# Molecular geometry and TADF photophysics:

# the strange case of DMAC-py-TRZ

Ettore Crovini,<sup>a‡</sup> Rama Dhali,<sup>b‡</sup> Dianming Sun,<sup>\*a</sup> Tomas Matulaitis, <sup>a</sup> Thomas Comerford, <sup>a</sup> Alexandra M. Z. Slawin,<sup>a</sup> Cristina Sissa,<sup>b</sup> Francesco Azzolin, <sup>b</sup> Francesco Di Maiolo, <sup>b</sup> Anna Painelli<sup>\*</sup>, <sup>b</sup> and Eli Zysman-Colman<sup>\*a</sup>

<sup>a</sup> Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, UK. E-mail: <u>eli.zysman-colman@st-andrews.ac.uk</u>; Web: <u>http://www.zysman-colman.com</u>; Tel: +44 (0)1334 463826
<sup>b</sup> Department of Chemistry, Life Science and Environmental Sustainability, University of Parma, 43124

<sup>b</sup> Department of Chemistry, Life Science and Environmental Sustainability, University of Parma, 43124 Parma, Italy

<sup>‡</sup> Equal contribution

#### Abstract

We present the synthesis, optoelectronic characterization, and a detailed theoretical study of **DMAC-py-TRZ**, a novel, efficient TADF emitter. This compound is a structural relative of the well-known TADF compound **DMAC-TRZ**, substituting the bridging phenylene for a pyridyl group. This marginal change has an enormous impact on the structure and hence on the photophysics as the steric interactions between the DMAC donor and the bridge that force DMAC-TRZ into an orthogonal conformation are attenuated and permit **DMAC-py-TRZ** to adopt a planar and slightly bent structure in the ground state. The large degree of conjugation in the bent **DMAC-py-TRZ** structure, demonstrated by the strong intensity of the lowest excitation with CT character, is responsible for a large singlet triplet gap, hence hindering TADF of this bent conformer. The computational analysis predicts that emission occurs, however, from a relaxed orthogonal excited-state geometry, as confirmed by the huge Stokes shift observed in nonpolar solvents. In this relaxed orthogonal geometry TADF is indeed observed. Emission from the unrelaxed state is recovered in glassy frozen solvents, where the emission band is largely blue-shifted compared with measurements in liquid solvent, and TADF is quenched. In amorphous matrices, structural disorder leads to the coexistence of both conformers, even if, depending on the emitter concentration, dual fluorescence may disappear due to a fast energy transfer from the bent to the orthogonal conformers. We maintain that this efficient energy transfer is responsible for the good efficiency of DMAC**py-TRZ** devices, because of the presence in the matrix of a sizable proportion of compounds that adopt the bent structure, favorable to act as the host for the orthogonal TADF conformer of **DMAC-py-TRZ**.

Keywords: TADF, OLED, conformational dynamics, triazine, TD-DFT

#### Introduction

In an organic light-emitting diode (OLED), electrons and holes, injected in the device from opposite electrodes, combine to form excitons. According to spin statistics, 25% of the electrically generated excitons are in a singlet state and 75% are in a triplet state. If the excitons form on a fluorescent molecule, emission will only occur from the singlet excitons, effectively limiting the device Internal Quantum Efficiency (IQE). Phosphorescent dyes harvest both singlet and triplet excitons to emit light from the triplet excited state resulting in an IQE of up to 100%. Most phosphorescent emitters, however, contain noble metals such as platinum or iridium, among the scarcest elements on Earth.<sup>1-</sup> <sup>3</sup> Thermally activated delayed fluorescence (TADF) offers a different yet equally appealing strategy to triplet harvesting where 100% IQE is also possible in the device. In TADF emitters, dark triplet excitons are thermally upconverted into emissive singlets via reverse intersystem crossing (RISC). RISC is possible when the energy gap,  $\Delta E_{ST}$ , between the lowest lying singlet and triplet excited states is of the order of the thermal energy (ca. < 0.02 eV), provided that spin-orbit coupling (SOC) between the two states is nonnegligible. To minimize  $\Delta E_{ST}$ , the overlap between the HOMO and LUMO of the molecule must be reduced, localizing the two orbitals in separate electron-donating (for the HOMO) and electron-accepting (for the LUMO) parts of the molecule.<sup>4</sup> This separation is most often obtained by enforcing a large dihedral angle between the electron donor and acceptor moieties.<sup>5</sup> This strategy, however, leads to a reduction of the fluorescence efficiency and, according El Sayed rule,<sup>6</sup> to a reduction of the spin-orbit coupling between the singlet and triplet states as well.

Two of the most common moieties employed as donors and acceptors, respectively, are 9,9-dimethy-9,10-dihydroacridine (DMAC) and 2,4,6-triphenyl-1,3,5-triazine (TRZ), and the combination of the two produces the emitter **DMAC-TRZ**, first reported by Tsai *et al.*<sup>7</sup> **DMAC-TRZ** shows a very high photoluminescence quantum yield,  $\Phi_{PL}$ , of 90%, at  $\lambda_{PL}$  of

495 nm, as an 8 wt% doped film in mCPCN [9-(3-(9H-carbazol-9-yl)phenyl)-9*H*carbazole-3-carbonitrile]. In **DMAC-TRZ**, the  $\Delta E_{ST}$  amounts to a few tens of meV, depending on the host matrix, with a delayed fluorescence lifetime of 1.9 µs in mCBPBN, in line with an efficient RISC process.<sup>8</sup> The OLED shows a high maximum external quantum yield, EQE<sub>max</sub>, of 26.5% at  $\lambda_{EL}$  of 500 nm, while devices prepared from neat **DMAC-TRZ** films show a comparable EQE<sub>max</sub> of 20.0%.<sup>7</sup> The modest reduction of the EQE<sub>max</sub> at high concentration can be understood in terms of the orthogonal conformation of the emitter, which effectively prevents aggregation. Both the doped and non-doped devices show a relatively small efficiency roll-off, with an EQE<sub>100</sub> of 25.1% and 18.9%, respectively.

The emitters a-DMAC-TRZ<sup>9</sup> and MA-TA<sup>10</sup> are derivatives of DMAC-TRZ where adamantane groups are incorporated into the structure (Figure 1). In **a-DMAC-TRZ**, the adamantane-functionalization of the donor moiety leads to a deformed structure that results in an increased optical gap and thus a bluer emission. Dual fluorescence is observed from two different conformers, but overall, the electroluminescence (EL) performance remains similar to the **DMAC-TRZ** OLED, with an EQE<sub>max</sub> of 28.9%, yet with a  $\lambda_{EL}$  of 488 nm. In the report by Wada *et al.*<sup>10</sup> the replacement of the distal phenyl moieties on the TRZ with adamantyl groups results in a weaker acceptor, leading to a blue-shifted electroluminescence compared to DMAC-TRZ. The adamantyl substitution also reduces the non-radiative decay leading to a  $\Phi_{PL}$  of 99%. The blue solution-processed device ( $\lambda_{EL}$  of 475 nm) shows an EQE<sub>max</sub> at 22.1%. Conversely, replacement of the distal phenyl rings in TRZ by electron-withdrawing pyrimidines (DMAC-bPmT) results in a redshifted emission ( $\lambda_{PL}$  of 520 nm vs 500 nm for **DMAC-TRZ** in toluene).<sup>11</sup> The delayed emission lifetime of DMAC-bPmT is 3.3 µs in toluene, which is shorter than that of DMAC-**TRZ** at 8.8  $\mu$ s in the same medium. The RISC rate constant,  $k_{RISC}$ , of **DMAC-bPmT** is  $8.8 \times 10^5$  s<sup>-1</sup>, is three times faster than that of **DMAC-TRZ** ( $2.9 \times 10^5$  s<sup>-1</sup>). However, its  $\Phi_{PL}$ of 70% in toluene is reduced compared to that of **DMAC-TRZ** ( $\Phi_{PL}$  = 93% in toluene). Rajamalli et al., <sup>12</sup> and Dos Santos et al., <sup>13</sup> showed that the introduction of a heteroaromatic bridge in sulfone-based D-A TADF emitters can prevent structural relaxation, enhance  $\Phi_{PL}$ and improve the color purity due to the narrower emission, and demonstrated an improvement in the efficiency of the devices compared to that with the reference emitter **pDTCz-DPS**. The materials in the study of Rajamalli *et al.*, <sup>12</sup> **pDTCz-2DPyS**, and **pDTCz-3DPyS**, both show good  $\Phi_{PL}$  of ca. 60%. The blue OLEDs, at  $\lambda_{EL}$  of 466 nm and 452 nm for the devices with **pDTCz-2DPyS**, and **pDTCz-3Dpy**, respectively, showed EQE<sub>max</sub> ~12-13%, which are considerably improved over the parent device with **pDTCz-DPS** (EQE<sub>max</sub> of 4.7%). Dos Santos *et al.*, <sup>13</sup> showed that the addition of second nitrogen atom within the bridging heterocycle in **pDTCz-DPzS**, and **pDTCz-DPmS** contributed to a further enhancement of the EQE<sub>max</sub> to 18% and 14%, respectively, at  $\lambda_{EL}$  of 522 nm and 461 nm for the devices with **pDTCz-DPzS**, and **pDTCz-DPmS**, respectively.



Figure **1**. Molecular structures of selected emitters from the literature with selected photophysical and device performance data.

The impact of intramolecular H-bonding on the photophysics of TADF emitters was also investigated by Chen *et al.* in two phenoxazine-based emitters **PXZ-PPO** and **PXZ-BOO**.<sup>14</sup> **PXZ-BOO** shows TADF, relevant devices having EQE<sub>max</sub> of 19.4% at  $\lambda_{EL}$  of 528 nm. In THF solution, **PXZ-PPO** is present as a mixture of two conformers, a more planar structure with N-H interaction and a twisted structure, where hydrogen bonding is not present. The planar conformation emits in the deep blue at 420 nm but shows no TADF, while the twisted conformer shows green TADF (610 nm) but with a very short lifetime of 170 ns.

The planar conformer is dominant in the crystalline phase, while in solution the twisted conformer is largely responsible for the observed photophysics, giving rise to TADF. The **PXZ-PPO**-based device, with EQE<sub>max</sub> of 14.1% at  $\lambda_{EL}$  of 528 nm, is slightly inferior to the OLED based on **PXZ-BOO**, which has an EQE<sub>max</sub> of 19.4% at  $\lambda_{EL}$  of 528 nm.

The presence of two conformers of a TADF emitter has also been documented by Shi *et al.* in the TRZ derivative compounds **TP2P-PXZ** and **TP5P-PXZ**.<sup>15</sup> Phenoxazine and a central pyridine bridge were used to promote the formation of an intramolecular hydrogen bond in **TP2P-PXZ**, while in the control compound **TP5P-PXZ** this interaction is absent. The presence of quasi-equatorial (QE) and quasi-axial (QA) conformations of **TP2P-PXZ** led to a self-doped system, where the QA conformer effectively acts as the host material. This led to an efficient OLED with an EQE<sub>max</sub> of 25.4% at  $\lambda_{EL}$  of 548 nm while the performance of the device with **TP5P-PXZ** was somewhat attenuated with an EQE<sub>max</sub> of 14.6% at a slightly red-shifted  $\lambda_{EL}$  of 560 nm.

These examples show that modification of the nature of the aromatic bridge in a TADF emitter can lead to significant changes in the molecular geometry, with the co-existence of different conformers that show distinctive photophysics. In this work, we introduce the emitter **DMAC-py-TRZ**, where the phenylene bridge in **DMAC-TRZ**<sup>7</sup> is replaced by a 2-pyridyl bridge. **DMAC-py-TRZ** emits at  $\lambda_{PL}$  of 539 nm and has a  $\Phi_{PL}$  of 58% in toluene solution while as a 10 wt% doped mCP film the  $\lambda_{PL}$  is 496 nm and the  $\Phi_{PL}$  is 57%. Its crystal structure (Figure **2**) documents a small dihedral angle between the DMAC and pyridyl bridge of 19.7(2)° and a V-shaped or bent structure of the DMAC donor, with an associated bending angle (deviation from a planar conformation) of 45°. This behaviour is in line with that observed by Shi *et al.*<sup>15</sup> We present an in-depth computational study and an extensive optoelectronic and photophysical characterization that showcases the impact that conformational changes in the excited state and not just in the ground state have on the photophysics of the compound.



Figure **2**. a) and b) The crystal structure shown as ORTEP at 50% ellipsoid probability; c) and d) the molecular structure; e) and f) the calculated ground state structure of **DMAC-TRZ** and **DMAC-py-TRZ**.

#### **Computational Analysis**

The ground-state geometries of **DMAC-TRZ** and **DMAC-py-TRZ** were optimized in the gas phase using density functional theory (DFT) at the M062X/6-31G(d) level of theory.<sup>16,17,18</sup> The excited-state energies were calculated using time-dependent density functional theory (TD-DFT) within the Tamm-Dancoff approximation<sup>19</sup> at the same level of theory (TDA-DFT). We employ the term "orthogonal" to describe the structure with a dihedral angle between the DMAC and the bridge that is close to 90° and we dub as "bent" the structure with the small dihedral angle and V-shaped geometry of the DMAC.

In a recent publication,<sup>20</sup> an extensive computational analysis of **DMAC-TRZ** set the basis for a few-state model that was carefully validated against spectroscopic properties in solution. Then the same model was exploited to calculate ISC and RISC rate constants, also accounting for environmental effects including dielectric and conformational disorder.<sup>21,22</sup> In the ground-state equilibrium geometry of **DMAC-TRZ**, the **DMAC** and **TRZ** moieties are mutually orthogonal (Figure 2), in line with the crystal structure.<sup>20</sup> In this orthogonal geometry, the S<sub>1</sub> and T<sub>1</sub> states each have a pure charge transfer (CT) character. In other terms, the HOMO and LUMO have negligible overlap so that the singlettriplet gap is almost closed, with  $\Delta E_{ST} = 0.01$  eV. The close similarity between the orbitals involved in  $S_1$  and  $T_1$  states implies a vanishing SOC, according to El Sayed's rule<sup>6</sup>, as to hinder direct RISC from  $T_1$  to  $S_1$ .

As for the excited states of **DMAC-TRZ**,  $S_1$  (with a strong <sup>1</sup>CT character) retains an orthogonal geometry, while  $T_1$  (<sup>3</sup>CT) undergoes a large conformational deformation where the dihedral becomes ~60°. At this angle,  $\Delta E_{ST}$  increases as does SOC. A rigid scan of the dihedral angle of **DMAC-TRZ** (Figure **S9c**)<sup>20</sup> is informative. Specifically, starting from the optimized ground-state geometry, we calculated the ground and excited state energies upon gradual rotation of the DMAC unit about the phenylene bridge without allowing for any additional molecular relaxation (the dihedral angle for the scan is defined in Figure **S9a**). The resulting S<sub>0</sub>, S<sub>1</sub>, T<sub>2</sub> and T<sub>3</sub> potential energy surfaces (PES) all show a flat minimum for the orthogonal geometry, while T<sub>1</sub> shows a double minimum around (90±30)° angle.<sup>19</sup> The molecular orbitals (MOS) and natural transition orbitals (NTOS) shown in Figure **S11** and **S12** reveal that in the orthogonal structure, the HOMO is localized on DMAC and the LUMO is on the TRZ.

In contrast with **DMAC-TRZ**, the ground-state optimized geometry of **DMAC-py-TRZ** has a bent structure (Figure **2f**), as also observed in the crystal structure (Figure **2b**). To better understand the structural differences between DMAC-TRZ and DMAC-py-TRZ, a rigid dihedral angle scan of **DMAC-py-TRZ** starting from an analogous orthogonal conformation to that of **DMAC-TRZ** has been performed. The rigid scan leads to a qualitatively similar picture for the two compounds (Figure **S9**), with relevant MOs and NTOs in Figures **S11** and **S12**, showing the HOMO and LUMO localized on the donor and acceptor moieties, respectively. The presence of the nitrogen atom in the pyridine bridge effectively increases the electron-withdrawing strength of the acceptor, resulting in a stabilized LUMO and a smaller HOMO-LUMO gap in **DMAC-py-TRZ** (E<sub>HOMO-LUMO</sub> = 4.78 eV for the orthogonal structure) vs **DMAC-TRZ** ( $E_{HOMO - LUMO} = 4.99$  eV for the orthogonal structure). Accordingly, the S<sub>1</sub> and T<sub>1</sub> excitations occur at lower energy in **DMAC-py-TRZ** than in **DMAC-TRZ** and both the S<sub>1</sub> and T<sub>1</sub> states are stabilized compared to those of **DMAC-TRZ** (Figures **S9c** and **S9d**). The rigid energy scan, however, points to a large increase of the ground-state energy when the dihedral angle deviates significantly from orthogonality, so that non-orthogonal conformations are hardly accessible. To address the bent conformer, we performed a relaxed scan of the dihedral angle, relevant results being shown in Figure **3**.



Figure **3**. (a) and (b) compare the ground state (S<sub>0</sub>) energy calculated as a function of the dihedral angle in a rigid (dashed lines) and relaxed scan (continuous lines) for **DMAC-TRZ** and **DMAC-py-TRZ**, respectively; (c) and (d) show the energies of the S<sub>0</sub>, S<sub>1</sub> and T<sub>1</sub> energies as a function of dihedral angle between DMAC calculated at the relaxed S<sub>0</sub> geometry for **DMAC-TRZ** and **DMAC-py-TRZ**, respectively.

The relaxed scans show that for each of the emitters, two minima are present, corresponding to the orthogonal and bent structures. For **DMAC-TRZ**, the energy difference between the two conformers amounts to 0.04 eV, slightly larger than thermal energy at room temperature. The energy barrier for the interconversion between the two conformers, 0.22 eV (21.2 kcal/mol), is, however, much larger than thermal energy so that only the orthogonal geometry is expected to be significantly populated at room temperature. The situation is very different for **DMAC-py-TRZ** where the bent conformer (dihedral angle  $\sim 10^{\circ}$ ) is lower in energy than the orthogonal conformer by 0.20 eV and the energy barrier for the interconversion between the bent and orthogonal conformers is 0.20 eV (19.3 kcal/mol). Thus, at room temperature only the bent conformer is

populated. The MOs and NTOs calculated for the bent structure (Figures **S11** and **S12**) show that in both molecules there is a partial delocalization of the HOMO onto the acceptor moiety and, for **DMAC-py-TRZ** also a partial delocalization of the LUMO onto the donor moiety.

Divergent results are obtained for the excited state energies at the geometries relevant to the rigid/relaxed scans of the dihedral angle (Figures **3c** and **3d**) of the two compounds. For **DMAC-TRZ**, the rigid (Figure **S9c**) and the relaxed scans (Figure **3c**) lead to the same picture: the S<sub>1</sub> state maintains the same orthogonal conformation as the ground state, while the  $T_1$  state is stabilized and adopts a twisted structure (dihedral angle: ~60°). Full optimisations of S<sub>1</sub> and T<sub>1</sub> confirm this result.<sup>20</sup> In the orthogonal geometry, the S<sub>1</sub> state is an almost pure CT state and, hence, has a negligible oscillator strength. The scenario is much more interesting for DMAC-py-TRZ. In the bent geometry (the energy minimum, Figure **3b**), the vertical excitation energy to  $S_1$  amounts to 4.1 eV and the  $\Delta E_{ST}$  is 0.78 eV, which is far too large for TADF to be operational at ambient temperature. Moreover, the oscillator strength for the  $S_0 \rightarrow S_1$  is large (1.27, Figure **S12c**) in this geometry due to the significant overlap of the orbitals involved in the transition (Figure **4a**). However, the bent geometry is not the equilibrium geometry for  $S_1$  (Figure 4d) and a huge structural deformation is predicted in the S<sub>1</sub> state from the bent to the orthogonal structure. In other terms, in **DMAC-py-TRZ** the absorption occurs from the bent geometry and the lowest energy transition is both high in energy and has a large oscillator strength. By contrast, fluorescence occurs from the orthogonal structure at a much lower energy (3.17 eV) and with negligible oscillator strength (as per the non-overlapping orbitals, in Figure **4b**). In this orthogonal geometry the  $\Delta E_{ST}$  reduces to only 8.2 meV), making TADF possible.

In **DMAC-py-TRZ**, the T<sub>1</sub> state is predicted to exist as a twisted geometry in both the rigid (Figure **S9d**) and relaxed scans (Figure **3d**). The full optimization of the excited state geometry, however, yields conflicting results. For S<sub>1</sub> the situation is clear: taking either the bent or the orthogonal geometry as starting points for the excited state optimization, the S<sub>1</sub> geometry (Figure **3d**) always converges to the orthogonal conformation, supporting the results from the relaxed scan analysis. For T<sub>1</sub>, instead, two different structures are reached depending on the starting geometry (Figure **S10**), with slightly different  $\Delta E_{S1-T1}$  values (0.93 eV where the dihedral angle is 30° and 0.41 eV where the dihedral angle is 60°). The energy of the two triplet conformations is similar ( $\Delta E_{T1_{60°-30°}} = 0.07$  eV), so that a firm conclusion about the equilibrium geometry for T<sub>1</sub> cannot be reached.



Figure 4. NTOs of **DMAC-py-TRZ** calculated for the  $S_0$ - $S_1$  transition a) at the  $S_0$ -optimized geometry, which is relevant to the absorption process; b) at the  $S_1$ -optimized geometry, which is relevant to the emission process

# **Optoelectronic properties**



Figure 5. a) Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of **DMAC-TRZ** (black) and **DMAC-py-TRZ** (red) in DCM (scan rate = 100 mV/s, tetrabutylammonium hexafluorophosphate as electrolyte, reported relative to a saturated calomel electrode (SCE) with a ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple as the internal standard, 0.46 V vs SCE for DCM<sup>23</sup>). b) UV-vis absorption spectra of **DMAC-TRZ** (black) and **DMAC-py-TRZ** (red) in 10<sup>-5</sup> M toluene. c) Solvatochromism photoluminescence study of **DMAC-py-TRZ** ( $\lambda_{exc}$ , = 340 nm); d Prompt fluorescence and phosphorescence spectra at 77 K in 10<sup>-5</sup> M 2-methyltetrahydrofuran (2-MeTHF) glass ( $\lambda_{exc}$  = 343 nm, prompt and delayed fluorescence spectra were obtained in the 1–100 ns and 1–8.5 ms time range, respectively).

Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) of **DMAC-py-TRZ** and **DMAC-TRZ** were measured in degassed DCM with tetra-*n*-butylammonium hexafluorophosphate as the electrolyte and Fc/Fc<sup>+</sup> as the internal reference. The voltammograms in Figure **5a** are reported versus a Saturated Calomel Electrode (SCE). Both materials show pseudo-reversible reduction and oxidation waves. Both oxidation

and reduction waves for **DMAC-py-TRZ** ( $E_{ox}/E_{red} = 1.11/-1.64$  V) are anodically shifted compared to those of **DMAC-TRZ** (0.97/-1.72 V). The corresponding HOMO and LUMO energies are -5.31 / -2.62 eV and -5.45 eV/ -2.70 eV for DMAC-TRZ and DMAC-py-TRZ, respectively. Comparing electrochemical redox gaps measured in solution with gas-phase DFT results is tricky. Experimentally, the HOMO-LUMO gap of DMAC-py-TRZ, ~ 2.75 eV, is larger than the HOMO-LUMO gap of **DMAC-TRZ** ~2.69 eV. Considering an orthogonal geometry for both dyes, DFT results for the HOMO-LUMO gaps are 4.78 eV and 4.99 eV for **DMAC-py-TRZ** and **DMAC-TRZ**, respectively, showing the opposite trend vs experiment. The same is true if the bent geometry is considered for both dyes, with calculated HOMO-LUMO gaps of 5.73 eV and 5.77 eV for DMAC-py-TRZ and DMAC-TRZ, respectively. However, if we properly consider an orthogonal structure for **DMAC-TRZ** (E<sub>HOMO-LUMO</sub> = 4.99 eV for orthogonal geometry) and a bent structure for **DMAC-py-TRZ** (E<sub>HOMO-LUMO</sub> = 5.73 eV for bent geometry) calculated HOMO-LUMO gaps reflect the trend observed experimentally. In any case, the HOMO stabilization in DMAC-py-TRZ vs DMAC-TRZ is ascribed to the presence of the electron-withdrawing pyridyl bridge, which reduces the electron density on the donor. Similarly, the electron density of the acceptor is reduced, resulting in a more stabilized LUMO level.

Figure **5b** compares the absorption spectra of **DMAC-TRZ** and **DMAC-py-TRZ** in toluene. The CT band of **DMAC-py-TRZ** at 370 nm is slightly blue-shifted with respect to **DMAC-TRZ** at 382 nm. The most striking difference is, however, in the much larger intensity of the band measured for **DMAC-py-TRZ** ( $\varepsilon$  =43,800 M<sup>-1</sup> cm<sup>-1</sup>) vs **DMAC-TRZ** ( $\varepsilon$  = 2100 M<sup>-1</sup> cm<sup>-1</sup>). This is a direct consequence of the different conformations adopted by the two compounds in the ground state: the orthogonal conformation of **DMAC-TRZ** (observed in the crystal structure and predicted by DFT) hinders an effective conjugation and suppresses the intensity of the low-energy CT transition. On the other hand, the bent conformation of **DMAC-py-TRZ** (observed in the crystal structure and predicted by DFT) promotes an efficient conjugation of the two moieties, perfectly in line with the oscillator strength calculated with TD-DFT (oscillator strengths are reported in Figure **S12**, together with NTOs).

Neither the absorption spectra of **DMAC-TRZ** and **DMAC-py-TRZ** (Table **S27**) show solvatochromism, in line with a very small permanent dipole moment of the molecule in the ground state. Photoluminescence (PL) spectra or **DMAC-py-TRZ** in Figure **5c** (Table **S27**) show a strong positive solvatochromism akin to that observed for **DMAC-TRZ** (Figure **S13** 

and Ref. 20) The large positive PL solvatochromism observed for both compounds suggests that the emissive excited state has a large permanent dipole moment, thus confirming the CT character of this state in both compounds.<sup>24,25</sup> The progressive broadening of the emission band in the solvatochromism study is a result of polarityinduced inhomogeneous broadening.<sup>25,26</sup> The well-resolved vibronic structure of the emission band in non-polar solvents is often considered an indication of a local nature of the relevant excitation. Therefore, to prove the CT nature of the lowest transition in DMAC-py-TRZ in all solvent, including non-polar ones, Figure S14 shows spectra collected for the two molecular fragments, **DMAC** and **py-TRZ**. For **py-TRZ**, only absorption spectra are shown since the species is not emissive. The spectroscopic features of both molecular fragments are located at higher energies than the lowest energy feature seen in DMAC-py-**TRZ**, confirming that this specific feature is related to a CT state. An important and unusual result is recognized in the large Stokes shift observed for DMAC-py-TRZ in non-polar solvents (Table **S27**): in methylcyclohexane, the absorption band is located at 370 nm, while the emission is seen at 472 nm, amounting to a Stokes shift of  $\sim 0.7$  eV. This large Stokes shift can only be explained in terms of a very large molecular relaxation upon photoexcitation, well in line with the TD-DFT results that predict the relaxation of the S<sub>1</sub> state from the bent to the orthogonal geometry.

In degassed toluene, **DMAC-TRZ** and **DMAC-py-TRZ** have similar  $\Phi_{PL}$  of 67% and 58%, respectively, in line with emission originating in both compounds from a similar orthogonal geometry. The  $\Phi_{PL}$  decrease in air ( $\Phi_{PL}$  = 22% and 17%, respectively), indicating the presence of accessible triplet excited states. The prompt and delayed lifetimes,  $\tau_p$  and  $\tau_d$ , for **DMAC-TRZ** in degassed toluene are of 20.8 ns (1.1%) and 5.2 µs (98.9%), in line with those previously reported,<sup>7</sup> while the  $\tau_p$  and  $\tau_d$  for **DMAC-py-TRZ** are 44.0 ns (8.1%) and 1.5 µs (91.9%), respectively (Figure **S15**).

To summarize, theoretical and spectroscopic studies agree with the picture where **DMAC-TRZ** maintains the same orthogonal conformation in both the ground and the S<sub>1</sub> states. However, **DMAC-py-TRZ** undergoes a significant geometric reorganization from the bent geometry in the ground state to the orthogonal geometry in the excited state.

Spectra collected in a glassy 2-MeTHF matrix at 77 K (Figure **5d**) shed further light on the geometrical relaxation of **DMAC-py-TRZ** upon photoexcitation. In the frozen matrix, the emission peaks at 404 nm, blue-shifted compared to that in liquid 2-MeTHF at ambient

conditions ( $\lambda_{PL}$  = 596 nm, Table **1** and Figure **S16**). Apparently, in the frozen matrix the excited compound cannot relax, so that emission occurs from the bent structure and hence peaks at much higher energy than in the (non-polar) liquid solvent. The gated signal collected in the glassy matrix (red line in Figure **5d**) is ascribed to phosphorescence, suggesting a large  $\Delta E_{ST}$  for this conformer under these conditions, again in line with that calculated for the bent structure.

The PL behavior of **DMAC-py-TRZ** was also characterized in polyTHF, a viscous solvent where conformational relaxation is hindered. Interestingly, two emission bands are observed in this viscous medium (Figure **S17**). The first emission band at 410 nm is similar to the one observed in the glassy matrix at 77 K while the second emission at 600 nm is similar to the emission observed in DMSO at room temperature. Apparently, at ambient temperature, the excited state relaxation, fully hindered in glassy matrices at low temperature, is only partially hindered in the viscous polyTHF. Accordingly, the presence of the two emission bands is evidence of the simultaneous presence of the unrelaxed (bent) emissive species (as in the glassy matrix) as well as of relaxed (orthogonal) species (as in the liquid solvent).

Having observed that the S<sub>1</sub> relaxation of DMAC-py-TRZ in frozen glassy matrices at low temperature is fully hindered while it is only partially hindered in viscous solvents at ambient condition, we next transitioned to an investigation of the behavior of this compound in amorphous matrices where large geometric reorganization is also likely to be hindered. Spin-coated thin films of DMAC-py-TRZ doped into PMMA at 10 wt% were first prepared (Figure **7a**). Emission at  $\lambda_{PL}$  of 516 nm was observed with a  $\Phi_{PL}$  of 63.8% under a  $N_2$  atmosphere, which decreased to 58.0% upon exposure to oxygen. Biexponential decay kinetics were observed in the time-resolved PL measurements, with  $\tau_{\rm p}$  of 26.0 ns and an average  $\tau_{\rm d}$  of 4.7 µs [ $\tau_1$ =1.0 µs (32.6%),  $\tau_2$ =7.4 µs (67.4%)], respectively. The presence of a delayed fluorescence suggests that at least some emitter molecules adopt an orthogonal conformation, as to allow for TADF. Compared to the data obtained in toluene ( $\tau_p$  of 44.0 ns and  $\tau_d$  of 1.5 µs), **DMAC-py-TRZ** possesses a shorterlived prompt component and a slightly longer-lived delayed component. We then investigated the photophysics in mCP (1,3-bis(*N*-carbazolyl)benzene) as the host matrix, a suitable high triplet energy host for both compounds that would be relevant for OLEDs. Figure **7d** shows results at a 10 wt% doping concentration. The emission in mCP is blueshifted at  $\lambda_{PL}$  of 496 nm, compared to that of the doped PMMA film. The  $\Phi_{PL}$  of the doped film in mCP is 57.4% under N<sub>2</sub>, which decreased to 53.5% in air. The  $\tau_p$  = 24.9 ns and the average  $\tau_d$  = 5.3 µs [ $\tau_1$ =1.4 µs (46.8%),  $\tau_2$ =7.7 µs (53.2%)]. In both PMMA and mCP matrices at 10% doping the delayed emission is thermally activated (Figure 7). However, extracting detailed information from such highly doped matrices is dangerous because of spurious phenomena, including homo energy-transfer and inner filter effects (self-absorption).



Figure **7**. a) PL spectra of **DMAC-py-TRZ** in spin-coated 10 wt% mCP film, spin-coated 10 wt% PMMA film ( $\lambda_{exc}$  = 340 nm); b) time-resolved PL decay in spin-coated 10 wt% mCP film of **DMAC-py-TRZ** ( $\lambda_{exc}$  = 378 nm); c) Temperature-dependent delayed fluorescence decays in spin-coated 10 wt% mCP film of **DMAC-py-TRZ** ( $\lambda_{exc}$  = 378 nm); d) Prompt fluorescence and phosphorescence spectra at 77 K in drop-cast 10 wt% mCP film ( $\lambda_{exc}$  = 343 nm, prompt and delayed fluorescence spectra were obtained in the 1–100 ns and 1–8.5 ms time range, respectively).



Figure **8.** a) emission spectra of **DMAC-py-TRZ** in spin-coated 1-5 wt% mCP films ( $\lambda_{exc}$  = 340 nm); b) time-resolved PL decay in spin-coated 1 wt% mCP film of **DMAC-py-TRZ** collected at  $\lambda_{em}$  = 490 nm and  $\lambda_{em}$  = 430 nm ( $\lambda_{exc}$  = 378 nm).

To minimize spurious concentration effects, low-concentration (down to 1 wt%) films were fabricated, relevant spectra being shown in Figure **8**. In these films both the high frequency emission originating from the bent structure, and the low-frequency emission from the orthogonal structure, are present, suggesting that both conformers are present in all films. The high frequency emission decays much more rapidly (Figure **8b**), again confirming that it originates from the bent conformer. Upon increasing concentration, the high frequency emission progressively weakens and disappears for doping concentrations above 3 wt%. Two phenomena may exist to explain this observation, both related to the large transition dipole moment (large oscillator strength) of the  $S_0 \rightarrow S_1$ transition in the bent geometry: (1) self-absorption; and (2) energy transfer from the bent to the orthogonal structure. Both phenomena are expected to become more efficient upon increasing the concentration of the emitter in the host matrix.

Material	Environment	$\lambda_{\rm PL} / nm^a$	$\Phi_{\rm PL} N_2$ (air) <sup>b</sup> /%	$ au_{ m p}$ , $ au_{ m d}$ $^{e}/$ ns; µs	<b>S</b> <sub>1</sub> <i>f</i> /	T <sub>1</sub> <sup>g</sup> /	$\Delta E_{\rm ST}^{i}/$
					eV	eV	eV
DMAC-TRZ	Toluene (10 <sup>-5</sup> M) <sup>27</sup>	499	67 (22) <sup>c</sup>	20.8; 5.2	2.88	2.57	0.31
	mCP 10 wt%	499	47 (45)	22.9; 15.3			
	PMMA 10 wt%	523	18 (15)	41.6; 17.0			

Table 1. Photophysical properties of DMAC-TRZ and DMAC-py-TRZ.

DMAC-py-TRZ	Toluene (10 <sup>-5</sup> M)	539	58 (17) <sup>c</sup>	44.0; 1.5	3.21	2.77	0.44
	mCP 10 wt%	496	57 (54) <sup>d</sup>	24.9; 5.3			
	PMMA 10 wt%	516	64 (58) <sup>d</sup>	26.0; 4.7			

<sup>*a*</sup> measured at room temperature; <sup>*b*</sup>  $\lambda_{exc}$  = 340 nm; <sup>*c*</sup> obtained *via* the optically dilute method<sup>28</sup> (see SI), quinine sulfate (0.5 M) in H<sub>2</sub>SO<sub>4</sub> (aq) was used as the reference,  $\Phi_{PL}$ : 54.6%,  $\lambda_{exc}$  = 360 nm;<sup>29</sup> <sup>*d*</sup> obtained using an integrating sphere; <sup>*e*</sup>  $\tau_p$  (prompt lifetime) and  $\tau_d$  (delayed lifetime) were obtained from the transient PL decay of degassed solution/doped film,  $\lambda_{exc}$  = 378 nm; <sup>*f*</sup>S<sub>1</sub> was obtained from the onset of the prompt fluorescence measured at 77 K, obtained in the 1–100 ns time range; <sup>*g*</sup>T<sub>1</sub> was obtained from the onset of the phosphorescence spectrum measured at 77 K, obtained in the 1–8.5 ms time range; <sup>*h*</sup>S<sub>1</sub> was obtained from the onset of the fluorescence spectrum measured at room temperature <sup>*i*</sup>  $\Delta E_{ST}$  = S<sub>1</sub> - T<sub>1</sub>; <sup>*j*</sup> assigned to the bent conformer of **DMAC-py-TRZ**; <sup>*k*</sup> assigned to the twisted conformer of **DMAC-py-TRZ**.

#### Conclusions

The synthesis of a new TADF emitter, **DMAC-py-TRZ**, is presented, together with an extensive computational analysis and experimental characterization. The chemical structure of **DMAC-py-TRZ** only marginally differs from that of the parent **DMAC-TRZ** compound. However, this minor change of the bridging moiety between the donor and acceptor has an enormous impact on the conformation and hence on the photophysics of the compound. Specifically, while DMAC-TRZ maintains the same orthogonal geometry in both the ground and the first excited singlet states, DMAC-py-TRZ assumes a bent geometry in the ground state, as highlighted by the large oscillator strength measured in solution for this dye. However, upon excitation to the S<sub>1</sub> state, the system undergoes a large geometrical rearrangement to the orthogonal structure. This large relaxation is confirmed by the very large Stokes shift measured in non-polar solvents. In frozen 2-MeTHF glass at very dilute conditions, the relaxation is hindered and only a blue-shifted emission is seen from the unrelaxed bent conformer, without any hint of emission from the orthogonal structure. In mCP films a distribution of conformers exists and at low concentrations dual emission is observed, originating both from both the bent and orthogonal structures. However, upon increasing the doping concentration, the emission from the orthogonal conformer dominates. While self-absorption can be partly responsible for the phenomenon, we conclude that an efficient energy transfer from one conformer to the other also contributes to the spectral change. Indeed, TADF is not expected nor observed in the bent structure, due to a too large  $\Delta E_{ST}$ . The good TADF efficiency of **DMAC-py-TRZ** in solution, similar as for **DMAC-TRZ**, is in line with the very

fast molecular relaxation from the bent (TADF-silent) to the orthogonal geometry (TADFactive) in solution. The situation is more delicate in matrices where the host rigidity hinders a large molecular rearrangement. The observed good efficiency of TADF in matrices then suggests efficient energy transfer of excitons created on the bent (and TADF silent) structures towards molecules in the orthogonal (and TADF-active) structure as to retrieve all photogenerated singlet states for TADF activity. Most probably, efficient triplet-to-triplet energy transfer is also required to explain the good efficiency of **DMACpy-TRZ** OLEDs, but this will be subject of a subsequent study.

### **Supporting information**

Supporting information file 1 includes synthesis protocols, NMR spectra, supplementary photophysical measurements and computational data. Supporting information file 2 includes the xyz coordinates corresponding to the ground state optimized geometry of **DMAC-py-TRZ**.

## Acknowledgments

We thank EU Horizon 2020 Grant Agreement No. 812872 (TADFlife) for funding. The St Andrews team acknowledges support from the Engineering and Physical Sciences Research Council of the UK (grant EP/P010482/1). The authors from the University of Parma acknowledge the support from the HPC (High Performance Computing) facility of the University of Parma, Italy. Moreover, authors from University of Parma benefited from the equipment and support of the COMP-HUB Initiative, funded by the "Departments of Excellence" program of the Italian Ministry for Education, University and Research (MIUR, 2018-2022).

#### References

- (1) Adachi, C. Third-Generation Organic Electroluminescence Materials. *Jpn. J. Appl. Phys.* **2014**, *53*, 060101. https://doi.org/10.7567/JJAP.53.060101.
- (2) Wong, M. Y.; Zysman-Colman, E. Purely Organic Thermally Activated Delayed Fluorescence Materials for Organic Light-Emitting Diodes. *Adv. Mater.* **2017**, *29*, 1605444. https://doi.org/10.1002/adma.201605444.
- (3) Xie, F. M.; Zhou, J. X.; Li, Y. Q.; Tang, J. X. Effects of the Relative Position and Number of Donors and Acceptors on the Properties of TADF Materials. *J. Mater. Chem. C* 2020, 8 (28), 9476–9494. https://doi.org/10.1039/d0tc02252g.
- (4) Dias, F. B.; Penfold, T. J.; Monkman, A. P. Photophysics of Thermally Activated Delayed Fluorescence Molecules. *Methods Appl. Fluoresc.* 2017, 5 (1), 012001. https://doi.org/10.1088/2050-6120/aa537e.
- Milián-Medina, B.; Gierschner, J. Computational Design of Low Singlet-Triplet Gap All-Organic Molecules for OLED Application. *Org. Electron.* 2012, *13* (6), 985–991. https://doi.org/10.1016/j.orgel.2012.02.010.
- (6) M. A. El-Sayed. Spin Orbit Coupling and the Radiationless Processes in Nitrogen. *J. Chem. Phys.* **1963**, *38*, 2834–2838.
- (7) Tsai, W. L.; Huang, M. H.; Lee, W. K.; Hsu, Y. J.; Pan, K. C.; Huang, Y. H.; Ting, H. C.; Sarma, M.; Ho, Y. Y.; Hu, H. C.; Chen, C. C.; Lee, M. T.; Wong, K. T.; Wu, C. C. A Versatile Thermally Activated Delayed Fluorescence Emitter for Both Highly Efficient Doped and Non-Doped Organic Light Emitting Devices. *Chem. Commun.* **2015**, *51* (71), 13662–13665. https://doi.org/10.1039/c5cc05022g.
- (8) Stavrou, K.; Franca, L. G.; Monkman, A. P. Photophysics of TADF Guest-Host Systems: Introducing the Idea of Hosting Potential. ACS Appl. Electron. Mater. 2020, 2 (9), 2868–2881. https://doi.org/10.1021/acsaelm.0c00514.
- (9) Li, W.; Cai, X.; Li, B.; Gan, L.; He, Y.; Liu, K.; Chen, D.; Wu, Y. C.; Su, S. J. Adamantane-Substituted Acridine Donor for Blue Dual Fluorescence and Efficient Organic Light-Emitting Diodes. *Angew. Chemie - Int. Ed.* **2019**, *58* (2), 582–586. https://doi.org/10.1002/anie.201811703.
- Wada, Y.; Kubo, S.; Kaji, H. Adamantyl Substitution Strategy for Realizing Solution-Processable Thermally Stable Deep-Blue Thermally Activated Delayed Fluorescence Materials. *Adv. Mater.* 2018, *30* (8), 1705641. https://doi.org/10.1002/adma.201705641.
- (11) Wada, Y.; Nakagawa, H.; Kaji, H. Acceleration of Reverse Intersystem Crossing Using Different Types of Charge Transfer States. *Chem. - An Asian J.* 2021, *16* (9), 1073– 1076. https://doi.org/10.1002/asia.202100091.
- (12) Rajamalli, P.; Chen, D.; Li, W.; Samuel, I. D. W.; Cordes, D. B.; Slawin, A. M. Z.; Zysman-Colman, E. Enhanced Thermally Activated Delayed Fluorescence through Bridge Modification in Sulfone-Based Emitters Employed in Deep Blue Organic Light-Emitting Diodes. *J. Mater. Chem. C* 2019, 7 (22), 6664–6671. https://doi.org/10.1039/c9tc01498e.
- (13) Paloma Lays dos Santos, Dongyang Chen, Pachaiyappan Rajamalli, Tomas Matulaitis, David B. Cordes, Alexandra M. Z. Slawin, Denis Jacquemin, Eli Zysman-

Colman, and I. D. W. S. Use of Pyrimidine and Pyrazine Bridges as a Design Strategy To Improve the Performance of Thermally Activated Delayed Fluorescence Organic Light Emitting Diodes. *ACS Appl. Mater. Interfaces* **2019**, *11*, 45171–45179.

- (14) Chen, J. X.; Xiao, Y. F.; Wang, K.; Fan, X. C.; Cao, C.; Chen, W. C.; Zhang, X.; Shi, Y. Z.; Yu, J.; Geng, F. X.; Zhang, X. H.; Lee, C. S. Origin of Thermally Activated Delayed Fluorescence in a Donor-Acceptor Type Emitter with an Optimized Nearly Planar Geometry. *J. Mater. Chem. C* **2020**, *8* (38), 13263–13269. https://doi.org/10.1039/d0tc03747h.
- (15) Shi, Y.; Wang, K.; Zhang, S.; Fan, X.; Tsuchiya, Y.; Lee, Y.; Dai, G.; Chen, J.; Zheng, C.; Xiong, S.; Ou, X.; Yu, J.; Jie, J.; Lee, C.; Adachi, C.; Zhang, X. Characterizing the Conformational Distribution in an Amorphous Film of an Organic Emitter and Its Application in a "Self-Doping" Organic Light-Emitting Diode. *Angew. Chemie* **2021**, *133* (49), 26082–26087. https://doi.org/10.1002/ange.202108943.
- (16) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Function. *Theor. Chem. Acc.* 2008, 120 (1– 3), 215–241. https://doi.org/10.1007/s00214-007-0310-x.
- (17) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. A Complete Basis Set Model Chemistry. I. The Total Energies of Closed-Shell Atoms and Hydrides of the First-Row Elements. *J. Chem. Phys.* **1988**, *89* (4), 2193–2218. https://doi.org/10.1063/1.455064.
- (18) Al-Laham, G. A. P. and M. A. A Complete Basis Set Model Chemistry. II. Open-Shell Systems and the Total Energies of the First-Row Atoms. *J. Chem. Phys.* **1988**, *94* (4), 6081–6090. https://doi.org/10.1063/1.455064.
- (19) Hirata, S.; Head-Gordon, M. Time-Dependent Density Functional Theory within the Tamm-Dancoff Approximation. *Chem. Phys. Lett.* **1999**, *314* (3–4), 291–299. https://doi.org/10.1016/S0009-2614(99)01149-5.
- (20) Dhali, R.; Phan Huu, D. K. A.; Bertocchi, F.; Sissa, C.; Terenziani, F.; Painelli, A. Understanding TADF: A Joint Experimental and Theoretical Study of DMAC-TRZ. *Phys. Chem. Chem. Phys.* 2021, 23 (1), 378–387. https://doi.org/10.1039/d0cp05982j.
- (21) Phan Huu, D. K. A.; Saseendran, S.; Painelli, A. Effective Models for TADF: The Role of the Medium Polarizability. *J. Mater. Chem. C* **2022**, *10* (12), 4620–4628. https://doi.org/10.1039/d1tc05296a.
- (22) Phan Huu, D. K. A.; Saseendran, S.; Dhali, R.; Franca, L. G.; Stavrou, K.; Monkman, A.; Painelli, A. Thermally Activated Delayed Fluorescence: Polarity, Rigidity, and Disorder in Condensed Phases. J. Am. Chem. Soc. 2022, 144 (33), 15211–15222. https://doi.org/10.1021/jacs.2c05537.
- (23) Connelly, N. G., and Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. *Chem. Rev.* **1996**, *96* (2), 877–910.
- (24) Painelli, A.; Terenziani, F. A Non-Perturbative Approach to Solvatochromic Shifts of Push-Pull Chromophores. *Chem. Phys. Lett.* **1999**, *312* (2–4), 211–220. https://doi.org/10.1016/S0009-2614(99)00960-4.

- (25) Boldrini, B.; Cavalli, E.; Painelli, A.; Terenziani, F. Polar Dyes in Solution: A Joint Experimental and Theoretical Study of Absorption and Emission Band Shapes. *J. Phys. Chem. A* **2002**, *106* (26), 6286–6294. https://doi.org/10.1021/jp020031b.
- (26) Terenziani, F.; Painelli, A.; Girlando, A.; Metzger, R. M. From Solution to Langmuir-Blodgett Films: Spectroscopic Study of a Zwitterionic Dye. *J. Phys. Chem. B* 2004, *108* (30), 10743–10750. https://doi.org/10.1021/jp047954m.
- (27) Zhang, Z.; Crovini, E.; dos Santos, P. L.; Naqvi, B. A.; Cordes, D. B.; Slawin, A. M. Z.; Sahay, P.; Brütting, W.; Samuel, I. D. W.; Bräse, S.; Zysman-Colman, E. Efficient Sky-Blue Organic Light-Emitting Diodes Using a Highly Horizontally Oriented Thermally Activated Delayed Fluorescence Emitter. *Adv. Opt. Mater.* **2020**. https://doi.org/10.1002/adom.202001354.
- (28) Crosby, G. A.; Demas, J. N. Measurement of Photoluminescence Quantum Yields. Review. J. Phys. Chem. **1971**, 75 (8), 991–1024. https://doi.org/10.1021/j100678a001.
- (29) Song, F.; Xu, Z.; Zhang, Q.; Zhao, Z.; Zhang, H.; Zhao, W.; Qiu, Z.; Qi, C.; Zhang, H.; Sung, H. H. Y.; Williams, I. D.; Lam, J. W. Y.; Zhao, Z.; Qin, A.; Ma, D.; Tang, B. Z. Highly Efficient Circularly Polarized Electroluminescence from Aggregation-Induced Emission Luminogens with Amplified Chirality and Delayed Fluorescence. *Adv. Funct. Mater.* **2018**, *28* (17), 1800051. https://doi.org/10.1002/adfm.201800051.

## **TOC Graphic**

