

# Synthesis and Properties of Triphenylamine- and 9-Phenylcarbazole-cored Star-shaped Terfluorenes: Understanding the Effect of Molecular Dimensionality

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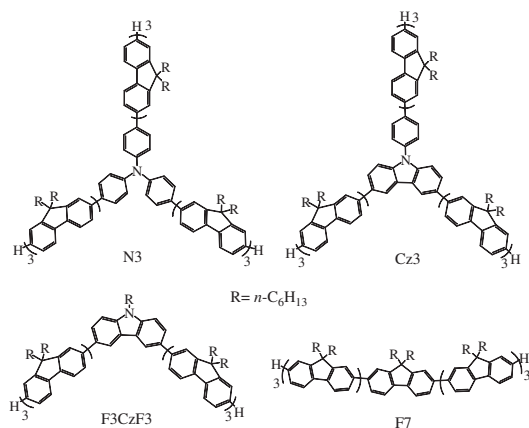
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Two star-shaped terfluorenes with either triphenylamine or 9-phenylcarbazole core structure with different dimensionality were synthesized. The optical, thermal, electrochemical, and electroluminescent properties were investigated in comparison with those of the low-dimensional linear counterparts. Strong correlation between the molecular dimensionality and associated optoelectronic properties was demonstrated.

Over the past few years, low-dimensional linear oligo- and polyfluorenes have been among the most prominent candidates for applications in organic electronics, i.e. organic light-emitting diodes (OLEDs).<sup>1,2</sup> New intrinsic electrical, optical, and morphological properties are becoming available with increased molecular complexity and dimensionality.<sup>3–5</sup> In particular, two/three-dimensional (2D/3D) star-shaped  $\pi$ -conjugated systems have been attracting much interest.<sup>3,4</sup> Among them, starburst terfluorenes appeared to be rather attractive with superior functional properties.<sup>4</sup> Despite this progress, little effort has been devoted to elucidating the effect of molecular dimensionality.<sup>3</sup> Further insight into the influence of material architectures and topologies on associated physical properties is still needed.<sup>3</sup> Better understanding of the structure–property relationships is a crucial aspect for designing novel organic optoelectronic materials with tailor-made properties for a specific application.

For this purpose, we synthesized two new star-shaped terfluorene analogues N3 and Cz3 with either triphenylamine or 9-phenylcarbazole as the core structure (Scheme 1). The only difference between the molecular structures of Cz3 and N3 lies in the additional single bond that connects the two adjacent phenyl units in 9-phenylcarbazole, which limits the free rotation and compels the resulting Cz3 molecule to adopt a more planar arrangement (c.f. Supporting Information, SI).<sup>7</sup> As for the mo-

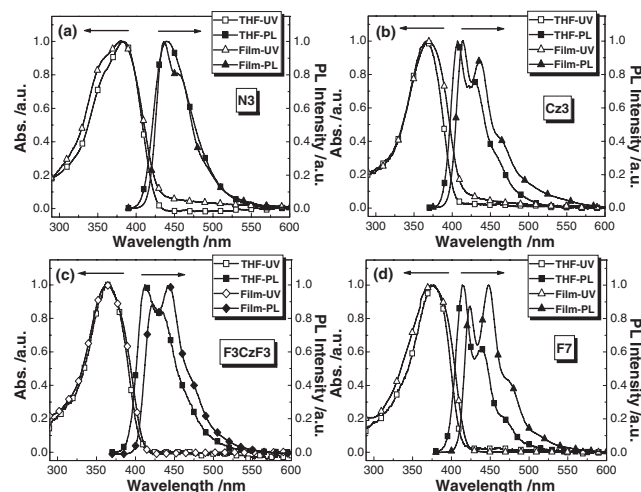


**Scheme 1.** Chemical structures of N3, Cz3, F3CzF3, and F7.

lecular structure of N3, three substituents attached at the fringes of nitrogen can undergo free rotation in three dimensions, thus adopting a propeller-shaped 3D molecular architecture (c.f. SI).<sup>7</sup> As we know, no such terfluorene compounds with either triphenylamine or 9-phenylcarbazole as the core structure have been reported so far.<sup>5</sup> Herein we explore them as ideal platforms for investigating the impact of molecular topology especially the molecular dimensionality on the material functional properties. The optical, thermal, electrochemical, and electroluminescent properties of the as-synthesized star-shaped terfluorenes N3 and Cz3 were investigated in comparison with those of their low-dimensional linear counterparts (F3CzF3 and F7) as an attempt to elucidate structure–property relationships. Strong correlation between the molecular dimensionality and associated optoelectronic properties was demonstrated.

The chemical structures of N3, Cz3, F3CzF3, and F7 are depicted in Scheme 1. The compounds were synthesized via a microwave-assisted multiple Suzuki coupling methodology in good yields (78–89%) and high purity.<sup>7</sup>

Investigation of the photophysical properties of the model compounds revealed their distinct dependence on the molecular topology and dimensionality. These results are documented in Figure 1 and summarized in Table 1. In the PL spectra, the thin film of Cz3 showed a notable red shift relative to its solution spectra, while the emission spectra of the linear counterparts, F3CzF3 and F7, in film state significantly differ in both spectral shapes and peak positions from those in their dilute solution states. In contrast however, the optical properties of N3 in the solid state are almost identical to those in solution. Only a split-



**Figure 1.** Absorption and photoluminescence (PL) spectra of N3 (a), Cz3 (b), F3CzF3 (c), and F7 (d) in THF and as films.

**Table 1.** Optical, electrochemical, and thermal properties of the compounds

	$M_r$	$\lambda_{\text{abs}}^a/\text{nm}$ (THF)	$\lambda_{\text{em}}^a/\text{nm}$ (THF)	$\lambda_{\text{abs}}/\text{nm}$ (film)	$\lambda_{\text{PL}}/\text{nm}$ (film)	$\Phi_f^b$ (THF)	$\Phi_f^b$ (film)	$E_{\text{HOMO}}^c$ /eV	$E_{\text{LUMO}}^c$ /eV	$T_g/^\circ\text{C}$	$T_d/^\circ\text{C}$
N3	3239.0	383	440	379	436,455sh	0.87	0.76	-5.66	-2.02	89.1	415
Cz3	3237.0	366	407,431sh	367.5	414,436,464sh	0.81	0.72	-5.75	-2.07	84.5	378
F3CzF3	2246.5	362.5	412,436sh	363	422,444	0.69	0.46	-5.67	-2.08	80.0	375
F7	2329.7	376.5	414,439	373.5	424,448,475sh	0.84	0.68	-5.75	-2.11	61.7	372

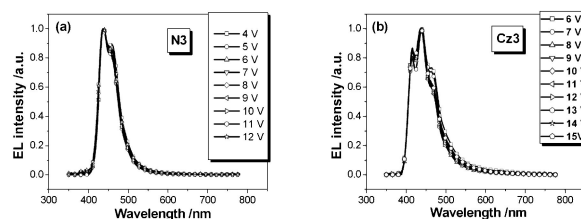
<sup>a</sup>All spectra were measured in dilute THF solution at 295 K. <sup>b</sup>Estimated error in PL quantum efficiencies  $\approx \pm 10\%$ . 9,10-Diphenylanthracene ( $\Phi_f = 0.91$  in ethanol) was used as standard. <sup>c</sup>Estimated from the onset oxidation or reduction potential by using  $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.71)$  and  $E_{\text{LUMO}} = -(E_{\text{red}} + 4.71)$ . <sup>d</sup>c

ting shoulder at 455 nm appeared in the PL spectra was observed in spin-coated film, indicating that neither conformational changes nor aggregation or excimer formation occurred upon entering the solid state. This is a significant signal for enhanced solid-state luminescence by retaining an isolated-molecule-like emission in the condensed solid state, since detrimental  $\pi$ -stacking-induced molecular interaction can occur in many conjugated compounds upon entering the solid state.<sup>6</sup> Clearly, the novel 3D propeller-shaped molecular architecture of N3 that could significantly depress the intermolecular interactions (e.g., dimer or excimer formation) plays an important role. The higher quantum yields of N3 and the smaller difference between those in the film state (0.76) and in solution state (0.87) relative to those of Cz3, F3CzF3, and F7 (Table 1) also support this proposal.

N3, Cz3, F3CzF3, and F7 showed weight losses of 5% at 415, 378, 375, and 372 °C (Table 1), respectively. The phase-transition temperatures (i.e.  $T_g$ ), investigated with DSC, were progressively increased with increasing the molecular complexity and dimensionality from linear compound to star-shaped compound with an order of  $F7 < F3CzF3 < Cz3 < N3$  (Table 1). Upon heating beyond  $T_g$ , no distinct crystalline and melting processes were identified for N3 and Cz3. In addition, a diffuse halo around  $2\theta = 20^\circ$  in their wide-angle X-ray diffraction (WAXD) patterns<sup>7</sup> is observed, whereas no distinct peaks corresponding to the stacking periodicity could be detected in the wide-angle region, indicating a high degree of amorphous properties in the solid state. In contrast, sharp peaks in the WAXD for the linear counterpart F7 were clearly identified.<sup>7</sup> These results suggest that increasing the molecular dimensionality helps to decrease the intermolecular interactions and thus improve the amorphous glassy properties.

The electrochemical properties were investigated and the HOMO and LUMO values were summarized in Table 1. No distinct correlation between the electrochemical properties and the molecular topology was found. Most probably, in this case, the molecular topology is relatively unimportant in determining the electrochemical properties for these terfluorene compounds.

Solution-processed single-layer OLEDs using N3, Cz3, F3CzF3, and F7 as active emissive materials were fabricated. The device configuration was ITO/PEDOT:PSS/sample/LiF/Ca/Al. Because of the poor film quality of the linear compounds F3CzF3 or F7, we did not succeed in lighting the OLED devices. As shown in Figure 2, the EL spectra of N3 centered at 437 nm with a shoulder at 455 nm, which are quite similar to the PL spectra in both spectra shapes and peak positions. Stable pure deep blue emission with CIE coordinative of (0.16, 0.08) was obtained, which showed no significant changes upon various driving voltages. In contrast, the EL spectra of Cz3 changed significantly in both spectral shapes and peak positions compared to its PL spectra, resulted in red-shifted emission CIE coordinates of (0.18, 0.11). Moreover, nearly four-times higher maximum



**Figure 2.** EL spectra of N3 (a) and Cz3 (b) based devices at various driving voltages.

luminance (830  $\text{cd}/\text{m}^2$  vs. 220  $\text{cd}/\text{m}^2$ ) and lower turn-on voltage (4.0 V vs. 6.0 V) was measured for OLED based on N3, compared with that of Cz3, under the identical experimental conditions. This is consistent with the conclusion that there is an additional enhancement from increasing the molecular dimensionality.

In summary, two new star-shaped terfluorenes with either triphenylamine or 9-phenylcarbazole core structure have been synthesized. Their optical, thermal, electrochemical, and electroluminescent properties have been investigated in comparison with those of the linear counterparts. The results show straightforward evidence that increasing molecular dimensionality is quite effective for improving the morphological and thermophysical properties and on enhancing the luminescence properties by suppressing the intermolecular interactions. Higher electroluminescent performance was obtained for N3 with higher dimensionality.

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#### References and Notes

- J. U. Wallace, S. H. Chen, *Adv. Polym. Sci.* **2008**, *212*, 145.
- a) K.-T. Wong, Y.-Y. Chien, R.-T. Chen, C.-F. Wang, Y.-T. Lin, H.-H. Chiang, P.-Y. Hsieh, C.-C. Wu, C. H. Chou, Y. O. Su, G.-H. Lee, S.-M. Peng, *J. Am. Chem. Soc.* **2002**, *124*, 11576. b) E. Lim, B.-J. Jung, S. M. Kim, B. O. Kim, H.-K. Shim, *Chem. Lett.* **2008**, *37*, 686.
- J. Roncali, P. Leriche, A. Cravino, *Adv. Mater.* **2007**, *19*, 2045.
- a) W.-Y. Lai, R. Zhu, Q.-L. Fan, L.-T. Hou, Y. Cao, W. Huang, *Macromolecules* **2006**, *39*, 3707. b) W.-Y. Lai, Q.-Q. Chen, Q.-Y. He, Q.-L. Fan, W. Huang, *Chem. Commun.* **2006**, 1959. c) W.-Y. Lai, Q.-Y. He, R. Zhu, Q.-Q. Chen, W. Huang, *Adv. Funct. Mater.* **2008**, *18*, 265. d) P. A. Levermore, R. Xia, W. Lai, X. H. Wang, W. Huang, D. D. C. Bradley, *J. Phys. D: Appl. Phys.* **2007**, *40*, 1896.
- a) K. Kreger, M. Jandke, P. Stroehriegel, *Synth. Met.* **2001**, *119*, 163. b) M. Sonntag, K. Kreger, D. Hanft, P. Stroehriegel, *Chem. Mater.* **2005**, *17*, 3031.
- S. A. Jenekhe, J. A. Osaheni, *Science* **1994**, *265*, 765.
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