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Effect of the Number and Substitution Pattern of Carbazole Donors on the Singlet and Triplet State Energies in a Series of Carbazole-Oxadiazole Derivatives Exhibiting Thermally Activated Delayed Fluorescence

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Supporting Information

ABSTRACT: Substitution of a varying number of 9H-carbazole donors onto 2-(pentafluorophenyl)-5-phenyl-1,3,4-oxadiazole yields a series of donor-acceptor compounds with similar electrochemical band gaps, but dissimilar optical properties. Each substitution of a carbazole onto the 2- and 4-positions results in a 150-200 meV stabilization of the first singlet excited state, evident in the fluorescent emission. The first triplet excited state is less sensitive to these substitutions, leading to a reduced energy separation between the singlet and triplet states, ΔE_{ST} , with increasing carbazole content. OLED devices made using the donoracceptor compounds exhibiting the lowest $\Delta E_{\rm ST}$ were fabricated and exhibit sky blue emission with an external quantum efficiency of up to 24.4% at a luminance of 10 cd m⁻², and 9.2% at 1000 cd m⁻².



INTRODUCTION

Organic light-emitting diodes (OLEDs) have received significant attention, both academically and in industry, since the pioneering work of Tang and VanSlyke.¹ Due to spin statistics, devices made using conventional fluorescent emitters are limited to roughly 25% internal quantum efficiency (IQE) owing to the formation of ca. 75% of triplet excitons upon charge recombination in the device.² In emitters that exhibit thermally activated delayed fluorescence (TADF), however, the energy difference the lowest energy singlet excited state (S_1) and the lowest energy triplet state (T_1) , ΔE_{ST} , is sufficiently low for a significant fraction of the triplets to be thermally upconverted to singlets through reverse intersystem crossing (RISC) before they decay to the ground state (S_0) ; this can then be followed, in some cases, by efficient fluorescent emission from the S₁ state.^{3,4} The approach most often used to minimize $\Delta E_{\rm ST}$, and to increase RISC rates, is predicated on the assumption that the S₁ state for donoracceptor molecules can be well-described as a transition between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Increasing the charge-transfer (CT) character of S₁ by increasing spatial separation of the HOMO and LUMO through increasing localization of these orbitals on donor and an acceptor moiety,

respectively, will decrease $\Delta E_{\rm ST}$.⁵ There is, however, a trade-off with retaining efficient fluorescence, since the radiative transition probability will also decrease with increasing HOMO-LUMO spatial separation. By utilizing TADF emitters, OLEDs approaching 100% IQE and over 20% external quantum efficiency (EQE) have been realized.⁶⁻⁸

2,5-Diphenyl-1,4,5-oxadiazole (DPO), which is well-known for its electron transport properties, as well as high thermal stability and photoluminescence quantum yield, and its derivatives have been widely used as electron-transport materials in OLEDs.⁹⁻¹⁴ The relatively high electron affinity of this moiety has been utilized by incorporating DPO as the acceptor into bipolar donor-acceptor (D-A) hosts for phosphorescent emitters in OLED devices,¹⁵⁻¹⁷ including both molecular compounds and polymers in which it is combined with the ubiquitous 9-carbazolyl (Cz) donor.^{15,16,18-20} Furthermore, CzDPO D-A compounds have themselves been exploited as tunable emitters in conventional fluorescent OLEDs.^{21–25} Use of DPO as the acceptor in TADF emitters, however, has been limited. To date, DPO has been

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paired with relatively strong electron donors phenoxazine^{26,27} and 5-phenyl-5,10-dihydrophenazine,²⁸ resulting in devices with emission in the blue-green to green range and EQE_{max} values of under 15%. Despite the common use of Cz as a donor in TADF applications,²⁹ examples of CzDPO emitters that exhibit TADF have only very recently been demonstrated.³⁰

The effect of an increasing number of donor substituents on the photophysics of the resulting fluorophore has been observed experimentally as a method for decreasing the HOMO-LUMO gap, the S₁ energy, and ΔE_{ST} .³¹ Several recent computational studies have focused on elucidating the mechanism for the purpose of developing advanced design rules for TADF compounds. It has been calculated that a model series of Cz-phthalonitrile-based TADF molecules show a monotonic decrease in both S1- and T1-state energy with increased number of Cz donors,³² with a larger decrease for the S_1 energy, leading to a parallel monotonic decrease in $\Delta E_{\rm ST}$. The effect on the CT-like S₁ state has been explained through stabilization of the acceptor LUMO via inductive electron withdrawal from the acceptor by the Cz substituents, with each additional carbazole increasing this effect.³³⁻³⁵ The smaller effect on the T_1 -state energy, conversely, is due to the T_1 state, at least for the less substituted compounds, being well described by a localized excitation (LE) rather than an intramolecular CT HOMO-LUMO transition.^{32,36} Additionally, for efficient RISC, not only low ΔE_{ST} but also high spinorbit coupling between the triplet and singlet manifolds is desirable,^{37,38°} and it has also been shown that increased substitution by donors can increase spin-orbit coupling when the S₁ and T₁ states differ in character, whether they are CT vs LE states, respectively, or have different CT character from one another.^{36,39}

The specific topology of the D-A TADF compound has only very recently come under systematic investigation. Kim described calculations on Cz-phthalonitrile TADF compounds, suggesting that attachment of the donor at chemically inequivalent positions significantly affects not the LUMO of the acceptor, but the nature and energy of the donor HOMO instead. The effect on the triplet state was, again, less pronounced and exhibited diminishing significance as the number of donors increased and the additive inductive effects began to dominate over mesomeric effects.⁴⁰ Geng et al. found very little change in the energy of the S1 state by varying the connectivity in xanthone-phenylene-carbazole compounds, but were able to raise the T1 energy by moving from para- to metato ortho-substitution patterns.41 To contribute to the understanding of the role of topology and substitution in the design of TADF molecules, we have synthesized a series of $Cz_nF_{(5-n)}DPO$ compounds in which the effect of the number of Cz groups on the acceptor has been partially decoupled from the inductive stabilization of the LUMO on the acceptor. This allows us to examine the mesomeric effects on the S₁ and T₁ states more directly. OLEDs made utilizing the CzDPO compounds as the emitter yielded EQE_{max} values ranging from 6% to over 24%, and include the most efficient OLEDs containing DPO-based emitters reported to date.

EXPERIMENTAL SECTION

All reagents were purchased from commercial sources and were used without further purification. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded using a Bruker Avance IIIHD 500 instrument operating at 500, 125, and 470.4 MHz, respectively, or on a Varian Mercury Vx 400 operating at 400, 100, and 376.5 MHz, respectively. Chemical

shifts are listed in parts per million (ppm) and were referenced using the residual nondeuterated solvent $^{1}\mathrm{H}$ signal or the solvent $^{13}\mathrm{C}$ resonance, or using an internal standard (trifluoroacetic acid, -76.55 ppm) for ¹⁹F NMR. Column chromatography was carried out using silica gel (60 Å, 40-63 μ m, Sorbent) as the stationary phase. Mass spectra were measured on an Applied Biosystems 4700 Proteomics Analyzer using MALDI or a VG Instruments 70-SE using electron impact (EI) mode. UV-vis spectra were measured using a Cary 5000 UV-vis-NIR spectrophotometer. Fluorescence, phosphorescence, and emission transients were collected on a Jobin Yvon Fluorolog-3 equipped with a pulsed xenon lamp, photomultiplier tube (Horiba R928), and pulsed LED excitation source (NanoLED). Fluorescent lifetimes were fit using DAS6 decay analysis software. Solution and solid-state absolute photoluminescence quantum yields were determined on a Quantaurus-QY C11347 spectrometer. Electrochemical data were acquired using cyclic voltammetry in 0.1 M $^{n}Bu_{4}N^{+}PF_{6}^{-}$ in dry tetrahydrofuran (for reductive scans) or dichloromethane (oxidative scans) under nitrogen, using a CH Instruments 620D potentiostat, a glassy carbon working electrode, a platinum wire auxiliary electrode, and, as a pseudo-reference electrode, a silver wire anodized in 1 M aqueous potassium chloride solution. The scan rate was 50 mV s⁻¹, and ferrocene was added as an internal reference. Thermogravimetric analysis was carried out using a PerkinElmer Pyris 1 TGA with a heating rate of 10 $^{\circ}$ C min⁻¹.

Computational Methodology. The molecular geometries in the ground (S_0) state were optimized using the B3LYP⁴² functional and the 6-31G(d,p) basis set using the Gaussian 09 program.⁴³ Excited-state geometries and energies were derived by time-dependent density functional theory (TD-DFT) at the MPW1B95/6-31G(d,p)⁴⁴ level of theory. Electronic properties were calculated by TD-DFT.

2-(Pentafluorophenyl)-5-phenyl-1,3,4-oxadiazole (2a). To a solution of benzohydrazide (5.9 g, 43 mmol) in dry THF (100 mL) was slowly added 2,3,4,5,6-pentafluorobenzoyl chloride (10 g, 43 mmol) at room temperature under nitrogen. During addition a white solid appeared. After the addition was complete, the reaction was warmed to room temperature. The reaction mixture was stirred for 18 h at room temperature. Pyridine (10 mL) was then added, the mixture was stirred for an additional 1 h, and water (500 mL) was added. The white solid was collected by filtration and dried under vacuum. The product (N'-benzoyl-2,3,4,5,6-pentafluorobenzohydrazide) was obtained as a white powder (14 g) and was used for the next step without any future purification.

N'-Benzoyl-2,3,4,5,6-pentafluorobenzohydrazide (14.0 g, 42.4 mmol) from the previous step was suspended in POCl₃ (50 mL), and the reaction was stirred in an oil bath at 120 °C. During heating, the white solid starting materials dissolved, and a solution was obtained. The reaction was monitored by thin-layer chromatography (dichloromethane as eluent). After 4 h, the reaction mixture was brought to room temperature and was carefully dropped into ice water (700 mL). A white solid precipitated, which was collected by filtration, and was washed with water. After drying, the crude product was purified by column chromatography, eluting with 5% ethyl acetate in dichloromethane. After evaporating solvents, the white solid was recrystallized from acetone/water. The white solid was filtered and then dried under vacuum (11.5 g, 87%, two steps).

¹H NMR (400 MHz, CDCl₃): δ 8.14 (dt, *J* = 8, 1.6 Hz, 2H), 7.63– 7.54 (m, 3H). ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃COOH): δ –135.38 (m, 2F), –147.14 (m, 1F), –159.46 (m, 2F). The NMR data are similar to those previously reported for the same compound synthesized by oxidative coupling of 2-phenyl-1,3,4-oxadiazole and pentafluorobenzene.⁴⁵

2-(4-(tert-Butyl)phenyl)-5-(pentafluorophenyl)-1,3,4-oxadiazole (2b). To a solution of 4-(*tert*-butyl)benzohydrazide (5.0 g, 26 mmol) in dry THF (100 mL) was slowly added 2,3,4,5,6pentafluorobenzoyl chloride (6.0 g, 26 mmol) at room temperature under nitrogen, during which a white solid appeared. After the addition was complete, the reaction mixture was stirred at room temperature for 2 h. Pyridine (8.0 mL) was added and stirred for additional 1 h. Water (500 mL) was added to the reaction mixture, and a brown solid was collected by filtration and dried under vacuum. The product (N'-(4-(tert-butyl)benzoyl)-2,3,4,5,6-pentafluorobenzohydrazide) was obtained as a brown powder (9.8 g) and was used for the next step without any further purification.

N'-(4-(*tert*-Butyl)benzoyl)-2,3,4,5,6-pentafluorobenzohydrazide (9.0 g, 27 mmol) was suspended in POCl₃ (50 mL). The reaction was stirred at 100 °C (oil bath). During heating, the white solid starting materials dissolved and a clear solution was obtained. The reaction was monitored by thin-layer chromatography (dichloromethane as eluting solution). After 6 h, the reaction mixture was brought to room temperature and was carefully dropped into ice water (700 mL). A white solid precipitated, which was collected by filtration and washed with water. After drying, the crude product was purified by column chromatography, eluting with dichloromethane. After evaporating solvents, the product was recrystallized from acetone/water; a white solid was collected by filtration and dried under vacuum (8.5 g, 84%, two steps).

¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, J = 8 Hz, 2H), 7.57 (d, J = 8 Hz, 2H), 1.37 (s, 9H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 165.83, 156.22 154.40 (m), 145.17 (dm, ¹ $J_{CF} = 256$ Hz), 143.21 (dtt, ¹ $J_{CF} = 259$ Hz, $J_{CF} = 13$, 5 Hz), 138.13 (dm, ¹ $J_{CF} = 252$ Hz), 127.08, 126.22, 101.00 (td, $J_{CF} = 15$, 5 Hz), 35.16, 31.05. ¹⁹F NMR (376.5 MHz, CDCl₃, CF₃COOH): δ –135.45 (m, 2F), –147.04 (m, 1F), –159.56 (m, 2F). HRMS (EI, m/z): Calcd for C₁₈H₁₃N₂OF₅ (M⁺), 368.0948; Found, 368.0944.

2-(4-(9H-Carbazol-9-yl)-2,3,5,6-tetrafluorophenyl)-5-phenyl-1,3,4-oxadiazole (CzDPO). In a round-bottom flask, 2-(pentafluorophenyl)-5-phenyl-1,3,4-oxadiazole (1.03 g, 3.30 mmol), carbazole (0.570 g, 3.41 mmol), and potassium carbonate (4.42 g, 32.0 mmol) were placed under vacuum and then under nitrogen. DMSO (20 mL) was added and the reaction mixture was stirred overnight at room temperature. The reaction progress was monitored via thin-layer chromatography. Upon completion, the mixture was precipitated with water and the crude product was collected via filtration. Column chromatography (9:1 ethyl acetate/hexanes as eluent) yielded the higher R_f fluorescent product as a white powder (0.819 g, 54%). ¹H NMR (500 MHz, CDCl₃): δ 8.21 (d, J = 6.5 Hz, 2H), 8.16 (d, J = 7.5 Hz, 2H), 7.63–7.57 (m, 3H), 7.50 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 8 Hz, 2H), 7.22 (d, J = 8 Hz, 2H). ¹³C{¹H} (125 MHz, CDCl₃): δ 165.84, 155.16, 145.33 (ddt, ${}^{1}J_{CF}$ = 260 Hz, J_{CF} = 14 Hz, J_{CF} = 4 Hz), 144.14 (ddt, ${}^{1}J_{CF}$ = 255 Hz, J_{CF} = 14 Hz, J_{CF} = 4 Hz), 139.40, 132.50, 129.27, 127.30, 126.66, 124.35, 123.01, 121.65, 120.61, 119.83 (t, J_{CF} = 14 Hz), 109.94, 104.51 (t, J_{CF} = 14 Hz). ¹⁹F NMR (470 MHz, $CDCl_3$): δ -134.94 (m, 2F), -140.38 (m, 2F). HRMS (EI, m/z): Calcd for C₂₆H₁₃N₃OF₄ (M⁺), 459.0995; Found, 459.0995

2-(2,4-Di(9H-carbazol-9-yl)-3,5,6-trifluorophenyl)-5-phenyl-1,3,4-oxadiazole (2,4CzDPO). In a round-bottom flask, 2-(pentafluorophenyl)-5-phenyl-1,3,4-oxadiazole (0.482 g, 1.54 mmol), carbazole (0.408 g, 2.44 mmol), and potassium carbonate (3.5 g, 25 mmol) were placed under vacuum and then under nitrogen. DMSO (10 mL) was added and the reaction mixture was stirred overnight at room temperature. Upon completion, the mixture was precipitated with water and the crude product was separated via filtration. Column chromatography (10% ethyl acetate in hexanes as eluent) yielded the product as a white powder (0.177 g, 19%). $^1\mathrm{H}$ NMR (500 MHz, $CDCl_3$: δ 8.16 (d, J = 5 Hz, 2H), 8.06 (d, J = 10 Hz, 2H), 7.52 (t, J =10 Hz, 2H), 7.44-7.38 (m, 5H), 7.31-7.28 (m, 4H), 7.25 (t, J = 10 Hz, 2H), 7.20 (d, J = 10 Hz, 2H), 7.13 (d, J = 10 Hz, 2H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 165.09, 155.69, 152.77 (d, ${}^{1}J_{CF}$ = 259 Hz), 147.97 (dd, ${}^{1}J_{CF}$ = 262 Hz, J_{CF} = 16 Hz), 146.93 (dd, ${}^{1}J_{CF}$ = 265 Hz, $J_{CF} = 16$ Hz) 140.83, 139.46, 131.99, 128.71, 126.76, 126.75, 126.69, 124.38, 123.95, 122.30, 121.64, 121.35, 121.14, 120.66, 120.58, 119.84 (t, $J_{\rm CF}$ = 15 Hz), 114.47 (d, $J_{\rm CF}$ = 11 Hz), 114.42, 109.93, 109.07. $^{19}{\rm F}$ NMR (470 MHz, CDCl₃): δ –120.34 (d, J = 14 Hz, 1F), -131.78 (d, J = 24 Hz, 1F), -131.89 (dd, J = 24 Hz, 14 Hz, 1F). HRMS (ESI, m/z): Calcd for $C_{38}H_{22}N_4OF_3$ (M⁺), 607.174; Found, 607.1723.

2-Phenyl-5-(2,4,6-tri(9H-carbazol-9-yl)-3,5-difluorophenyl)-1,3,4-oxadiazole (2,4,6CzDPO) and 2-Phenyl-5-(2,4,5-tri(9Hcarbazol-9-yl)-3,6-difluorophenyl)-1,3,4-oxadiazole (2,4, 5CzDPO). To a round-bottom flask were added 2-(pentafluorophenyl)-5-phenyl-1,3,4-oxadiazole (0.50 g, 1.60 mmol), carbazole (0.803 g, 4.80 mmol), and potassium carbonate (2.20 g, 16.0 mmol). The flask was evacuated and purged with nitrogen and DMSO (20 mL) was added. The reaction mixture was stirred overnight at room temperature. Upon completion, the reaction mixture was precipitated with water and the crude product was separated via filtration. Column chromatography (silica gel, 10% hexanes/dichloromethane as eluent) was performed to yield the higher R_f product 2-phenyl-5-(2,4,6-tri(9H-carbazol-9-yl)-3,5-difluorophenyl)-1,3,4-oxadiazole as a yellow powder, and the lower R_f product 2-phenyl-5-(2,4,5-tri(9H-carbazol-9-yl)-3,6-difluorophenyl)-1,3,4-oxadiazole as a white crystalline powder.

2,4,6CzDPO. Yield: 0.226 g (19%). ¹H NMR (500 MHz, CDCl₃): δ 8.19 (d, J = 4 Hz, 2H), 8.11 (d, J = 8 Hz, 4H), 7.58 (t, J = 8 Hz, 2H), 7.51 (t, J = 8 Hz, 4H), 7.46–7.37 (m, 8H), 7.33 (t, J = 8 Hz, 4H), 7.17 (t, J = 8 Hz, 2H), 6.89 (d, J = 8 Hz, 2H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 164.59, 156.65 (t, $J_{CF} = 2.5$ Hz), 156.41 (dd, ¹ $J_{CF} = 268$ Hz, $J_{CF} = 5$ Hz), 140.90, 139.49, 131.64, 128.46, 126.67, 126.62, 126.54, 126.35, 124.39, 124.04, 123.66 (dd, $J_{CF} = 14$ Hz, $J_{CF} = 5$ Hz), 122.18, 121.60, 120.69, 119.84 (t, $J_{CF} = 15$ Hz), 109.89, 108.96. ¹⁹F NMR (470 MHz, CDCl₃): δ –113.00 (s). HRMS (MALDI, m/z): Calcd for C₅₀H₂₉N₅OF₂ (M⁺), 754.2413; Found, 754.2410. Anal. Calcd for C₅₀H₂₉N₅OF₂: C, 79.67; H, 3.88; N, 9.29. Found: C, 79.75; H, 3.73; N, 9.45.

2,4,5CzDPO. Yield: 0.273 g (23%). ¹H NMR (500 MHz, CDCl₃): δ 8.12 (d, J = 4 Hz, 2H), 7.80–7.78 (m, 2H), 7.76–7.74)m, 2H), 7.52 (t, J = 8 Hz, 2H), 7.44 (d, J = 8 Hz, 2H), 7.41 (d, J = 8 Hz, 1H), 7.35 (t, J = 8 Hz, 2H), 7.28 (t, J = 8 Hz, 2H), 7.24–7.21 (m, 4H), 7.15–7.08 (m 10H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 165. 05, 156.11 (q, J_{CF} = 2.5 Hz), 154.22 (dd, $^{1}J_{CF}$ = 263 Hz, J_{CF} = 3.8 Hz), 153.27 (dd, $^{1}J_{CF}$ = 255 Hz, J_{CF} = 3.8 Hz), 140.76, 138.58, 138.43, 131.91, 128.71, 128.12 (dd, J_{CF} = 14 Hz, J_{CF} = 3.8 Hz), 128.76, 126.75, 125.73, 125.71, 125.10 (dd, J_{CF} = 15 Hz, J_{CF} = 3.8 Hz), 124.14, 124.13, 124.05, 122.45, 121.26, 121.15, 121.03, 120.62, 120.04, 120.02, 114.01 (d, J_{CF} = 14 Hz), 109.91, 109.83, 109.35. ¹⁹F NMR (470 MHz, CDCl₃): δ –111.64 (d, J = 14 Hz, 1F), –120.54 (d, J = 14 Hz, 1F). HRMS (MALDI, m/z): Calcd for C₅₀H₂₉N₅OF₂ (M⁺), 754.2413; Found, 753.2347. Anal. Calcd for C₅₀H₂₉N₅OF₂: C, 79.67; H, 3.88; N, 9.29. Found: C, 79.60; H, 4.00; N, 9.32.

2-Phenyl-5-(2,3,4,6-tetra(9H-carbazol-9-yl)-5-fluorophenyl)-1,3,4-oxadiazole (2,3,4,6CzDPO). A solution of 2-(pentafluorophenyl)-5-phenyl-1,3,4-oxadiazole (1.0 g, 3.2 mmol), carbazole (2.13 g, 12.7 mmol), and potassium carbonate (7.0 g, 50. mmol) in DMSO (20 mL) was stirred at room temperature for 27 h under nitrogen. Water (100 mL) was added and a pale yellow solid was obtained. The solid product was collected by filtration, and washed with water. After drying, the crude product was purified by column chromatography using dichloromethane/hexane (8:2) as eluent. After removal of solvent, the yellow solid was dissolved in dichloromethane, and methanol (100 mL) was added. Dichloromethane was removed and a pale-yellow solid was recrystallized from methanol solution. The solid product was collected by filtration. After drying under vacuum, the product was obtained (1.6 g, 55%). ¹H NMR (500 MHz, CDCl₃): δ 8.09 (d, J = 8 Hz, 2H), 7.74–7.73 (m, 2H), 7.62 (d, J = 8 Hz, 2H), 7.49-7.44 (m, 4H), 7.39 (d, J = 8 Hz, 2H), 7.32-7.27 (m, 3H), 7.23-7.20 (m, 4H), 7.15-7.06 (m, 8H), 7.03 (t, J = 8 Hz, 2H), 6.85–6.80 (m, 4H), 6.73 (t, J = 8 Hz, 2H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 164.30, 157.14 (d, J = 4 Hz), 156.39 (d, ${}^{1}J_{CF}$ = 261 Hz), 140.95, 139.71, 138.72, 138.12, 136.64 (d, J = 2.5 Hz), 134.13 (d, *J* = 4 Hz), 131.47, 129.35 (d, *J* = 14 Hz), 128.37, 127.16 (d, *J* = 15 Hz), 126.95 (d, J = 1 Hz), 126.55, 126.48, 125.61, 125.55, 124.68, 124.14, 124.01, 123.72, 122.26, 121.04, 120.97, 120.70, 120.56, 120.47, 120.04, 119.54, 110.05, 109.30, 109.28. ¹⁹F NMR (470 MHz, CDCl₃): δ -113.83 (s). HRMS (MALDI, m/z): Calcd for C₆₇H₃₇N₆OF (M⁺) 900.3013; Found 900.3005. Anal. Calcd for C₆₇H₃₇N₆OF: C, 82.65; H, 4.14; N, 9.33. Found: C, 82.43; H, 4.08; N, 9.32.

2-(4-(tert-Butyl)phenyl)-5-(2,3,4,5,6-penta(9H-carbazol-9-yl)phenyl)-1,3,4-oxadiazole (2,3,4,5,6CzDPO). A solution of 2-(4-(*tert*-butyl)phenyl)-5-(pentafluorophenyl)-1,3,4-oxadiazole (0.20

g, 0.54 mmol), carbazole (0.50 g, 3.0 mmol), and potassium carbonate (2.0 g, 14 mmol) in DMSO (10 mL) was stirred at 100 °C for 10 h under nitrogen. After cooling to room temperature, water (75 mL) was added and a pale yellow solid was obtained. The solid product was collected by filtration and washed with water. After drying, the crude product was purified by column chromatography using dichloromethane/hexane (7:3) as eluent. After removal of solvents, the solid was dissolved in dichloromethane, methanol (30 mL) was added, dichloromethane was removed, and the resulting yellow solid was collected by filtration and dried under vacuum (0.55 g, 92%). ¹H NMR (500 MHz, CDCl₃): δ 7.64–7.61 (m, 4H), 7.36 (d, J = 8 Hz, 4H), 7.30 (d, J = 4 Hz, 2H), 7.24–7.20 (m, 10H), 7.08 (d, J= 8.5 Hz, 2H), 6.97–6.95 (m, 8H), 6.79–6.73 (m, 6H), 6.68–6.65 (m, 6H), 6.61 (t, J = 7.5 Hz, 2H), 1.22 (s, 9H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 164.12, 157.34, 154.83, 139.73, 139.57, 138.34, 137.95, 137.04, 127.30, 126.30, 125.49, 125.24, 124.37, 124.23, 123.80, 123.60, 120.49, 120.31, 120.21, 120.02, 119.57, 119.41, 119.31, 110.75, 110.51, 109.38, 34.86, 30.98. HRMS (MALDI, m/z): Calcd for C78H53N7O 1103.4312 (M+); Found 1103.4295. Anal. Calcd for C78H53N7O: C, 84.84; H, 4.84; N, 8.88. Found: C, 84.65; H, 4.72; N, 8.91.

OLED Fabrication. The performance of three of the emitters was evaluated in OLEDs with the structure: glass/ITO/MoO3 (15 nm)/ Poly-TriCZ (80 nm)/DPEPO:emitter (25 nm, 25 wt %)/TP3PO (4 nm)/TPBi (50 nm)/LiF (1 nm)/Al (50 nm)/Ag (100 nm) as shown in Figure 4a (see Chart S1 in the Supporting Information for molecular structures of the materials used). The thin layer of molybdenum trioxide was evaporated as a hole-injection layer. The 80 nm thick Poly-TriCZ⁴⁶ hole-transporting layer was spin-coated (500 rpm for 60 s) from a chlorobenzene solution (10 mg mL⁻¹) and thermally annealed (110 °C for 2 min) in a nitrogen-filled glovebox. The emissive layer (EML) was deposited via a co-evaporation of DPEPO:emitter with a dopant concentration of 25 wt %. Sequentially deposited TP3PO and TPBi layers were used as electron transport layers. Lithium fluoride was deposited to improve the electron injection between a 50 nm thick aluminum cathode and the organic layers. A silver layer was deposited atop the aluminum to assist with the contact between the devices and the test setup. The chemical structures of all organic materials used in the devices are shown in the Supporting Information. The typical OLED active area was 3.0 mm × 3.0 mm. All thermal depositions were performed at pressures below 1.0×10^{-7} Torr.

RESULTS AND DISCUSSION

The carbazole donor/2,5-diphenyl-1,3,4-oxadiazole acceptor compounds in this study (Chart 1) were synthesized through nucleophilic aromatic substitution with differing stoichiometries of 9H-carbazole on the pentafluorophenyl DPO precursors 2-(pentafluorophenyl)-5-phenyl-1,3,4-oxadiazole or 2-(4-(tert-butyl)phenyl)-5-(pentafluorophenyl)-1,3,4-oxadiazole. Very recently, a close analogue of 2,3,4,5,6CzDPO, differing only in lacking the tert-butyl group, has been obtained through similar chemistry.³⁰ Compounds 2,4,6CzDPO and 2,4,5CzDPO were obtained from the same reaction in a 0.8:1 ratio (based on isolated yields). Detailed synthetic procedures and characterization data can be found in the Experimental Section. The CzDPO compounds were characterized by ¹H, ¹³C{¹H}, and, when appropriate, ¹⁹F NMR, and highresolution mass spectrometry (HRMS), and purity was confirmed through elemental analysis (EA). In particular, the regiochemistry of 2,4CzDPO, 2,4,6CzDPO, 2,4,5CzDPO, and 2,3,4,6CzDPO was confirmed through ¹⁹F NMR and ¹³C{¹⁹F} NMR spectroscopy. Additional purification by vacuum sublimation was performed on compounds before incorporation into OLEDs.

The thermal stability of the compounds was examined using thermogravimetric analysis (TGA) under a nitrogen atmos-

Chart 1. Compounds Studied



phere; decomposition temperatures (T_d) , defined here as the temperature at which 5% mass loss in the TGA curve was observed (Figure S5 in the Supporting Information), are summarized in Table 1. All six compounds show decomposition temperatures in excess of 300 °C, and T_d increases with increasing replacement of fluorine with carbazole.

Oxidation and reduction potentials were measured using cyclic voltammetry in dichloromethane and tetrahydrofuran, respectively, and all values were referenced against an FeCp₂⁺/ FeCp₂ internal standard. In the case of nonreversible oxidation processes, potentials were estimated from the onset at a scan rate of 50 mV s^{-1} . The reduction waves were sufficiently reversible processes that $E_{1/2}$ values could be estimated. The compounds became slightly more difficult to reduce as additional carbazole groups were added, with reduction potentials shifting from -2.00 V for CzDPO to -2.19 V for 2,3,4,5,6CzDPO, suggesting fluoro has a greater stabilizing effect on the LUMO than carbazolyl, consistent with it acting as a slightly stronger electron-withdrawing group. All compounds showed irreversible oxidation behavior during the cathodic sweep, consistent with electrochemical oxidation occurring on the Cz donor.⁴⁷ The compounds are increasingly easily oxidized with additional Cz substitution, again consistent with the slightly greater electron-withdrawing effects of fluoro substituents. Values ranged from +1.17 V for CzDPO down to +1.00 V for 2,3,4,5,6CzDPO. Taken together, the electrochemical gap $(E_{ec}^{g} = e(E^{ox} - E^{red}))$ changed minimally within the series, only varying between 3.12 and 3.19 eV.

The B3LYP/6-31G(d,p)-calculated energies of the HOMO and LUMO (illustrated in Figure 2) are included in Table 1 for comparison. Although the energies do not precisely track with the observed electrochemical potentials, HOMO and LUMO energies are in good agreement and, similarly, increase slightly relative to **CzDPO** with increased Cz substitution. The resulting difference in energy of the HOMO and LUMO,

Table 1. Thermal and Electrochemical Potentials of Compounds vs FeCp₂⁺/FeCp₂ and DFT-Calculated Frontier-Orbital Energies

		ele	ctrochemical pote	ntial	calculated orbital energies				
compound	$T_{\rm d}/^{\circ}{\rm C}^{a}$	$E^{\rm ox}/{ m V}$	$E^{\rm red}/{ m V}$	E^{g}/eV^{b}	HOMO/eV	LUMO/eV	$\Delta E_{ m HL}/ m eV^c$		
CzDPO	308	1.17	-2.00	3.17	-5.78	-2.14	3.64		
2,4CzDPO	373	1.15	-1.99	3.14	-5.54	-2.08	3.46		
2,4,6CzDPO	421	1.11	-2.04	3.15	-5.54	-2.03	3.52		
2,4,5CzDPO	409	1.08	-2.05	3.13	-5.61	-2.10	3.51		
2,3,4,6CzDPO	426	1.02	-2.10	3.12	-5.52	-1.97	3.55		
2,3,4,5,6CzDPO	478	1.00	-2.19	3.19	-5.42	-1.89	3.53		
^{<i>a</i>} From 5% weight loss temperature by TGA at 10 °C min ⁻¹ . ^{<i>b</i>} $E^{g} = e(E^{ox} - E^{red})$. ^{<i>c</i>} $\Delta E_{HL} = E_{LUMO} - E_{HOMO}$.									

Table 2. Solution Photophysical Properties in Dilute Toluene Solution

		fluorescence phosphorescence ^a		rescence ^a				
compound	$\lambda_{\rm abs}/{ m nm}$	$\lambda_{\rm max}/{\rm nm}$	onset/eV	$\lambda_{\rm max}/{\rm nm}$	onset/eV	$\Delta E_{\mathrm{ST}}^{}b}$ /eV	$\phi_{ m Fl}{}^c$	$ au_{ m Fl}/ m ns$
CzDPO	288, 344	444	3.24	508	2.75	0.49	0.21/0.27	6.7
2,4CzDPO	288, 315, 329, 347	449	3.10	516	2.72	0.38	0.06/0.08	4.8
2,4,6CzDPO	288, 316, 329, 345	490	2.85	521	2.73	0.12	0.04/0.06	3.9
2,4,5CzDPO	289, 314, 329, 361	459	3.06	484	2.71	0.35	0.12/0.20	7.7
2,3,4,6CzDPO	290, 319, 331	483	2.86	471	2.79	0.07	0.06/0.10	3.2
2,3,4,5,6CzDPO	291, 333	482	2.93	459	2.81	0.12	0.03/0.13	2.9

^aRecorded in toluene matrix at 77 K. ^bEstimated from the difference of onset of fluorescence and onset of phosphorescence. ^cPhotoluminescence quantum yield in aerated/nitrogen sparged solution.

 $\Delta E_{\rm HL}$, ranges from a maximum 3.64 eV in CzDPO to a minimum of 3.46 eV, a difference of 0.17 eV.

Solution state photophysical data were collected in dry toluene unless otherwise stated and are shown in Table 2. All compounds exhibit UV absorptions from ca. 288 to 297 nm and weaker absorptions from 314 to 333 nm, attributable to $\pi - \pi^*$ absorptions by electronic states localized on the Cz and DPO moieties. The broad, featureless absorptions at wavelengths above ca. 340 nm are assigned to intramolecular charge-transfer (ICT) transitions from the Cz donor to DPO acceptors. As seen in Figure 1a, fluorescent emission of all molecules displayed the broad, structureless line shape expected from an emission from a CT S₁ state. Furthermore, the emission for all compounds is solvent-dependent, while the absorption spectra were largely insensitive to solvent (see the Supporting Information). The emission maximum for CzDPO, for example, in dichloromethane (475 nm) is red-shifted by 350 meV versus that in cyclohexane (419 nm). If solvation is similar for all the compounds studied, electron density from Cz moieties contributing to the S1 state and aligned partially against the overall direction of the excited-state dipole, specifically those in the 2- and 6-positions, would be expected to decrease the difference in dipole between the ground and excited states, and subsequently the emission dependence on solvent polarity.⁴⁸ Thus, as expected, more highly substituted compounds show less solvatochromic fluorescence. The pentasubstituted 2,3,4,5,6CzDPO, for example, exhibits a lower red shift of 240 meV between cyclohexane (461 nm) and dichloromethane (506 nm).

The energy of the S_1 state, estimated using the onset of fluorescence, differs more significantly over the series (0.39 eV variation) than the electrochemical gap (0.07 eV variation). Compound **4CzDPO** exhibits a fluorescence onset at 3.24 eV. Substituting one fluorine with carbazole yields **2,4CzDPO** and lowers the S_1 -state energy to 3.10 eV. Trisubstituted compounds **2,4,6CzDPO** and **2,4,5CzDPO** are at 2.85 and 3.06 eV, respectively. Addition of a fourth Cz donor on



Figure 1. (a) Steady-state fluorescence spectra collected at room temperature in dilute toluene solution. (b) Photoluminescence spectra collected in toluene matrix at 77 K with a 500 μ s delay before data collection and attributed to phosphorescence.

2,3,4,6CzDPO resulted in onset at 2.86 eV, and pentasubstituted 2,3,4,5,6CzDPO is at 2.93 eV. Fluorescence maxima follow the same trend as the onsets.



Figure 2. HOMO, LUMO, and singlet and triplet NTOs for compounds studied. NTO hole (blue) and particle (red) wave functions are shown superimposed.

When interpreting the structural effects on the singlet state energies, two observations stand out. First, the range of S₁-state energies (ca. 400 meV) is significantly higher than in the electrochemical gaps, (ca. 70 meV). Similarly, the TD-DFT calculated singlet energies vary by up to 330 meV, while the calculated HOMO-LUMO gap varies by only 170 meV. Second, substitution of Cz into the 2- and 6-positions provides strong stabilization of S1, while substitution at the 3- and 5positions has relatively little effect. The molecules can be classified into three groups based on their S₁ energies, and on how many donors are substituted in the critical 2- and 6positions: compounds with 2,6-donors exhibit the most redshifted fluorescence (red shifts of 0.39, 0.38, and 0.31 eV for the onsets of 2,4,6CzDPO, 2,3,4,6CzDPO, and 2,3,4,5,6Cz-**DPO** vs that of **CzDPO**); compounds substituted in only the 2-position exhibit intermediate S₁-state energies (red shifts of 0.14 and 0.18 eV for 2,4CzDPO and 2,4,5CzDPO vs **CzDPO**), while **CzDPO** has the highest S_1 energy.

Delayed photoluminescence spectra (500 μ s delay before detection) were collected at 77 K and are attributable to phosphorescence. The T₁ energy was estimated using the onset of phosphorescence, and $\Delta E_{\rm ST}$ was calculated as the difference in estimated S₁- and T₁-state energies, as is common in the literature. In contrast to the S₁ energy, which, as noted above, varied by ca. 400 meV in the series, the T₁-state energy was relatively insensitive to donor substitution, varying by ca. 100 meV. However, the line shapes of the phosphorescence spectra do fall into two distinct classes. The compounds that retain the fluoro substituent in both 3- and 5-positions (Figure 1b, lower left) displayed a line shape resembling the phosphorescent emission of an isolated donor or acceptor; specifically, a Czlike line shape⁷ is seen in 4CzDPO and a DPO-like emission¹⁵ is seen for 2,4CzDPO and 2,3,5CzDPO. Previously reported quantum-chemical calculations have found the T1 state on similar CzDPO compounds to be an LE state located on the DPO moiety.¹⁸ The compounds that contain Cz in the 3- and/ or 5-positions show an emission line shape distinct from the previous compounds, with a well-resolved 0,0-peaked highfrequency (ca. 1300 cm⁻¹) vibronic structure (Figure 1b, lower right). This may indicate a different T₁-state character. In particular, the line shape indicates that the T_1 and S_0 geometries are primarily related through high-frequency modes; this could possibly be due to suppression of lowfrequency torsional relaxations by the steric crowding of adjacent carbazole groups in the 3- and/or 5-Cz-substituted species. Noda et al. have also recently described donor substitution in the 3- and 5-positions of benzonitrile as modifying the energies of the triplet states independent of those of the CT state.49

The highest T_1 energies of the series were found for the more highly substituted **2,3,4,6CzDPO** (2.79 eV) and **2,3,4,5,6CzDPO** (2.81 eV). Due to the relatively small variation in T_1 energies, the estimated ΔE_{ST} values roughly followed the trend for the S₁ energy and are shown in Table 2. Compounds **2,4,6CzDPO**, **2,3,4,6CzDPO**, and **2,3,4,5,6Cz-DPO**—the compounds with the lowest energy S₁ states—

exhibit the smallest ΔE_{ST} values, suggesting they are the most promising candidates for TADF emission.

DFT calculations (Figure 2) indicate that the HOMOs are, as expected, primarily located on one or more of the electronrich carbazoles, with small coefficients on the bridging phenyl. The LUMOs are more broadly spread across the entire 2,5diphenyl-1,3,4-oxadiazole moiety, with higher coefficients on the bridging phenyl that is substituted with the inductively electron-withdrawing carbazolyl and fluoro substituents than on the terminal C_6H_5 or C_6H_4 'Bu group.

Natural transition orbitals (NTOs), based on TD-DFT calculations at optimized S_1 and T_1 geometries, are shown alongside the HOMOs and LUMOs. The NTOs indicate a singlet emission generally well represented by a LUMO-to-HOMO CT-type transition, although the partitioning of the hole wave function between the different carbazole moieties differs a little in some cases from that seen for the HOMO wave function. For all compounds besides **CzDPO**, significant density of the hole wave function is located on carbazoles in the 2- and/or 6-positions. This is consistent with the experimentally observed decrease in the sensitivity of the Stokes shift to solvent polarity in the series, and with the key role of donor substitution in the 2- and 4-positions to stabilizing the fluorescent emission, perhaps due to electrostatic stabilization of more closely adjacent hole and electron.

In contrast to the NTOs of the lowest singlet emission, the T_1 NTOs show mixed CT and LE character, with that of **CzDPO** showing particularly predominant DPO LE character. As in the S_1 NTOs, the particle wave functions are well confined to the DPO moiety. The hole wave functions in the T_1 states, while displaying significant density on the Cz donors, are not as strongly Cz-localized as those in the S_1 states and also have significant density on the bridging phenyl groups and the oxadiazoles. It has been calculated that, for a given ΔE_{ST} , compounds containing S_1 and T_1 states with different orbital nature exhibit increased RISC rates relative to those for which S_1 and T_1 have similar orbital character due to increased spin–orbit coupling between the singlet and triplet manifolds.

To probe the potential application of these compounds as TADF emitters, fluorescence transients were collected for the more promising compounds in toluene solution that had been sparged by bubbling nitrogen for ca. 15 min; these are shown in Figure 3. Compound 2,3,4,5,6CzDPO displayed a biexponential fluorescent decay composed of a prompt component with a lifetime of 3.2 ns and a strong delayed luminescence component, attributed to TADF, with a lifetime of 62.8 µs. Compounds 2,4,6CzDPO and 2,3,4,6CzDPO also displayed biexponential fluorescent decay (prompt fluorescence $\tau_{\rm fl} = 3.9$ and 3.2 ns, respectively) with minor delayed fluorescence components that, while distinguishable from the instrument response function (IRF), could not be reliably fitted to determine the delayed lifetime. The long-lived luminescence components were quenched after exposure to air, consistent with TADF, where the triplet state can be quenched by oxygen before undergoing RISC. It is worth noting that, while 2,4,6CzDPO exhibited detectable TADF, regioisomer 2,4,5CzDPO, which exhibits a larger ΔE_{ST} value, does not, illustrating the importance of D-A topology in the design of TADF compounds.

Thin films of the three compounds displaying TADF properties were deposited by co-evaporation of the fluorophore (25 wt %) with a bis[2-(diphenylphosphino)phenyl]-ether oxide (DPEPO) host on a quartz substrate. The emission

Article



Figure 3. Transient photoluminescent decay curves at 300 K. (a) Data in toluene solution at room temperature after sparging with nitrogen. The instrument response function (IRF) is shown in black; although its width and the weakness of delayed fluorescence preclude extraction of $\tau_{\rm DF}$ values for **2,4,6CzDPO** and **2,3,4,6CzDPO**, the data clearly show a delayed component for these compounds that is much weaker than that for **2,3,4,5,6CzDPO**. (b) Data for evaporated thin films in which fluorophores (25 wt %) are doped into DPEPO (transients collected under nitrogen).

maxima of the films were 472, 484, and 479 nm for 2,4,6CzDPO, 2,3,4,6CzDPO, and 2,3,4,5,6CzDPO, respectively. Each compound displayed fluorescent decay with contribution from fast and slow components when measured under a nitrogen stream. When fit with a biexponential decay function, delayed fluorescent lifetimes ($\tau_{\rm DF}$) of 308.7, 166.2, and 75.0 μ s, respectively, were determined. Absolute photoluminescent quantum yields were significantly higher than when determined in toluene solution, presumably due to decreased nonradiative relaxation rates in thin film vs in solution. Under a stream of nitrogen, the PLQYs were 0.32, 0.54 and 0.61, respectively.

The performance of the three emitters exhibiting TADF discussed above was evaluated in OLEDs with the structure shown in Figure 4a (see Chart S1 in the Supporting Information for chemical structures of the materials). Figure 4b displays the normalized electroluminescence (EL) spectra of the three devices. The EL spectra of the devices exhibit more structure than the corresponding solution fluorescence spectra; in addition to the peak at ca. 490 nm, each device also exhibits a subsidiary peak or shoulder at ca. 470 nm, and longer wavelength shoulders. However, the positions of the strongest

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Figure 4. (a) Device structure, (b) electroluminescence (EL) spectra, (c) current–voltage–luminance (*J*–*V*–*L*) characteristics, and (d) EQE of three devices containing 2,4,6CzDPO, 2,3,4,6CzDPO, and 2,3,4,5,6CzDPO as emitters, respectively.

Table 3.	Device	Performance	of	OLEDs	Made	Using	CzDPO	Emitters	
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emitter	$V_{ m on}/{ m V}$	$EQE_{max}/\%$	$CE_{max}/cd A^{-1}$	$PE_{max}/lm W^{-1}$	CIE/(x, y)
2,4,6CzDPO	5.1	6.1	12.3	7.7	(0.17, 0.30)
2,3,4,6CzDPO	5.5	17.8	40.6	22.8	(0.18, 0.36)
2,3,4,5,6CzDPO	4.1	24.4	46.3	34.6	(0.16, 0.29)
			2		

^aTurn-on voltage (V_{on}), defined as that required to achieve 10 cd m⁻², external quantum efficiency (EQE), current efficacy (CE), power efficacy (PE), and CIE coordinates of OLEDs (from EL spectra under a bias of 5 V).

maximum and the overall emission widths are consistent with those seen in the solution fluorescence spectra. Similar differences have been seen between the fluorescence and EL spectra of other emitters; e.g., the EL of a benzofurocarbazoletriazine TADF emitter has recently been found to exhibit concentration-dependent structure,⁵⁰ while the corresponding fluorescence spectra are structureless.⁵¹ Although the EL spectra are similar for all three emitters, as are the corresponding fluorescence spectra, the relative intensity of the component at 470 nm is significantly smaller for the device containing the **2,3,4,6CzDPO** emitter, leading to a greener light emission of the device.

Current–voltage–luminance characteristics and EQE as a function of luminance are shown in Figure 4c,d, respectively, and device data are summarized in Table 3. Despite having similar estimated $\Delta E_{\rm ST}$ in solution, the compounds in which there are donors in the 3- and 5-positions displayed stronger delayed fluorescence with shorter delayed fluorescent lifetimes. This trend of spectroscopic characteristics favoring TADF was continued in the device efficiencies. EQE_{max} values in the

devices ranged from 6.1% in **2,4,6CzDPO**, to 17.8% in **2,3,4,6CzDPO**, and up to 24.4% at a reference luminance of 10 cd/m² in **2,3,4,5,6CzDPO**.⁵² Note that, under higher injection conditions and at a luminance of 1000 cd/m², more relevant for applications, devices with **2,3,4,5,6CzDPO** yield EQE values of 9.2% in nonoptimized devices. The highest EQE_{max} values are large despite moderately large τ_{DF} values; however, these lifetimes likely contribute, via processes such as triplet-triplet or triplet-polaron annihilation, to the substantial roll-off in EQE seen with luminance (Figure 4c). Moreover, values of EQE_{max} increase with decreased thin-film τ_{DF} values.

CONCLUSIONS

In summary, we have synthesized a series of DPO compounds with a varying number and connectivity of fluorine atoms and carbazole groups. The compounds exhibit very similar electrochemical gaps but display S₁-state energies that have a strong dependence on D-A topology. In previously studied systems, additional donors attached through electronegative heteroatoms can change the S₁ energy due to inductive effects stabilizing the LUMO regardless of position. In this system, where the substitution of carbazole replaces an electronegative fluorine instead of hydrogen, the inductive effect on the LUMO is largely negated. Substitution in the 2- and/or 6-positions is shown to lead to stabilization of the S₁ state relative to that of 4-CzDPO. However, substitution in the 3- and/or 5-positions does not affect the S₁ state significantly. Triplet state energies were much less sensitive to the substitution of Cz versus fluorine atoms; however, there is some evidence that the substitution pattern plays a more important role in the nature of the triplet state and, as a result, reverse intersystem crossing.

In the compounds that displayed TADF, delayed fluorescent lifetimes decreased and fluorescence quantum yield under a stream of nitrogen increased as carbazole substitution in the 3- and 5-positions increased. OLEDs were fabricated using the three compounds with the lowest estimated $\Delta E_{\rm ST}$ values as the emitters. Despite similar estimates of $\Delta E_{\rm ST}$, controlled largely by stabilization of the S₁ states, devices exhibited a range of EQE_{max} from 6.1% to 24.4% at a luminance of 10 cd/m², increasing with increased donor substitution in the 3- and 5-positions of the emitters. At a luminance of 1000 cd/m², an EQE of 9.2% was achieved with the best compound. This work helps elucidate the importance of the regiochemistry of the donor and acceptor in TADF compounds, beyond the previously postulated ability of the donor to simply inductively stabilize the LUMO on the acceptor.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.8b02632.

Oxidative and reductive cyclic voltammograms; absorption and photoluminescence spectra in cyclohexane, toluene, dichloromethane, and chloroform; transient photoluminescence in air-saturated toluene solution; TGA curves; structures for compounds used in OLEDs; ¹H, ¹³C{¹H}, ¹³C{¹⁹F}, and ¹⁹NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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