109.55. Anal. Calcd. For $C_{19}H_{11}BrN_2$: C, 65.73; H, 3.19; Br, 23.01; N, 8.07. Found: C, 65.72; H, 3.20; N, 8.07.

Supplementary Figures and Tables

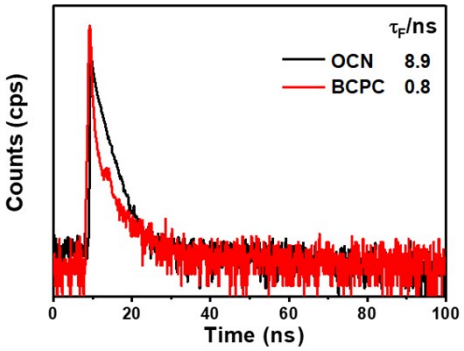


Figure S1. Time-resolved emission decay curves of **OCN** and **BCPC** crystal powder fluorescence under ambient conditions. τ_F is the fluorescence lifetime.

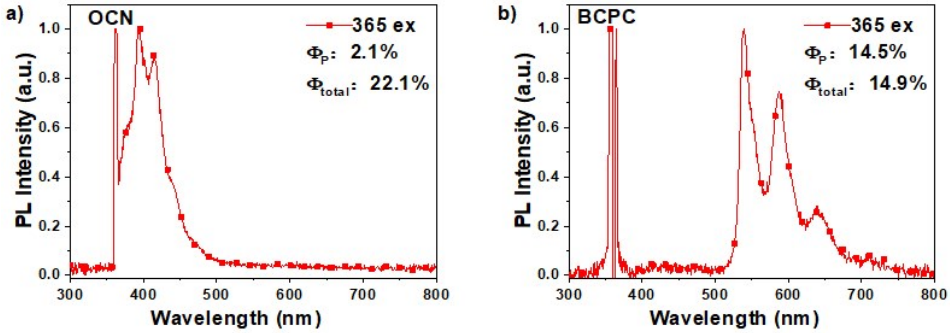


Figure S2. The transient PL spectra and the measured total absolute efficiency (Φ_{total}) and the calculated phosphorescence efficiency (Φ_P) by a PL integration sphere for **OCN** a) and **BCPC** b) crystals under ambient conditions.

Table S1. Crystal Structural data of **OCN** and **BCPC**.

Compound reference	colorless **OCN** crystal[1]	colorless **BCPC** crystal
Chemical formula	$C_{19}H_{12}N_2$	$C_{19}H_{11}BrN_2$
Formula weight	268.31	347.21
Crystal system	Orthorhombic	Monoclinic
Space group	Iba2	P 21
a/ Å	14.7314(14)	8.338(6)
b/ Å	24.585(2)	12.528(9)

c/ Å	8.0451(8)	14.752(11
α/°	90	90
β/°	90	92.607(13)
γ/°	90	90
Unit cell volume/ Å^3	2913.7(5)	1539.2(18)
Temperature/K	296	100
Z	8	2
Density (calculated) /g cm^{-3}	1.223	1.498
F(000)	1120	696
Theta range for data collection	2.765 to 7.571 deg.	2.863 to 25.997 deg.
Index ranges	-19<=h<=18, -32<=k<=24, -10<=l<=10	-9<=h<=10, -15<=k<=14, -18<=l<=17
Completeness to theta	25.242 99.9%	25.242 99.7%
Absorption coefficient	None	None
Max. and min. transmission	0.984 and 0.988	0.487 and 0.454
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3248 / 1 / 190	4872 / 1 / 397
Goodness-of-fit on F^2	0.968	0.828
CCDC number	1918562	1980041

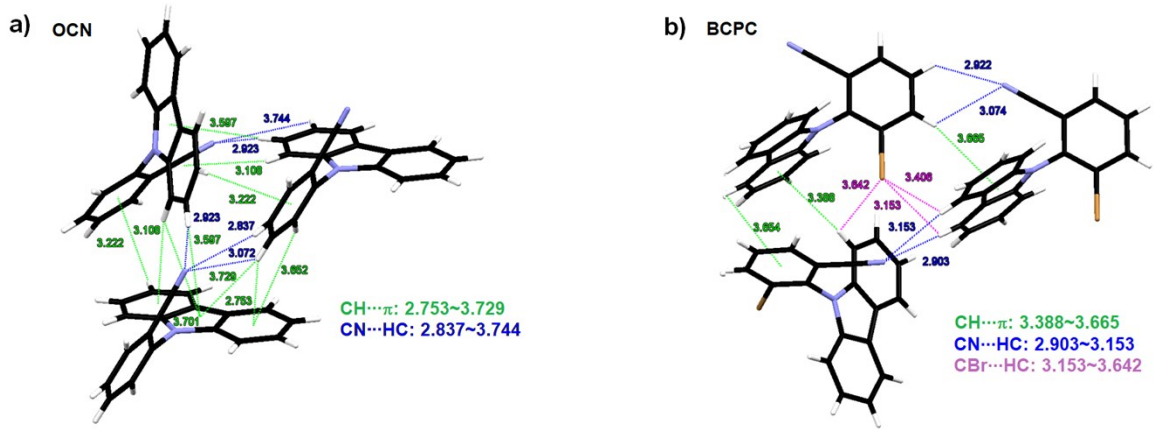


Figure S3. The intermolecular interactions in **OCN** a) and **BCPC** b) crystals.

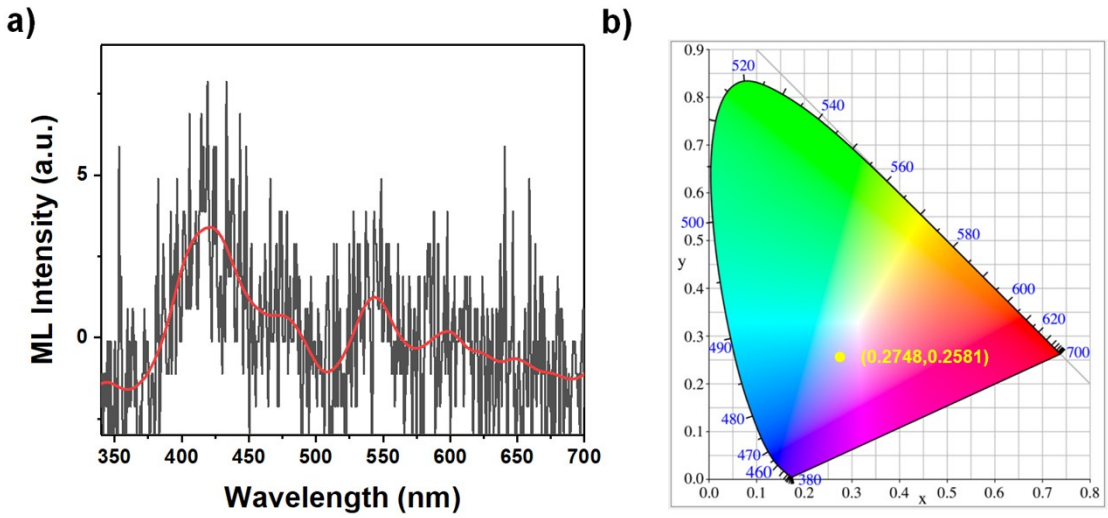


Figure S4. The ML spectrum a) and the ML CIE coordinates b) of the crystalline mixture (10/2) of **OCN** and **BCPC.**

Table S2. Summary of photophysical parameters of **OCN** and **BCPC** crystals.

Sample	τ_F /ns	λ_{ex} /nm	Φ_F /%	K_F /s^{-1}	τ_P /ms	Φ_P /%	K_P /s^{-1}	K_{nr} /s^{-1}	K_{ISC} /s^{-1}
OCN	8.9	365	20	$2.2*10^7$	574.2	2.1	$3.7*10^{-2}$	1.7	$2.3*10^6$
BCPC	0.8	365	0.4	$4.9*10^6$	239.4	14.5	$6.0*10^{-1}$	3.5	$1.8*10^8$

τ_F: lifetime of fluorescence; Φ_F: absolute quantum yield of fluorescence; K_F: rate constant of fluorescence; τ_P: lifetime of phosphorescence; Φ_P: absolute quantum yield of phosphorescence; K_P: rate constant of phosphorescence; K_{nr}: rate constant of non-radiative decay of T_1; K_{ISC}: rate constant of intersystem crossing (ISC) from singlet to triplet states. $K_F = \Phi_F/\tau_F$; $K_P = \Phi_P/\tau_P$; $K_{nr} = (1-\Phi_P)/\tau_P$; $K_{ISC} = \Phi_P/\tau_F$.[2-5]

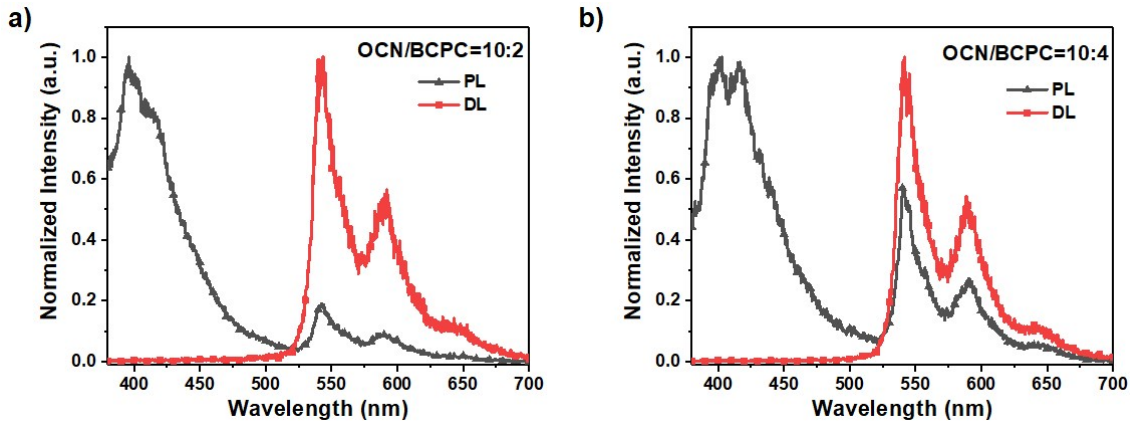


Figure S5. Steady (PL) and delayed (DL) photoluminescence of crystalline mixture (10/2) a) and (10/4) b) of **OCN** and **BCPC.**

Photophysical properties of the L-OCN and L-BCPC in crystalline states:

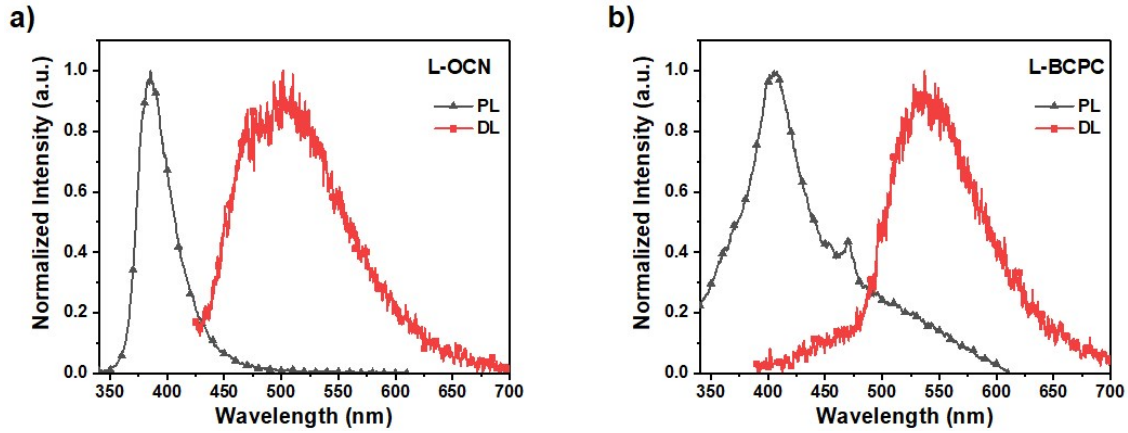


Figure S6. Steady (PL) and delayed (DL) photoluminescence of **L-OCN** a) and **L-BCPC** b).

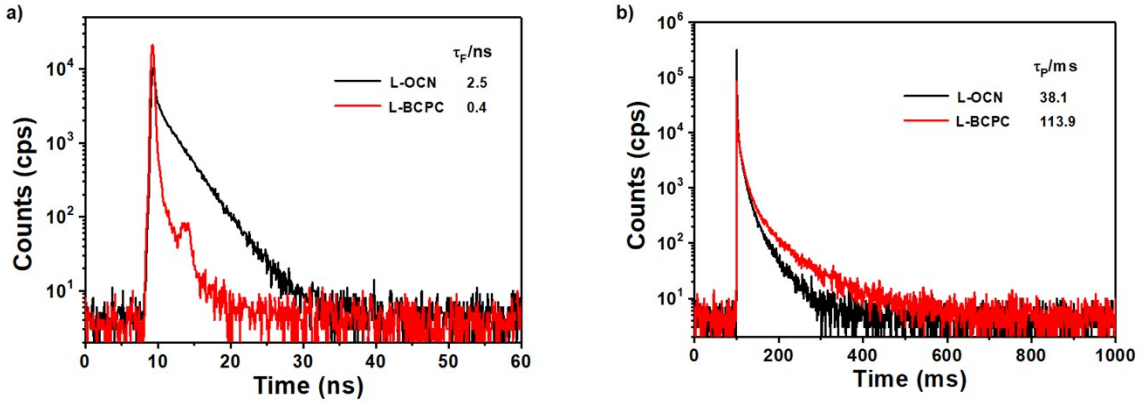


Figure S7. Time-resolved emission decay curves of **L-OCN**, **L-BCPC** crystal powder fluorescence a) and phosphorescence b) under ambient conditions. τ_F is the fluorescence lifetime, and τ_p is the phosphorescence lifetime.

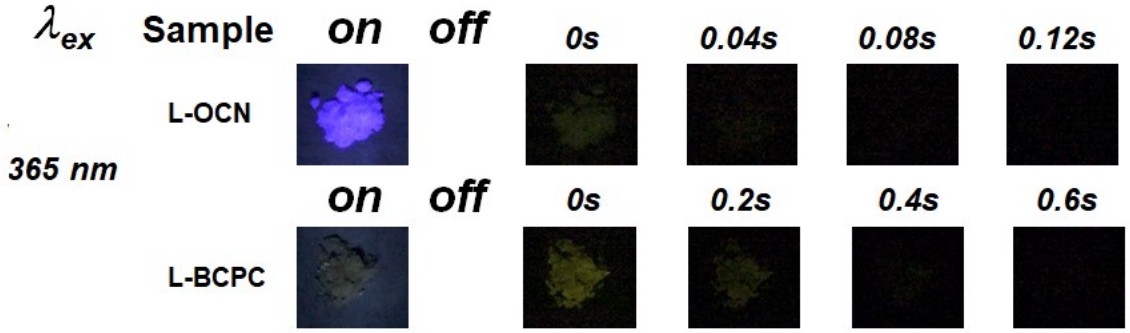


Figure S8. The PL photographs of **L-OCN** and **L-BCPC** crystals under 365 nm excitation light before and after removing exaction light in the dark.

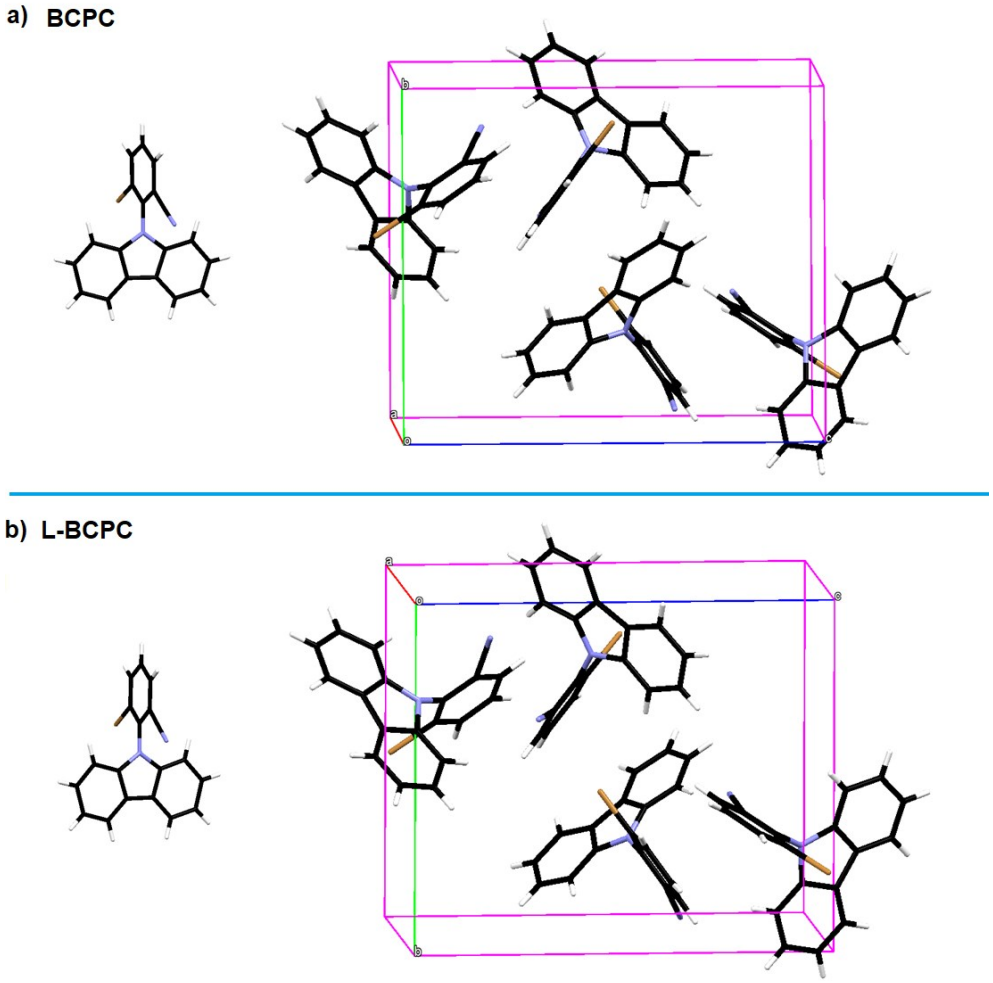


Figure S9. The unit cell structures of **BCPC** a) and **L-BCPC** b) single crystal.

Table S3. Crystal Structural data of **BCPC** and **L-BCPC**.

Compound reference	colorless **BCPC** crystal	colorless **L-BCPC** crystal
Chemical formula	$C_{19}H_{11}BrN_2$	$C_{19}H_{11}BrN_2$
Formula weight	347.21	347.21
Crystal system	Monoclinic	Monoclinic
Space group	P 21	P 21
a/ Å	8.338(6)	8.2827(16)
b/ Å	12.528(9)	12.474(2)
c/ Å	14.752(11	14.700(3)
α/°	90	90
β/°	92.607(13)	92.458(3)
γ/°	90	90

Unit cell volume/ Å^3	1539.2(18)	1517.5(5)
Temperature/K	100	100
Z	2	2
Density (calculated) /g cm^{-3}	1.498	1.520
F(000)	696	696
Theta range for data collection	2.863 to 25.997 deg.	2.773 to 24.999 deg.
Index ranges	-9<=h<=10, -15<=k<=14, -18<=l<=17	-9<=h<=9, -8<=k<=14, -17<=l<=16
Completeness to theta	25.242 99.7%	24.999 99.8%
Absorption coefficient	None	None
Max. and min. transmission	0.487 and 0.454	0.614 and 0.542
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4872 / 1 / 397	4413 / 7 /397
Goodness-of-fit on F^2	0.828	0.984
CCDC number	1980041	2051715

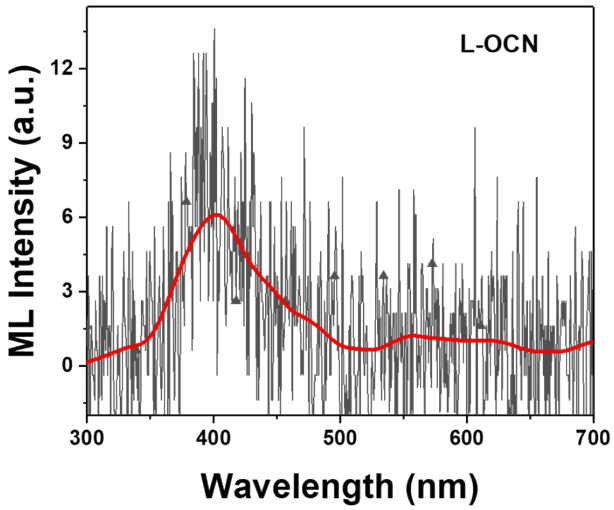


Figure S10. Mechanofluorescence (MF) spectra of **L-OCN** crystals.

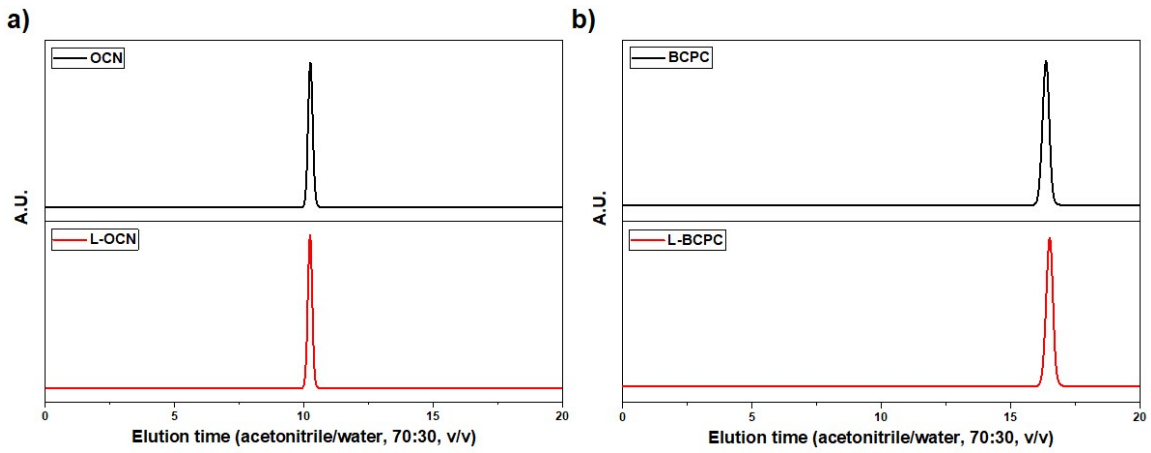


Figure S11. a) HPLC spectra of **OCN** and **L-OCN** monitored at the onset absorption of 346 nm with 70/30 acetonitrile (ACN)-water ratio (v/v). b) HPLC spectra of **BCPC** and **L-BCPC** monitored at the onset absorption of 346 nm with 70/30 acetonitrile (ACN)-water ratio (v/v).

NMR Spectra

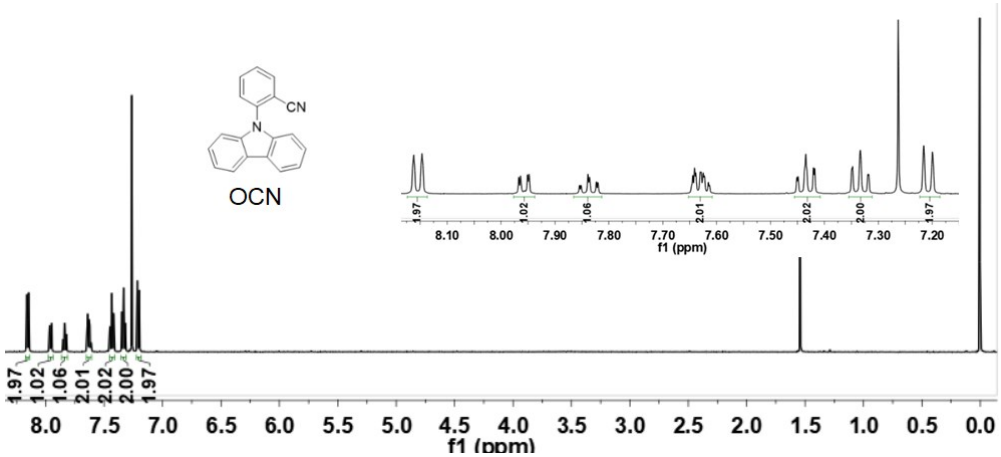


Figure S12. ^{1}H NMR spectrum of **OCN** in $CDCl_3$.

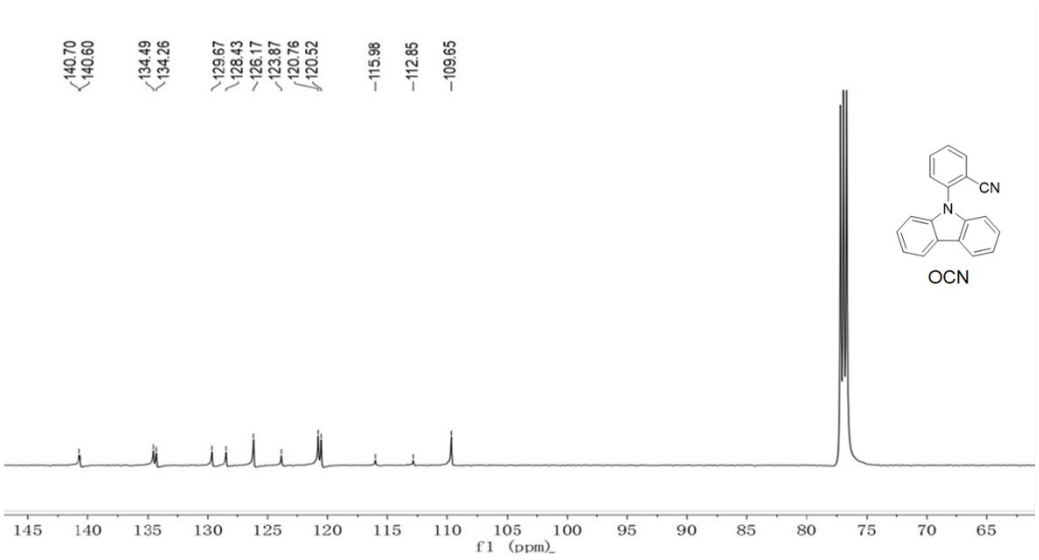


Figure S13. ^{13}C NMR spectrum of **OCN** in $CDCl_3$.

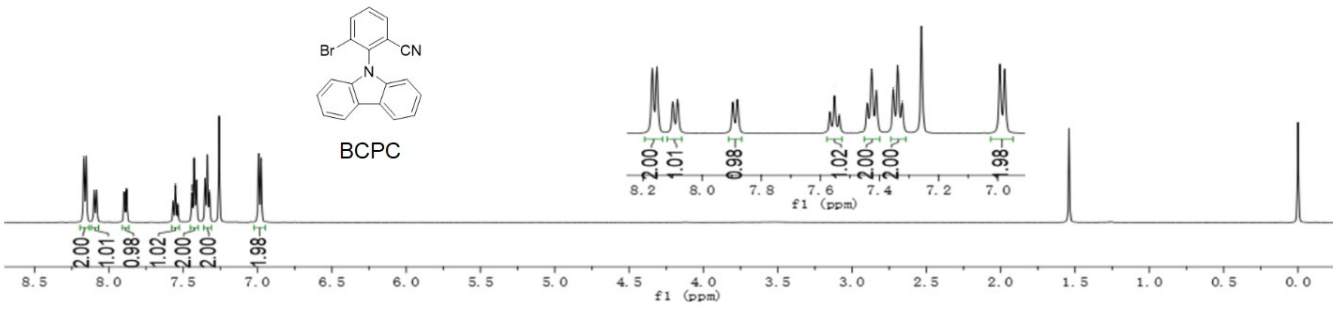


Figure S14. ^{1}H NMR spectrum of **BCPC** in $CDCl_3$.

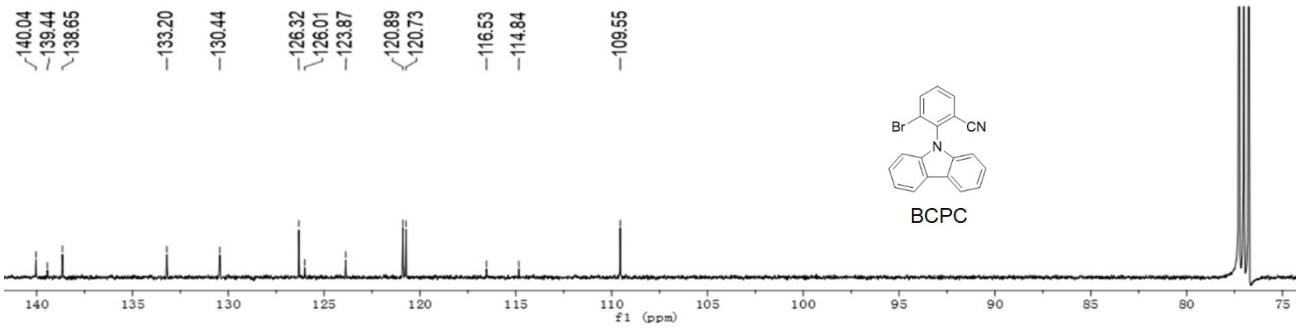


Figure S15. ^{13}C NMR spectrum of **BCPC** in $CDCl_3$.

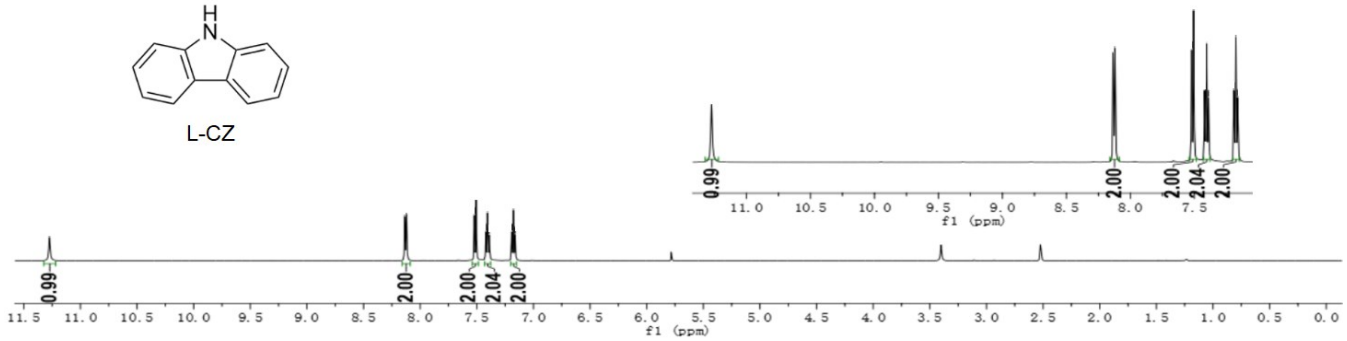


Figure S16. ^{1}H NMR spectrum of **L-CZ** in DMSO-d_6.

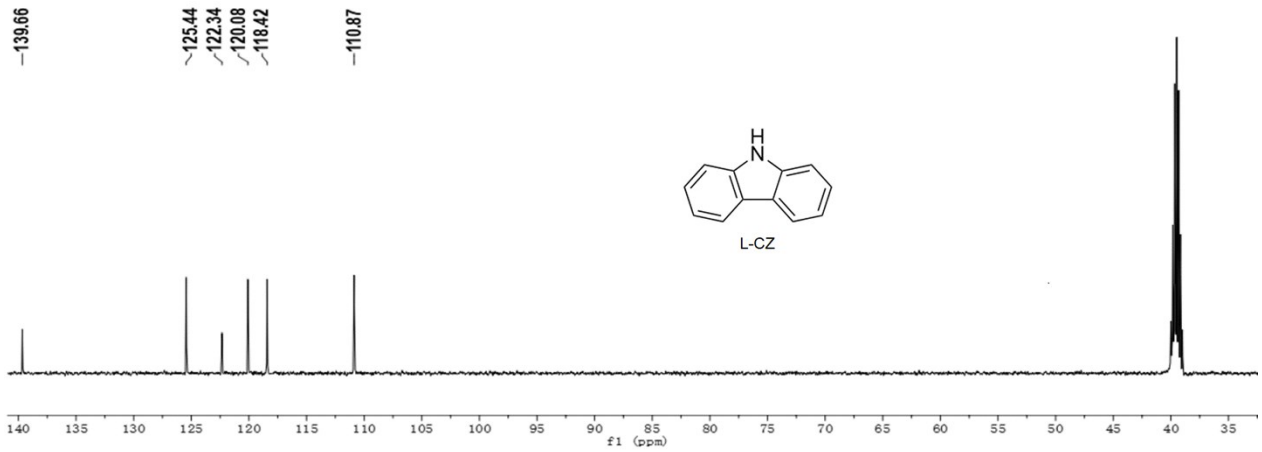


Figure S17. ^{13}C NMR spectrum of **L-CZ** in DMSO-d_6.

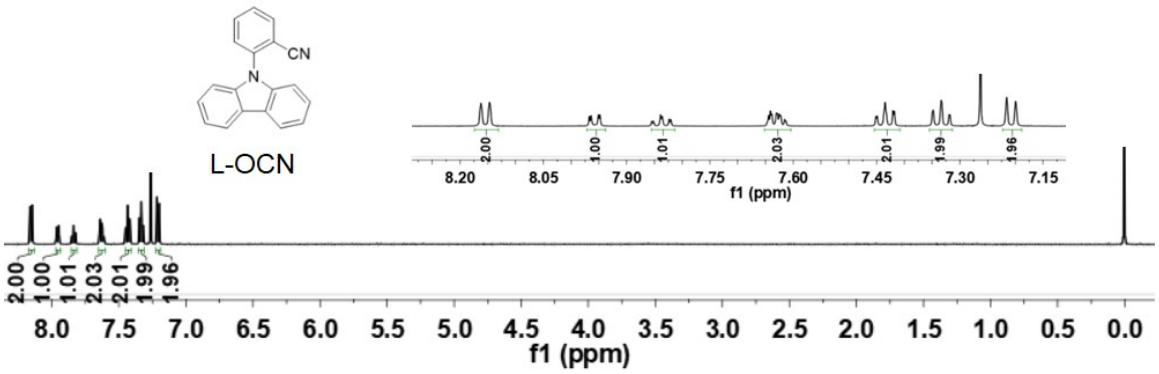


Figure S18. ^{1}H NMR spectrum of **L-OCN** in $CDCl_3$.

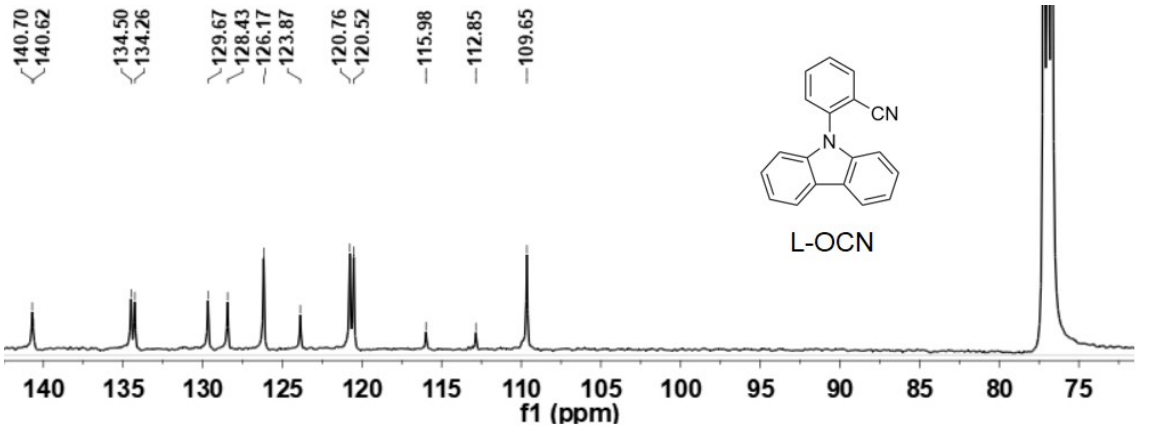


Figure S19. ^{13}C NMR spectrum of **L-OCN** in $CDCl_3$.

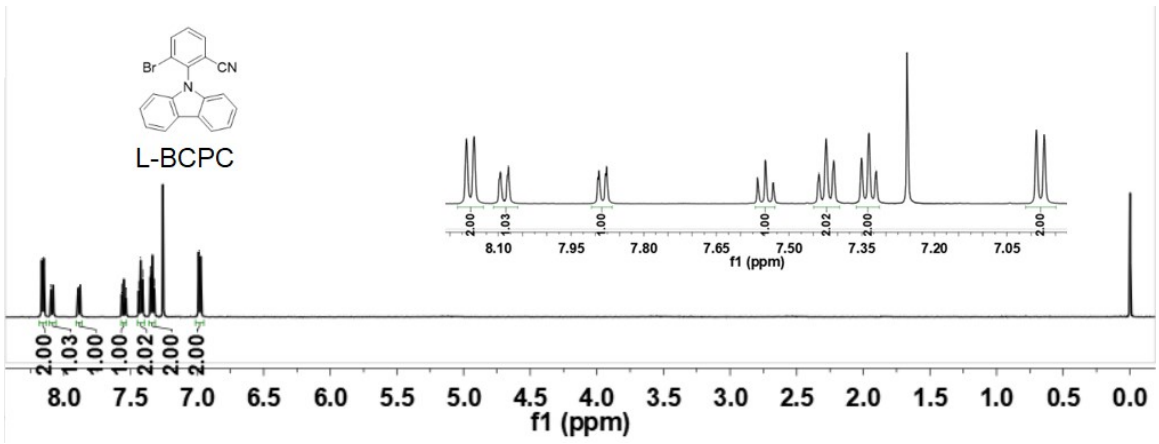


Figure S20. ^{1}H NMR spectrum of **L-BCPC** in $CDCl_3$.

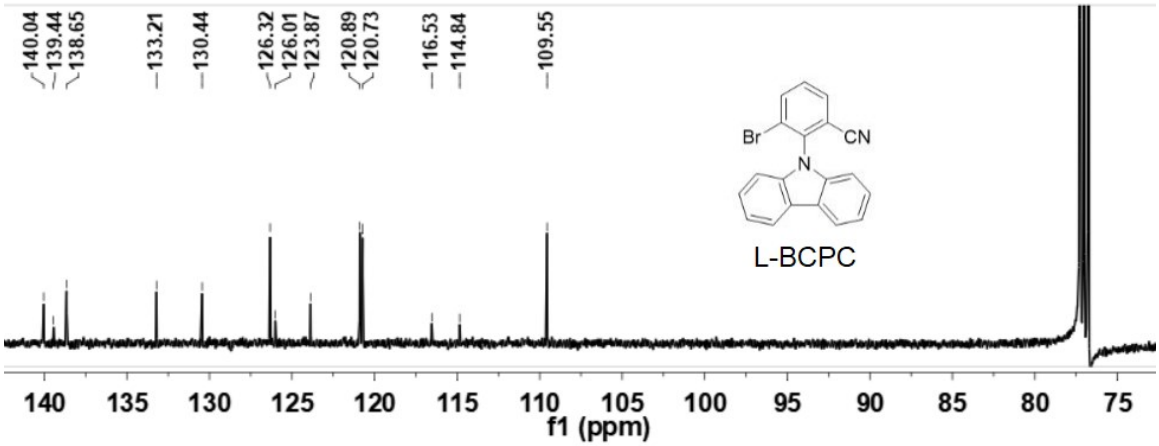


Figure S21. ^{13}C NMR spectrum of **L-BCPC** in $CDCl_3$.

Reference

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