The Critical Role of nπ* States in the Photophysics and Thermally Activated Delayed Fluorescence of Spiro Acridine-Anthracenone

Larissa Gomes Franca, Yun Long, Chunyong Li, Andrew Danos, and Andrew Monkman*

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ABSTRACT: The molecular photophysics and thermally activated delayed fluorescence (TADF) in spiro compounds are distinct because of the rigid orthogonal C–C bridging bond between donor and acceptor. The photophysics is found to be highly complex, with unprecedented multiple anti-Kasha emissions from three different singlet states, two of which are one-photon forbidden. The TADF mechanism is critically controlled by local acceptor nπ* states; the singlet nπ* state undergoes rapid intersystem crossing populating an energetically close acceptor ππ* triplet state. The acceptor triplet nπ* state couples nonadiabatically to a CT triplet state mediating reverse intersystem crossing. When the nπ* and CT states are energetically close, TADF is greatly enhanced with rISC rate reaching 10^7 s⁻¹. We observe neither DF from the singlet nπ* state nor electron transfer (ET) to form the 1CT because there is no ET driving force; however, ET from the higher-energy donor singlet ππ* state readily occurs along with donor emission.

Organic light-emitting diodes (OLEDs) now underpin a large section of the display market because of their many appealing characteristics, including being high efficiency, flexible, and solution processable, and their ability to be fabricated on low-cost substrates.1–4 Development of suitable emitters for OLEDs is fundamental in increasing their output efficiency and optimizing device performance. One of the key requirements is an emitter that utilizes triplet excited states to maximize the achievable internal quantum efficiency close to 100%. Phosphorescent materials currently used in OLED displays have provided one route, using heavy-metal-containing organic complexes to facilitate spin–orbit coupling and efficient spin-mixing to give efficient phosphorescence.5,6 In addition, nonradiative decay of triplet excitons formed in the emission layer host material can be suppressed by ensuring that the triplet energy of the host is higher than that of the phosphorescent emitter.7

An alternative method for harvesting triplet states, thermally activated delayed fluorescence (TADF), has attracted tremendous interest for OLED applications by providing a means of harvesting triplet excitons without the need for rare and expensive heavy metals.8,9 Thermal activation of triplet excitons causes them to undergo reverse intersystem crossing (rISC) back to the singlet manifold, producing delayed fluorescence. To achieve efficient rISC, TADF molecules must meet several key criteria, starting with a small S₁−T₁ energy gap, ΔE_{ST}. One way to achieve this is through a lowest-energy excited state of charge-transfer (CT) character. Charge-transfer states achieve effective separation of electron and hole wave functions and small associated ΔE_{ST} values, either by possessing structurally orthogonal D and A moieties (decoupling their individual electronic systems) or through a large spatial separation of D and A fragments (e.g., in exciplexes).10 Either approach results in minimal electron exchange interaction energy and a very small ΔE_{ST}, frequently <50 meV.11–13 However, when the electron exchange energy is so small, the singlet (1CT) and triplet (3CT) orbitals become degenerate and transition between the two is spin-forbidden as no change in orbital angular momentum can occur.14 To facilitate TADF a third triplet excited state, very close in energy to the 3CT state but having different orbital character, is required to mix (nonadiabatically) with 3CT to mediate a spin flip and couple the triplet back to the singlet manifold. This can be either a local triplet state (3LE) or a higher-lying triplet CT state.15

An orthogonal N–C donor–acceptor bridge is typically used in TADF materials to give the appropriate energy level ordering, but such bonding is not a prerequisite for TADF.16–18 While only a few examples have been reported, in spiro-linked D–A molecules the rigid and orthogonal donor–acceptor C–C bridge can yield efficient rISC.19–21 This is very important as a bridging C–N bond between D and A in a typical D–A TADF material is considered to be a very weak bond, prone to degradation. This is one of the suspected main causes of the short lifetimes achievable by TADF emitters.
in devices. Moving away from this architecture, to a spiro system for example, could greatly enhance emitter lifetime, and this provides a very compelling motivation for these studies to provide a better understanding of spiro TADF emitters.

The spiro-linked acridine anthracenone derivative 10-phenyl-10H,10’H–spiro[acridine-9,9’-anthracene]-10’-one (ACRSA, Scheme 1) was one of the first reported spiro-linked TADF materials. It showed efficient solution-state photoluminescence (PL efficiency of 81%), with similar performance (∼75%) doped in the OLED host bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) leading to moderately high device EQE of 16.5% in the same host.22,23 The generally moderate (but never outstanding) device performances reported for spiro-linked TADF materials (compared with up to 25% EQE in C–N linked D–A molecules) suggest a different photophysics and/or rISC mechanism may be active in the presence of the C–C spiro-bridge, warranting further investigation.

Lykov and Marian have recently presented a very detailed quantum chemistry analysis of the ACRSA molecule. They highlight the complex interactions between charge transfer and local states, the role of state mixing (with high-lying excitonic states of A1 to A2 symmetry) in overcoming the forbidden nature of radiative decay from these states, and the potential for rapid nanosecond rISC mediated by n–π* decay from these states, and the potential for rapid nanosecond local states, the role of state mixing (with high-lying excitonic states) and the potential for rapid nanosecond decay channels reconfigured by the positive solvatochromic shift character is confirmed by the positive solvatochromic shift observed in this absorption band (Supporting Figure S3).

As both the emission of the 1LE0 ππ* state and a portion of the 1CT emission are not fully quenched by oxygen, this indicates that the exciton can undergo electron transfer yielding the 1CT state directly. High-energy triplet states formed by electron transfer and additionally by ISC from the 1LE0 ππ* state will cascade down to the lowest-energy triplet state—which can be harvested to give oxygen-sensitive TADF emission.

The relative yields of each emissive state for different excitation wavelengths are shown in Figure 2. Excitation of the solution below the onset of the 1LE1 transition (>350 nm, 3.54 eV, Figure 1b,c) reveals emission from another new structured fluorescence (DF) component that otherwise dominates the total emission. The reduced 1CT emission in aerated solution allows us to additionally detect the presence of a further high-energy emission band (onset, 3.7 eV). Upon comparing this emission to that previously observed in acridine14 it is clear that this emission emanates from the acridine 1LE0 ππ* state (1B1 in Supporting Scheme 1 and Figure S2). The fast radiative decay of this 1LE0 excitonic state competes effectively with internal conversion (IC), electron transfer, and intersystem crossing (ISC) nonradiative decay channels. The ππ* character is confirmed by the positive solvatochromic shift observed in this absorption band (Supporting Figure S3).

As we observe emission from both 1LE1 and 1CT in aerated solution (380 nm excitation, well below the absorption tail of the 1LE0 excitonic state), we must conclude that both states are directly populated, yielding prompt emission. Calculation of oxygen-quenched delayed CT emission contribution (Supporting Figure S4) shows that direct 1CT absorption is more efficient at populating the 1CT state than ET from the 1LE0 exciton; 330 nm gives a PF/DF ratio of 6.8%, while at 380 nm PF/DF increases to 11.1% (lower triplet yield so lower DF). From the strong DF component we infer that the 1CT–3CT energy gap (11A2−11A1 gap, Supporting Scheme 1)
must be small, indicating very low electron exchange energy from near degenerate orbitals. Consequently, ISC between \(^1\)CT and \(^3\)CT will be forbidden\(^{14,26}\) and the strong DF CT emission observed when exciting at \(\geq 350\) nm can arise only through the photoexcited \(^1\)LE\(\alpha\) state forming a large triplet population by ISC. Such efficient quenching by ISC resulting in a large \(^3\)CT population and strong DF—fully supports the proposal made by Lyskov and Marian\(^{24}\) that the \(^1\)LE\(\alpha\) n\(\pi^*\) state couples strongly to a \(^1\)LE\(\alpha\) n\(\pi^*\) triplet state (\(^1\)A\(_1\), Supporting Scheme 1) in competition with radiative decay.

These interpretations are further supported by excitation profiles measured at different emission collection wavelengths (Figure 3 and Supporting Figure S5). Monitoring emission from the \(^1\)CT state (at 515 and 600 nm), we observe emission arising from excitation of both the \(^1\)LE\(\alpha\) state (at \(<350\) nm) and a second CT transition (at \(\sim 400\) nm). Again, the CT emission is dominated by DF (degassed conditions), which is thoroughly quenched in aerated measurements. Monitoring at 412 nm (the peak of the \(^1\)LE\(\alpha\) n\(\pi^*\) emission), excitation into the \(^1\)LE\(\alpha\) n\(\pi^*\) state gives weak emission, which indicates active ISC from \(^1\)LE\(\alpha\) n\(\pi^*\) to \(^1\)LE\(\alpha\) n\(\pi^*\). Much stronger \(^1\)LE\(\alpha\) n\(\pi^*\) emission is observed with excitation in the \(350\)–\(400\) nm range, resulting from direct \(^1\)LE\(\alpha\) n\(\pi^*\) excitation. The \(^1\)LE\(\alpha\) n\(\pi^*\) emission increases slightly on degassing, probably from enhancement of underlying delayed CT emission (with direct absorption from 350 to 415 nm). Excitation at wavelengths \(>425\) nm yields no \(^1\)LE\(\alpha\) n\(\pi^*\) emission, although we do observe weak CT emission (Supporting Figure S6), indicating that the onset of direct CT absorption is at lower energy than the \(^1\)LE\(\alpha\) n\(\pi^*\) state. These excitation measurements demonstrate that excitation of the high-energy \(^1\)LE\(\alpha\) state gives rise to emission from three singlet excited states simultaneously: \(^1\)LE\(\alpha\) exciton, \(^1\)LE\(\alpha\) n\(\pi^*\), and \(^1\)CT. While dual-emission TADF and room-temperature phosphorescent (RTP) materials are now frequently reported,\(^{27–30}\) extreme anti-Kasha behavior such that a molecule is capable of emitting from three singlet excited states (\(^1\)LE\(\alpha\) exciton, \(^1\)LE\(\alpha\) n\(\pi^*\), and \(^1\)CT) simultaneously is exceedingly rare. We believe this is the first report of concurrent triple-pathway singlet emission from a single molecule.

Extending to solvents of different polarity, Figure 4 shows the emission spectra of ACRSA in MCH, toluene, and DCM (aerated and degassed) at different excitation wavelengths. Supporting Figure S7 directly compares emission between excitation at 330 and 380 nm in each solvent for additional clarity. In MCH and DCM, the same general trends are observed as in toluene. However, the structured emission from the \(^1\)LE\(\alpha\) n\(\pi^*\) state is clearly not affected by polarity (Supporting Figure S8). In MCH the \(^1\)CT emission is only
very weakly stabilized, lies underneath the local \(^1\text{LE}_D\) \(\pi^*\) emission, but is readily distinguished by the strong CT emission observed with 330 nm excitation (into the \(^1\text{LE}_A\) state). The appearance of the structured local emission increasing on removal of oxygen is in fact due to this underlying CT emission increasing (Supporting Figure S9). This is confirmed by the apparent relative decrease in local emission on degassing in DCM, where the CT band is red-shifted out from underneath the local emission band (but still partially overlapping) such that the true behavior of the local transition can been seen clearly.

It is interesting to compare this general emission behavior of ACRSA to its separate acridine donor and anthracenone acceptor units. Acridine emits at 337 nm (Supporting Figure S2), whereas anthracenone (or anthrone) is reported as nonemissive. However, Fujii et al. also report that the tautomeric form of anthrone, 9-anthrol, is emissive. In benzene the spectra are almost identical to the ACRSA emission in MCH: well structured with similar vibronic contributions. Moreover, 9-anthrol in strongly basic solvents (NaOH) emits with a broad Gaussian band, centered at ca. 550 nm, very similar to ACRSA in toluene. This shows that charge transfer is...
efficient in ACRSA and that even in the excited state, the D and A units are strongly decoupled. It may also highlight the mixed nature of the excited states (local and CT) and also possible similarities between the excited-state structure of the A unit in ACRSA and that of 9-anthrol. However, this cannot come from such a tautomeric form as proton transfer is impossible for the anthracenone unit that is spiro linked to the acridine in ACRSA.

We observe the largest 1CT DF emission contribution in toluene (Supporting Figures S10 and 11). The oxygen-dependent spectra in MCH and DCM (Supporting Figure S12) show that exciting into the 1LEA state leads to an oxygen-dependent CT population (DF increasing by a factor 4 in MCH and 2 in DCM), whereas via direct excitation the increase in CT emission is only a factor of 2 in MCH and DCM. This clearly indicates that 1CT is populated significantly through the triplet manifold and most efficiently via the 1LEA state.

Time-resolved emission was measured following excitation at both 337 and 355 nm (Figure 5), starting with (degassed) toluene solution. The 337 nm pulses excite the 1LEA excitonic state and produce rapidly decaying emission from this state at 370 nm, within the time response of the laser/iCCD system (<1 ns). 1CT emission is also observed in the earliest spectrum (2 ns), indicating an ET rate (estimated at $10^8-10^9$ s$^{-1}$) that does not out-compete radiative decay and IC of the 1LEA state.

Figure 5. Area-normalized time-resolved emission decay of ACRSA in degassed MCH (a), toluene (b), and DCM (c) solutions (50 μM) excited at 337 nm into the 1B1 exciton transition and at 355 nm into the direct mixed 2A2 and 1A2 transitions (d–f). Poor solubility in MCH leads to the observed emission from dimer/excimer states at long wavelengths. A corresponding set of peak normalized spectra are given in Supporting Figure S13.

Figure 6. Emission decay kinetics for ACRSA in MCH (a), toluene (b), and DCM (c) (50 μM) as a function of excitation wavelength. Three main kinetic decay regions can be defined for (i) fast 1LEA state decay, (ii) slow prompt 1CT decay, and (iii) delayed 1CT decay. Panels d, e, and f show the effect of oxygen quenching on the kinetic decays (in aerated solvents).
population. In contrast, excitation at 355 nm directly into the rates of 5.29 × 10^5 and 6.2 × 10^5 s⁻¹, respectively, with all kinetic data summarized in Supporting Table 1. Isoemissive points in the time-resolved area-normalized emission spectra (Figure 5) indicate that the 1LEA nπ* and 1CT states decay independently of each other, consistent with simultaneous photoexcitation but no IC, electron or energy transfer, or vibronic coupling between them. This all indicates very slow radiative decay rates from the CT state consistent with a forbidden transition. This slow decay also demonstrates that ISC to the isoenergetic 2CT is highly forbidden, as there are no close-lying local triplet states to mediate ISC to the 3CT. Nonradiative decay must also be strongly suppressed, indicating few coupling vibrational modes to mediate IC.

In DCM excitation at both 337 and 355 nm photoexcites a much larger initial 1LEA population than in toluene, which is not well-structured (in line with the steady-state measurements). The 1LEA emission also persists for longer, 10 and 16 ns, respectively. This increase in lifetime reflects a potential blue shift of the 1LEA nπ* and red shift of 3LEA nπ* with increasing solvent polarity, reducing the ISC rate between them. The total emission intensity is however much lower in DCM than in either toluene or MCH, which may result from increased nonradiative quenching of the lower-energy 1CT and 3CT states (energy gap law). In comparison with the decay kinetics in toluene (Figure 6), at 355 nm excitation the prompt 1CT state decays much more rapidly than in toluene (91 ± 3 ns). The DF component in DCM dominates emission after 300 ns (lifetime 2.38 ± 0.06 μs) and has a slower ISC rate (1.18 × 10^5 s⁻¹) than in toluene. The rISC rate is also slower at 4.83 × 10^5 s⁻¹. The CT triplet state involved in rISC, which relaxes in energy with increasing polarity, must therefore open up the gap between itself and the TADF-mediating local triplet state, reducing the rate of rISC and thus DF contribution in polar DCM. In toluene the DF is much stronger but the rISC rate is similar, again indicative of the lower-energy DCM CT states experiencing increased nonradiative decay (energy gap law). The faster radiative decay rates calculated in DCM compared to toluene coupled with the lower overall emission intensity is also explained by an increased nonradiative decay rate; our kinetic model assumes no nonradiative decay (other than ISC) and the fitted “radiative” rate will include both radiative and nonradiative rates.

In MCH the picture is different again. As the 1CT and 1LEA nπ* states are much closer in energy, it is difficult to deconvolute the behavior of each. From the decay kinetics, the 1LEA nπ* decays very rapidly as in toluene, with lifetime of 1.2 ns. The prompt CT states decay much faster; the prompt CT state decays much more rapidly than in toluene (91 ± 3 ns). The DF component in DCM dominates emission after 300 ns (lifetime 2.38 ± 0.06 μs) and has a slower ISC rate (1.18 × 10^5 s⁻¹) than in toluene. The rISC rate is also slower at 4.83 × 10^5 s⁻¹. The CT triplet state involved in rISC, which relaxes in energy with increasing polarity, must therefore open up the gap between itself and the TADF-mediating local triplet state, reducing the rate of rISC and thus DF contribution in polar DCM. In toluene the DF is much stronger but the rISC rate is similar, again indicative of the lower-energy DCM CT states experiencing increased nonradiative decay (energy gap law). The faster radiative decay rates calculated in DCM compared to toluene coupled with the lower overall emission intensity is also explained by an increased nonradiative decay rate; our kinetic model assumes no nonradiative decay (other than ISC) and the fitted “radiative” rate will include both radiative and nonradiative rates.

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with energy 2.88 eV (0–0 vibronic peak) and well-resolved structure. From the spectral shape we conclude that the emission emanates from the acceptor anthracenone unit, i.e., 3LEA nπ* state. At very long delay times (80 ms) we observe the emergence of another phosphorescence band. With little structure and onset of 3.2 eV, this matches well with reported acridine phosphorescence.22 Such dual phosphorescence was previously reported by us in other TADF D–A systems arising from a thermal equilibrium between D and A triplet states which are vibrationally coupled.25,34 The observation of dual phosphorescence establishes ACRSA as an anti-Kasha material on the triplet manifold in addition to its profoundly anti-Kasha singlet behavior.

We also examine the effect of oxygen quenching on the emission dynamics (Figure 6 and Supporting Figure S18). In toluene and DCM the early time emission spectra and decays are unaffected by oxygen, as would be expected from prompt emitting states, but lifetimes are a little longer, which we have no clear idea about at this time. In toluene, the prompt CT emission is quenched after ca. 36 μs (presumably by oxygen), but we observe weak DF, lifetime of ca. 120–240 ns accounting for about 5% of the total intensity. It is therefore remarkable to observe DF CT emission for such a long time in air.

Figure 7 shows transient absorption spectra of ACRSA in oxygen-free toluene for the first 6 ns (343 nm excitation) and 400 ns after pump (355 nm excitation). A band centered at 620 nm is seen to grow in after an induction time of ∼25 ps. The induced band can be resolved into two peaks centered at 619 and 675 nm. Both of these peaks have the same decay kinetics, with the entire band growing in for ∼8–10 ns and decaying after ∼200 ns. Estimation of the band edge energy of each peak (assuming a Gaussian peak shape) yields energies of 1.84 and 1.65 eV, giving an energy separation of 190 meV, corresponding precisely with the C=O stretch of anthracenone.

As the induced absorption has a lifetime of 200 ns it cannot correspond to transitions from the short-lived local singlet 1LE, or 1LEA states. It also cannot be a transition from the long-lived (>3 μs) 1/1CT population, and the CT emission energy is too low to accommodate an induced absorption at the observed energies. By elimination, this induced absorption is assigned to a transition from a 3LE triplet state. Supporting this, measurements in aerated solution gave very poor signal, consistent with oxygen quenching of triplet states. The grow-in kinetics of this induced band matches well with the fast decay of the local 1LEA state with 343 nm excitation. We thus conclude that the induced absorption comes from a transient 1LEA nπ* population, having lifetime of ∼200 ns as it undergoes subsequent IC to the lower energy 1LEA nπ* triplet state. With excitation at 355 nm we initially populate the 1LEA nπ* state which rapidly undergoes ISC to populate the 3LEA nπ*. In both cases we observe the same photoinduced absorption spectra, confirming the common 3LEA nπ* assignment. The induction time observed with 343 nm excitation corresponds to the slower ISC and subsequent IC steps required to reach the 3LEA nπ* state from the 1LEA (ISC to 3LEA then IC). At low temperatures when vibrational coupling and ISC/IC are inefficient, these 1LE D/A states give rise to the observed dual phosphorescence.

The molecular photophysics of TADF in ACRSA is substantially different from that of established TADF molecules, with different ISC and rISC channels.36 Strong solvatochromic relaxation of the lowest-energy singlet 1CT state occurs, while a close-lying 1LEA nπ* state remains unaffected by polarity. Both of these A2 states are emissive despite being one-photon symmetry forbidden. The 1LEA nπ* is quenched to its 3LE nπ* triplet state through very fast ISC in accordance with El Sayed’s rule. In transient absorption a rapid grow-in of a 3LE nπ* induced absorption is in agreement with this explanation. This ISC step out competes any vibrational coupling to the 1CT state, as confirmed by the time-resolved emission spectra showing that these states decay independently. In MCH the 1CT state has strong LE character giving fast radiative decay rates and a short PF CT lifetime compared to toluene and DCM (Supporting Table 1). The PF CT emission has a long lifetime in toluene and DCM because the 1CT state is energetically distant from the 1LEA nπ* state, precluding second-order vibronic coupling to any local state (singlet or triplet). This, along with the forbidden nature of direct 1CT to 3CT SOC, is clearly observed through the extremely long 1CT lifetime. In DCM, the CT states shift so low in energy that coupling to the ground state increases nonradiative decay (energy gap law). However, the presence of TADF in all solvents confirms that isolation of the 1CT is not important in the formation of a long-lived 1CT population because of the role of the 1LEA nπ* state.

Optically the DF emission intensity is low in MCH despite more appropriate energy level ordering. This we suggest is due to rISC from the 1CT state being in continuous competition with IC back to the strongly coupled 1LEA nπ* state. This is also why we can observe resolved phosphorescence from this local triplet state. In MCH we do still identify a fast DF signal quenched by oxygen. This confirms the strong enhancement of both radiative decay and rISC in MCH, achieved through near resonant 1CT and 1CT states (with high local character) and closely spaced 1LEA nπ* singlet, 1LEA nπ*, and 1LEA nπ* triplet states. This alignment of energy levels yields both small energy gaps for efficient nonadiabatic vibronic coupling and large SOC matrix elements, giving very fast rISC rate of ∼1 × 107 s−1. This fast rISC rate is required for it to compete with rapid IC to the well-coupled lowest-energy 1LEA nπ* state.

As the polarity of the solvent increases 1CT and 1CT energetically relax, with 1CT becoming the lowest-energy triplet state. A larger gap opens to the local states especially to the 3LEA nπ*, which increases in energy with increasing solvent polarity, as observed in other aromatic ketone systems.27,36 The measured rISC rates consequently fall by nearly 2 orders of magnitude with increasing polarity (Supporting Table 1), reflecting the increasing energy gap between 1CT and local states (but uniform energy gaps between the local singlet and triplet acceptor states).39 The highly structured phosphorescence from the anthracenone acceptor unit indicates that in nonpolar solvents the 1LEA nπ* triplet state must be below the TADF-active 1CT state. In all solvents we never observe DF from the 1LEA nπ*, but we do observe dual 1LEA nπ* and 1CT emission. This clearly indicates the two states are decoupled. In MCH we see that the 1LEA nπ* and unrelated 1CT energies are very close, resulting in a very low driving force for ET from the 1LEA nπ* state insufficient to drive charge transfer, especially in competition with fast quenching by ISC.
From the time-resolved emission spectra (Figure 5) it is clear that in all solvents the CT state that gives prompt and DF emission does not red shift significantly with time. This emission is also relatively narrow, indicating solvent shell reorganization is very fast and there is no electronic relaxation of the CT state caused by slow molecular reorganization.

ACRSA is unique in that it allows excitation into more than one singlet state. Below 350 nm, excitation of the 1LEA ππ* exciton yields fast emission from this high-energy excitonic singlet state observed in aerated solutions, in competition with exciton yields fast emission from this high-energy excitonic manifold to populate 3CT triplet states, yielding DF from subsequent rISC. This is confirmed by the strong oxygen dependence of the DF CT emission we observe and the results from photoinduced absorption measurements. Nonradiative decay can occur via other triplet states that do not couple to the rISC-active lowest-energy CT triplet state, leading to excited-state quenching. Excitation above 350 nm directly populates the CT and LE, ππ* excitonic states, yielding simultaneous prompt emission from both states.

These results confirm the very fast ISC channel from LEA, ππ* to LEA, ππ* in ACRSA, as predicted by Lyskov and Marian. rISC remains much slower than this in polar solvents, typically with 2−5 μs lifetime. However, in MCH far higher rISC rates are seen as the TADF-active CT state rises in energy toward the LE states.24

This leads us to a proposed “experimental” energy level scheme given in Figure 8, based on the calculations of Lyskov and Marian and our experimental observations.

Combining all of our experimental observations we conclude the following ISC and rISC channels populate the CT states in ACRSA via direct optical excitation of the LEA, ππ*.

**1LEA ππ* ISC channel:**

\[ 1LEA, \pi\pi^* \xrightarrow{SOC} 3LEA, \pi\pi^* \xrightarrow{SOC} 3LEA, \pi\pi^* \xrightarrow{Vib} 1CT, \pi\pi^* \]

**1CT ππ* rISC channel:**

\[ 3CT, \pi\pi^* \xrightarrow{Vib} 1LEA, \pi\pi^* \xrightarrow{SOC} 1CT, \pi\pi^* \]

We observe that the LE, ππ* and ππ* singlet states are not affected by polarity, but from calculation and reports of other ketones, the triplet ππ* states are more affected, shifting up in energy, which we depict in Figure 7. Thus, the SOC step via LE, ππ* states should be minimally affected by polarity changes. The rate-limiting step is likely the CT coupling to the LE, ππ* through vibronic coupling and so is not as impacted by the increasing energy gap in toluene and DCM. The overall rISC rate is controlled by this vibronic coupling, decreasing rISC rates in toluene and DCM compared to MCH from 10^7 s^-1 to ca. 5 × 10^6 s^-1. In air we observe CT quenching because of the very long natural lifetime in toluene and DCM. We propose this simpler rISC mechanism compared to that of Lyskov and Marian because we never observe delayed emission from the LE, ππ* state.

In this study, the “simple” spiro TADF molecule ACRSA is demonstrated to be anything but. We find both strong excitation energy and solvent polarity dependencies in its emission. Exciting the first allowed local ππ* excitonic state of the donor acridine gives rise to three different emissions: one from the excitonic state itself (that competes with both ISC and IC, and electron transfer to two lower lying, one-photon forbidden A5 symmetry states), one from the local ππ* state of the anthracenone acceptor, and also emission from a CT state. The green band represents the energy range over which we observe solvatochromic states. Red arrows represent nonradiative transitions. (b) The effect of solvent polarity on the states and the SOC (yellow arrows) and vibronic coupling (gray arrows) between states giving rise to ISC and rISC.

**Figure 8.** Energy level scheme for ACRSA. (a) Measured energy levels from spectral onsets of ACRSA in different polarity solvents, following the nomenclature of Lyskov and Marian.24 The green band represents the energy range over which we observe solvatochromic states. Red arrows represent nonradiative transitions. (b) The effect of solvent polarity on the states and the SOC (yellow arrows) and vibronic coupling (gray arrows) between states giving rise to ISC and rISC.

In this study, the “simple” spiro TADF molecule ACRSA is demonstrated to be anything but. We find both strong excitation energy and solvent polarity dependencies in its emission.
DF from the \( ^1\text{LE}_\text{A}\pi\pi^* \) state however. Both direct and indirect excitation (via the excitonic state) gives very large DF emission in degassed solutions.

In agreement with DFT/MRCl calculations, fast ISC between the lowest-energy \( ^1\text{LE}_\text{A}\pi\pi^* \) singlet state and \( ^3\text{LE}_\text{A}\pi\pi^* \) triplet state is established from the correspondence of \( ^1\text{LE}_\text{A}\pi\pi^* \) emission decay and grow-in of induced absorption from the \( ^3\text{LE}_\text{A}\pi\pi^* \) state, confirming strong SOC between these states. In MCH we observe very strong enhancement of both radiative decay and rISC, achieved through near-resonant \( ^1\text{CT} \) and \( ^3\text{CT} \) states (having high local character) as well as nearby \( ^1\text{LE}_\text{A}\pi\pi^* \) singlet and \( ^3\text{LE}_\text{A}\pi\pi^* \) triplet states. This alignment yields high radiative decay rates for the \( ^1\text{CT} \) state, small energy gaps for nonadiabatic vibronic coupling, and high SOC rates. The net result is very high rISC rates of \( 10^7 \text{ s}^{-1} \). However, rapid ISC from excitation to higher-energy singlet states yields fewer triplet states and lower DF. This indicates competing decay channels on the triplet manifold, with not all excitons reaching the lowest-energy TADF-active triplet state.

In devices, similar ISC from high-energy excitons terminating in TADF-inactive triplet states may be a mechanism that explains the generally unexceptional OLED performance of ACRSA and other spiro-linked derivatives.

Throughout our optical measurements ACRSA gives radiative decay from up to three different excited states simultaneously (at early times) and two states even at tens of nanoseconds. Combined with observed dual phosphorescence this “simple” molecule therefore utterly disregards Kasha’s law. The perpendicular and rigid geometry of the molecule—which very effectively decouples A and D as required—is what allows us to see identifiable photophysical properties of the donor (\( ^1\text{LE}_\text{D}\pi\pi^* \) exciton emission, in competition with slow ET and nonradiative decay), alongside formally forbidden \( ^1\text{CT} \) and \( ^3\text{LE}_\text{A}\pi\pi^* \) emission. ACRSA’s “simple” spiro structure therefore bestows it with unprecedented and previously unrecognized richness in its optical properties because of this very effective electronic decoupling of the donor and acceptor units, apart from the molecular CT state. This is not limited to ACRSA, nor spiro TADF molecules in general, but all TADF molecules because of the requirement to effectively decouple the D and A to yield CT states with vanishing singlet–triplet energy gaps, a necessary (but not sufficient) requirement for efficient TADF. This whole class of materials can be thought of as a combination of donor, acceptor, and molecular CT state giving their own photophysics, as is the case for an exciplex TADF systems and emerging through-space TADF materials, where the linkage and coupling between the D and A is even less well-defined. Thus, in its original form, does Kasha’s rule still apply to such a “system”?

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**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c03314.

Experimental details; additional photophysical data such as absorption spectra, time-resolved emission decays and steady-state spectra of ACRSA in different solvents, excitation, and concentrations; phosphorescence spectra of ACRSA in zeonex matrix; absorption and emission spectra of acridine; lifetime fittings (PDF)

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**AUTHOR INFORMATION**

Corresponding Author

Andrew Monkman — OEM Research Group, Department of Physics, Durham University, Durham DH1 3LE, United Kingdom; orcid.org/0000-0002-0784-8640; Email: a.p.monkman@durham.ac.uk

Authors

Larissa Gomes Franca — OEM Research Group, Department of Physics, Durham University, Durham DH1 3LE, United Kingdom

Yun Long — OEM Research Group, Department of Physics, Durham University, Durham DH1 3LE, United Kingdom

Chunyong Li — OEM Research Group, Department of Physics, Durham University, Durham DH1 3LE, United Kingdom

Andrew Danos — OEM Research Group, Department of Physics, Durham University, Durham DH1 3LE, United Kingdom; orcid.org/0000-0002-1752-8675

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c03314

Author Contributions

L.G.F., Y.L., A.D., and C.L. made the presented optical and time-resolved spectroscopy measurements. A.M. devised the research, undertook the data analysis, and supervised the work. A.M. wrote the manuscript with L.G.F. and A.D., with contributions from all authors.

Notes

The authors declare no competing financial interest.

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