Supplementary Information (SI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2025

Liquid-crystalline Dual Fluorescent Dyes for White Light Emission

Alfiya F. Suleymanova[a], James R. Fortwengler[b], Xinrui Chen[d], Rafal Czerwieniec[c], Yafei Wang[d]*, Marsel Z. Shafikov[c]* and Duncan W. Bruce[a]*

[a]Department of Chemistry
University of York
Heslington
YORK
YO10 5DD
UK
Tel: (+44) 1904 324085
E-mail: duncan.bruce@york.ac.uk

[b]Department of Chemistry,
University of Southern California,
Los Angeles,
California,
90089, USA

[c]Institut für Physikalische und Theoretische Chemie,
Universität Regensburg,
Universitätsstrasse 31,
Regensburg, D-93053,
GERMANY
E-mail: shafikoff@gmail.com

[d]School of Materials Science & Engineering,
Changzhou University,
CHANGZHOU 213164,
PR CHINA
E-mail: qiji830404@hotmail.com

Supporting Information

General methods

NMR spectra were recorded on a JEOL ECX spectrometer at 298 K. ^{1}H NMR (400 MHz) chemical shifts are referenced to residual, non-deuterated $CHCl_3$ (δ = 7.26 ppm) in $CDCl_3$, DCM (δ = 5.32 ppm) in methylene chloride-d_2 and DMSO in DMSO-d_6 (δ = 2.49 ppm). $^{13}C\{^{1}H\}$ NMR (100 MHz) chemical shifts are reported relative to $CDCl_3$ (δ 77.3), DCM-d_2 (δ 54.00) and DMSO-d_6 (δ 39.52). Elemental analysis was carried out on an Exeter Analytical Inc. CE-440 analyser. Accurate mass measurement analyses were conducted using matrix-assisted laser desorption/ionisation (MALDI). Optical textures were recorded using an Olympus BX50 polarising microscope equipped with a Linkam scientific LTS350 heating stage, Linkam LNP2 cooling pump and Linkam TMS92 controller. DSC was performed on a Mettler DSC822e fitted with an autosampler operating with Mettler Star-E software and calibrated before use against an indium standard (onset = 156.55 ± 0.2°C, Δ*H* = 28.45 ± 0.40 J g^{-1}), with all runs performed under an atmosphere of dry nitrogen. Small angle X-ray scattering was recorded using a Bruker D8 Discover equipped with a temperature controlled, bored graphite rod furnace, custom built at the University of York. Cu-Kα (λ = 0.154056 nm) radiation was used, generated from a 1 μS microfocus source. Diffraction patterns were recorded on a 2048 × 2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample, allowing simultaneous collection of small-angle and wide-angle scattering data. Samples were measured in 1 mm capillary tubes in a magnetic field of *ca* 1 T.

All reagents were purchased from commercial sources and used as received. 2,9-Dibromophenanthroline[1] and 3,8-dibromophenanthroline[2, 3] were synthesised according to the literature. Solvents were purified with drying cartridges through a solvent delivery system. Reactions were monitored by TLC using silica gel (F_{254} plates, 60 Å porosity). TLC analysis was visualized using UV light. The products were purified by chromatography on silica gel (60 Å porosity, 35-75 μm).

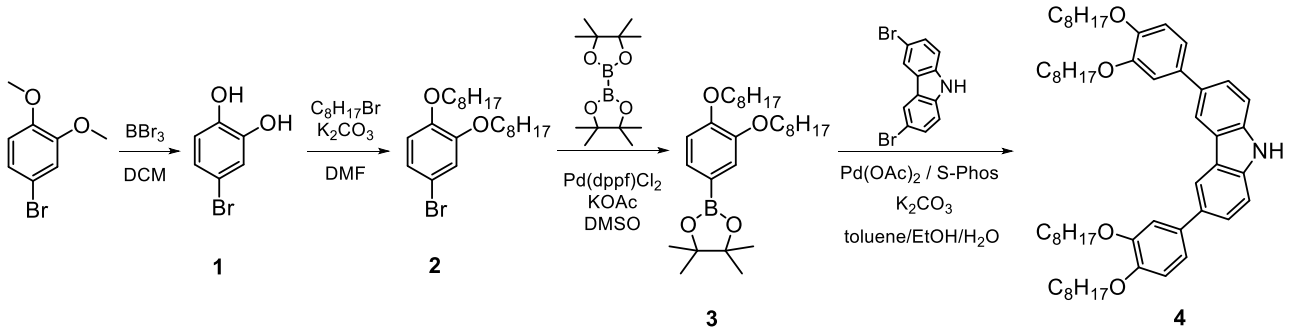
The UV-Vis absorption spectra were measured with a Varian Cary 300 double beam spectrometer. The emission and excitation spectra were measured with a Horiba Jobin Yvon Fluorolog-3 steady-

state fluorescence spectrometer. The emission decay times were measured with a PicoBright PB375 pulsed diode laser (λ_{exc} = 378 nm, pulse width 100 ps) used as the excitation source, and the PL signal was detected with a cooled photomultiplier attached to a FAST ComTec multichannel scalar PCI card with a time resolution of 250 ps. The PL quantum yield was determined with a Hamamatsu C9920-02 system equipped with a Spectralon® integrating sphere.

All calculations were carried out with the Gaussian 09 package1 utilising the DFT approach with the M11L functional2 and the def2-SVP basis set3. Geometry optimisations were conducted with 'tight' criteria.

Synthesis

Synthesis of 3,6-bis-(3,4-dioctyloxybenzene)-9H-carbazole



1-Bromo-3,4-dihydroxybenzene (1)

1-Bromo-3,4-dimethoxybenzene (20 mL, 157 mmol) was dissolved in DCM (100 mL). Argon was bubbled for 30 min to remove the oxygen. After cooling down to -78 °C for 30 min in dry ice/acetone bath, a solution of BBr_3 in heptane (360 mL, 360 mmol, 1 M) was added drop by drop and the solution was kept at -78 °C for 30 min. White-brownish precipitate was observed (dissolved during further warming process). Solution was slowly warmed to room temperature, and then to 40 °C and stirred overnight. After reacted for 24 h, saturated NH_4Cl aqueous solution was added slowly at 0 °C to quench the reaction. The mixture was extracted with ethyl acetate. Organic solvents were collected, over anhydrous $MgSO_4$, and evaporated. Obtained product was used without further purification. Yield was 95% (R_f = 0.23 in petroleum ether/ethyl acetate

system (3/1)). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 7.02 (1H, d, J = 2.3 Hz), 6.91 (1H, dd, J = 8.6, 2.3 Hz), 6.74 (1H, d, J = 8.6 Hz), 6.00 (1H, s, OH), 5.79 (1H, s, OH).

1-Bromo-3,4-dioctyloxybenzene (2)

1-Bromo-3,4-dihydroxybenzene (7.45 g, 39.15 mmol) was dissolved in anhydrous dimethylformamide (130 mL) and degassed by flushing argon through the solution for 15 min in a sonicator. Potassium carbonate (21.6 g, 156.6 mmol) was added and the suspension was stirred for another 15 min at room temperature. After addition of the 1-bromooctane (21.6 mL, 125.3 mmol), the reaction mixture was stirred overnight at 80 °C. After cooling to room temperature, the reaction mixture was poured into water (500 mL), and then extracted with hexane (2x300 mL). The combined organic layers were washed with water, and dried over anhydrous $MgSO_4$. The product was dried under vacuum to give white solid with yield of 98% (16 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 6.98 (2H, m, Ph), 6.73 (1H, d, *J* = 9.2 Hz, Ph), 3.95 (2H, t, *J* = 6.6 Hz, $OC\underline{H_2}$), 3.94 (2H, t, *J* = 6.6 Hz, $OC\underline{H_2}$), 1.79 (4H, m, alkyl), 1.45 (4H, m, alkyl), 1.28 (4H, m, alkyl), 0.88 (6H, m, CH_3).

4,4,5,5-tetramethyl-2-(3,4-dioctyloxybenzene)-1,3,2-dioxaborolane (3)

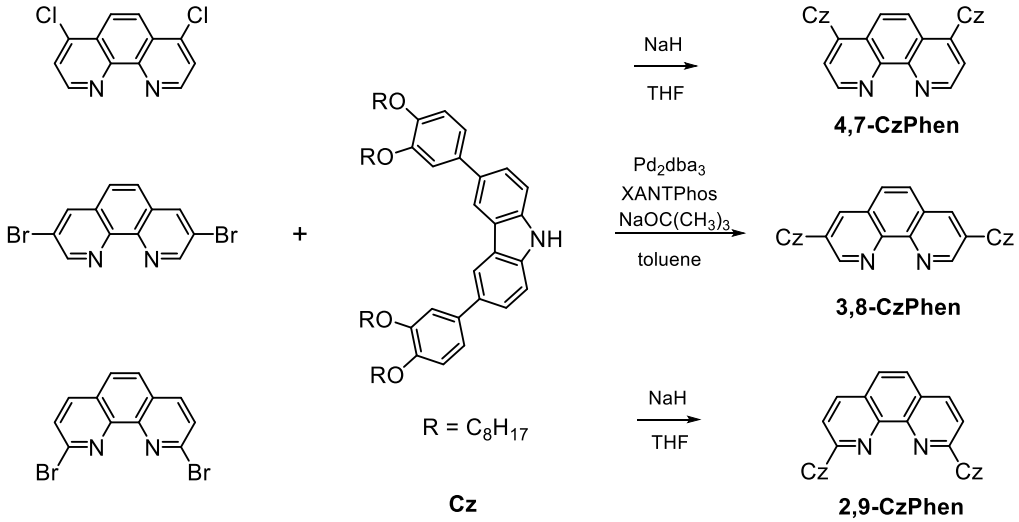
A flask charged with [$PdCl_2$(dppf)] (425 mg, 0.58 mmol), KOAc (11.4 g, 116 mmol), and bis(pinacolato)diboron (14.7 g, 58 mmol) was flushed with nitrogen. DMSO (120 mL) and compound **2** (16 g, 38.7 mmol) were then added. After being stirred at 90 ^{o}C for 24 h, the product was extracted with toluene, washed with water, and dried over anhydrous $MgSO_4$. The compound was purified by column chromatography (silica gel, DCM/PE = 1/1, R_f = 0.34) to give the product as white solid with yield of 55% (9.79 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 7.38 (1H, dd, *J* = 7.9, 1.5 Hz), 7.29 (1H, d, *J* = 1.5 Hz), 6.86 (1H, d, *J* = 7.9 Hz), 4.01 (4H, t, *J* = 6.6 Hz), 1.81 (4H, m), 1.46 (4H, m), 1.33 (12H, s), 1.25 (16H, m), 0.88 (6H, m). ^{11}B NMR (128 MHz, $CDCl_3$): δ 31.88.

3,6-bis-(3,4-dioctyloxybenzene)-9H-carbazole (4)

A solution of 3,6-dibromocarbazole (1.63 g, 5 mmol) and compound **3** (5.3 g, 11.5 mmol) in a mixture of toluene (90 mL), ethanol (45 mL) and aqueous saturated K_2CO_3 solution (6.9 g, 50 mmol

in 20 mL of water) was degassed by argon bubbling for 30 min. [$Pd_3(OAc)_6$] (225 mg, 0.33 mmol) and *S*-Phos (820 mg, 2 mmol) were added, and the mixture was refluxed for 48 h. After hydrolysis (150 mL of water), the mixture was extracted with ethyl acetate (2 x 150 mL), washed with brine and dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure and the crude material was purified by flash chromatography (deactivated alumina, petroleum ether/ethyl acetate = 5/1, R_f = 0.56) to give white powder in 72% yield (3 g). ^{1}H NMR (400 MHz, DCM-d_2): δ/ppm 8.31 (2H, d, *J* = 1.8 Hz), 8.28 (1H, s, NH), 7.66 (2H, dd, *J* = 8.4, 1.8 Hz), 8.52 (2H, d, *J* = 8.4 Hz), 7.25 (4H, m), 7.00 (2H, d, *J* = 8.3 Hz), 4.10 (4H, t, *J* = 6.6 Hz), 4.04 (4H, t, *J* = 6.6 Hz), 1.84 (8H, m), 1.51 (8H, m), 1.31 (32H, m), 0.90 (12H, m). ^{13}C NMR (100 MHz, DCM-d_2): δ 150.0, 148.9, 139.8, 135.6, 133.4, 125.8, 124.4, 120.0, 118.8, 114.9, 113.8, 111.5, 70.0, 70.0, 32.4, 30.1, 30.0, 30.0, 29.9, 26.7, 23.3, 14.4. Anal. Calcd for $C_{56}H_{81}NO_4$: C, 80.82; H, 9.81; N, 1.68. Found: C, 81.12; H, 10.10; N, 1.67%. MS (ESI): $C_{56}H_{82}NO_4$, 832.6238, found 832.6229.

Synthesis of carbazolyl-phenanthrolines



4,7-(3,6-bis-(3,4-dioctyloxybenzene)carbazolyl)-1,10-phenanthroline (4,7-CzPhen)

Sodium hydride (48 mg, 1.2 mmol) was washed with anhydrous hexane (5 mL) twice under the nitrogen atmosphere. Anhydrous THF (6 mL) and carbazole **4** (668 mg, 0.8 mmol) was added, and the mixture was heated to reflux. After 2 h, suspension of 4,7-dichloro-1,10-phenanthroline (50 mg, 0.2 mmol) in THF (1 mL) was added dropwise, and the reflux was maintained overnight. After cooling to room temperature, the mixture was filtered to remove inorganics. Solvent was

evaporated, and the product was purified by column chromatography (silica gel, DCM/ethyl acetate as 10/1) to obtain the product as yellow powder with yield of 38% (140 mg). ^{1}H NMR (400 MHz, DCM-d_2): δ/ppm 9.46 (2H, d, *J* = 4.9 Hz, Phen), 8.38 (4H, d, *J* = 1.8 Hz, Cz), 7.92 (2H, d, *J* = 4.9 Hz, Phen), 7.58 (4H, dd, *J* = 8.7, 1.8 Hz, Cz), 7.41 (2H, s, Phen), 7.24-7.18 (8H, m, Ph), 7.15 (4H, d, *J* = 8.7 Hz, Cz), 6.96 (4H, d, *J* = 7.0 Hz, Ph), 4.07 (8H, t, *J* = 6.6 Hz), 4.02 (8H, t, *J* = 6.6 Hz), 1.82 (16H, m), 1.49 (16H, m), 1.30 (64H, m), 0.88 (24H, m). ^{13}C{^{1}H} (100 MHz, DCM-d_2): δ/ppm 152.0, 150.0, 149.4, 149.2, 143.5, 141.4, 135.0, 134.9, 126.9, 126.2, 125.0, 123.3, 123.3, 120.1, 119.1, 114.8, 113.8, 110.9, 70.0, 69.9, 32.4, 30.0, 30.0, 29.9, 26.6, 23.2, 14.4. Anal. Calcd for $C_{124}H_{166}N_4O_8$: C, 80.91; H, 9.09; N, 3.04. Found: C, 81.31; H, 9.02; N, 2.95%. MS (MALDI): $C_{124}H_{167}N_4O_8$, 1840.2778, found 1840.2691.

3,8-bis(3,6-dioctyloxy-carbazolyl)-1,10-phenanthroline (3,8-CzPhen)

A mixture of 3,8-dibromo-1,10-phenanthroline (100 mg, 0.3 mmol) and carbazole **4** (1.24 g, 1.5 mmol) was dissolved in toluene (40 ml). Sodium-tert-butoxide (200 mg, 2.1 mmol), tris(dibenzylideneacetone)dipalladium(0) ([$Pd_2(dba)_3$], 55 mg, 0.06 mmol) and 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (XANTPhos) (70 mg, 0.12 mmol) were added to the solution. The reaction mixture was stirred at 100 °C for 24 h under the nitrogen atmosphere. After cooling to room temperature, the mixture was quenched by an aqueous solution of EDTA-2K (100 ml), and the product was extracted with DCM. The crude product was purified by column chromatography on silica gel using DCM as eluent. The product was obtained as yellow powder with yield of 29% (157 mg). ^{1}H NMR (400 MHz, DCM-d_2): δ/ppm 9.53 (2H, d, *J* = 2.5 Hz, Phen), 8.62 (2H, d, *J* = 2.5 Hz, Phen), 8.45 (4H, d, *J* = 1.8 Hz, Cz), 8.08 (2H, s, Phen), 7.74 (4H, dd, *J* = 8.6, 1.8 Hz, Cz), 7.66 (4H, d, *J* = 8.6 Hz, Cz), 7.30 (8H, m, Ph), 7.02 (4H, d, *J* = 8.2 Hz, Ph), 4.13 (8H, t, *J* = 6.6 Hz), 4.05 (8H, t, *J* = 6.6 Hz), 1.85 (16H, m), 1.50 (16H, m), 1.32 (64H, m), 0.91 (12H, t, *J* = 6.9 Hz), 0.89 (12H, t, *J* = 6.9 Hz). ^{13}C{^{1}H} (100 MHz, DCM-d_2): δ/ppm 150.1, 149.6, 149.2, 145.1, 140.8, 135.1, 134.9, 134.3, 132.9, 130.0, 128.1, 126.3, 125.1, 120.1, 119.1, 114.8, 113.8, 110.4, 70.1, 69.9, 32.4, 30.1, 30.0, 29.9, 26.7, 23.3, 14.5. Anal. Calcd for $C_{124}H_{166}N_4O_8$: C, 80.91; H, 9.09; N, 3.04. Found: C, 80.81; H, 9.41; N, 3.13%. MS (MALDI): $C_{124}H_{167}N_4O_8$, 1840.2778, found 1840.2730.

2,9-(3,6-bis-(3,4-dioctyloxybenzene)carbazolyl)-1,10-phenanthroline (2,9-CzPhen)

Sodium hydride (28 mg, 0.71 mmol) was washed with anhydrous hexane (5 mL) twice under the nitrogen atmosphere. Anhydrous THF (6 mL) and carbazole **4** (394 mg, 0.47 mmol) was added, and the mixture was heated to reflux. After 2 h, suspension of 2,9-dibromo-1,10-phenanthroline (40 mg, 0.118 mmol) in THF (1 mL) was added dropwise, and the reflux was maintained overnight. Solvent was evaporated, and the product was purified by column chromatography (silica gel, DCM/Hex as 5/1). The product was obtained as yellow powder with yield of 44% (95 mg). ^{1}H NMR (400 MHz, DCM-d_2): δ/ppm 8.51 (2H, d, *J* = 8.6 Hz, Phen), 8.46 (4H, d, *J* = 8.7 Hz, Cz), 8.36 (4H, d, *J* = 1.9 Hz, Cz), 8.11 (2H, d, *J* = 8.6 Hz, Phen), 7.94 (2H, s, Phen), 7.71 (4H, dd, *J* = 8.7, 1.9 Hz, Cz), 7.27 (4H, d, *J* = 2.2 Hz, Ph), 7.15 (4H, dd, *J* = 8.3, 2.2 Hz, Ph), 6.85 (4H, d, *J* = 8.3 Hz, Ph), 4.03 (8H, t, *J* = 6.7 Hz), 4.01 (8H, t, *J* = 6.7 Hz), 1.82 (16H, m), 1.50 (16H, m), 1.33 (64H, m), 0.91 (12H, t, *J* = 6.8 Hz), 0.87 (12H, t, *J* = 6.8 Hz). ^{13}C{^{1}H} (100 MHz, DCM-d_2): δ/ppm 151.5, 150.0, 149.2, 145.9, 139.6, 139.2, 135.1, 134.9, 127.5, 126.2, 126.0, 125.9, 120.1, 118.7, 118.4, 114.7, 113.6, 113.2, 70.0, 69.9, 32.5, 32.5, 30.1, 30.1, 30.1, 30.0, 29.9, 26.8, 26.7, 23.3, 23.3, 14.5, 14.5. Anal. Calcd for $C_{124}H_{166}N_4O_8$: C, 80.91; H, 9.09; N, 3.04. Found: C, 80.80; H, 9.04; N, 3.24%. MS (MALDI): $C_{124}H_{167}N_4O_8$, 1840.2778, found 1840.2736.

NMR spectra

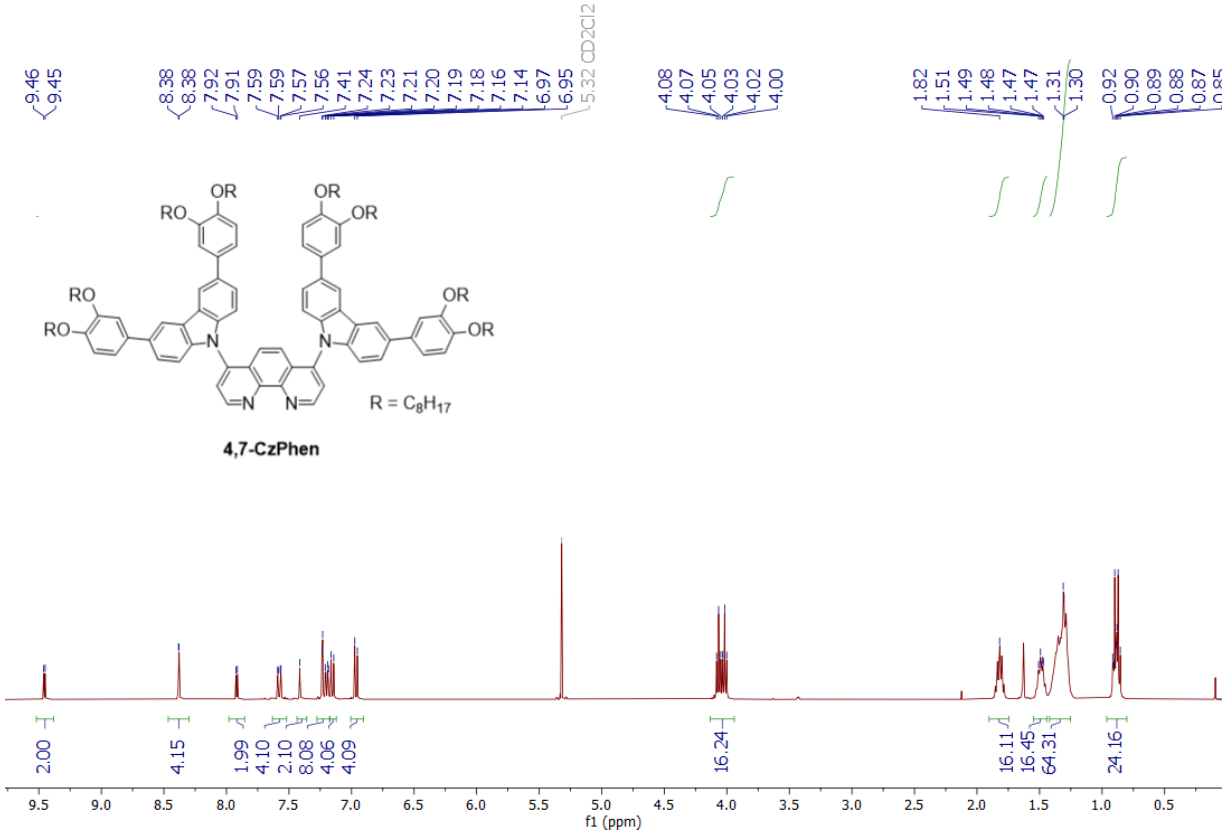


Figure S1. ^{1}H NMR spectrum of compound 4,7-CzPhen

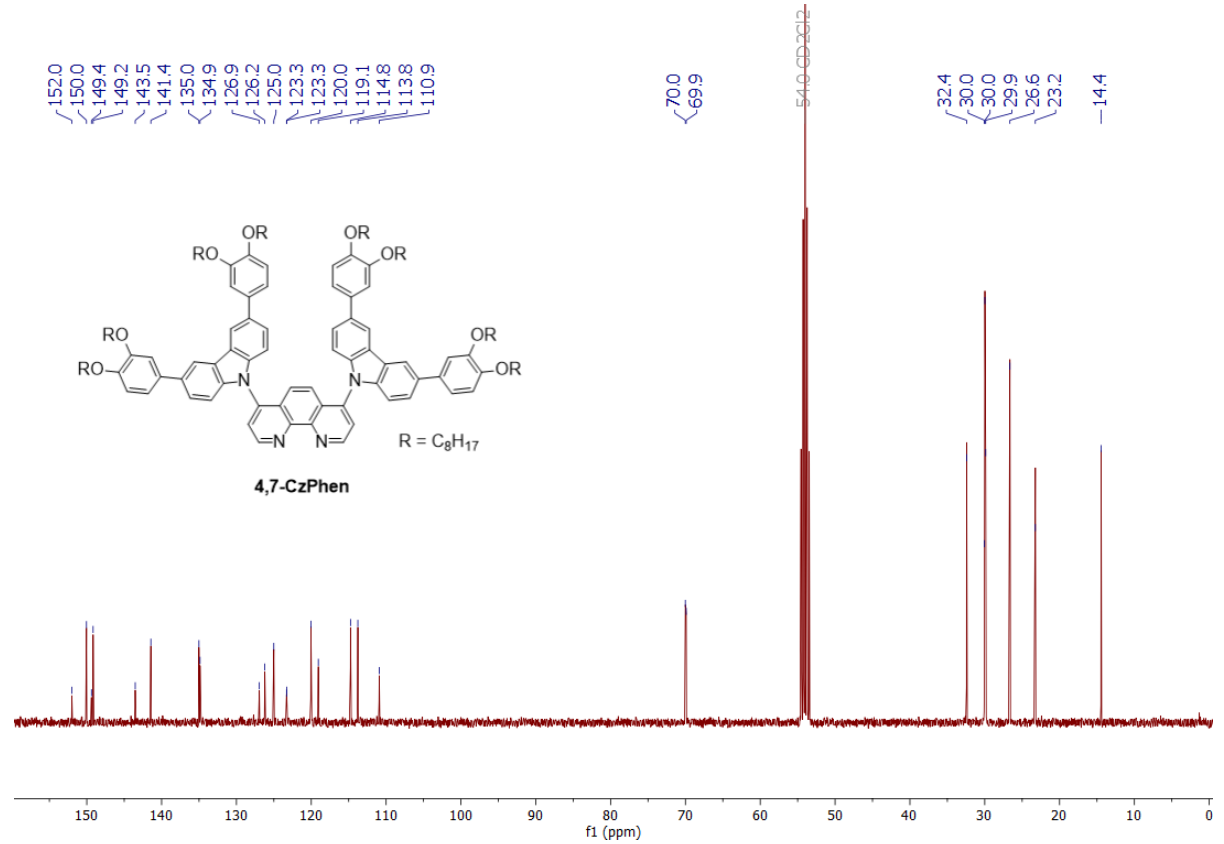


Figure S2. ^{13}C{^{1}H} NMR spectrum of compound 4,7-CzPhen

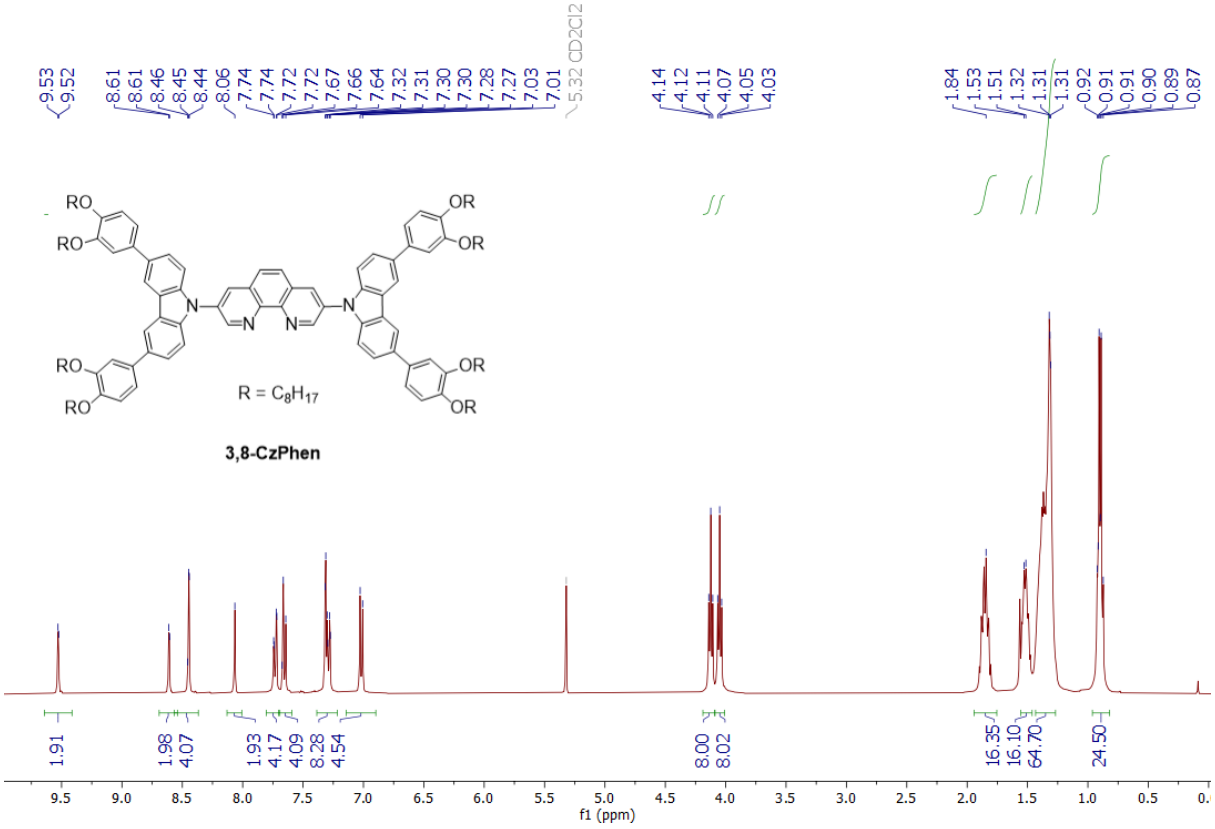


Figure S3. ^{1}H NMR spectrum of compound 3,8-CzPhen

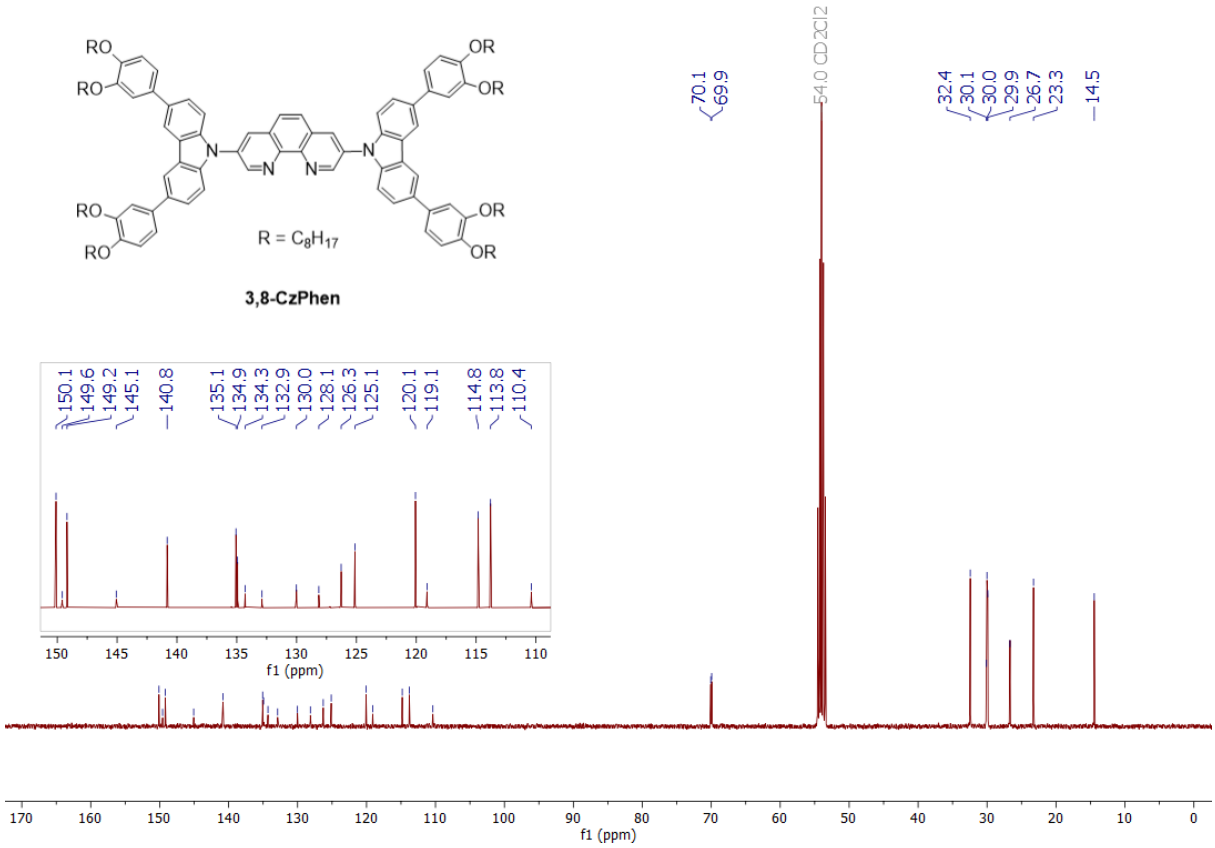


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of compound 3,8-CzPhen

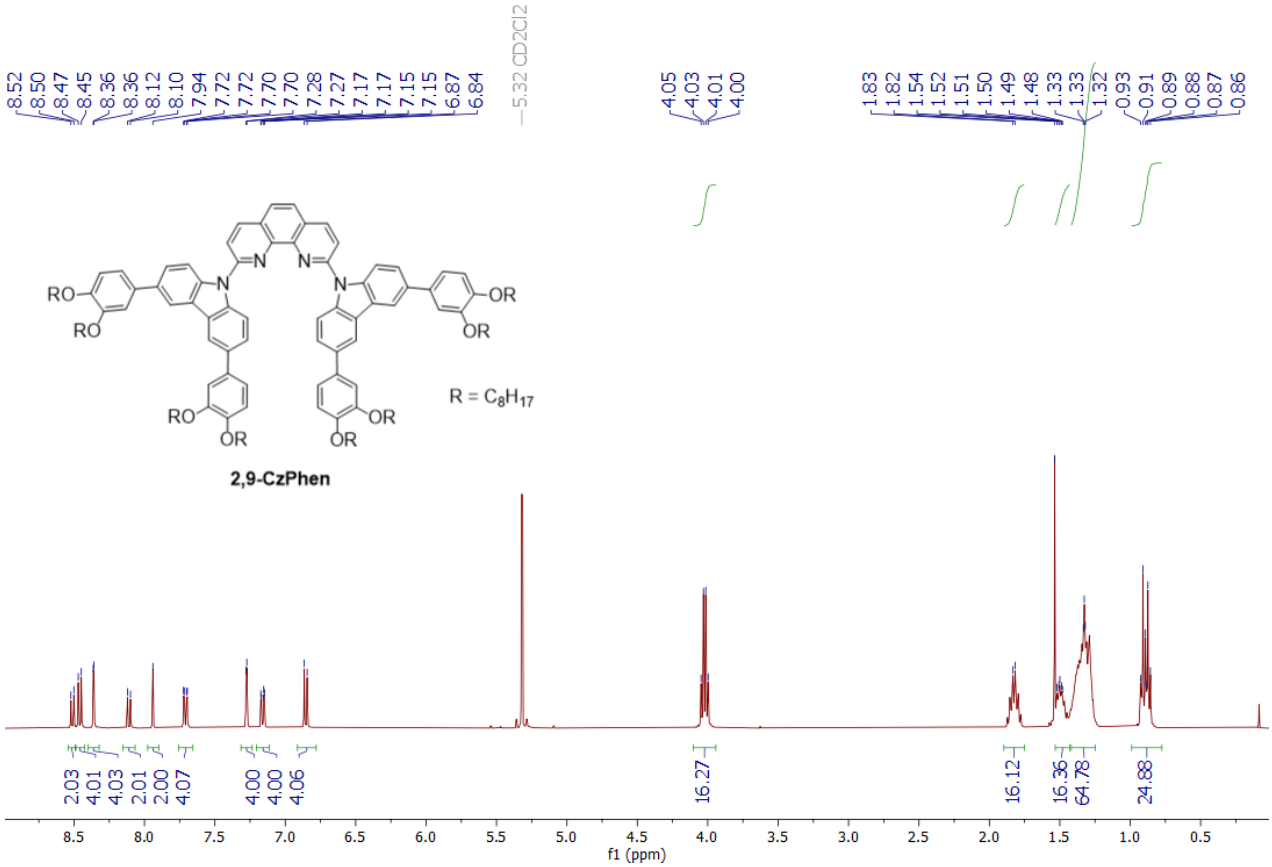


Figure S5. ^{1}H NMR spectrum of compound 2,9-CzPhen

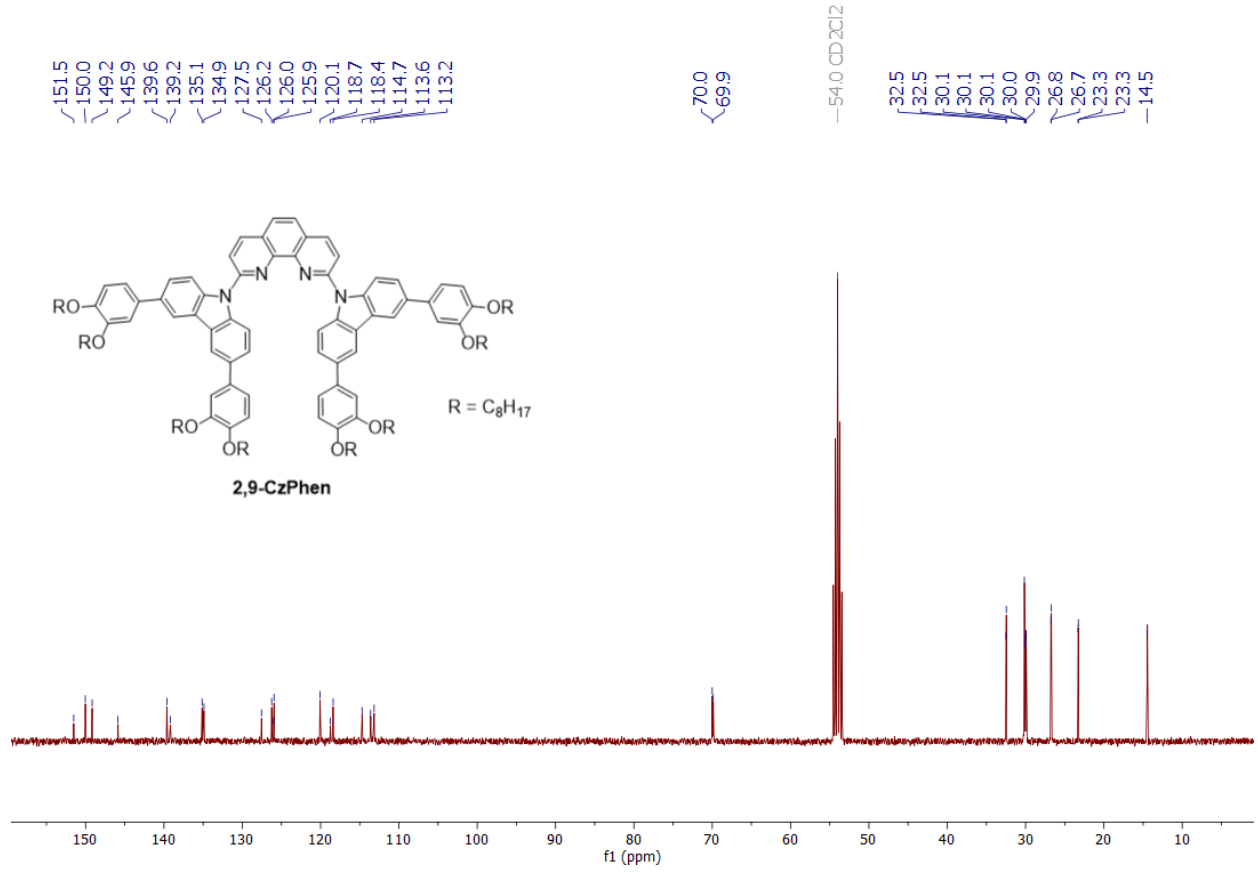


Figure S6. ^{13}C{^{1}H} NMR spectrum of compound 2,9-CzPhen

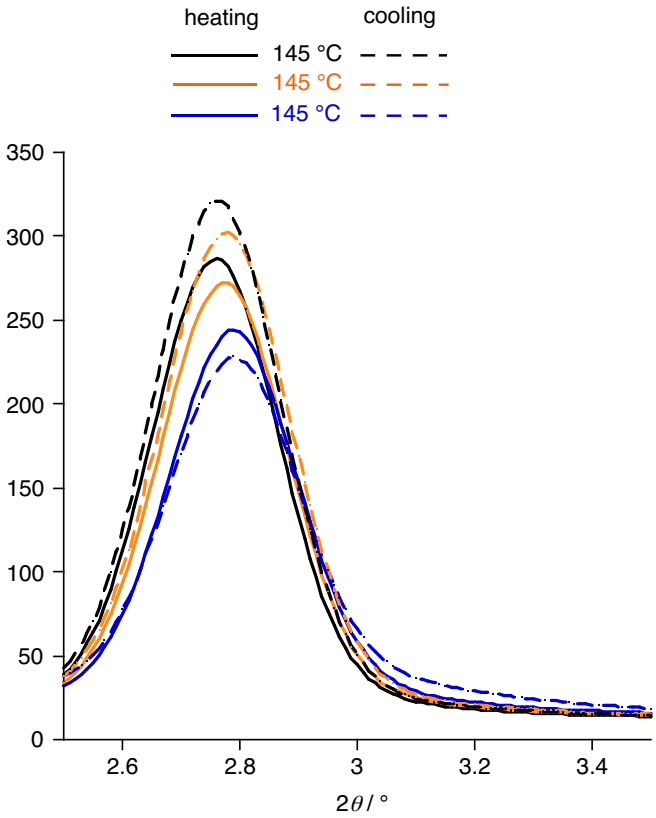


Figure S7 SAXS pattern for **4,7-CzPhen** on heating and cooling either side of the clearing point.

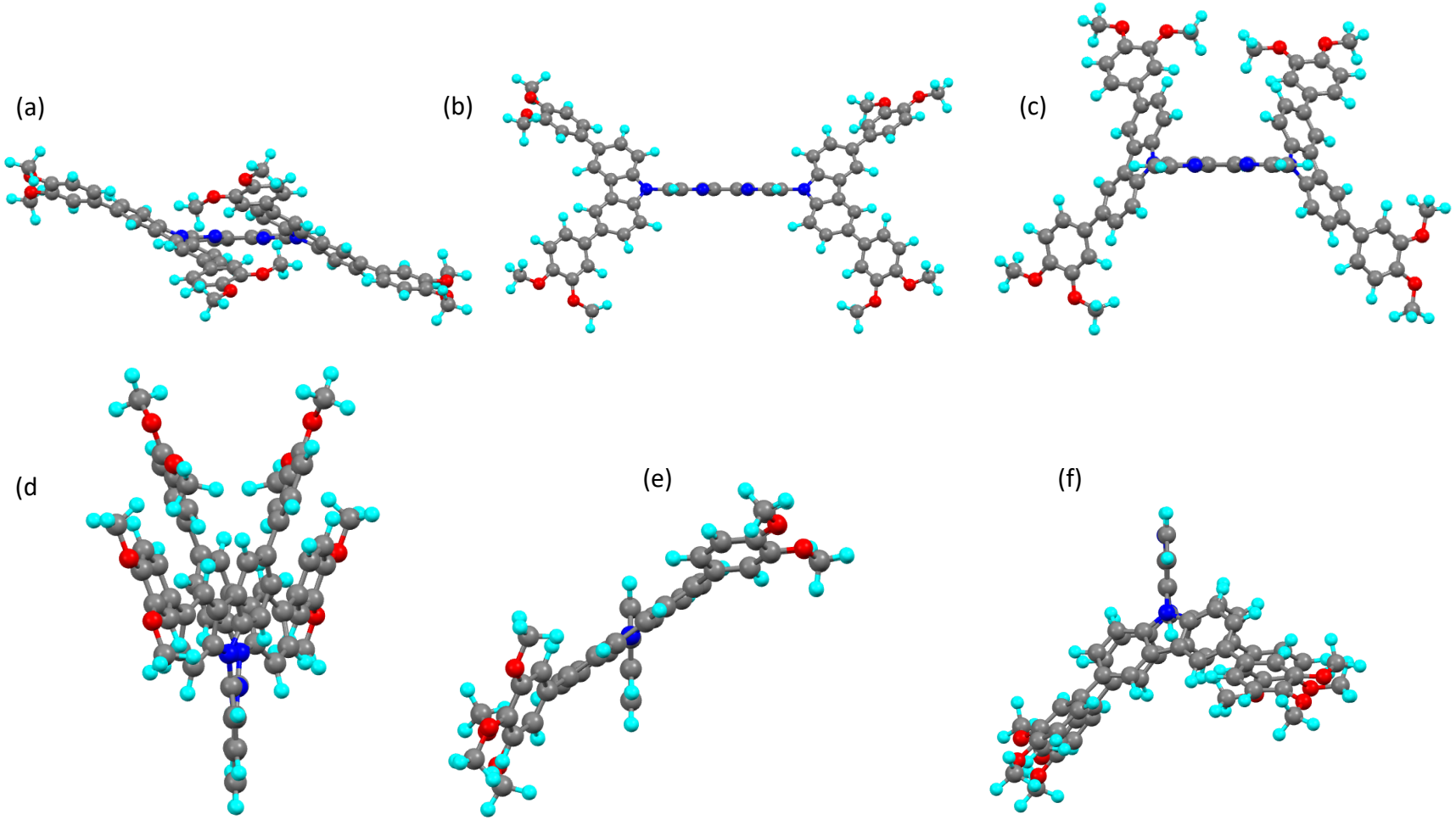


Figure S8. View of the DFT-optimized structures of (a) **2,9-CzPhen'**, (b) **3,8-CzPhen'** and (c) **4,7-CzPhen'** viewed along the axis coincident with the plane of the phenanthroline ring that bisects its two nitrogen atoms and (d)-(f) viewed along axis containing the 3- and 8-carbon atoms of the ring with ring nitrogen atoms pointing up.

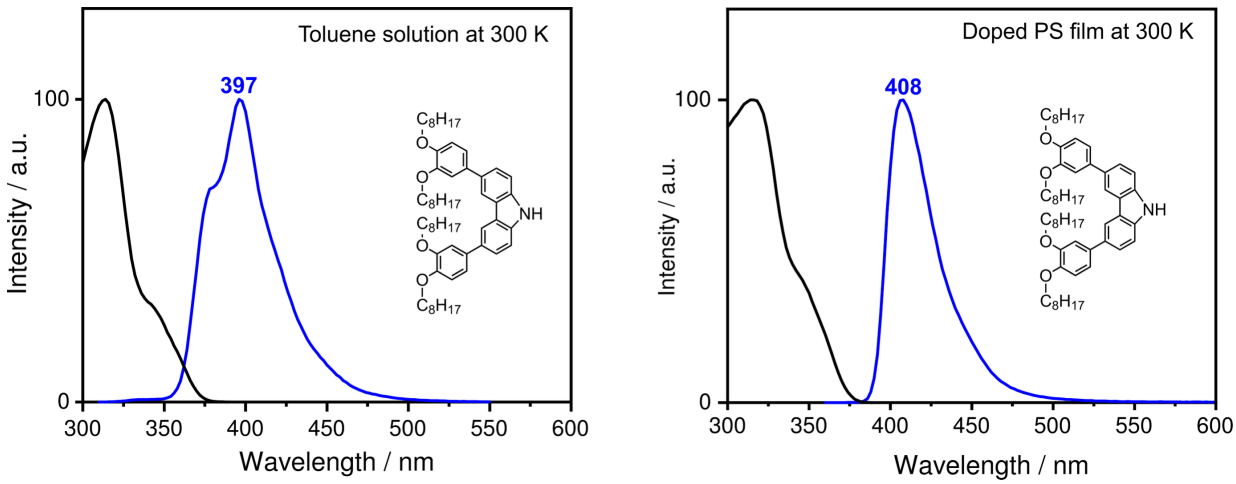


Figure S9 Emission (blue) and excitation (black) spectra of bis(dioctyloxyphenyl)carbazole measured at 300 K doped in a PS film and in toluene solution as indicated in the insets.

Tables S1-S3 Cartesian (xyz) coordinates of atomic positions of ground state optimised geometries.

Table S1

2,9-CzPhen' S0 state geometry (M11L/def2-SVP)

6	0.651603120	7.504688556	0.195278044
6	-0.651626981	7.504684587	-0.195274986
6	1.354248158	6.284804449	0.385399058
6	0.700923101	5.050170373	0.167895042
6	-0.700925006	5.050165383	-0.167902984
6	-1.354261044	6.284794500	-0.385402000
6	2.693636263	6.208731462	0.808347088
6	3.306138296	4.992017344	0.944509099
6	2.570039233	3.837112261	0.601560076
7	1.319449134	3.880592273	0.243405047
6	-2.693649148	6.208713470	-0.808347035
6	-3.306141207	4.991994404	-0.944513041
6	-2.570030163	3.837094306	-0.601575015
7	-1.319442065	3.880581298	-0.243417990
7	-3.134285217	2.573553213	-0.675123022
7	3.134297266	2.573574158	0.675109078
6	-4.454380318	2.241440201	-0.433372004
6	-2.442375174	1.419037123	-1.020888050
6	-3.349155252	0.343315047	-1.051743053
6	-4.629773344	0.864256098	-0.666936020
6	-5.507816405	3.007881272	0.052327033
6	-6.733150508	2.392860233	0.235052047
6	-6.949458535	1.031911130	-0.037593974
6	-5.870320442	0.271034064	-0.481392008
6	-1.103873071	1.223127096	-1.345632073
6	-0.705459055	-0.054260007	-1.693209100
6	-1.585179131	-1.148735083	-1.732850101
6	-2.920833228	-0.930760052	-1.400575076
6	4.454391362	2.241456124	0.433358062
6	2.442383202	1.419060079	1.020875107
6	3.349161258	0.343336987	1.051742111
6	2.920835218	-0.930735107	1.400581135
6	4.629781361	0.864273016	0.666934078
6	5.507829475	3.007888172	-0.052352975
6	6.733161515	2.392861112	-0.235070989
6	6.949467531	1.031915009	0.037590032
6	5.870326474	0.271045960	0.481397066
6	1.103880098	1.223156073	1.345614134
6	1.585179115	-1.148705110	1.732850159
6	0.705462055	-0.054229019	1.693196156
6	-8.274317649	0.425960097	0.166131042
6	-1.112804106	-2.486154188	-2.123772131
6	-8.412184674	-0.878798000	0.621805075
6	-9.440537733	1.161063161	-0.093679979
6	-10.696223803	0.612617134	0.093060036
6	-10.817573830	-0.713883970	0.554856072
6	-9.668516764	-1.442282033	0.813223091
6	1.112800063	-2.486121209	2.123778190
6	-0.167660037	-2.930010231	1.760739165
6	1.927320120	-3.350473285	2.844463246
6	1.491431074	-4.623895376	3.191976274

6	0.228291974	-5.060355400	2.829586243
6	-0.614421084	-4.193892325	2.102877192
6	8.274324635	0.425958950	-0.166128984
1	1.184473169	8.452506605	0.359855056
1	-1.184504015	8.452498667	-0.359846999
1	3.237714313	7.131754488	1.056876109
1	4.324088375	4.918249326	1.344834132
1	-3.237737184	7.131732580	-1.056868050
1	-4.324095287	4.918218406	-1.344831074
1	-5.386803357	4.061547349	0.330742054
1	-7.558293523	2.989951286	0.649695076
1	-6.002817482	-0.798489019	-0.702338026
1	-0.373934009	2.038208149	-1.302879071
1	0.348993026	-0.210626028	-1.966672122
1	-3.635700293	-1.767904114	-1.400988078
1	3.635700266	-1.767880174	1.401002138
1	5.386819444	4.061550255	-0.330781996
1	7.558305588	2.989945153	-0.649724022
1	6.002820445	-0.798475122	0.702353081
1	0.373943049	2.038238143	1.302853130
1	-0.348993026	-0.210591022	1.966654178
1	-7.520914612	-1.471564056	0.870820098
1	-9.350007677	2.181234240	-0.487673008
8	-11.845524873	1.237290191	-0.142554982
8	-12.061468931	-1.156308990	0.703155081
1	-0.809607080	-2.274964178	1.155505117
1	2.922279200	-3.020185267	3.174760270
1	2.155061117	-5.277841433	3.770853316
8	-0.284576076	-6.253806463	3.109134269
8	-1.804775179	-4.695110351	1.795776166
6	9.440546729	1.161060997	0.093671036
6	10.696230841	0.612608943	-0.093065978
6	10.817575841	-0.713898162	-0.554846013
6	9.668515706	-1.442296204	-0.813202035
6	8.412186632	-0.878805150	-0.621789020
6	0.167657988	-2.930043236	-1.760740107
6	0.614415009	-4.193927335	-2.102872133
6	-0.228305060	-5.060395395	-2.829568187
6	-1.491446155	-4.623935350	-3.191953213
6	-1.927330175	-3.350510248	-2.844446191
1	9.350020747	2.181237076	0.487651066
8	11.845534927	1.237280978	0.142540040
8	12.061469937	-1.156329205	-0.703142026
1	9.741916718	-2.470963287	-1.186788060
1	7.520914559	-1.471571189	-0.870794036
1	0.809610044	-2.274993187	-1.155515060
8	1.804770099	-4.695145383	-1.795777108
8	0.284558968	-6.253848479	-3.109112208
1	-2.155082210	-5.277885392	-3.770820258
1	-2.922292249	-3.020223215	-3.174738214
1	-9.741921745	-2.470945110	1.186821118
6	-12.237245950	-2.451116087	1.142099115
6	-2.656423238	-3.926258286	1.028892105
6	11.795656902	2.538609078	0.593255073
6	12.237241928	-2.451141307	-1.142071058
6	-0.503961100	-7.148064525	-3.799952259
6	0.503936977	-7.148018539	3.799986317

6	2.656426170	-3.926288332	-1.028907049
1	-11.810657913	-2.614064102	2.153656194
1	-11.790013915	-3.194270146	0.449700063
1	-13.322524034	-2.630053092	1.190484120
1	-2.229387200	-3.703204270	0.028371031
1	-2.920053248	-2.966957212	1.522549146
1	-3.579645314	-4.511115321	0.893637099
1	11.284019868	2.625462093	1.574301152
1	11.288964871	3.214127136	-0.127040981
1	12.836412023	2.877084097	0.713927082
1	11.810651880	-2.614100314	-2.153626137
1	11.790008887	-3.194286360	-0.449663006
1	13.322520012	-2.630082329	-1.190456063
1	-0.779390117	-6.775482518	-4.808589338
1	-1.436639172	-7.396851546	-3.252008221
1	0.084852936	-8.070680613	-3.920260273
1	0.779360002	-6.775429548	4.808623396
1	1.436619048	-7.396810588	3.252051275
1	-0.084879077	-8.070633622	3.920296326
1	2.229399138	-3.703225310	-0.028383973
1	2.920053200	-2.966991259	-1.522575086
1	3.579649235	-4.511144384	-0.893656038
6	-11.795641873	2.538613290	-0.593285014
1	-11.284001823	2.625453293	-1.574331092
1	-11.288949842	3.214138339	0.127004038
1	-12.836395936	2.877089326	-0.713964023

Table S2

3,8-CzPhen' S0 state geometry (M11L/def2-SVP)

7	-4.761082366	-0.197210015	0.046324004
6	-5.535080410	0.939704074	-0.015248001
6	-5.589615407	-1.296714098	0.060617005
6	-6.928581540	-0.864682065	0.000073000
6	-6.894007533	0.569865042	-0.046091004
6	-5.155595393	2.275098176	0.005543000
6	-6.154954459	3.229234247	-0.033536003
6	-7.520881591	2.896649220	-0.081251006
6	-7.877519593	1.549769119	-0.078964006
6	-7.956830615	-1.798504138	-0.015939001
6	-7.663963605	-3.160091239	0.020037002
6	-6.314364502	-3.555497273	0.058368004
6	-5.271999401	-2.648338204	0.077810006
1	-4.100497314	2.577654199	0.045231003
1	-5.864567438	4.289609329	-0.053946004
6	-8.548577676	3.948805300	-0.129056010
1	-8.939373699	1.262094094	-0.068370005
1	-9.003301697	-1.458958112	-0.030187002
6	-8.735767672	-4.168338319	0.011823001
1	-6.076321472	-4.628777353	0.040120003
1	-4.230591323	-2.997251228	0.082313006
6	-8.368607616	5.156012395	0.562516045
6	-9.323172728	6.156042448	0.528600040
6	-10.506056815	5.968405456	-0.215226017
6	-10.687228795	4.778262364	-0.899121068
6	-9.719389748	3.781026288	-0.856997067
6	-9.916234742	-3.947064302	-0.713242056
6	-8.617891641	-5.356567387	0.721131057
6	-9.639828742	-6.299344493	0.716097052
6	-10.804383823	-6.076249451	0.001309000
6	-10.940129852	-4.876324375	-0.726669056
8	-11.364026864	6.982561535	-0.189537014
6	-12.542201961	6.848021501	-0.892005069
8	-9.235137690	7.318863573	1.166117090
6	-8.099258619	7.568664603	1.905681147
8	-11.837420893	-6.908622509	-0.070702005
6	-11.752386872	-8.101720616	0.614052046
8	-12.079892925	-4.748296364	-1.398031109
6	-12.277252914	-3.594927276	-2.126378160
1	-7.466445551	5.292146407	1.172193087
1	-11.594417885	4.618816354	-1.494714116
1	-9.876366739	2.862702219	-1.440109109
1	-10.010510791	-3.031369233	-1.310594099
1	-7.721766588	-5.548528445	1.327736103
1	-9.519869711	-7.221340545	1.298044100
1	-13.154373994	5.997093477	-0.527282040
1	-12.370279946	6.714688519	-1.980351153
1	-13.114058996	7.776934587	-0.742526059
1	-7.180735557	7.555622554	1.282859099
1	-7.969462605	6.844343507	2.736441210
1	-8.211965647	8.575053631	2.337753180
1	-11.647463883	-7.951911595	1.708751131
1	-10.906015859	-8.728317650	0.263514020

1	-12.689898983	-8.647865669	0.426967033
1	-11.523717900	-3.470968267	-2.931620226
1	-12.261004950	-2.686905208	-1.488417113
1	-13.271852031	-3.675107281	-2.591737199
6	0.800374059	-1.588004122	2.078838156
6	-0.554844044	-1.599852121	2.099165161
6	-1.305170101	-0.919796071	1.099618084
6	-0.641455051	-0.207501016	0.068062005
6	0.802260063	-0.194315015	0.046683004
6	1.508621116	-0.894890069	1.057759078
6	-2.705332207	-0.906710068	1.101639086
6	-3.371946255	-0.228650017	0.106957008
6	-2.602560196	0.430072033	-0.873106064
7	-1.303566102	0.446960034	-0.884936070
7	1.424144107	0.472596036	-0.924796071
6	2.723115209	0.479935037	-0.950275072
6	3.532495272	-0.165176013	0.006326000
6	2.907692223	-0.856577064	1.018794080
1	1.375531106	-2.114468163	2.854209220
1	-1.097188086	-2.136019161	2.891347223
1	-3.125698237	0.960813071	-1.689741131
1	3.212850247	1.021102076	-1.780667134
7	4.918560377	-0.106471008	-0.092741007
6	5.668276440	1.046109082	-0.165529013
6	5.768796464	-1.189360089	-0.102793008
6	7.033225547	0.703604056	-0.227947018
6	7.097384531	-0.730113058	-0.190718015
6	8.143851645	-1.642164128	-0.232804018
6	7.879508611	-3.009650232	-0.198735015
6	6.539573501	-3.432573262	-0.130454010
6	5.479184423	-2.547042195	-0.083813006
6	7.996576589	1.702609129	-0.276214021
6	7.613623555	3.042150235	-0.263284020
6	6.242664477	3.347341254	-0.185330014
6	5.263135402	2.373606183	-0.130051010
1	9.183073686	-1.283073099	-0.269042020
1	4.445422342	-2.917120224	-0.056576004
1	9.063773692	1.435621109	-0.289542022
6	8.619075675	4.114823317	-0.325556025
1	5.931113435	4.401831334	-0.194325015
1	4.203362322	2.655030200	-0.066319005
6	8.428020621	5.314981410	0.375267029
6	9.779153757	3.973990301	-1.076059081
6	10.725863814	4.990693379	-1.131203086
6	10.533705797	6.173886463	-0.438261034
6	9.361399699	6.334263471	0.328338025
8	11.371676862	7.204883556	-0.423484033
6	12.538565931	7.097442529	-1.149075090
8	9.261708685	7.492328563	0.972925075
6	8.136027600	7.714672597	1.736364134
6	8.974124663	-3.992012305	-0.246348019
6	10.122125756	-3.759627286	-0.992884075
6	8.882679659	-5.197932398	0.464572035
6	9.900002759	-6.134147474	0.431846033
6	11.059355868	-5.880326443	-0.328979025
6	11.152840850	-4.691603356	-1.032827077
8	11.983325909	-6.834650514	-0.298894023

6	13.142890001	-6.631635526	-1.015870079
8	9.894865770	-7.291333550	1.085689085
6	8.786480686	-7.603852562	1.842517143
1	6.321224491	-4.510186345	-0.149263012
1	7.534933576	5.430196421	1.002325079
1	9.943844776	3.061612236	-1.666315127
1	11.625013908	4.851853372	-1.743899131
1	12.348432969	6.965119536	-2.234506169
1	13.175052018	6.257851494	-0.800037063
1	13.094059006	8.037309637	-1.006437077
1	8.038276603	6.983780548	2.565798195
1	7.205501529	7.685084604	1.132163088
1	8.236269647	8.721171641	2.171251168
1	10.211791771	-2.842615216	-1.591983123
1	7.998846601	-5.383372437	1.088026085
1	12.040027939	-4.481959343	-1.642861123
1	13.698406042	-5.734587430	-0.671665050
1	12.952051963	-6.529208507	-2.104402159
1	13.778672071	-7.516355591	-0.856912065
1	7.861345608	-7.656687577	1.231614093
1	8.620905675	-6.879428541	2.666863202
1	8.968267676	-8.595834633	2.284384173
1	-3.261023247	-1.425440109	1.896843146
1	3.495951265	-1.365653103	1.796641138

Table S3

4,7-CzPhen' S0 state geometry (M11L/def2-SVP)

6	-0.784403061	-0.998510076	2.105113161
6	0.571852044	-0.970053072	2.111683162
6	1.303873098	-1.321250099	3.279043251
6	0.623779049	-1.755696133	4.446124338
6	-0.824292061	-1.810896141	4.430100338
6	-1.510429114	-1.399912107	3.259376247
6	2.715460205	-1.311230102	3.330772254
6	3.342237255	-1.730728132	4.481879342
6	2.553428195	-2.134651163	5.561995423
7	1.249587096	-2.146040164	5.553428414
7	-1.444866111	-2.271985175	5.513007422
6	-2.746027208	-2.354825179	5.492153393
6	-3.541593268	-1.962147149	4.411805336
6	-2.920470223	-1.463917111	3.290449249
7	-3.669813281	-1.031534080	2.195324166
7	3.469975266	-0.918810071	2.224265171
6	3.537327269	0.348373027	1.690517128
6	4.378174333	-1.723230129	1.573539120
6	5.031892384	-0.970040075	0.580176045
6	4.496732342	0.359706027	0.659098048
6	2.851774216	1.500831114	2.049305155
6	3.132241238	2.659954205	1.348636101
6	4.077397314	2.706569207	0.307735024
6	4.756450361	1.537590115	-0.028467002
6	5.975595440	-1.577990120	-0.238057018
6	6.277092484	-2.928135224	-0.071361006
6	5.601471411	-3.648977281	0.930527071
6	4.652548355	-3.071924234	1.753064132
6	-3.791929292	0.274994021	1.784034135
6	-4.500294345	-1.817848138	1.432092111
6	-4.707599358	0.336918026	0.715684056
6	-5.157502394	-1.007628075	0.485241037
6	-6.030325438	-1.585489123	-0.427607033
6	-6.259076486	-2.959860225	-0.399983031
6	-5.582600421	-3.736237287	0.558661042
6	-4.702734361	-3.189841245	1.474310110
6	-5.012032383	1.564238121	0.140940011
6	-4.425870338	2.729550211	0.631738049
6	-3.524176267	2.627463198	1.707192132
6	-3.194900243	1.419567110	2.292627173
1	-1.336229102	-0.738623059	1.190892089
1	1.119234086	-0.689645053	1.201116090
1	4.438263341	-1.733062132	4.549720347
1	3.046981232	-2.459951188	6.494451510
1	-3.232959247	-2.747358210	6.401937462
1	-4.636684352	-2.026758156	4.461025340
1	2.124070164	1.505159117	2.872750220
1	2.620496199	3.587898273	1.643023125
6	4.362635334	3.965553305	-0.399603031
1	5.485323408	1.543063120	-0.852442063
1	6.459246512	-0.999302074	-1.039167081
6	7.275311544	-3.593324276	-0.923949070
1	5.854435440	-4.707917361	1.083399081

1	4.145564319	-3.665641279	2.525766195
1	-6.518272477	-0.961940075	-1.191430093
1	-4.193303319	-3.824392290	2.212432170
1	-5.704994409	1.612565122	-0.712030055
6	-4.757510361	4.043294306	0.057254004
1	-3.090064234	3.546570270	2.126290163
1	-2.503346193	1.378561107	3.145646240
6	-3.797051289	5.064507388	0.007479001
6	-6.026158485	4.318059332	-0.437406033
6	-6.335124495	5.564002434	-0.970890077
6	-5.384282410	6.569585525	-1.016963079
6	-4.093533315	6.310135476	-0.514013039
8	-5.575099440	7.791958617	-1.500715113
6	-6.818520504	8.095376627	-2.012773155
8	-3.238142248	7.325059550	-0.599258044
6	-1.973178150	7.147475550	-0.086090007
6	3.340257253	4.886668372	-0.671709051
6	3.597111275	6.069516464	-1.341177105
6	4.910083375	6.367944492	-1.758556135
6	5.921835476	5.462317427	-1.488807111
6	5.650538419	4.276041325	-0.817082063
6	8.405048666	-2.894178221	-1.374486103
6	7.129395522	-4.918508374	-1.313327099
6	8.073998607	-5.535364420	-2.125893163
6	9.186837724	-4.841448372	-2.569895196
6	9.351176735	-3.495260265	-2.184238167
8	5.058873386	7.525605557	-2.392912183
6	6.320836498	7.860546603	-2.834922217
8	2.685921203	6.985193557	-1.655778128
6	1.378118106	6.752484528	-1.294280099
8	10.145768760	-5.335360397	-3.345503257
6	10.039058792	-6.650588485	-3.743868287
8	10.451407780	-2.905994220	-2.640883202
6	10.667833814	-1.587170123	-2.304279174
6	-7.190377537	-3.587914275	-1.350806104
6	-8.344999643	-2.937659223	-1.766545134
6	-6.934011534	-4.868923371	-1.861757144
6	-7.798210581	-5.475848437	-2.754621210
6	-8.964882688	-4.800354366	-3.167185241
6	-9.221347701	-3.535824268	-2.664958206
8	-9.733897724	-5.460556431	-4.026202310
6	-10.882432810	-4.841393369	-4.470369340
8	-7.621049606	-6.678112529	-3.292582251
6	-6.502769488	-7.394738541	-2.924515223
1	-5.780000416	-4.817161369	0.602048047
1	-2.779399210	4.857099371	0.361159027
1	-6.816343522	3.556631274	-0.378387029
1	-7.350765552	5.749871445	-1.341166103
1	-7.618683601	8.017726587	-1.247676094
1	-7.089540537	7.445635550	-2.870725218
1	-6.775852519	9.137383676	-2.365644182
1	-1.414182107	6.345293483	-0.615000046
1	-1.987756152	6.903749527	0.996818074
1	-1.434711110	8.099469602	-0.220376017
1	2.310829177	4.642835354	-0.379084029
1	6.952529509	5.681262450	-1.793443134
1	6.480908488	3.593588272	-0.587616044

1	8.555985628	-1.858102143	-1.045933078
1	6.239894499	-5.487321423	-1.008438076
1	7.921599581	-6.579540513	-2.425130187
1	6.719735494	7.125050553	-3.564081275
1	7.047043529	7.956259633	-2.001115153
1	6.237601468	8.837166659	-3.336346252
1	1.254231097	6.667241535	-0.193080015
1	0.967020076	5.834320461	-1.765261133
1	0.790475058	7.615523566	-1.646912123
1	9.128259708	-6.833526542	-4.351115331
1	10.032863767	-7.351285575	-2.883209218
1	10.920609826	-6.871080505	-4.365504332
1	10.771875829	-1.443332111	-1.208756092
1	9.858134731	-0.921757070	-2.669556206
1	11.610729880	-1.283438099	-2.784840211
1	-8.595455637	-1.948578150	-1.357952103
1	-6.008477456	-5.382820399	-1.572780122
1	-10.130696787	-2.999637230	-2.962913229
1	-10.668668803	-3.893660295	-5.006947381
1	-11.589657883	-4.623448353	-3.643235279
1	-11.371683847	-5.535078399	-5.171550394
1	-6.475329478	-7.600577590	-1.834253141
1	-5.560760430	-6.880773551	-3.207548246
1	-6.547102477	-8.356442625	-3.458738267

Table S4. Device performance data: ITO/PEDOT:PSS(40nm)/
PVK:OXD-7 (7:3):xwt% dopant (40nm)/DPEPO/TmPyPB(45 nm)/LiF(0.5 nm)/Al(120 nm)

Dopant	**Dopant, wt%**	V_{on} **/ V**	L_{max} **/ cd m^{-2}**	CE_{max} **/cd A^{-1}**	EQE_{max} **/ %**	***CIE* (x, y)**	$\lambda_{max\ (emission)}$ **/ nm**
4,7-CzPhen	1%	6.0	104.7	0.47	0.32	(0.27, 0.32)	464
	3%	6.4	87.87	0.62	0.44	(0.20, 0.24)	460
2,9-CzPhen	1%	6.0	117.6	0.86	0.60	(0.22, 0.26)	458
	3%	6.4	122.5	0.73	0.43	(0.22, 0.27)	462
3,8-CzPhen	1%	8.0	145.6	4.34	3.01	(0.23, 0.26)	456
	3%	7.6	183.6	1.38	0.75	(0.24, 0.29)	470

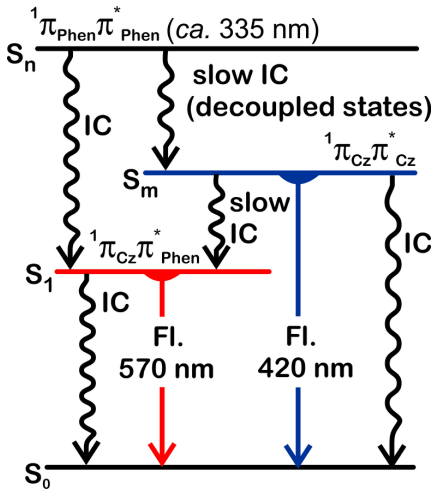


Figure S10. Jablonski diagram summarising luminescent properties of **3,8-CzPhen** in a PS film (Fl. = fluorescence), showing a little more detail than that in Figure 9.

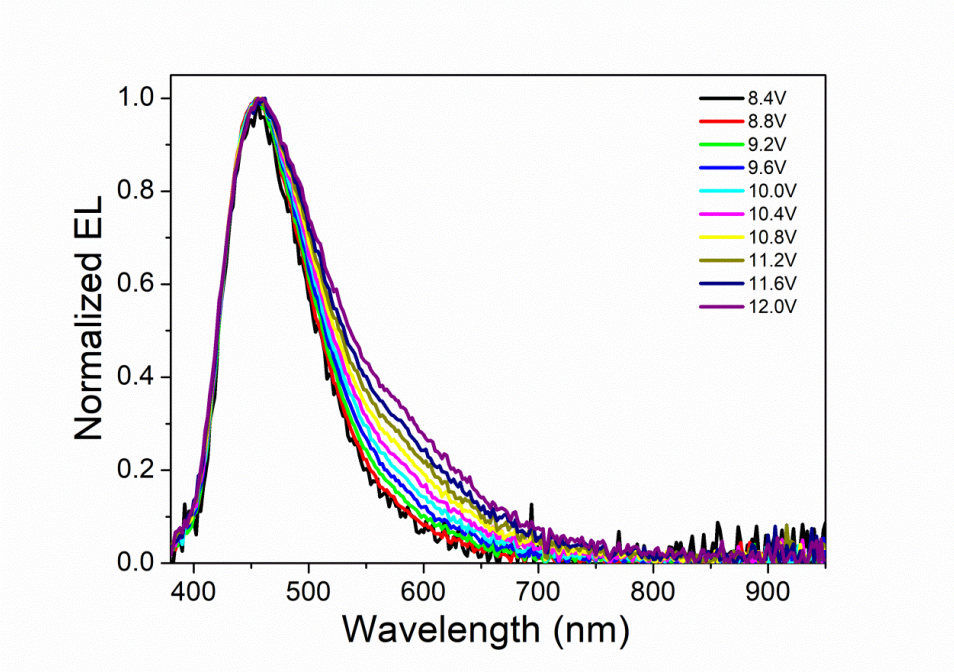


Figure S11 Normalised emission intensity of the OLED device at 1 wt% loading of **3,8-CzPhen** as a function of increasing drive voltage.

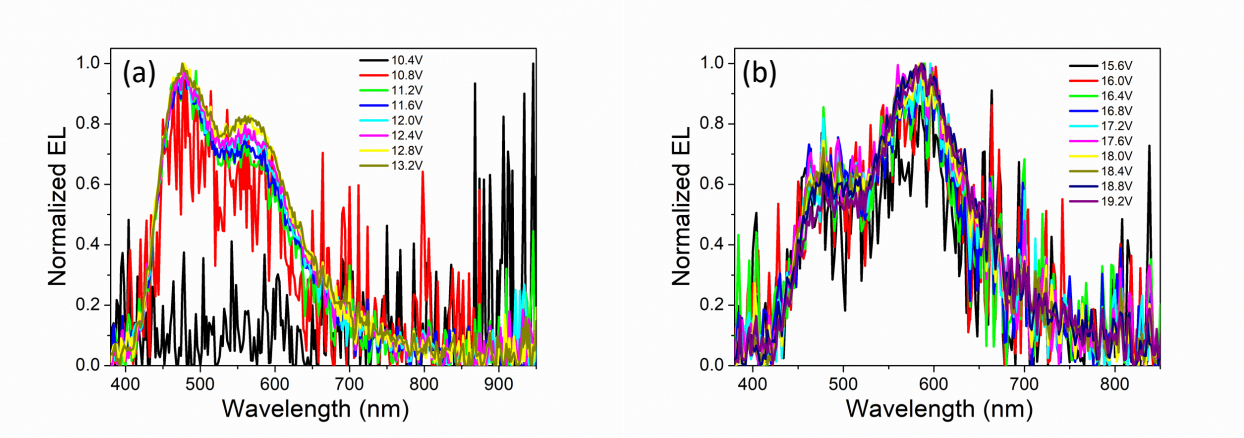


Figure S12 Normalised emission intensity of the OLED device at: (a) 20 wt% and (b) 40 wt% loading of **3,8-CzPhen** as a function of increasing drive voltage.

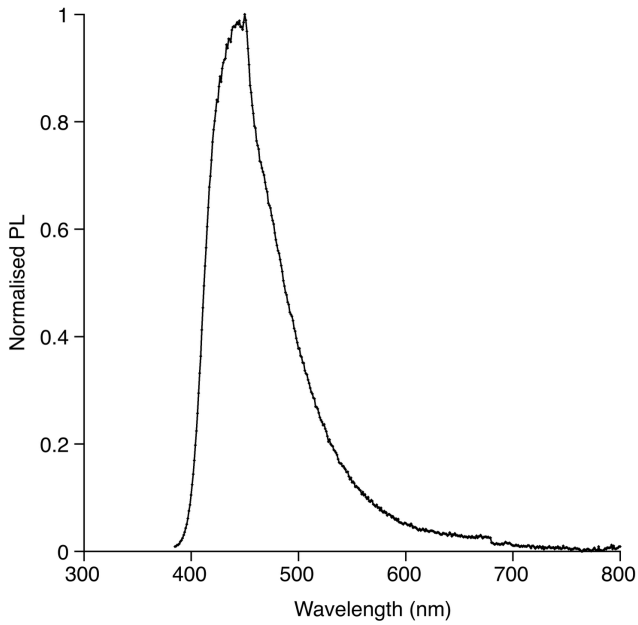


Figure S13 Photoluminescence of **3,8-CzPhen** at 20 wt.% in PVK/OXD-7 at 300 K.

References

1. H. C. Guo, R. H. Zheng and H. J. Jiang, *Organic Preparations and Procedures International*, 2012, **44**, 392-396.
2. Y. Saitoh, T.-a. Koizumi, K. Osakado, and T. Yamamoto, *Can. J. Chem.*, 1997, **75**, 1336-1339.
3. S. J. P. Bousquet and D. W. Bruce, *J. Mater. Chem.*, 2001, **11**, 1769-1771.