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Functional Pyrimidine-based Thermally Activated Delay Fluorescence Emitters: Photophysics, Mechanochromism and Fabrication of Organic Light-Emitting Diodes

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# **TOC Entry**

#### Abstract

A new series of molecules T1-T4 possessing thermally activated delay fluorescence (TADF) have been strategically designed and synthesized. T1-T4 bear the dimethyl acridine as the electron donor, which is linked to either symmetrical or unsymmetrical diphenyl pyrimidine as an acceptor. In comparison to the ubiquitous triazine acceptor, the selection of pyrimidine as an acceptor takes its advantage of facile functionalization and less stabilized unoccupied  $\pi$ -orbitals so that the energy gap toward blue can be accessed. Together with the acridine donors, the resulting D-A functional materials reveal remarkable TADF properties. In solid, all T1-T4 exhibit intriguing mechanochromism. The crystal structures, together with the spectroscopy and dynamics acquired upon application of stressing, lead us to propose two types of structure arrangement that give distinct emission properties, one with and the other without TADF. Upon fabricating OLEDs the T1-T4 films prepared from sublimation all exhibit dominant TADF behavior, accounting for their high performance where the 490 nm EL emission with an EQE of 14.2% can be attained when T2 is used as an emitter.

# 1. Introduction

Organic light-emitting diodes (OLEDs) are deemed to be the auspicious technology for lighting applications and new generation flexible displays.<sup>[1]</sup> Typically OLEDs are composed of electroluminescent materials and carrier transport materials embedded between metal cathode and transparent conducting oxide anode. Internal quantum efficiency (IQE) of the electroluminescent materials plays key role in determining the practical performance of the OLEDs. Theoretically, due to the fast rate of singlet-triplet intersystem crossing and allowed T<sub>1</sub>  $\rightarrow$  S<sub>0</sub> transition, organometallic phosphorescent emitters are able to harvest both singlet and triplet excitons and can achieve 100% IQE, superior to the fluorescent materials with limited IQE of 25%.<sup>[2]</sup> However, rare availability and high cost of phosphorescent materials hinder their practical applications, motivating researchers to develop new types of emitters with lower costs

and better performance. In light of this scenario, Adachi et al. pioneered a new generation lowcost and high-efficiency emitters based on the mechanism of thermally activated delayed fluorescence (TADF).<sup>[3]</sup> TADF emitters have extremely small singlet-triplet energy gap, allowing up-conversion of triplet excitons to the radiative singlet excited state via reverse intersystem crossing by harvesting environmental thermal energy. Without employing heavy metal atoms, TADF emitters are able to harvest both singlet and triplet excitons for light emission, providing an efficient pathway to achieve 100% IQE.<sup>[4]</sup>

TADF materials with minimized spatial overlap between the donor (D) and acceptor (A) fragments can aid in reducing the energy gap between the singlet and triplet states ( $\Delta E_{T.S.}$ , defined as T<sub>1</sub> minus S<sub>1</sub> in the lowest lying excited state). Tremendous efforts have been made to couple donor and acceptor units for realizing highly efficient TADF materials.<sup>[5]</sup> Electron deficient aromatic systems such as triazole,<sup>[6]</sup> oxadiazole,<sup>[7]</sup> anthraquinone,<sup>[8]</sup> cyano,<sup>[9]</sup> sulfones,<sup>[10]</sup> phosphine oxide,<sup>[11]</sup> and etc., are generally regarded as adequate accepting fragments. Of particular interest is the 1,3,5-triazine that has been widely utilized as acceptor unit of D-A system that exhibits remarkable TADF characteristic.<sup>[12]</sup> More recently, pyrimidine has emerged as an alternative acceptor fragment.<sup>[13]</sup> This selection is mainly due to its electron deficient character and easy functionalization of the donor moieties, which aid in constructing the required D-A arrangement. It is also expected that the pyrimidine acceptor possesses the less stabilized empty  $\pi$ -orbitals compared with the triazine based acceptor. Hence, by combining with suitable donors, the pyrimidine based D-A functional materials would provide a suitable motif for efficient sky-blue and blue emission.

Furthermore, the donor should attach to the acceptor in a partially orthogonal orientation to reduce the electron correlation and hence reduced  $\Delta E_{T-S}$  will be achieved.<sup>[14]</sup> From the view point of molecular design, carbazole has long been considered as an excellent donor fragment. Unfortunately, the central pyrrole ring is not capable of inducing sufficiently large steric effect against the pyrimidine to maintain the perpendicular arrangement upon excitation.<sup>[4, 15]</sup> We thus decided to switch to the dimethyl acridine, for which the six membered

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central ring is expected to increase spatial encumbrance with the acceptor fragment as envisaged in the literature.<sup>[6, 16]</sup> Scheme 1 displays the structural sketching of these pyrimidine based TADF molecules, T1-T4, among which T1 and T2 are endowed with the dimethyl acridine donor linked to either symmetrical or unsymmetrical diphenyl pyrimidine acceptor, and T3 and T4 are derivatives of T1 and T2 but with reduced  $\pi$ -conjugation at one phenyl group by introducing an ortho-methyl substituent. These structural changes within the emitters are expected to alter the associated optoelectronic properties systematically.



R = H, T1; R = Me, T3

R = H, T2; R = Me, T4

Scheme 1. Structural drawing of diphenyl pyrimidine based TADF molecules.

# 2. Results and discussion

### 2.1. Synthesis and characterization

The synthetic strategy for achieving the target molecules are shown in Scheme 2. Chalcone type intermediates (1 - 4) were prepared by simple Aldol condensation reactions with the corresponding aldehyde and acetophenone in good yields.<sup>[17]</sup> Accordingly, the prepared chalcones further reacted with respective amidine hydrochloride salts to yield the pyrimidine based acceptor unit (5 - 8). The donor fragment was then coupled with the acceptor unit via Buchwald Hartwig amination to yield the desired products (T1, T2, T3 and T4). They were subjected to recrystallization, followed by temperature gradient vacuum sublimation. Chemical structures of the final products were confirmed using <sup>1</sup>H and <sup>13</sup>C NMR, mass spectroscopy and elemental analysis.



Scheme 2. Synthesis of pyrimidine accepting unit and final TADF molecules. Experimental conditions: (i) KOH, EtOH, RT; (ii) KOH, EtOH/water, reflux. (iii) dimethylacridine, <sup>t</sup>BuONa, P(<sup>t</sup>Bu)<sub>3</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>, dry toluene, reflux, 24 h.

T1 and T2 were also examined by single-crystal X-ray diffraction and, to the best of our knowledge, they represent the first set of structural study based on pyrimidine TADF system, which should provide in-depth insight into the overall molecular structure and the relative orientation between the donor and acceptor in the ground state. As depicted in Figures 1 and 2, the planar dimethyl acridine for both molecules is nearly orthogonal (88.76° and 85.49° for T1 and T2 respectively) to the middle phenylene substituent that links to the central pyrimidine, fulfilling the requirement of minimizing orbital overlap between HOMO and LUMO (vide infra). The measured dihedral angles between each phenyl group and the central pyrimidine unit were

found to be 21.93°, 5.15°, 15.28° and 19.41°, 6.05°, 17.87° for T1 and T2, respectively, which confirm the formation of pseudo-planar arrangement for the central pyrimidine acceptor unit that is favorable for the extended  $\pi$ -conjugation.

Thermal properties of T1, T2, T3 and T4 were investigated by using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) at a heating rate of 10 °C min<sup>-1</sup>. The TGA and DSC graphs were displayed in Figure S1 and their relevant data are listed in Table S1. The temperature of decomposition (T<sub>d</sub>, which corresponds to 5% weight loss) was observed in the range of 357 to 382 °C, evidencing their robustness and excellent thermal stability under investigation. The insertion of methyl group in the pyrimidine acceptors (T3 and T4) slightly lower its T<sub>d</sub> compared to their parent analogues T1 and T2. The glass transition temperature (T<sub>g</sub>) of all samples was recorded to be around 95 °C.

### 2.3 TADF properties via photophysical measurements

Photophysical properties of these compounds were firstly analyzed by UV/Vis absorption and photoluminescence studies in different solvents at room temperature. The corresponding spectra are displayed in Figure 3 and their relevant photophysical data are summarized in Table 1. All T1-T4 compounds exhibit a higher energy band around 200 – 300 nm with high molar extinction coefficient ( $\varepsilon \sim 4 - 6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) arising from the  $\pi \rightarrow \pi^*$  transition and a lower lying band around 350 - 400 nm with relatively much weaker molar extinction coefficient ( $\varepsilon \leq 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) that can be attributed to the intramolecular charge transfer transition from the donor unit to the acceptor fragment as envisaged in literature.<sup>[13d, 13e]</sup> We then performed the time-dependent density functional theory (TD–DFT) calculations in aim to gain insight into the basic photophysical properties. All pertinent assignments of the lowest lying singlet  $S_0 \rightarrow S_1$  optical absorption transitions for T1 - T4 are listed in Table S2 - S5, Figure 4 and Figure S2 - S5 (Supporting Information). As a result, the  $S_0 \rightarrow S_1$  transitions are assigned to HOMO  $\rightarrow$  LUMO+1 for T1 and T3 and HOMO  $\rightarrow$  LUMO for T2 and T4. The electron density distribution of HOMO is mainly localized at the planar dimethyl acridine fragments for

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all compounds, while the electron density distribution of LUMO+1 (for T1 and T3) and LUMO (for T2 and T4) is localized at the central phenylene and the diphenyl pyrimidine fragments. Therefore, the  $S_0 \rightarrow S_1$  transition for T1 - T4 is unambiguously assigned to the charge transfer transition, in which HOMO and LUMO+1 (for T1 and T3) or LUMO (for T2 and T4) are spatially separated by the dimethyl acridine and the phenylene substituent. The dihedral angles between the dimethyl acridine and the central phenylene substituent are calculated to be ~90°, firmly supporting the orthogonal configuration (Figure 4). Because the calculated oscillator strengths are rather small (~10<sup>-4</sup>), in a result, the  $S_0 \rightarrow S_1$  transition is expected to reveal a charge-transfer character with small absorptivity, consistent with the rather weak low-lying absorption band observed experimentally (vide supra).<sup>[18]</sup>

The photoluminescence spectra of all titled compounds reveal significant solvent dependent luminescence, i.e., solvatochromism, leading to a trend of bathochromic shift upon increasing the solvent polarity from toluene to CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN. For example, the emission maximum of T2 appears at 473 nm in toluene, which is red shifted by 93 nm and 142 nm in CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN, respectively. Similar solvent dependent excited-state behavior was observed for T1, T3 and T4. It has been well established that solvatochromism is related to the large change of dipole moment in the electronically excited state versus that of the ground state, supporting the observed luminescence originating from the intramolecular charge transfer (ICT) transition,<sup>[19]</sup> which is the prerequisite characteristic to the TADF molecules.

The TADF behavior can be evidenced indirectly by the changes of steady state emission in aerated solution versus that in degassed solution. The delay fluorescence resulting from the  $T_1 \rightarrow S_1$  reverse intersystem crossing should be drastically quenched by  $T_1$  to dioxygen energy transfer process. Accordingly, the photoluminescence quantum yields (PLQY) of these compounds in both aerated and degassed conditions were measured and the data are summarized in Table 1. Apparently, except for T1 and T3 in toluene (vide supra), the results shown in Table 1 reveal a significant increase in quantum yields under degassed conditions. For instance, PLQY of the charge transfer emission for T1, T2, T3 and T4 in degassed CH<sub>2</sub>Cl<sub>2</sub> were

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recorded to be 63%, 43%, 80% and 88 % versus 14%, 16%, 25% and 25%, respectively, measured in aerated condition, supporting their potential TADF property. In a direct manner, the transient photoluminescence decay dynamics was then measured in different solutions to analyze their TADF behaviors. Figures 5 and 6 display the PL decay profiles in the both degassed toluene and CH<sub>2</sub>Cl<sub>2</sub>, and their corresponding lifetime data are listed in Table 1. For example, the emission of T2 in degassed CH<sub>2</sub>Cl<sub>2</sub> exhibited two single-exponential decay kinetics with time constants fitted to be 25 ns and 2.5 µs. Upon aerating the solution, in sharp contrast, the emission revealed only single exponential decay kinetics with a time constant of 18 ns (Figure S6). Therefore, the 2.5 µs long decay component is drastically quenched by O<sub>2</sub>, confirming its origin from the triplet state. Also, the required low excitation intensity of TSPC eliminates the possibility of the long-lived emission from triplet-triplet (T-T) annihilation. Therefore, the 2.5 µs decay component to TADF is unambiguous. Accordingly, the 25 ns decay component can be assigned to the prompt fluorescence.

Except for T1 and T3 that did not show double exponential decay in degassed toluene, similar TADF character, i.e. the prompt and long decay component, was observed for all other compounds in the studied solvents. The lack of TADF for T1 and T3 in toluene from both steady state and kinetic measurements may be rationalized by their lower charge transfer ability than that of T2 and T4. As elaborated in the cyclic voltammetry measurement (Table S7 in SI), the HOMO energy, within experimental error, was measured to be about the same (-5.34 eV), while the LUMO energy is T1 (-2.45 eV) > T2 (-2.48 eV) and T3 (-2.37 eV) > T4 (-2.40 eV). Therefore, the charge transfer T2 and T4 seems to be more exergonic than that for T1 and T3, respectively. Recent experimental evidence in the literature supports the involvement of local triplet excited states from the donor or acceptor units,  $^{3}D$  or  $^{3}A$ , other than the triplet CT in the reverse intersystem crossing (rISC). Therefore, the reverse intersystem crossing (rISC) may not occur between  $^{1}CT$  and  $^{3}CT$  but between  $^{1}CT$  and  $^{3}A/^{3}D$  may be below  $^{3}CT$  in low polarity solvent such

as toluene. In this case, the  ${}^{3}A/{}^{3}D \rightarrow {}^{1}CT$  rISC is inefficient. Conversely, in high polarity solvent such as CH<sub>2</sub>Cl<sub>2</sub>,  ${}^{3}CT$  is lower than  ${}^{3}A/{}^{3}D$  and  ${}^{3}CT \rightarrow {}^{1}CT$  rISC is rather efficient.

In theory, under the assumption of pre-equilibrium between  $S_1$  and  $T_1$  states, the difference in energy  $\Delta E_{T-S}$  (defined as T<sub>1</sub> minus S<sub>1</sub>) can be derived according to the relationship between  $\Delta E_{T-S}$  and S<sub>1</sub>-T<sub>1</sub> equilibrium constant  $K_{eq}$  expressed as  $\Delta E_{T-S}$  = -RTIn( $K_{eq}/3$ ) where the equilibrium constant  $K_{eq}$  can be deduced from the pre-exponential factors for prompt fluorescence versus delay fluorescence decay components. A factor of 3 stands for the triplet degenerate states,<sup>[21]</sup>  $\Delta E_{T-s}$  was then deduced to be -2.56, -1.79, -3.09 and -1.94 kcal/mol for T1, T2, T3 and T4 in CH<sub>2</sub>Cl<sub>2</sub>, respectively. For organic molecules, the TADF efficiency is mainly limited by the nonadiabatic electronic state coupling matrix associated with intersystem crossing. A designed strong charge-transfer character with small overlap of the frontier orbitals not only minimizes  $\Delta E_{T-S}$ , but also induces a mixing of the singlet and triplet states and thus enhances intersystem crossing for a high TADF efficiency. From our molecule design, comparing T1 and T2, the central pyrimidine acceptor of T1 is expected to countervail the electron withdrawing ability. Comparing the pair of compounds T1/T3 and T2/T4, the additional o-methyl group on T3 and T4 showed the slightly increased electron donation and reduced  $\pi$ -conjugation to the attached phenyl substituent, i.e. the reduced charge transfer ability. Overall, it can be speculated from the steady state and lifetime measurements that the derivative T2 has significant solvatochromism property and the smallest energy gap. As can be seen, the charge transfer ability follows the order of T2 > T4 > T1 > T3, consistent with early conclusion.

#### 2.4 The solid state property

Prior to present the TADF behavior for T1 - T4 in solid state, an intriguing phenomenon, namely the mechanochromism, is worth to report.<sup>[22]</sup> Herein, we take T2 as an example for detailed elaboration. The single crystal of T2 exhibits an emission band with peak maximum at 433 nm (Figure 7). Upon applying the mechanical force such as grinding, as shown in Figure 7, the maximum is red shifted to 483 nm indicating the alternation of solid packing arrangement

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and hence the electronic transition upon changing the morphology of solids. Such a change of emission can be visualized by the naked eyes. Figure 8 shows the photographic images of the luminescence color of T2 in response to mechanical grinding with a mortar and pestle. Apparently, upon UV lamp (366 nm) excitation the emission of the crystal sample (before grinding) appears to be blue, whereas the emission of the ground powder turns out to be prone to cyan. The phenomenon is much more dramatic when T2 is sublimed, for which the emission peak wavelength is completely shifted to 490 nm such that the luminescence appears to be greenish. Upon re-dissolving the ground powder or sublimed sample in solvent such as toluene, followed by slow recrystallization, the green-emitting sample is then recovered back to the blue emitting sample.

To gain further insight into the associated mechanochromism we then performed T2 transient PL decays of these three solid samples (see Figure S7 and Table S6). As for the crystalline sample, upon monitoring at the deep-blue region of 430 nm, the fluorescence exhibits solely single exponential decay kinetics with a lifetime fitted to be 5.1 ns. In stark contrast, the emission monitored at the long wavelength region of e.g. 550 nm reveals multiple decay components, consisting of a fast decay component with a lifetime of 5.1 ns, a relatively slow decay of 219 ns and a much longer decay component of 8.9  $\mu$ s. The 5.1 ns decay component is similar to that monitored at 430 nm and can be attributed to the same 430 nm band that tails down to 550 nm. Accordingly, we ascribe the 219 ns and 8.9 μs components to the same fluorescence band that possesses TADF property. Due to the small pre-exponential value, the long wavelength band should not be obvious in the steady state measurement, as seen in Figure 7 where almost only a blue 435 nm band appears for T2 in the crystalline form. In the ground powder this long-wavelength band appears around 490 nm (Figure 7), which is also supported by the increase of 219 ns and 8.9  $\mu$ s components (see Figure S7). In the sublimed sample, shown in Figure S7, the emission kinetics is dominated by the 219 ns and 8.9  $\mu$ s components, clearly revealing the dominant TADF property. In other words, the sublimed sample exhibits a blue-greenish 490 nm fluorescence that has thorough TADF property. Note

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that sublimation was also the method used in the fabrication of vacuum deposited OLEDs (vide infra). Mechanochromism is also observed for T1, T3 and T4 and similar excitation wavelength dependent relaxation dynamics with that of T2 are resolved, which are depicted in Figure S8 with pertinent data summarized in Table S6.

According to the results and discussion elaborated above, it is reasonable to propose the existence of two kinds of structure alignment in solid state, for which the intermolecular interaction plays a key role to account for the observed mechanochromism and hence different photophysics. To gain more insight into the associated intermolecular interaction, we have then carefully examined the crystal packing of T1 and T2. As depicted in Figure S9, the crystal structure of T1 and T2, which contains four molecules in the unit cell, it belongs to the monoclinic crystal system and with space group  $P2_1/C$ . There exist a pair of molecules that adopt a head-to-head stacking and with a close  $\pi$ - $\pi$  intermolecular interaction showing a distance in the range of 3.5 - 3.8 Å. This H-type like interaction (the h aggregation), in theory, should lead to a blue shift of the lowest lying transition in both singlet and triplet states.<sup>[23]</sup> Moreover, the  $\pi$ - $\pi$  stacking interaction may enhance the  $\pi$ -electron correlation and hence increase the electron exchange energy. The net result is to increase the singlet-triplet  $(S_1-T_1)$ energy gap such that the  $T_1 \rightarrow S_1$  is thermally inaccessible and TADF is no longer observed. The other packing adopts a loosely head-to-tail alignment via perhaps the weak C-H $\cdots\pi$  interactions. This loosely packing mode has negligible effect to the electronic property of T1 - T4 per se, which then exhibits TADF behavior similar to that observed in the solution.<sup>[24]</sup>

Upon exerting the mechanic force to the crystal such as grinding, the well aligned *h*-like dimers collapse, in part, and become loosely packed, or both packing modes even turn to the amorphous structure under a more radical scenario. Accordingly, grinding T1 and T2 increases the single molecule entity free from strong intermolecular interaction and hence increases the contribution of long-wavelength emission band with strong TADF property. Especially, the sublimation of T1 - T4 causes the fast condensation and hence the formation of amorphous structure, resulting in the dominant TADF property, which is what we observed in the OLED

fabrication, particularly when T1 - T4 films are prepared by sublimation. Detail is elaborated below.

# 2.5 Electrochemical properties and OLED fabrication

For the application of OLED, the information of electrochemical properties is necessary, which was scrutinized by using cyclic voltammetry measurements and the voltammograms. The results are depicted in Figure S10 and the corresponding numerical data are listed in Table S7. All the compounds exhibit reversible oxidation process in the range of 0.53 - 0.54 V and reduction process lies between -2.32 and -2.43 V versus FcH<sup>+</sup>/FcH couple, for which the small variation of oxidation potential is due to the presence of same donor fragment in all compounds. The insertion of methyl group to T1 and T2 slightly increases their reduction potential by 80 mV for T3 and T4, respectively.

Electroluminescent properties of the four materials were investigated with a device configuration of ITO/TAPC (50 nm)/mCP:10 wt% dopant (15 nm)/DPEPO:10 wt% dopant (15 nm)/TmPyPB (60 nm)/LiF (1 nm)/Al (100 nm). As shown in Figure 9a and Table 2, these devices show similar turn-on voltages of 3.0 - 3.2 V. Figure 9b shows their EQE vs. luminance. T1 shows a maximum EQE of 7.2% in device, whereas T2, T3 and T4 based OLEDs deliver higher EQEs of 11.8 - 12.6%. The EQE of T2 based device could be improved to 14.2% by using an emitting layer of 12 nm. Considering that OLEDs based on conventional fluorescent emitters will deliver maximum EQEs of 5 - 7.5% assuming an optical out-coupling efficiency of 20 - 30%,<sup>[25]</sup> the high EQEs (> 10%) of the T2, T3 and T4 based OLEDs suggest the contribution of the triplet excitons that are thermally repopulated back to the singlet manifold to account for the enhanced light emission. The finding confirms the existence of TADF in these materials. Figure 9c reveals EL spectra of the OLEDs, which show that EL peaks for T1, T2, T3 and T4 are 472, 492, 464 and 476 nm, respectively. The results indicate that all four materials are efficient blue emitters. By inserting an orange-red phosphorescent emitting layer of DPEPO:4 wt% Ir(2-phq)<sub>2</sub>acac (5 nm) into the blue OLEDs, where Ir(2-phq)<sub>2</sub>acac is bis(2-phenylquinoline)(acetylacetonate)

iridium(III),<sup>[26]</sup> four white OLEDs were fabricated. As shown in Figure 10 and listed in Table 2, the white OLEDs turned on at ca. 3.0 V. High EQEs over 10% have been realized in these devices.

# 3. Conclusion

In summary, we report the design and synthesis of a new series of T1 - T4 molecules bearing dimethyl acridine and pyrimidine as the electron donor and acceptor, respectively. In comparison to the ubiquitous triazine acceptor, the selection of pyrimidine as an acceptor is due to its less stabilized unoccupied  $\pi$ -orbitals and facile functionalization. The resulting D-A functional materials reveal remarkable TADF properties in solution, among which T2 exhibited the smallest  $\Delta E_{T-S}$ , which could be due to the asymmetric arrangement of pyrimidine nitrogen atoms. The crystal structures, together with the intriguing mechanochromism observed for T1 - T4, lead us to propose two type of structure arrangement that give distinct emission properties, showing emission lifetimes in both the ns and  $\mu$ s regime. OLEDs based on T1 - T4 exhibit dominant TADF behavior; in particular, the device incorporating T2 as the emitter delivers blue emission with a high EQE of 14.2%. By inserting an orange-red phosphorescent emitting layer into the blue devices, the white OLEDs with turn-on voltage ca. 3.0 V and EQEs over 10% were realized. These results suggest pyrimidine (A)/acridine(D) hybrids as promising materials for mechanochromism and OLEDs.

**Supporting information**. Details of synthetic procedures, theoretical calculation, photophysical and electrochemical measurements, single crystal X-ray diffraction studies and procedures for OLED device fabrication.

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**Figure 1**. Structural drawing of T1 with ellipsoids shown at the 30% probability level. The curved arrows depict the dihedral angle between the adjacent rings.



**Figure 2**. Structural drawing of T2 with ellipsoids shown at the 30% probability level. The curved arrows depict the dihedral angle between the adjacent rings.

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**Figure 3**. Absorption and emission spectra of a) T1, b) T2, c) T3 and c) T4, in toluene (blue),  $CH_2Cl_2$  (red), acetonitrile (brown) and solid state (black) at 298 K.



**Figure 4.** Frontier molecular orbitals pertinent to the lowest optical transitions for T1-T4 in CH<sub>2</sub>Cl<sub>2</sub>. Pink and green meshes represent HOMO and LUMO (or LUMO+1), respectively. The calculated optimized dihedral angles between the planar dimethyl acridine to the central phenylene substituent are also displayed.



Figure 5. Transient photoluminescence characteristics of T1 (upper) and T2 (lower) in degassed toluene and  $CH_2Cl_2$  ( $\lambda_{ex}$  = 355 nm).



**Figure 6.** Transient photoluminescence characteristics of T3 (upper) and T4 (lower) in degassed toluene and  $CH_2Cl_2$  ( $\lambda_{ex}$  = 355 nm).



**Figure 7**. Photoluminescence spectra of T2 in single crystal (black), powder (red), sublimation state (blue) and ground state (green) respectively.



**Figure 8.** Photographic images of the color and luminescence changes of T2 in response to mechanical grinding: (a) and (c) unground sample, (b) and (d) ground sample. Photographs were taken under ambient light and UV irradiation (365 nm).



**Figure 9.** (a) Current density-voltage-luminance, (b) external quantum efficiency-luminance plots and (c) EL spectra of the blue OLEDs.



**Figure 10.** (a) Current density-voltage-luminance and (b) external quantum efficiencyluminance plots of the white OLEDs. The device structure of the white OLEDs consists of a multilayer structure of ITO/TAPC (50 nm)/mCP:10 wt% dopant (15 nm)/DPEPO:10 wt% dopant (15 nm)/DPEPO:4 wt% Ir(2-phq)<sub>2</sub>acac (5 nm)/TmPyPB (60 nm)/LiF (1 nm)/Al (100 nm), where dopant is T1 - T4, respectively.

Table 1. Selec	ted photophysica:	l properties of	T1, T2,	T3 and T4 i	in toluene,	$CH_2Cl_2$ and	CH <sub>3</sub> CN at
RT.							

compound	CT / LAN			$\Delta E_{T-S}$	k <sub>isc</sub> ;
(solvent)	CI / nm	Q.Y. / %	$\tau$ (pre-exp factor)	[kcal/mol]	k <sub>risc</sub> (s <sup>-1</sup> )
T1 (toluene)	471	24.3, <sup>[a]</sup> 33.9 <sup>[b]</sup>	6.48ns (-)		
T1 (CH <sub>2</sub> Cl <sub>2</sub> )	525	14.0, <sup>[a]</sup> 63.2 <sup>[b]</sup>	18.2ns (0.9956),	-2 56	5.49×10 <sup>7</sup> ;
			16.5µs (0.0044)	-2.50	2.43×10 <sup>5</sup>
T1 (CH₃CN)	575	1.0, <sup>[a]</sup> 1.8 <sup>[b]</sup>			
T2 (toluene)	473	16.0, <sup>[a]</sup> 33.6 <sup>[b]</sup>	4.23ns (0.9997),	4.22	2.36×10 <sup>8</sup> ;
			78.5µs (0.0003)	-4.23	6.22×10 <sup>4</sup>
T2 (CH <sub>2</sub> Cl <sub>2</sub> )	566	15.74, <sup>[a]</sup> 42.83 <sup>[b]</sup>	25.0ns (0.9839),	1 70	3.93×10 <sup>7</sup> ;
			2.52µs (0.0161)	-1.79	6.42×10 <sup>5</sup>
T2 (CH₃CN)	615	4.4, <sup>[a]</sup> 7.4 <sup>[b]</sup>			
T3 (toluene)	469	24.8, <sup>[a]</sup> 38.5 <sup>[b]</sup>	8.76ns (-)		
T3 (CH <sub>2</sub> Cl <sub>2</sub> )	517	25.4, <sup>[a]</sup> 79.6 <sup>[b]</sup>	24.3ns (0.9982),	2.00	4.10×10 <sup>7</sup> ;
			24.5µs (0.0018)	-3.09	7.42×10 <sup>4</sup>
T3 (CH₃CN)	563	4.9, <sup>[a]</sup> 12.5 <sup>[b]</sup>			
T4 (toluene)	479	21.31, <sup>[a]</sup> 77.75 <sup>[b]</sup>	2.76ns (0.9980),	2.02	3.62×10 <sup>8</sup> ;
			61.5µs (0.0020)	-3.02	7.39×10 <sup>5</sup>
T4 (CH <sub>2</sub> Cl <sub>2</sub> )	558	24.65, <sup>[a]</sup> 88.39 <sup>[b]</sup>	22.7s (0.9875),	1.04	4.35×10 <sup>7</sup> ;
			3.79µs (0.0125)	-1.94	5.51×10 <sup>5</sup>
T4 (CH₃CN)	605	4.9, <sup>[a]</sup> 10.1 <sup>[b]</sup>			

<sup>[a]</sup> those measured in aerated solution, and <sup>[b]</sup> measured in degassed solution.

	Von	L <sub>max</sub>	EQE (%) <sup>[c]</sup>	η <sub>c</sub>	η <sub>ρ</sub>	CIE(x,y) <sup>[d]</sup>
	(V)	(cd/m²)		(cd·A <sup>-1</sup> ) <sup>[c]</sup>	(lm·W <sup>-1</sup> ) <sup>[c]</sup>	
T1 <sup>[a]</sup>	3.0	2868	7.2/5.6	13.4/10.4	12.0/8.2	(0.17,0.27)
T2 <sup>[a]</sup>	3.2	7606	12.6/12.6	30.4/30.3	23.2/22.4	(0.21,0.39)
T2 <sup>[b]</sup>	3.0	7385	14.2/11.5	34.2/28.1	29.8/21.0	(0.20,0.39)
T3 <sup>[a]</sup>	3.0	1269	11.8/4.2	18.8/6.5	19.6/4.7	(0.17,0.21)
T4 <sup>[a]</sup>	3.0	1867	11.8/10.3	24.0/21.0	21.5/15.5	(0.18,0.30)
T1 <sup>[a]</sup> (white)	3.0	3458	10.7/7.1	18.5/12.2	19.4.8.5	(0.34,0.30)
T2 <sup>[b]</sup> (white)	3.0	5401	11.3/9.0	23.8/18.9	24.9/13.8	(0.34,0.37)
T3 <sup>[a]</sup> (white)	3.1	1727	11.9/5.7	20.3/9.5	21.2/6.1	(0.33,0.28)
T4 <sup>[a]</sup> (white)	3.1	2969	14.3/10.6	29.3/21.4	26.3/15.2	(0.30,0.34)

**Table 2.** The EL data of the OLEDs using T1 - T4 as the emitters.

<sup>[a]</sup> EMLs: mCP:10 wt% dopant (15 nm)/DPEPO:10 wt% dopant (15 nm).

<sup>[b]</sup> EMLs: mCP:10 wt% dopant (12 nm)/DPEPO:10 wt% dopant (12 nm).

<sup>[c]</sup> Efficiencies at maximum and 100 cd/m<sup>2</sup>.

<sup>[d]</sup> At 100 cd/m<sup>2</sup>.

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