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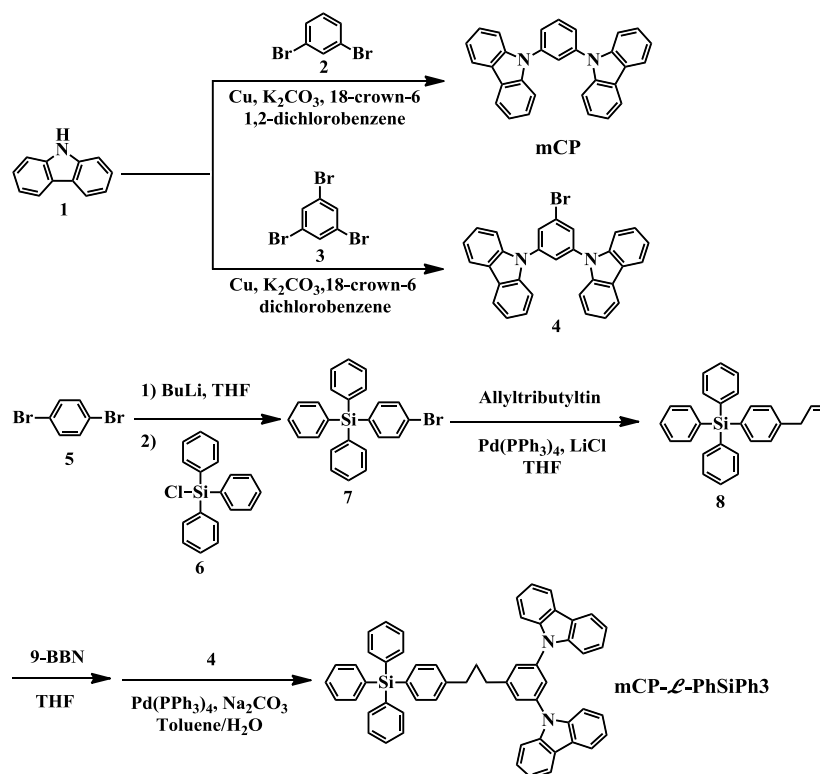
Supplementary Information

Temporal Stability of Blue Phosphorescent Organic Light-Emitting Diodes

Affected by Thermal Annealing of Emitting Layers

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Material Synthesis: All chemicals, reagents, and solvents were used as received from commercial sources without further purification except toluene and tetrahydrofuran (THF) that had been distilled over sodium and benzophenone. All reactions were carried out under argon and anhydrous conditions unless noted otherwise.



Scheme S1. Synthesis of model compounds

9,9'-(5-Bromo-1,3-phenylene)bis(9H-carbazole), **4**. A mixture of **1** (5.31 g, 31.77 mmol), **3** (5.00 g, 15.88 mmol), Cu (4.04 g, 63.53 mmol), K₂CO₃ (17.56 g, 127.06 mmol), and 18-crown-6 (2.29 g, 6.35 mmol) was stirred in *o*-dichlorobenzene (60 ml) at 190 °C for 48 h. The crude mixture was filtered, and the solvent was distilled off under reduced pressure. The mixture was extracted with chloroform and the organic extracts were combined, washed with water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane:chloroform at 8:1 by volume as the eluent to yield **4** (1.61 g, 21%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 8.16-8.14 (d, *J* = 8.0 Hz, 4H), 7.87-7.86 (d, *J* = 4.0 Hz, 2H), 7.80-7.78 (m, 1H), 7.55-7.53 (m, 4H), 7.48-7.44 (m, 4H), 7.35-7.31 (m, 4H).

(4-Bromophenyl)triphenylsilane, **7**. *n*-BuLi (2.5 M in hexane, 5.09 ml, 12.72 mmol) was added dropwise to a solution of **5** (3.00 g, 12.72 mmol) in THF (45 ml) at -78 °C, where the mixture was stirred for 3 h before adding **6** (3.75 g, 12.72 mmol) slowly. The reaction mixture was allowed to warm up to room temperature, quenched with water, and then extracted with chloroform. The organic extracts were combined, washed with brine and water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane:methylene chloride at 4:1 by volume as the eluent to yield **7** (3.00 g, 56%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 7.56-7.55 (m, 3H), 7.54-7.52 (m, 4H), 7.51-7.50 (m, 1H), 7.47-7.42 (m, 4H), 7.41-7.36 (m, 7H).

(4-Allylphenyl)triphenylsilane, **8**. THF (60 ml) was added to a mixture of **7** (1.00 g, 2.41 mmol), allyltributyltin (2.22 g, 7.22 mmol), Pd(PPh₃)₄ (0.14 g, 0.12 mmol), and LiCl (0.20 g, 4.81 mmol). The reaction mixture was stirred at 90 °C for 24 h, cooled down to room temperature, and extracted with chloroform. The organic extracts were combined, washed with water, and dried over MgSO₄. After evaporating off the solvent, the crude product was purified by gradient column chromatography on silica gel with hexane:chloroform at 49:1 to 24:1 by volume as the eluent to yield **8** (0.80g, 88%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 7.57-7.55 (m, 6H), 7.51-7.49 (m, 2H), 7.44-7.40 (m, 3H), 7.38-7.34 (m, 6H), 7.22-7.20 (m, 2H), 6.02-5.95 (m, 1H), 5.12-5.06 (m, 2H), 3.42-3.40 (d, *J* = 8.0 Hz, 2H).

1,3-Bis(9-carbazolyl)benzene, **mCP**. *o*-dichlorobenzene (120 ml) and **2** (2.56 ml, 21.20 mmol) were added to a mixture of **1** (10.62 g, 63.59 mmol), Cu (8.08 g, 127.17 mmol), K₂CO₃ (35.15 g, 254.35 mmol), and 18-crown-6 (4.58 g, 12.72 mmol). The reaction mixture was stirred at 190 °C

for 36 h. The crude mixture was filtered and the solvent was distilled off under reduced pressure. The mixture was extracted with chloroform and the organic extracts were combined, washed with water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane:methylene chloride at 9:1 volume as the eluent to yield **mCP** (5.01 g, 58%) as a pale purple powder. The synthesized **mCP** was further purified by sublimation to give a white solid in 55% yield. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 8.17-8.15 (d, *J* = 8.0 Hz, 4H), 7.87-7.82 (m, 2H), 7.72-7.69 (m, 2H), 7.55-7.53 (m, 4H), 7.46-7.42 (m, 4H), 7.33-7.29 (m, 4H). LDI TOF MS *m/z* ([M]⁺): 408.5. Anal. calcd for C₃₀H₂₀N₂ (%): C 88.21, H 4.93, N 6.86; found: C 87.77, H 4.80, N 6.79.

(4-(3-(3,5-Bis(9-carbazolyl)phenyl)propyl)phenyl)triphenylsilane, **mCP-ℒ-PhSiPh3**. 9-BBN (0.5 M in THF, 9 ml, 4.5 mmol) was added dropwise to a solution of **8** (0.54 g, 1.44 mmol) in THF (8 ml) at 0 °C. The mixture was stirred at room temperature for 15 min and then at 35 °C for 3 h before transferring to a mixture of **4** (0.77 g, 1.59 mmol), Pd(PPh₃)₄ (0.033 g, 0.029 mmol), Na₂CO₃ (3.82 g, 36.04 mmol), H₂O (18 ml) and Toluene (30 ml). The reaction mixture was stirred at 90 °C for 24 h, cooled down to room temperature, and extracted with chloroform. The organic extracts were combined, washed with water, and dried over MgSO₄. Upon evaporating off the solvent, the crude product was purified by gradient column chromatography on silica gel with hexane:chloroform at 3:1 to 2:1 by volume as the eluent to yield **mCP-ℒ-PhSiPh3** (0.86 g, 76%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 8.16-8.14 (d, *J* = 8.0 Hz, 4H), 7.47-7.46 (m, 1H), 7.56-7.49 (m, 14H), 7.45-7.39 (m, 7H), 7.36-7.28 (m, 10H), 7.25-7.22 (m, 2H), 2.92-2.89 (m, 2H), 2.81-2.78 (m, 2H), 2.18-2.10 (m, 2H). LDI TOF MS *m/z* ([M]⁺): 785.0. Anal. calcd for C₅₇H₄₄N₂Si (%): C 87.20, H 5.65, N 3.57; found: C 87.06, H 5.67, N 3.55.

Tetraphenylsilane, **SiPh4**. ¹H NMR (400 MHz, CDCl₃, 298K): δ (ppm) 7.58-7.56 (d, *J* = 8.0 Hz, 8H), 7.46-7.34 (m, 12H). Anal. calcd for C₂₄H₂₀Si (%): C 85.66, H 5.99; found: C 85.82, H 6.03.

Morphology, Thermal Stability, and Phase Transition Temperatures: Decomposition temperatures were characterized by thermogravimetric analysis (Q500, TA Instruments) at a ramping rate of 10 °C/min under a nitrogen flow of 60 ml/min. Thermal transition temperatures were acquired on a differential scanning calorimetry (Perkin-Elmer DSC 8500) with nitrogen flow at 20 ml/min. The mixed samples, **mCP:SiPh4**, **mCP:SiPh4:FIrpic** and **mCP-ℒ-PhSiPh3:FIrpic**, were prepared by codissolution in dichloromethane, followed by drying

thoroughly *in vacuo*. All samples were preheated to above their melting point, and then cooled down to $-30\text{ }^{\circ}\text{C}$ at $-100\text{ }^{\circ}\text{C}/\text{min}$ before the second heating and cooling scans were recorded at $20\text{ }^{\circ}\text{C}/\text{min}$. The nature of phase transition was characterized by hot-stage polarizing optical microscopy (DMLM, Leica, FP90 central processor and FP82 hot-stage, Mettler Toledo).

Photophysical Properties: Absorption of thin films on the fused silica substrate was characterized by UV-Vis-NIR spectrophotometer (Lambda-900, Perkin-Elmer). For phosphorescence measurements, thin films held on a cryostat (HC-2, APD Cryogenic Inc.) at 20 K in a vacuum chamber were excited at 355 nm with a 45° incident angle using a pulsed frequency-tripled neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (GCR-100, Quanta-Ray Spectra-Physics). Phosphorescence spectra were collected using the detector of CCD camera (DH50118F-01, Andor) with a monochromatic system (260i, ORIEL).

Electrochemical Characterization: Cyclic voltammetry was conducted on an EC-Epsilon potentiostat (Bioanalytical Systems Inc.) A silver/silver chloride (Ag/AgCl) wire, a platinum wire, and a glassy carbon disk with a diameter of 3 mm were used as the reference, counter, and working electrodes, respectively. Tetraethylammonium tetrafluoroborate was used as supporting electrolyte, which had been purified as described previously [1]. The sample was dissolved at a concentration of 10^{-3} M in acetonitrile/toluene (1:1 by volume) containing 0.1 M supporting electrolyte. Acetonitrile and toluene were distilled with calcium hydride and sodium/benzophenone, respectively. The dilute sample solution exhibited oxidation scans against the Ag/AgCl reference electrode. The oxidation potentials were adjusted to ferrocene (Fc) as an internal standard with an oxidation potential of $0.51\pm 0.02\text{ V}$ over Ag/AgCl. The resultant oxidation potential, $E_{1/2}(\text{oxd})$, relative to (Fc/Fc⁺) was used to calculate the HOMO level in neat solid film as $-1.4\times qE_{1/2}(\text{oxd})-4.6\text{ eV}$, where q is electron charge [2].

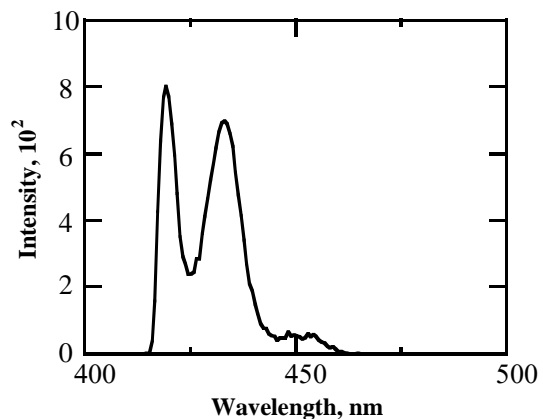


Figure S1. Phosphorescence spectrum at 20 K of vacuum-sublimed **mCP-L-PhSiPh3** film with excitation at 355 nm. The triplet energy was estimated from the highest energy band.

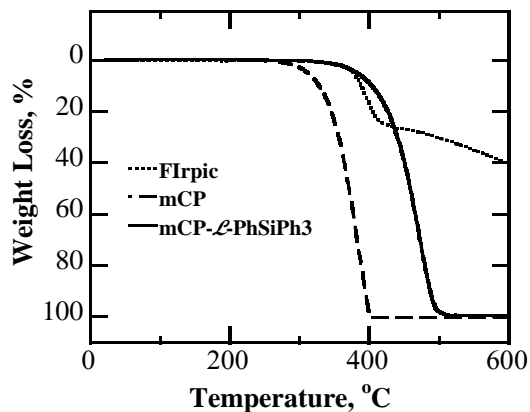


Figure S2. TGA thermograms of **FIrpic**, **mCP** and **mCP-L-PhSiPh3** recorded at a heating rate of 10 °C/min under nitrogen atmosphere.

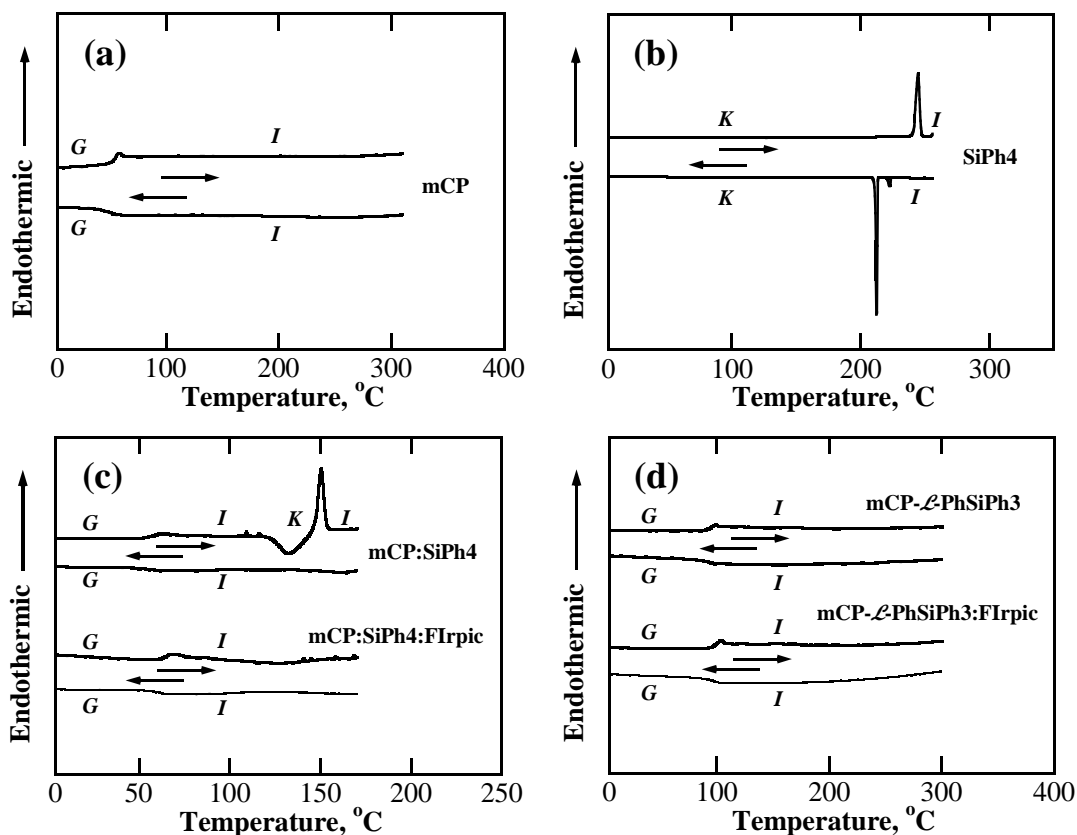


Figure S3. DSC heating and cooling scans at ± 20 °C/min of (a) **mCP**, (b) **SiPh4**, (c) **mCP:SiPh4** and **mCP:SiPh4:FIrpic**, and (d) **mCP- \mathcal{L} -PhSiPh3** and **mCP- \mathcal{L} -PhSiPh3:FIrpic** preheated to above their melting points followed by cooling down to -30 °C at -100 °C/min. The melting points were determined from the first heating scans of **mCP**, **SiPh4**, **mCP:SiPh4**, **mCP:SiPh4:FIrpic**, **mCP- \mathcal{L} -PhSiPh3** and **mCP- \mathcal{L} -PhSiPh3:FIrpic** at 176, 252, 170, 166, 115 and 120 °C, respectively. Symbols: *G*, glassy; *K*, crystalline; *I*, isotropic.

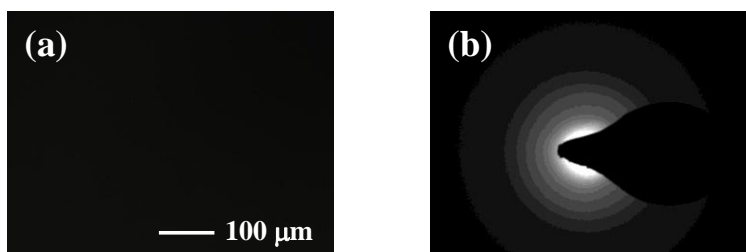


Figure S4. Freshly deposited TmPyPB(10 nm)/BPhen(30 nm)/LiF(1 nm): (a) polarizing optical micrograph, and (b) electron diffraction image.

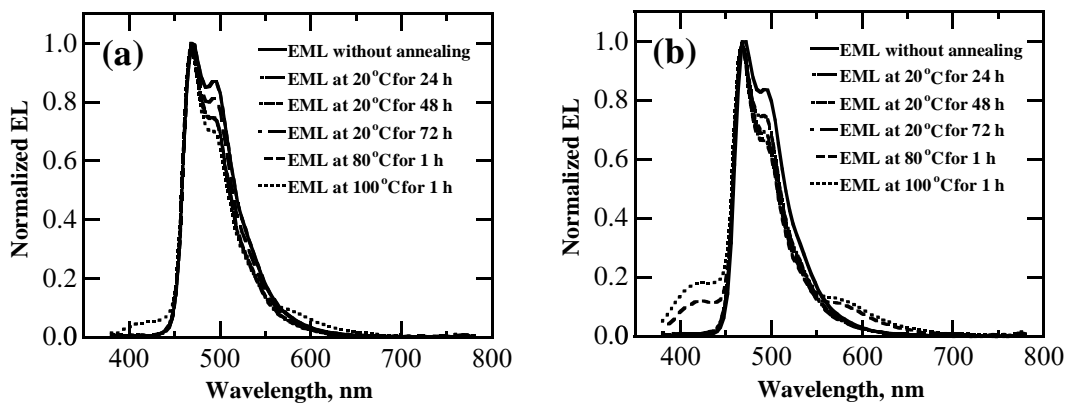


Figure S5. Electroluminescence spectra of PhOLEDs, ITO/MoO₃/TAPC/EML/ TmPyPB/BPhen/LiF/Al, where EML consists of (a) **mCP-ℓ-PhSiPh3:FIrpic**, and (b) **mCP:SiPh4:FIrpic** with ITO/MoO₃/TAPC/EML, annealed at 20 °C for 0, 72 h and at 80 and 100 °C for 1 h before subsequent depositions of TmPyPB/BPhen/LiF/Al.

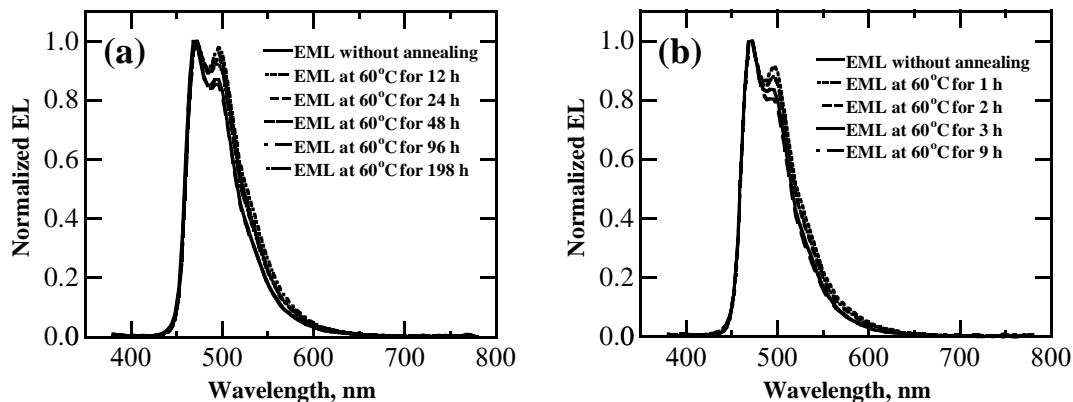


Figure S6. Electroluminescence spectra of PhOLED devices, ITO/MoO₃/TAPC/EML/TmPyPB/BPhen/LiF/Al, where EML consists of (a) **mCP-ℒ-PhSiPh₃:FIrpic**, and (b) **mCP:SiPh₄:FIrpic** with ITO/MoO₃/TAPC/EML/TmPyPB annealed at 60 °C for varying time periods before subsequent depositions of BPhen/LiF/Al.

References:

- [1] L. Zeng, F. Yan, S. K.-H. Wei, S. W. Culligan, S. H. Chen, *Adv. Funct. Mater.* 2009, **19**, 1978.
- [2] B. W. D'Andrade, D. Datta, S. R. Forrest, P. Djurovich, E. Polikarpov, M. E. Thompson, *Org. Electron.* 2005, **6**, 11.