

Carbene metal amides as high-efficient emitters for OLEDs

Carbene metal amides (CMAs) based on cyclic (alkyl)(amino)carbenes (CAAC) are highly efficient emitters for solution phase processed and vacuum deposited OLEDs. They show sub-microsecond emission lifetimes involving rotationally accessed delayed fluorescence. Steric hindrance increases quantum yields by minimizing structural deformations in the excited state. Recent development will be discussed, such as CMA dendrimers.

Theoretical study of compounds containing monoaza[5]helicene and diaza[5]helicene acceptor units

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods have played a key role in the screening of potential thermally-activated delayed fluorescence (TADF) candidates, reducing the synthetic chemistry effort. Using these calculations, properties that are key in enabling efficient TADF such as singlet-triplet energy gap (ΔE_{ST}), HOMO/LUMO spatial overlap and oscillator strength can be predicted and compared, prior to time-consuming organic synthesis.

Amongst the many acceptor units used in materials for organic electronics, helicenes have generated unique interest due to their non-planar chiral structure and have been used effectively in applications such as OLEDs,¹ non-linear optics (NLO)² and circularly polarized light.³ Furthermore, recent work by Jelfs et al⁴ has predicted that the molecular packing of chiral helicenes can lead to high electron mobility highlighting the potential for these materials in organic electronic devices.

In this work we have studied novel compounds containing electron-deficient monoaza[5]helicene and diaza[5]helicene cores using DFT and TDDFT. The effect of introducing different donor units into the structure and a comparison between the mono and di-substituted analogues will be analysed by studying the ground state and excited state structures, orbital overlap, energy levels and oscillator strength. Additionally, a study into the suitability of functionals used for the calculations will be presented.

- (1) W. Hua et al, RSC Adv., 2015, 5, 75–84
- (2) A. Bossi et al, J. Phys. Chem. C, 2008, 112, 7900–7907
- (3) A. J. Campbell et al, Nat. Photonics, 2013, 7, 634–638
- (4) K. E. Jelfs et al, Nanoscale, 2018, 10, 1865-1876

Investigating novel donor materials for TADF emitters

At the present time, the pool of donor materials used in TADF emitter materials remains small. Most often used are carbazole, acridine, phenoxazine or diphenylamine based materials. This research focusses on the development of new donor materials for TADF emitters by repurposing donor units that are often found in different fields of organic electronics, such as organic photovoltaics (OPVs), and coupling them in an atypical fashion to a variety of acceptor units. In addition to synthesizing these materials, a quantum chemical study using density functional theory is performed to investigate the optical and electronic properties. Time dependent fluorescence spectroscopy is performed to analyse the presence of delayed fluorescence.

Pyridine Carbazole Based Bipolar Host Material for TADF OLEDs

Two pyridine carbazole based materials were synthesized and characterized. The two materials were applied as host while yellow TADF emitter tri-PXZ-TRZ was used as guest to construct OLEDs. The results exhibited enhanced EQE and reduced efficiency rolling-off comparing to non-polar materials.

Utilising Indolo[3,2-b] Indoles as TADF Capable Materials For Application in OLEDs.

This poster concerns the synthesis and photophysical investigation of indolo[3,2-b] indole derivatives, to produce materials capable of thermally activated delayed fluorescence, TADF, for application in organic light emitting diodes, OLEDs.

Owing to the larger proportion of pyrrole units in its core, the indolo[3,2-b] indole ring has extended conjugation and much greater electron donor strength than carbazole. As a result, indolo[3,2-b] indole is gaining increasing interest for use in TADF materials and continues to be the centre of much research.

[4-(5,10-indolo[3,2-b] indole)] N-benzophenone, CC4, was first prepared in low yield and was shown to exhibit both prompt and delayed fluorescence, with a photoluminescence quantum yield of 18 % in a degassed toluene solution. The TADF capability of this molecule is attributed to the low singlet-triplet energy gap of 0.2 eV. The photophysical properties of CC4 were investigated using both thin-film and solution studies, and comparisons were drawn.

Despite the promising nature of the emission of CC4, the photoluminescence quantum yield remains low, and more time will need to be spent optimising this before it becomes a viable candidate for application in OLEDs.

Photophysics of hyperfluorescent TADF emitter pairs

Thermally activated delayed fluorescence (TADF) is an established mechanism for harvesting triplet excitons in “metal-free” OLEDs, increasing their maximum attainable IQEs to 100%. Although several highly efficiency TADF emitters have been discovered¹, developing general design rules for the organic structures of efficient TADF compounds remains at the forefront of ongoing research. At present, without the ability to customize emission colour while also maintaining emission efficiency, TADF emitter OLEDs have not yet reached widespread commercial deployment.

As part of the EU’s Horizon 2020 HyperOLED project², research at Durham University aims to address the limitations of current generation TADF emitters by pairing them with traditional fluorescent OLED emitters. Fluorescent dyes, while possessing excellent stability and colour selectivity, cannot harvest triplet excitons in devices by themselves - leading to maximum IQEs of 25%. When paired with a triplet harvesting TADF material, sequential energy transfer and emission from the fluorescent material (hyperfluorescence) can allow for emissive layer devices that combine the best features of the TADF and fluorescent emitters.³

This poster will demonstrate current efforts to characterize the energy transfer step between TADF and fluorescent emitter in hyperfluorescent materials. Of critical interest are the contributions of triplet exciton quenching, and changes in the rate of rISC induced by accelerated depopulation of the TADF singlet state.

(1) Dias, F. B.; Bourdakos, K. N.; Jankus, V.; Moss, K. C.; Kamtekar, K. T.; Bhalla, V.; Santos, J.; Bryce, M. R.; Monkman, A. P. *Adv. Mater.* **2013**, *25* (27), 3707–3714.

(2) HyperOLED <http://www.hyperoled.eu/>.

(3) Nakanotani, H.; Higuchi, T.; Furukawa, T.; Masui, K.; Morimoto, K.; Numata, M.; Tanaka, H.; Sagara, Y.; Yasuda, T.; Adachi, C. *Nat. Commun.* **2014**, *5* (May), 1–7.

Maximising the reverse intersystem crossing rate in thermally activated delayed fluorescence emitters: a matter of spin-vibronic coupling

Organic light emitting diodes offers a wide range of application in the domain of lights and displays. Upon electrical excitation, 25% of the excited molecule is in an emitting singlet states while the 75% remaining are in a dark triplet state, considerably reducing the efficiency of the device. [1]

Thermally activated delayed fluorescence (TADF) has been investigated for several years as an alternative to the use of expensive heavy metals. It consists in a thermally activated reverse intersystem crossing (rISC) from the triplet state to the higher lying singlet state.

In order to observe an efficient rISC, the molecule should exhibit a small singlet-triplet energy gap. This has lead efforts to be put into the synthesis of system exhibiting low lying charge transfer states. However because of their similar nature, the lowest singlet and triplet states are only very weakly coupled making the simple picture of a direct singlet to triplet transfer unlikely. More complex mechanisms involving higher lying states acting as intermediate states have been proposed, and emphasize the crucial importance of both SOC and vibronic coupling. [2,3]

In this work, we will focus on showing the importance of spin-vibronic and how to maximise the rISC in TADF emitters.

[1] F. B. Dias et al., *Methods Appl. Fluoresc.*, 2017, 5, 012001.

[2] J. Gibson et al., *ChemPhysChem*, 2016, 17, 2956-2961

[3] M. K. Etherington et al., *Nat. Commun.*, 2016, 7:13680

Spirocycle Containing Conjugated Polymers: Manipulating Excited States

We present theory and synthetic development of polymeric systems with adjustable singlet-triplet energy gap of 0.7-0.015eV (ΔE_{s-t}). These materials computationally display characteristics indicative of thermally activated delayed fluorescence (TADF). The feasibility of these systems has been previously shown within the group. TADF has been demonstrated within small molecule systems where it is used to enhance electroluminescent efficiencies, we wish to transplant this technology into polymeric materials. This necessitates the manipulation of the materials ΔE_{s-t} allowing for the thermally activated conversion of triplet excitons into singlet excited states. The structure of the spirocycle monomeric unit allows for the placement of electron withdrawing groups orthogonal to the polymer backbone. This orientation induces the spatial separation of HOMO and LUMO orbitals upon the chain, lowering the singlet-triplet energy gap and fulfilling the prerequisite conditions for TADF to occur. The singlet-triplet energy gap of these materials is shown computationally to be modifiable by the substitution of the orthogonal groups within the materials. We present computational studies of postulated TADF demonstrating polymeric materials and ongoing synthetic approaches to achieving an analogous series of spirocycle based polymers

TADF: Making OPVs into better OLEDs to minimise non-radiative voltage loss

Archetypical organic photovoltaic (OPV) donor materials have a large exchange energy ($\Delta EST \approx 0.7$ eV). Consequently, spin triplet charge transfer states (3CTs) formed by the non-geminate recombination of free charges can transfer to the low energy donor triplet (T1) state and become energetically trapped, where they ultimately decay non-radiatively. Thermally activated delayed fluorescence (TADF) materials possess a very small ΔEST (~ 25 meV). By increasing the energy of the T1 to be almost isoenergetic with the singlet (S1), the T1 state is raised above the 3CT level, thus removing this non-radiative recombination pathway. In this work, we demonstrate the feasibility of a TADF donor OPV device and highlight the opportunity to develop low ΔEST donor materials to reduce non-radiative voltage losses in OPVs.

Probing geminate recombination in organic solar cells containing TADF molecules

Thermally-activated delayed fluorescence (TADF) molecules can convert spin-triplet excitons into spin-singlet excitons due to its high-lying triplet energy level. This high-energy triplet, in the context of organic solar cells, can potentially suppress geminate recombination from charge-transfer (CT) states at electron-donating and electron-accepting interfaces. Here, we utilize a novel ultrafast photocurrent technique, namely pump-push photocurrent spectroscopy, to probe the amplitude and kinetics of geminate recombination in working solar cells based on TADF molecules. Our initial result shows that geminate recombination is not severe but its kinetics can be controlled by the relative energy levels of CT and triplet states. This has implications to kinetically suppress recombination from low-lying triplet states in organic solar cells.

The Influence of Molecular Conformation on the Photophysics of Organic Room Temperature Phosphorescent Luminophores

A series of novel donor-acceptor-donor (D–A–D) compounds featuring dibenzothiophene (DBT) and phenothiazine (PTZ) units are presented. A different degree of steric hindrance between the donor and acceptor fragments is achieved by the systematic changes of donor substituents (methyl, *iso*-propyl, *tert*-butyl groups). This leads to the tuning of photophysical properties by conformational control. The unsubstituted DPTZ–DBT molecule exists in both equatorial and axial forms in the ground state, but the equatorial conformer prevails in the excited state. This leads to strong room temperature phosphorescence (RTP) in the green region with an unusually high phosphorescence quantum yield (71%). Under the influence of bulky substituents, the alkyl–DPTZ–DBT derivatives change molecular conformation, preventing formation of the excited charge transfer state. Hence, blue phosphorescence characterized by shorter fluorescence and phosphorescence lifetimes, dominates in DPTZ–*iPr*–DBT and DPTZ–*tBu*–DBT. The less bulky methyl substituent on the donor results in dual RTP (blue and green), apparently violating Kasha's rule imposed by the modulation of the barriers between excited states. The experimental results are supported by DFT calculations in the ground and excited state. Control of conformation with substituents is an effective strategy for tuning the excited state properties of D–A–D molecules for RTP emission.

Accessing Emitter Orientation in Organic Thin Films - a Simulation-Free Approach

Blue TADF emitters relying on carbazole donors surrounding a central acceptor group

Organic light-emitting diodes (OLEDs) are currently the dominating technology in smartphone and other small-medium displays. Problems like difficult upscaling, high power consumption and relatively short device lifetime prevent OLEDs from becoming the common technology for all display and lighting applications. Current state-of-the-art commercial OLED displays contain molecular phosphorescent emitters. The highly efficient emission process in these compounds relies on efficient spin-orbit coupling on a central heavy metal ion like Ir or Pt. Hence, future applications of this technology may suffer from the scarcity and price level of the respective precious resources. Moreover, photochemically sufficiently stable phosphorescent blue emitters have not been found yet.

Recently, thermally activated delayed fluorescence (TADF) has emerged as an attractive alternative, where up to 100% internal quantum efficiency can be achieved by harvesting the triplet excitations via reverse intersystem crossing (rISC). TADF emitters are purely organic and offer potentially cheaper material and device production as well as higher colour tunability. In this work, we present photoluminescence (PL) and OLED results for TADF emitters consisting of rather weak acceptor groups like trifluoromethyl-benzene or methyl benzoate surrounded by carbazoles. These materials have high PL quantum yield and a PL emission with a maximum around 470 nm. We observe substantial changes in emission spectra and quantum yield resulting from modifying the electron-donating carbazole moieties or from exchanging the acceptor units. Preliminary OLED devices show external quantum efficiency (EQE) values exceeding 5% together with driving voltages as low as 3 V. Interestingly, emitter concentration appears to play a key role in both EQE and device lifetime, which will be investigated in further experiments.

Exploring the photophysics of Carbene Metal Amides

Carbene Metal Amides (CMAs) have been recently reported, and show promising application in OLED devices, and interesting photophysical behaviour differing from the normal form of organic TADF materials. A number of variants on these molecules have been studied using cryogenic TRPL techniques. We discuss the role of the metal bridge atom in Reverse Inter System Crossing rates, and explore design rules for this class of materials.

Delayed fluorescence in planar indolo[3,2-b]indole derivatives

Heteroacenes form a family of organic conjugated molecules that are well known for their extraordinary charge carrier mobility. Despite the fact that heteroacenes attract a lot of attention due application in field effect transistors, the optical properties of many molecules possessing high charge mobility remain relatively unexplored. Understanding the photophysics of high mobility semiconductors could lead to improvements in solar cells, light emitting transistors and organic lasing. We studied photophysical properties of planar indolo[3,2-b]indole (ININ) derivatives in solutions and in thin films. We use steady-state and transient absorption and emission spectroscopy at a range of temperatures. We find that the ININ derivatives exhibit unity photoluminescence quantum efficiency in deoxygenated solution due the slow intersystem crossing (80ns). Unexpectedly, the singlet state emission of these molecules persists for up to 5 μ s. This delayed fluorescence doesn't follow the kinetics of triplets, instead showing a power-law dependence, suggestive of recombining charges. I will discuss our work towards understanding of the origin of the long-lived emission.

The Importance of Vibronic coupling and Solid State Solvation on Thermally Activated Delayed Fluorescence Molecules

Developing a comprehensive understanding of the mechanism of Thermally Activated Delayed Fluorescence (TADF) is crucial to optimising the design of heavy-metal-free organic light emitting diodes (OLEDs). Previously, this research area has concentrated on the energy gap between the lowest singlet and triplet states. We demonstrate that, in fact, a crucial role is played by non-Born-Oppenheimer effects in the rate of reverse intersystem crossing (krISC). We see that vibronic coupling between the lowest local exciton triplet (3LE) and the lowest charge transfer triplet (3CT) occurs within the TADF mechanism, and increases the krISC by approximately four orders of magnitude. This mixing of states is of particular interest when considering the solid state solvation effects (SSSE), as the effect of the host on these intermediate states, as well as the CT states, must be examined. Crucially, we show that the magnitude of the SSSE depends on the dipole moment and rigidity of the emitter as well as the host, opening new design routes for the development of highly efficient TADF emitters [1, 2].

[1] J. Gibson, A. P. Monkman and T. Penfold, *Chem. Phys. Chem.*, 2016, 17, 2956-2961

[2] T. Northey, J. Stacey and T. Penfold, *J. Mat. Chem. C*, 2017, 5, 11001-11009.

Experimental Setup of Broadband Impulsive Vibrational Spectroscopy

The reverse intersystem crossing (rISC) between singlet and triplet charge transfer (CT) states in donor-acceptor CT molecules is mediated by one of the local triplet states. The vibronically coupling between the CT triplet state and the local triplet state is crucial for the thermally activated delayed fluorescence (TADF) process, so we believe it is important to study the vibronic states of the excited electronic states in TADF molecules. We are building a broadband impulsive vibrational spectroscopy (BB-IVS) setup that was proved to be a powerful technique to record the vibrational spectra of excited states in the time domain. I will present the experimental setup of two-beam BB-IVS and some results on organic molecules.

Investigation of Raman-Active modes in an organic TADF molecule using Broad-Band Impulsive Vibrational Spectroscopy

Thermally Activated Delayed Fluorescence (TADF) provides an attractive means for harvesting triplet states without necessitating heavy metals.¹⁻² Consequently, TADF molecules have been reported as attractive light emitters for enhancing the output efficiency in Organic Light Emitting Diodes (OLEDs). In TADF molecules the non-emissive triplet state undergoes reverse intersystem crossing (rISC) back to the emissive singlet state with assistance of thermal energy.¹ Recent investigations show that in donor-acceptor TADF molecules, the rISC process between singlet and triplet charge transfer (CT) excited states is mediated by a local triplet state. This mechanism is dependent on vibronic coupling of the local excited (LE) and CT triplet states.³ Investigation of the vibronic coupling is therefore crucial in controlling the TADF process. The technique of Broad-Band Impulsive Vibrational Spectroscopy (BBIVS) has been developed as an efficient technique for measuring vibronic coherence in electronic states in the time domain, being able to combine structural sensitivity with high temporal resolution.⁴⁻⁵

In this investigation, BBIVS is used to monitor the evolution of Raman-Active vibrational modes in the ground state of TADF molecule Triquinolonobenzene, a compound with high chemical stability and photostability, in which intramolecular electronic transfer has been utilised to achieve highly efficient TADF.⁶ A two beam BBIVS setup is used to collect the time-domain Raman spectra in the ground state. To measure the vibrational coherence in the excited state, a third actinic pump is currently being introduced into the system in order to create excited states for which the vibronic coherence can be probed.

1. Fernando, B. D.; Thomas, J. P.; Andrew, P. M., Photophysics of thermally activated delayed fluorescence molecules. *Methods and Applications in Fluorescence* 2017, 5 (1), 012001.
2. Fukagawa, H.; Shimizu, T.; Iwasaki, Y.; Yamamoto, T., Operational lifetimes of organic light-emitting diodes dominated by Förster resonance energy transfer. *Scientific Reports* 2017, 7 (1), 1735.
3. Etherington, M. K.; Gibson, J.; Higginbotham, H. F.; Penfold, T. J.; Monkman, A. P., Revealing the spin–vibronic coupling mechanism of thermally activated delayed fluorescence. *Nature Communications* 2016, 7, 13680.
4. Liebel, M.; Schnedermann, C.; Wende, T.; Kukura, P., Principles and Applications of Broadband Impulsive Vibrational Spectroscopy. *The Journal of Physical Chemistry A* 2015, 119 (36), 9506-9517.
5. Liebel, M.; Kukura, P., Broad-Band Impulsive Vibrational Spectroscopy of Excited Electronic States in the Time Domain. *J. Phys. Chem. Lett.* 2013, 4, 1358.
6. Mamada, M.; Inada, K.; Komino, T.; Potscavage, W. J.; Nakanotani, H.; Adachi, C., Highly Efficient Thermally Activated Delayed Fluorescence from an Excited-State Intramolecular Proton Transfer System. *ACS Central Science* 2017, 3 (7), 769-777.

Blue TADF emitters with High Photoluminescence and Electroluminescence Efficiencies

Four blue TADF emitters were designed and synthesized, using indenocarbazole derivatives as the electron-donating moiety, and 2,4,6-Triphenyl-1,3,5-triazine as the acceptor unit. In contrast with other six-membered heterocycles, like phenothiazine, phenoxazine and dihydroacridine, which often are affected by less TADF efficient conformers, indenocarbazole derivatives are conformational stable. The indenocarbazole derivatives, InCz23FITz, InCz23DPhTz, InCz23DMeTz and InCz34DPhTz were chosen to investigate the effect of different substituents and substitution positions on their photophysical behavior and electroluminescence performances. Luminescence from a charge transfer state is observed in the four compounds, showing a bathochromic shift with increasing solvent polarity. The compounds show high PLQY in doped films that range from 70 to 88%. The substituted positions on carbazole have deeper influence on the TADF properties of the indenocarbazole derivatives studied here. The four compounds show relatively small TADF contribution under optical excitation, due to the relatively large ST gap (≈ 0.2 eV) and slow reverse intersystem crossing rate ($\approx 10^3$ s⁻¹). In spite of this, the compounds performed well in electroluminescence devices. Especially, InCz34DPhTz with the shortest delayed lifetime and the highest PLQY among the four compounds, showing turn on voltage around 4.5 V and a maximum EQE around 26%, even about 14% at 100 cd/m², with no method for enhancement outcoupling.

Isomeric Derivatives of 9,9-dimethyl-9,10-dihydroacridine and Benzonitrile

Probably the most attractive donor in the construction of blue and green TADF emitters is 2,7-di-tert-butyl-9,9-dimethyl-9,10-dihydroacridine. When compared with carbazole, acridine possesses more pronounced electron donating ability, therefore it is easier to push the singlet emission of the resulting compound from the UV region to the visible blue region in acridine containing compounds. Acridine consists of a hexagonal inner ring, whereas the inner ring of carbazole is pentagonal. Due to the extension of the inner ring, each ortho-hydrogen (related to the nitrogen atom) in an acridine unit is ca. 0.48 Å closer to the N–C carbon atom (the N–C bond of the aromatic substituent), which results in almost 1 Å shorter length of the rotational freedom for the substituent – this makes it possible to ensure the perpendicular orientation of the substituent. This fundamental advantage, along with the high triplet energy (3.05 eV) and the strong electron donating ability brought the fame to the acridine moiety as the ideal building block for blue-emitting TADF materials. In this work we decided to employ the stronger electron donor acridine in low-molar-mass emitting systems and to investigate them thoroughly in order to show how a combination of D and A units, as well as the linking pattern between them, can lead to the achievement of the desirable properties of the resulting compound. Molecular geometry optimizations of benzonitrile-substituted acridine derivatives confirmed the above described steric influence of the ortho-hydrogens to the torsion of the substituent: independently from the linking pattern in use, the benzonitrile unit was found to be perpendicular to the acridine plane in all the series of compounds under investigation. The compound with the ortho-linkage between chromophores possesses glass-forming ability with a glass transition temperature of 97 °C. The sublimation temperatures of the compounds were discovered to be within the temperature range of 241–252 °C. The compounds possess small singlet-triplet energy splitting gaps (<100 meV) and exhibit blue thermally activated delayed fluorescence. The compound with the ortho-linkage between the donor and the acceptor moieties exhibits the highest triplet formation yield of 0.88, which makes it the most efficient blue TADF emitter within the series.

Rational Design of Near-Infrared Absorbing D- π -A Organic Dye Molecule

We developed rational design principles to lower the HOMO-LUMO gap and in turn the optical gap using very simple model systems, disentangling electronic and geometric factors which control them. Furthermore, we used these design principles to model an organic dye which exhibits a near-IR (NIR) absorption maximum with a favourable intramolecular charge-transfer (ICT) excitation nature. To achieve this, we did an in-depth study of the individual effect of, and interplay between, factors like introduction of substituents¹, variation of torsional angle, size of aromatic core and heteroatom mono-substitution in the aromatic core, on the electronic structure of the molecule. Our analysis is based on quantitative Kohn-Sham MO analysis² in conjunction with Time Dependent Density Functional Theory (TD-DFT) at CAMY-B3LYP/TZ2P/COSMO (DCM Solvent) level. Using these design rules, we were able to rationally design a generic D- π -A organic dye which shows absorption at 900 nm. Our findings would help to develop strategies for harvesting near-IR (NIR) photons of the solar spectrum as well as for designing new NIR emitters in the field of organic electronics.

Pyridine derived sulfone based TADF emitter for deep blue organic light emitting diodes

Enhancement of color purity in thermally activated delayed fluorescence (TADF) emitters is highly desired for the practical application of these materials. We designed and synthesized TADF emitter, based on a di(pyridinyl)sulfone (DPyS) core as the new electron-accepting units and di(tert-butyl)carbazole (DtBCz) as the electron-donating units. Here, the sulfone core is used to increase the energy gap of the materials to achieve the deep blue emission. As we expected, these materials shows deep blue emission with an emission maximum of 450 nm in co-doped thin film. In addition, these materials show small ΔE_{ST} and higher color purity due to intramolecular H-bonding. An electroluminescent device of this material as the dopant shows the external quantum efficiency of 7.3% with CIE value of 0.15; 0.11. Moreover, this device shows narrow emission with full width and half maximum (FWHM) of 73 nm, which is much narrower than most of the reported blue TADF emitters.

1. M. Y. Wong and E. Zysman-Colman, *Adv. Mater.*, 2017, 1605444.
2. P. Rajamalli, D. Rota Martir and E. Zysman-Colman, *ACS Appl. Energy Mater.*, 2018, 1, 649.
3. P. Rajamalli, D. Rota Martir and E. Zysman-Colman, *J. Photon. Energy*, 2018, 8, 032106.
4. P. Rajamalli, N. Senthilkumar, P.-Y. Huang, C.-C. Ren-Wu, H.-W. Lin, and C.-H. Cheng, *J. Am. Chem. Soc.*, 2017, 139, 10948.

Photophysical characterization of new organic molecules with TADF

Owing to the oxygen and temperature dependences, TADF can be used both in molecular thermometry and oxygen sensing. In addition, TADF is at the heart of 3rd generation organic light-emitting diodes (OLEDs). To have an efficient TADF emission, several conditions are required. One of the most important requirements is a small value for the singlet-triplet energy gap (DEST). The design of new molecules for OLEDs has as one of the main goals a reduced DEST. Herein, we use several methods of analysis to estimate the DEST of several molecules, designed by us. In addition, further important parameters such as the singlet and triplet formation quantum yields and the phosphorescence lifetime are also discussed.

Photophysics and Solvatochromism of Novel Blue-emitting Organometallic Materials based on Carbene-metal-amides

During the last decade, the field of organic light-emitting diodes (OLEDs) has seen rapid progress and commercial adoption in display and lighting applications owing to significant improvements in efficiency and stability. One remaining challenge for OLED technology is the lack of efficient and stable blue emitters, despite the commercial availability of efficient and stable red and green emitters. We have previously reported efficient green emitters from a novel class of organometallic small molecules based on carbene-metal-amides (CMAs). Here we explore structurally related blue variants from this class of materials using steady-state and transient spectroscopy techniques. By attaching electron-withdrawing groups to the amide moiety, emission wavelengths can be tuned significantly into the blue without compromising photoluminescence quantum efficiency (PLQE). We realise deep blue emitters with above-70% PLQEs and sub-microsecond emission lifetimes from these CMAs. We investigate how structural variation of amide groups play a role in determining their photophysics and how these alterations could contribute to realising blue OLEDs from CMA derivatives. Detailed transient spectroscopy measurements reveal that the key to achieving high PLQEs in these materials is their extremely rapid intersystem crossing, which causes the reservoir of non-emissive triplets to be readily converted into emissive singlets on much shorter timescales than is typically achieved with current organic thermally-activated delayed fluorescence (TADF) materials. Furthermore, we investigate the solvatochromism of these CMA variants to explore the nature of their excited states. We find that blue emitters with strong electron-withdrawing groups on their amide moiety are heavily quenched and have fundamentally different photoluminescence spectra in polar solvents, while those with weaker electron-withdrawing groups, as well as our best-performing green emitters, are significantly more tolerant to the polarity of the environment. This suggests an interplay between multiple charge-transfer and localised states within each molecule, controlled by the strength of electron-withdrawing groups involved, and points to design rules for efficient emission from CMA materials.

Solution Processability via Bonding of Carbazole Units to a TADF Core

The competition between the rate of fluorescence, and the singlet-triplet energy gap, in TADF compound, necessitates a relatively long lived excited state. This can lead to problems of roll-off in devices, which is usually reduced by dispersing the emitting material within a conductive host. However such systems can present problems when solution processed, namely aggregation. Further the lack of control of solubility can lead to problems of dissolving prior layers in the device upon fabrication. In recent years covalently binding carbazole to the TADF core had shown potential as a strategy to control solution processability. Further the self-hosting nature of the resulting compounds naturally prevents issues of aggregation within the host upon device formation by eliminating the host.

First Mononuclear Silver Complexes for the Efficient Solution and Vapor-processed OLEDs

Molecular design has gone a long way towards commercially viable and efficient organic light emitting diodes (OLEDs). Each generation of the emissive materials (fluorescent, phosphorescent, thermally activated delayed fluorescent or hyperfluorescent) has been focused on complete harvesting of singlet and “dark” triplet excited states. Here, we report an initial observation of efficient electroluminescence (EL) from a group of mononuclear silver(I) complexes. Silver complexes show good light, oxygen/moisture and thermal stability. Materials display green emission, good photoluminescence quantum yields up to 67% in host matrices while delayed emission is one of the shortest known to date (200–400 ns). First organic light-emitting diodes (OLEDs) using silver emitting molecules as dopants demonstrate moderate external quantum efficiencies up to 11 and 14% via solution processing or vacuum deposition. A maximum luminance of 21000 cd m⁻² is achieved. From spectroscopic studies, we identified structural and electronic correlations leading to minimal singlet-triplet gap and efficient utilization of triplet states. Comparison and key differences with analogous gold- and copper-based carbene-metal-amides will be presented.

Deconstruction of an OLED: EL Transients in TADF Devices

Thermally activated delayed fluorescence (TADF) is of great importance to achieve higher external quantum efficiency (EQE) in organic light emitting diodes (OLEDs), allowing for the harvesting of triplet states in metal-free organic emitters and overcoming the 1:3 ratio between singlet and triplet excited states that limits the internal quantum efficiency (IQE) to 25% of purely fluorescent OLEDs. [1–3] TADF-based devices, however, continue to suffer from the roll-off effect, a major limitation for different types of applications. The roll-off effect corresponds to a decrease of the devices' EQE at higher brightness, and its causes are still unclear, being believed that it can, among others, be related to layer morphology changes, triplet-triplet annihilation (TTA), or polaron quenching caused by the charges injected onto the devices. [4, 5]

In this work, a transient electroluminescence (EL) spectroscopy technique was assembled for collecting the EL transients in OLEDs under operation conditions, as an attempt to better understand the mechanisms that drive light emission and decay in TADF devices. Through this technique, morphology changes appear to be observed, however allowing for a more intense EL, indicating that it does not directly promote roll-off. In addition, the possibility of TTA was denied under different excitation pulse's duration measurements. Finally, we observed that charge-trapping is strongly present in these devices, suggesting that these trapped charging could, indeed, be resulting in polaron quenching, thus decreasing device efficiency at a higher brightness.

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Reverse Intersystem Crossing from Upper Triplet States: Triplet Harvesting by Aromatic Carbonyls

Previous works from the Gilch and Monkman group have shown that simple aromatic carbonyls such as thioxanthone (TX) can convert triplet excitation into light. The conversion involves reverse intersystem crossing (rISC) from the T₂ state of TX to its emissive S₁ state. This was proven by exciting a triplet sensitizer, whose energy was transferred to that T₂ state. Subsequent fluorescence emission of TX could be observed by time-resolved spectroscopy. TX is not well suited as an emitter molecule for OLEDs since its fluorescence quantum yield is low (~ 12 %). Recent results suggest that structurally related compounds, e.g. acridone (AC), ought to be better emitters due to their intrinsically higher fluorescence quantum yields. Furthermore the energy difference between upper triplet and emissive singlet state can be raised to maximize the rISC and obtain efficient emitters.

Buchwald-Hartwig cross coupling amination reactions as a valuable tool in the preparation of the organic compounds for high efficiency OLEDs

Over the past few years the synthesis of thermally activated delayed fluorescence (TADF) emitters has become very popular. Nevertheless, most of the literature describes only the superior photophysical properties of the organic compounds without an in-depth explanation of the involved chemical reactions.¹ Here we discuss the utilization of the Buchwald-Hartwig cross-coupling amination reaction and show its application in the synthesis of new compounds with TADF properties.

Different synthetic techniques used to obtain the desired compounds are discussed. In addition, a brief discussion of the photophysical properties of the prepared compounds is shown

This work shows the possibility of scale-up preparation of TADF emitters starting from commercially available precursors. Using modified reaction conditions we were able to upscale the chemical synthesis of the desired compounds based on the dibenzothiophene-S,S-dioxide acceptor core.^{2,3}

Using the Buchwald-Hartwig reaction with our conditions new compounds based on naphthalimide core were prepared. Some of these compounds show TADF properties. In addition, their crystal structures are disclosed to observe cross-conjugation, which is crucial for decreasing ΔE_{st} .

We report a procedure to linearly scale-up the synthesis of compounds based on dibenzothiophene-S,S-dioxide by modifying Buchwald-Hartwig cross-coupling reaction conditions. In addition, we applied the previously investigated reaction in the preparation of new organic compounds based on the naphthalimide core to show the successful utilization of our chemical method.

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Development of new molecules for TADF and room temperature phosphorescence

By systematic analysis of different TADF molecules with varying substituents we have uncovered the relationship between TADF and RTP in these molecules. We have also demonstrated that molecular conformation can be controlled by both excitation wavelength and by the solvent polarity.

Probing geminate recombination in organic solar cells containing TADF molecules

TADF molecules can convert spin-triplet excitons into spin-singlet excitons due to its high-lying triplet energy level. This high-energy triplet, in the context of organic solar cells, can potentially suppress geminate recombination from charge-transfer (CT) states at electron-donating and electron-accepting interfaces. Here, we utilize a novel ultrafast photocurrent technique, namely pump-push photocurrent spectroscopy, to probe the amplitude and kinetics of geminate recombination in working solar cells based on TADF molecules. Our initial result shows that geminate recombination is not severe but its kinetics can be controlled by the relative energy levels of CT and triplet states. This has implications to kinetically suppress recombination from low-lying triplet states in organic solar cells.