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Acridan Grafted Poly(biphenyl germanium) with High Triplet Energy, Low Polarizability and External Heavy-Atom Effect for Highly Efficient Sky-Blue TADF Electroluminescence

*Miao-Ken Hung, Kuen-Wei Tsai, Sunil Sharma, Jun-Yi Wu, and Show-An Chen**

Abstract: We propose the novel σ-π conjugated polymer, poly(biphenyl germanium) grafted with two electron-donating acridan moieties on the germanium (Ge) atom for use as the host material in polymer light-emitting diode (PLED) with sky-blue emitting thermally activated delayed fluorescence (TADF) material, DMAC-TRZ as the guest. It gives the high triplet energy (E_T) 2.86 eV, which is significantly higher than those of conventional π-π conjugated polymers (E_T= 2.65 eV as the limit) and this guest emitter (E_T= 2.77 eV). The TADF emitter emits bluer emission than other host materials due to the low orientation polarizability of this Ge-based polymer host. Additionally, the Ge atom provides an external heavy-atom effect leading to the promoted rate of reversed intersystem crossing (RISC) in this TADF guest, and thus harvesting more triplet excitons for light emission. The sky-blue TADF electroluminescence using this host/guest pair gives the record-high external quantum efficiency (EQE) 24.1% at maximum and 22.8% at 500 cd/m^2. Thus, the present study opens up a new promising design route of polymer host for various TADF guests for highly efficient TADF PLED.

Organic light-emitting diodes (OLEDs) using TADF emitters have emerged as a next-generation electroluminescence for illumination and display applications.[1] An effective TADF emitter can harvest both singlet and triplet excitons to potentially achieve 100% internal quantum efficiency by converting triplets to singlets via RISC due to the small difference of singlet and triplet energy levels (ΔE_{ST}) below 0.1 eV.[1a] Similar to phosphors, the triplet exciton lifetimes of TADF emitters are usually several microseconds, which is prone to result in triplet-triplet annihilation (TTA) for neat TADF emitter (i.e. without host) in the emitting layer (EML).[2] Thus, the EML with host-guest strategy is usually employed with TADF material as guest dispersed uniformly in the host matrix for suppressing TTA.[3] To date, the state-of-the-art TADF OLEDs with EQEs over 30% were reported using the host-guest strategy in the EML.[4] Like phosphorescence OLEDs, an efficient host for TADF guest requires higher E_T level than the guest to suppress the non-radiative process,[5] reasonable charge balance to reduce efficiency roll-off,[6] and well-matched HOMO/LUMO levels to guest to reduce charge injection barrier.[3] Besides, the host with low polarizability and heavy-atom is also crucial to enhance emission color purity[7] and spin-orbit coupling interaction in the TADF guest[8], respectively, and the latter can promote the RISC rate and compensate the increased intersystem crossing (ISC) rate that efficiently harvests triplet excitons for light emission.[8b, 9]

TADF OLEDs are generally fabricated by the expensive vacuum deposition process (dry process). For low-cost and large area fabrication, it is desirable to use solution-process to fabricate the devices. Since film quality of solution-processed film of small molecular materials is poor in general, polymeric TADF materials including intrinsic TADF-polymers and conjugated polymer with small molecular TADF materials (host-guest system) must be used for forming high quality film of the EML. For the TADF-polymers (denotes as intrinsic TADF-polymers),[1d, 10] the reported studies can be classified into conjugated and non-conjugated types based on their different main-chain structures. From the viewpoint of charge balance, conjugated TADF-polymers with good charge-transport properties are much more desirable than non-conjugated TADF-polymers whose devices usually give low brightness (below 2000 cd/m^2) and high efficiency roll-off.[11] To date, the reported EQEs of conjugated TADF-polymer electroluminescence devices can achieve 18.1% and 19.4% for green and orange emissions,[12] respectively. However, the blue conjugated TADF-polymer device with CIE coordinate of $y < 0.4$ giving EQE only 6.1% as the reported record value which is far inferior in performance to the other emission colors due to the limitation of triplet energy (E_T) level of its backbone structure (below 2.65 eV).[13] Therefore, a development of blue conjugated TADF-polymer emitter is highly constrained. For the host-guest system with conjugated polymer as host and small molecular TADF materials as guest, up to the present, there is no report employing this strategy to fabricate TADF PLEDs (denotes as the EML using the blend of polymer host/ TADF guest).

Here, we report the host-guest TADF PLED for the first time by developing the σ-π conjugated polymer host P(DMAC-Ge) (Figure 1a) with Ge-biphenyl polymer as backbone and two electron-donating acridan groups (DMAC) grafting on the Ge central atom as the side arms for charge transport. It gives the high E_T (2.86 eV) and well-matched energy levels to the adopted highly efficient sky-blue TADF emitter DMAC-TRZ (E_T=2.77 eV)[14] here. Moreover, the polymer host P(DMAC-Ge) with symmetric arrangement in polar transport moieties leading to bluer emission from the guest, and the Ge atom on the host can generate external heavy-atom effect. To the TADF guest for enhancing spin-orbit coupling and promote the rate of RISC, which can efficiently harvest triplet excitons for light emission. As using P(DMAC-Ge) as host and DMAC-TRZ as guest, this TADF PLED shows an EQE of 17.6% with sky-blue emission at the CIE coordinates (0.16, 0.31). Upon further adopting the cohost strategy in the EML, the sky-blue device gives new record EQE$_{max}$ over 24%.

To meet the requirements of high E_T, reasonable charge mobility and heavy-atom effect for the host design, the σ-π conjugated polymer is a candidate structure,[15] in which the repeat unit can be composed of a biphenyl unit linking with a heavy Group IV atom such as Ge.[16] In our previous work,[15] the silicon-based σ-π conjugated polymer has been realized having semiconducting characteristic with charge mobility at the level of 10^{-5} and 10^{-7} cm^2/Vs for hole and electron, respectively, its E_T (2.67 eV) though higher than π-π conjugated polymers, however, is still insufficient to develop the polymer host for the common

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blue TADF emitters. To design a new σ-π conjugated polymer with higher E_T, we need to promote the E_T of the backbone structure due to the existence of multiple-triplet states.[15] Since Ge atom has larger atomic radius (125 pm) than the original Si central atom (110 pm),[17] a replacement of Si by Ge in the backbone may reduce the extent of π-electron delocalization along the backbone and therefore to promote its E_T energy. For clarifying if such strategy of varying the size of central atom can lead to a promotion of the E_T level of σ-π conjugated polymer backbone, we prepare the analogues of σ-π conjugated polymer backbone structures P(dBu-Si) and P(dBu-Ge) (Figure 1a). As expected, P(dBu-Ge) obviously has higher E_T of 2.85 eV than P(dBu-Si) with 2.78 eV (Table S1), and both are much higher than the π-π conjugated polymer with 2.65 eV as the limit.[18]

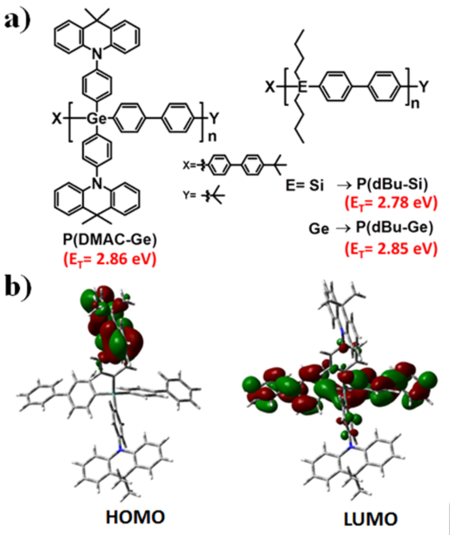

Figure 1. a) Molecular structures of the σ-π conjugated polymers P(DMAC-Ge), P(dBu-Si) and P(dBu-Ge), and their E_T values are show in the brackets. b) DFT calculation of HOMO/LUMO distributions for the repeat unit of P(DMAC-Ge) using the Gaussian 09 package at the B3LYP/6-13G(d) level.

Based on the above results, P(dBu-Ge) is further modified by replacing two butyl side arms with the two electron-donating moieties 9,9-dimethyl acridan (DMAC) to give P(DMAC-Ge). For demonstrating the significance of the σ-π conjugated backbone in charge transport, the control polymer P(V-DMAC) containing non-conjugated backbone was also synthesized (Figure 2d). The detailed synthesis procedures for all polymers in Figure 1a and P(V-DMAC) are given in the Supporting Information. The ultraviolet-visible (UV-vis) absorption, photoluminescence (PL) and phosphorescence spectra of these polymers are shown in Figures S1 and S2, and their corresponding physical property data are listed in Table S1. The phosphorescence spectra measured at 77K show that P(DMAC-Ge) has E_T of 2.86 eV (Figure S2c), which is significantly higher than the TADF emitter 9,9-Dimethyl-9,10-dihydroacridine (DMAC-TRZ, 2.77eV) used as guest here. The HOMO/ LUMO levels of the polymer host P(DMAC-Ge) measured by cyclic voltammetry (Figure S3) are -5.43/-2.27 eV, respectively. Besides, the density functional theory (DFT) calculation shows the major LUMO distribution on the Ge-biphenyl backbone (Figure 1b), indicating that the σ-π conjugated characteristics on Ge-biphenyl units have stronger electron-deficient nature than DMAC group, which may provide an additional channel for electron transport. For the TADF guest, we choose the sky-blue TADF DMAC-TRZ because it has a rather high PLQY of 90% that could facilitate high device efficiency[14] and has the well-matched HOMO/LUMO of -5.38/-3.10 eV (Table S1) to those of P(DMAC-Ge).

For the PL measurements of the host-guest system (Figure **2**a), we find that the P(DMAC-Ge) film doped with 8wt% DMAC-TRZ exhibits the maximum PL emission ($\lambda_{PL, max}$) at 480 nm and the relatively narrow full-width at half-maximum (FWHM) of PL with 77.8 nm, which show the obvious blue-shift of $\lambda_{PL, max}$ and the narrower FWHM relative to the same emitter in the other hosts: in P(V-DMAC) film ($\lambda_{PL, max}$= 488 nm, FWHM= 84.0 nm) and in the common host materials, PVK film ($\lambda_{PL, max}$= 493 nm, FWHM= 91.3 nm) and TAPC film ($\lambda_{PL, max}$= 502 nm, FWHM= 91.4 nm). While the doped P(dBu-Ge) films ($\lambda_{PL, max}$= 473 nm, FWHM= 76.2 nm) shows more blue-shift of $\lambda_{PL, max}$ and narrower FWHM as compared to the doped P(DMAC-Ge) film. All the PL emission colors of the doped films in the CIE 1931 color space are shown in Figure 2b. As can be seen, the doped P(DMAC-Ge) and P(V-DMAC) films are located in the sky-blue region ($CIE_y < 0.4$),[19] while the doped PVK and TAPC films shift to the green region ($CIE_y \geqq 0.4$).[20] Evidently, these differences in PL spectra arise from the difference in the emitter's environments. For instance, P(DMAC-Ge) gives the blue-shift of $\lambda_{PL, max}$ by 8 nm compared to P(V-DMAC) with non-conjugated vinyl backbone, indicating the molecular configuration of host is a crucial factor to affect PL emission; while P(V-DMAC) with acridan group gives the blue-shift of $\lambda_{PL, max}$ by 5 and 13 nm as compared to PVK and TAPC that contain carbazole and triphenylamine groups, and the P(dBu-Ge) gives 7 nm blue-shift of $\lambda_{PL, max}$ than P(DMAC-Ge), both are suggesting the influences of various functional groups. These results reveal that the PL emissions of DMAC-TRZ are largely affected by the natural properties of hosts, which inspire us to consider the possibility if the PL emission of DMAC-TRZ affected by the polarizability of host.

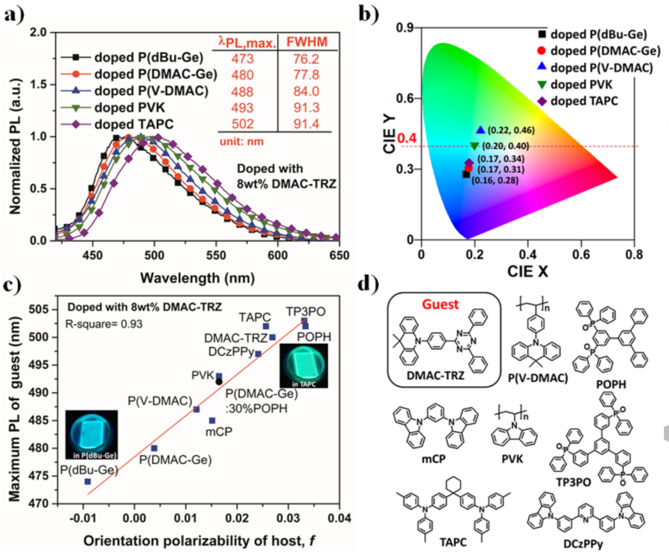

Figure 2. a) PL spectra of 8wt% DMAC-TRZ doped in the various host films, where the $\lambda_{PL, max}$ and FWHM are maximum PL emission and narrow full-width at half-maximum of PL, respectively and b) the CIE coordinates for their PL emissions. c) Plot for the maximum PL of 8wt% DMAC-TRZ doped in various host films versus the orientation polarizability of host (Inset: the photographs of the doped P(dBu-Ge) film (left) and the doped TAPC film (right) under photoexcitation by UV-lamp), and d) the structures of the molecular materials used in this measurement.

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It has been reported that the PL emission of TADF can be affected by the environmental polarity, so-called as solid-state solvation.[7a, 21] However, no investigation on the relationship between TADF emission and host configuration is given. To explore the host-guest interaction in solid state on the photophysical properties of the guest, the measurements for the $\lambda_{PL,\ max}$ of 8wt% DMAC-TRZ doped host materials with various orientation polarizabilities (*f*) are carried out for the first time (Figure 2c). The orientation polarizability of the host material is calculated from the equation $f(\varepsilon_r,n)=[(\varepsilon_r-1)/(2\varepsilon_r+1)]-[(n^2-1)/(2n^2+1)]$, where ε_r and n are the relative permittivity and refractive index, respectively.[22] The measured $\lambda_{PL,\ max}$ and *f* values are given in Table S2. The magnitude of *f* value decides the ability to form instantaneous dipoles of the host in the presence of applied electric field,[7b] and the structures of the host molecules we used in this measurement are shown in Figure 2d. The $\lambda_{PL,\ max}$ shift of DMAC-TRZ is then plotted versus *f* as shown in Figure 2c and showing that a linear relationship is found, the emission $\lambda_{PL,\ max}$ increases from 473 to 503 nm with increasing the *f* values of host in the range from -9.12×10^{-3} to 33.4×10^{-3}, and reflecting that the PL emission shift of DMAC-TRZ is highly correlating to the polarizability of the host. The *f* value of P(DMAC-Ge) (3.9×10^{-3}) giving about one-third smaller than that of P(V-DMAC) (1.2×10^{-2}) can be attributed to more symmetric arrangement for the former than the latter, which are supported by the lower dipole moment (μ) of the repeat unit of P(DMAC-Ge) with μ= 2.21 D than the repeat unit of P(V-DMAC) with μ= 2.58 D (Figure S5). For the influence of functional group on host, P(V-DMAC), mCP, PVK and TAPC containing electron-donating groups show increased *f* values with the sequence of acridan (1.2×10^{-2}) < carbazole (1.5-1.6×10^{-2}) < triphenylamine (2.6×10^{-2}). In contrast, the molecules DCzPPy, DMAC-TRZ, TP3PO and POPH containing electron-withdrawing groups such as pyridine, triazine and diphenylphosphine oxide generally give high *f* values (2.4×10^{-2}~3.3×10^{-2}). Consequently, P(DMAC-Ge) is an ideal host for DMAC-TRZ because the Ge-based polymer backbone give it much low molecular polarizability to make its PL emission color purer and bluer.

On the other hand, Figure 2c also suggests that the extent of intramolecular charge transfer (ICT) between DMAC (electron donor) and TRZ (electron acceptor) on DMAC-TRZ that varying its emission color not only occurs in solution state but also exists in the solid state, in which the slight emission color modulation can be achieved by controlling the polarizability of host material. Besides, the same linear trends for the other TADF emitters consisting of fixed 8wt% doping to the hosts with different orientation polarizabilities were also observed (Figure S6a), indicating that the effect of host orientation polarizability could be also applicable to the emission color adjustment for other TADF emitters.

Concerning the external heavy-atom effect on TADF guest, we believe that the Ge atom with high atomic number in P(DMAC-Ge) should exist heavy-atom effect, which can enhance the spin-orbit coupling (H_{SO}) and then promote the RISC rate in the TADF guest that converts more triplet excitons to singlet excitons for generating more delayed fluorescence.[8b, 23] To confirm if the heavy-atom Ge on P(DMAC-Ge) has an opportunity to provide the H_{SO} to the guest DMAC-TRZ molecule, the accommodation of the guest into the vicinity of the host is presented in a 3D plot as shown in Figure 3a. The open space in the repeat unit analogue of P(DMAC-Ge) shows sufficiently large to allow the guest DMAC-TRZ molecule to approach the Ge central atom, and the closest distance between the center of the guest molecule and the central atom Ge is 5.4 Å, which is close to the reported effective distance of external heavy-atom effect 5.6~7.4 Å.[24] Based on this simulation result, we infer that the external heavy atom effect on DMAC-TRZ should occur by using P(DMAC-Ge) as the host.

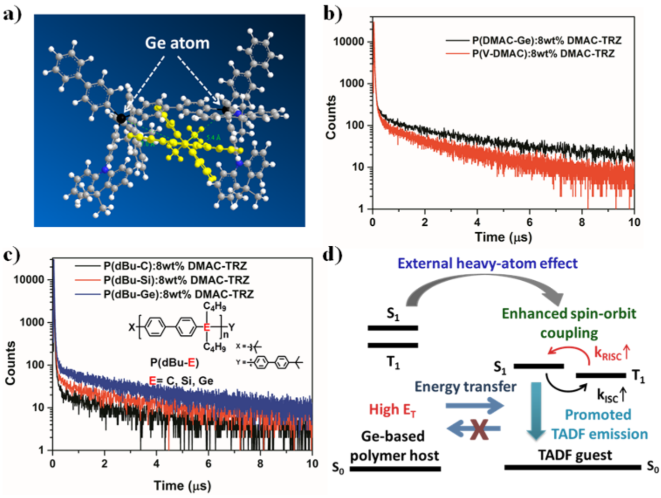

Figure 3. a) Molecular modeling study for the repeat unit analogue of P(DMAC-Ge) doped with DMAC-TRZ (expressed in yellow color). The schematic 3D chemical structures were under minimized energy by use of Chem3D (version 15.1). PL decays of b) P(DMAC-Ge) and P(V-DMAC) films, and c) P(dBu-E), E= C, Si and Ge films doped with 8wt% DMAC-TRZ under excitation by a *fs* pulse laser (350nm) at room temperature, and the emissions were monitored at their maximum PL values. d) Schematic single-triplet interaction between Ge-based polymer host and TADF guest.

Table 1. Photophysical data and rate constants of the host doped with 8wt% DMAC-TRZ films.

EML	PLQY [%]	Φ_p^{a} [%]	Φ_d^{b} [%]	τ_p [ns]	τ_d [μs]	% of τ_d^{c} [%]	k_{ISC}^{d} [$10^7 s^{-1}$]	k_{RISC}^{e} [$10^6 s^{-1}$]	$\chi^{2\ g}$
P(DMAC-Ge): DMAC-TRZ	91	16.0	75.0	36.4	2.16	82.5	2.27	2.64	1.42
P(V-DMAC) : DMAC-TRZ	89	21.9	67.1	42.9	1.81	75.4	1.76	2.25	1.52
P(dBu-C): DMAC-TRZ	81	23.4	57.6	36.2	2.03	71.1	1.96	1.70	1.26
P(dBu-Si): DMAC-TRZ	83	18.6	64.4	31.3	2.16	77.6	2.48	2.07	1.30
P(dBu-Ge): DMAC-TRZ	92	14.2	77.8	31.1	2.38	84.6	2.72	2.73	1.23

[a] PLQY for the prompt fluorescent (Φ_p) component calculated from ϕ_p=PLQY×(% of τ_p). [b] PLQY for the delayed fluorescent (Φ_d) component calculated from Φ_d=PLQY×(% of τ_d). [c] % of τ_d= A2/(A1+A2)×100. [d&e] The rate constants of intersystem crossing (k_{ISC}) and reverse intersystem crossing (k_{RISC}), and their detailed calculation methods are demonstrated in Supporting Information.[f] Chi-spaure value for exponentially fitting of the decay curve.

Thus, the followed up transient PL measurement on the DMAC-TRZ doped P(DMAC-Ge), P(V-DMAC) and P(dBu-E), E= C, Si, Ge films were carried out (Figure 3), from which various quantum yields, exciton lifetimes, rate constants and ΔE_{ST} are listed in Table 1. First, we compare the transient PL curves of the doped P(DMAC-Ge) and P(V-DMAC) films (Figure 3b), and find that the prompt lifetime (τ_p) for former (τ_p =36.4 ns) is obviously smaller than that of the latter (τ_p= 42.9 ns), and the decrease of τ_p indicates that the radiative transition is quenched by an incresed ISC process[25] arising from the heavy-atom Ge on P(DMAC-Ge). The delayed lifetime (τ_d) and delayed component (% of τ_d) for the doped P(DMAC-Ge) film are 2.16 μs and 82.5%, which are larger than the doped P(V-DMAC) film (τ_d= 1.81 μs, 75.4%) and can be attributed to the increased RISC process leading to more delayed fluorescence production.[23] Second, we calculate their rate constants of ISC (k_{ISC}) and RISC (k_{RISC}) via the results of PLQY and exiton lifetime (Table 1). The doped P(DMAC-Ge) film shows k_{ISC} and k_{RISC} of 2.27×10^{7} s^{-1} and 2.64×10^{6} s^{-1}, respectively, which are larger than the doped P(V-DMAC) film (k_{ISC}= 1.76×10^{7} s^{-1} and k_{RISC}= 2.25×10^{6} s^{-1}), and the increased k_{ISC} and k_{RISC} for the doped P(DMAC-Ge) film suggest that the spin-orbit coupling interaction in TADF could be intensified by the heavy-atom Ge.

For further exploring the heavy-atom effect of the host on the influence of k_{RISC} in DMAC-TRZ, we also prepare the polymers comprising of various IV A group central atoms with the same non-polar butyl side arm P(dBu-E), E= C, Si, Ge (Figure 3c) for comparison. Among them, the doped P(dBu-Ge) film shows more pronounced TADF character (τ_d= 2.38 μs, % of τ_d= 84.6%) than the doped P(dBu-C) film (τ_d=2.03 μs, 71.1%) and the doped P(dBu-Si) film (τ_d=2.16 μs, 77.6%). The k_{ISC} and k_{RISC} values for the doped P(dBu-Ge) film are 2.72×10^{7} and 2.73×10^{6}, which are higher than the doped P(dBu-Si) film (k_{ISC}=2.48×10^{7} and k_{RISC}=2.07×10^{6}) and the doped P(dBu-C) film (k_{ISC}=1.96×10^{7} and k_{RISC}=1.70×10^{6}). These enhanced TADF characters and rate constants for the Ge-based host confrim the existance of extenal heavy-atom effect. In addition, the higher PLQY for the doped P(dBu-Ge) film (92%) than the doped P(dBu-C) film (81%) and P(dBu-Si) film (83%) also indicats that presence of Ge atom has a positive effect on TADF emitter. In Figure 3d, we show the advantages of introducing the Ge atom to the σ-π conjugated polymer host. First, it can give high E_T to avoid the back energy transfer from TADF guest. Second, it can generate external heavy-atom effect to enhance spin-orbit coupling and promote the rate of RISC in the TADF guest, Both of the aboves can efficiently harvest triplet excitons for promoting light emission.

To investigate the electroluminescence (EL) properties of these polymer hosts, the devices were fabricated with the following configuration of ITO/PEDOT:PSS /host: 8wt% DMAC-TRZ (30nm)/TP3PO (3nm)/ TmPyPB (52nm) /CsF (1nm)/Al, in which the hosts including P(DMAC-Ge) and P(V-DMAC). All of the structures of molecules used in the devices and the energy diagram are shown in Scheme S4 and the device performances are shown in Figure 4 and their parameters are listed in Table S3. For the EL emissions, the inset of Figure 4b shows that the EL spectra of 8wt% DMACT-TRZ doped in P(DMAC-Ge) gives EL_{max} at 482 nm with the CIE coordinates of (0.16, 0.31) as sky-blue emission, which is more blue-shifting compared to the P(V-DMAC) based device at 487 nm with CIE (0.17, 0.34), the PVK based device at 497 nm with CIE (0.19, 0.45) and the TAPC based device at 495 nm with CIE (0.21, 0.41) (Figure S7). For charge transport behaviors, Figure 4a shows that P(DMAC-Ge) based device gives better charge injection capability than P(V-DMAC) based device under the same electrical field, which also reflects on their brightness profiles and specifically on maximum brightness (B_{max}) values, the former B_{max} ~11000 cd/m^2 being ~2.8 times higher than that of the latter (B_{max}~4000 cd/m^2). For the device performance, Figure 4b shows the maximum EQEs with 17.6% and 10.0% for P(DMAC-Ge) and P(V-DMAC) based devices, respectively, and the charge balance factor (γ) values are 0.77 for the former and 0.45 for the latter (Table S3). The EQE and the corresponding efficiency roll-off extent relative to EQE_{max} at 500 cd/m^2 are 15.9% (-9.7%) for P(DMAC-Ge) based device, but decrease to 7.0% (-30%) for P(V-DMAC) based device (Table S3). The P(DMAC-Ge) giving higher EQE and γ and lower efficiency roll-off than P(V-DMAC) is due to that the Ge-based σ-π conjugated backbone could act as an additional electron transport channel. In addition, we believe that this high device performance partly contributed from the increased H_{SO} of TADF guest by external heavy-atom effect of the Ge based host, which is able to harvest more triplet excitons and thus give higher EL efficiency.

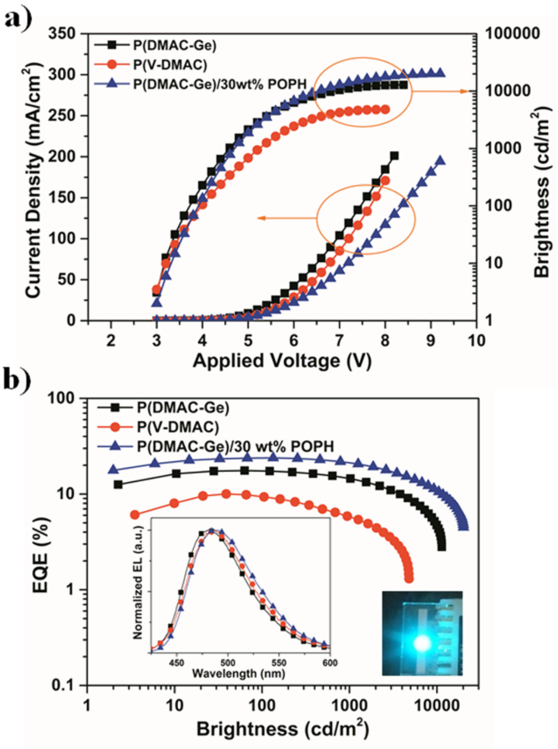

Figure 4. Performances of P(DMAC-Ge), P(V-DMAC) and P(DMAC-Ge)/POPH based sky-blue TADF PLEDs: a) current density-voltage-brightness (I-V-B) characteristics and b) EQE versus brightness (inset: the EL spectra at 7V and the photograph of P(DMAC-Ge) based device).

We further improve the performance of P(DMAC-Ge) based sky-blue device by blending the electron transport material 5-terphenyl-1,3-phenylene-bis(diphenylphosphine oxide) (POPH) [26] into the EML, under the same device configuration as the above sky-blue TADF PLEDs (Figure S9 and Table S4). Impressively, the device using P(DMAC-Ge)/ POPH (70:30 by weight ratio) as the host gives maximum λ_{EL} at 490 nm with CIE (0.17, 0.37) and the extremely high device performance EQE_{max}=24.1%, LE_{max}= 55.0 cd/A and PE_{max}= 48.0 lm/W, as well as very low efficiency roll-off showing high EQE= 22.8% at 500 cd/m^2. The EL spectrum has a slighly red-shift because its *f* value of P(DMAC-Ge)/ POPH increses to 1.6×10^{-2} (Figure 2b), but it still locates in the sky-blue emission region. Moreover, the high efficiency for this cohost device is attributed to chage balance, which is supported by more balanced hole and electron current (Figure S10) and higher γ value (0.99) (Table S3) as compared to P(DMAC-Ge) based device. This successful cohost strategy on device performance indicates that if we want to construct a bipolar polymer host with high device efficiency but without cohost, an electron transport moiety with diphenylphosphine oxide could be a good candidate. Note that although the E_T of HIL (PEDOT:PSS) is low, a triplet energy transfer from the EML to it does not occur since the emission zones are located away from the HIL (Scheme S5 and Figure S10). To the best of our knowledge, this device performance is much higher than the reported state-of-the-art performance of the sky-blue TADF-polymer device (EQE$_{max}$= 12.1% and B_{max}~6000 cd/m^2),[27] and the solution-processed sky-blue TADF OLEDs using small molecule as the host at the pratical application range 500cd/m^2, which shows serverly efficiency roll-off (the EQE below 15%) and low B_{max} (~2000 cd/m^2) although its EQE$_{max}$ 25.8% is 1.7% higher than our device. Besides, the EQE$_{max}$ for our device is very close to the EQE$_{max}$ 27.4% of dry-processed TADF-OLED by using the same TADF dopant DMAC-TRZ, but its CIE coordinates (0.21, 0.51) is within the green emission region.[4a]

In summary, the proposed novel polymer P(DMAC-Ge) gives high E_T of 2.86 eV allowing it be used as the host for sky-blue TADF emitter and its symmetric arrangement provides low polarizability making spectral blue-shift of the sky-blue emitting TADF guest DMAC-TRZ and thus better blue color purity. In addition, the external heavy-atom effect of Ge atom on host can promote spin-orbit coupling of the guest that enlarges its k_{RISC}, suggesting that more triplet excitons can be harvested to generate more delayed fluorescence. The sky-blue emitting device of this host/guest pair gives the record-high EQE 24.1% by further adopting the cohost strategy of P(DMAC-Ge)/ POPH (70:30 by weight ratio) in the emitting layer. Thus, the present study opens up a new promising design route of polymer host for various TADF guests for highly efficient TADF PLED.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: polymer light-emitting diode (PLED), thermally activated delayed fluorescence (TADF), high triplet energy, heavy-atom effect, spin-orbit coupling

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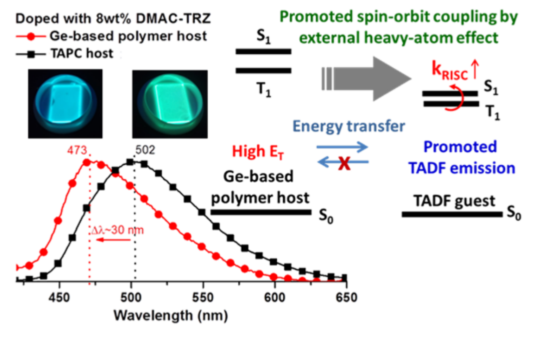
COMMUNICATION



Heavy-atom germanium in σ-π conjugated polymer host provides high E_T level to give efficient energy transfer from host to guest, low orientation polarizability leading to bluer emission from the guest, and the enhancement of spin-orbit coupling to promote the RISC rate of guest to host and thus harvesting more triplet excitons for light emission. The sky-blue TADF electroluminescence using this host/guest pair gives the record-high EQE 24.1%.

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Acridan Grafted Poly(biphenyl germanium) with High Triplet Energy, Low Polarizability and External Heavy-Atom Effect for Highly Efficient Sky-Blue TADF Electroluminescence