# Peripheral halogen atoms in multi-resonant thermally activated delayed fluorescence emitters: The role of heavy atom on intermolecular interactions and spin orbit coupling.

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### **General information:**

#### General synthetic information.

All reagents and solvents for the synthesis and characterization were obtained from commercial sources. Anhydrous THF, toluene and DCM were obtained from an MBRAUN solvent purification system. Anhydrous 1,4-dioxane was freshly distilled over calcium hydride before use. Other chemicals were used directly without additional purification. Air-sensitive reactions are conducted under a nitrogen atmosphere using Schlenk techniques. Flash column chromatography was carried out using silica gel (Silia-P from Silicycle, 60 Å, 40-63 µm). Analytical thin-layer-chromatography (TLC) was performed with silica plates with aluminum backings (250 µm with F-254 indicator). TLC visualization was accomplished by 254/365 nm UV lamp. Melting points were measured using open-ended capillaries on an Electrothermal 1101D Mel-Temp apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured using a Bruker AVII 400 NMR spectrometer. The following abbreviations have been used for multiplicity assignments: "s" for singlet, "d" for doublet, "t" for triplet, "q" for quartet and "m" for multiplet. High-resolution mass spectrometry (HRMS) was obtained at the University of Edinburgh Mass Spectrometry Facility. Elemental analyses were performed by Joe Casillo at the University of Edinburgh.

#### Theoretical Calculations.

All calculations in the ground state, including geometry optimization, have been carried out using Density Functional Theory (DFT) with Gaussian 09 using the PBE0<sup>1</sup> functional and the 6-31G(d,p) basis set.<sup>2</sup> Excited-state calculations have been performed using Time-Dependent DFT (TD-DFT) within the Tamm-Dancoff approximation (TDA)<sup>3, 4</sup> using the same functional and basis set as for ground-state geometry optimization. Molecular orbitals were visualized using GaussView 6.0 software.<sup>5</sup> Vertical excited-states were also calculated using Spin-Component Scaling second-order algebraic diagrammatic construction (SCS-ADC2)/cc-pVDZ calculations based on the ground-state optimized structure using DFT.<sup>6, 7</sup> Difference density plots were used to visualize change in electronic density between the ground and excited state and were visualized using the VESTA package.<sup>8</sup> Calculations were submitted and processed using Silico V3,<sup>9</sup> which incorporates a number of publicly available software libraries, including: cclib<sup>10</sup> for parsing of result files, VMD<sup>11</sup>/Tachyon<sup>12</sup> for 3D rendering, Matplotlib<sup>13</sup> for drawing of graphs, Open Babel<sup>14</sup>/Pybel<sup>15</sup> for file interconversion and PySOC<sup>16</sup> for the calculation of spin-orbit coupling.

Electrochemistry measurements.

Cyclic Voltammetry (CV) analysis was performed on an Electrochemical Analyzer potentiostat model 620E from CH Instruments at a sweep rate of 100 mV/s. Differential pulse voltammetry (DPV) was conducted with an increment potential of 0.01 V and a pulse amplitude, width, and period of 50 mV, 0.06, and 0.5 s, respectively. All measurements were performed in degassed DCM with 0.1 M tetra-n-butylammonium hexafluorophosphate ([<sup>n</sup>Bu<sub>4</sub>N]PF<sub>6</sub>) as the supporting electrolyte and ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as the internal reference (0.46 V vs SCE)<sup>17</sup>. An Ag/Ag<sup>+</sup> electrode, a glassy carbon electrode and a platinum electrode were used as the reference electrode, working electrode and counter electrode, respectively. The HOMO and LUMO energies were determined using the relation the relation HOMO/LUMO =  $-(E_{ox}/E_{red} vs Fc/Fc^{+} + 4.8)^{18, 19}$ , where  $E_{ox}$  and  $E_{red}$  are the oxidation and reduction peak potentials versus Fc/Fc<sup>+</sup>, respectively, calculated from the DPV.

#### Photophysical measurements.

Steady-state absorption and emission spectra were measured using a double beam Shimadzu UV-3600 UV/VIS/NIR spectrophotometer and a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer, respectively. Solid-state samples were prepared from toluene solutions of host and guest molecules at specific mass ratios, and dried following drop-casting upon sapphire or quartz substrates. An integrating sphere (Edinburgh Instruments FS5, SC30 module) was employed for quantum yield measurements for thin film samples. The  $\Phi_{PL}$  of the films were then measured in air and in N<sub>2</sub> by purging the integrating sphere with N<sub>2</sub> gas flow for 5 min. Time-resolved measurements were performed using a spectrograph (Horiba Triax) and a Stanford Computer Optics 4Picos ICCD camera, where samples were excited with a Nd:YAG laser (EKSPLA, 10 Hz, 355 nm) under vacuum.

#### Device Fabrication.

OLEDs were fabricated on patterned indium tin oxide (ITO)-coated glass (VisionTek Systems) with a sheet resistance of 15  $\Omega$ /sq. Oxygen-plasma cleaned substrates were loaded into a Kurt J. Lesker Super Spectros deposition chamber, and both the small molecule and cathode layers were thermally evaporated at pressure below 10<sup>-7</sup> mbar. The materials used for the production of the MR-TADF-only devices were N,N-bis(naphthalene-1-yl)-N,-bis(phenyl)benzidine (NPB) as the hole injection/transport layer (HIL/HTL), 1,3-di(9H-carbazol-9-yl)benzene, N,N'-dicarbazolyl-3,5-benzene (mCP) as the electron blocking layer (EBL), the emissive layer (EML) had mCP as a host and the MR-TADF emitter, 2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine (T2T) as the hole blocking layer (HBL), T2T and 8-hydroxyquinolinolato lithium (Liq) as the electron transport/injection layer (ETL/EIL), and aluminum (AI) cathode. NPB, mCP and T2T were purchased from SigmaAldrich and sublimed before use.

#### Device Characterization

Freshly evaporated devices were transferred into a calibrated 6-inch integrating sphere (Labsphere) in a glovebox, and their electrical properties were measured using a source meter (Keithley 2400). Emission spectra were simultaneously measured using both a calibrated fiber coupled spectrometer (Ocean optics USB4000) and a photodiode, for low luminance. All devices were evaluated at 293 K and under  $N_2$  atmosphere.

Synthesis:



Figure **S1**. Synthesis scheme of **dBr-tBu-DiKTa**.

## Dimethyl 2,2'-((4-(tert-butyl)phenyl)azanediyl)dibenzoate (1)

4-(*tert*-butyl)aniline (4.27 mL, 26.8 mmol, 1 equiv.), methyl 2-iodobenzoate (11.8 mL, 80.4 mmol, 3 equiv.), copper tin alloy (977 mg, 5.36 mmol, 0.2 equiv.), copper(I) iodide (255 mg, 1.34 mmol. 0.05 equiv.), anhydrous potassium carbonate (7.78 g, 56.3 mmol, 2.1 equiv.), and 25 mL anhydrous di-*n*-butyl ether were added to a 2-neck Schlenk tube. The resulting reaction mixture was heated to 150 °C under nitrogen and stirred for 4 days. After cooling to room temperature, the reaction mixture was filtered and rinsed with dichloromethane. The solution was then concentrated under reduced pressure. The resulting dark brown oil was purified by column chromatography on silica gel (ethyl acetate: hexane = 1: 10) to obtain compound **1** as a yellowish powder after recrystallized and washed with hexane. **Yield**: 67%, 7.51 g. **Mp**: 104-106 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 (dd, J = 7.7, 1.6 Hz, 2H), 7.38 (ddd, J = 8.2, 7.4, 1.7 Hz, 2H), 7.20 – 7.07 (m, 6H), 6.77 – 6.70 (m, 2H), 3.35 (s, 6H), 1.25 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.02, 146.70, 145.83, 144.94, 132.44, 130.82, 128.17, 127.53, 125.68, 123.55, 121.13, 51.69, 34.19, 31.39. HR-MS: [C<sub>24</sub>H<sub>17</sub>Br<sub>2</sub>NO<sub>2</sub> +H]<sup>+</sup> Calculated: 418.2013; Found: 418.2003.

## Dimethyl 6,6'-((4-(tert-butyl)phenyl)azanediyl)bis(3-bromobenzoate) (2)

To a suspension of **1** (3.50 g, 8.38 mmol, 1 equiv.) in acetonitrile (40 mL), *N*-bromosuccinimide (2.98 g, 16.8 mmol, 2 equiv.) in acetonitrile (20 mL) was added dropwise at 0 °C under nitrogen and the mixture was stirred at room temperature for 18 h. The reaction mixture was quenched with water and extracted with 150 mL dichloromethane. The organic layer was then separated and concentrated under reduced pressure. The resulting solid was purified by column chromatography on silica gel (ethyl acetate: hexane = 1: 40) to obtain compound **2** as a yellow powder. **Yield**: 67%, 3.23 g. **Mp**: 117-118 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73 (d, J = 2.4 Hz, 2H), 7.48 (dd, J = 8.7, 2.5 Hz, 2H), 7.21 – 7.14 (m, 2H), 7.01 (d, J = 8.7 Hz, 2H), 6.75 – 6.69 (m, 2H), 3.37 (s, 6H), 1.25 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.32, 145.93, 145.39, 145.00, 135.44, 133.61, 129.67, 128.82, 125.93, 121.49, 116.42, 52.02, 34.26, 31.35, 31.19. HR-MS:  $[C_{24}H_{17}Br_2NO_2 + H]^+$  Calculated: 574.0223; Found: 574.0197.

## 6,6'-((4-(tert-butyl)phenyl)azanediyl)bis(3-bromobenzoic acid) (3)

Compound **2** (800 mg, 1.39 mmol, 1 equiv.) was combined with sodium hydroxide (278 mg, 6.95 mmol, 5 equiv.) in 10 mL of an ethanol/water (1:1) mixture. The reaction mixture was heated to 100 °C for 18 h. After cooling to room temperature, the pH was adjusted to 2-3 by addition of dilute hydrochloric acid. The diacid was precipitated as a light yellow solid and was collected by vacuum filtration, washed thoroughly with water, dried under vacuum, and used without further purification and characterization. **Yield**: 99%, 751 mg.

## 3,11-dibromo-7-(tert-butyl)quinolino[3,2,1-de]acridine-5,9-dione (dBr-tBu-DiKTa)

The diacid **3** (700 mg, 1.28 mmol, 1 equiv.) was dispersed in 15 mL dichloromethane under a nitrogen atmosphere. Thionyl chloride (187  $\mu$ L, 2.56 mmol, 2 equiv.) and 2 drops of DMF were added to the reaction mixture sequentially. After 3 h under reflux, the reaction mixture was cooled to room temperature. Under a positive flow of nitrogen, aluminium chloride (1.71 g, 12.8 mmol, 10 equiv.) was added slowly. After heating to 47 °C for 18 h, the reaction mixture was cooled to room temperature and quenched by dropwise addition of water with vigorous stirring. The resulting mixture was extracted with 150 mL dichloromethane, the organic layer was then separated and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (dichloromethane: hexane = 2: 1) to afford compound dBr-tBu-DiKTa as a yellow powder. Yield: 73%, 480 mg. Mp: 271-273 °C. Litt.: 194.8–196.2°C.<sup>11 1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.79 – 8.75 (m, 2H), 8.60 (dd, J = 7.2, 2.4 Hz, 2H), 7.96 (d, J = 9.0 Hz, 2H), 7.77 (dd, J = 9.0, 2.4 Hz, 2H), 1.47 (s, 9H). <sup>13</sup>C NMR (101 **MHz, CDCl**<sub>3</sub>) δ 177.57, 147.92, 138.21, 137.22, 135.60, 130.50, 130.43, 127.80, 123.19, 121.68, 118.63, 35.12, 31.30. HR-MS: [C<sub>24</sub>H<sub>17</sub>Br<sub>2</sub>NO<sub>2</sub> +H]<sup>+</sup> Calculated: 509.9699; Found: 509.9696. Anal. Calcd. for C24H17Br2NO2: C, 56.39%; H, 3.35%; N, 2.74%. Found: C, 56.24%; H, 3.38%; N, 2.83%. HPLC (65% THF and 35% Water): 99.41% pure, retention time 9.917 min. The analytical data match those of the literature.<sup>20</sup>



Figure **S2**. <sup>1</sup>H NMR of **1** in CDCl<sub>3</sub>.



Figure **S3**. <sup>13</sup>C NMR of **1** in CDCl<sub>3</sub>.



Figure S4. HRMS of 1.



Figure **S5**. <sup>1</sup>H NMR of **2** in CDCl<sub>3</sub>.



Figure **S6**. <sup>13</sup>C NMR of **2** in CDCl<sub>3</sub>.



Figure **S7**. HRMS of **2**.



Figure **S8**. <sup>1</sup>H NMR of **dBr-tBu-DiKTa** in CDCl<sub>3</sub>.



Figure **S9**. <sup>13</sup>C NMR of **dBr-tBu-DiKTa** in CDCl<sub>3</sub>.



Figure **S10**. HRMS of **dBr-tBu-DiKTa**.

# **Elemental Analysis Service Request Form**

# Researcher name \_\_\_\_\_\_ Wang

# Researcher email jw357@st-andrews.ac.uk

## NOTE: Please submit ca. 10 mg of sample

Sample reference number	JXW-I54
Name of Compound	
Molecular formula	C24H17Br2NO2
Stability	Stable in air and in most solvents
Hazards	
Other Remarks	

## Analysis type:

	/-	
Single	Duplicate 🗹 Triplicate	

# **Analysis Result:**

Element	Expected %	Found (1)	Found (2)	Found (3)
Carbon	56.39	\$5.79	56.68	
Hydrogen	3.35	3.34	3.42	
Nitrogen	2.74	2.79	2.87	
Oxygen				

# Authorising Signature:

Date completed	21.05.21
Signature	J-PL-
comments	

Figure **S11**. Elemental analysis report of **dBr-tBu-DiKTa**.

# HPLC Trace Report23Nov2023

## <Sample Information>

Sample Name Sample ID Method Filename	: dBr : : 65% THF 35% water 0.6 mlmin 20 m	nins.lcm	
Batch Filename Vial # Iniection Volume	: dbr tbr mes.lcb : 1-7 : 10 ul	Sample Type	: Unknown
Date Acquired Date Processed	23/11/2023 21:18:52 23/11/2023 21:38:53	Acquired by Processed by	: System Administrator : System Administrator

#### <Chromatogram>



100.000

## <Peak Table>

Total

Detect	or A 280nm					
Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	1.141	2487	303	0.014	8.210	0.250
2	2.379	81636	2334	0.462	34.974	0.764
3	7.580	20117	616	0.114	32.644	1.023
4	9.917	17568405	415793	99.410	42.253	1.302

419046

Figure **S12**. HPLC report of **dBr-tBu-DiKTa**.

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Figure **S13**. Calculated HOMO, LUMO and energy levels of **Mes<sub>3</sub>-DiKTa**, **dBr-tBu-DiKTa** and **tBr-DiKTa** in gas phase at PBE0/6-31G(d,p) level and SOCME based on optimized T<sub>1</sub> geometry.



Figure **S14**. CV and DPV of **dBr-tBu-DiKTa**, **tBr-DiKTa**, and **Mes<sub>3</sub>-DiKTa** in DCM (CV was performed at a sweep rate of 100 mV/s. DPV was conducted with an increment potential of 0.01 V and a pulse amplitude, width, and period of 50 mV, 0.06, and 0.5 s, respectively).

	E <sub>ox</sub> / V	$E_{red} / V$	HOMO / eV	LUMO/ eV	$\Delta E / eV$
dBr-tBu-DiKTa	1.33	-1.73	-6.13	-3.07	3.06
tBr-DiKTA	1.35	-1.61	-6.15	-3.19	2.96
Mes₃-DiKTa	1.20	-1.85	-6.00	-2.95	3.05

Table S1. Electrochemical data of dBr-tBu-DiKTa, tBr-DiKTa and Mes<sub>3</sub>-DiKTa.<sup>a</sup>

<sup>*a.*</sup> In degassed DCM with 0.1 M [<sup>*n*</sup>Bu<sub>4</sub>N]PF<sub>6</sub> as the supporting electrolyte and Fc/Fc<sup>+</sup> as the internal reference (0.46 V vs. SCE)<sup>17</sup>. The HOMO and LUMO energies were determined using the relation HOMO/LUMO =  $-(E_{ox} / E_{red} + 4.8)$  eV, where  $E_{ox}$  and  $E_{red}$  are the peak of anodic and cathodic potentials from DPV relative to Fc/Fc<sup>+</sup>.  $\Delta E$  is the energy gap between HOMO and LUMO.



Figure **S15**. Absorption and PL solvatochromatism studies of a) **dBr-tBu-DiKTa** and b) **tBr-DiKTa**, using different solvents with 20  $\mu$ M concentration.  $\lambda_{exc}$ =330 nm.



Figure **S16**. Contour plots of normalised time-resolved spectra and decay of **Mes<sub>3</sub>-DiKTa** in zeonex 0.1 wt% film, degassed at a) 300 K and b) 80 K.



Figure **S17**. Time-resolved decay and spectra at different time ranges, for **Mes<sub>3</sub>-DiKTa** in a zeonex matrix at 0.1 wt% at a) 300 K and b) 80 K.



Figure **S18**. Contour plots of normalised time-resolved spectra and decay of **dBr-tBu-DiKTa** in zeonex 0.1 wt% film, degassed at a) 300 K and b) 80 K.



Figure **S19**. Time-resolved decay and spectra at different time ranges, for **dBr-tBu-DiKTa** in a zeonex matrix at 0.1 wt% at a) 300 K and b) 80 K.



Figure **S20**. Contour plots of normalised time-resolved spectra and decay of **tBr-DiKTa** in zeonex 0.1 wt% film, degassed at a) 300 K and b) 80 K.



Figure **S21**. Time-resolved decay and frames at different time ranges, for **tBr-DiKTa** in a zeonex matrix at 0.1 wt% at a) 300 K and b) 80 K.



Figure **S22**. Contour plots of normalised time-resolved spectra and decay of **Mes<sub>3</sub>-DiKTa** in mCP 1 wt%, degassed at a) 300 K and b) 80 K.



Figure **S23**. Time-resolved decay and spectra at different time ranges, for **Mes<sub>3</sub>-DiKTa** in a mCP matrix at 1 wt% at a) 300 K and b) 80 K.



Figure **S24**. Contour plots of normalised time-resolved spectra and decays of **dBr-tBu-DiKTa** in mCP 1 wt% film, degassed at a) 300 K and b) 80 K.



Figure **S25**. Contour plots of normalised time-resolved spectra and decay of **tBr-DiKTa** in mCP 1 wt% film, degassed at a) 300 K and b) 80 K.



Figure **S26**. PL spectra of different concentrations of **dBr-tBu-DiKTa** in zeonex host, at 300 K.  $\lambda_{exc}$  = 355 nm.



Figure **S27**. a) **dBr-tBu-DiKTa** 300 K in zeonex decays at different concentrations, b) time-resolved ns and early  $\mu$ s and c) late  $\mu$ s and ms regions spectra frames, in zeonex at 4 wt%.

Method 1 <sup>21</sup>	Φ <sub>DF</sub> /Φ <sub>PF</sub>	$\Phi_{\text{DF}}/\Phi_{\text{PF}}+\Phi_{\text{DF}}$	<b>k</b> <sub>f</sub> <b>/ s</b> <sup>-1</sup>	k <sub>isc</sub> ∕s⁻¹	k <sub>risc</sub> / s <sup>-1</sup>
tBr-DiKTa <sup>a</sup>	5.66×10 <sup>0</sup>	8.50×10 <sup>-1</sup>	3.86×10 <sup>8</sup>	3.28×10 <sup>8</sup>	8.82×10 <sup>3</sup>
dBr-tBu-DiKTa <sup>a</sup>	4.97×10 <sup>0</sup>	8.33×10 <sup>-1</sup>	2.48×10 <sup>8</sup>	2.06×10 <sup>8</sup>	7.02×10 <sup>3</sup>
Mes <sub>3</sub> -DiKTa <sup>a</sup>	$1.32 \times 10^{0}$	5.69×10 <sup>-1</sup>	1.47×10 <sup>8</sup>	8.37×10 <sup>7</sup>	2.54×10 <sup>3</sup>
tBr-DiKTa <sup>b</sup>	3.11×10 <sup>1</sup>	9.69×10 <sup>-1</sup>	3.34×10 <sup>8</sup>	3.24×10 <sup>8</sup>	3.87×10 <sup>5</sup>
dBr-tBu-DiKTa <sup>b</sup>	$8.94{\times}10^{0}$	8.99×10 <sup>-1</sup>	2.49×10 <sup>8</sup>	2.24×10 <sup>8</sup>	3.58×10 <sup>4</sup>
Mes <sub>3</sub> -DiKTa <sup>b</sup>	$1.38 \times 10^{0}$	5.80×10 <sup>-1</sup>	2.20×10 <sup>8</sup>	1.27×10 <sup>8</sup>	4.39×10 <sup>3</sup>

Table **S2**. Decay analysis using different methods.

Method 2 <sup>22</sup>	$\Phi_{PF}$	$\Phi_{\text{DE}}$	<b>k</b> <sub>f</sub> / s⁻¹	$k_{isc ave}/s^{-1}$	$k_{risc ave}/s^{-1}$	k <sub>r singlet</sub> / S <sup>-1</sup>	k <sub>nr singlet</sub> max/S <sup>-1</sup>	k <sub>nr triplet</sub> max/S <sup>-1</sup>	Φ <sub>PL</sub> N2
tBr-DiKTa <sup>a</sup>	5.98×10 <sup>-2</sup>	1.69×10 <sup>-1</sup>	3.86×10 <sup>8</sup>	2.26×10 <sup>8</sup> ± 3.89×10 <sup>7</sup>	$4.53 \times 10^3 \pm 5.43 \times 10^2$	2.31×107	7.78×10 <sup>7</sup>	1.09×10 <sup>3</sup>	0.229
dBr-tBu- DiKTaª	7.43×10 <sup>-2</sup>	1.85×10-1	2.48×10 <sup>8</sup>	1.48×10 <sup>8</sup> ± 2.63×10 <sup>7</sup>	$3.63 \times 10^3 \pm 4.70 \times 10^2$	1.84×10 <sup>7</sup>	5.26×107	9.40×10 <sup>2</sup>	0.259
Mes₃-DiKTa <sup>a</sup>	3.17×10 <sup>-1</sup>	2.09×10 <sup>-1</sup>	1.47×10 <sup>8</sup>	$8.22 \times 10^8 \pm 2.10 \times 10^7$	$1.44 \times 10^3 \pm 3.80 \times 10^2$	4.67×10 <sup>7</sup>	4.21×10 <sup>7</sup>	7.61×10 <sup>2</sup>	0.526
tBr-DiKTa <sup>♭</sup>	3.68×10 <sup>-2</sup>	5.71×10 <sup>-1</sup>	3.34×10 <sup>8</sup>	$3.53 \times 10^8 \pm 4.06 \times 10^6$	$1.97 \times 10^5 \pm 2.45 \times 10^3$	1.23×107	7.93×10 <sup>6</sup>	4.90×10 <sup>3</sup>	0.608
dBr-tBu- DiKTa <sup>b</sup>	1.50×10 <sup>-1</sup>	6.70×10 <sup>-1</sup>	2.49×10 <sup>8</sup>	$2.76 \times 10^8 \pm 4.11 \times 10^6$	$1.93 \times 10^4 \pm 3.82 \times 10^2$	3.74×10 <sup>7</sup>	8.21×10 <sup>6</sup>	7.64×10 <sup>2</sup>	0.82
Mes <sub>3</sub> -DiKTa <sup>b</sup>	5.33×10 <sup>-1</sup>	3.67×10 <sup>-1</sup>	2.20×10 <sup>8</sup>	$1.37 \times 10^8 \pm 6.51 \times 10^5$	$2.92 \times 10^3 \pm 2.23 \times 10^1$	1.17×10 <sup>8</sup>	1.30×107	3.95×10 <sup>2</sup>	0.90

<sup>a</sup> In zeonex. <sup>b</sup> In mCP.



Figure **S28**. JVL results. a) EL spectra, b) JVL curves, c) EQE vs luminance of **dBr-tBu-DiKTa** at 3.5 wt% (blue) and 1 wt% (red) in mCP host. d) EQE vs current density and e) normalized EQE vs current density above 4mAcm<sup>-2</sup> to highlight the efficiency roll-off at this region of **dBr-tBu-DiKTa** at 3.5 wt% (blue), 1 wt% (red) and **Mes<sub>3</sub>-DiKTa** 3.5 wt% (green) in mCP host.

Emitter in n	nCP host	V <sub>on</sub> / V	Lum <sub>max</sub> / cdm <sup>-2</sup>	EQE <sub>max</sub> / %	EQE <sub>10</sub> / %	EQE <sub>100</sub> /%	EQE <sub>1000</sub> / %	FWHM / nm	λ <sub>ει</sub> / nm	CIE / (x,y)
dBr-tBu-	1 wt%	3.7	6810	17.9	15.5	5.7	1.1	52	474	(0.15, 0.25)
DiKTa	3.5 wt%	3	2441	21.2	15.8	11.4	1.95	54	480	(0.16, 0.35)
Mes₃-DiKTa	3.5 wt%	3.1	1917	21.6	17.5	10.2	3.2	36	479	(0.13, 0.29)

Table S3. Device metrics for dBr-tBu-DiKTa and Mes<sub>3</sub>-DiKTa OLEDs.

#### **Other examples of HAE-TADF**

Xu *et al.* designed a series of chlorine-substituted molecules **3-CCP-BP-PXZ**, **9-CCP-BP-PXZ** and **3,9-CCP-BP-PXZ** in 2019.<sup>23</sup> The chlorine-carbon bond is stronger than bromine-carbon and iodine-carbon bonds, which ensures relatively higher chemical stability. Besides, the external HAE could be greatly amplified in the aggregated state due to more surrounding heavy atoms. The neat films showed shorter  $\tau_d$  of 0.70, 0.68, 0.42 µs and faster  $k_{RISC}$  of  $1.73 \times 10^6$ ,  $1.97 \times 10^6$ ,  $3.10 \times 10^6$  s<sup>-1</sup>, respectively for **3-CCP-BP-PXZ**, **9-CCP-BP-PXZ** and **3,9-CCP-BP-PXZ**, than the chlorine-free **CP-BPPXZ** (2.1 µs and  $0.63 \times 10^6$  s<sup>-1</sup>). The non-doped OLED with **3,9-CCP-BP-PXZ** exhibited an EQE<sub>max</sub> of 20.6%, with a negligible efficiency roll-off of 4.4% at 1000 cd m<sup>-2</sup>. Liu *et al.* coupled fluorine, chlorine and bromine substituted benzophenone with DMAC and obtained **BD-F**, **BD-CI** and **BD-Br**.<sup>24</sup> **BD-CI** and **BD-Br** exhibited faster  $k_{RISC}$  of  $2.23 \times 10^5$  and  $2.67 \times 10^5$  s<sup>-1</sup> than **BD-H** ( $1.63 \times 10^5$  s<sup>-1</sup>), which was ascribed to the enhanced SOC interaction in the presence of heavy atoms. The fastest  $k_{RISC}$  of  $6.20 \times 10^5$  s<sup>-1</sup> for **BD-F** was attributed to multiple conversion channels for triplet excitons. OLED using **BD-CI** as emitter showed an EQE<sub>max</sub> of 23.7% and 20.2% at 1000 cd m<sup>-2</sup>. A lower EQE for **BD-Br** (11.2% EQE<sub>max</sub>) could be blamed on its low thermal stability (thermal decomposition temperature ~200 °C).



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Heavier chalcogen atoms (sulfur and selenium) are commonly substituted for oxygen to enhance SOC. In 2019, de Sa Pereira *et al.* investigated the photophysical characterisation of sulfur and selenium substituted **PTZ-TRZ** and **PSeZTRZ**.<sup>25</sup> They found that substitution from sulfur to selenium on the donors could lead to an enhancement in the phosphorescence radiative decay with little effect on  $k_{RISC}$ . The heavy atom did not affect the TADF performance of **PSeZTRZ**. Schott *et al.* studied a series of sulfur- and selenium-containing fused-ring molecules with central thiophene or selenophene moieties and determined that the position of heavy atom within a molecule was important for tuning the strength of SOC.<sup>26</sup> Drummond *et al.* reported new DF emitter **SeXO<sub>1</sub>-TPA** by substituting Se for S in **TXO<sub>1</sub>-TPA**.<sup>27</sup> The substitution enhanced SOC between singlet ( $S_1$ ) and triplet ( $T_1$  or  $T_2$ ) excited states. Based on this, **SeXO<sub>1</sub>-TPA** showed  $k_{ISC}$  of 1.18×10<sup>10</sup> s<sup>-1</sup> and  $k_{RISC}$  of 2.8×10<sup>5</sup> s<sup>-1</sup>, more than 250 times and 22 times, respectively, faster than those of **TXO<sub>1</sub>-TPA**. Han *et al*. designed two twisted D–A–D type emitters **CzSe** and **TMCzSe** both containing selenium.<sup>28</sup> Through improving the twist angles between donors and acceptor by using tetramethyl-9H-carbazole moieties, TMCzSe realized mixed RTP and TADF emission and exhibited a  $\tau_d$  of 26.71  $\mu$ s. OLEDs using **TMCzSe** as the emitter showed a high EQE<sub>max</sub> of 25.5% and 12.5% efficiency roll-off up to 1000 cd m<sup>-2</sup>. Ren et al. reported a S-containing TADF emitter **MCz-TXO**, which exhibited a very fast  $k_{RISC}$  of  $1.2 \times 10^8$  s<sup>-1</sup> when compared with the Ocontaining emitter MCz-XT (~10<sup>4</sup> s<sup>-1</sup>).<sup>29</sup> They also designed CC-TXO-I that contains a bicarbazole donor, which showed  $k_{RISC}$  of 2.1×10<sup>7</sup> s<sup>-1</sup> in 6 wt% doped films in PPF and where the device showed an EQE<sub>max</sub> of 19.0% and showed an efficiency roll-off of 45.8% at 1000 cd m<sup>-2.30</sup> Recently, they further investigated in silico the effect of changing the chalcogenide on the RISC rates by DFT calculations.<sup>31</sup> A much faster  $k_{R/SC}$  of >10<sup>10</sup> s<sup>-1</sup> was predicted for selenium- and tellurium-containing TADF molecules, MCz-SeXO, MCz-TeXO. However, due to the strong HAE, polonium-containing molecule MCz-PoXO would only show phosphorescence instead of TADF. Zhang *et al.* designed two through-space charge transfer (TSCT) emitters **DPTZ-QX** and **DPTZ-DFQX**.<sup>32</sup> These compounds have  $\Phi_{PL}$  of 49 and 61% in 5 wt% doped films in mCP. Despite the higher calculated SOCME values of 0.38 and 0.40 cm<sup>-1</sup> between the S<sub>1</sub> and T<sub>1</sub> states, **DPTZ-QX** and **DPTZ-DFQX** exhibited long  $\tau_d$  of 255 and 144.3 µs and slow  $k_{RISC}$  of 2.31 and 2.65 ×10<sup>4</sup> s<sup>-1</sup>, respectively, which is caused by the large  $\Delta E_{ST}$  of 0.14 and 0.15 eV. Wang *et al.* designed DMAC-DPS-DOPTZ and PXZ-DPS-DOPTZ with diphenyl sulfone and phenothiazine dioxides as the acceptor, respectively.<sup>33</sup> Both emitters showed large  $k_{RISC}$  of up to 10<sup>6</sup> s<sup>-1</sup> with  $\Delta E_{ST}$  of 0.1 and 0.03 eV in 10 wt% doped films in mCBP. Both devices gave 11.3% EQE<sub>max</sub> and the device with PXZ-DPS-**DOPTZ** gave lower efficiency roll-off of 13.7% at 1000 cd m<sup>-2</sup>.



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A TADF polymer **Pac-BSS** containing **BSS** and acridan as host was used as an emitter in a solutionprocessed OLED, which exhibited blue emission at 458 nm with small FWHM of 31 nm and an EQE<sub>max</sub> of 13.1%.<sup>34</sup> Park *et al.* demonstrated a Se-doped emitter **CzBSe**, which emits at 479 nm and has a  $\Phi_{PL}$ of 98% in 1 wt % doped films in mCBP.<sup>35</sup> Larger calculated SOCME values of 0.87 cm<sup>-1</sup> (0.02 cm<sup>-1</sup> for **CzBO** and 0.07 cm<sup>-1</sup> for **CzBS**) between S<sub>1</sub> and T<sub>1</sub> states explains why **CzBSe** has a shorter  $\tau_d$  of 14 µs and faster  $k_{RISC}$  of 1.8×10<sup>8</sup> s<sup>-1</sup>. The OLED with **CzBSe** showed a high EQE<sub>max</sub> of 30.1% and low efficiency roll-off of 13% at 1000 cd m<sup>-2</sup>. Li *et al.* also reported similar structures **Cz-BSeN** and **DCz-BSeN**.<sup>36</sup> The  $k_{RISC}$  of these two compounds is 7.5 and 8.8×10<sup>8</sup> s<sup>-1</sup> in 1 wt% doped film in polystyrene and the OLEDs with **Cz-BSeN** and **DCz-BSeN** showed EQE<sub>max</sub> of 20.3 and 22.3%, with efficiency roll-off of 32.5 and 30% at 500 cd m<sup>-2</sup>. This group also combined second- and third-generation carbazole donor dendrons with a selenium-containing polycyclic aromatic hydrocarbon emitter in **BSeN-DCz** and **BSeN-TCz**.<sup>37</sup> These two compounds have high  $k_{RISC}$  of 9×10<sup>6</sup> s<sup>-1</sup> in 1 wt% doped film in polystyrene. Intermolecular aggregation is effectively suppressed due to the large steric hindrance, which explains the narrow emission at 472 nm (FWHM of 32 nm) of **BSeN-TCz** as a neat film. OLEDs with 20 wt% **BSeN-TCZ** showed an EQE<sub>max</sub> of 19.7%. Cao *et al.* then extended the  $\pi$ -system of the MR-TADF skeleton in **BN–Se** to improve oscillator strength.<sup>38</sup> The toluene solution showed a  $\Phi_{PL}$  of 99 % at 502 nm, small  $\Delta E_{ST}$  of 0.08 eV and fast  $k_{RISC}$  of 1.6×10<sup>6</sup> s<sup>-1</sup>. The OLED showed an EQE<sub>max</sub> of 32.6% with an ultralow efficiency roll-off of 1.3% at 1000 cd m<sup>-2</sup>. Li *et al.* designed **BTC-BNCz** by incorporating a sulfur atom-fused donor unit.<sup>39</sup> This compound has a high  $\Phi_{PL}$  of 95 % at 488 nm, and a  $\Delta E_{ST}$  of 0.11 eV in toluene. The  $k_{RISC}$  was calculated to be 1.6×10<sup>5</sup> s<sup>-1</sup> in 3% doped film in PhCzBCz. The OLED with**BTC-BNCz** showed an EQE<sub>max</sub> of 27% and an efficiency roll-off of 20% at 100 cd m<sup>-2</sup>.

Hua et al. designed new MR-TADF emitters **2PXZBN** and **2PTZBN**.<sup>40</sup> Due to the HAE, **2PTZBN** containing S atom exhibited larger SOCME of 1.524 cm<sup>-1</sup> between  $S_1$  and  $T_2$  states, shorter DF lifetime of 5.0  $\mu$ s and faster  $k_{RISC}$  of 2.76×10<sup>5</sup> s<sup>-1</sup> over **2PXZBN** with O atom. The OLED employing **2PTZBN** as the emitter exhibited an improved EQE<sub>max</sub> of 25.5% compared to 17.7% for the device with **2PXZBN**. In addition, the efficiency roll-off was significantly reduced from 58% for 2PXZBN to 33% for 2PTZBN at 1000 cd m<sup>-2</sup>. The same group replaced the sulfur atom with selenium in **BNSSe** and **BNSeSe**.<sup>41</sup> The  $k_{RISC}$  was significantly improved to  $6.0 \times 10^5$  and  $2.0 \times 10^6$  s<sup>-1</sup>. The OLEDs with **BNSSe** and **BNSeSe** showed much higher EQE<sub>max</sub> of 35.7 and 36.8% and lower efficiency roll-off of only 10 and 7.6% at 1000 cd m<sup>-2</sup> when compared to the devices with 2PXZBN and 2PTZBN. In 2022, Pratik et al. did a computational investigation on the impact of replacing oxygen atoms with sulfur or selenium on three series of MR-TADF compounds, 1-X, 2-X and 3-X<sup>42</sup> and 1c-X, 1d-X, 1e-X and 1f-X<sup>43</sup>. Most of the Se-based molecules exhibited stronger SOC and faster  $k_{ISC}$  and  $k_{RISC}$  than the ones containing O and S. Large differences of SOC and  $k_{RISC}$  between different series indicated that the positions of chalcogen atoms would have a crucial impact on the properties of molecules. Li et al. introduced a S atom at the para position to the B-atom in the MR-TADF emitter (BN-Cz) and produced BN(p)SCH<sub>3</sub>, BN(p)SOCH<sub>3</sub> and BN(p)SO<sub>2</sub>CH<sub>3</sub>.<sup>44</sup> BN(p)SCH<sub>3</sub>, which differed only in the oxidation state of the sulfur, showed the bluest emission at 479 nm and the smallest  $\Delta E_{ST}$  of 0.12 eV and fastest  $k_{RISC}$  of 6.4×10<sup>4</sup> s<sup>-1</sup>. OLED with **BN(p)SCH<sub>3</sub>** showed an EQE<sub>max</sub> of 26.3% and an efficiency roll-off of 54.4% at 1000 cd m<sup>-2</sup>. Huang *et al.* decorated S-containing chains onto the same MR-TADF framework in **TCzBN-S** and **TCzBN-SO**.<sup>45</sup> Both emitters have the same

 $\Delta E_{ST}$  of 0.14 eV and the same  $\Phi_{PL}$  of 98%. **TCzBN-S** has a faster  $k_{RISC}$  of  $1.4 \times 10^5$  s<sup>-1</sup> comparted to **TCzBN-SO** (5.6×10<sup>4</sup> s<sup>-1</sup>), which contributed to the improved device performance, where the efficiency roll-off was 44% at 1000 cd m<sup>-2</sup> (EQE<sub>max</sub> of 30%). Similarly, Hu *et al.* introduced selenoxanthone at the *para* position to the B-atom in BN-Cz in **BN-STO**.<sup>46</sup> This compound showed strong SOCME of 1.61 cm<sup>-1</sup> between S<sub>1</sub> and T<sub>1</sub> states. The 5 wt% doped film in DMIC-TRZ has a small  $\Delta E_{ST}$  of 0.13 eV, high  $\Phi_{PL}$  of 96% and fast  $k_{RISC}$  of 1.2×10<sup>5</sup> s<sup>-1</sup>. The OLED showed green emission at 517 nm with FWHM of 34 nm, excellent EQE<sub>max</sub> of 40.1% and an efficiency roll-off of 30% at 1000 cd m<sup>-2</sup>.



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