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Bridging small molecules to conjugated polymers: drive efficient thermally activated delayed fluorescence with a methylsubstituted phenylene linker

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Abstract: Thermally activated delayed fluorescence (TADF) polymers are of great interest due to their compatibility with the lowcost wet methods (spin-coating, inkjet printing etc.). However, they have received less attention compared with small molecules. Based on a "TADF + Linker" strategy, here we demonstrate the successful construction of conjugated polymers allowing highly efficient delayed fluorescence. In this case, a small molecular TADF block is simply bonded together to form the polymers by a methyl-substituted phenylene linker, such as phenylene, dimethyl phenylene, tetramethyl phenylene. With the growing number of methyl, the energy level of the local excited triplet state (³LE_b) from the delocalized polymer backbone is found to be gradually increased, and finally surpass the charge transfer triplet state (³CT). As a result, the diminished delayed fluorescence can be recovered again for the tetramethyl phenylene containing polymer, revealing a record-high external quantum efficiency (EQE) of 23.5% (68.8 cd/A, 60.0 lm/W) and Commission Internationale de l'Eclairage (CIE) coordinates of (0.25, 0.52). Combined with an orange-red TADF emitter, furthermore, a bright warm white electroluminescence is also obtained with a peak EQE of 20.9% (61.1 cd/A, 56.4 lm/W) and CIE coordinates of (0.36, 0.51). Those results clearly indicate that methyl-substituted phenylene is a promising linker to bridge existing TADF small molecules to novel conjugated TADF polymers.

1. Introduction

Thermally activated delayed fluorescence (TADF) emitters, following the conventional fluorescent¹⁻² and phosphorescent ones³⁻⁴, are now recognized as the third generation electroluminescent materials for organic light-emitting diodes (OLEDs)⁵⁻⁸. Thanks to the small energy difference (ΔE_{ST}) between the lowest singlet (S₁) and triplet (T₁) states, they can realize a theoretical 100% internal quantum efficiency (IQE) through a thermal assisted reverse intersystem crossing from T₁ to S₁. In 2012, Adachi C. prepared a group of carbazolyl dicyanobenzene derivatives⁹, and demonstrated that their delayed fluorescence efficiencies were comparable to those of

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Generally, several principles could be adopted for the design of TADF polymers (Figure 1). The first one is based on the combination of electron donor (D) and electron acceptor (A)¹⁶⁻²¹. That is, both D and A are carefully aligned in the different sites to form a TADF polymer, such as D and A simultaneously in the main chain¹⁶, D and A simultaneously in the side chain¹⁷⁻¹⁸, or D in the main chain and A in the side chain¹⁹⁻²¹ etc. Unlike small molecules, it is not an easy task to realize TADF at a macromolecular level because the relative distance, strength and location of D and A all need to be well controlled to tune through-bond or through-space charge transfer (CT). The second one is directly from a small molecular TADF unit, which is introduced into the main chain or side chain of a polymeric host²²⁻²⁵. Unfortunately, the intrinsic low triplet energy especially for conjugated polymers often leads to the loss of triplet excitons and thus poor device performance.

To address these problems, we have a great interest in another concept, where the small molecular TADF unit is bonded to each other via an appropriate linker. By making full use of the diversity and richness of the entire library of existing small molecular TADF emitters, in this case, the gap from small molecules to polymers is anticipated to be removed easily. So such a "TADF + Linker" strategy is believed to be simple and applicable to varied emissive colors. There have been two limited examples to create non-conjugated TADF polymers according to this route²⁶⁻²⁷. However, its potential in conjugated TADF polymers remains unexplored, although the conjugated backbone possesses more favorable charge transport as well as intense absorption and emission than the non-conjugated counterpart²⁸⁻²⁹.

With methyl-substituted phenylene as the linker, herein, we report the successful construction of conjugated polymers allowing highly efficient delayed fluorescence (Figure 2). It is found that the conjugated linkage inevitably brings about a new decreased local excited triplet state (${}^{3}LE_{b}$) caused by the delocalized polymer backbone, which plays an important role on the TADF character. When the number of methyl grows, interestingly, the energy of ${}^{3}LE_{b}$ is gradually climbing up to surpass the CT triplet state (${}^{3}CT$) so that the diminished delayed fluorescence from the small molecular TADF fragment can be recovered again. Consequently, the target polymer containing tetramethyl phenylene achieves the best device performance,

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Figure 2. Molecular structures and frontier orbital distributions of the conjugated TADF polymers and the model compound AcBPCz.

revealing a record-high external quantum efficiency (EQE) of 23.5% (68.8 cd/A, 60.0 lm/W) and Commission Internationale de l'Eclairage (CIE) coordinates of (0.25, 0.52). Moreover, combined with an orange-red TADF molecule, the resulting warm-white emission exhibits a peak EQE of 20.9% (61.1 cd/A, 56.4 lm/W) and CIE coordinates of (0.36, 0.51).

2. Results and Discussion

2.1 Molecular design

As a proof of concept, (4-(9,9-dioctylacridin-10(9H)-yl))(4-(9H-carbazol-9-yl))benzophenone (AcBPCz) is selected as the TADF fragment on the basis of benzophenone as A and carbazole or acridine as D. The highest occupied molecular orbital (HOMO) is mainly localized on acridine because of its stronger electron-donating ability relative to carbazole, whereas the lowest unoccupied molecular orbital (LUMO) is distributed on benzophenone. Thereby the acridine to benzophenone CT is responsible for the weak absorption band in the range of 400-450 nm and the maximum emission at 500 nm (Figure S1). In addition, the observed separation between HOMO and LUMO

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Scheme 1. Synthesis of AcBPCz and TADF polymers: (i). SOCl₂, CH₃OH, 60 °C; (ii). C₈H₁₇MgBr, THF, 0 °C \rightarrow rt \rightarrow 50 °C; CH₃COOH, HCl/H₂O, 80 °C; (iii). Pd₂(dba)₃, dppf, Cs₂CO₃, toluene, 100 °C; (iv). t-BuOK, DMF, 110 °C; (v). bis(pinacolato)diboron, Pd(dppf)Cl₂, KOAc, DMF, 100 °C; (vi). Pd₂(dba)₃, SPhos, Aliquat 336, K₂CO₃/H₂O, toluene, 95 °C.

leads to a theoretically small ΔE_{ST} of 0.19 eV³⁰, which is in well agreement with the experimental value (0.12 eV). This ensures the effective T_1 -to- S_1 reverse intersystem crossing, followed by an obvious delayed fluorescence. The photoluminescence (PL) transient decay of AcBPCz further verifies its TADF nature, exhibiting a prompt and delayed fluorescent lifetime of 29.5 ns and 2.96 us, respectively.

With AcBPCz in hand, subsequently, it is tied together by phenylene³¹⁻³², dimethyl phenylene and tetramethyl phenylene to afford three conjugated TADF polymers poly(AcBPCz-P), poly(AcBPCz-DMP) and poly(AcBPCz-TMP) (Figure 2). To begin with, their ground state geometries are optimized at B3LYP³³/6-31G(d)³⁴ level by Gaussian 09 software package³⁵. Noticeably, they display almost the same HOMO and LUMO distributions as AcBPCz. Although the extended conjugation from the carbazole side has resulted in the elevated HOMO level (Figure S2), the calculated value (ranging from -5.13 to -5.35 eV) is still lower than that of acridine (-5.04 eV). As a consequence, the CT transition still happens from acridine to

benzophenone for poly(AcBPCz-P), poly(AcBPCz-DMP) and poly(AcBPCz-TMP). In other words, these polymers are expected to give similar CT emission whatever different methyl-substituted phenylene linker is used.

2.2 Synthesis and characterization

The synthetic route of the conjugated TADF polymers is depicted in Scheme 1. Starting from 2-(phenylamino)benzoic acid, 2-(phenylamino)benzoic methylester (1) was prepared, which further reacted with octylmagnesium bromide, followed by an acid-catalyzed cyclization to get the key intermediate 9,9dioctyl-9,10-dihydroacridine (2). Then a successive Ullmann reaction, nucleophilic substitution, boron esterification were carried out to produce the borate monomer (M1). Combined with 1,4-dibromobenzene, 1,4-dibromo-2,5-dimethylbenzene or 1,4-dibromo-2,3,5,6-tetramethylbenzene as the bromide monomer, finally, poly(AcBPCz-P), poly(AcBPCz-DMP) and poly(AcBPCzsynthesized through a typical TMP) were Suzuki polycondensation^{1,25}. With a flexible polystyrene as the

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Compound	$\lambda_{abs}{}^{a}$ [nm]	$\lambda_{PL}^{b} [nm]$	$\tau_p^{\ c} [ns]$	$\tau_d^{\ c} \ [us]$	Φ^{d}	$S_1 / T_1 / \Delta E_{ST}^{e} [eV]$
AcBPCz	328, 341	500	29.5	2.96	0.66 (0.91)	2.76 / 2.64 / 0.12
poly(AcBPCz-P)	370	495	33.0	n. d.	0.22 (0.28)	2.76 / 2.27 / 0.49
poly(AcBPCz-DMP)	324	497	27.3	1.57	0.38 (0.70)	2.76 / 2.58 / 0.18
poly(AcBPCz-TMP)	304, 328, 341	498	27.2	4.44	0.68 (0.95)	2.76 / 2.64 / 0.12

 Table 1. Summary of photophysical properties.

^aAbsorption measured in toluene solution; ^bFluorescence measured in neat film; ^cPrompt and delayed lifetimes obtained in neat film under nitrogen atmosphere with an excitation wavelength of 375 nm; ^dAbsolute PLQY measured in neat film and in 15 wt.% doped mCP film (in brackets) under nitrogen atmosphere with an excitation wavelength of 400 nm; ^eS, and T₁ are estimated by onset of fluorescence and phosphorescence in neat film respectively and $\Delta E_{sT} = S_1 - T_1$.



Figure 3. Absorption in toluene solution (dashed lines) and fluorescence in neat film (solid lines) of AcBPCz and TADF polymers under ambient conditions. Inset: enlarged CT absorption band in the range of 400-450 nm.



Figure 4. PL transient decay curves of AcBPCz and TADF polymers in neat film under nitrogen atmosphere.



Figure 5. Energy-level diagram of AcBPCz and TADF polymers.

reference, an acceptable number-averaged molecular weight (M_n) ranging from 8.3 to 39.7 kDa is determined for these resultant stiff polymers (Table S1), associated with the good solubility in common organic solvents (dichloromethane, tetrahydrofuran, toluene, chlorobenzene etc.). Furthermore, they are thermally stable, showing a decomposition temperature around 370 °C (Figure S4).

2.3 Photophysical properties

Figure 3 plots the UV-Vis absorption in toluene and PL spectra in neat film of poly(AcBPCz-P), poly(AcBPCz-DMP) and poly(AcBPCz-TMP) compared with AcBPCz. On one hand, the major intense absorption band below 400 nm, correlated to the polymeric backbone (Figure S5), is gradually blue-shifted from poly(AcBPCz-P) to poly(AcBPCz-DMP) and poly(AcBPCz-TMP). On the other hand, a weak but discernible band in the 400-450 nm range is observed for these three polymers, which is also present in the absorption spectrum of AcBPCz. Meanwhile, they all emit a bright greenish-blue emission peaked at 495-498 nm together with an almost identical spectral profile. As mentioned above, the same CT transition from acridine to benzophenone in the polymer contributes to the observed similarity. Despite of this, they behave quite different in the PL transient decay (Figure 4). It is noteworthy that the delayed fluorescence is gradually enhanced following a sequence of poly(AcBPCz-P) < poly(AcBPCz-DMP) < poly(AcBPCz-TMP). At last, the decay profile of poly(AcBPCz-TMP) matches with that of AcBPCz, suggesting the fully

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	V _{on} ^c	$L_{ m max}$	LE [cd A ⁻¹]	PE [lm W-1]	EQE [%]	λ _{em}	CIE ^d
Device	[V]	[cd m ⁻²]	Maxim	um value / at 1000	[nm]	(x, y)	
poly(AcBPCz-P) ^a	4.2	5400	4.2 / 3.9	2.4 / 2.0	1.4 / 1.3	514	0.27, 0.52
poly(AcBPCz-DMP) ^a	4.4	9800	28.3 / 25.4	16.4 / 13.6	8.7 / 7.8	517	0.29, 0.55
poly(AcBPCz-TMP) ^a	3.8	12700	36.9 / 35.9	24.1 / 22.8	12.3 / 12.0	508	0.25, 0.54
poly(AcBPCz-TMP) ^b	3.2	13500	68.8 / 53.4	60.0 / 34.3	23.5 / 18.0	507	0.25, 0.52
poly(AcBPCz-TMP) : NAI-DMAC b	3.2	8500	61.1 / 22.4	56.4 / 13.7	20.9 / 7.7	510, 552	0.36, 0.51

Table 2. Summary of device performance.

^aDevices using PEDOT:PSS as the hole-injection layer; ^bDevices using PEDOT:PSS + PFI as the hole-injection layer; ^cTurn-on voltage at 1 cd/m²; ^dCIE coordinates at 1000 cd/m². L_{max}: maximum brightness; LE: luminous efficiency; PE: power efficiency.



Figure 6. Optimized device performance for poly(AcBPCz-TMP) with PEDOT:PSS + PFI as the hole-injection layer: EQE as the function of luminance and EL spectrum (Inset) for (a) the monochromic device and (b) the warm white device; (c) Lifetime characteristics at an initial luminance of 200 cd/m².

recovered TADF when four methyl groups are incorporated into the phenylene linker. And the film PL quantum yield (PLQY) is accordingly up from 0.22 of poly(AcBPCz-P) to 0.38 of poly(AcBPCz-DMP) and 0.68 of poly(AcBPCz-TMP) (Table 1). Compared with AcBPCz, moreover, a similar temperaturedependent transient PL behavior is observed for poly(AcDBCz-TMP) (Figure S6). As the temperature rises, the delayed component below 30 μ s is found to be gradually increased, indicative of the TADF nature^{16, 24}.

Considering their molecular structures, the slight difference among these linkers may have a significant impact on the varied TADF behavior. To demonstrate such a point, the phosphorescence spectra of the conjugated TADF polymers as well as each independent component are measured at 77 K (Figure S7) in order to establish the three-excited-state energy diagram. As one can see in Figure 5, the ³LE from either D or A lies above ³CT for the small molecular TADF block AcBPCz. Thus it possesses efficient TADF, consistent with the literature³⁷⁻³⁸. After AcBPCz is bonded by methyl-substituted phenylene to form the polymer, both the CT singlet state (¹CT) and ³CT remain nearly unchanged. By contrast, a reduced ³LE from the polymeric backbone (denoted as ³LE_b) newly appears due to the conjugated linkage. For example, in poly(AcBPCz-P) based on phenylene as the linker, the ³LE_b (2.27 eV) is much lower than ³CT (2.64 eV) and becomes a non-emissive quenching center, leading to the disappearance of TADF. Ongoing from poly(AcBPCz-P) to poly(AcBPCz-DMP) and poly(AcBPCz-TMP), the energy level of ³LE_b is elevated from 2.27 eV to 2.58 eV and 2.74 eV. This is further confirmed by the theoretical simulation³⁹ (Figure S3). With the growing methyl number, the torsion angle between carbazole and methylsubstituted phenylene is increased from 37.5° to 55.8° and 84.9°. So the conjugation along the whole main chain can be tuned via methyl substitution to achieve the improved triplet energy. As a result of the higher ³LE_b (2.74 eV) relative to ³CT (2.64 eV), the delayed fluorescence is found to be fully recovered in poly(AcBPCz-TMP) with tetramethyl phenylene as the linker.

2.4 Electroluminescence properties

To evaluate the electroluminescent (EL) properties, solution-processed devices are assembled with a configuration of ITO/PEDOT:PSS (40 nm)/EML (50 nm)/TSPO1 (8

nm)/TmPyPB (42 nm)/LiF (1 nm)/Al (100 nm) (Figure S8). Here TSPO1 (diphenyl-4-triphenylsilylphenyl-phosphine oxide) and TmPyPB (1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene) are employed as the exciton-blocking and electron-transporting layers, respectively. The emitting layer (EML) is composed of the conjugated TADF polymer dispersed into mCP (1,3-bis(9Hcarbazol-9-yl)benzene), because there exists aggregation induced quenching to some degree (Figure S9). And the doping concentration is adjusted to be 15 wt.% with poly(AcBPCz-TMP) as an example (Figure S10 and Table S2). Then we compare the device performance among poly(AcBPCz-P), poly(AcBPCz-DMP) and poly(AcBPCz-TMP) at such an optimized doping concentration (Figure S11 and Table 2). Although they exhibit EL spectra almost identical to each other, the peak EQE is monotonically increased from 1.4% to 8.7% to 12.3%. The trend is in well agreement with their transient PL behaviors, implying that the delayed component mainly affects the device efficiency.

EQE can be described by the following equation:

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

where γ is the ratio of the recombined carriers to the injected carriers; η_r is the fraction of radiative excitons, and is supposed to be 1 for TADF emitters when neglecting non-radiative pathways; η_{PL} is the PLQY; η_{out} is the light out-coupling constant and is often assumed to be 25%⁴⁰. Given the high PLQY of 0.95 for mCP : 15 wt.% poly(AcBPCz-TMP) (Table 1), the γ in the present device is estimated to be 0.52, indicative of the charge imbalance. And the upper limit of EQE should be 23.8% by setting γ as 1. So there is still enough space for the efficiency improvement.

With this idea in mind, the PEDOT:PSS layer is mixed with perfluorinated ionomer (PFI) to favor the hole injection⁴¹. Similar to its PL counterpart, a bright greenish-blue EL is achieved for poly(AcBPCz-TMP) together with CIE coordinates of (0.25, 0.52) (Figure 6a). It should be noted that the turn-on voltage at 1 cd/m² is distinctly reduced from 3.8 V to 3.2 V after device optimization (Figure S12 and Table 2). the Correspondingly, the maximum luminous efficiency, power efficiency and EQE are improved from 36.9 cd/A, 24.1 lm/W and 12.3% to 68.8 cd/A, 60.0 lm/W and 23.5%, respectively. The obtained EQE approaches to the theoretical limit of 23.8% now, which suggests that the PFI modification is beneficial for balanced charge injection and transporting. Moreover, it still remains as high as 18.0% even at a high luminance of 1000 cd/m², indicative of the small efficiency roll-off. Taking advantage of the efficient greenish-blue emission of poly(AcBPCz-TMP), an orange-red TADF emitter NAI-DMAC⁹ is further doped into the EML. A warm white EL is realized (Figure 6b and Figure S13), giving a record-high EQE of 20.9% (61.1 cd/A, 56.4 lm/W) as well as CIE coordinates of (0.36, 0.51). To the best of our knowledge, both the monochromic and warm white device efficiencies are the highest ever reported for TADF polymers (Figure S14 and Table S3). Those results clearly indicate that the methyl-substituted phenylene is a promising linker to construct high-performance conjugated TADF polymers based on the "TADF + Linker" strategy.

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Besides efficiency, the device stability is investigated preliminarily (Figure 6c). As can be seen, the T₅₀ lifetime at an initial luminance of 200 cd/m² is determined to be 3.8 min and 32 min for the monochromic devices of AcBPCz and poly(AcBPCz-TMP), respectively. Compared with AcBPCz, the lifetime of poly(AcBPCz-TMP) is increased by about one order of magnitude, clearly illustrating the superiority of polymer to small molecule in solution-processed devices. Also, the warm white device displays a lifetime of 27 min. To be honest, the reported values are still far away from those of vacuumdeposited small molecular TADF emitters⁴²⁻⁴⁴. However, the stability improvement can be expected through material screening and device engineering, such as using a host with high glass transition temperature to replace mCP and inserting an additional hole-transporting layer between PEDOT:PSS and EML etc.

3. Conclusion

In summary, a series of conjugated TADF polymers named poly(AcBPCz-P), poly(AcBPCz-DMP) and poly(AcBPCz-TMP) have been designed and synthesized with AcBPCz as the small molecular TADF block and phenylene, dimethyl phenylene or tetramethyl phenylene as the linker, respectively. Owing to the conjugated linkage, a reduced ³LE_b from the delocalized polymer backbone newly appears, so that no obvious delayed fluorescence is observed in poly(AcBPCz-P). Nevertheless, the energy level of ³LE_b could be enhanced to surpass that of ³CT with the increasing methyl number. As a consequence, the diminished TADF is recovered again for poly(AcBPCz-TMP), whose corresponding monochromic and warm white devices both achieve a state-of-art EQE over 20%. This work, we believe, will shed light on the development of high-performance conjugated TADF polymers based on the "TADF + Linker" strategy.

4. Experimental Section

In Supporting Information: General methods including theoretical computation, measurement and characterization, device fabrication and testing; Synthetic details with corresponding structural characterization data for all compounds; TADF properties of AcBPCz; Computational results of geometry optimization, frontier orbital distribution and vertical excitation analysis; Extra tables and figures of physical properties and EL devices; Comparisons of device performances with currently reported OLEDs based on TADF polymers; ¹H-NMR and ¹³C-NMR spectra of AcBPCz, monomers and polymers.

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Keywords: TADF, conjugated polymer, methyl-substituted phenylene, local excited triplet state, charge transfer triplet state

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RESEARCH ARTICLE

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Layout 2:

RESEARCH ARTICLE



A "TADF + Linker" strategy has been proposed for the successful construction of conjugated polymers allowing efficient delayed fluorescence. With the increasing methyl number in the methyl-substituted phenylene linker, the energy of the local excited triplet state (³LE_b) from the delocalized polymer backbone can be well tuned to surpass that of the charge transfer triplet state (³CT). Consequently, the diminished TADF is recovered again, leading to a record-high EQE of 23.5% and 20.9% for the monochromic and warm white devices, respectively.

J. Rao, X. Liu, X. Li, L. Yang, L. Zhao, S. Wang*, J. Ding* and L. Wang

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Bridging small molecules to conjugated polymers: drive efficient thermally activated delayed fluorescence with a methylsubstituted phenylene linker