

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

Title: Meta Junction Promoting Efficient Thermally Activated Delayed Fluorescence in Donor-Acceptor Conjugated Polymers

Authors: Junqiao Ding

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202006034

Link to VoR: https://doi.org/10.1002/anie.202006034

WILEY-VCH

WILEY-VCH

Meta Junction Promoting Efficient Thermally Activated Delayed Fluorescence in Donor-Acceptor Conjugated Polymers

Jiancheng Rao, Liuqing Yang, Xuefei Li, Lei Zhao, Shumeng Wang, * Junqiao Ding, * Lixiang Wang

Abstract: The meta junction is proposed to realize efficient thermally activated delayed fluorescence (TADF) in donor-acceptor (D-A) conjugated polymers. Based on triphenylamine as D and dicyanobenzene as A, as a proof of concept, a series of D-A conjugated polymers has been developed by changing their connection sites. When the junction between D and A is tuned from para to meta, the singlet-triplet energy splitting (ΔE_{ST}) is found to be significantly decreased from 0.44 to 0.10 eV because of the increasing hole-electron separation. Unlike the para-linked analogue with no TADF, consequently, the meta-linked polymer shows a strong delayed fluorescence. Its corresponding solution-processed organic light-emitting diodes (OLEDs) achieve a promising external quantum efficiency (EQE) of 15.4% (51.9 cd A⁻¹, 50.9 lm W⁻¹) and Commission Internationale de l'Eclairage (CIE) coordinates of (0.34, 0.57). The results first highlight the bright future of D-A conjugated polymers used for TADF OLEDs.

1. Introduction

Nowadays thermally activated delayed fluorescence (TADF) has been widely adopted in organic light-emitting diodes (OLEDs) to achieve a theoretical 100% internal quantum efficiency without using rare metals.^[1-4] Unlike the traditional fluorescence,^[5] the singlet-triplet energy splitting (ΔE_{ST}) is required to be negligible (< 0.3 eV) for TADF, so that triplets generated upon electrical excitation could be up-converted into singlets via a thermally-aided reverse intersystem crossing (RISC).^[6] From the molecular viewpoint, a donor-acceptor (D-A) geometry is proposed to meet such a demand,^[7] where the initial and final molecular orbitals of the lowest excitation tend to localize on the D and A units, respectively. Hence a small ΔE_{ST} is within our expectation due to the limited molecular orbital overlap.^[8,9] Also, the electronic coupling between the local triplet and the charge transfer states together with the effect of

J. Rao, L. Yang, X. Li, Dr. L. Zhao, Dr. S. Wang, Prof. J. Ding, Prof. [*] L. Wang State Key Laboratory of Polymer Physics and Chemistry Changchun Institute of Applied Chemistry Chinese Academy of Sciences, Changchun 130022, P. R. China E-mail: wangshumeng@ciac.ac.cn; junqiaod@ciac.ac.cn J Rao University of Chinese Academy of Sciences Beijing 100049, P. R. China L. Yang, X. Li, Prof. J. Ding, Prof. L. Wang University of Science and Technology of China Hefei 230026, P. R. China Prof. J. Ding School of Chemical Science and Technology, Yunnan University Kunming 650091, P. R. China Supporting information for this article is given via a link at the end of the document.

dynamic rocking of the D–A units about the orthogonal geometry plays a crucial role on the achievement of efficient TADF.^[10] On the basis of these criteria, a great number of TADF small molecules^[11-17] have been successfully reported to give various emission colors in the whole visible region as well as comparable electroluminescent device efficiencies to phosphors.^[18,19]

Starting from D and A, however, it remains a big challenge to design TADF polymers that are suitable for low-cost and easily-scalable wet methods (Figure 1). For example, the manipulation of ΔE_{ST} is assumed impossible in conjugated polymers because they often display the lowest triplet state (T_1) to be 0.7 \pm 0.1 eV below the lowest singlet state (S1). $^{[20]}$ Accordingly, few reports have focused on D-A conjugated polymers to realize TADF, where both D and A are incorporated into the main chain.^[21,22] To avoid this bottleneck, one approach is to fix D in the main chain and graft A in the side chain directly or via a spiro-linkage,^[23-27] the other is to tether D and A in the side chain simultaneously.^[28-31] Benefitting from the intentional separation between D and A in location, the developed Backbone-D/Pendant-A and through-space charge transfer (TSCT) polymers show a reduced molecular orbital overlap and thus a small ΔE_{ST} . As a consequence, high-performance delayed fluorescence is obtained, revealing a state-of-art external quantum efficiency (EQE) over 15%.[26,29] Despite the effectiveness, there still leaves a doubt whether D-A conjugated polymers have a real potential in the TADF generation. Additionally, D-A conjugated polymers possess some unique features beneficial for OLEDs, such as the favored charge transporting and ease tuning of the bandgap, because the existed guinoidal structure can increase the planarity of the polymeric backbone and enable π -delocalization along the polymeric chain.^[32,33] Therefore, much effort should be paid back to the development of TADF polymers based on the D-A conjugated backbone.

Herein, we demonstrate that meta junction can promote efficient TADF in D-A conjugated polymers. As a proof of concept (Figure 2), triphenylamine (TPA) and dicyanobenzene (DCB) are selected as the D and A, respectively. By changing their connection sites, four D-A conjugated polymers named poly(TPAp-DCBp), poly(TPAp-DCBm), poly(TPAm-DCBp) and poly(TPAm-DCBm) are constructed, where p and m denote para and meta junctions, respectively. Following this sequence, the energy of T_1 is found to ascend faster with the para-to-meta alteration than the energy of S_1 , in agreement with the decreased hole-electron overlap. Compared with the non-TADF poly(TPAp-DCBp) (0.44 eV), as a result, the ΔE_{ST} drops significantly to 0.10 eV of poly(TPAm-DCBm), endowing it with a strong delayed fluorescence. The corresponding solutionprocessed OLEDs achieve a promising EQE as high as 15.4% (51.9 cd A⁻¹, 50.9 lm W⁻¹) and Commission Internationalede l'Eclairage (CIE) coordinates of (0.34, 0.57). To the best of our knowledge, this is the first report on D-A type conjugated TADF

WILEY-VCH





Figure 2. Molecular structures, hole and electron analysis of the S_1 states for the D-A conjugated polymers. S_m is the overlap function between hole and electron distributions, quantified by a S_m index ranging from 0 (no overlap) to 1 (complete overlap).

polymers, whose performance can well compete with the Backbone-D/Pendant-A and TSCT polymers.

2. Results and Discussion

2.1 Theoretical computation

Initially, theoretical computation was carried out to study the effect of the junction between D and A in the designed four D-A

conjugated polymers poly(TPAp-DCBp), poly(TPAp-DCBm), poly(TPAm-DCBp) and poly(TPAm-DCBm). Firstly, their ground-state geometries are optimized at B3LYP/6-31G(d) level by Gaussian09 software package. Since they contain the same D and A units in the backbone, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels are taken to almost match with each other (Table S1). Subsequently, considering that ΔE_{ST} is sensitive to

fable 1	. Summary	of the	molecular	weight,	photophysical,	electrochemical	and thermal	properties
---------	-----------	--------	-----------	---------	----------------	-----------------	-------------	------------

Compound	M _n ^a	PDI ^b	λ_{abs}^{c}	λ_{PL}^{d}	$\tau_{\rm p}/\tau_{\rm d}^{\rm e}$	$\Phi^{ m f}$	$S_1/T_1/\Delta E_{ST}^{g}$	HOMO / LUMO ^h	T _d ⁱ	T _g ^j
	[KDa]		LIIIII	լասյ	[lis / µs]		[ev]	[EV]		Įυ
poly(TPAp-DCBp)	13.1	1.42	301, 354, 438 (514)	533 (71)	1.20 / n. d.	0.82 (0.90)	2.55 / 2.11 / 0.44	-5.14/-2.42	459	149
poly(TPAp-DCBm)	6.1	1.33	303, 344, 420 (496)	531 (77)	1.85 / 1.35	0.61 (0.85)	2.59 / 2.34 / 0.25	-5.17 / -2.49	453	152
poly(TPAm-DCBp)	4.1	1.29	301 (455)	524 (79)	8.10 / 1.90	0.25 (0.64)	2.63 / 2.42 / 0.21	-5.18 / -2.48	452	114
poly(TPAm-DCBm)	7.5	1.92	305 (448)	529 (88)	10.9 / 6.37	0.39 (0.80)	2.63 / 2.53 / 0.10	-5.15 / -2.51	449	123

^aNumber-averaged molecular weight; ^bPolydispersity index; ^cAbsorption peaks and onset values (in brackets) measured in neat films; ^dFluorescence peaks and FWHM values (in brackets) measured in neat films; ^ePrompt and delayed fluorescence lifetimes obtained in neat films under nitrogen atmosphere with an excitation wavelength of 375 nm; ¹Absolute PLQYs measured in neat films and in 5 wt.% doped mCP films (in brackets) under nitrogen atmosphere with an excitation wavelength of 400 nm; ^gS₁ and T₁ are estimated from the onsets of the film fluorescence and phosphorescence spectra, respectively, and $\Delta E_{ST} = S_1 - T_1$; ^hHOMO and LUMO levels are determined by cyclic voltammetry; ⁱDecomposition temperature corresponding to 5% weight loss; ⁱGlass transition temperature determined by the middle value between break points.

the exchange interactions on the overlap between hole and electron wave functions,^[20] the vertical excitation calculation is conducted by TD-DFT at the same level using the optimized molecular structures, followed by the hole and electron analysis $^{\left[34,35\right] }$ on S_{1} and T_{1} states. As one can see in Figure 2, both the hole and electron of S_1 are distributed along the polymeric chain, and a large electron-hole overlap (S_m index = 0.1609) is determined for poly(TPAp-DCBp). When the D-A junction is varied from para to meta, we note that the hole and electron distributions are becoming more and more discrete. With poly(TPAm-DCBm) as an example, the S_1 hole and S_1 electron are independently centered on TPA and DCB, respectively, leading to a decreased S_m index of 0.0321. Also, a similar trend is observed for the T₁ state (Figure S1). These observations imply that the meta junction plays an important role on the reduction of the hole-electron overlap in D-A conjugated polymers, which may further decrease the correlated ΔE_{ST} .

To verify this point, finally, the energies of S₁ and T₁ are calculated according to a semi-empirical descriptor-based optimal Hartree-Fock (OHF) method, the so-called *K*-OHF method.^[36] Because of the reduced hole-electron overlap, as mentioned above, the estimated ΔE_{ST} is found to be down from 0.3416 eV of poly(TPAp-DCBp) to 0.1638 eV of poly(TPAm-DCBm) (Table S2). Furthermore, a much lower oscillator strength *f* is predicted for poly(TPAm-DCBm) (0.0110) compared to poly(TPAp-DCBp) (1.3988). The prediction is consistent with the largely separated hole and electron distributions observed in poly(TPAm-DCBm), which is also an indicator of the charge transfer (CT) nature for S₁.

2.2 Synthesis and characterization

The synthetic route of the designed D-A conjugated polymers is depicted in Scheme S1. At first, 4-octylaniline was reacted with 1-bromo-4-iodobenzene and 1-bromo-3-

iodobenzene via a Buchwald-Hartwig C-N coupling^[37] to get 4bromo-N-(4-bromophenyl)-N-(4-octylphenyl)aniline (1) and 3bromo-N-(3-bromophenyl)-N-(4-octylphenyl)aniline (2), which were then converted to their corresponding borate monomers M1 and M2 by esterification, respectively. With the bromide monomers 2,5-dibromoterephthalonitrile and 2.6dibromoterephthalonitrile in hand, а typical Suzuki polymerization^[38,39] was then performed to afford four polymers with different D-A junctions, namely poly(TPAp-DCBp), poly(TPAp-DCBm), poly(TPAm-DCBp) and poly(TPAm-DCBm). The molecular structures of these polymers were characterized by gel permeation chromatography (GPC), ¹H and ¹³C NMR, and elementary analysis. The number-averaged weight (M_n) ranges from 4.1 kDa to 13.1 kDa with polydispersity index (PDI) from 1.29 to 1.92 (Table 1). Noticeably, the meta-involved polymers poly(TPAp-DCBm), poly(TPAm-DCBp) and poly(TPAm-DCBm) seem to have a smaller Mn than that of poly(TPAp-DCBp). The similar trend was also observed by A. D. Schlüter early in 2005, but without a definite explanation.^[40] At present, we could tentatively deduce that, compared with the para polymerization, the steric hinderance caused by the metainvolved polymerization may slow down the transmetalation,^[41] leading to deborylation and thus small Mn. Furthermore, they are readily soluble in common organic solvents, such as toluene, chlorobenzene and chloroform etc., ensuring their capability to form high quality films via solution processing. Also, all of them possess a decomposition temperature (T_d) around 450 °C and a glass transition temperature (T_{α}) ranging from 114 to 152 °C, indicative of the excellent thermal stability (Figure S2). And their HOMO (-5.14 ~ -5.18 eV) and LUMO levels (-2.42 ~ -2.51 eV), determined by cyclic voltammetry (CV), are found to be nearly independent on the D-A conjunction (Figure S3).

2.3 Photophysical properties



Figure 3a plots the UV-Vis absorption, fluorescence and phosphorescence spectra for neat films of poly(TPAp-DCBp), poly(TPAp-DCBm), poly(TPAm-DCBp) and poly(TPAm-DCBm). Compared with those of the components TPA and DCB (Figure S4), the absorption in the range of 350-500 nm can be reasonably ascribed to the π - π * transition of the conjugated polymeric backbone mixed with CT from TPA to DCB. As discussed above, the hole-electron separation is monotonically enhanced due to the meta junction, leading to a strengthened CT character. So the relative intensity of the longestwavelength absorption band declines following the sequence of poly(TPAp-DCBp) > poly(TPAp-DCBm) > poly(TPAm-DCBp) > poly(TPAm-DCBm) (Figure S5). And a concomitant hypsochromic shift is observed because the continuity of the backbone conjugation is broken by the meta junction. Ongoing from poly(TPAp-DCBp) to poly(TPAm-DCBm), the fluorescence spectra are blue-shifted correspondingly, accompanied by an increased S1 energy from 2.55 to 2.63 eV (Table 1). Moreover, the structureless spectral profile and broadened full width at half maximum (FWHM) from 71 to 88 nm further confirm the existence of CT in poly(TPAm-DCBm).



Figure 4. PL decay comparison between the neat films of the D-A conjugated polymers (a), and the temperaturedependent transient PL spectra of poly(TPAm-DCBm) (b).

In addition, the phosphorescence spectra are also measured at 77 K, and the energy of T₁ is estimated to be up from 2.11 eV of poly(TPAp-DCBp) to 2.53 eV of poly(TPAm-DCBm). According to the literatures, [42,43] the shortened longest poly(pphenyl) chain in the molecular structure is responsible for the elevated T₁ energy when the meta junction is adopted. Although the energies of S_1 and T_1 are both increased with the para-to-meta modification, it should be noted that the increment of T₁ (0.42 eV) is much larger than that of S₁ (0.08 eV) from to poly(TPAm-DCBm) poly(TPAp-DCBp) (Figure 3b). Consequently, a smaller ΔE_{ST} of 0.10 eV is measured for poly(TPAm-DCBm) with regard to poly(TPAp-DCBp) (0.44 eV). This is in well agreement with the theoretical predictions, proving that the meta junction can effectively reduce the ΔE_{ST} of D-A conjugated polymers induced by the enhanced holeelectron separation.

Table 2. Summary of device performance.

Davias	$V_{on}^{\ \ c}$	$L_{ m max}$ d	LE ^e [cd A ⁻¹]	PE $^{\rm f}$ [lm W ⁻¹]	EQE ^g [%]	$\lambda_{em}^{\ \ h}$	CIE ⁱ
Device	[V]	[cd m ⁻²]	Maximum value /	[nm]	(x, y)		
poly(TPAp-DCBp) ^a	4.0	11200	14.4 / 14.2 / 14.0 / 13.5	9.6 / 9.5 / 8.9 / 8.1	4.2 / 4.1 / 4.0 / 3.9	517	0.28, 0.61
poly(TPAm-DCBm) ^a	4.2	7200	29.6 / 28.2 / 20.9 / 17.1	19.4 / 17.4 / 11.9 / 9.3	8.8 / 8.6 / 6.3 / 5.2	533	0.34, 0.57
poly(TPAm-DCBm) ^b	3.2	6800	51.9 / 36.7 / 22.3 / 16.8	50.9 / 27.4 / 14.6 / 10.2	15.4 / 10.9 / 6.6 / 5.0	532	0.34, 0.57

^aDevice using PEDOT:PSS as the hole-injection layer; ^bDevice using PFI modified PEDOT:PSS as the hole-injection layer; ^cTurn-on voltage at 1 cd m⁻²; ^dMaximum luminance; ^eLuminous efficiency; ^fPower efficiency; ^gExternal quantum efficiency; ^hPeak wavelength at 1000 cd m⁻²; ^cCIE coordinates at 1000 cd m⁻².



Figure 5. Device performance comparison between poly(TPAp-DCBp) and poly(TPAm-DCBm): (a) EL spectra at 1000 cd m⁻²; (b) Current density-voltage-luminance characteristics; (c) EQE and luminous efficiency as a function of luminance; (d) Power efficiency as a function of luminance.

Given the obtained low ΔE_{ST} , poly(TPAm-DCBm) is expected to be able to generate efficient TADF. Therefore, the transient photoluminescent (PL) spectra are recorded in solid states under nitrogen atmosphere. As shown in Figure 4a, poly(TPAp-DCBp) exhibits only a prompt fluorescence without any delayed fluorescence, while both prompt and delayed fluorescence are observed for poly(TPAp-DCBm), poly(TPAm-DCBp) and poly(TPAm-DCBm) showing a delayed lifetime (t_d) of 1.35 µs, 1.90 µs and 6.37 µs, respectively. In accordance with the decreased ΔE_{ST} , the RISC rate constant (k_{RISC}) goes up from 2.83×10⁴ of poly(TPAp-DCBm) to 5.94×10⁴ of poly(TPAm-DCBp) and 1.01×10⁵ of poly(TPAm-DCBm) (Table S3). As a result of the more and more rapid RISC process, the

Scepted ManuScr



delayed fluorescence is found to be obviously enhanced. Among them, poly(TPAm-DCBm) displays the strongest delayed fluorescence, illustrating the superiority of the meta junction in D-A conjugated polymers. The TADF nature of poly(TPAm-DCBm) is further confirmed by the temperature-dependent transient PL decay.^[44] With the increasing temperature from 50 to 300 K, the delayed component is gradually increased in a scan time range of 0-25 µs (Figure 4b).

2.4 Electroluminescent properties

To evaluate the validity of poly(TPAm-DCBm) as the TADF polymer, solution-processed OLEDs are fabricated with the configuration of ITO/PEDOT:PSS (40 nm)/EML (50 nm)/TSPO1 (8 nm)/TmPyPB (42 nm)/LiF (1 nm)/Al (100 nm) (Figure S6). PEDOT:PSS (poly(3,4-ethylenedioxythiophene): Here, sulfonate)), TSPO1 (diphenyl-4poly(styrene triphenylsilylphenyl-phosphine oxide) and TmPyPB (1,3,5-tri[(3pyridyl)-phen-3-yl]benzene) serve as the hole-injection layer, exciton-blocking and electron-transporting layer layer, respectively. In order to suppress the aggregation caused quenching, poly(TPAm-DCBm) is doped into mCP (1,3bis(9Hcarbazol-9-yl)benzene) at a 5 wt.% concentration to constitute the emitting layer (EML), which has a higher PL quantum yield (PLQY) than that of the nondoped film (0.80 versus 0.39, Table 1). Also, the control device of poly(TPAp-DCBp) is prepared under the same conditions for comparison.

Similar to their PL counterparts, poly(TPAm-DCBm) displays a broader electroluminescence (EL) spectrum than poly(TPAp-DCBp) because of the strengthened CT character (Figure 5a). Although a hypsochromic EL onset is observed from poly(TPAp-DCBp) to poly(TPAm-DCBm), their corresponding CIE coordinates are red-shifted from (0.28, 0.61) to (0.34, 0.57) (Table 2). In addition, the current density and luminance of poly(TPAm-DCBm) are decreased compared with those of poly(TPAp-DCBp) at the same driving voltage (Figure

5b). The observed tendency may be from the torsional backbone and shortened conjugation length in the meta-linked poly(TPAm-DCBm), which is believed to be detrimental to intermolecular stacking and thus charge transporting. In spite of this, the maximum luminous efficiency, power efficiency and EQE are increased from 14.4 cd A⁻¹, 9.6 lm W⁻¹ and 4.2% of poly(TPAp-DCBp) to 29.6 cd A⁻¹, 19.4 lm W⁻¹ and 8.8% of poly(TPAm-DCBm) (Figure 5c and 5d). As discussed above, poly(TPAp-DCBp) is a non-TADF emitter, whereas poly(TPAm-DCBm) possesses a strong TADF due to a reduced ΔE_{ST} . Therefore, both singlet and triplet excitons can be harvested in poly(TPAm-DCBm) rather than poly(TPAp-DCBp), resulting in a nearly doubled device efficiency.

Frankly speaking, the superior device performance of poly(TPAm-DCBm) is achieved by partly sacrificing the charge transporting capability. To solve this problem, a preliminary try is performed by modifying the PEDOT:PSS layer with PFI (perfluorinated ionomer).^[45-47] After such an optimization, both the current density-voltage and luminance-voltage plots move backwards along the voltage axis (Figure S7). For example, the turn-on voltage is distinctively lowered from 4.2 to 3.2 V, and the luminance at a driving voltage of 5 V is elevated from 65 to 780 cd m⁻². Meanwhile, the peak EQE is optimized to 15.4% (51.9 cd A⁻¹, 50.9 lm W⁻¹) but with almost unchanged EL spectrum (Figure 6). To our knowledge, the obtained performance is comparable to those of Backbone-D/Pendant-A and TSCT polymers, [26,29] and even among the highest ever reported for TADF polymers.^[48-50] Even though the PFI modified PEDOT:PSS is used as the hole injection layer, we note that, the current density of poly(TPAm-DCBm) is not recovered completely yet in comparison to poly(TPAp-DCBp) (Figure S8). Additionally, an obvious efficiency roll-off does exist, and the EQE drops to 10.9% at 100 cd m^{-2} and 5.0% at 1000 cd m^{-2} (Table 2). This could be attributed to the charge imbalance originating from the enhanced hole injection and transporting as a result of the PFI modification and the unipolar feature of the mCP host. On the other hand, when assuming the ratio of the recombined carriers to the injected carriers (y), the fraction of radiative excitons (η_r) and the light out-coupling constant (η_{out}) to be 1, 1 and 25%, respectively,^[44] a high PLQY (η_{PL}) of 0.80 would correspond to an EQE limit of 20% according to the equation:

$$EQE = \gamma \cdot \eta_r \cdot \eta_{PL} \cdot \eta_{out}.$$

Therefore, a systematic investigation on device engineering (such as using a higher conductive hole injection layer combined with high-mobility electron-transporting layer, and replacing mCP with a bipolar or an exciplex-type host etc.) is further required to improve device efficiency and its roll-off, which is under way.

3. Conclusion

In summary, four D-A conjugated polymers named poly(TPAp-DCBp), poly(TPAp-DCBm), poly(TPAm-DCBp) and poly(TPAm-DCBm) have been designed and synthesized with TPA as D and DCB as A. Thanks to the para-to-meta tuning, the hole-electron overlap is found to be obviously reduced from

poly(TPAp-DCBp) to poly(TPAm-DCBm), and the corresponding ΔE_{ST} goes down from 0.44 eV to 0.10 eV. As a result, poly(TPAm-DCBm) with the meta junction exhibits a much stronger TADF than that of poly(TPAp-DCBp) with the para junction, and reveals a promising EQE over 15% in solution-processed devices. This work does demonstrate that D-A conjugated polymers can also achieve highly efficient delayed fluorescence, paving the way to their development and application in TADF OLEDs.

4. Experimental Section

In Supporting Information: Descriptions for measurement and characterization methods, theoretical computation, device fabrication and testing procedures, synthetic details with corresponding structural characterization data; Tables for theoretical computations rate constants following the threeenergy-level model; Figures for hole-electron distributions of T₁, TGA, DSC and CV profiles, PL spectra for the components TPA and DCB, comparison of UV-vis absorption spectra, device configuration with molecular structures of used materials and some device performances; MALDI-TOF, ¹H-NMR and ¹³C-NMR spectra for synthesized borate monomers; ¹H-NMR and ¹³C-NMR spectra for D-A conjugated polymers.

ORCID

Junqiao Ding: 0000-0001-7719-6599

Notes

The authors declare no competing financial interest.

Acknowledgements

The authors acknowledge the National Key Research and Development Program (2016YFB0401301) and the National Natural Science Foundation of China (51873205) for the financial support.

Keywords: OLEDs; D-A conjugated polymer; TADF; meta junction; hole-electron overlap

References:

- 1. C. Adachi, Jpn. J. Appl. Phys. 2014, 53, 060101.
- Y. Tao, K. Yuan, T. Chen, P. Xu, H. Li, R. Chen, C. Zheng, L. Zhang, W. Huang, *Adv. Mater.* 2014, *26*, 7931.
- Z. Yang, Z. Mao, Z. Xie, Y. Zhang, S. Liu, J. Zhao, J. Xu, Z. Chi, M. P. Aldred, *Chem. Soc. Rev.* 2017, 46, 915.

- Y. Liu, C. Li, Z. Ren, S. Yan, M. R. Bryce, *Nat. Rev. Mater.* 2018, 3, 18020.
- A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* 2009, *109*, 897.
- H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* **2012**, 492, 234.
- A. Endo, K. Sato, K. Yoshimura, T. Kai, A. Kawada, H. Miyazaki, C. Adachi, *Appl. Phys. Lett.* **2011**, *98*, 083302.
- 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.
- L. S. Cui, H. Nomura, Y. Geng, J. U. Kim, H. Nakanotani, C. Adachi, *Angew. Chem. Int. Ed.* 2017, *56*, 1571.
- F. B. Dias, J. Santos, D. R. Graves, P. Data, R. S. Nobuyasu, M. A. Fox, A. S. Batsanov, T. Palmeira, M. N. Berberan-Santos, M. R. Bryce, A. P. Monkman, *Adv. Sci.* **2016**, *3*, 1600080.
- 11. D. Y. Lee, M. Kim, S. K. Jeon, S.-H. Hwang, C. W. Lee, J. Y. Lee, *Adv. Mater.* **2015**, *27*, 5861.
- 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.
- 13. W. Li, B. Li, X. Cai, L. Gan, Z. Xu, W. Li, K. Liu, D. Chen, S.-J. Su, *Angew. Chem. Int. Ed.* **2019**, *58*, 11301.
- T.-L. Wu, M.-J. Huang, C.-C. Lin, P.-Y. Huang, T.-Y. Chou, R.-W. Chen-Cheng, H.-W. Lin, R.-S. Liu, C.-H. Cheng, *Nat. Photon.* 2018, *12*, 235.
- D. H. Ahn, S. W. Kim, H. Lee, I. J. Ko, D. Karthik, J. Y. Lee, J. H. Kwon, *Nat. Photon.* **2019**, *13*, 540.
- W. Zeng, H. Y. Lai, W. K. Lee, M. Jiao, Y. J. Shiu, C. Zhong, S. Gong, T. Zhou, G. Xie, M. Sarma, K. T. Wong, C. C. Wu, C. Yang, *Adv. Mater.* **2018**, *30*, 1704961.
- W.-C. Chen, B. Huang, S.-F. Ni, Y. Xiong, A. L. Rogach, Y. Wan, D. Shen, Y. Yuan, J.-X. Chen, M.-F. Lo, C. Cao, Z.-L. Zhu, Y. Wang, P. Wang, L.-S. Liao, C.-S. Lee, *Adv. Funct. Mater.* **2019**, *29*, 1903112.
- G. Zhou, W.-Y. Wong, X. Yang, Chem. Asian J. 2011, 6, 1706.
- 19. S. Shao, J. Ding, L. Wang, *Chin. Chem. Lett.* **2016**, *27*, 1201.
- 20. A. Köhler, D. Beljonne, Adv. Funct. Mater. 2004, 14, 11.
- 21. S. Y. Lee, T. Yasuda, H. Komiyama, J. Lee, C. Adachi, *Adv. Mater.* **2016**, *28*, 4019.
- 22. Y. Hu, W. Cai, L. Ying, D. Chen, X. Yang, X.-F. Jiang, S. Su, F. Huang, Y. Cao, *J. Mater. Chem. C* **2018**, *6*, 2690.
- Y. Zhu, Y. Zhang, B. Yao, Y. Wang, Z. Zhang, H. Zhan, B. Zhang, Z. Xie, Y. Wang, Y. Cheng, *Macromolecules* **2016**, 49, 4373.
- D. M. E. Freeman, A. J. Musser, A. K. Forster, K. J. Fallon, A. G. Rapidis, F. Cacialli, I. McCulloch, T. M. Clarke, R. H. Friend, H. Bronstein, *J. Am. Chem. Soc.* 2017, *139*, 11073.
- Q. Wei, P. Kleine, Y. Karpov, X. Qiu, H. Komber, K. Sahre, A. Kiriy, R. Lygaitis, S. Lenk, S. Reineke, B. Voit, *Adv. Funct. Mater.* 2017, *27*, 1605051.
- 26. Y. Yang, S. Wang, Y. Zhu, Y. Wang, H. Zhan, Y. Cheng, *Adv. Funct. Mater.* **2018**, *28*, 1706916.
- 27. B. Zhang, Y. Cheng, Chem. Rec. 2019, 19, 1624.
- S. Shao, J. Hu, X. Wang, L. Wang, X. Jing, F. Wang, J. Am. Chem. Soc. 2017, 139, 17739.

10.1002/anie.202006034

WILEY-VCH

- 29. J. Hu, Q. Li, X. Wang, S. Shao, L. Wang, X. Jing, F. Wang, *Angew. Chem. Int. Ed.* **2019**, *131*, 8493.
- 30. F. Chen, J. Hu, X. Wang, S. Shao, L. Wang, X. Jing, F. Wang, *Front. Chem.* **2019**, *7*, 854.
- S. Shao, J. Ding, L. Wang, Chin. J. Appl. Chem. 2018, 35, 993
- 32. L. Lu, T. Zheng, Q. Wu, A. M. Schneider, D. Zhao, L. Yu, *Chem. Rev.* 2015, *115*, 12666.
- 33. H. Zhou, L. Yang, W. You, Macromolecules 2012, 45, 607.
- 34. L. Lin, Z. Wang, J. Fan, C. Wang, *Org. Electron.* **2017**, *41*, 17.
- J. Yuan, Y. Yuan, X. Tian, Y. Liu, J. Sun, *J. Phys. Chem. C* 2017, *121*, 8091.
- C. Wang, C. Deng, D. Wang, Q. Zhang, J. Phys. Chem. C 2018, 122, 7816.
- P. Ruiz-Castillo, S. L. Buchwald, Chem. Rev. 2016, 116, 12564.
- K. Bai, S. Wang, L. Zhao, J. Ding, L. Wang, Macromolecules 2017, 50, 6945.
- Y. Yang, L. Zhao, S. Wang, J. Ding, L. Wang, *Acta Polym. Sin.* 2019, *50*, 685.
- R. M. Kandre, F. Kutzner, H. Schlaad, A. D. Schlüter, *Macromol. Chem. Phys.* 2005, 206, 1610.
- 41. R. J. Lundgren, M. Stradiotto, Chem. Eur. J. 2012, 18, 9758.
- K. Brunner, A. Dijken, H. Börner, J. J. A. M. Bastiaansen, N. M. M. Kiggen, B. M. W. Langeveld, *J. Am. Chem. Soc.* 2004, *126*, 6035.
- A. Dijken, J. J. A. M. Bastiaansen, N. M. M. Kiggen, B. M. W. Langeveld, C. Rothe, A. Monkman, I. Bach, P. Stössel, K. Brunner, *J. Am. Chem. Soc.* 2004, *126*, 7718.
- 44. A. Endo, M. Ogasawara, A. Takahashi, D. Yokoyama, Y. Kato, C. Adachi, *Adv. Mater.* **2009**, *21*, 4802.
- 45. T. W. Lee, Y. Chung, O. Kwon, J. J. Park, *Adv. Funct. Mater.* **2007**, *17*, 390.
- X. Liu, J. Rao, X. Li, S. Wang, J. Ding, L. Wang, *iScience* 2019, *15*, 147.
- J. Rao, X. Liu, X. Li, L. Yang, L. Zhao, S. Wang, J. Ding, L. Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 1320.
- 48. A. E. Nikolaenko, M. Cass, F. Bourcet, D. Mohamad, M. Roberts, *Adv. Mater.* **2015**, *27*, 7236.
- 49. Z. Ren, R. S. Nobuyasu, F. B. Dias, A. P. Monkman, S. Yan, M. R. Bryce, *Macromolecules* **2016**, *49*, 5452.
- 50. G. Xie, J. Luo, M. Huang, T. Chen, K. Wu, S. Gong, C. Yang, *Adv. Mater.* **2017**, *29*, 1604223.

WILEY-VCH

Efficient

Delayed

Entry for the Table of Contents (Please choose one layout)

Layout 2:

RESEARCH ARTICLE



Meta junction has been introduced to promote efficient TADF in D-A conjugated polymers for the first time. As a result of the enhanced hole-electron separation, the singlet-triplet energy splitting (ΔE_{ST}) is found to be significantly decreased from 0.44 eV to 0.10 eV with the para-to-meta modification. And a strong delayed fluorescence is achieved for the meta-linked polymer, revealing a peak EQE of 15.4% in solution-processed devices.