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Donor-σ-Acceptor Motif Thermally Activated Delayed Fluorescence Emitters with Dual Upconversion

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Abstract: A family of organic emitters having a donor- σ -acceptor (D- σ -A) motif is demonstrated. Based on the weakly coupled D- σ -A intramolecular charge transfer state, a transition from the localized excited triplet states (³LE) and charge transfer triplet states (³CT) to the charge transfer singlet states (¹CT) with a small activation energy and high photoluminescence quantum efficiency is accomplished. Two thermally activated delayed fluorescence (TADF) components are identified, one of which has a very short lifetime of 200-400 ns and another a longer TADF lifetime of the μ s order. In particular, two D- σ -A materials present strong blue emission with TADF properties in toluene. This result will shed light on the molecular design of new TADF emitters having short delayed lifetimes.

Nowadays, organic light-emitting diodes (OLEDs) are widely utilized in flat-panel displays and solid-state lighting, and attract considerable interest both in academia and industry.^[1] The internal electroluminescence (EL) quantum efficiency (IQE) of OLEDs with conventional organic fluorophores is in practice limited to 25% because 75% of the electrically generated excitons are statistically triplets that decay nonradiatively.^[2] In comparison with fluorescent OLEDs, phosphorescent OLEDs (PHOLEDs) with precious-metal complexes as emitters can achieve IQEs of 100%, since both singlet and triplet excitons can be harvested as a result of singlet-triplet state mixing *via* efficient spin-orbit coupling.^[3] However, PHOLEDs still suffer from the high cost, scarcity and toxicity of these precious

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metals, which hinder their long-term mass production and utilization. Recently, however, the application of metal-free thermally activated delayed fluorescence (TADF) emitters has led to the development of TADF-OLEDs. These are among the most promising classes of practical next-generation OLEDs, since high-performance EL characteristics can be obtained through the molecular design of conventional aromatics, which is in effect unlimited.^[4]

In TADF-OLEDs, electrically generated triplet excitons can be efficiently upconverted from the lowest triplet excited state (T1) to the lowest singlet excited state (S1) via reverse intersystem crossing (RISC) when the energy difference between the two excited states (ΔE_{ST}) is small enough, generally less than a few hundreds meV.^[5] Recently, TADF-OLEDs have made substantial progress in achieving an external EL quantum efficiency of over 30%, which is comparable with the best PHOLEDs.[6] The TADF process is central to the formation of a charge-transfer (CT)excited state from donoracceptor (D-A) molecules, where the highest occupied molecular orbital (HOMO) is located on the donor moiety, and the lowest unoccupied molecular orbital (LUMO) is offered by the acceptor moiety. For the conventional D-A type TADF emitters, the overlap between HOMO and LUMO must be minimized to decrease ΔE_{ST} , which is crucial for efficient thermal upconversion via RISC.[4]

well-established single-molecule Besides the TADF emitters, exciplex emitters based on intermolecular CT transitions were also confirmed to function via TADF by our group in 2012.^[7] Compared with single-molecule TADF emitters, a wide variety of exciplex TADF emitters have been developed by the appropriate combination of donor and acceptor molecules. While some technical issues, such as low photoluminescence quantum yield (PLQY), complex device fabrication and delicate requirements for energy level alignment, represent a barrier to the development of high-performance exciplex TADF OLEDs, recent studies suggest the crucial importance of control over the distance between donor and acceptor moieties.^[8] All the studies to date highlight the necessity of CT state in TADF mechanism.

In this context, we explored an improved design of TADF molecules having a donor- σ -acceptor (D- σ -A) structure where the σ -group allows to some extent to control the distance in an intramolecular way.^[9] In principle, hyperconjugation in such D- σ -A molecules would not only favor the wide separation of the HOMO and LUMO, resulting in small ΔE_{ST} , but also overcome the disadvantages of exciplex TADF emitters, where the charge transfer state is reached through intermolecular charge transfer. The D-A geometries in exciplexes are uncontrollable in solid films, which increases nonradiative decay.^[8] More importantly, we aim for very fine tuning and alignment of the CT and local excited (LE) state energy levels, so that the mixing of the

different excited-state species enhances their radiative decay rate and hence their emission properties.



Figure 1. Molecular structures, calculated HOMO and LUMO energies and molecular orbital distribution of HOMO and LUMO for 1-3.

The D- σ -A type molecules (1-3) designed in this study are composed of triazine (TRZ) as acceptor (A), connected to tetramethyl-substituted carbazole (TMCz), dihydroacridine (DMAC) or triphenylamine (TPA) moieties as donors (D) *via* hexafluoroisopropylidene as a σ -bridge, as illustrated in Fig.1. They could be easily prepared by a multi-step synthesis, finishing with a Buchwald-Hartwig amination reaction, in good yields of *ca.* 80% (Scheme S1). Details of the synthetic route are provided in the supporting information. All materials were fully characterized by ¹H-NMR, ¹³C-NMR, ¹⁹F-NMR, mass spectrometry and elemental analysis.

The three-dimensional geometries, frontier molecular orbital energy levels and ΔE_{ST} of these molecules were calculated using density functional theory with the Gaussian 09 package at the B3LYP/6-31G(d) level.^[10] Similar to previously reported TADF emitters, the HOMO and LUMO of the three molecules are mainly dispersed over the electron-donating moiety and the acceptor moiety, respectively (Fig.1). The overlap between the HOMO and LUMO is clearly minimized by the effective separation of their electron densities caused by the introduction of the σ -bridge, implying a small energy difference between the singlet and triplet excited states. Based on the ground-state geometries, the ΔE_{ST} values of compounds 1-3 are calculated to be extremely small, i.e., 0.0006, 0.0009 and 0.0165eV, respectively, as illustrated in detail in the supporting information (Table S1a). Despite different values using different calculation methods (Table S1c), the ΔE_{ST} values of 1-3 always showed the same trend of increasing in that order.

To investigate the intramolecular and intermolecular contacts within these materials, single crystals of **1** and **3**, obtained by the vapor diffusion method with dichloromethane (DCM) and hexane, were analyzed. The single-crystal X-ray analysis revealed that both molecules present an asymmetric molecular geometry. In both molecules, the donor segment (DMAC or TPA) and acceptor segment (TRZ) adopt a highly twisted configuration. As evident from the packing pattern, neither intramolecular nor intermolecular spatial contact between donor and acceptor molecules is observed in **1** (Fig.S1).

In **3**, the distance between two TRZ units is above 3.6 Å. These twisted configurations and the lack of molecular contact prevent both materials from forming excimers and exciplexes in the solid state.^[11]

To determine experimentally the HOMO and LUMO energies of these molecules, the first oxidation and reduction potentials were measured in DCM and dimethylformamide (DMF) solutions, respectively, by cyclic voltammetry (CV). As shown in Fig.S2, all of the materials present the same reduction potential of -1.92 V, which can be assigned to the reduction of the TRZ acceptor moleties. The oxidation potentials are in the range of 0.47 to 0.59 V, which is in good agreement with the electron-donating capabilities of those units. Thus, the LUMO energy levels of **1-3** were estimated to be -2.50 eV for all three molecules, and the HOMO energy levels as -5.26, -5.42 and - 5.41 eV, respectively.^[12]



Figure 2. a) Absorption, fluorescence (298 K in toluene) and phosphorescence (77 K in toluene matrix) spectra of molecules 1-3.

The photophysical properties of the three materials were investigated using absorption and fluorescence spectroscopy and compared with those of the control molecules, DMAC-TRZ, TMCz-TRZ and DPA-TRZ (D-A structure), having no σ -bridge (Fig.S3). All the D-A molecules exhibit absorption bands in the region of 350 to 420 nm, with moderately weak molar absorption coefficient ε , which can be ascribed to the intramolecular charge-transfer (ICT) transition from the HOMO to the LUMO. Unlike their D-A analogs, the absorption spectra of molecules 1-3 do not present observable ICT states in the longer-wavelength region, as shown in Fig.2, indicating no CT interaction in their ground states. Nevertheless, the photoluminescence (PL) spectra exhibit broad and structureless emission, indicating that their emissive S1 excited states are ICT states in nature, which is compatible with conventional exciplex emission, and with the computational values. Further, the emission maxima of 2 and 3 are blue-shifted relative to that of 1, corresponding to their lower electron-donating capabilities. Meanwhile, the phosphorescence spectra of the three molecules captured at 77 K are all well resolved and show characteristic vibrational structures, indicating that their lowest emissive T₁ excited states are ³LE (Fig.2) at this temperature.^[6] Based on values calculated from their fluorescence and the phosphorescence spectra, the ΔE_{ST} of materials 1, 2 and 3 are estimated to be 0.06, 0.07 and 0.18eV, respectively. Extremely small ΔE_{ST} values are often accompanied by low PLQY, since

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the oscillator strength (f) is proportional to the HOMO-LUMO overlap integral. Therefore, it is crucial to take both parameters, $\Delta E_{\rm ST}$ and f, into account in the design of highly efficient TADF.^[13] The computational data (Table S1) of oscillator strength with extremely small values of 0.0008, 0.0012 and 0.0054 for 1-3, respectively, repeat our concern to some extent. For all three Dσ-A molecules, the PLQY values in toluene before degassing are below 10%, with particularly low values of 1.6% for 1 and 2. Interestingly, the PLQY values are dramatically increased in oxygen-free toluene, reaching 70%, 36% and 20% for 1-3, respectively, which is also a common observation in conventional TADF molecules (Table S3). Importantly, the PL spectra of the three materials in toluene before degassing are all composed of the superposition of ¹LE and ¹CT emission, which can be recognized from the characteristic vibrational structure (around 360 nm) and broad emission peak (around 450 nm) in the spectra, respectively (Fig. S4). The emission peaks at the shorter-wavelength region can be attributed to emission from the ¹LE state, and agree well with the emission spectra of the donor moieties themselves.



Figure 3. a) Transient PL decay profiles of 1-3 in toluene (black line) and oxygen-free toluene (red line); b)Transient PL decay profiles of 1-3 in oxygen-free toluene measured by streak camera experiments on a short time scale.

It is noteworthy that three decay components were revealed in the transient PL decay profiles of materials 1and 2 in oxygen-free toluene, as shown in Fig.3. The first decay components clearly appeared as a small bump in 1 and 2 but could not be discerned in 3. These small, fast amplitudes indicate that the ISC process is much faster than the fluorescent radiative decay.^[5c, 14] In comparison, there is only one component decay for molecule 3 in the transient PL decay profile, and an appreciable enhancement of the lifetime and

PLQY after removing oxygen. To define the nature of those three component decays, streak camera experiments in toluene solution were performed. These revealed that the first, rapid decays of 1 and 2 both originate from the mixture of ¹LE and ¹CT emissions (Fig. S5), similar to the behavior in toluene before degassing as revealed in Fig. S4. Meanwhile, the second decay can be ascribed to the ¹CT emission with a rather longer lifetime. Further, we also identified the third delayed component, having a redshifted broad CT-type emission in molecules 1 and 2 (Fig. S5). Based on the PLQY enhancement and different lifetimes of the ¹CT emission, we conclude that the first delayed ¹CT emission (380 ns for 1 and 190 ns for 2) and subsequent delayed emission both originate from TADF processes. To clarify the detailed mechanism, we further measured the temperature dependence of the PL decay characteristics. For 1 and 2, the first delayed lifetime increased with decreasing temperature (Figs.S6 and S7). Meanwhile, material 3 presented no second TADF component.





In Fig. 4, we show the most probable dual TADF mechanism. For these D-\sigma-A emitters, the excitation energy must be higher than those of their donor and acceptor analogs, to ensure ¹LE emission of the donors. Then, because of the fast ISC process, most of the excitons transfer to ${}^{3}\text{LE}_{(\text{Donor})},$ where they are effectively quenched in the presence of ³O₂, resulting in very low PLQY for 1 and 2 in toluene before degassing. After degassing, in contrast, the excitons in ³LE_(Donor) are able to convert to the ¹CT state by the RISC process, and from here they radiatively decay (the first TADF emission) to the ground state. Here the upconversion process is rather fast, i.e., 200-400 ns, because the transition is spin-allowed based on El Sayed's rule in particular, the emission efficiency in molecule 1 is quite high at 63% (Table S5). The increase of τ_d with decreasing temperature, with almost no change of PLQY, in molecules **1** and **2** indicates that the transition from the ${}^{3}LE_{(Donor)}$ to the ¹CT states is an endothermic process, but nonradiative decay is heavily suppressed even at room temperature. However, when the triplet exciton cannot overcome the gap, this results in the characteristic phosphorescence from the ³LE_(Donor) state, as shown in Fig. 2. Here, we also mention the presence

of the second delayed component, which can be ascribed to the upconversion from the ³CT state to the ¹CT state after the forward ISC decay. Note that the efficiency of this process is only 6% and 3% in molecules 1 and 2, respectively, indicating that the first delayed channel is the major TADF delay process. In the case of 3, the PL behavior is appreciably different from the other two. The PLQY is 10% and 20% with and without O₂, respectively, indicating the presence of highly efficient nonradiative decay processes, which can be ascribed to the donor unit of TPA. Since the TPA unit is rather rotationally flexible compared with the other donors, the excitons in ³LE_(Donor) undergo efficient nonradiative decay, and the decrease of temperature contributes to a slight enhancement of the upconversion. Also, the lack of a clearly observed second TADF component indicates that nonradiative decay is also dominant from the ³CT state. Overall, we have confirmed that molecules 1 and 2 have very fine-tuned energy alignments, demonstrating two sources of upconversion.

Finally, we note further aspects of this molecular design concept with respect to OLED application. In view of crucial issues such as device lifetime and efficiency roll-off in OLEDs, the decrease of delayed lifetime in TADF emitters will undoubtedly enhance device performance. However, at the current stage of design, the presence of the second delayed component will prevent their effective application because of the direct exciton formation at this energy level. In a follow-up study, we intend to finely tune the σ length to enable the complete mixing of ^3CT and ^1CT , allowing the disappearance of the second slow TADF component.

In summary, we have demonstrated a novel molecular design strategy for TADF emitters based on donor- σ -acceptor molecules. By separating the HOMO and LUMO through the introduction of hyperconjugation, a small ΔE_{ST} with dual TADF was obtained, arising from fine-tuned energy alignment of the ¹CT, ³CT and ³LE states. In spite of the weakly coupled intramolecular CT state, considerably high PLQY values can be achieved using these materials because of their rigid molecular structures. More interestingly, relatively short TADF decayed lifetimes of less than 400 ns were achieved with **1** and **2**. We believe our present study provides a new design strategy using hyperconjugation for advanced TADF materials.

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Conflicts of interest

The authors declare no conflicts of interest.

Keywords: Delayed fluorescence · donor-σ-acceptor · hyperconjugation · lifetime · organic light-emitting diodes

- [1] C. W. Tang, S. A. van Slyke, *Appl. Phys. Lett.* **1987**, *51*, 913.
- [2] a) M. A. Baldo, D. F. O'Brien, M. E. Thompson, S. R. Forrest, *Phys. Rev. B: Condens Matter Mater. Phys.* **1999**, *60*, 14422; b) M. Segal, M.

A. Baldo, R. J. Holmes, S. R. Forrest, Z. G. Soos, *Phys. Rev.B:* Condens Matter Mater. Phys. 2003, 68, 075211.

- [3] a) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forres, *Nature* **1998**, *395*, 151; b) C. Adachi, M. A. Baldo, M. E. Thompson, S. R. Forrest, *J. Appl. Phys.* **2001**, *90*, 5048; c) H.-C. Su, H.-F. Chen, F.-C. Fang, C.-C. Liu, C.-C. Wu, K.-T. Wong, Y.-H. Liu, S.-M. Peng, *J. Am. Chem. Soc.* **2008**, *130*, 3413; d) S.-C. Lo, R. E. Harding, C. P. Shipley, S. G. Stevenson, P. L. Burn, I. D. W. Samuel, *J. Am. Chem. Soc.* **2009**, *131*, 16681; e) Y. Zhang, S. R. Forrest, *Phys. Rev. Lett.* **2012**, *108*, 267404.
- a) H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, Nature 2012, [4] 492, 234; b) Q. Zhang, B. Li, S. Huang, H. Nomura, H. Tanaka, C. Adachi, Nature Photon. 2014, 8, 326; c) F. B. Dias, K. N. Bourdakos, V. Jankus, K. C. Moss, K. T. Kamtekar, V. Bhalla, J. Santos, M. R. Bryce, and A. P. Monkman, Adv. Mater. 2013, 25, 3707; d) W.-L. Tsai, M.-H. Huang, W.-K. Lee, Y.-J. Hsu, K.-C. Pan, Y.-H. Huang, H.-C. Ting, M. Sarma, Y.-Y. Ho, H.-C. Hu, C.-C. Chen, M.-T. Lee, K.-T. Wong, C.-C. Wu, Chem. Commun. 2015, 51, 13662; e) M. Moral, L. Muccioli, W.-J. Son, Y. Olivier, J. C. Sancho-García, J. Chem. Theory Comput. 2015, 11, 168; f) T. Hatakeyama, K. Shiren, K. Nakajima, S. Nomura, S. Nakatsuka, K. Kinoshita, J. Ni, Y. Ono, T. Ikuta, Adv. Mater. 2016, 28, 2777; g) R. Gómez-Bombarelli, J. Aguilera-Iparraguirre, T. D. Hirzel, D. Duvenaud, D. Maclaurin, M. A. Blood-Forsythe, H. S. Chae, M. Einzinger, D.-G. Ha, T. Wu, G. Markopoulos, S. Jeon, H. Kang, H. Miyazaki, M. Numata, S. Kim, W. Huang, S. I. Hong, M. Baldo, R. P. Adams, A. Aspuru-Guzik. Nat. Mater. 2016, 15, 1120; h) L.-S. Cui, J. U. Kim, H. Nomura, H. Nakanotani, C. Adachi, Angew. Chem. Int. Ed. 2016, 55, 6864; Angew. Chem. 2016, 128, 6978; i) L.-S. Cui, H. Nomura, Y. Geng, J. U. Kim, H. Nakanotani, C. Adachi, Angew. Chem. Int. Ed. 2017, 56, 1571; Angew. Chem. 2017, 129, 1593. j) M. Y. Wong, E. Zysman-Colman, Adv. Mater. 2017, 29, 1605444.

 a) J. C. Fister III, D. Rank, J. M. Harris, *Anal. Chem.* **1995**, *67*, 4269; b)
 F. A. Salazar, A. Fedorov, M. N. Berberan-Santos, *Chem. Phys. Lett.* **1997**, *271*, 361; c) L. Bergmann, G. J. Hedley, T. Baumann, S. Bräse, I. D. Samuel, *Sci. Adv.* **2016**, *2*, e1500889.

- [6] a) Q. Zhang, Q. Zhou, Y. Cheng, L. Wang, D. Ma, X. Jing, F. Wang, *Adv. Mater.* 2014, *16*, 432; b) H. Kaji, H. Suzuki, T. Fukushima, K. Shizu, K. Suzuki, S. Kubo, T. Komino, H. Oiwa, F. Suzuki, A. Wakamiya, Y. Murata, C. Adachi, *Nat. Commun.* 2015, *6*, 8476; c) K. Suzuki, S. Kubo, K. Shizu, T. Fukushima, A. Wakamiya, Y. Murata, C. Adachi, H. Kaji, *Angew. Chem. Int. Ed.* 2015, *54*, 15231; *Angew. Chem.* 2015, *127*, 15446; d) D. R. Lee, M. Kim, S. K. Jeon, S. H. Hwang, C. W. Lee, J. Y. Lee, *Adv. Mater.* 2015, *27*, 5861; e) Y. J. Cho, S. K. Jeon, B. D. Chin, E. Yu, J. Y. Lee, *Angew. Chem. Int. Ed.* 2015, *54*, 5201; *Angew. Chem.* 2015, *127*, 5290. f) T.-A. Lin, T. Chatterjee, W.-L. Tsai, W.-K. Lee, M.-J. Wu, M. Jiao, K.-C. Pan, C.-L. Yi, C.-L. Chung, K.-T. Wong, C.-C. Wu, *Adv. Mater.* 2016, *28*, 6976.
- [7] K. Goushi, K. Yoshida, K. Sato, C. Adachi, *Nat. Photon.* 2012, *6*, 253.
 [8] a) Y. S. Park, S. Lee, K. H. Kim, S.Y. Kim, J. H. Lee, J. J. Kim, *Adv. Funct. Mater.* 2013, *23*, 4914; b) D. Chen, G. Xie, X. Cai, M. Liu, Y. Cao, S.-J. Su, *Adv. Mater.* 2016, *28*, 239; c) W. Liu, J.-X. Chen, C.-J. Zheng, K. Wang, D.-Y. Chen, F. Li, Y.-P. Dong, C.-S. Lee, X.-M. Ou, Chen, C. Suberger, Computer Science, Co
- X.-H. Zhang, *Adv. Funct. Mater.* 2016, *26*, 2002.
 a) C. A. van Walree, M. R. Roest, W. Schuddeboom, L. W. Jenneskens, J. W. Verhoeven, J. M. Warman, H. Kooijman, A. L. Spek, *J. Am. Chem. Soc.* 1996, *118*, 8395; b) Y. Gu, L. Zhu, Y. Li, L. Yu, K. Wu, T. Chen, M. Huang, F. Wang, S. Gong, D. Ma, J. Qin, C. Yang, *Chem. Eur.J.* 2015, *21*, 8250.
- [10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al., Gaussian 09, revision E.01, Gaussian, Inc., Wallingford, CT, 2009.
- [11] H. Wang, L. Xie, Q. Peng, L. Meng, Y. Wang, Y. Yi, P. Wang, Adv. Mater. 2014, 16, 5198.
- [12] P. I. Djurovich, E. I. Mayo, S. R. Forrest, M. E. Thompson, Org. Electron. 2009, 10, 515.

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- [13] S. Hirata, Y. Sakai, K. Masui, H. Tanaka, S. Y. Lee, H. Nomura, N. Nakamura, M. Yasumatsu, H. Nakanotani, Q. Zhang, K.Shizu, H. Miyazaki, C. Adachi, *Nat. Mater.* **2014**, *14*, 330.
- [14] a) M. Iwamura, S. Takeuchi, T. Tahara, *Acc. Chem. Res.* 2015, *48*, 782; b) M. Z. Shafikov, A. F. Suleymanova, R. Czerwieniec, H. Yersin, *Chem. Mater.* 2017, *29*, 1708.

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We explored a novel molecular design strategy for TADF emitters based on a donor- σ -acceptor motif. Two D- σ -A emitters displayed short TADF decayed lifetimes of less than 400 ns. Since the decrease of delayed lifetime in TADF emitters is highly beneficial fordevice performance, we believe this work provides an effective approach for advanced TADF materials.

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