

Northumbria Research Link

Citation: Higginbotham, Heather F., Etherington, Marc and Monkman, Andrew P. (2017) Fluorescence and Phosphorescence Anisotropy from Oriented Films of Thermally Activated Delayed Fluorescence Emitters. *The Journal of Physical Chemistry Letters*, 8 (13). pp. 2930-2935. ISSN 1948-7185

Published by: American Chemical Society

URL: <http://dx.doi.org/10.1021/acs.jpcllett.7b00729> <<http://dx.doi.org/10.1021/acs.jpcllett.7b00729>>

This version was downloaded from Northumbria Research Link: <http://nrl.northumbria.ac.uk/41871/>

Northumbria University has developed Northumbria Research Link (NRL) to enable users to access the University's research output. Copyright © and moral rights for items on NRL are retained by the individual author(s) and/or other copyright owners. Single copies of full items can be reproduced, displayed or performed, and given to third parties in any format or medium for personal research or study, educational, or not-for-profit purposes without prior permission or charge, provided the authors, title and full bibliographic details are given, as well as a hyperlink and/or URL to the original metadata page. The content must not be changed in any way. Full items must not be sold commercially in any format or medium without formal permission of the copyright holder. The full policy is available online: <http://nrl.northumbria.ac.uk/policies.html>

This document may differ from the final, published version of the research and has been made available online in accordance with publisher policies. To read and/or cite from the published version of the research, please visit the publisher's website (a subscription may be required.)



Northumbria
University
NEWCASTLE



UniversityLibrary

Fluorescence and Phosphorescence Anisotropy from Oriented Films of Thermally Activated Delayed Fluorescence Emitters

Heather Fay Higginbotham, Marc Kenneth Etherington, and Andrew P. Monkman

J. Phys. Chem. Lett., **Just Accepted Manuscript** • Publication Date (Web): 26 May 2017

Downloaded from <http://pubs.acs.org> on June 1, 2017

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Fluorescence and Phosphorescence Anisotropy from Oriented Films of Thermally Activated Delayed Fluorescence Emitters.

*Heather F. Higginbotham, Marc. K. Etherington, Andrew P. Monkman**

Department of Physics, Durham University, South Road. DH1 3LE. UK

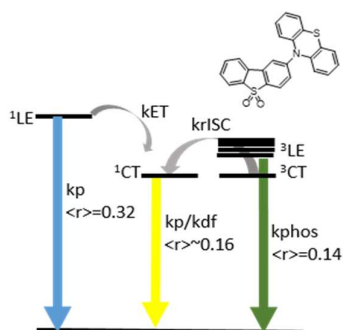
AUTHOR INFORMATION

Corresponding Author

*a.p.monkman@durham.ac.uk

1
2
3 Anisotropy within three TADF materials has been observed using steady-state fluorescence
4 polarisation. This technique has allowed for the observation of differences in polarisation
5 within dilute solution, and both un-stretched and stretched films; the latter producing highly
6 aligned molecules within the sample. Using these aligned films differences in anisotropy can
7 be observed between the emission from the ^1LE and ^1CT states and upon exciting different
8 absorption bands. Furthermore, polarisation observed from time-resolved measurements,
9 highlights the strong vibronic coupling between charge-transfer and local triplet states.

21 TOC GRAPHICS



39 **KEYWORDS** Thermally-activated delayed fluorescence, polarisation, outcoupling, charge-
40 transfer
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

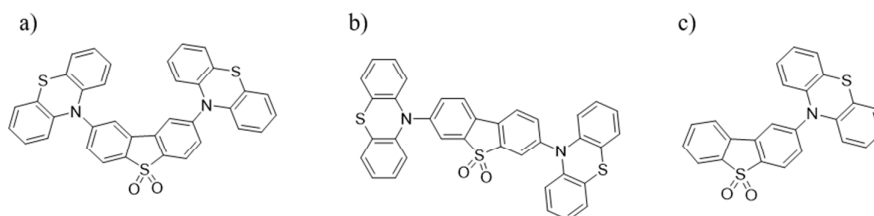
1
2
3 Organic light-emitting diodes (OLEDs) have come to the forefront of electronic applications
4 due to their superior light output, colour purity and low toxicity.^{1,2} Moreover, precise design
5 of OLED materials has yielded compounds with internal quantum efficiency (IQE) of 100%
6 without the use of expensive inorganic phosphor materials.^{3,4} In many cases this has been
7 achieved using materials capable of thermally-activated delayed fluorescence (TADF),⁵⁻⁸
8 where fast reverse intersystem crossing (rISC) is capable of harvesting 100% of triplets back
9 to emissive singlets.^{9,10} With an abundance of OLED emitting materials exploiting TADF, a
10 more comprehensive understanding of its mechanism is required to further knowledge of how
11 OLED efficiency can be improved in the future.
12
13
14
15
16
17
18
19
20
21
22

23
24 As well as optimising the emitter for 100% efficient charge to light conversion, extracting
25 light from a device is also a critical aspect of attaining an overall efficient OLED.² The
26 process by which emission is trapped stems from how light from the emitting layer passes
27 through further device barriers/layers of differing refractive indexes, creating total internal
28 reflection and waveguiding within the different layers. With this in mind, the ratio of light
29 generated internally to that which escapes the device, defines the outcoupling parameter.
30
31
32
33
34
35
36

37
38 Although outcoupling is often an overlooked parameter within device fabrication research,
39 the term is of paramount importance when describing external quantum efficiency (EQE),
40 arguably the most important parameter when determining OLED efficiency. With the fraction
41 of light extracted limited to an estimated 20-30%, outcoupling therefore limits the EQE of a
42 device to discouraging values.^{2,11-13} The estimation of outcoupling efficiency in normal
43 devices is based upon the assumption that within the device structure, the emitting layer
44 contains molecules that are deposited in non-uniform orientations, creating random or
45 isotropic emission. However research has shown that orientated emitters reduce coupling to
46 surface plasmon modes within the interfaces of the device, increasing light extracted.¹⁴⁻¹⁶
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 With this knowledge in mind, there have been some investigations of molecular alignment of
4 OLED phosphorescent¹⁶⁻²³ and TADF^{14,24} emitters within films, using predominantly angular-
5 dependent photoluminescence techniques in order to map the average angle of the transition
6 dipole moment (TDM), which is fit to computational simulations. These comprehensive
7 works, pioneered by Brütting, have shown that in some cases spontaneous horizontal
8 molecular alignment occurs during vacuum deposition²³ therefore an investigation *via*
9 artificial molecular alignment would prove an ideal model for studying light emission within
10 a device structure.
11
12
13
14
15
16
17
18
19

20
21 Here we present an alternate technique to obtain the physical orientation of the TDM within a
22 film; fluorescence polarisation spectroscopy. Using this experimental method, the relative
23 angles between ground and excited state dipole moments can be determined, in order to map
24 molecular anisotropy within three known TADF materials (Scheme 1). The results show that
25 within mechanically stretched films, small organic emitters do align to give anisotropic
26 emission and the absolute alignments of TDMs can be used to design better OLED emitting
27 materials that can be deposited with enhancement of outcoupling in mind. It is therefore
28 anticipated that comprehension of the TDM within TADF materials will help improve
29 methods to increase outcoupling and assist quantum chemists in obtaining better models of
30 molecular excited state properties.
31
32
33
34
35
36
37
38
39
40
41
42
43
44



Scheme 1 Structures of three TADF emitters a) 2,8-DPTZ-DBTO₂ , b) 3,7-DPTZ-DBTO₂ and c) 2-PTZ-DBTO₂ used for anisotropy studies using fluorescence polarisation spectroscopy

The anisotropy a sample is determined *via* the following equation,

$$\langle r \rangle = \frac{I_{vv} - GI_{vh}}{I_{vv} + (2GI_{vh})}, \quad \text{-Equation 1}$$

where $\langle r \rangle$ is the anisotropy of the sample, I_{vv} denotes the intensity of light with an excitation polariser and emission polariser in the vertical position, I_{vh} denotes the intensity of light obtained with the excitation polariser in the vertical and emission polariser in the perpendicular position, and G is the instrument calibration factor, which corrects for any dependencies upon polarisation within the instrument's optical components.^{25,26} Anisotropy ($\langle r \rangle$) can be related to the angle between the absorption and emission transition dipole (θ) *via* the following,

$$\langle r \rangle = \frac{2}{5} \frac{3\cos^2\theta - 1}{2}, \quad \text{-Equation 2}$$

where a $\langle r \rangle$ value of 0.4 denotes complete alignment of the absorption and emission dipole moments and -0.2 denotes a 90 ° angle between the absorption and emission dipole moments. Within stretch orientated films, alignment of the absorption dipole moment with the z-axis incident light polarisation, removes the probability of photoselection observed within isotropic materials and subsequently the 2/5 parameter from the equation. This factor however remains, due to the low symmetry of the molecules, as only in highly symmetrical molecules can $\cos^2\theta$ theoretically be 1.²⁷

The three molecules studied, 2,8-DPTZ-DBTO₂, 3,7-DPTZ-DBTO₂ and 2-PTZ-DBTO₂, were chosen for their documented TADF properties and strong charger-transfer (CT) character, (all

1
2
3 of which are published by our group in the literature),^{9,28,29} and similar structure (Scheme 1).
4
5 This structural similarity was chosen so that all changes in anisotropy could be attributed to
6
7 molecular alignment and subunit conformation, rather than dipole changes due to a change in
8
9 molecular structure. Absorbance of each compound in polyethylene (PE) film reproduces
10
11 literature results (Figure S1), with the spectra showing a characteristic absorption band in the
12
13 blue ($\text{abs}_{\text{max}} \sim 340 \text{ nm}$), indicative of phenothiazine absorption, and a characteristic red shifted
14
15 ‘tail’, previously identified as direct CT absorption.²⁸ This indicates that the structural
16
17 integrity of the compounds is preserved even after heating and casting within the PE film.
18
19

20
21 To obtain a complete picture of the anisotropy of each compound and to ensure the validity of
22
23 results, the compounds were analysed in dilute ($10 \mu\text{M}$) toluene solution, in un-stretched PE
24
25 film as well as oriented films containing aligned molecules, formed through mechanical
26
27 stretching. Fluorescence polarisation spectroscopy of 2-PTZ-DBTO₂ in dilute solution shows
28
29 an anisotropy close to 0, indicating, not a dipole change of 54.7° , but the molecules’ freedom
30
31 to rotate on a timescale faster than the emission lifetime, resulting in emission at a large
32
33 distribution of angles (Figure 1a).³⁰ Solution anisotropy of 2,8-DPTZ-DBTO₂ and 3,7-DPTZ-
34
35 DBTO₂ show identical depolarisation effects and can be found in the supporting information
36
37 (Figure S2). Depolarised emission within dilute solution is indiscriminate of emitting
38
39 pathway from the excited state as both the ¹LE ($\lambda_{\text{em}} \sim 430 \text{ nm}$) and ¹CT ($\lambda_{\text{em}} \sim 570 \text{ nm}$) emission
40
41 in the 3,7-DPTZ-DBTO₂ and 2-PTZ-DBTO₂ samples display an anisotropy of close to 0
42
43 across the whole emission spectrum. The result is expected due to the low viscosity of the
44
45 toluene solvent and the low concentration of the solute.
46
47
48
49

50
51 Casting 2,8-DPTZ-DBTO₂, 3,7-DPTZ-DBTO₂ and 2-PTZ-DBTO₂ in solid PE film removes
52
53 the depolarisation due to rotation seen in dilute solutions. Regardless, the un-stretched PE
54
55 films also show an anisotropy of close to 0 for both ¹LE and ¹CT emission bands (Figure 1b
56
57
58
59
60

and S3). This means that at a concentration of 1% emitter, each molecule is randomly oriented when dispersed within the film, and thus no spontaneous alignment is found. Such depolarisation proves that the estimation of the outcoupling factor in devices using these compounds, assuming random orientation, is most likely accurate and that previously reported EQEs of more than 5% can be attributed to the increase in the charge recombination parameter (due to the presence of TADF) and not an increase in outcoupling.

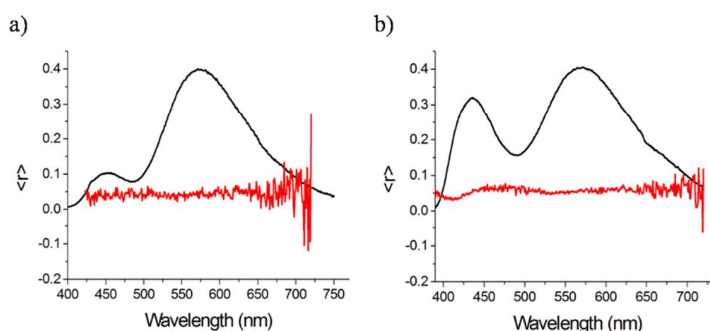


Figure 1 a) Anisotropy of 2-PTZ-DBTO₂ in a) a 10 μ M toluene solution (red line) and b) an un-stretched PE film containing 1% w/w of the emitter (red line) (λ_{ex} 370 nm). Note: The normalised emission spectrum is added in black for clarity

By stretching the film along a single axis, one can then induce molecular alignment to mimic anisotropy within an ideal OLED emissive layer. Stretched films with a stretch ratio of above 10 were analysed at different excitation wavelengths and through rotation of the film from 0-90 $^{\circ}$; with 0 $^{\circ}$ implying the film is placed with the stretch direction aligned with the vertically polarised excitation light, and 90 $^{\circ}$ implying that the stretch direction is perpendicular to the vertically polarised excitation light. Upon excitation at 370 nm (into the donor phenothiazine absorption band) the stretched films emit with an anisotropy related to the film orientation (Figure 2). In the 2,8-DPTZ-DBTO₂ film (Figure 2a), aligned with the vertical polarisation (0 $^{\circ}$), an anisotropy of 0.13 ± 0.01 is observed for emission from the ¹CT state (at emission of 570 nm), a value denoting a difference between the absorption and emission dipole moment of 42

1
2
3 °. Rotation of the film within the holder to 20, 45, 60 and 90 °, the latter giving a
4
5 perpendicular orientation of the stretch direction to the excitation polarisation, shows a
6
7 reduction in anisotropy down to below 0. We observe an anisotropy specifically of 0 when
8
9 the stretched film is oriented at the magic angle with respect to the light polarisation. This
10
11 phenomenon is also observed in the 3,7-DPTZ-DBTO₂ and 2-PTZ-DBTO₂ samples. This loss
12
13 in anisotropy is a direct result of film rotation, highlighting the alignment of the molecules
14
15 within the sample.
16
17

18
19 For the 0 ° aligned films of 3,7-DPTZ-DBTO₂, an anisotropy of 0.23±0.01 at 580 nm, within
20
21 the ¹CT emission band, is observed. This value denotes an angle between the absorption and
22
23 emission dipole moments of 32 °. This difference in TDM angle between the 2,8-DPTZ-
24
25 DBTO₂ and 3,7-DPTZ-DBTO₂ molecules highlights the effect of different donor positioning
26
27 within the two molecules and therefore the importance of molecular configuration when
28
29 designing CT emitting TADF molecules, if orientation is a target parameter. The 2-PTZ-
30
31 DBTO₂ molecule, shows CT emission with an anisotropy of 0.18±0.01 at the emission
32
33 maxima of 570 nm, showing a 37 ° angle between dipole moments. Although both 2,8-
34
35 DPTZ-DBTO₂ and 2-PTZ-DBTO₂ contain donor/s placed in the same position of the
36
37 acceptor, the presence of a single donor in 2-PTZ-DBTO₂ means that its absorption and
38
39 emission must come from the same donor upon each photoexcited event, unlike 2,8-DPTZ-
40
41 DBTO₂ which may depolarise somewhat, assuming both donors are likely to photoexcite, and
42
43 may indicate different orientations of each donor.^{29,31} Local excited state (¹LE) phenothiazine
44
45 emission can also be seen in both the 2-PTZ-DBTO₂ and 3,7-DPTZ-DBTO₂ stretched films,
46
47 with an anisotropy of 0.32±0.01 at the emission maxima of 430 nm in the former and
48
49 0.41±0.03 in the latter at 0 ° film orientation. This highlights that within the dispersed host,
50
51 there is no energy migration between emitter molecules and absorption and emission from
52
53 ¹LE arises through the same orbitals. As excitation at 370 nm initially populates the local
54
55
56
57
58
59
60

excited state (^1LE) it is trivial to see that emission from the same ^1LE state (at 430 nm) should induce a smaller TDM change than emission subsequently arising from the ^1CT state. Furthermore, emission from both ^1LE and ^1CT states shows depolarisation upon film rotation and so it can be concluded that the ensemble of emitter molecules are all highly aligned.

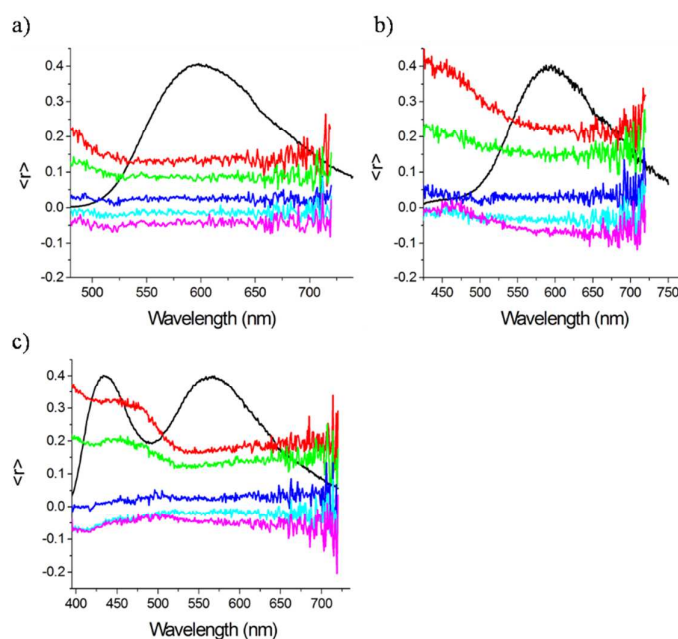


Figure 2 Anisotropy of stretched films of 1% a) 2,8-DPTZ-DBTO₂ b) 3,7-DPTZ-DBTO₂ and c) 2-PTZ-DBTO₂ (λ_{ex} 370 nm) with the stretched film aligned at 0° (red), 20° (green), 45° (blue), 60° (cyan), and 90° (pink). Note: The normalised emission spectrum is added in black for clarity

As well as probing anisotropy upon phenothiazine donor excitation, changes in polarisation can also be seen upon direct CT absorption. Dias *et al.* identified the presence of a direct CT absorbance band on the red edge (visible from \sim 400-470 nm) of a UV-visible spectrum of 2,8-DPTZ-DBTO₂ in both film and in solution.²⁸ To further corroborate this work, stretched films of 2,8-DPTZ-DBTO₂, 3,7-DPTZ-DBTO₂ and 2-PTZ-DBTO₂ were excited from 310 nm (exciting the phenothiazine donor) through to 480 nm, selectively exciting the CT absorption

1
2
3 band (Figure 3). Regarding 2,8-DPTZ-DBTO₂ with the film stretch axis aligned with the
4
5 vertical polarisation, the same anisotropy of ~ 0.14 (for emission from the ¹CT state, λ_{em} 570
6
7 nm) is seen when exciting the molecule between 310-370 nm, identified as excitation of the
8
9 phenothiazine ¹LE state (Figure 3a-red plot). Excitation between 390-480 nm produces a very
10
11 significant increase in anisotropy up to 0.35 ± 0.02 , close to the maximum anisotropy and
12
13 denoting a difference of only 16° between absorption and emission dipole moments. This
14
15 alignment of absorption and emission dipoles clearly verifies this red edge absorption band as
16
17 direct CT absorption.
18
19

20
21
22 In all three molecules, the anisotropy of the un-stretched film and the dilute solutions is not
23
24 affected by the change in excitation wavelength, showing the same depolarisation in all cases.
25
26 As the un-stretched film was measured in the same holder and under identical conditions as
27
28 the stretched materials, it acts as an effective control for the experiment. The increase in
29
30 anisotropy upon change in excitation is also seen in the 3,7-DPTZ-DBTO₂ molecule,
31
32 displaying an anisotropy of 0.42 ± 0.04 (when emitting from the ¹CT state, λ_{em} 580 nm) when
33
34 excited at 480 nm, when the film is vertically aligned (Figure 3b-red plot). This value denotes
35
36 complete alignment of the absorption dipole moment and the emission dipole moment,
37
38 expected if attributed to the same CT state.
39
40
41

42
43 In all cases the anisotropy is reduced upon rotation of the film. As the film is rotated, the
44
45 anisotropy diminishes to below 0, further reiterating the high degree of orientation through
46
47 the stretching process. Interestingly, both the 3,7-DPTZ-DBTO₂ and 2-PTZ-DBTO₂ film,
48
49 with their two distinct emission peaks, displays discrete anisotropic behaviour for both the
50
51 ¹LE and ¹CT states (Figure 3c and d). In Figure 3a, b and c the presence of two absorption
52
53 states (¹LE and ¹CT) is further highlighted, by monitoring the anisotropy of the CT emission
54
55 as a function of excitation wavelength. In Figure 3d we show the anisotropy as a function of
56
57
58
59
60

excitation wavelength when monitoring the emission from the ^1LE ($\lambda_{\text{em}}430\text{ nm}$) state in 2-PTZ-DBTO₂. While excitation between 310-390 nm shows no increase in the anisotropy of the CT emission, (beginning to increase only after 390 nm-Figure 3c), we observe increasing anisotropy from the ^1LE emission, starting at 0.25 ± 0.02 , at 310 nm excitation, and steadily rising to 0.35 ± 0.01 at 390 nm excitation. Assuming that the emission dipole moment of the ^1LE state is not changing (at a single film position), it again shows that there is more than one absorbing transition in this region which gives rise to ^1LE emission. Emission from the locally excited state ($\lambda_{\text{em}}430\text{ nm}$) is also affected by film rotation (due to the rotation of the aligned molecules and their emission dipole moment away from the excitation polarisation). We believe this is clear evidence of the mixing of $\pi\text{-}\pi^*$ and $\text{n-}\pi^*$ transitions in the absorption band tails as described by Marion³² and in our previous work.^{28,33}

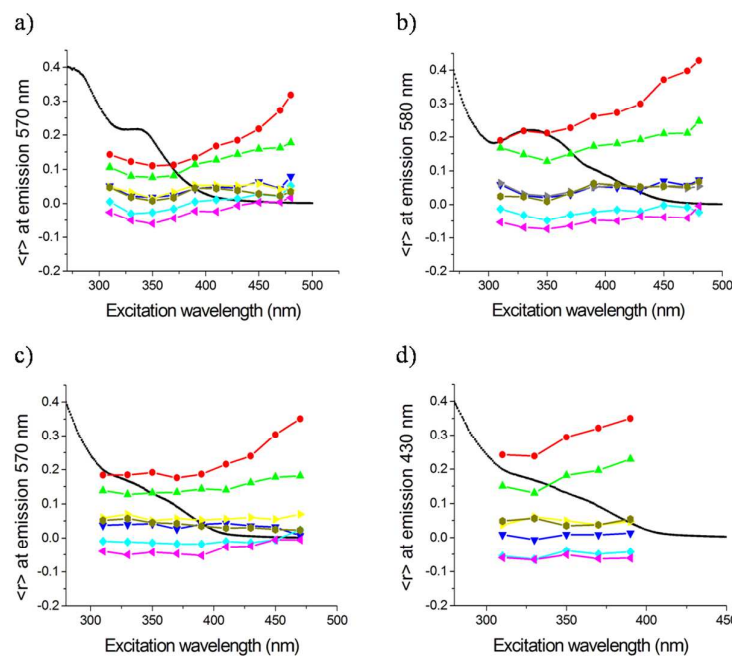


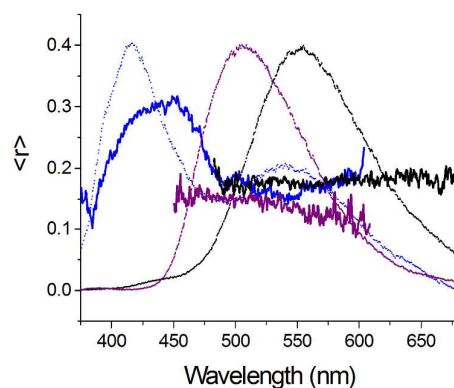
Figure 3 Anisotropy of films of 1% a) 2,8-DPTZ-DBTO₂ b) 3,7-DPTZ-DBTO₂ and c) 2-PTZ-DBTO₂ with emission at 570 nm or 580 nm (^1CT emission) d) 2-PTZ-DBTO₂ with emission at 430 nm (^1LE), at different excitation wavelengths, with the stretched film aligned

1
2
3 at 0 ° (red), 20 ° (green), 45 ° (yellow), 60 ° (cyan), 90 ° (pink), an un-stretched film (mustard)
4
5 and a 10 μM solution (blue). Note: The normalised excitation spectrum is added in black for
6
7 clarity
8
9

10
11 To further characterise the position of the dipole moments within these complex molecules,
12
13 we turn to time-resolved anisotropy measurements. The anisotropy of 2-PTZ-DBTO₂ was
14
15 investigated in the nanosecond (prompt emission), early microsecond (TADF emission) and
16
17 late microsecond (phosphorescence) regions, allowing for a more comprehensive picture of
18
19 each TDM within this molecule (Figure S5). Polarisation was recorded using a vertically
20
21 polarised Nd:YAG laser, to create a polarised excitation source, coupled with a visible
22
23 polariser, placed after the sample in the set-up. As seen in the steady state measurements, a 2-
24
25 PTZ-DBTO₂ stretched film placed parallel (0 °) to the polarised laser produces ¹LE emission
26
27 anisotropy of 0.28±0.06 (λ_{em} =430 nm), with an onset of 2.98 eV and a CT anisotropy of
28
29 0.16±0.03 (λ_{em} =540 nm) at 2 ns time delay from the 0 time of the laser (Figure 4-blue plot).
30
31 These values are similar to those seen in steady-state spectroscopy (Figure 2c) and can thus
32
33 be considered as indicative of the TDM of the pure fluorescence states, ¹LE and ¹CT. At 3 μs
34
35 time delay, clear delayed ¹CT emission is observed, already fully characterised by Ward *et.*
36
37 *al.*, and identified as TADF. At 0 ° film alignment, this delayed emission has an anisotropy of
38
39 0.17±0.04, identical to the prompt ¹CT value within experimental error. This highlights that
40
41 the dipole moment of the CT state is stationary, regardless of any excursions to the triplet
42
43 state and back *via* rISC within the TADF mechanism. As seen in steady state polarisation
44
45 spectroscopy, rotation of the film depolarises the anisotropic output (Figure S6).
46
47
48
49

50
51 At a delay time of 200 μs there is a blue shift in emission to an onset of 2.44 eV, identified as
52
53 emission from the triplet, ³LE state. Along with this hypsochromic shift in emission,
54
55 manifests an additional change in anisotropy. At 0 ° film alignment, the anisotropy is reduced
56
57
58
59
60

1
2
3 to 0.14 ± 0.04 , therefore showing a significant change between the dipole moment position of
4
5 the ^1LE (found at very short timescales- $\lambda_{\text{em}} 430$ nm) and the ^3LE state. In contrast, the
6
7 phosphorescence anisotropy observed at long delay times appears similar to the anisotropy of
8
9 the singlet CT emission. This result is therefore surprising but not unprecedented within
10
11 literature. A study by Herbich *et. al.*, observed that some organic molecules displayed
12
13 phosphorescence anisotropy close to that of the ^1CT state, not of the ^1LE state.³⁴ The data
14
15 resulting from this literature is in line with the current model published by this group of the
16
17 efficient rRISC process within TADF molecules, whereby spin-orbit coupling (SOC)
18
19 between the ^1CT state and the ^3LE state (and vice versa) is mediated through ^3CT - ^3LE
20
21 vibronic coupling and second-order SOC.^{35,36} These anisotropy results therefore clearly
22
23 suggest that the presence of strong ^3CT - ^3LE vibronic coupling, mixes these states, resulting in
24
25 the observed equivalence of the ^3LE and ^1CT anisotropy. Therefore, this time-resolved
26
27 polarisation spectroscopy technique not only further corroborates the theory of ^3CT - ^3LE
28
29 coupling within TADF materials but can be further used as a method for identifying good
30
31 TADF materials in the future.
32
33
34
35
36
37



38
39
40
41
42
43
44
45
46
47
48
49
50
51
52 **Figure 4** Time resolved anisotropy of 1% 2-PTZ-DBTO₂ stretched film (0 °) excited at 355
53 nm at 2 ns (blue), 3 μs (black), and 200 μs (purple). Note: The normalised emission spectrum
54 (dashed lines) is added in blue (2 ns), black (3 μs) and purple (200 μs) for clarity
55
56
57
58
59
60

1
2
3 Polarisation spectroscopy has allowed for the identification of changes in TDM upon
4
5 emission from the local and charge-transfer states. In relation to research of enhancing
6
7 outcoupling, it is possible to induce TADF molecular alignment within films, allowing for the
8
9 development of an accurate experimental model for dipole alignment within OLED
10
11 structures, which is consistent with the observation of increased yield for outcoupled
12
13 emission within devices. Nevertheless care should be taken by both experimental and
14
15 computation researchers, due to the complicated excited state dynamics within these
16
17 seemingly simple TADF materials. It is hoped that this and other such studies will assist
18
19 quantum chemists in obtaining better models to be applied to OLED research and design.
20
21

22 23 ASSOCIATED CONTENT

24
25
26
27 Supporting Information: The Supporting Information is available free of charge on the ACS
28
29 Publications website at DOI: XXXXXXXXX. Provided are the experiment methods,
30
31 absorbance spectra of films and additional anisotropy data.
32
33

34 35 AUTHOR INFORMATION

36 37 **Corresponding author**

38
39 A.P.M: Email: a.p.monkman@durham.ac.uk
40
41

42 43 **Notes**

44
45 The authors declare no competing financial interests.
46
47

48 49 ACKNOWLEDGMENT

50
51 H.F.H M.K.E and A.P.M acknowledge the EU's Horizon 2020 for funding the PHEBE
52
53 project under grant no. 6,41,725.
54

55 56 REFERENCES

57
58
59
60

- 1
2
3
4
5 (1) Tao, Y.; Yuan, K.; Chen, T.; Xu, P.; Li, H.; Chen, R.; Zheng, C.; Zhang, L.; Huang, W.
6
7 Thermally Activated Delayed Fluorescence Materials Towards the Breakthrough of
8
9 Organoelectronics. *Adv. Mater.* **2014**, *26*, 7931–7958.
10
11
12 (2) Chang, Y. L. *Efficient Organic Light-Emitting Diodes (OLEDs)*; Pan Stanford Publishing,
13
14 2015.
15
16
17 (3) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.;
18
19 Forrest, S. R. Highly Efficient Phosphorescent Emission from Organic Electroluminescent
20
21 Devices. *Nature* **1998**, *395*, 151–154.
22
23
24 (4) Baldo, M. A.; Thompson, M. E.; Forrest, S. R. High-Efficiency Fluorescent Organic
25
26 Light-Emitting Devices Using a Phosphorescent Sensitizer. *Nature* **2000**, *403*, 750–753.
27
28
29 (5) Yang, Z.; Mao, Z.; Xie, Z.; Zhang, Y.; Liu, S.; Zhao, J.; Xu, J.; Chi, Z.; Aldred, M. P.
30
31 Recent Advances in Organic Thermally Activated Delayed Fluorescence Materials. *Chem.*
32
33 *Soc. Rev.* **2017**, *46*, 915–1016.
34
35
36 (6) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. Highly Efficient Organic
37
38 Light-Emitting Diodes from Delayed Fluorescence. *Nature* **2012**, *492*, 234–238.
39
40
41 (7) Zhang, Q.; Li, B.; Huang, S.; Nomura, H.; Tanaka, H.; Adachi, C. Efficient Blue Organic
42
43 Light-Emitting Diodes Employing Thermally Activated Delayed Fluorescence. *Nat. Photon.*
44
45 **2014**, *8*, 326–332.
46
47
48 (8) Jankus, V.; Data, P.; Graves, D.; McGuinness, C.; Santos, J.; Bryce, M. R.; Dias, F. B.;
49
50 Monkman, A. P. Highly Efficient TADF OLEDs: How the Emitter–Host Interaction Controls
51
52
53
54
55
56
57
58
59
60

1
2
3 Both the Excited State Species and Electrical Properties of the Devices to Achieve Near
4
5 100% Triplet Harvesting and High Efficiency. *Adv. Funct. Mater.* **2014**, *24*, 6178–6186.
6
7

8
9 (9) Ward, J. S.; Nobuyasu, R. S.; Batsanov, A. S.; Data, P.; Monkman, A. P.; Dias, F. B.;
10
11 Bryce, M. R. The Interplay of Thermally Activated Delayed Fluorescence (TADF) and Room
12
13 Temperature Organic Phosphorescence in Sterically-Constrained Donor-Acceptor Charge-
14
15 Transfer Molecules. *Chem. Commun.* **2016**, *52*, 2612–2615.
16
17

18
19 (10) Dias, F. B.; Pollock, S.; Hedley, G.; Pålsson, L. O.; Monkman, A.; Perepichka, I. I.;
20
21 Perepichka, I. F.; Tavasli, M.; Bryce, M. R. Intramolecular Charge Transfer Assisted by
22
23 Conformational Changes in the Excited State of Fluorene-dibenzothiophene-S,S-dioxide Co-
24
25 oligomers. *J. Phys. Chem. B* **2006**, *110*, 19329–19339.
26
27

28
29 (11) Gather, M. C.; Reineke, S. Recent Advances in Light Outcoupling from White Organic
30
31 Light-Emitting Diodes. *J. Photon. Energy* **2015**, *5*, 057607-1–057607-20.
32
33

34
35 (12) Saxena, K.; Jain, V. K.; Mehta, D. S. A Review on the Light Extraction Techniques in
36
37 Organic Electroluminescent Devices. *Opt. Mater.* **2009**, *32*, 221–233.
38
39

40
41 (13) Patel, N. K.; Cina, S.; Burroughes, J. H. High-Efficiency Organic Light-Emitting
42
43 Diodes. *IEEE J. Sel. Top. Quantum Electron.* **2002**, *8*, 346–361.
44
45

46
47 (14) Mayr, C.; Lee, S. Y.; Schmidt, T. D.; Yasuda, T.; Adachi, C.; Brütting, W. Efficiency
48
49 Enhancement of Organic Light-Emitting Diodes Incorporating a Highly Oriented Thermally
50
51 Activated Delayed Fluorescence Emitter. *Adv. Funct. Mater.* **2014**, *24*, 5232–5239.
52
53

54
55 (15) Nowy, S.; Krummacher, B. C.; Frischeisen, J.; Reinke, N. A.; Brütting, W. Light
56
57 Extraction and Optical Loss Mechanisms in Organic Light-Emitting Diodes: Influence of the
58
59 Emitter Quantum Efficiency. *J. Appl. Phys.* **2008**, *104*, 123109-1–123109-9.
60

1
2
3 (16) Flämmich, M.; Frischeisen, J.; Setz, D. S.; Michaelis, D.; Krummacher, B. C.; Schmidt,
4
5 T. D.; Brütting, W.; Danz, N. Oriented Phosphorescent Emitters Boost OLED Efficiency.
6
7 *Org. Electron.* **2011**, *12*, 1663–1668.

8
9
10 (17) Lampe, T.; Schmidt, T. D.; Jurow, M. J.; Djurovich, P. I.; Thompson, M. E.; Brütting,
11
12 W. Dependence of Phosphorescent Emitter Orientation on Deposition Technique in Doped
13
14 Organic Films. *Chem. Mater.* **2016**, *28*, 712–715.

15
16
17 (18) Schmidt, T. D.; Setz, D. S.; Flämmich, M.; Frischeisen, J.; Michaelis, D.; Krummacher,
18
19 B. C.; Danz, N.; Brütting, W. Evidence for Non-Isotropic Emitter Orientation in a Red
20
21 Phosphorescent Organic Light-Emitting Diode and its Implications for Determining the
22
23 Emitter's Radiative Quantum Efficiency. *Appl. Phys. Lett.* **2011**, *99*, 163302-1–163302-3.

24
25
26 (19) Kim, K. H.; Moon, C. K.; Lee, J. H.; Kim, S. Y.; Kim, J. J. Highly Efficient Organic
27
28 Light-Emitting Diodes with Phosphorescent Emitters Having High Quantum Yield and
29
30 Horizontal Orientation of Transition Dipole Moments. *Adv. Mater.* **2014**, *26*, 3844–3847.

31
32
33 (20) Liehm, P.; Murawski, C.; Furno, M.; Lüssem, B.; Leo, K.; Gather, M. C. Comparing the
34
35 Emissive Dipole Orientation of Two Similar Phosphorescent Green Emitter Molecules in
36
37 Highly Efficient Organic Light-Emitting Diodes. *Appl. Phys. Lett.* **2012**, *101*, 253304-1–
38
39 253304-4.

40
41
42 (21) Kim, S. Y.; Jeong, W. I.; Mayr, C.; Park, Y. S.; Kim, K. H.; Lee, J. H.; Moon, C. K.;
43
44 Brütting, W.; Kim, J. J. Organic Light-Emitting Diodes with 30% External Quantum
45
46 Efficiency Based on a Horizontally Oriented Emitter. *Adv. Funct. Mater.* **2013**, *23*, 3896–
47
48 3900.

1
2
3 (22) Kim, K.-H.; Liao, J. L.; Lee, S. W.; Sim, B.; Moon, C. K.; Lee, G. H.; Kim, H. J.; Chi,
4
5 Y.; Kim, J. J. Crystal Organic Light-Emitting Diodes with Perfectly Oriented Non-Doped Pt-
6
7 Based Emitting Layer. *Adv. Mater.* **2016**, *28*, 2526–2532.

8
9
10 (23) Jurow, M. J.; Mayr, C.; Schmidt, T. D.; Lampe, T.; Djurovich, P. I.; Brutting, W.;
11
12 Thompson, M. E. Understanding and Predicting the Orientation of Heteroleptic Phosphors in
13
14 Organic Light-Emitting Materials. *Nat. Mater.* **2016**, *15*, 85–91.

15
16
17 (24) Sun, J. W.; Kim, K. H.; Moon, C. K.; Lee, J. H.; Kim, J. J. Highly Efficient Sky-Blue
18
19 Fluorescent Organic Light Emitting Diode Based on Mixed Cohost System for Thermally
20
21 Activated Delayed Fluorescence Emitter (2CzPN). *ACS Appl. Mater. Interf.* **2016**, *8*, 9806–
22
23 9810.

24
25
26 (25) Vaughan, H. L.; Dias, F. M. B.; Monkman, A. P. An Investigation into the Excitation
27
28 Migration in Polyfluorene Solutions via Temperature Dependent Fluorescence Anisotropy. *J.*
29
30 *Chem. Phys.* **2005**, *122*, 014902.

31
32
33 (26) Vaughan, H. L.; Monkman, A. P.; Pålsson, L.-O.; Nehls, B. S.; Farrell, T.; Scherf, U. On
34
35 the Angular Dependence of the Optical Polarization Anisotropy in Ladder-Type Polymers. *J.*
36
37 *Chem. Phys.* **2008**, *128*, 044709.

38
39
40 (27) Thulstrup, E.W. and Michl, J. Polarized Absorption Spectroscopy of Molecules Aligned
41
42 in Stretched Polymers. *Spectrochim. Acta* **1988**, *44A*, 767-782.

43
44
45 (28) Dias, F. B.; Santos, J.; Graves, D. R.; Data, P.; Nobuyasu, R. S.; Fox, M. A.; Batsanov,
46
47 A. S.; Palmeira, T.; Berberan-Santos, M. N.; Bryce, M. R.; Monkman, A. P. The Role of
48
49 Local Triplet Excited States and D-A Relative Orientation in Thermally Activated Delayed
50
51 Fluorescence: Photophysics and Devices. *Adv. Sci.* **2016**, *3*, 1600080.
52
53
54
55
56
57
58
59
60

1
2
3 (29) Etherington, M. K.; Franchello, F.; Gibson, J.; Northey, T.; Santos, J.; Ward, J. S.; Data,
4 P.; Kurowska, A.; Higginbotham, H. F.; dos Santos, P. L.; Graves, D. R.; Batsanov, A. S.;
5
6
7 Dias, F. B.; Bryce, M. R.; Penfold, T. J.; Monkman, A. P. Regio- and Conformational
8
9 Isomerisation Critical to Design of Efficient Thermally-activated Delayed Fluorescence
10
11 Emitters. *Nat. Commun.* **2017**, *8*, 1–11.
12

13
14
15 (30) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Springer, 2006
16
17

18
19 (31) Okazaki, M.; Takeda, Y.; Data, P.; Pander, P.; Higginbotham, H.; Monkman, A. P.;
20
21 Minakata, S. Thermally Activated Delayed Fluorescent Phenothiazine-
22
23 Dibenzo[a,j]phenazine-phenothiazine Triads Exhibiting Tricolor-Changing Mechanochromic
24
25 Luminescence. *Chem. Sci.* **2017**, *8*, 2677–2686.
26
27

28
29 (32) Marian, C. M. A New Pathway for the Rapid Decay of Electronically Excited Adenine.
30
31 *J. Chem. Phys.* **2005**, *122*, 104314.
32
33

34 (33) Dias, F. B.; Bourdakos, K. N.; Jankus, V.; Moss, K. C.; Kamtekar, K. T.; Bhalla, V.;
35
36 Santos, J.; Bryce, M. R.; Monkman, A. P. Triplet Harvesting with 100% Efficiency by Way
37
38 of Thermally Activated Delayed Fluorescence in Charge Transfer OLED Emitters. *Adv.*
39
40 *Mater.* **2013**, *25*, 3707–3714.
41
42

43
44 (34) Herbich, J.; Kapturkiewicz, A.; Nowacki, J. Phosphorescent Intramolecular Charge
45
46 Transfer Triplet States. *Chem. Phys. Lett.* **1996**, *262*, 633–642.
47
48

49
50 (35) Gibson, J.; Monkman, A. P.; Penfold, T. J. The Importance of Vibronic Coupling for
51
52 Efficient Reverse Intersystem Crossing in Thermally Activated Delayed Fluorescence
53
54 Molecules. *ChemPhysChem* **2016**, *17*, 2956–2961.
55
56
57
58
59
60

1
2
3 (36) Etherington, M. K.; Gibson, J.; Higginbotham, H. F.; Penfold, T. J.; Monkman, A. P.
4
5 Revealing the Spin-Vibronic Coupling Mechanism of Thermally Activated Delayed
6
7 Fluorescence. *Nat. Commun.* **2016**, *7*, 13680.
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60