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Carbazole Dendrimers as Solution-Processable Thermally Activated Delayed-Fluorescence Materials**

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Abstract: *Recently, thermally activated delayed fluorescence (TADF) materials have received increasing attention as effective emitters for organic light-emitting diodes (OLEDs). However, most of them are usually employed as dopants in a host material. In this report, carbazole dendrimers with a triphenyl-s-triazine core are reported, which are the first solution-processable, non-doped, high-molecular-weight TADF materials. The dendrimers were obtained by a new and facile synthetic route using the tert-butyldimethylsilyl moiety as a protecting group. All dendrimers showed TADF in toluene. Measurements of the temperature-dependent luminescence lifetime revealed that spin-coated neat films also showed TADF with moderate quantum yields. OLED devices incorporating these dendrimers as spin-coated emitting layers gave external quantum efficiencies of up to a 3.4%, which suggests that this device is harvesting triplet excitons. This result indicates that carbazole dendrimers with attached acceptors are potential TADF materials owing to their polarized electronic structure (with HOMO–LUMO separation).*

After the pioneering work by Tang and co-workers,[1] the electronics of thin organic films, such as light-emitting diodes (OLEDs),[2] photovoltaics,[3] transistors,[4] and memory architectures,[5] have rapidly evolved. OLEDs are already in practical use; however, such devices are still mainly fabricated by vacuum deposition of low-molecular-weight materials ($M_W \leq 1000$). For truly inexpensive and large-scale fabrication processes, the solution processability of the materials is very important.[6] Generally, for OLED materials, a uniform amorphous film is necessary. Therefore, polymeric materials have been the most intensively studied solution-processable materials,[6] but they suffer from a wide molecular-weight distribution, inhomogeneity, low solubility, and impurities. Thus, several solution-processable materials with definite molecular weights have recently been reported.[7]

Dendrimers[8] are perfectly branched polymers with absolute molecular weights. Owing to their unique structure with a high steric hindrance, they are generally soluble, amorphous, and can isolate chromophores at the core to prevent concentration quenching. They have been widely studied as solution-processable OLED materials,[9] and carbazole dendrimers,[10] in particular, have been used as efficient hole-transporting materials,[11] phosphorescence hosts,[12] and single-component emitting materials,[13,14] because of their good hole-transporting properties, high triplet energies and thermal stabilities, and excellent crosslinking abilities.[15]

The development of emitting materials for OLEDs started with systems based on fluorescence,[1a,b] moved to phosphorescence-based devices,[16] and recently reached triplet–triplet annihilation (TTA)[17] and thermally activated delayed fluorescence (TADF) materials.[18] TADF has the advantages of a high internal quantum efficiency (up to 100%) and inexpensive (rare-metal-free) materials. However, to the best of our knowledge, a non-doped, solution-processable TADF material has still not been developed. The important design principle of a TADF material is to spatially separate HOMO and LUMO as this reduces the difference between the singlet and triplet energy levels ($\Delta E_{\mathrm{S-T}}$). Previously, we revealed that simple carbazole dendrimers feature a potential gradient with an electron-rich periphery, with the LUMO at the core, and the HOMO at the periphery. This dendrimer still has a $\Delta E_{\mathrm{S-T}}$ value (>0.5 eV) that is too large for TADF, but it is expected that the attachment of an acceptor molecule to the core will extend this potential gradient and reduce the $\Delta E_{\mathrm{S-T}}$ value, thus enabling TADF. Furthermore, it is expected that owing to the bulky dendrimer structure, intermolecular interactions are inhibited, and concentration quenching is minimized. We now report a carbazole dendrimer with a triazine core as the first solution-processable, single-component, and high-molecular-weight TADF material for OLEDs.

The carbazole dendrons were synthesized by a facile synthetic route using *tert*-butyldimethylsilyl (TBS) groups to protect the carbazole nitrogen atoms (I_2CzTBS^{19}; see the Supporting Information, Scheme S1). Previously reported routes for the synthesis of carbazole dendrons used tosyl (Ts),[10b] benzyl (Bn),[10c–e] *tert*-butoxycarbonyl (Boc),[10a] or acetyl (Ac)[10f] groups as protecting groups, but the cleavage conditions were harsh, required extended periods of time, or the yields were not high. On the other hand, the TBS group

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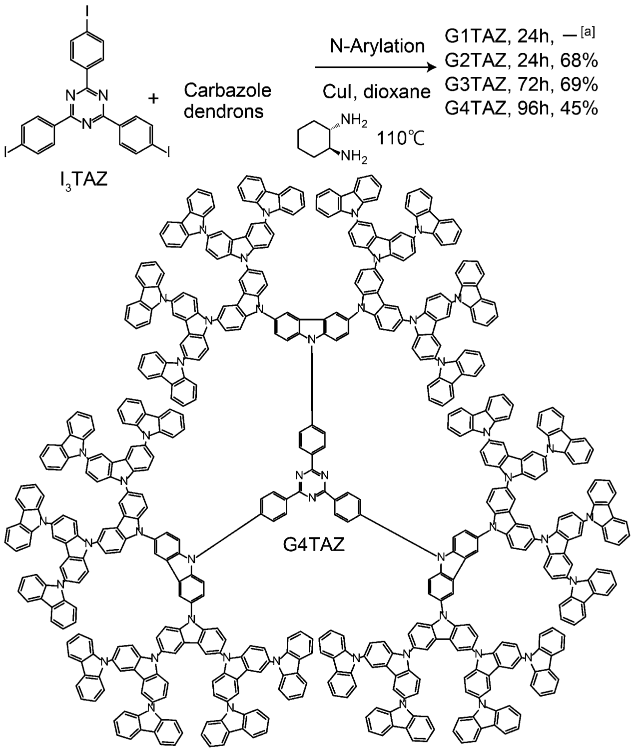
could be quantitatively cleaved within a few minutes using tetrabutylammonium fluoride (TBAF). Furthermore, the cleavage reaction could be directly performed in the reaction mixture of the N-arylation step. This procedure effectively reduces the number of purification steps and the total time required to synthesize the high-generation carbazole dendrons. The dendrimers with the 2,4,6-triphenyl-s-triazine core (G*n*TAZ, *n* = generation) were synthesized by reacting the carbazole dendrons with 2,4,6-tris(4-iodophenyl)-1,3,5-triazine (Scheme 1).[20] The formation of the G1 dendrimers (G1TAZ) was confirmed by MALDI-TOF mass-spectrometric analysis of the reaction mixture, but the solubility of the dendrimers was extremely low, and they could not be isolated. Other generation dendrimers, however, were successfully isolated and highly soluble in common organic solvents, such as toluene, THF, and chloroform. All new compounds were analyzed by ^{1}H and ^{13}C NMR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis (see the Supporting Information for details).



Scheme 1. Synthesis of dendrimers with carbazole dendrons and an s-triazine core (G*n*TAZ). [a] Very low solubility.

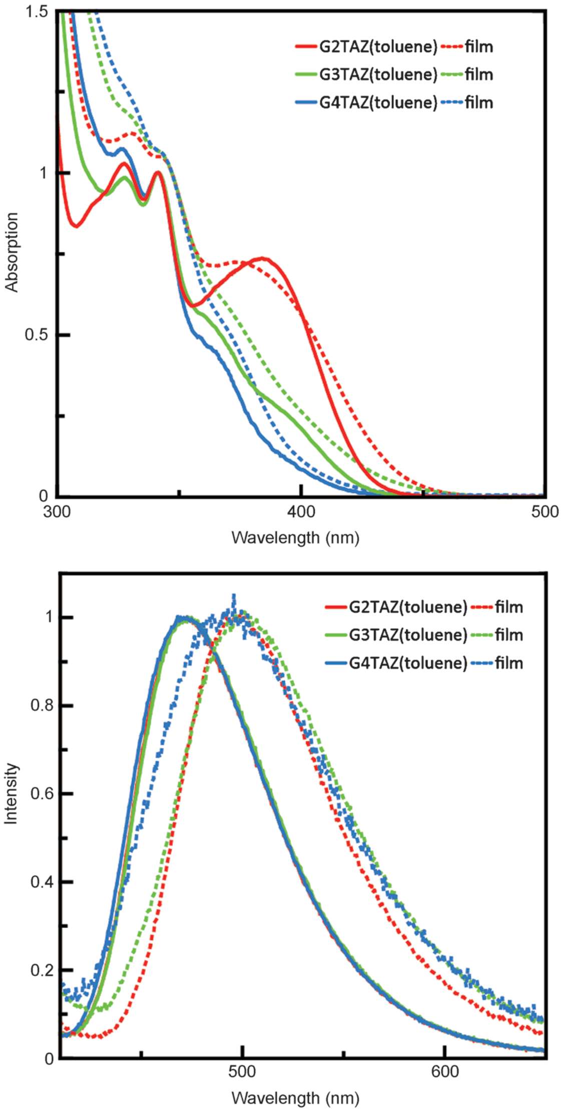


Figure 1. UV/Vis (top) and PL spectra (bottom; excitation at 390 nm) of toluene solutions and neat films of the G*n*TAZ dendrimers.

The UV/Vis absorption spectra of the G*n*TAZ dendrimers in toluene showed a charge–transfer (CT) band with an absorption coefficient on the order of $10^3\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ at approximately 390 nm (Figure 1, top). The absorption coefficient decreased when the generation number was increased, indicating that the oscillator strength of direct transitions from the carbazole (HOMO) to the triazine (LUMO) decreases when the generation number is increased. In line with this result, a calculation of the molecular orbitals[21] showed that the distance between HOMO and LUMO increased when the generation number is increased because the carbazole dendrons have a large HOMO density at the outer periphery (Figures S9–S11). The photoluminescence (PL) spectra in toluene showed a broad emission band at 473 nm (Figure 1, bottom), and the emission peak was drastically shifted by changing the solvent. Thus, this emission band could be assigned to emission from the CT state. The spectra were almost identical for the different dendrimer generations. This finding indicates that emission occurs from a CT state near the core, that is, that conjugation in the excited state of the carbazole dendron is limited to two or three carbazole moieties because of the highly twisted molecular structure (direct transitions from the outer carbazole ring to the triazine core are difficult).[10a] The UV/Vis absorption and PL spectra were also recorded for the neat films (Figure 1). The UV/Vis spectra showed a slight bathochromic shift compared to the toluene solution owing to intermolecular interactions. The PL spectra showed a much greater shift of the emission peak. The CT state is strongly affected by the external environment and the conformation (conjugation) of the excited state. Therefore, the shift in the PL spectra can be explained by the change in the external environment, changes in the conformation of the dendrimer in the solid state, and intermolecular interactions (π–π stacking). In fact, the shifts in the absorption and PL spectra between the solution and film samples were smaller for G4TAZ than for other dendrimer generations. This result implies that intermolecular interactions are inhibited by the large shell of the carbazole dendron. The ΔE_{S-T} values of the neat films were also determined from the fluorescence and phosphorescence spectra (Table 1; see also Figure S12). Values of 0.03 eV (G2TAZ), 0.06 eV (G3TAZ), and 0.06 eV (G4TAZ) were measured, which are low enough to allow for reverse intersystem crossing from the triplet state to the singlet state at room temperature.

Table 1: Energy levels and thermal stabilities of G*n*TAZ dendrimers.

Compound	HOMO [eV][a]	LUMO [eV][b]	S_1 [eV][c]	T_1 [eV][c]	ΔE_{S-T} [eV]	$T_{d5\%}$ [°C][d]
G2TAZ	5.76	3.01	2.77	2.74	0.03	592
G3TAZ	5.72	2.97	2.79	2.74	0.06	620
G4TAZ	5.68	2.80	2.86	2.79	0.06	633

[a] Determined by photoelectron spectroscopy of the film in air. [b] Estimated from the HOMO level and the absorption edge. [c] See Figure S12 for the spectra that were used for determining these values. [d] $T_{d5\%}$ = 5 % weight loss temperature. See Figure S13 for a plot of weight loss versus temperature.

The photoluminescence quantum yields (PLQYs) were measured for the dendrimers both in toluene solution and as neat films (Table 2). The PLQY of the dendrimers in toluene solution was nearly 100 % for all generations, and relatively high even for the neat film under an inert atmosphere. Interestingly, the PLQY decreased when it was measured in air, which implies that the emission lifetime is relatively long, and that the emission is effectively quenched by the diffusion of oxygen. The greater decrease in the PLQY of the higher-generation dendrimers indicates that they have longer PL lifetimes in solution than the lower-generation dendrimers. The PLQYs of the neat films were higher for the lower-generation dendrimers. The intermolecular interactions between the emissive cores decrease when the generation number is increased, as indicated by the absorption and PL spectra. However, the PL lifetime in solution (isolated molecules) is longer for higher-generation dendrimers, which implies that the longer lifetime increases the chances that the excited state is quenched by intermolecular interactions, such as excimer formation. Therefore, the higher-generation dendrimers have a lower PLQY in the neat film in spite of greater intermolecular interactions. For further investigations of the PL behavior, the PL lifetimes of the neat film were measured at several temperatures (Figure 2; see also Table S1). When the temperature was increased, the contribution of a long-lifetime component (on the order of microseconds) also increased. This behavior is typical for a TADF material. Nevertheless, the contribution of the long-lifetime component decreased slightly at the highest temperature (300 K), which might be due to an increase in non-radiative processes through vibration or molecular interactions that increase in intensity with temperature.[22] Intriguingly, the spectra of the delayed component showed a bathochromic shift compared to the prompt component (Figure S14). This phenomenon was previously reported for some TADF materials and was explained by the difference in the nuclear configuration between the initial S1 state and the S1 state that is formed from the T1 state.[23] The differences in the spectra were greater for the higher-generation dendrimers, indicating that the differences between the conformations of the S1 and T1 states are greater for the larger dendrimers. The contributions of the delayed fluorescence at 300 K were calculated to be 43 % (G2TAZ), 81 % (G3TAZ), and 72 % (G4TAZ). The contribution typically increased from G2TAZ to G3TAZ, implying that HOMO–LUMO separation was more effective. This result suggests that the HOMO structure of the carbazole dendron (with a higher density at the outer periphery) is very critical to controlling TADF efficiency.

OLED devices with a ITO/PEDOT:PSS(30 nm)/G*n*TAZ (35 nm)/TPBI(40 nm)/Ca(10 nm)/Al structure were then fabricated. The dendrimers were expected to act as the emitting layer, and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) as the hole-blocking and electron-transfer layer. The corresponding energy diagram is summarized in Figure S15, and the device characteristics are summarized in Figures 3 and S16 and Tables 2 and S2. The EL spectra of the devices confirmed that emission occurred only from the dendrimers (Figure 3 c). However, the EL spectra showed a slight bathochromic shift compared to the PL spectra (Figure S17). As the delayed fluorescence, which is based on intersystem crossing, occurs at a longer wavelength than prompt singlet emission, the slight bathochromic shift in the EL spectra could be explained by the greater number of triplet excitons produced by the electric excitation in the EL process. The maximum external quantum efficiencies (EQEs) of the

Table 2: PLQYs of G*n*TAZ dendrimers and EQEs of OLEDs with G*n*TAZ dendrimers as the emitting layer.

Compound	Φ_{PL} solution in air [%]	Φ_{PL} solution in N_2 [%]	Φ_{PL} film in N_2 [%]	Φ prompt [%]	Φ delayed [%]	EQE calcd [%][a,b]	EQE calcd [%][c]	EQE exp. [%]
G2TAZ	76	94	52	28.6	22.4	8.0	2.9	2.4
G3TAZ	59	1.0×10^2	31	6.2	24.8	6.1	1.7	3.4
G4TAZ	6.4	94	8.5	2.5	6.0	1.8	0.5	1.5

[a] According to Ref. [24]. [b] Assuming a hole–electron recombination efficiency of 1 and a light-extraction efficiency of 0.22.[25] [c] Theoretical maximum by assuming that the PLQY of the neat films originates solely from the singlet states. Φ_{PL} = photoluminescence quantum yield.

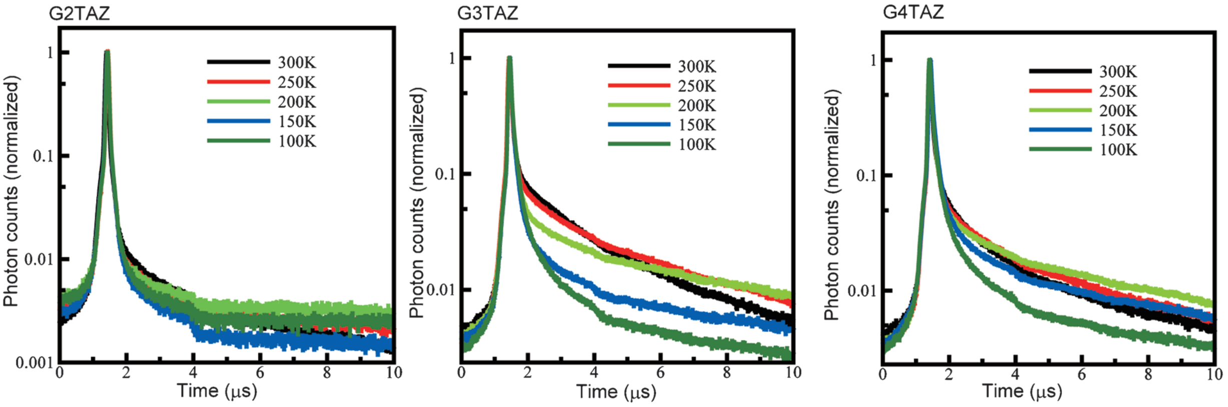


Figure 2. Transient PL decay of G*n*TAZ dendrimers at various temperatures (excitation at 355 nm).

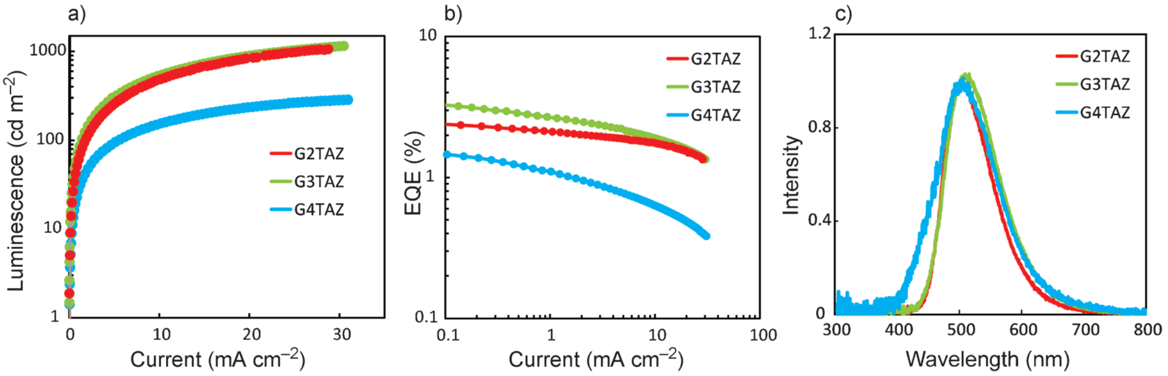


Figure 3. Properties of OLEDs containing G*n*TAZ dendrimers as the emitter. a) Dependence of the luminescence on the current density. b) Dependence of the external quantum efficiency on the current density. c) Electroluminescence spectra.

OLED devices reached 2.4 % (G2TAZ), 3.4 % (G3TAZ), and 1.5 % (G4TAZ). These values are definitely higher than the EQEs that were calculated with the assumption that the singlet states generated electrically, that is, 25 % of the excitons, can contribute to the emission. This result indicates that the spin-coated G*n*TAZ neat films harvest the electrically generated triplet excitons through TADF processes. Even though the observed values are still lower than the calculated theoretical maximum EQE values with TADF,[24,25] further structural optimization of the devices could lead to improvements. The dependence of the EQE on the current density was determined by a roll-off analysis employing the TTA model (Figure S18).[26] The values were in good agreement with the model, and J_0 values (the current density at the half maximum of the EQE) of 59.34 mA cm^{-2} (G2TAZ), 18.31 mA cm^{-2} (G3TAZ), 7.15 mA cm^{-2} (G4TAZ) were determined. As the density of the chromophore should decrease as the generation number was increased, the annihilation probability should decrease, leading to higher J_0 values as the generation number is increased. However, the J_0 values decreased as the generation number was increased owing to the longer lifetime of the exciton in the higher-generation dendrimer as the PLQY decreased for the higher-generation dendrimers. To further elucidate the relation between the J_0 value and the dendrimer generation number, further investigations to study the influence of the molecular packing and orientation, for example, will be necessary.

In conclusion, an effective route for the synthesis of carbazole dendrons was developed. Carbazole dendrimers with a triphenyl-s-triazine core were then synthesized and shown to exhibit thermally activated delayed fluorescence. The TADF emission was also observed to occur for neat spin-coated films with a moderate PLQY. OLEDs devices with G*n*TAZ dendrimers as the emitting layer were fabricated, and a maximum external quantum efficiency of 3.4 % (G3TAZ) was observed. The device performance should be improvable by careful optimization, but more importantly, the recorded EQE value indicated that the dendrimer emitting layer is harvesting the triplet excitons. Thus, the G*n*TAZ dendrimers are the first solution-processable, single-component (non-doped), and high-molecular-weight TADF materials for OLEDs. The intrinsic HOMO–LUMO separation in the carbazole dendron[10a] was confirmed to play an important role; therefore, other carbazole dendrimers with attached acceptor moieties should also be promising TADF materials. Furthermore, carbazole derivatives are known to become insoluble by crosslinking.[15] This feature may enable the fabrication of a fully solution-processed TADF OLED device.

Keywords: carbazoles · dendrimers · electroluminescence · fluorescence

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