

Supplementary Information

High-efficiency and long-lifetime deep-blue phosphorescent OLEDs using deuterated exciplex-forming host

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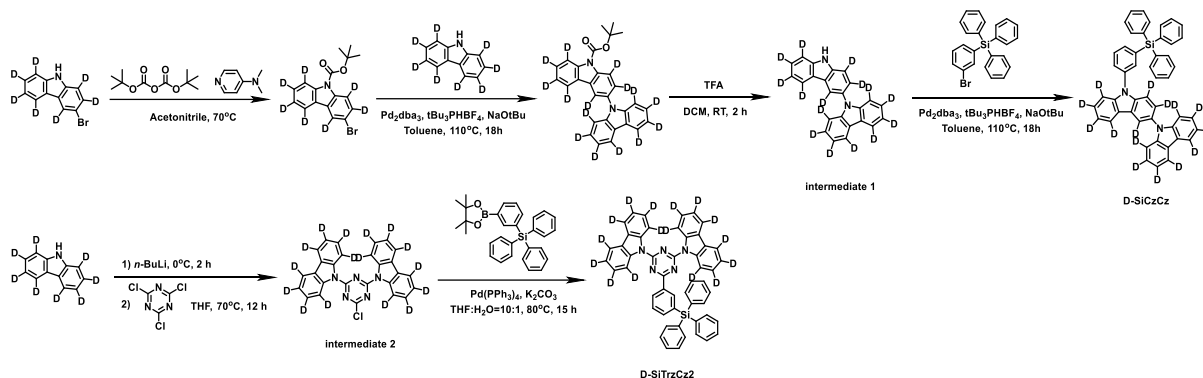
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1. Supplementary Methods

Synthesis and characterization of *D*-SiCzCz and *D*-SiTrzCz2



Supplementary Fig. 1 The synthetic routes of *D*-SiCzCz and *D*-SiTrzCz2.

Synthesis of 9H-3,9'-bicarbazole-1,1',2,2',3',4,4',5,5',6,6',7,7',8,8'-d₁₅ (intermediate 1):

3-Bromo-9H-carbazole-1,2,4,5,6,7,8-*d*₇ (10.00 g, 39.50 mmol), di-*tert*-butyl decarbonate (25.86 g, 118.51 mmol) and *N,N*-dimethylpyridin-4-amine (4.83 g, 39.50 mmol) were dissolved in acetonitrile (60 mL) at room temperature. After stirring overnight, the reaction mixture was purified by flash chromatography on silica gel with petroleum ether/CH₂Cl₂ (4:1, v/v) to give a white solid. Then, a mixture of the solid (8.00 g, 22.65 mmol), 9H-carbazole-1,2,3,4,5,6,7,8-*d*₈ (4.76 g, 27.17 mmol), Pd₂dba₃ (2.07 mg, 2.26 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.99, 3.40 mmol) and NaOtBu (5.44 g, 56.61 mmol) in dry toluene (100 mL) was stirred at 110°C for 18 h. After cooling to room temperature, the reaction mixture was extracted with CH₂Cl₂ and the combined organic layer was dried over anhydrous MgSO₄. The crude product was purified by flash chromatography on silica gel with petroleum ether/CH₂Cl₂ (3:1, v/v). The resulting product was dissolved in CH₂Cl₂ and 4.98 mL trifluoroacetic acid (TFA) was then added drop by drop. After reacting for 2 h at room temperature, the mixture was extracted with CH₂Cl₂ and the combined organic layer was dried over anhydrous MgSO₄. The crude product was purified by flash chromatography on silica gel with petroleum ether/CH₂Cl₂ (3:1, v/v) to give **intermediate 1** as a white solid, 3.73 g, total yield of 63%. ¹H NMR (400 MHz, Methylene Chloride-*d*₂) δ (ppm): 8.21 (s, 1H). MALDI-TOF: Calculated: 347.23, Found: 347.35.

Synthesis of (9-(3-(triphenylsilyl)phenyl)-9H-3,9'-bicarbazole-1,1',2,2',3',4,4',5,5',6,6',7,7',8,8'-d₁₅ (D-SiCzCz):

A mixture of **intermediate 1** (1.00 g, 2.88 mmol), (3-bromophenyl)triphenylsilane (2.39 g, 5.76 mmol), Pd₂dba₃ (263.52 mg, 0.29 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (125.24 mg, 0.43 mmol) and NaOtBu (1.11 g, 11.51 mmol) in dry toluene (60 mL) was stirred

at 110°C for 18 h. After cooling to room temperature, the reaction mixture was extracted with CH₂Cl₂ and the combined organic layer was dried over anhydrous MgSO₄. The crude product was purified by flash chromatography on silica gel with petroleum ether/CH₂Cl₂ (3:1, v/v) to give **D-SiCzCz** as a white solid, 1.78 g, yield of 89%. ¹H NMR (600 MHz, Methylene Chloride-*d*₂) δ (ppm) 7.85 (s, 1H), 7.77 (dt, *J* = 7.3, 2.0 Hz, 1H), 7.72 (dd, *J* = 3.3, 1.8 Hz, 1H), 7.68 – 7.66 (m, 6H), 7.49 – 7.46 (m, 3H), 7.45 – 7.42 (m, 6H), 7.30 (s, 1H). ¹³C NMR (151 MHz, Methylene Chloride-*d*₂) δ (ppm) 142.21, 141.76, 140.17, 137.75, 137.57, 136.77, 135.77, 134.83, 134.80, 134.04, 130.35, 130.19, 130.07, 128.51, 128.32, 124.73, 123.39, 123.32, 119.80, 110.11. MALDI-TOF: Calculated: 681.34, Found: 680.24 (M-H).

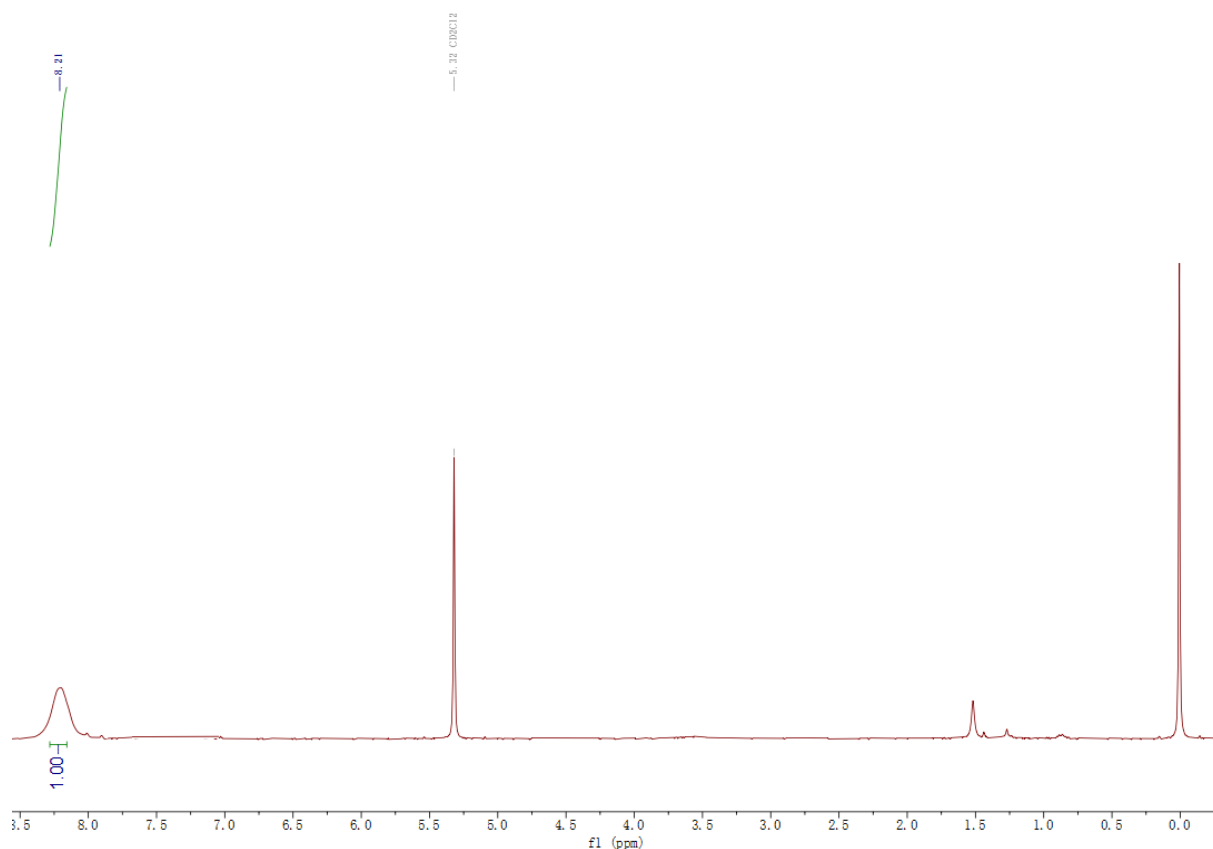
*Synthesis of 9,9'-(6-chloro-1,3,5-triazine-2,4-diyl)bis(9H-carbazole-1,2,3,4,5,6,7,8-*d*₈) (intermediate 2):*

9H-Carbazole-1,2,3,4,5,6,7,8-*d*₈ (5.00 g, 28.53 mmol) was dissolved in tetrahydrofuran (100 mL) under nitrogen atmosphere. The reaction solution was cooled to 0°C, *n*-BuLi (2.4M in hexane, 10.70 mL, 25.68 mmol) was added slowly. After 2 h, a solution of cyanuric chloride (2.53 g, 13.69 mmol) in anhydrous tetrahydrofuran (10 mL) was added slowly via dropping funnel. The reaction mixture was heated to 70°C for 12 h. The reaction was quenched by distilled water and the resultant solid was purified by flash chromatography on silica gel with petroleum ether/CH₂Cl₂ (2:1, v/v) to give **intermediate 2** as a white solid, 6.34 g, yield of 48%. MALDI-TOF: Calculated: 462.01, Found: 462.90.

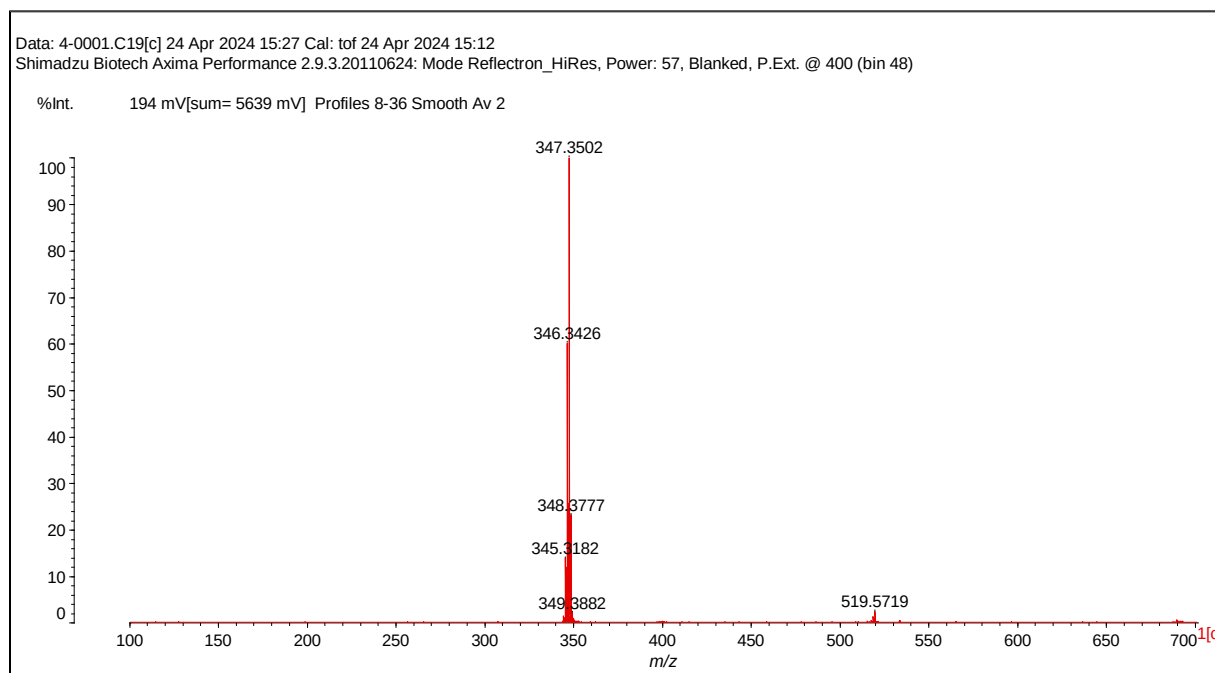
*Synthesis of 9,9'-(6-(3-(triphenylsilyl)phenyl)-1,3,5-triazine-2,4-diyl)bis(9H-carbazole-1,2,3,4,5,6,7,8-*d*₈) (D-SiTrzCz2):*

A mixture of **intermediate 2** (2.00 g, 4.33 mmol), triphenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (2.40 g, 5.19 mmol), Pd(PPh₃)₄ (0.5 g, 0.43 mmol) and K₂CO₃ (1.50 g, 10.82 mmol) in tetrahydrofuran and water (10: 1, 70 mL) was stirred at 80°C for 15 h. After cooling to room temperature, the reaction mixture was extracted with CH₂Cl₂ and the combined organic layer was dried over anhydrous MgSO₄. The crude product was purified by flash chromatography on silica gel with petroleum ether/CH₂Cl₂ (3:1, v/v) to give **D-SiTrzCz2** as a white solid, 2.88 g, yield of 87%. ¹H NMR (600 MHz, Methylene Chloride-*d*₂) δ (ppm) 9.09 (s, 1H), 8.83 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.89 (dt, *J* = 7.2, 1.3 Hz, 1H), 7.73 – 7.69 (m, 7H), 7.49 – 7.46 (m, 3H), 7.44 (s, 2H), 7.43 (s, 3H), 7.41 (d, *J* = 1.3 Hz, 1H). ¹³C NMR (151 MHz, Methylene Chloride-*d*₂) δ (ppm) 173.64, 165.18, 141.27, 139.27, 137.17, 136.81, 136.15, 135.94, 134.26, 130.93, 130.31, 129.10, 128.55, 128.50, 126.93, 126.77, 123.21, 119.69, 117.52. MALDI-TOF: Calculated: 761.37, Found: 761.64.

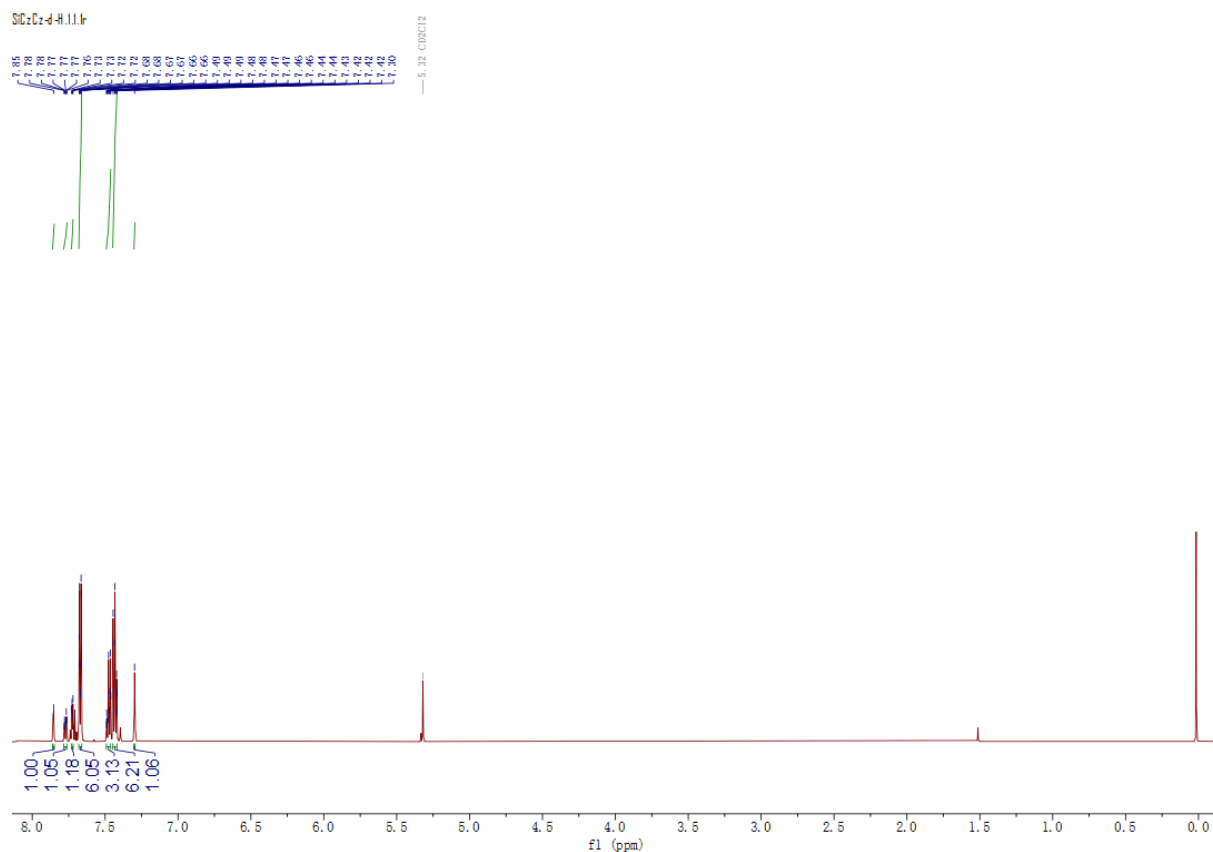
2. Supplementary Figures and Tables



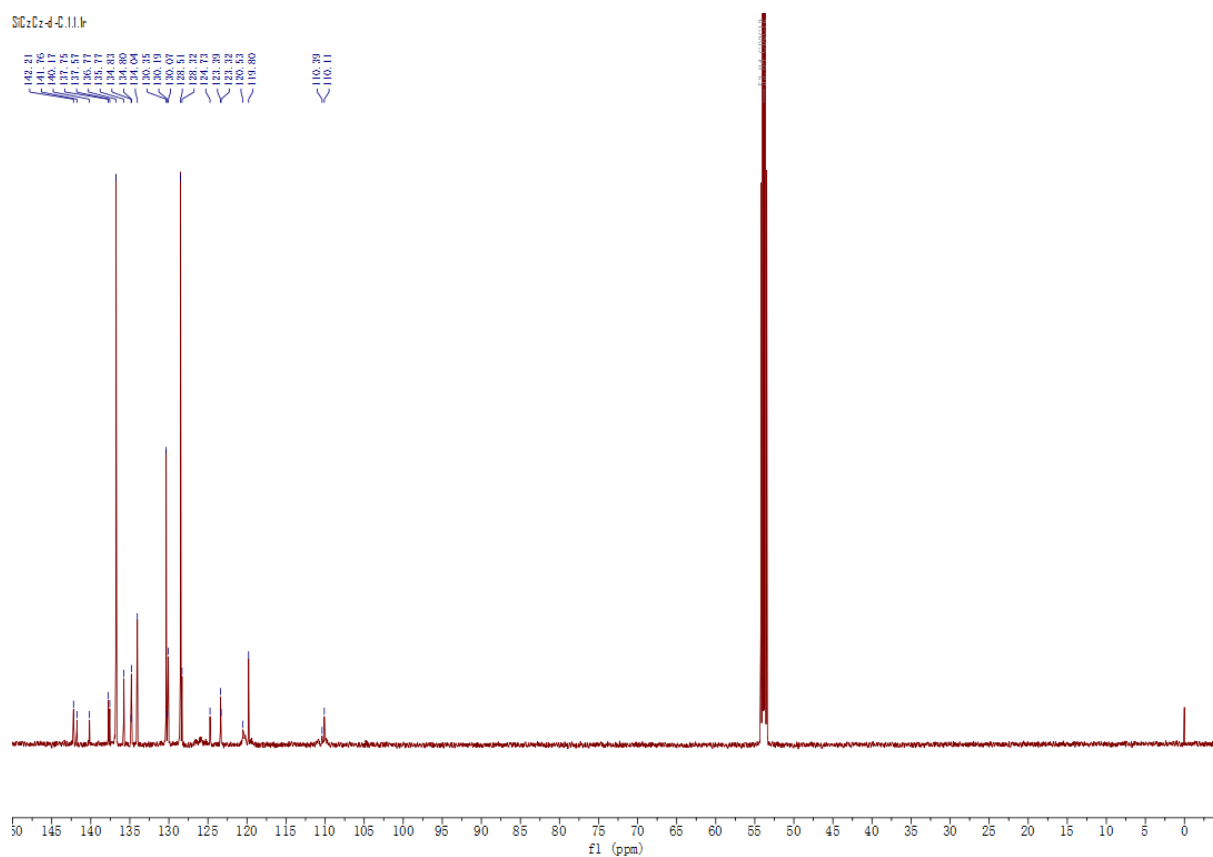
Supplementary Fig. 2 ¹H NMR spectra for intermediate 1.



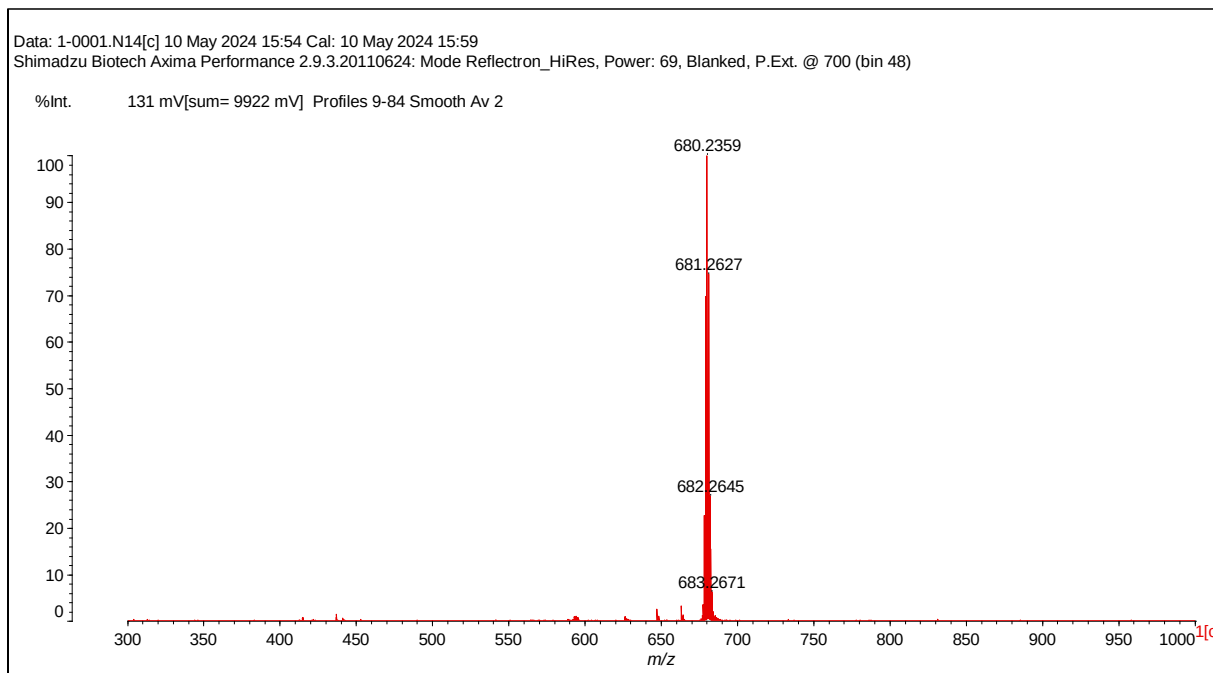
Supplementary Fig. 3 MALDI-TOF Mass spectrometry for intermediate 1.



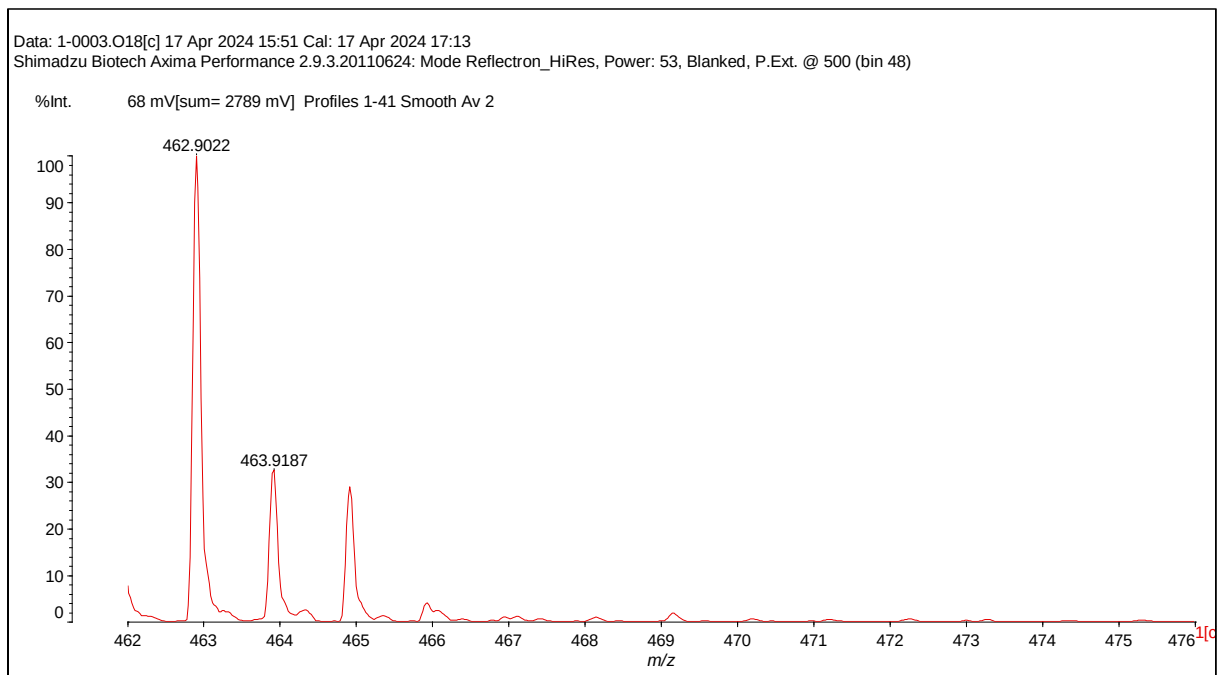
Supplementary Fig. 4 ^1H NMR spectra for compound *D*-SiCzCz.



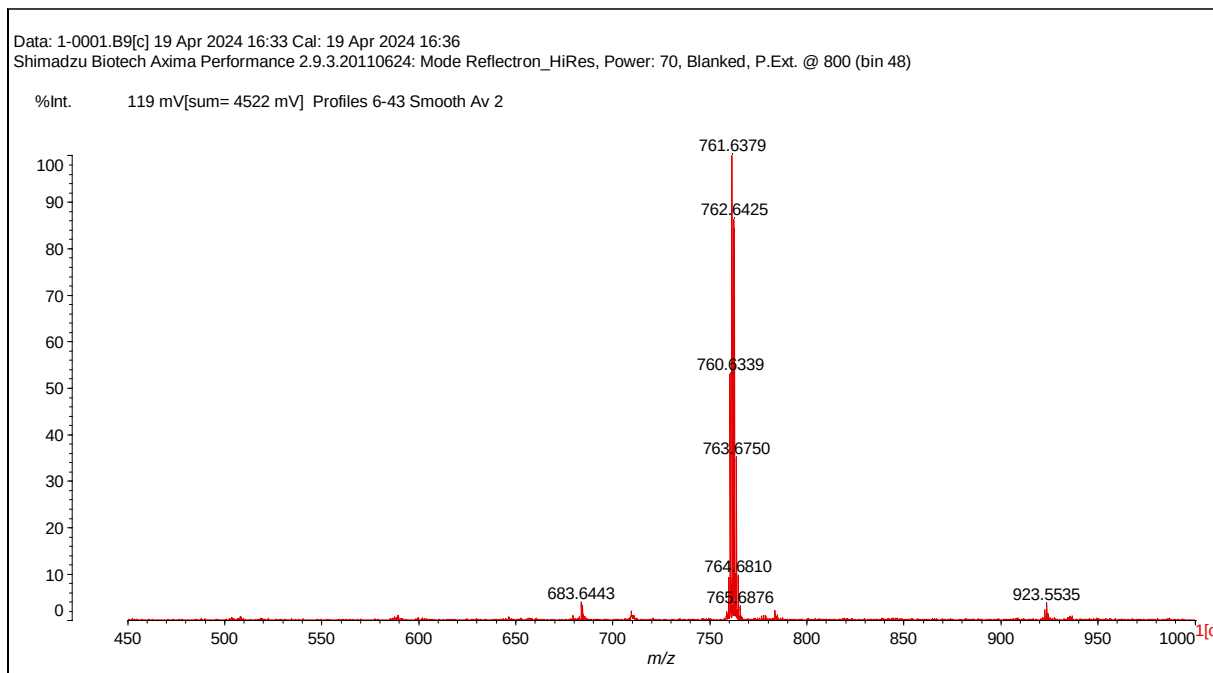
Supplementary Fig. 5 ^{13}C NMR spectra for compound *D*-SiCzCz.



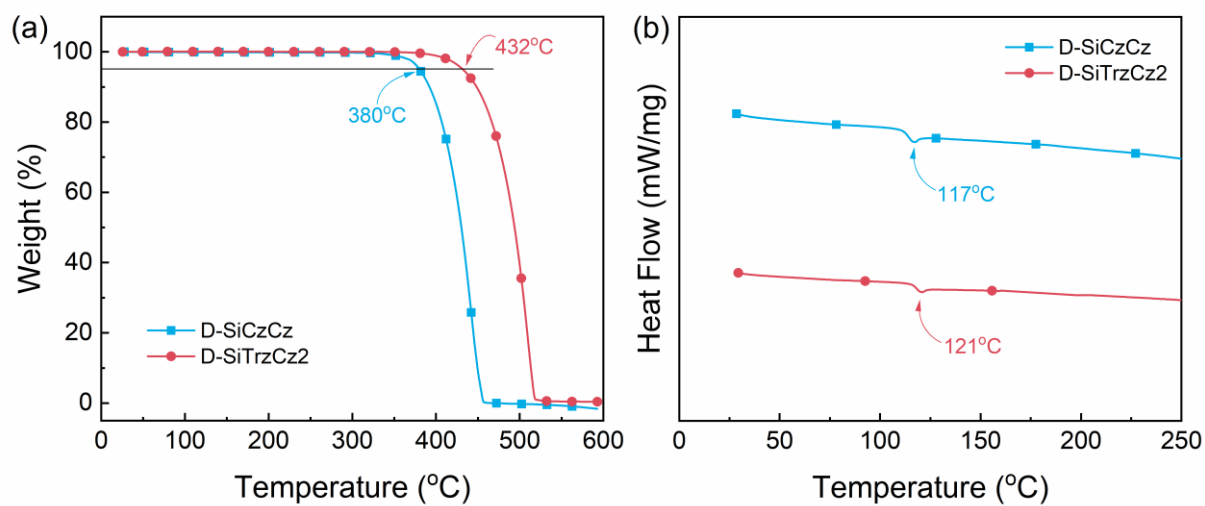
Supplementary Fig. 6 MALDI-TOF Mass spectrometry for compound *D*-SiCzCz.



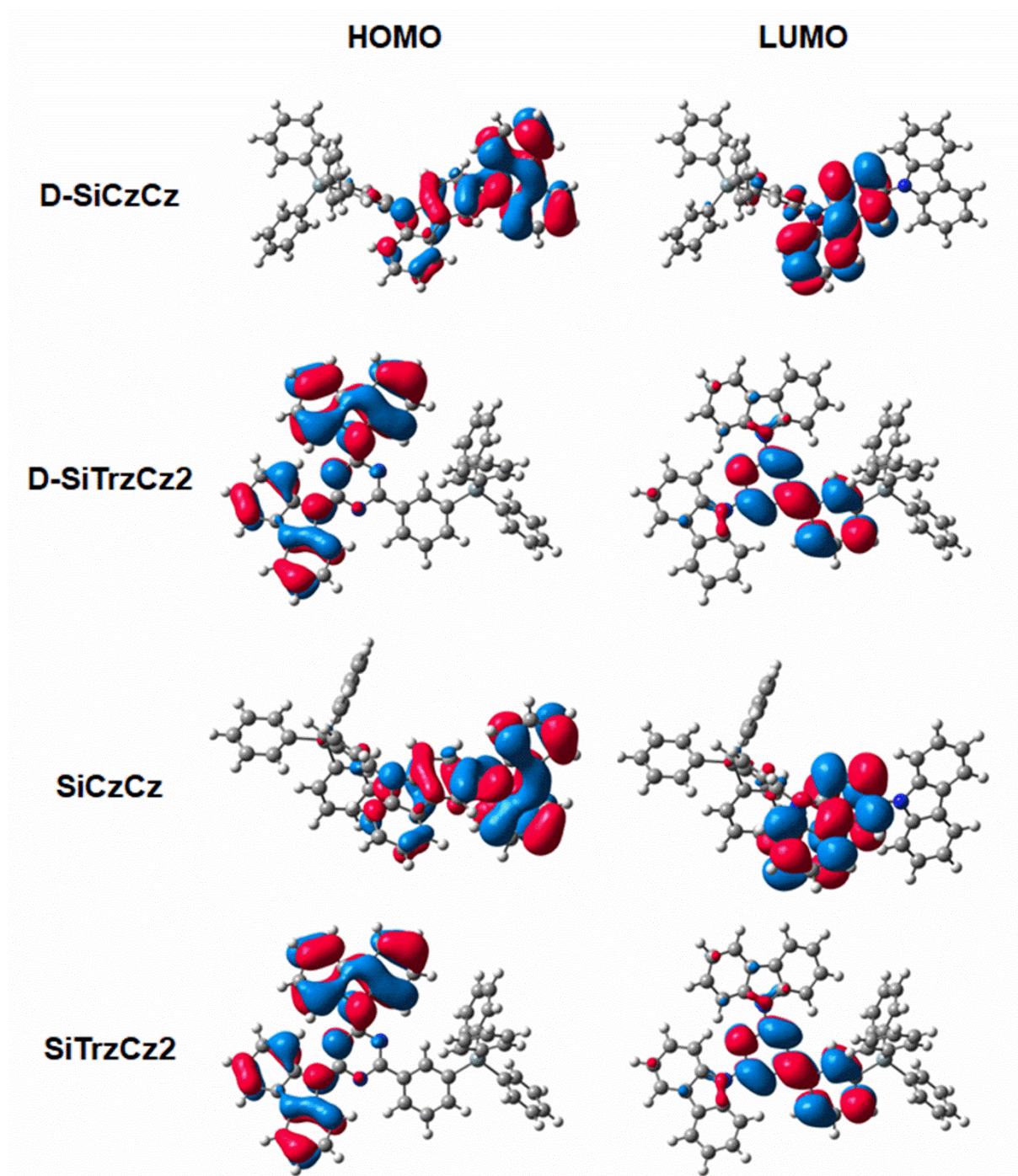
Supplementary Fig. 7 MALDI-TOF Mass spectrometry for intermediate 2.



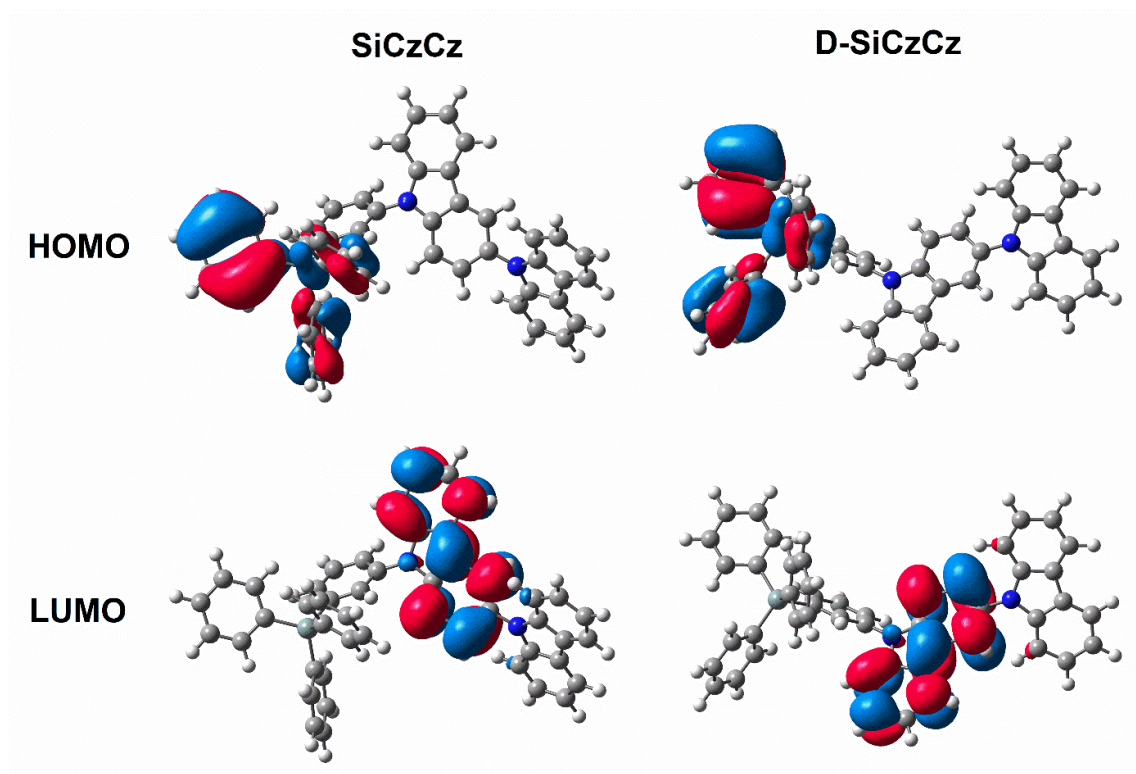
Supplementary Fig. 10 MALDI-TOF Mass spectrometry for compound *D*-SiTrzCz2.



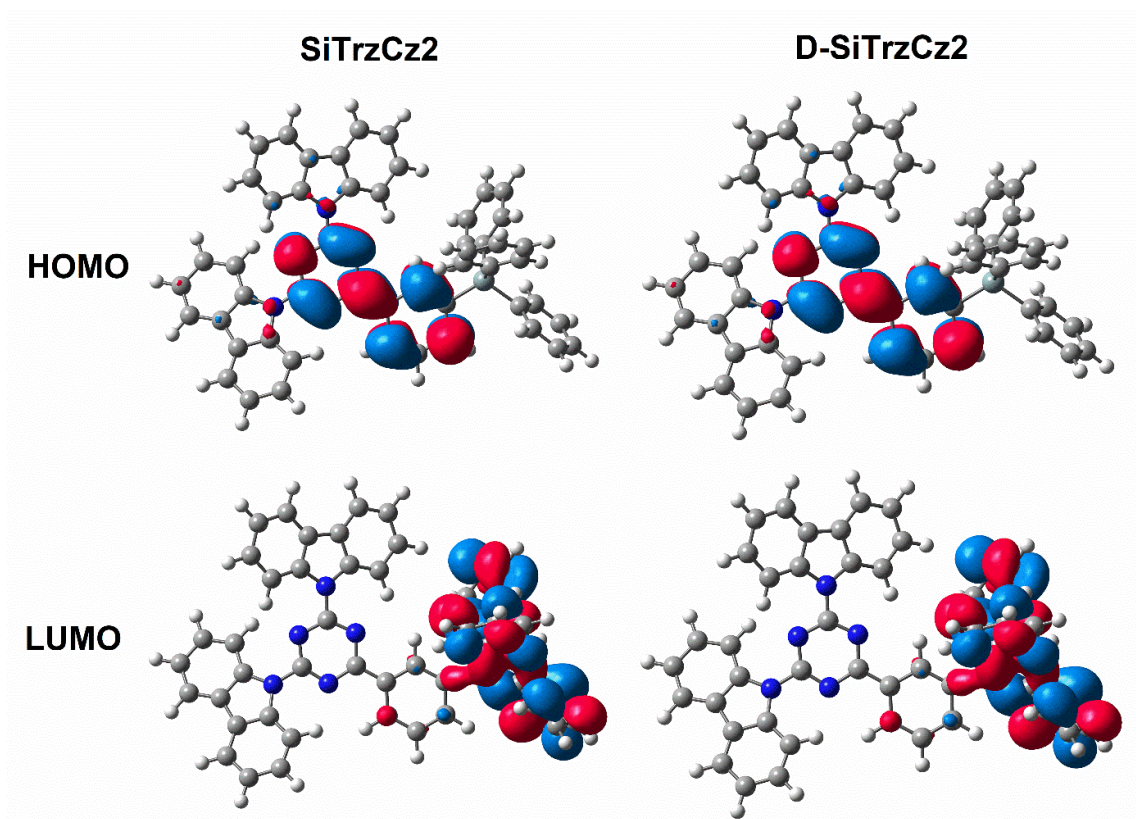
Supplementary Fig. 11 (a) Thermogravimetric analysis (TGA) and (b) differential scanning calorimetry (DSC) curves for *D*-SiCzCz and *D*-SiTrzCz2.



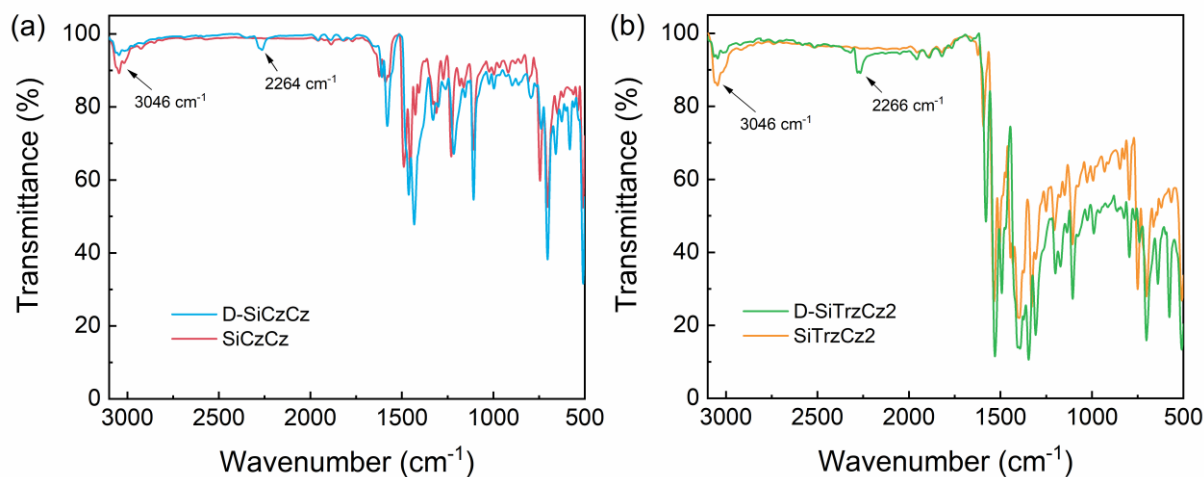
Supplementary Fig. 12 HOMO and LUMO distribution for *D*-SiCzCz, *D*-SiTrzCz2, SiCzCz and SiTrzCz2.



Supplementary Fig. 13 HOMO and LUMO distribution for SiCzCz and *D*-SiCzCz in cationic state.



Supplementary Fig. 14 HOMO and LUMO distribution for SiTrzCz2 and *D*-SiTrzCz2 in anionic state.



Supplementary Fig. 15 The experimental FT-IR spectra of (a) *D*-SiCzCz and SiCzCz, (b) *D*-SiTrzCz2 and SiTrzCz2.

Supplementary Table 1 BDE values for the deuterated and non-deuterated compounds.

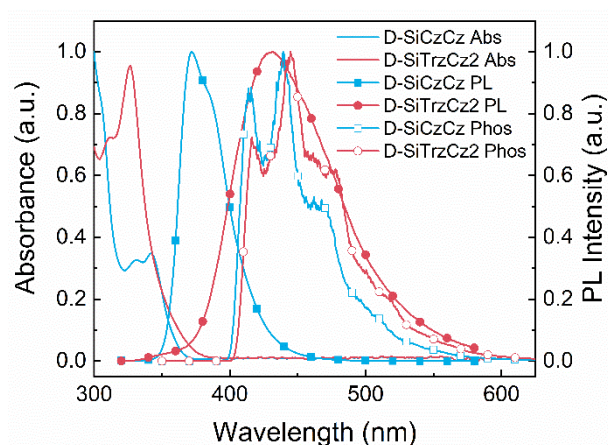
		①	②	③
BDE [eV]	SiCzCz	4.82	3.56	3.48
	<i>D</i> -SiCzCz	4.90	3.59	3.51
BDE(+) [eV]	SiCzCz	5.82	6.53	5.80
	<i>D</i> -SiCzCz	6.83	6.56	5.82
BDE [eV]	SiTrzCz2	4.82	5.52	4.79
	<i>D</i> -SiTrzCz2	4.93	5.55	4.82
BDE(-) [eV]	SiTrzCz2	1.25	2.59	2.67
	<i>D</i> -SiTrzCz2	1.36	2.61	2.69

SiCzCz

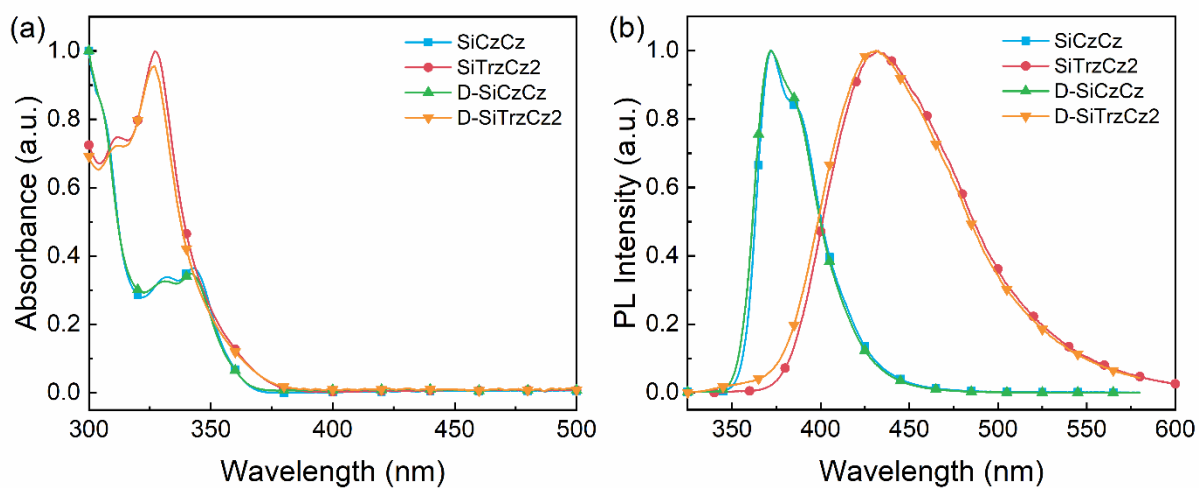
D-SiCzCz

SiTrzCz2

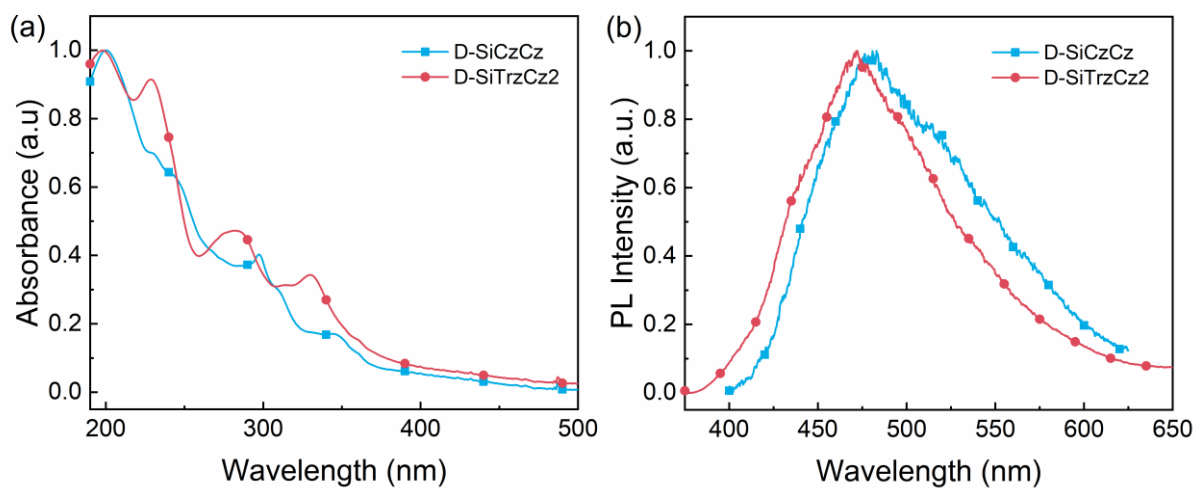
D-SiTrzCz2



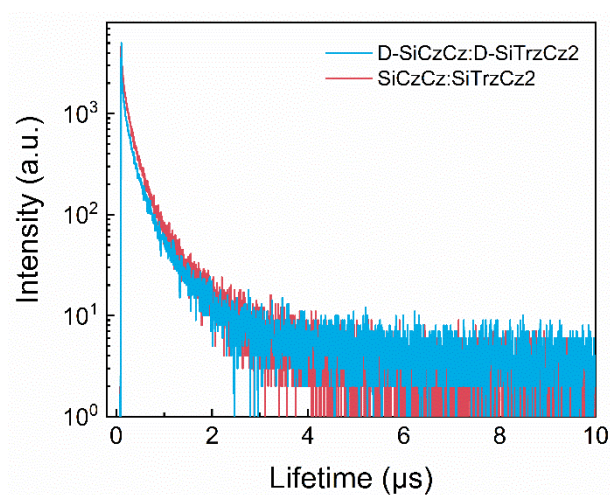
Supplementary Fig. 16 Normalized UV-Vis absorption, PL and phosphorescence spectra in toluene solution of *D*-SiCzCz and *D*-SiTrzCz2.



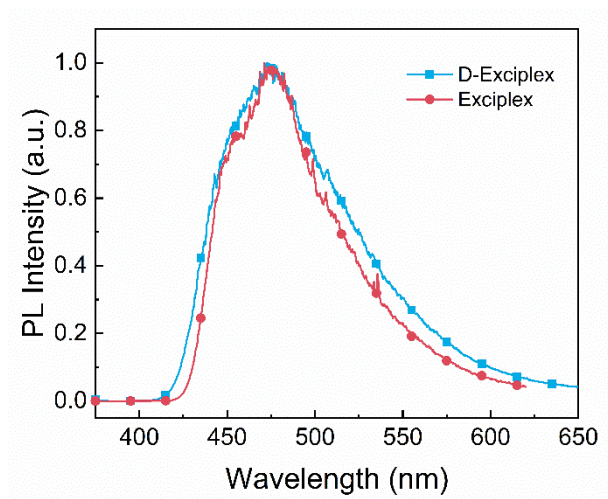
Supplementary Fig. 17 (a) Normalized UV-vis absorption spectra, (b) PL spectra of SiCzCz, SiTrzCz2, *D*-SiCzCz and *D*-SiTrzCz2 in toluene solution.



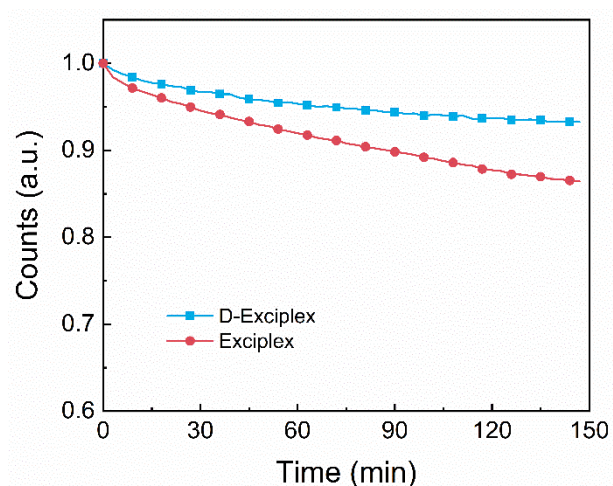
Supplementary Fig. 18 (a) Normalized UV-Vis absorption and (b) phosphorescence spectra in neat film for *D*-SiCzCz and *D*-SiTrzCz2.



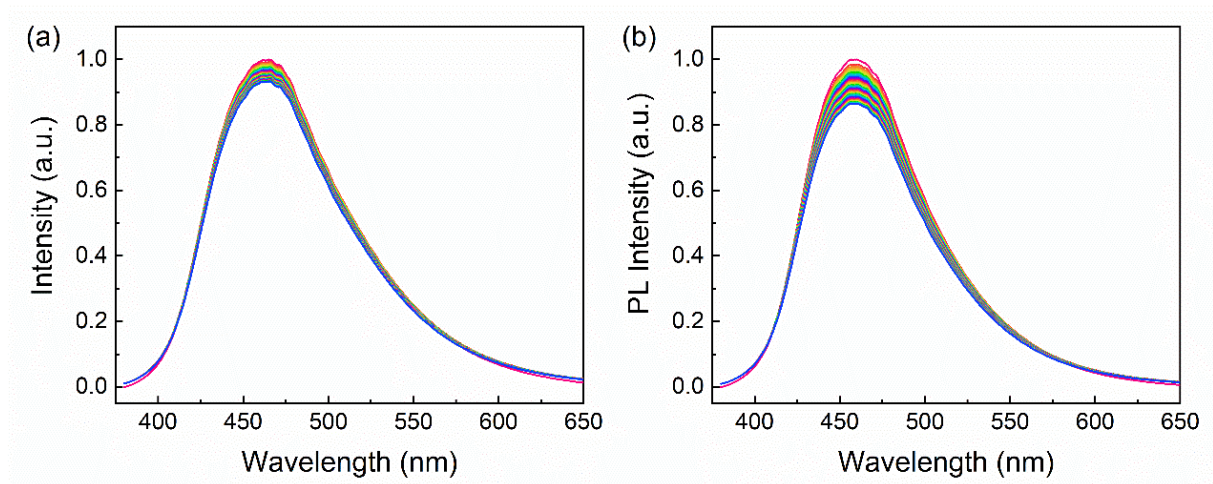
Supplementary Fig. 19 Transient decay curves of deuterated and non-deuterated exciplexes.



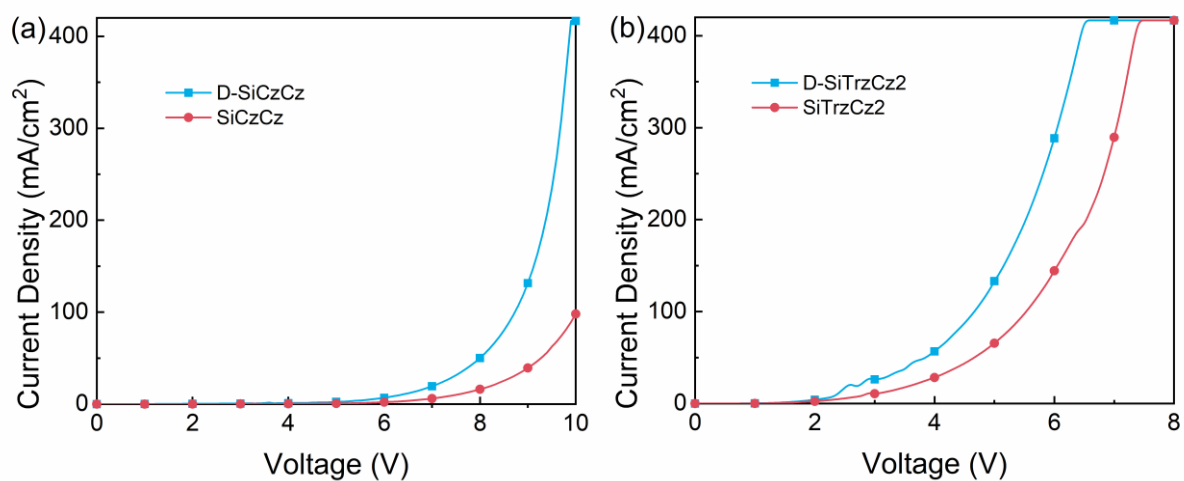
Supplementary Fig. 20 The phosphorescence spectra at 77 K for exciplexes of *D*-SiCzCz: *D*-SiTrzCz2 and SiCzCz: SiTrzCz2.



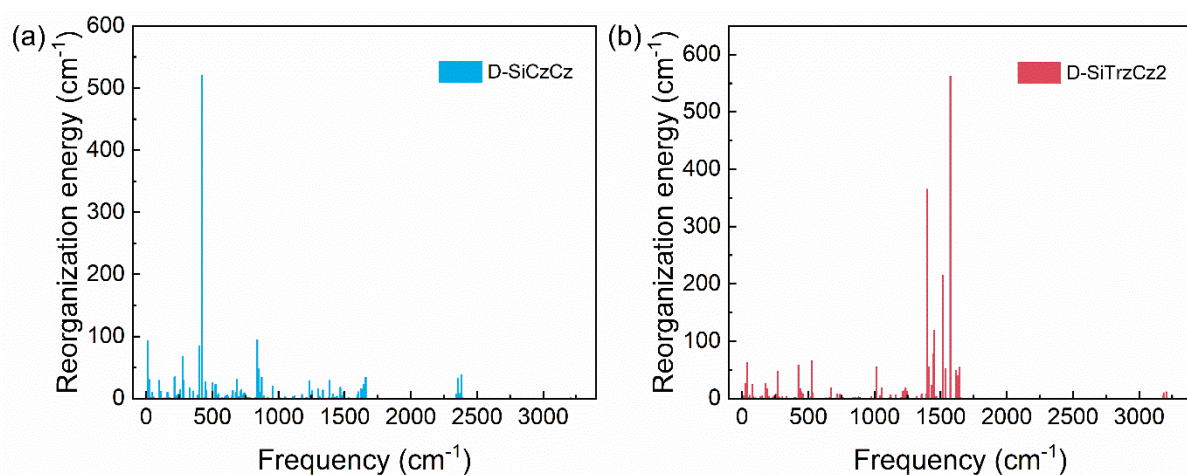
Supplementary Fig. 21 Photo-aging diagram of evaporated thin films (100 nm) of *D*-SiCzCz: *D*-SiTrzCz2 and SiCzCz: SiTrzCz2 mixtures under continuous ultraviolet irradiation of 360 nm.



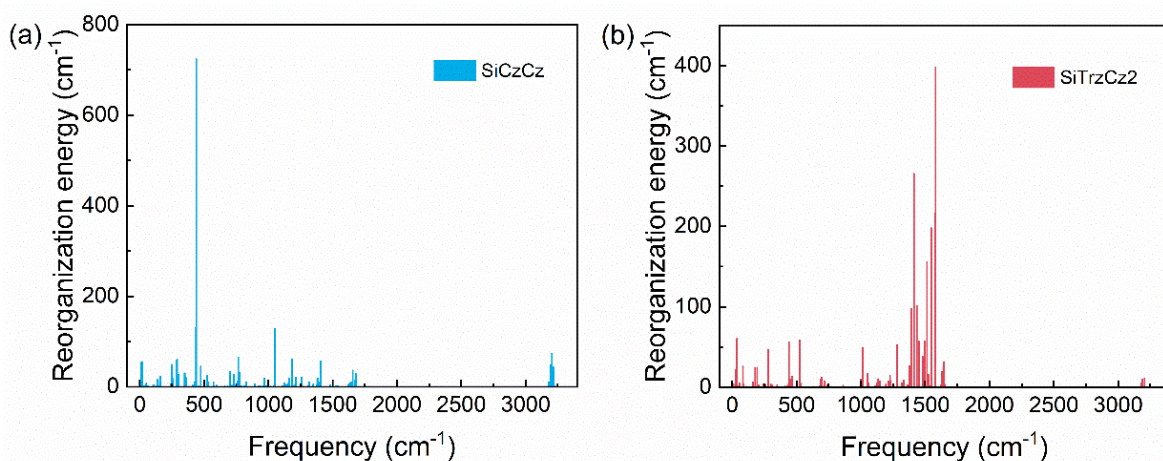
Supplementary Fig. 22 Photo-aging fluorescent spectra of (a) *D*-SiCzCz: *D*-SiTrzCz2 and (b) SiCzCz: SiTrzCz2 films under continuous ultraviolet irradiation of 360 nm.



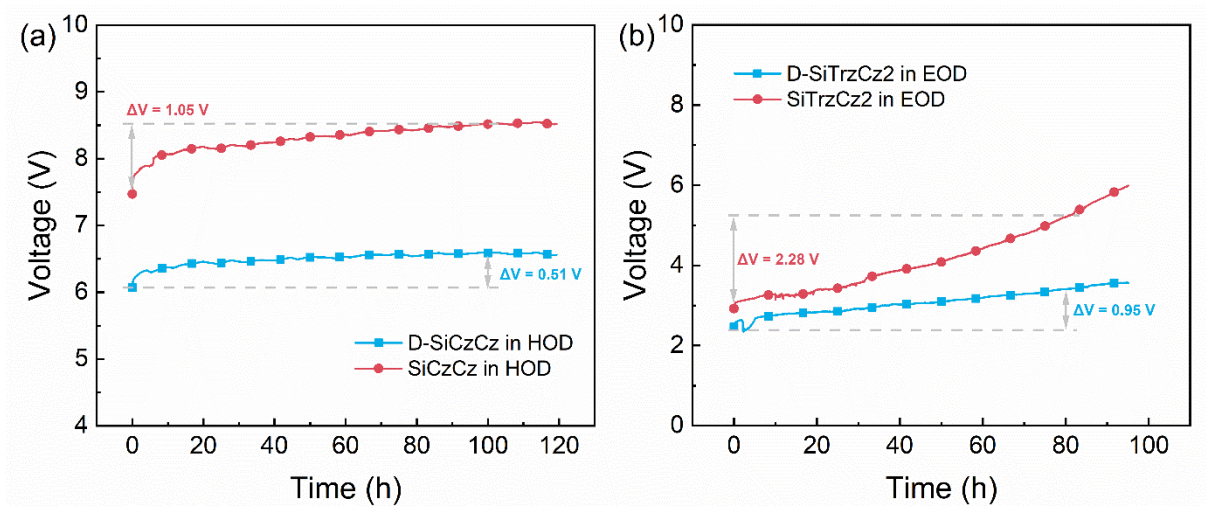
Supplementary Fig. 23 (a) HODs for electron donating *D*-SiCzCz and SiCzCz, (b) EODs for electron accepting *D*-SiTrzCz2 and SiTrzCz2.



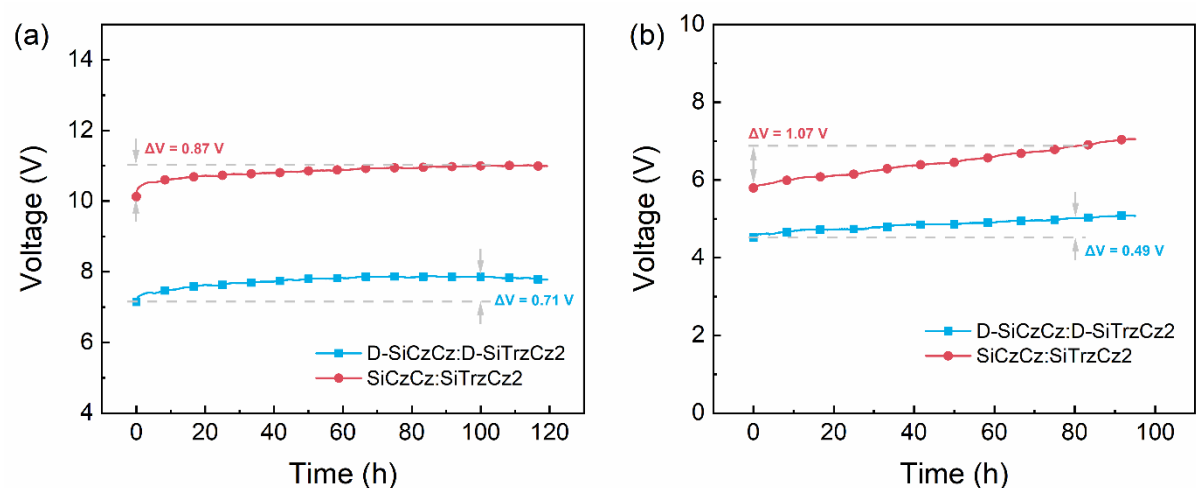
Supplementary Fig. 24 The reorganization energies of (a) *D*-SiCzCz and (b) *D*-SiTrzCz2.



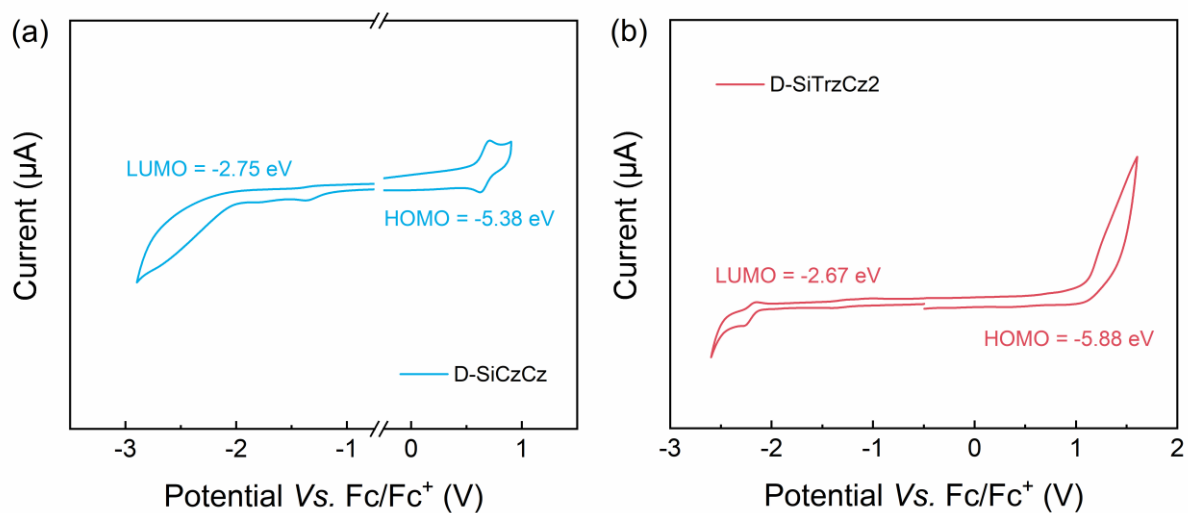
Supplementary Fig. 25 The reorganization energies of (a) SiCzCz and (b) SiTrzCz2.



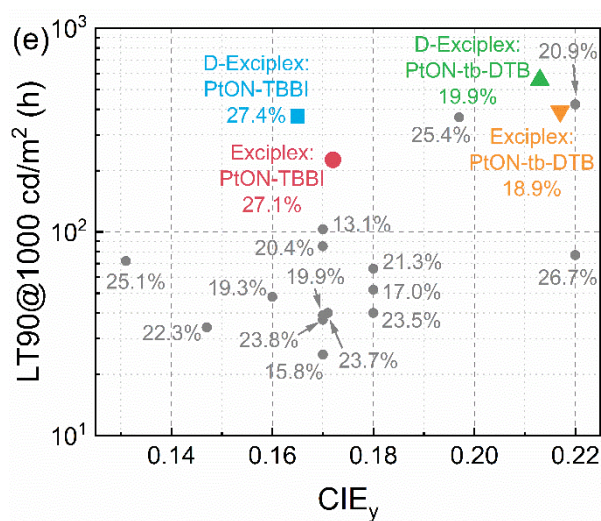
Supplementary Fig. 26 Electrical-aging curves of (a) *D*-SiCzCz and SiCzCz in HODs, (b) *D*-SiTrzCz2 and SiTrzCz2 in EODs.



Supplementary Fig. 27 Electrical aging curves of deuterated and non-deuterated mixtures in (a) HODs and (b) EODs.



Supplementary Fig. 28 Oxidation and reduction curves of (a) *D*-SiCzCz and (b) *D*-SiTrzCz2 by cyclic voltammetry.



Supplementary Fig. 29 Summarized CIE_y/LT90@1000 cd m⁻² of blue phosphorescent OLEDs with maximum EQE values.

Supplementary Table 2 Photophysical properties of *D*-SiCzCz and *D*-SiTrzCz2.

Compounds	$\lambda_{\text{abs}}^{\text{a}}$ [nm]	$\lambda_{\text{em}}^{\text{a}}$ [nm]	E_{S}^{b} [eV]	E_{T}^{b} [eV]	E_{g}^{c} [eV]	HOMO/LUMO ^d [eV]	$\tau_{\text{p}}^{\text{e}}$ [ns]	$\tau_{\text{d}}^{\text{e}}$ [ns]	$\Phi_{\text{PL}}^{\text{e}}$ [%]
<i>D</i> -SiCzCz	331,342 297,345	372 377	3.51	3.09	3.20	-5.38/-2.75	21.7	648.8	46
<i>D</i> -SiTrzCz2	311,327 283,330	431 427	3.29	3.06	3.31	-5.88/-2.67			

^aMeasured in toluene (up line) and film (down line) at room temperature (RT). ^bSinglet energy (E_{S}) measured through RT fluorescence and Triplet energy (E_{T}) measured through low temperature (77 K) phosphorescence spectra in toluene. ^cOptical bandgap (E_{g}) evaluated from the absorption edge of film state UV-Vis spectra. ^dHOMO and LUMO measured from the onset of oxidation and reduction curves from CV. ^eTransient decay curves and PLQY measured in vacuum-evaporated exciplex-forming films.

Supplementary Table 3 Summary of recent reported the state-of-art stable blue phosphorescent OLEDs.

Host	Phosphor	CIE (y)	Lifetime	Ref
<i>D</i> -SiCzCz: <i>D</i> -SiTrzCz2	PtON-TBBI	0.165	LT90@1000cd/m ² =370 h	This work
SiCzCz:SiTrzCz2	PtON-TBBI	0.172	LT90@1000cd/m ² =226 h	This work
<i>D</i> -SiCzCz: <i>D</i> -SiTrzCz2	PtON-tb-DTB	0.213	LT90@1000cd/m ² =557 h	This work
SiCzCz:SiTrzCz2	PtON-tb-DTB	0.217	LT90@1000cd/m ² =390 h	This work
SiCzCz:SiTrzCz2	PtON-TBBI	0.197	LT95@1000cd/m ² =150 h	1
SiCzCz:SiTrzCz2	PtON-tb-DTB	0.22	LT95@1000cd/m ² =235.1 h	2
SiCzCz:SiTrzCz2	PtON-tb-TTB	0.22	LT95@1000cd/m ² =43 h	2
SiCzCz:BO-Cz-Si-1	PtON-TBBI	0.18	LT70@1000 cd/m ² =180 h	3
SiCzCz:BO-Cz-Si-2	PtON-TBBI	0.17	LT70@1000 cd/m ² =168 h	3
SiCzCz:SiTrzCz2	PtON5-dtb	0.16	LT90@1000 cd/m ² =48 h	4
SiCzCz:SiTrzCz2	PtON5N-dtb	0.17	LT90@1000 cd/m ² =85 h	4
SiCzCz:SiTrzCz2	PtON-TBBI	0.147	LT70@1000 cd/m ² =160 h	5
SiCzCz:SiTrzCz2	Pt-SPCz	0.131	LT70@1000 cd/m ² =233 h	5
CzBTPCNmSi	Ir(cb) ₃	0.18	LT70@100 cd/m ² =332 h	6
CNCzBTPmSi	Ir(cb) ₃	0.18	LT70@100 cd/m ² =500 h	6
CzBTPmSi	Ir(cb) ₃	0.17	LT70@100 cd/m ² =355 h	6
SiCzCz:SiTrzCz2	PtON-TBBI	0.171	LT95@1000 cd/m ² =19.8 h	7
mCBP	f-ct1c	0.19	LT70@500 cd/m ² =31 h	8
mCBP	f-ct1d	0.19	LT70@500 cd/m ² =25 h	8
SiDBFCz	Ir(dpbic) ₂	0.17	LT80@500 cd/m ² =83 h	9
SiDBFCz	Ir(dpbic) ₂	0.17	LT80@500 cd/m ² =253 h	9

3. Supplementary References

1. Sun, J. et al. Exceptionally stable blue phosphorescent organic light-emitting diodes. *Nat. Photonics* **16**, 212-218 (2022).
2. Jung, Y. H. et al. Modified t-butyl in tetradentate platinum (II) complexes enables exceptional lifetime for blue-phosphorescent organic light-emitting diodes. *Nat. Commun.* **15**, 2977 (2024).
3. Park, J., et al. Boron-based thermally activated delayed fluorescence host materials as universal hosts for blue phosphorescent organic light-emitting diodes. *Mater. Today* **75**, 27-36 (2024).
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8. Yan, J., et al. Electroluminescence and hyperphosphorescence from stable blue Ir(III) carbene complexes with suppressed efficiency roll-off. *Nat. Commun.* **14**, 6419 (2023).
9. Kim, K. J., Lee, H., Kang, S. & Kim, T. Superbly long lifetime over 13,000 h for multiple energy transfer channels in deep blue phosphorescence organic light-emitting diodes with Ir complex under CIEy of 0.17. *Chem. Eng. J.* **448**, 137671 (2022).