

Synthesis and Functional Properties of End-Dendronized Oligo(9,9-diphenyl)fluorenes

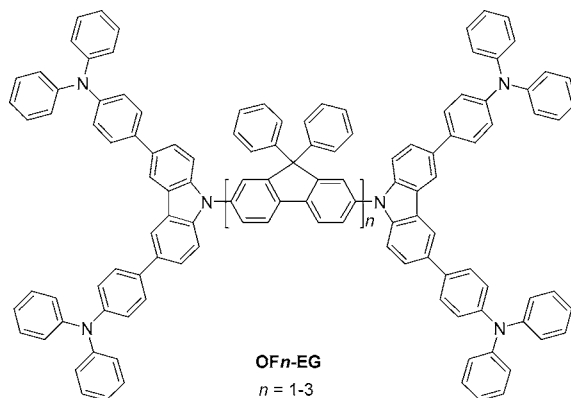
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ABSTRACT



A facile approach for the synthesis of a family of dendrimers OF_n-EG with hole-transporting ability moieties by copper-catalyzed Buchwald's double-amination as a key reaction has been developed. These novel dendrimers exhibit good energy transfer efficiencies and very high thermal and electrochemical stabilities and have potential applications as hole transfer and emitting layers in the field of organic emitting diodes (OLEDs) or as host materials for electrophosphorescent applications.

Triarylamine-based dendrimers have been intensively used as promising molecular materials for molecular magnetism and information storage,¹ energy transfer,² and organic light-emitting diodes.³ Monodisperse oligofluorenes have recently attracted much attention because of their chemical and thermal stabilities and the possibility to vary the properties

of the resulting compounds via the substitution pattern of the 9-position of the fluorenyl unit, as well as potential applications for optoelectronic molecular materials.⁴ Remarkably, end-capping polyfluorenes with hole-transporting moieties have also been shown to improve the performance of polyfluorene-based light-emitting diodes (PLEDs).⁵ Conjugated triarylamine-based dendrimers with redox gradients have been investigated;^{1a} however, oligofluorenes end-capped with dendrons comprising triarylamine and carbazole moi-

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(1) (a) Selby, T. D.; Blackstock, S. C. *J. Am. Chem. Soc.* **1998**, *120*, 12155. (b) Selby, T. D.; Blackstock, S. C. *Chem. Mater.* **2002**, *14*, 1685. (c) Louie, J.; Hartwig, J. F.; Fry, A. J. *J. Am. Chem. Soc.* **1997**, *119*, 1165.

(2) Ranasinghe, M. I.; Varnavski, O. L.; Pawlas, J.; Hauck, S. I.; Louie, J.; Hartwig, J. F.; Goodson, T. *J. Am. Chem. Soc.* **2002**, *124*, 6520.

(3) (a) Wang, P. W.; Liu, W.; Yu, J.; Devadoss, C.; Bharathi, P.; Moore, J. S. *Adv. Mater.* **1996**, *8*, 237. (b) Freeman, A. W.; Koene, S. C.; Malenfant, P. R. L.; Thompson, M. E.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2000**, *122*, 12385. (c) Satoh, N.; Cho, J.-S.; Higuchi, M.; Yamamoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 8104.

(4) (a) Grell, M.; Knoll, W.; Lupo, D.; Meisel, A.; Miteva, T.; Neher, D.; Nothofer, H. G.; Scherf, U.; Yasuda, A. *Adv. Mater.* **1999**, *11*, 671. (b) Li, Z. H.; Wong, M. S.; Tao, Y.; Lu, J. P. *Chem. Eur. J.* **2005**, *11*, 3285. (c) Li, Z. H.; Wong, M. S.; Fukutani, H.; Tao, Y. *Chem. Mater.* **2005**, *17*, 5032. (d) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416. (e) Marsitzky, D.; Klapper, M.; Müllen, K. *Macromolecules* **1999**, *32*, 8685.

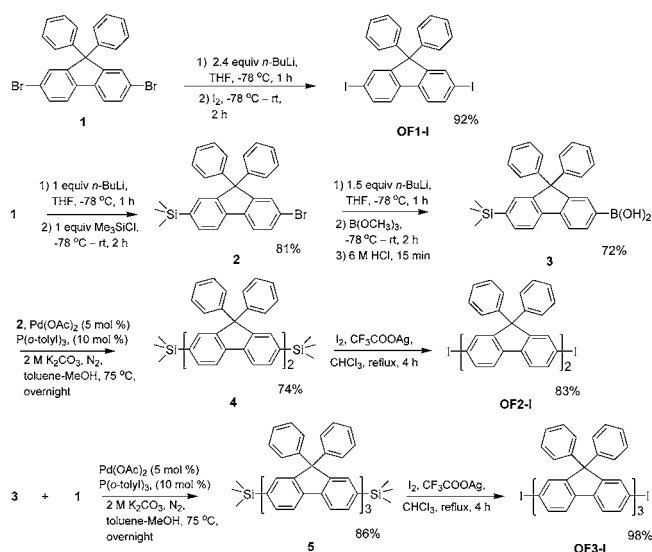
(5) Miteva, T.; Meisel, A.; Knoll, W.; Nothofer, H. G.; Scherf, U.; Müller, D. C.; Meerholz, K.; Yasuda, A.; Neher, D. *Adv. Mater.* **2001**, *13*, 565.

eties may be expected to improve the physical properties of oligofluorenes; this still remains to be explored.

In this paper, we describe the synthesis and functional properties of end-dendronized oligofluorenes with a redox gradient, **OF n -EG**, $n = 1-3$, in which the dendron is constructed by triarylamine and carbazole moieties and the core is constructed by oligo(9,9-diphenyl)fluorene. Since the peripheral triarylamine-based moieties exhibit lower oxidation potentials than those of carbazole units in the interior, this configuration constructs a redox gradient and facilitates the migration of electrons from the core to the periphery of the dendron.

The strategy for preparation of triarylamine- and carbazole-based dendritic oligofluorenes **OF n -EG**, $n = 1-3$, is outlined in Schemes 1 and 2. Transformation of the dibromide **1**⁶ into

Scheme 1. Synthesis of Diiodo-oligo(9,9-diphenyl)fluorenes **OF n -I**

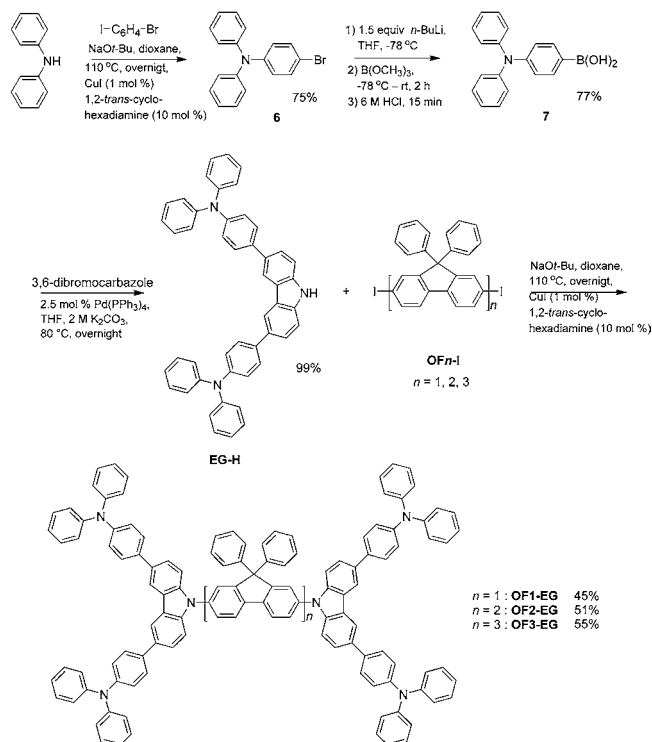


the corresponding diiodide **OF1-I** was carried out in 92% high yield by lithium–bromine exchange at low temperature, followed by reaction with iodine at room temperature. Transformation of the dibromide **1** into the corresponding monobromide **2** was carried out in 81% yield by lithium–bromine exchange, followed by reaction with trimethylsilyl chloride. Then, transformation of the monobromide **2** into the corresponding boronic acid **3** was easily carried out in a yield of 72% by lithium–bromine exchange, followed by reaction with trimethyl borate and subsequently acid hydrolysis. Suzuki cross-coupling between the boronic acid **3** and monobromide **2** using Pd(OAc)₂/2P(*o*-tolyl)₃ as a catalyst afforded the desired double-trimethylsilyl end-capped bifluorene **4** in an excellent yield. Transformation of **4** into diiodide **OF2-I** was achieved in a good yield by iodo-desilylation at 80 °C in the presence of silver trifluoroacetate.⁷ Diiodide **OF3-I** was also prepared by a method similar to

(6) Wong, K.-T.; Wang, Z.-J.; Chien, Y.-Y.; Wang, C.-L. *Org. Lett.* **2001**, *3*, 2285.

(7) Wilson, S. R.; Jacob, L. A. *J. Org. Chem.* **1986**, *51*, 4833.

Scheme 2. Synthesis of End-Dendronized Oligo(9,9-diphenyl)fluorenes **OF n -EG**



the synthesis of **OF2-I**. Importantly, the dendron **EG-H** was gained by the palladium-catalyzed direct Suzuki cross-coupling of boronic acid **7** with *N*-unprotected 3,6-dibromocarbazole in 99% high yield. It should be noted that the catalytic activity of Pd(PPh₃)₄ is remarkably higher than that of Pd(OAc)₂/2P(*o*-tolyl)₃ in this coupling reaction. Then, copper-catalyzed Buchwald double-amination⁸ of the corresponding diiodide **OF n -I**, $n = 1-3$, with the dendron **EG-H** using 1:10 of CuI/1,2-trans-cyclohexadiamine as a catalyst afforded the target products in a moderate yield.

The decomposition temperatures (T_{dec}) of these dendrimers **OF n -EGs** are about 600 °C, indicating that all of the new dendrimers have very high thermal stability. This good stability may be induced by the dendritic wedges **EG-H**, which have T_{dec} up to 565 °C (Table 1). The glass transition temperatures (T_{g}) of the newly synthesized dendrimers are 192, 225, and 254 °C, respectively, and gradually increase as the core chain length increases. The dendron **EG-H** also exhibits high T_{g} up to 124 °C, indicating that an incorporation of the dendrons **EG** onto the backbone of oligofluorene is very important for inducing a high T_{g} of resulting molecules. On the other hand, the DSC analyses further confirmed that all of the **OF n -EGs** form an extremely stable amorphous glass because neither melting transitions nor crystallization transitions were detected after their glass transition temperatures.

In view of electronic absorption spectra, the absorption bands/maxima of these new dendrimers peaked at 347, 348,

(8) (a) Antilla, J. C.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 11684. (b) Antilla, J. C.; Baskin, J. M.; Barder, T. E.; Buchwald, S. L. *J. Org. Chem.* **2004**, *69*, 5578.

Table 1. Summary of Physical Measurements of **OF n -EG**, $n = 1-3$, and **EG-H**

	$\lambda_{\max}^{\text{abs}}/ \text{nm}$ ($\epsilon \cdot 10^5/ \text{M}^{-1} \text{cm}^{-1}$)	$\lambda_{\max}^{\text{em}}/ \text{nm}$	$\Phi_{\text{a,c}}$	ETE ^{a,d} /%	HOMO ^e /eV	$E_{1/2}$ ^f /V	E_g ^f /eV	T_g ^g /°C	T_{dec} ^h /°C
OF1-EG	347 (1.31)	404	<0.01	78	5.18	0.38, 0.71	2.08	192	596
OF2-EG	348 (1.49)	436	0.31	68	5.19	0.39, 0.69	2.17	225	601
OF3-EG	356 (1.66)	436	0.38	69	5.19	0.39, 0.68	2.20	254	601
EG-H	324 (0.65)	396	<0.01		5.17	0.40, 0.75	1.87	124	565

^a Measured in CHCl_3 . ^b Excited at the absorption maxima. ^c Using quinine sulfate monohydrate ($\Phi_{313} = 0.48$) as a standard. ^d Energy-transfer efficiency is determined by comparing the absorption maximum of the dendritic wedges of the absorption and fluorescence excitation spectra. ^e $E_{1/2}$ vs Fc^+/Fc estimated by CV method using platinum disk electrode as a working electrode, platinum wire as a counter electrode, and SCE as a reference electrode with an agar salt bridge connecting to the oligomer solution. All of the potentials were calibrated with ferrocene, $E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.45 \text{ V vs SCE}$. ^f Estimated from the edge of electronic absorption spectra. ^g Determined by differential scanning calorimeter from remelt after cooling with a heating rate of $10^\circ \text{C}/\text{min}$ under N_2 . ^h Determined by thermal gravimetric analyzer with a heating rate of $10^\circ \text{C}/\text{min}$ under N_2 .

and 356 nm, respectively, and were generally structureless and blue shifted ($\sim 30 \text{ nm}$) relative to the corresponding diphenylamino end-capped oligofluorenes^{4b} (Figure 1a and

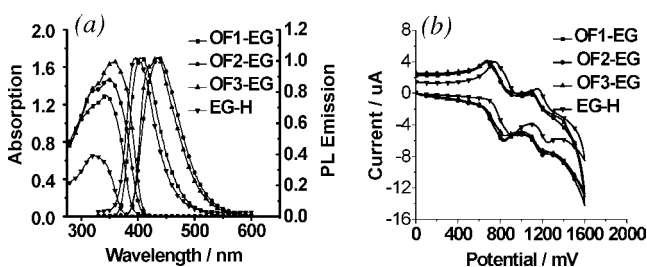
**Figure 1.** (a) Absorption and fluorescence spectra of **OF n -EG** and **EG-H**, measured in CHCl_3 . (b) Cyclic voltammograms of **OF n -EG** and **EG-H**, measured in CH_2Cl_2 .

Table 1). There is a substantial red-shift of the absorption maxima (λ_{\max}) of oligofluorenes ($\Delta 25-54 \text{ nm}$) upon incorporation of strongly electron-donating diphenylamino group(s) which is attributed to the asymmetric destabilization of the HOMO and the LUMO levels leading to the decrease in the energy gap;⁹ however, the introduction of dendrons onto the oligofluorene backbone causes the resulting molecule less planar than the analogues end-capped with diphenylamino groups in their electronic ground state leading to a blue shift in $\lambda_{\max}^{\text{abs}}$ ($\Delta 30-54 \text{ nm}$).¹⁰ The absorption maxima ($\lambda_{\max}^{\text{abs}}$) and molar absorptivities (ϵ_{\max}) of **OF n -EGs** increase sequentially as the core chain length increases (Figure 1a and Table 1). Surprisingly, the emission maxima ($\lambda_{\max}^{\text{em}}$: 404, 436, and 436 nm, respectively) of these dendrimers first red-shifted ($\Delta 5 \text{ nm}$) and then remained fairly constant at 436 nm (Figure 1a and Table 1). Upon excitation either at 324 nm attributed to the $n \rightarrow \pi^*$ transition of triarylamine- and carbazole-based dendron or at 350 nm corresponding to the $\pi \rightarrow \pi^*$ transition of oligofluorene core, the emission spectra obtained are identical, suggesting that energy or exciton can efficiently transfer from the peripheral

triarylamine to the fluorene core. The energy transfer efficiency (ETE) of this dendritic wedge is approximately 70% as estimated by comparing the difference in intensity at the absorption maximum of the dendritic wedges of the absorption spectrum and the fluorescence excitation spectrum. The fluorescence quantum yields (Φ_{PL}) measured in chloroform using quinine sulfate monohydrate as a standard are less than 0.01, 0.31, and 0.38, respectively, and increase as the core chain length increases, indicating the longer homologue has better coplanarity in the excited state than the shorter one; however, these Φ_{PL} values are quite smaller than those (~ 0.90) of the corresponding analogues only end-capped with diphenylamino groups,^{4b} suggesting that introduction of dendrons onto the oligofluorene skeleton perturbs the planarity and alters the fluorescent nature of oligofluorene core.

The electrochemical behaviors of these newly synthesized dendrimers are tabulated in Table 1 and Figure 1b. In contrast to the triaryldiamine,^{4b,c} the new dendrimers **OF n -EG** exhibit an electrochemical behavior similar to that of the triarylamine- and carbazole-based dendron **EG-H**, in which one reversible four-electron anodic redox couples ($E_{1/2} \sim 0.38 \text{ eV}$), corresponding to removal of electrons from the peripheral arylamino group of the dendrons, and another reversible two-electron anodic redox couple ($E_{1/2} \sim 0.70 \text{ eV}$), corresponding to removal of electrons from the interior carbazole moieties forming radical tetracations and hexylcations, respectively (Figure 1b). Both first oxidation potential and second oxidation potentials are essentially unaffected by the length and structure of the oligofluorene core as the oxidation occurs only at the wedges; however, both first oxidation potential values and second oxidation potential values of **OF n -EGs** are a bit smaller than those of **EG-H** ($E_{1/2}$: 0.40 and 0.75 eV, respectively) (Table 1), indicating that the incorporation of dendron **EG** makes the resulting dendrimers more susceptible for electrochemical oxidation. In general, with an incorporation of triarylamine-based dendritic end-caps, the HOMO energy level of oligofluorenes moves up to $\sim 5.20 \text{ eV}$ (relative to the vacuum level) as estimated by the electrochemical method. Such a high HOMO energy level greatly reduces the energy barrier for the hole injection from ITO ($\phi = 5.0 \text{ eV}$) to the emissive oligofluorenes. As a result, **OF n -EGs** can also be used as hole transport/injection materials.

(9) Wong, M. S.; Li, Z. H. *Pure Appl. Chem.* **2004**, *76*, 1409.

(10) (a) Berlmann, I. B.; *J. Phys. Chem.* **1970**, *74*, 3085. (b) Nijegorodov, N. I.; Downey, W. S. *J. Phys. Chem.* **1994**, *98*, 5639.

In summary, we have presented a facile approach for the synthesis of a family of dendrimers with hole-transporting ability moieties by copper-catalyzed Buchwald's double-amination as a key reaction. We believe that this approach will be applicable for the construction of other structurally uniform and well-defined π -conjugated functional dendronized compounds. All of the end-dendronized oligofluorene compounds were characterized by a combination of ^1H NMR, ^{13}C NMR, and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy.¹¹ These dendrimers exhibit very high thermal and electro-

(11) Yang, J.-X.; Tao, X.-T.; Yuan, C. X.; Yan, Y. X.; Wang, L.; Liu, Z.; Ren, Y.; Jiang, M. H. *J. Am. Chem. Soc.* **2005**, *127*, 3278.

chemical stabilities. The details on the OLEDs' performance using these materials as hole transfer and emitting layers or as host materials for electrophosphorescent applications will be reported in the future.

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Supporting Information Available: The synthetic procedures and physical data of all intermediates and **OF*n*-EG**, $n = 1-3$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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