Hot Exciplexes in U-Shaped TADF Molecules with Emission from Locally Excited States

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Hot exciplexes in U-shaped TADF molecules with emission from locally excited states

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Rapid reverse intersystem crossing and high color purity are vital characteristics of emitters with thermally activated delayed fluorescence in opto-electronic devices. We present a new approach, called “hot exciplexes” that enables access to both attributes at the same time. Hot exciplexes are produced by coupling facing donor and acceptor moieties to an anthracene bridge, yielding an exciplex with large T₁ to T₂ spacing. The hot exciplex model is investigated using optical spectroscopy and quantum chemical simulations. Reverse intersystem crossing is found to occur preferentially from the T₃ to the S₁ state within only a few nanoseconds. Application and practicality of the model are shown by fabrication of organic light-emitting diodes with up to 32 % hot exciplex contribution and low efficiency roll-off.

Thermally activated delayed fluorescence (TADF) has emerged as a powerful approach to improve the performance of opto-electronic devices by converting passive triplet excitons into fluorescent singlet excitons.¹–⁵ This way, the internal device efficiency can be improved theoretically from 25 % to 100 %, by harvesting virtually all generated excitons. Conventional TADF luminophores make use of geometrical confinement of the HOMO and LUMO, and precise interplay of electron donor and acceptor moieties. This geometry evokes a charge transfer type excited state (CT) allowing a small energy gap ΔEₘ between the lowest excited singlet state (S₁) and the lowest excited triplet state (T₁). The small ΔEₘ allows reverse intersystem crossing (RISC) in combination with vibronic coupling from
T$_1$ to S$_1$ and fluorescence from there (see Figure 1a). Following this approach, TADF-based OLEDs with internal quantum efficiencies of ~100% and high external quantum efficiencies (EQEs) of ~40% could be obtained.\textsuperscript{6–8} Alternatively, charge transfer can also occur in exciplexes formed by individual electron donor and acceptor molecules. While both donor and acceptor possess locally excited singlet states (1LE), the emission occurs from the generated exciplex charge transfer singlet state 1CT (see Figure 1b).\textsuperscript{9} Connecting donor and acceptor by a molecular bridge increases the yield of exciplex formation.\textsuperscript{10,11} However, the involvement of a CT as the emissive state entails low oscillator strengths $f$ and therefore inferior radiative relaxation efficiency and poor color purity. One strategy to overcome this problem is \textit{via} hot triplet excitons that enable upper-level RISC, evading limitation to emissive 1CT states of conventional TADF materials (see Figure 1c).\textsuperscript{12–14} These emitters often incorporate anthracene with its low lying T$_1$ state, making it an obvious candidate for hot exciton TADF.\textsuperscript{15–19} However, bilateral functionalization with electron donor and acceptor groups on opposite sides of the anthracene core leads to a mixture of LE and CT states, generating hybridized local and charge transfer states (HLCT).\textsuperscript{19–23} Unfortunately, the emission characteristics of such HLCT geometries exhibit strong dependence on the polarity of the environment, thus limiting the choice of matrix and the OLED device architecture.\textsuperscript{24–26} Moreover, hot exciton luminophores with HLCT states show detrimental roll-off behavior in current efficiency and low EQE.\textsuperscript{27–29}

New molecular designs that make use of precisely localized 1LE states for emission, while utilizing hot excitonic states for fast transfer to these 1LE states, would advance the field and understanding of TADF and enable the development of emissive materials with superior device performance in view of efficiency and color purity. Energetic alignment of these emissive 1LE states with 3CT states should boost RISC rates, leading to increased long-term stability and low efficiency roll-off.\textsuperscript{30,31}

Here, we present and characterize a new class of TADF materials, where we achieve precise matching of LE to CT states. To accomplish this, we utilize a bridged exciplex geometry, which aligns donor and acceptor moieties. As bridge, we employ the anthracene motif, which gives access to hot exciton states and their innate fast upper-level RISC pathway (see Figure 1d). This new “hot exciplex” design suppresses HLCT behavior, even in strongly polar environment, allowing high RISC rates and emission with high oscillator strength ($f$) from a 1LE state. Emission from the 1LE state leads to short fluorescence lifetimes, and high color purity in the blue spectrum.\textsuperscript{24,32} We compare
four different donor substituents and characterize our molecules by density functional theory (DFT) simulations and transient spectroscopy.

Results and discussion

Molecular Design

In our molecular design, we aim at aligning CT and LE states to enable spin-orbit coupling between excited triplet and excited singlet states and to promote fast RISC.\textsuperscript{33–35} However, CT and LE must not mix in such a way that they form HLCT states. To avoid HLCT formation, we devise a molecular architecture by unilateral functionalization of anthracene with electron donor and acceptor units (U-shaped, as depicted in Figure 1e). This U-shaped molecular design aligns donor and acceptor to enable \textit{through-space} charge transfer, like in an exciplex. The non-polar anthracene bridge that accommodates LE states connects donor and acceptor units hosting the CT states (see Figure 1d,e). This molecular design confines CT and LE states to separate hemispheres of the molecule, thus avoiding mixing of CT with LE and HLCT behavior. As an acceptor we opt for isophthalonitrile, which has demonstrated excellent performance in various TADF active materials.\textsuperscript{3,4} We compare four different donor units, namely methylfuran (MeFuPAI), benzofuran (BeFuPAI), methylthiophene (MeThPAI), and benzothiophene (BeThPAI). The

![Figure 1](image-url)
opposite anthracene hemisphere is decorated with a phenyl ring, which is twisted with respect to the anthracene, to increase solubility and obviate their tendency to crystallize.

**Synthesis**

To develop a rationalized synthetic approach towards these molecules, we first convert commercially available 1,8-dichloroanthraquinone (1) to 1,8-dibromo-anthraquinone (2) to increase reactivity during subsequent coupling reactions.\(^{36}\) 2 is selectively reduced to 1,8-dibromo-10-anthrone (3) before introduction of the phenyl ring to the anthracene core, giving 1,8-dibromo-10-phenylanthracene (4).\(^{37,38}\) As 4 is symmetrical, it is not possible to address the two halide groups individually during Suzuki coupling of the acceptor or donor moieties.\(^{39}\) We first introduce the donor moiety to give compounds (5-8), and then the acceptor moiety to give the target hot exciplex molecules (see Figure 2 and Experimentals in the Supplementary Information).

**Photophysical Characterization**

We perform absorption and photoluminescence experiments to characterize our synthesized molecules. All four molecules exhibit absorption in the near UV to violet spectrum and emission in the blue to green spectrum, which is typical for emission from an anthracene moiety (see Figure 3a). To corroborate our claim that the \(S_1\) is an LE state located on the anthracene moiety, we investigate solvatochromism of our four molecules. Strong solvatochromism is expected for emission from a CT or HLCT state, while the solvent should have only small effect on
emission from an LE state. We record absorption and photoluminescence spectra of our emitters in various solvents with different polarity. We observe that BeFuPAI, MeThPAI, and BeThPAI show narrow emission bands in polar as well as non-polar solvents with the smallest full width at half maximum (FWHM) in n-hexane (see Figures 3b and Supplementary Figure 1). Both, the small solvatochromic effect and the high color purity substantiate that emission occurs from an LE state, which is beneficial for the photoluminescence quantum yield ($\eta_{PL}$) with values between 26 and 55 % (see Table 1). Interestingly, the emission spectrum of MeFuPAI reveals higher dependence on the relative polarity of the solvent than the other three molecules (see Figure 3b). In non-polar solvents MeFuPAI demonstrates satisfying color purity and acceptable $\eta_{PL}$ of 8 % (see Figure 3c and Table 1). To further exclude HLCT contributions in our compounds, we plot the Stokes shift ($\nu_a - \nu_e$) in each solvent against its orientational polarizability $\alpha(\varepsilon, n)$ to obtain Lippert-Mataga plots. Our compounds display only one component with constant slope for increasing solvent polarity (from non-polar n-hexane to polar acetonitrile, in Figure 3c). By contrast, two linear components of different slope would be expected for HCLT states in this polarity range. Furthermore, Lippert-Mataga plots allow estimation of the change in dipole moment upon excitation $\Delta\mu = (\mu_g - \mu_e)$, in accordance with the Lippert-Mataga equation:

$$hc(\nu_a - \nu_e) = hc(\nu_a^0 - \nu_e^0) - \frac{2(\mu_g - \mu_e)^2}{r^3} \alpha(\varepsilon, n)$$  (1)
With \( r \) being the Onsager radius of the compound, as determined by DFT simulations (see Supplementary Information). The slopes of the Lippert-Mataga plots remain below \( \Delta \mu < 10 \) D and are therefore much smaller than in typical anthracene-based HLCT emitters (see Table 1). The small \( \Delta \mu \) in combination with the narrow emission bands and the negligible solvatochromic effects substantiate our claim that emission occurs from LE states in our hot exciplex molecules. To investigate participation of triplet states in the emission process, we perform oxygen quenching experiments. In all four compounds, the blue emission is reduced when excited in ambient atmosphere, whereas when under an argon blanket the emission is strong. This effect is fully reversible (see Figure 3d). This behavior presents a first indication that the emission occurs with participation of triplet states, as these are quenched by triplet oxygen. From the ratio of decreased intensity in the presence of oxygen versus the full intensity under argon, we estimate that triplet participation in furan-containing compounds is stronger than in thiophene-containing compounds (see Figure 3d). Upper-level RISC in hot exciton TADF materials has been reported to be fast and practically indistinguishable from fluorescence. We expect the same behavior in our hot exciplexes and investigate the photoluminescence decay of our molecules in the solid state. Indeed, the transient photoluminescence profile is composed of two fast decaying components with \( \tau_{pr} = 0.80 \pm 0.20 \) ns, indicating prompt fluorescence, and \( \tau_{del} = 5.9 \pm 0.82 \) ns, representing delayed fluorescence (see Figure 3e and Table 1). The ratios of prompt to delayed fluorescence components indicate enhanced triplet contribution in furan-containing MeFuPAI and BeFuPAI over the thiophene-containing MeThPAI and BeThPAI (see Figure 3e and Table 1). Upon exposure to oxygen, the lifetimes of the furan-containing compounds decrease significantly, whereas in the thiophene-based compounds the decay rates are almost identical under oxygen and argon (cf. dashed and solid lines in Figure 3e). This behavior is in line with the fluorescence quenching results, where we observed less quenching in the thiophene-based compounds (cf. Figure 3d and e). Altogether, the differences in photoluminescence lifetime under oxygen and argon

### Table 1 | Empirical photoluminescence data and theoretical investigation of excited state energies.

| Compound    | \( \Delta \mu \) [D] | \( \eta_{\text{RL}} \) [%] in CHCl\(_3\) | \( \eta_{\text{RL}} \) sol solid [%] | \( \tau_{pr} \) (Ar/O\(_2\)) [ns] | \( \tau_{det} \) (Ar/O\(_2\)) [ns] | \( E_{\text{vert}}\) (S\(_1\)) (eV) / [nm] | \( E_{\text{adib}}\) (S\(_1\)) (eV) / [nm] | \( f\) (S\(_1\))
|-------------|---------------------|---------------------------------|---------------------|-----------------|-----------------|---------------------|---------------------|-------------------|
| MeFuPAI     | 7.1                 | 41                             | 6                   | 1.2/0.7         | 8.2/5.2         | 3.08 / 402         | 2.61 / 475         | 3.05 / 407        | 2.76 / 449        | 0.37              |
| BeFuPAI     | 4.9                 | 55                             | 20                  | 2.0/1.6         | 7.8/5.1         | 3.09 / 401         | 2.64 / 470         | 3.08 / 403        | 2.79 / 444        | 0.50              |
| MeThPAI     | 6.1                 | 8                              | 6                   | 0.8/0.7         | 8.17/5.7        | 3.12 / 397         | 2.63 / 471         | 3.22 / 385        | 2.88 / 431        | 0.38              |
| BeThPAI     | 8.1                 | 26                             | 17                  | 1.5/1.4         | 5.95/5.1        | 3.17 / 391         | 2.64 / 469         | 3.24 / 383        | 2.90 / 428        | 0.48              |

*Maxima in absorption/emission spectra measured chloroform solution. Vertical excitation energy obtained from DFT/MRCI simulations for the optimized ground state geometry; Adiabatic excitation energy obtained from DFT/MRCI calculations at the (TD)-DFT-optimized geometry.
are smaller than expected. This behavior can be explained by incomplete quenching by oxygen during the overall short photoluminescence lifetimes in the (sub)nanosecond regime. Photoluminescence is so abrupt that only little quenching can occur.\textsuperscript{42}

Characterization and Evaluation of the Excited States

Our empirical experiments indicate that our design principles appear correct. The emission in our molecules occurs fast, involves triplet states, and decays from an LE singlet state. However, we have no direct insight into the electronic states involved in this process. Often, time dependent (TD)-DFT simulations are carried out to delineate the electronic properties of TADF molecules.\textsuperscript{43-45} However, linear response TD-DFT calculations tend to underestimate triplet energies, which obviates a clear representation of our hot exciplex mechanism involving several triplet states.\textsuperscript{46} Even individually tuned long-range corrections appear unsuitable for our hot exciplex systems, since the optimum long-range correction may vary for the individual donor, acceptor, and bridge moieties.\textsuperscript{47} To compensate for these shortcomings, we perform density functional theory multi-reference configuration interaction (DFT/MRCI) calculations of electronic states.\textsuperscript{48,49} The respective ground- and excited state geometries are obtained with Kohn-Sham DFT and Tamm-Dancoff-approximated TD-DFT. To evaluate the accuracy of this modelling approach we first reproduce the optical properties determined empirically. We start by performing a conformational analysis at the semiempirical GFN2-xTB level.\textsuperscript{50,51} The obtained conformers are reoptimized and energetically re-ranked with the Kohn-Sham DFT-based composite method PBEh-3c. Only the lowest energy conformers are considered for our subsequent analysis (see Supplementary Figure 3).\textsuperscript{52}

To obtain insight into the excited state characteristics, we perform natural transition orbital (NTO) analysis at the $S_0$ geometry.\textsuperscript{53,54} From this, we identify that for all molecules considered, the $S_1$ state corresponds to an LE state, predominantly localized on the anthracene unit, with high $f > 0.37$ (see Figure 4a and Supplementary Figure 3). This is in line with our design principle and the empirical observations, and these values for $f$ correspond well with the measured medium to high $\eta_{PL}$ (see Table 1). Furthermore, the $S_2$ states show strong CT character, indicating that our design concept of bringing CT and LE close together is reflected by the NTOs (see Figure 4a and Supplementary Figure 3). Among the triplet states, we identify $T_1$ as an LE state, which is similar in character to $S_1$, while $T_2$ is also an LE state that is mostly located on the furan or thiophene moieties as well as on the anthracene bridge. For $\text{MeFuPAI}$, $\text{BeFuPAI}$, and $\text{MeThPAI}$, the $T_3$ state represents a CT state, with similarity to the $S_2$ state, but
with a slightly more delocalized occupied NTO. For **BeThPAI**, this CT state is found as T₄, while T₃ is an LE state (see Supplementary Figure 3). This reversal of T₃ and T₄ states in **BeThPAI** indicates that our molecules exhibit multiple high-energy triplet states of almost degenerate character, which would be in good agreement with our model of hot exciplexes.

In the next step, we refine the energies using the DFT/MRCI method (R2018 “tight” model⁵⁵) with the TZVP basis set, based on the obtained Tamm-Dancoff-approximated TD-PBElh-3c geometries.⁴⁸,⁴⁹,⁵⁶ The vertical excitation energies $E_{\text{vert}}$, required for reaching $S_1$ from the ground state during absorption, are in good agreement with the empirical absorption $\lambda_a$ obtained by UV/Vis spectroscopy (see Table 1). In much the same way, the calculated adiabatic excitation energies $E_{\text{adia}}$ correspond well with the blue emission $\lambda_e$ recorded by fluorescence spectroscopy (see Table 1 and Figure 3a).

Upon excitation and (R)ISC, molecules undergo geometry adaptations due to change of the potential energy surface. As a consequence, energy levels and gaps strongly depend on the nature of the exited state geometry assumed by the respective molecule. To account for this dependence, we determine all energies of the electronic states involved in the hot exciplex mechanism in their respective minimum geometries (see Figure 4b). At all geometries we observe the apparent large energy gaps of ~1 eV between $T_1$ and $T_2$ supporting our concept of hot exciplex states. In the $T_3$ geometry, the energy differences between $S_1$, $S_2$, $T_2$, and $T_3$ become diminishingly small, so that these states can be considered thermally degenerate, and strong RISC is expected (see Figure 4b). As a result of this degeneracy, we find that $T_3$ in **BeThPAI** is a LE state and that we are unable to optimize a CT triplet state. Therefore we do not display the energy states of this geometry in Figure 4b.

To investigate whether our model is in accordance with the observed delayed fluorescence with lifetimes of the order of only a few nanoseconds, we calculate spin-orbit coupling (SOC) matrix elements for $T_2\rightarrow S_1$ and $T_3\rightarrow S_1$ and estimate the rate of reverse intersystem crossing $k_{\text{RISC}}$ in the Condon approximation using a time-dependent approach.⁵⁷ While SOC of $T_2\rightarrow S_1$ is strong, ranging between 0.35 – 2.33 cm⁻¹, RISC is slow with $k_{\text{RISC}} < 10^9$ s⁻¹ (see Table 2). Apparently, in the $T_2$ geometry RISC from $T_2$ to $S_1$ is hindered due to negative adiabatic energy gap between the two states – the $T_2$ minimum is below the $S_1$ minimum. While SOC for $T_3\rightarrow S_1$ is of the same order of magnitude as for $T_2\rightarrow S_1$, a positive adiabatic energy gap is present here and RISC occurs from $T_3$ to $S_1$ within nanoseconds (see Table 2, Figure 4b, and Supplementary Table 1).
This result is in accordance with our conclusions drawn from the spectroscopic experiments, where MeThPAI exhibited low $\eta_{PL}$ in solution and solid state and only minor influence of oxygen quenching (see Figures

| Table 2 | Overview of excited state energies, spin orbit coupling and transfer rates obtained from theoretical investigation. |
|---------|---------------------------------------------------------------|
|         | $\Delta E_{\text{exc}}$ (T<sub>2</sub>→S<sub>1</sub>) [eV] | SOC (T<sub>2</sub>→S<sub>1</sub>) [cm<sup>-1</sup>] | $k_{\text{RISC}}$ (T<sub>2</sub>→S<sub>1</sub>) [s<sup>-1</sup>] | $\Delta E_{\text{exc}}$ (T<sub>3</sub>→S<sub>1</sub>) [eV] | SOC (T<sub>3</sub>→S<sub>1</sub>) [cm<sup>-1</sup>] | $k_{\text{RISC}}$ (T<sub>3</sub>→S<sub>1</sub>) [s<sup>-1</sup>] | $\Delta E_{\text{exc}}$ (T<sub>2</sub>→T<sub>3</sub>) [eV] | $\Delta E_{\text{exc}}$ (T<sub>3</sub>→T<sub>2</sub>) [eV] |
| MeFuPAI | −0.10             | 0.35       | $1.1 \times 10^5$ | 0.19       | 1.00       | $6.3 \times 10^7$     | 0.97       | 0.29 |
| BeFuPAI | −0.16             | 0.38       | $1.1 \times 10^4$ | 0.28       | 0.38       | $1.2 \times 10^7$     | 0.94       | 0.44 |
| MeThPAI | −0.16             | 2.33       | $3.8 \times 10^5$ | 0.28       | 0.93       | $3.1 \times 10^7$     | 0.95       | 0.44 |
| BeThPAI | −0.21             | 1.18       | $4.2 \times 10^4$ | −<sup>a</sup> | −<sup>a</sup> | −<sup>a</sup>         | 0.90       | −<sup>a</sup> |

<sup>a</sup> T<sub>3</sub> in BeThPAI is a LE state. The CT states could not be optimized.
3d and e). By contrast, MeFuPAI and BeFuPAI displayed susceptibility to oxygen quenching, which correlates with the longer $T_2$ lifetime. Appreciating these longer lifetimes in MeFuPAI and BeFuPAI and assuming that a nuclear wavepacket can partially equilibrate on the $T_2$ potential energy surface, we turn to determining the minimum energy conical intersections (MECI) to estimate the long-time behavior of the remaining population on $T_2$ (see Supplementary Table 6). For MeFuPAI, we find the $T_1/T_2$ MECI to be 11.5 kcal/mol above the $T_2$ minimum, while it is only 7.3 kcal/mol for the $T_2/T_3$ MECI. For BeFuPAI the $T_1/T_2$ and $T_2/T_3$ MECIs are found at 9.5 kcal/mol and 9.6 kcal/mol, respectively. From these results we expect that the population of $T_2$ can remain for periods of the order of microseconds with a greater amount of non-radiative up-funneling to $T_3$ in MeFuPAI and a 1:1 ratio of up- ($T_3$) and down-funneling ($T_1$) states in BeFuPAI.

Applying conditions representing electrical excitation, we observe rapid up-conversion for MeFuPAI and BeFuPAI from $T_2$ to $T_3$. Within ~15 fs the population of $T_1$ saturates at about 32 % for MeFuPAI and 25 % for BeFuPAI (see Figure 4c). As a consequence, vibronic up-conversion within the triplet manifold is possible in furan-containing emitters, particularly since only negligible down-funneling to $T_1$ is observed.

Taken together, the empirical and theoretical experiments suggest that efficient RISC in the furan-based systems is occurring via the hypothesized $T_2$ (LE) $\rightarrow$ $T_3$ (CT) $\rightarrow$ $S_1$ (LE) mechanism. Assuming that all up-funnelled triplet excitons follow the described RISC path, we expect a radiative exciton production efficiency of approximately 44 – 49 % in electroluminescent devices. This value is estimated by combining $\frac{1}{4}$ of inherently radiative singlet excitons (given by spin-statistics) with the above determined 25 – 32 % of the residual $\frac{3}{4}$ triplet excitons that are converting fast via hot exciplex TADF.

**Electroluminescent Properties**

To verify that the hot exciplex mechanism is also present in its intended application of light emitting diodes, we fabricate devices and determine their electroluminescence characteristics. In this context, we focus on oxygen-containing emitters MeFuPAI and BeFuPAI as they exhibit superior $\eta_{PL}$, distinct SOC, and better $T_2$ to $T_3$ up-funneling compared to MeThPAI and BeThPAI. We fabricate OLEDs with neat emitter layers (see Figure 5a). The electroluminescence spectra are almost identical to the photoluminescence spectra and independent of the current density between 1 – 100 mA/cm$^2$ (see Supplementary Figure 5). We obtain EQEs of 0.5 % for MeFuPAI and
2 % for BeFuPAI. The radiative exciton production efficiencies $\eta$ of the MeFuPAI and BeFuPAI devices are determined as 45 % and 50 %, respectively, using:

$$\text{EQE} = \gamma \cdot \eta_r \cdot \eta_{PL} \cdot \eta_0$$

(2)

with $\gamma$ as the carrier balance factor being close to unity, $\eta_{PL}$ in the solid state (see Table 1) and $\eta_0$ as the outcoupling efficiency of around 20 %. As expected, $\eta_r$ exceeds the 25 % limit in radiative exciton production efficiencies of conventional fluorescent OLEDs, and coincides with the interval predicted by FOMO-CASCI simulations.

We perform transient electroluminescence to verify the hot exciplex mechanism in electroluminescent devices and study the potential contribution of triplet-triplet interactions, which are to be expected in neat emitter layers. The transient emission spectra for these devices exhibit a prompt component, accounting for ~ 80 % of the emission in the nanosecond regime, and a delayed component of ~ 20 % in the microsecond regime (see Figure 5b and Supplementary Figure 6). This delayed component is surprising at first, acknowledging that the hot exciplex based TADF is expected to occur on the nanosecond regime. However, the delayed component fits a recently described model for triplet-triplet annihilation up-conversion (TTA-UC), and can therefore not be assigned to the hot exciplex emission (see red dashed lines for TTA-UC fit in Figure 5b): 22,60

$$\frac{I_{\text{del}}}{I_{\text{pr}}} = 4\eta_r - 1. \quad (3)$$

The contribution of TTA-UC is plausible because the emitter concentration is high and intermolecular emitter-emitter interactions are therefore allowed. As a result, our hot exciplex RISC pathway is so fast, that it needs to be
assigned to the prompt emission decay. From the difference between $\eta_{\text{EQE}} = 45 – 50\%$ determined from EQE (Equation 2) and $\eta_{\text{transEL}} = 30\%$ obtained from transient electroluminescence (Equation 3) (see Figure 5c), we can derive the contribution of hot exciplexes to the overall emission $I_{\text{HE}}$ by:

$$I_{\text{HE}} = \frac{1}{4\eta_{\text{transEL}}} - \frac{1}{4\eta_{\text{EQE}}} \quad (4)$$

(see Supplementary Information for derivation of Equation 4).

This analysis shows that hot exciplexes account for up to 24% and 32% of the electroluminescence in MeFuPAI and BeFuPAI devices, respectively. The presence of a hot exciplex RISC mechanism, is further substantiated by the diminishing contribution of TTA-UC for decreasing current densities (Figure 5c). Even at low current density the observed EQEs exceed the fluorescent OLED limit (see Figure 5d). As described above, a hot exciton mechanism utilizing HLCT states would show roll-off at high current density. By contrast, our hot exciplex pathway contributes to the electroluminescence process across the entire range of current densities (see Figure 5d).

Conclusions

In summary, we have devised a design strategy that produces a so far unexplored hot exciplex mechanism yielding an LE state as the emissive singlet. By capitalizing on a molecular toolbox design, the respective donor and acceptor moieties can be varied, in the future, to evoke emitters with superior $\eta_{\text{PL}}$ and EQE. Combined with the inherently fast RISC process, short luminescence lifetimes, as well as high color purity and low efficiency roll-off, hot exciplexes are primed for advanced opto-electronic applications such as blue-emitting OLEDs and might contribute to new material concepts for organic laser diodes.

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Author contributions

A.L.S. and A.J.C.K. devised, planned and supervised the project. A.L.S. and P.J.W. performed material synthesis. A.L.S. and B.H. performed optical characterization of the materials. C.B. and A.L.S. conducted calculations. K.G. and C.A. performed and supervised device fabrication and characterization. A.L.S. and A.J.C.K. evaluated the data and results, all authors contributed to writing the manuscript.

Additional information
Supplementary Information, including the experimental section and details on the computational study, is available in the online version of the paper.

**Competing financial interests**

The authors declare no competing financial interests.

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**Graphical abstract**
Hot exciplexes in U-shaped TADF molecules with emission from locally excited states

Supplementary Information

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Optical spectroscopy

Absorption and emission spectra of the compounds are measured in the following solvents:

| Solvent           | Polarity | Orientational polarizability |
|-------------------|----------|------------------------------|
| Acetone           | 0.355    | 0.284                        |
| Acetonitrile      | 0.460    | 0.305                        |
| Chloroform        | 0.259    | 0.148                        |
| Dichloromethane   | 0.309    | 0.217                        |
| Diethylamine      | 0.145    | 0.127                        |
| Diethyl ether     | 0.117    | 0.167                        |
| Dimethylformamide | 0.386    | 0.276                        |
| Ethyl acetate     | 0.228    | 0.200                        |
| n-Hexane          | 0.009    | 0.0012                       |
| Tetrahydrofuran   | 0.207    | 0.210                        |
| Toluene           | 0.099    | 0.014                        |
| Triethylamine     | 0.043    | 0.048                        |

The Onsager radius \( r \) – required for evaluation of the Lippert-Mataga plots – is estimated from DFT simulations on the B3LYP/6-31+G(d) level using the *Volume* keyword in the Gaussian09 software program.1

Supplementary Figure 1: Absorption (solid line) and photoluminescence (dashed line) spectra of MeFuPAI, BeFuPAI, MeThPAI, and BeThPAI in different solvents as indicated by the color code.
Supplementary Figure 2: TCSPC measurements of MeFuPAI, BeFuPAI, MeThPAI, and BeThPAI solid films under argon (solid data points) and oxygen (brighter, empty data points) atmosphere.
Computational study of the hot exciplex emitters

Natural Transition Orbitals

During conformational analysis of our four emitters we find local energy minima for conformers with regard to rotation around the donor-anthracene bond. We determine two preferred conformers – one with the heteroatom of the donor pointing towards the isophthalonitrile acceptor (“in”) and one with the heteroatom pointing away from the isophthalonitrile (“out”). While furan-containing compounds prefer the “out” conformation, “in” conformers are preferred from the thiophene-containing compounds. Since the conformers are found within an energy window of 1 kcal/mol (at the PBEh-3c level), we expect the presence of both conformers at room temperature we calculate Natural Transition Orbitals (NTOs) for both conformers. However, we observe only a small effect of the conformation on the character of the NTOs. Hence, we only used the most stable conformer for the subsequent analysis. We verified that the state ordering for the lowest three singlet and triplet states agrees with DFT/MRCI at the $S_0$ geometry (see below).

Supplementary Figure 3: Natural Transition Orbitals (determined via Tamm-Dancoff-approximated TD-DFT calculations employing the PBEh-3c density functional approximation) of “out” and “in” conformers of all four emitters – in energetic order from S1 (left columns, bottom) to S2 (left columns, top) and T1 (right columns, bottom) to T5 (right columns, top). While the “out”
conformers are lowest in energy for the methylfuranyl derivatives, the “in” conformers are found to be lower for the thiophenyl derivatives.

Calculation of spin-forbidden nonradiative transitions

To simulate the intersystem crossing (ISC) and reverse ISC (RISC) rates between the energetically close lying triplet and singlet states, we employ the two-state time-dependent approach of Marian and coworkers in the Condon approximation based on harmonic oscillators.7 For this approach, the geometries of the respective electronic states need to be optimized and the harmonic frequencies to be computed at the respective minima.

Since the state ordering at the $S_0$ geometry is found to be in agreement with high level density functional theory-based multi-reference configuration interaction (DFT-MRCI) calculations (except for BeThPAI, where the triplet CT state is $T_3$ with DFT/MRCI), we perform these geometry optimizations also at the TDA-TDDDT-PBEh-3c level. We include all states through the respective CT state of each spin manifold. To avoid ambiguity in the case of state flips during the optimizations, we denote the included states as $1^3$LE and $1^1$CT for the excited singlet and $3^1$LE1, $1^3$LE2, and $1^3$CT for the triplet states (only $1^1$LE, $3^1$LE1, and $1^3$LE2 in the case of BeThPAI) in the following. It is noted that at the TDA-TDDFT-PBEh-3c level, the CT geometry optimization leads to a crossing of the $1^1$CT and $3^1$LE states, which complicates the geometry optimization of the $1^1$CT state. For technical reasons, we thus preoptimize the $1^3$CT state at the TDA-TDDDT-B3LYP-D3(BJ) level first, since the $1^3$CT state is obtained as $S_1$ here, thus simplifying the optimization of that state. We then continued with the TDA-TDDDT-PBEh-3c optimization, which is now also possible, since the $1^3$CT has dropped to the $S_1$ position at the TDA-TDDDT-B3LYP-D3(BJ)-preoptimized geometry. We use the permanent dipole moment of the state to distinguish it from the LE states – the CT states show static dipole moments that are larger in magnitude by at least 10 Debye compared to the LE states. For BeThPAI, optimizations of the $1^3$CT and the $3^1$CT state geometries is not possible, due to state slips during the optimization.

We verify each geometry as a minimum by numerical Hessian calculations and use the corresponding harmonic frequencies in the time-dependent harmonic oscillator approach as implemented in the VIBES program.12 All optimized geometries are given in a zip file with this supporting information.

Instead of using the adiabatic energy gap computed at the TDA-TDDDT directly, higher level DFT-MRCI calculations employing the R2018 Hamiltonian with “tight” parametrization (for $\text{esel}=0.8$ a.u.) and Ahlrichs’ TZVP basis set are used to compute the electronic energies at each geometry. The DFT-MRCI method is a comparably efficient but highly accurate excited state electronic structure method and often on a par with the CC2 approximate coupled cluster method.15,16 The DFT-MRCI/TZVP/TDA-TDDFT-PBEh-3c are then used to specify the adiabatic energy gap of the two states between which the ISC rate has been calculated with the VIBES program. Furthermore, the spin-orbit coupling matrix elements between the spin-pure DFT-MRCI/TZVP states are evaluated at the respective initial state geometry. The electronic energies obtained at this level are given in Supplementary Tables 1–4. The equation for the (R)ISC rate in the Condon approximation is given as

$$k_{(R)ISC}^{(i\rightarrow f)} = \left( < \Psi_i | \hat{H}_{SOC} | \Psi_f > \right)^2 k_{vib}^{(i\rightarrow f)},$$

with the vibrational component being computed via numerical integration of the time correlation function:

$$k_{vib}^{(i\rightarrow f)} = \int_{-\infty}^{\infty} G(t) e^{i(t\Delta E_{if}^0 + E_{ZPVE}^i)} dt.$$ 

Here $G(t)$ is the generation function (see Ref.2), $\Delta E_{if}^0$ is the adiabatic energy difference between the initial and final states (computed at the DFT-MRCI/TZVP/TDA-TDDFT-PBEh-3c level in this work), and the last term is the zero-point vibrational energy (ZPVE) of the initial state (computed at the TDA-TDDFT-PBEh-3c level in this work). We test the method parameters for the $1^3$LE2 to $1^1$LE RISC in MeFuPAI and find the RISC rate to be very insensitive with respect to them. We use a time interval of
100 fs, a Gaussian damping width of 1 cm\(^{-1}\) and 8192 grid points for the time integration in all cases. The RISC rates are computed for a temperature of 300 K throughout.

We note that for all systems, we find that at the TDA-TDDFT-PBEh-3c-optimized 3\(^\text{CT}\) geometry, the 3\(^\text{CT}\) state remains in the T\(_2\) position with TDA-TDDFT-PBEh-3c, while it drops below the 3\(^\text{LE2}\) state (i.e., it takes the T\(_3\) position) at the DFT-MRCI/TZVP/TDA-TDDFT-PBEh-3c level. We notice furthermore that at the DFT/MRCI/TZVP level, the 3\(^\text{CT}\) energy is always lower at the TDA-TDDFT-PBEh-3c 3\(^\text{CT}\) state minimum than on the respective 3\(^\text{CT}\) state minimum geometry. This may be due to stronger mixing with LE states in the triplet manifold at the TDA-TDDFT-PBEh-3c level of theory. Given that for pure CT states, the singlet and triplet states are expected to be isoenergetic, we also consider the 3\(^\text{CT}\) state geometry to be a plausible geometry to represent the 3\(^\text{CT}\) state minimum. For comparison, we decide to consider the TDA-TDDFT-PBEh-3c 3\(^\text{CT}\) and 3\(^\text{CT}\) minimum geometries (and their harmonic frequencies), for the DFT/MRCI single-point calculations to estimate the RISC from the 3\(^\text{CT}\) state (cf. Supplementary Table 5). In all cases, we identify the respective DFT-MRCI states by visual inspection of the dominantly contributing orbitals to the respective excitations.

The Turbomole program\(^{17}\) is used to conduct all DFT and TDA-TDDFT calculations, while the standalone mrci program of Marian and coworkers along with related tools is used to perform the DFT-MRCI calculations (based on the BLYP\(^5,6,9\) orbitals generated with Turbomole) and calculations of spin-orbit coupling matrix elements.

**Supplementary Table 1** | Electronic state energies computed for MeFuPAI at the DFT-MRCI/TZVP level on the corresponding PBEh-3c geometries. The TDA-TDDFT formalism has been used for the excited state geometry calculations. The relative energies w.r.t. the S\(_0\) energy at the S\(_0\) geometry are given in electron volts (eV) on the right next to the total energy (in Hartree) of the respective state.

| MeFuPAI | Minimum geometry | Electronic state | S\(_0\) | 3\(^\text{LE}\) | 3\(^\text{CT}\) | 3\(^\text{LE1}\) | 3\(^\text{LE2}\) | 3\(^\text{CT}\) |
|---------|------------------|-----------------|---------|------------|------------|------------|------------|------------|
| S\(_0\)  | -1453.8766       | 0.00            | -1453.8876 | 0.25       | -1453.8632 | 0.17        | -1453.8664 | 0.28        | -1453.8643 | 0.23        | -1453.8639 | 0.15        |
| LE      | -1453.7646       | 1.05            | -1453.7753 | 2.76       | -1453.7627 | 1.10        | -1453.7738 | 2.80        | -1453.7727 | 2.83        | -1453.7632 | 3.09        |
| CT      | -1453.7547       | 3.32            | -1453.7662 | 3.28       | -1453.7653 | 3.00        | -1453.7532 | 3.30        | -1453.7566 | 3.28        | -1453.7666 | 3.01        |
| LE1     | -1453.8025       | 2.02            | -1453.8123 | 1.75       | -1453.8001 | 2.06        | -1453.8147 | 1.69        | -1453.8096 | 1.82        | -1453.8013 | 2.05        |
| LE2     | -1453.7647       | 2.05            | -1453.7754 | 2.81       | -1453.7633 | 1.08        | -1453.7695 | 2.91        | -1453.7788 | 2.66        | -1453.7636 | 1.08        |
| CT      | -1453.7771       | 2.25            | -1453.7885 | 3.21       | -1453.7846 | 2.94        | -1453.7774 | 2.25        | -1453.7854 | 2.22        | -1453.7684 | 2.58        |

**Supplementary Table 2** | Electronic state energies computed for BeFuPAI at the DFT-MRCI/TZVP level on the corresponding PBEh-3c geometries. The TDA-TDDFT formalism has been used for the excited state geometry calculations. The relative energies w.r.t. the S\(_0\) energy at the S\(_0\) geometry are given in electron volts (eV) on the right next to the total energy (in Hartree) of the respective state.

| BeFuPAI | Minimum geometry | Electronic state | S\(_0\) | 3\(^\text{LE}\) | 3\(^\text{CT}\) | 3\(^\text{LE1}\) | 3\(^\text{LE2}\) | 3\(^\text{CT}\) |
|---------|------------------|-----------------|---------|------------|------------|------------|------------|------------|
| S\(_0\)  | -1568.1779       | 0.00            | -1568.1695 | 0.23       | -1568.1681 | 0.32        | -1568.168 | 0.27        | -1568.1097 | 0.22        | -1568.1084 | 0.34        |
| LE      | -1568.0648       | 3.08            | -1568.0756 | 2.75       | -1568.0642 | 3.09        | -1568.0741 | 2.83        | -1568.0718 | 2.89        | -1568.062 | 3.16        |
| CT      | -1568.0532       | 3.39            | -1568.0549 | 3.35       | -1568.0644 | 3.09        | -1568.0533 | 3.39        | -1568.0536 | 3.38        | -1568.0613 | 3.17        |
| LE1     | -1568.1035       | 2.02            | -1568.1141 | 1.74       | -1568.1039 | 2.04        | -1568.1116 | 1.69        | -1568.1058 | 1.85        | -1568.1053 | 2.11        |
| LE2     | -1568.0664       | 3.03            | -1568.0754 | 2.79       | -1568.0651 | 3.07        | -1568.0711 | 2.91        | -1568.0814 | 2.63        | -1568.063 | 3.13        |
| CT      | -1568.0559       | 3.32            | -1568.0574 | 3.28       | -1568.0579 | 2.99        | -1568.0559 | 3.32        | -1568.0561 | 3.32        | -1568.0552 | 3.07        |
Supplementary Table 3 | Electronic state energies computed for MeThPAI at the DFT-MRCI/TZVP level on the corresponding PBEh-3c geometries. The TDA-TDDFT formalism has been used for the excited state geometry calculations. The relative energies w.r.t. the S\textsubscript{0} energy at the S\textsubscript{0} geometry are given in electron volts (eV) on the right next to the total energy (in Hartree) of the respective state.

| MeThPAI | Minimum geometry |
|---------|------------------|
| Electronic state | S\textsubscript{0} | ¹LE | ¹CT | ³LE1 | ³LE2 | ³CT |
| S\textsubscript{0} | -1776.8535 | -1776.8535 | 0.32 | 0.37 | 0.32 | 0.32 | 0.33 |
| LE | -1776.7468 | -1776.7468 | 0.32 | 0.37 | 0.32 | 0.32 | 0.33 |
| CT | -1776.7563 | -1776.7563 | 3.43 | 3.17 | 3.51 | 3.46 | 3.29 |
| LE1 | -1776.7377 | -1776.7377 | 1.81 | 1.90 | 1.75 | 1.90 | 2.11 |
| LE2 | -1776.7439 | -1776.7439 | 2.03 | 1.90 | 1.75 | 1.90 | 2.11 |
| CT | -1776.7399 | -1776.7399 | 3.37 | 3.05 | 3.42 | 3.39 | 3.16 |

Supplementary Table 4 | Electronic state energies computed for BeThPAI at the DFT-MRCI/TZVP level on the corresponding PBEh-3c geometries. The TDA-TDDFT formalism has been used for the excited state geometry calculations. The relative energies w.r.t. the S\textsubscript{0} energy at the S\textsubscript{0} geometry are given in electron volts (eV) on the right next to the total energy (in Hartree) of the respective state. For BeThPAI, we could not obtain the CT geometries due to state crossings during optimization.

| BeThPAI | Minimum geometry |
|---------|------------------|
| Electronic state | S\textsubscript{0} | ¹LE | ¹LE1 | ¹LE2 | ¹LE3 |
| S\textsubscript{0} | -1891.0192 | -1891.0192 | 0.53 | 0.30 | 0.32 | 0.18 |
| LE | -1891.0063 | -1891.0063 | 2.96 | 0.94 | 0.94 | 3.13 |
| CT | -1891.0077 | -1891.0077 | 3.54 | 3.54 | 3.54 | 3.54 |
| LE1 | -1891.0018 | -1891.0018 | 1.84 | 0.94 | 0.94 | 3.13 |
| LE2 | -1891.0014 | -1891.0014 | 2.91 | 0.94 | 0.94 | 3.13 |
| CT | -1891.0014 | -1891.0014 | 3.47 | 0.94 | 0.94 | 3.13 |

Supplementary Table 5 | Overview of excited state energies, spin orbit coupling and transfer rates for the T\textsubscript{3} (³CT) → S\textsubscript{1} (³LE) transitions obtained from theoretical investigation based on different geometries. While the Tamm-Dancoff approximated TD-PBEh-3c minimum T\textsubscript{3} (CT) geometry results are each given in the left columns, the S\textsubscript{1} (CT) optimized geometry results are given in the right columns each.

| ΔE\textsubscript{e}\textsubscript{A} (T\textsubscript{3}→S\textsubscript{1}) [eV] | SOC (T\textsubscript{3}→S\textsubscript{1}) [cm\textsuperscript{-1}] | k\textsubscript{RISC} (T\textsubscript{3}→S\textsubscript{1}) [s\textsuperscript{-1}] | ΔE\textsubscript{e}\textsubscript{A} (T\textsubscript{3}→T\textsubscript{2}) [eV] |
|-----------------|-------------------|---------------------------|-----------------|
| MeFuPAI | 0.19 | 0.18 | 1.00 | 1.05 | 6.3 ⋅ 10\textsuperscript{-7} | 20 | 0.29 |
| BeFuPAI | 0.28 | 0.20 | 0.38 | 0.85 | 1.2 ⋅ 10\textsuperscript{-7} | 20 | 0.44 |
| MeThPAI | 0.28 | 0.17 | 0.93 | 1.89 | 3.1 ⋅ 10\textsuperscript{-7} | 20 | 0.44 |

Simulation of internal conversion within the triplet state manifold

We find that RISC is more favorable to occur to the ¹LE state from the ³CT state than from the ³LE2 state (see Table 2 in the manuscript and Supplementary Table 5). Since the ³CT state is found to be higher in energy at the Franck-Condon point, we want to find out, if population transfer from the ³LE2 to the ³CT state may occur and if it is competitive to the transfer to the energetically lower ³LE1 state. Nonadiabatic dynamics simulations can be employed to elucidate this, but are also computationally elaborate, since many molecular dynamics trajectories need to be calculated.
In this work, we therefore use the ab initio floating occupation molecular orbital-complete active space configuration interaction (FOMO-CASCI) approach \(^{18}\) in combination with the spherical \(\text{def}_2\)-SV(P) \(^{19,20}\) basis set as implemented, including gradients \(^{21}\) and derivative coupling vectors, \(^{22}\) in the electronic structure program TeraChem.\(^{23}\) Here, the computationally expensive steps, i.e., the evaluation of two-electron integrals \(^{24,25}\) and the CASCI calculation \(^{26,27}\) are accelerated graphics processing units (GPUs). The FOMO-CASCI approach has been suggested as an efficient “one-shot” alternative to state-averaged complete active space self-consistent field (SA-CASSCF) calculations.\(^{18}\) Different from the latter, the orbitals in FOMO-CASCI are obtained from finite-temperature Hartree-Fock calculations enabling smearing of orbital populations, typically within the same active orbital space that is considered in the CASCI step. The electronic temperature is the key parameter of the method that is generally selected system specifically along with the respective active space. For our purpose, the relative state ordering and energetic splittings of the low-lying triplet states are important, and we find an active space of four electrons in six orbitals together with equal distribution of the active electrons in the active orbital space (i.e., infinite temperature smearing) to reproduce the relevant state orderings well. We refer to this approach as FOMO(\(\infty\))-CAS(4,6)CI/\(\text{def}_2\)-SV(P) in the following. We identify this approach to be very well-performing by comparison of the relative energies of the lowest three triplet states to the respective DFT-MRCI/TZVP energies each computed at the TDA-TDDFT-PBEh-3c-optimized geometries. The differences in relative triplet energies between both levels of theory are very small (root mean square deviation of 0.1 eV) and in no case exceed 0.3 eV.

The FOMO(\(\infty\))-CAS(4,6)CI/\(\text{def}_2\)-SV(P) electronic energies are furthermore augmented with a London-dispersion correction in the form of the pairwise D3(BJ) model \(^{8,10}\) (Hartree-Fock parametrization). Nonadiabatic dynamics simulations with this electronic structure approach are performed in the framework of ab initio multiple spawning (AIMS) as implemented in the FMS90 program.\(^{28-30}\) The AIMS method provides a semi-classical approximation to the nuclear wave packet by means of Gaussian basis functions traveling on a trajectory provided by the Born-Oppenheimer potential energy surface (termed trajectory basis functions or TBFs) of each electronic state. With this approach, we want to study the nonradiative spin-allowed population transfer starting from the \(^3\)LE2 state, but restrict this to the MeFuPAI, BeFuPAI, and MeThPAI systems.

To generate the initial conditions for the simulations, the \(S_0\) geometry is first reoptimized at the PBE0-D3(BJ)/\(\text{def}_2\)-TZVP(-f)-\(^{8,10,14,20,31,32}\) level with TeraChem and then the corresponding nuclear Hessian are calculated. Initial conditions, i.e., nuclear positions and velocities, are sampled from a harmonic Wigner distribution\(^{33}\) based on this Hessian. We chose the \(S_0\) state minima for generation of the initial conditions, because it best represents the points in phase space that are populated when being directly excited to the \(^3\)LE2 state such as in the electroluminescence experiment.

By monitoring the magnitudes of the FOMO(\(\infty\))-CAS(4,6)CI/\(\text{def}_2\)-SV(P) state dipole moments, we notice that the \(^3\)LE2 (dipole moment < 10 D) is not always lower than the \(^3\)CT state (dipole moment > 10 D) on some of the initial condition geometries. Instead a ratio of 57:33:10 (MeFuPAI), 61:27:12 (BeFuPAI), and 23:5:2 (MeThPAI) is observed. Here, the first value gives the counts among the initial condition geometries with \(^3\)LE2 being lower than \(^3\)CT, the second value indicating counts where the situation is reversed, and the last number corresponding to not clearly distinguishable situations. To estimate the situation in the photoluminescence experiment, we only consider initial conditions where the \(^3\)LE2 state is initially the lower one, i.e., the \(T_2\) state. In total, AIMS dynamics simulations based on 10 such initial conditions are carried out for each molecule. The TBFs are propagated using a 20 atomic unit (~0.5 fs) timestep, which is reduced to a timestep of 5 a.u. in regions of high nonadiabatic coupling. Due to the growing computational cost associated with running multiple trajectories after spawning events, we terminate the simulations at 120 fs (MeFuPAI), 90 fs (BeFuPAI), and 20 fs (MeThPAI). In the latter case, more than 60% of the population has decayed to the \(T_1\) (\(^3\)LE1) state, while for the furanyl systems, nearly all of the population remained on the \(^3\)LE2 with few population transfer events occurring mostly to the \(^3\)CT state (see Supplementary Figure 4). This is an indication that for these systems, decay to the \(^3\)LE1 state is unlikely and the systems can remain on the \(^3\)LE2 state for a substantial amount of time and eventually allowing population transfer to occur to the \(^3\)CT state from which RISC to the singlet manifold can occur efficiently (see Table 2 in the manuscript).
Supplementary Figure 4 | Development of the population distribution between T₁, T₂, T₃ where the T₂ state is initially the ³LE2 state. Population vs. time is shown for MeFuPAI (left), BeFuPAI (middle) and MeThPAI (right).

As mentioned above, a substantial number of initial condition geometries shows an inverted state ordering for the furanyl derivatives (37% and 31% for MeFuPAI and BeFuPAI, respectively). Particularly in the setting of an electroluminescence experiment, these initial conditions should also be accessible due to the high excess energy upon excitation. Using 10 of such initial conditions for each of the furanyl derivatives, we perform AIMS simulations for a duration of 15 fs. After this time, 80% of the original ³LE2 population has been transferred to the ³CT state. Hence, these points in phase space allow for increased population transfer to the ³CT state from which we expect the RISC to take place primarily. To obtain an approximated picture for electrical excitation, we use a combination of the previous simulations with the ³CT states having higher energy than the ³LE2 states and the inverted case. We calculate the respective weighted averages according to the distribution of both cases (57:33 for MeFuPAI and 61:27 for BeFuPAI).

To investigate the possible scenario that for MeFuPAI and BeFuPAI, the system might equilibrate to some extent on the T₂ (³LE2) state, we also consider minimum energy conical intersections (MECI) to. We find for MeFuPAI MECI(T₁/T₂) = 0.50 eV and MECI(T₂/T₃) = 0.32 eV relative to the respective T₂ minimum, and for BeFuPAI MECI(T₁/T₂) = 0.41 eV and MECI(T₂/T₃) = 0.42 eV. This indicates that population will reside on the T₂ for longer than a microsecond. At the same time, up-funneling to T₃ in MeFuPAI appears to be preferred, while a 1:1 ratio of up- (T₃) and down-funneled (T₁) states in BeFuPAI. These calculations were also performed at the FOMO(∞)-CAS(4,6)Cl/def2-SV(P) level in TeraChem.

Due to the small sample size and short time scales, our assessment is, of course, only qualitative. However, taken together the AIMS simulation results, we could collect more support for the hypotheses that, at least for the furanyl derivatives, internal conversion from the ³LE2 to the ³LE1 state is unlikely and instead, population transfer to the ³CT can take place.

Supplementary Table 6 | Electronic energies (in Hartree) for the T₂ minima and MECIs computed at the FOMO(∞)-CAS(4,6)Cl/def2-SV(P) level (including D3(BJ) dispersion energies. Relative energies in eV are given in parentheses.

|            | T₂ minimum       | T₁/T₂ MECI       | T₁/T₃,MECI minimum |
|------------|------------------|------------------|-------------------|
| MeFuPAI    | -1444.34161      | -1444.32328 (0.50 eV) | -1444.32993 (0.32 eV) |
| BeFuPAI    | -1557.91361      | -1557.90355 (0.41 eV) | -1557.90334 (0.42 eV) |
Electroluminescence

Supplementary Figure 5: Photoluminescence and electroluminescence spectra of MeFuPAI (a) and BeFuPAI (b) OLEDs at different current densities.

Supplementary Figure 6: Transient electroluminescence spectra of MeFuPAI (a) and BeFuPAI (b) OLEDs at different current densities.

Calculation of \( I_{\text{HE}} \)

The following formula gives the ratio of emission intensity of populated triplet to singlet states, which often is synonymous with the intensity-ratio of the prompt and delayed emission components.

\[
\frac{I_T}{I_S} = 4\eta_r - 1
\]

However, in our case, hot exciplex emission (\( I_{\text{HE}} \)) originating from triplets can be assigned to the prompt component:

\[
I_S + I_{\text{HE}} = I_{\text{pr}}
\]

\[
I_T = I_{\text{HE}} + I_{\text{TTA-UC}}
\]

\[
I_{\text{TTA-UC}} = I_{\text{del}}
\]

Inserting into the previous equation yields an expression for \( I_{\text{HE}} \):

\[
I_{\text{HE}} = \frac{I_{\text{pr}}(4\eta_r - 1)}{4\eta_r} - \frac{I_{\text{del}}}{4\eta_r}
\]

Normalizing the delayed and prompt components to unity:

\[
I_{\text{del}} = 1 - I_{\text{pr}}
\]

yields the simplified equation:
\[ I_{HE} = I_{pr} - \frac{1}{4\eta_r} \]

Normalizing the equation for transient EL analysis to unity, as well, allows expression of \( I_{pr} \) depending only on \( \eta_r \) (subscript transEL added for clarification of the \( \eta \) origin):

\[ I_{pr} = \frac{1}{4\eta_r, \text{transEL}} \]

Inserting into the previous, simplified equation for \( I_{HE} \) yields the final equation (subscript EQE added for clarification of the \( \eta \) origin):

\[ I_{HE} = \frac{1}{4\eta_r, \text{transEL}} - \frac{1}{4\eta_r, \text{EQE}} \]

## Experiments

### Materials

All reagents and solvents were purchased from commercial suppliers (abcr, TCI, Sigma Aldrich, VWR) and used without further purification.

### Synthetic Procedures

#### 1,8-Dibromoanthraquinone (2)

Under stirring with a mechanical stirrer, a suspension of 1 (150 g, 541 mmol), KBr (300 g, 2.52 mol), and CuCl\(_2\) (20.0 g, 149 mmol) in nitrobenzene (1 L) and phosphoric acid (85 wt\% in H\(_2\)O, 200 mL) is heated up to 200 °C. After all water has been evaporated and the reaction temperature has been reached, the reaction is stirred for 36 h at 200 °C. The dark green suspension is poured into methanol (5L). The resulting brown precipitate is isolated by filtration and washed with methanol (500 mL) and water (1L) to remove generated KCl. The crude product is re-dissolved in nitrobenzene (738 ml) and phosphoric acid (148 mL), and KBr (222 g, 1.86 mol) and CuCl\(_2\) (14.5 g, 108 mmol) is added. The reaction mixture is stirred at 200 °C for 20 h and then worked up as before, to give 1,8-dibromanthraquinon (2, 109 g, 298 mmol, 55 \%) as brown solid. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 8.25 (dd, \( J_{H,H} = 7.8 \text{ Hz} \), \( J_{H,H} = 1.2 \text{ Hz} \), 2H), 8.03 (dd, \( J_{H,H} = 7.9 \text{ Hz} \), \( J_{H,H} = 1.2 \text{ Hz} \), 2H), 7.55 (dd, \( J_{H,H} = 7.9 \text{ Hz} \), \( J_{H,H} = 7.8 \text{ Hz} \), 2H). APCI-MS (pos.): [M] = C\(_{14}\)H\(_8\)Br\(_2\)O\(_2\), experimental m/z = 366.8795 (found [M+H\(^+\)]), calculated m/z = 366.8792.

#### 1,8-Dibromo-10-anthrone (3)

Under stirring at -78 °C, NaBH\(_4\) (41.4 g, 1.09 mol) is added in portions to a solution of 2 (50.0 g, 137 mmol) in methanol (1.5 L). The reaction is kept at this temperature for three hours, and then concentrated HCl (150 mL) is added, and the reaction mixture is stirred for 16 hours under reflux. The resulting precipitate is filtered, washed with water (500 mL), dissolved in methanol (1.5 L), and cooled to -78 °C. NaBH\(_4\) (41.4 g, 1.09 mol) is added and the reaction mixture is stirred for 2 hours at -78 °C. Then, concentrated HCl (150 mL) is added and the reaction mixture is refluxed for 1 h. The precipitate is filtered, washed with water (500 mL) and purified by column chromatography (SiO\(_2\), hexane/DCM 10:1 \( \rightarrow \) 1:1) to give 3 (20.9 g, 59.4 mmol, 43 \%) as yellow solid. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 8.34 (dd, \( J_{H,H} = 7.9 \text{ Hz} \), \( J_{H,H} = 1.3 \text{ Hz} \), 2H), 7.90 (dd, \( J_{H,H} = 7.8 \text{ Hz} \), \( J_{H,H} = 1.3 \text{ Hz} \), 2H), 7.40 (dd, \( J_{H,H} = 7.9 \text{ Hz} \), \( J_{H,H} = 7.8 \text{ Hz} \), 2H), 4.19 (s, 2H). MALDI-MS (DCTB, pos.): [M] = C\(_{14}\)H\(_8\)Br\(_2\)O, experimental m/z = 351.8915 (found [M\(^+\)]), calculated m/z = 351.8921.

#### 1,8-Dibromo-10-phenylanthrone (4)

Under argon, a solution of 3 (20.0 g, 53.8 mmol) in anhydrous toluene (200 mL) is prepared in a heated Schlenk flask and cooled to -78 °C. A solution of phenyl lithium (1.9 M in dibutyl ether, 29.9 mL, 56.8 mmol) is added dropwise under stirring, and the reaction mixture is allowed to slowly warm up to
room temperature. After stirring for 20 h, concentrated HCl (50 mL) is added, and the reaction mixture is stirred under reflux for 3 h. The organic material is extracted with toluene (3x 200 mL) and dried over Na₂SO₄. After the solvent is removed under reduced pressure, the crude product is purified by column chromatography (SiO₂, hexane) to give 4 (16.2 g, 39.1 mmol, 69 %) as yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 9.37 (s, 1H), 7.85 (d, J_HH = 7.1 Hz, 2H), 7.62-7.55 (m, 5H), 7.39-7.36 (m, 2H) 7.21 (dd, J_HH = 8.8 Hz, J_HH = 7.1 Hz, 2H). APCI-MS (pos.): [M] = C₂₅H₁₂Br₂, experimental m/z = 419.9299 (found [M⁺]), calculated m/z = 419.9285.

General procedure for Suzuki coupling reactions

A sealed vial equipped with a magnetic stirring bar, K₃PO₄ (2.0 eq), Pd₂(dba)₃ (0.015 eq), P(o-tol)₃ (0.12 eq), anthracene compound 4-8 (1.0 eq), and the boronic acid (pinacol ester) (1.0/1.05 eq) is evacuated and charged with argon three times. Then, a solvent mixture from water, 1,4-dioxane, and toluene (1/5/1.8) is added, and the reaction mixture is degassed by bubbling with argon for 10 minutes. The reaction is stirred at 60 °C for 24 h and subsequently diluted with water. The diluted mixture is extracted with chloroform (3x 25 mL), and the combined organic extracts are dried over Na₂SO₄. After the solvent has been removed under reduced pressure, the crude product is purified via column chromatography over silica to obtain the desired compound.

2-(8-Bromo-10-phenylanthracen-1-yl)-5-methylfuran (5)

The reaction between K₃PO₄ (1.29 g, 6.07 mmol), Pd₂(dba)₃ (41.7 mg, 45.5 µmol), P(o-tol)₃ (111 mg, 364 µmol), 4 (1.25 g, 3.03 mmol), and 5-methylfurfurylboronic acid pinacol ester (619 mg, 3.03 mmol) is carried out in 60 mL solvent according to the general procedure. After column chromatography (SiO₂, hexane/DCM 1:0 → 9:1), 5 (480 mg, 1.16 mmol, 38 %) is obtained as yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 9.65 (s, 1H), 7.80-7.78 (m, 2H), 7.61-7.54 (m, 5H), 7.42-7.40 (m, 3H), 7.17 (dd, J_HH = 8.8 Hz, J_HH = 7.1 Hz, 1H), 6.90 (d, J_HH = 3.1 Hz, 1H), 6.29-6.28 (m, 1H), 2.52 (s, 3H). MALDI-MS (pos.): [M] = C₂₅H₁₂BrO, experimental m/z = 412.0451 (found [M(⁷⁹Br)⁺]), calculated m/z = 412.0463.

2-(8-Bromo-10-phenylanthracen-1-yl)benzofuran (6)

The reaction between K₃PO₄ (1.29 g, 6.07 mmol), Pd₂(dba)₃ (41.7 mg, 45.5 µmol), P(o-tol)₃ (111 mg, 364 µmol), 4 (1.25 g, 3.03 mmol), and 2-benzofuranylboronic acid (491 mg, 3.03 mmol) is carried out in 60 mL solvent according to the general procedure. After column chromatography (SiO₂, hexane/DCM 1:0 → 9:1), 6 (471 mg, 1.05 mmol, 35 %) is obtained as yellow oil. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 9.70 (s, 1H), 8.00 (d, 1H), 7.82 (d, J_HH = 7.1 Hz, 1H), 7.76 (d, J_HH = 7.6 Hz, 1H), 7.71 (d, J_HH = 8.9 Hz, 1H), 7.67 (d, J_HH = 8.0 Hz, 1H), 7.64-7.56 (m, 4H), 7.47 (dd, J_HH = 8.9 Hz, J_HH = 6.9 Hz 1H), 7.44-7.42 (m, 2H), 7.40-7.32 (m, 3H), 7.20 (dd, J_HH = 8.8 Hz, J_HH = 7.1 Hz, 1H). MALDI-MS (pos.): [M] = C₂₅H₁₂BrO, experimental m/z = 450.0435 (found [M(⁸⁰Br)⁺]), calculated m/z = 450.0442.

2-(Bromo-10-phenylanthracen-1-yl)-5-methylthiophene (7)

The reaction between K₃PO₄ (1.29 g, 6.07 mmol), Pd₂(dba)₃ (41.7 mg, 45.5 µmol), P(o-tol)₃ (111 mg, 364 µmol), 4 (1.25 g, 3.03 mmol), and 5-methylthiophene-2-boronic acid pinacol ester (668 mg, 3.03 mmol) is carried out in 60 mL solvent according to the general procedure. After column chromatography (SiO₂, hexane/DCM 1:0 → 9:1), 7 (520 mg, 1.21 mmol, 40 %) is obtained as yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 9.50 (s, 1H), 7.77 (d, J_HH = 7.1 Hz, 1H), 7.62-7.55 (m, 6H), 7.42-7.36 (m, 3H), 7.28 (d, J_HH = 3.4 Hz, 1H), 7.16 (dd, J_HH = 8.8 Hz, J_HH = 7.1 Hz, 1H), 6.95-6.94 (m, 1H), 2.63 (s, 3H). MALDI-MS (pos.): [M] = C₂₅H₁₂BrS, experimental m/z = 428.0222 (found [M(⁸⁰Br)⁺]), calculated m/z = 428.0234.

2-(8-Bromo-10-phenylanthracen-1-yl)benzo[b]thiophene (8)

The reaction between K₃PO₄ (1.29 g, 6.07 mmol), Pd₂(dba)₃ (41.7 mg, 45.5 µmol), P(o-tol)₃ (111 mg, 364 µmol), 4 (1.25 g, 3.03 mmol), and benzo[b]thien-2-ylboronic acid (540 mg, 3.03 mmol) is carried out in 60 mL solvent according to the general procedure. After column chromatography (SiO₂,
hexane/DCM 1:0 → 9:1), 8 (151 mg, 324 µmol, 11 %) is obtained as yellow solid. 1H-NMR (400 MHz, CDCl3): δ [ppm] = 9.54 (s, 1H), 7.97-7.93 (m, 1H), 7.78 (d, J_HH = 7.1 Hz, 1H), 7.72-7.68 (m, 2H), 7.63-7.58 (m, 3H), 7.46-7.41 (m, 4H), 7.18 (dd, J_HH = 8.9 Hz, J_HH = 7.1 Hz 1H), 7.09-7.06 (m, 2H) 6.74-6.71 (m, 2H). MALDI-MS (pos.): [M] = C_{26}H_{27}BrS, experimental m/z = 464.0226 (found [M(^{79}Br)^+]), calculated m/z = 464.0234.

5-(8-(5-Methylfuran-2-yl)-10-phenylanthracen-1-yl)isophthalonitrile (MeFuPAI)

The reaction between K$_2$PO$_4$ (493 mg, 2.32 mmol), Pd$_2$(dba)$_3$ (16.0 mg, 17.4 µmol), P(o-tol)$_3$ (42.4 mg, 139 µmol), 5 (480 mg, 1.16 mmol), and 5-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)isophthalonitrile (310 mg, 1.22 mmol) is carried out in 50 mL solvent according to the general procedure. After column chromatography (SiO$_2$, hexane/DCM 1:1 → 0:1), MeFuPAI (377 mg, 819 µmol, 71 %) is obtained as yellow solid. 1H-NMR (400 MHz, CDCl3): δ [ppm] = 8.90 (s, 1H), 8.14 (d, J_HH = 1.6 Hz, 2H), 8.05 (t, J_HH = 1.6 Hz, 1H), 7.76 (d, J_HH = 8.8 Hz, 1H), 7.71 (d, J_HH = 6.7 Hz, 1H), 7.64-7.58 (m, 4H), 7.46-7.36 (m, 5H), 6.50 (d, J_HH = 3.2 Hz, 1H), 6.19-6.18 (m, 1H), 2.35 (s, 3H). MALDI-MS (pos.): [M] = C_{34}H_{33}N$_2$O, experimental m/z = 460.1562 (found [M^+]$^+$), calculated m/z = 460.1576.

5-(8-(Benzofuran-2-yl)-10-phenylanthracen-1-yl)isophthalonitrile (BeFuPAI)

The reaction between K$_2$PO$_4$ (445 mg, 2.10 mmol), Pd$_2$(dba)$_3$ (9.6 mg, 10.5 µmol), P(o-tol)$_3$ (38.3 mg, 126 µmol), 6 (471 mg, 1.05 mmol), and 5-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)isophthalonitrile (280 mg, 1.10 mmol) is carried out in 50 mL solvent according to the general procedure. After column chromatography (SiO$_2$, hexane/DCM 1:1 → 0:1), BeFuPAI (379 mg, 763 µmol, 73 %) is obtained as yellow solid. 1H-NMR (400 MHz, CDCl3): δ [ppm] = 8.86 (s, 1H), 8.15 (d, J_HH = 1.5 Hz, 2H), 7.96 (t, J_HH = 1.5 Hz, 1H), 7.90-7.88 (m, 1H), 7.79-7.74 (m, 3H), 7.66-7.56 (m, 4H), 7.49-7.43 (m, 4H), 7.41-7.31 (m, 3H), 6.99 (s, 1H). MALDI-MS (DCTB, pos.): [M] = C_{30}H_{29}N$_2$O, experimental m/z = 496.1567 (found [M^+]$^+$), calculated m/z = 496.1576.

5-(8-(5-Methylthiophen-2-yl)-10-phenylanthracen-1-yl)isophthalonitrile (MeThPAI)

The reaction between K$_2$PO$_4$ (583 mg, 2.75 mmol), Pd$_2$(dba)$_3$ (18.9 mg, 17.4 µmol), P(o-tol)$_3$ (50.2 mg, 165 µmol), 7 (590 mg, 1.37 mmol), and 5-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)isophthalonitrile (367 mg, 1.44 mmol) is carried out in 50 mL solvent according to the general procedure. After column chromatography (SiO$_2$, hexane/DCM 1:1 → 0:1), MeThPAI (430 mg, 902 µmol, 66 %) is obtained as yellow solid. 1H-NMR (400 MHz, CDCl3): δ [ppm] = 8.81 (s, 1H), 8.14 (d, J_HH = 1.5 Hz, 2H), 8.00 (t, J_HH = 1.5 Hz, 1H), 7.77 (d, J_HH = 8.3 Hz, 1H), 7.67-7.55 (m, 5H), 7.46-7.38 (5H), 7.02 (d, J_HH = 3.4 Hz, 1H), 6.87-6.86 (m, 1H), 2.62 (s, 3H). MALDI-MS (DCTB, pos.): [M] = C_{33}H_{30}N$_2$S, experimental m/z = 476.1333 (found [M^+]$^+$), calculated m/z = 476.1347.

5-(8-(Benzothiophen-2-yl)-10-phenylanthracen-1-yl)isophthalonitrile (BeThPAI)

The reaction between K$_2$PO$_4$ (138 mg, 649 µmol), Pd$_2$(dba)$_3$ (4.5 mg, 4.9 µmol), P(o-tol)$_3$ (11.9 mg, 38.9 µmol), 8 (151 mg, 324 µmol), and 5-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)isophthalonitrile (86.6 mg, 341 µmol) is carried out in 15 mL solvent according to the general procedure. After column chromatography (SiO$_2$, hexane/DCM 1:1 → 0:1), BeThPAI (82.2 mg, 160 µmol, 49 %) is obtained as yellow solid. 1H-NMR (400 MHz, CDCl3): δ [ppm] = 8.80 (s, 1H), 8.13 (d, J_HH = 1.6 Hz, 2H), 8.09-8.07 (m, 1H), 7.90-7.88 (m, 1H), 7.85 (t, J_HH = 1.5 Hz, 1H), 7.79 (d, J_HH = 8.6 Hz, 1H), 7.74 (d, J_HH = 8.8 Hz, 1H), 7.69 (dd, J_HH = 8.6 Hz, J_HH = 1.2 Hz, 1H), 7.66-7.60 (m, 3H), 7.48-7.39 (m, 8H). MALDI-MS (DCTB, pos.): [M] = C_{33}H_{28}N$_2$S, experimental m/z = 512.1339 (found [M^+]$^+$), calculated m/z = 512.1347.

**Optical Spectroscopy**

UV/Vis absorption spectroscopy was carried out on a PerkinElmer Lambda 365 Spectrophotometer. Photoluminescence spectra were recorded on a PerkinElmer FL 6500 Fluorescence Spectrophotometer. Time correlated single photon counting (TCSPC) experiments were conducted between 411 nm and 693 nm on a setup containing a BDS-375-SM-FBE picosecond diode laser (375 nm excitation...
wavelength) and a PMC-100-4 photomultiplier tube (both from Becker&Hickl), a sCMOS Zyla sensor, and a SR-303i-B spectrograph (both from Andor Technology).

Device Fabrication

OLEDs were fabricated by vacuum deposition on ITO-coated glass substrates under a pressure of less than 5.0 × 10⁻⁴ Pa. Organic layers were deposited at a deposition rate of 0.05 nm/s through a metal mask. After deposition, the metal mask was replaced with another metal mask for cathode deposition in a nitrogen-filled glove box. The 8-quinolinolato lithium (Liq) and Al electrodes were deposited on the organic layers at deposition rates of 0.02 nm/s for Liq and 0.05–0.2 nm/s for Al. The device structure is ITO (100 nm)/HAT-CN (10 nm)/Tris-PCz (30 nm)/PAI (20 nm)/TmPyPB (40 nm)/Liq (4 nm)/Al (70 nm), where HAT-CN is hexaazatriphenylenehexacarbonitrile, Tris-PCz is 9,9′-diphenyl-6-(9-phenyl-9H-carbazol-3-yl)-9H,9′H-3,3′-bicarbazole, and TmPyPB is 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene.

Electroluminescence spectroscopy

EL spectra, and external EL quantum efficiency–current density characteristics were measured using an absolute EQE measurement system (C9920-12, Hamamatsu Photonics, Japan). Transient EL characteristics under pulse excitation with a pulse width of 100 µs were measured using a streak camera (C4334, Hamamatsu Photonics, Japan).
**Supplementary Figure 7**: $^1$H-NMR spectra of 5 in CDCl$_3$.

Supplementary Figure 8: $^1$H-NMR spectra of 6 in CDCl$_3$. The compound can be used for the subsequent reaction, despite minor impurities (*).
Supplementary Figure 9: $^1$H-NMR spectra of 7 in CDCl$_3$.

Supplementary Figure 10: $^1$H-NMR spectra of 8 in CDCl$_3$. The compound can be used in the subsequent reaction, despite impurities indicated by signals between 7 and 8 ppm.
Supplementary Figure 11: $^1$H-NMR spectra of MeFuPAI in CDCl$_3$.

Supplementary Figure 12: $^1$H-NMR spectra of BeFuPAI in CDCl$_3$. 
Supplementary Figure 13: $^1$H-NMR spectra of MeThPAI in CDCl$_3$.

Supplementary Figure 14: $^1$H-NMR spectra of BeThPAI in CDCl$_3$. 
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