

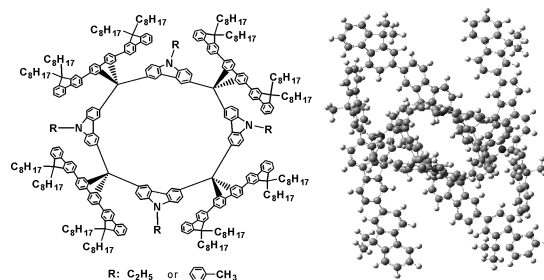
Macrospirocyclic Oligomers Based on
Carbazole and FluoreneYu Lu,[†] Yu Zhou,[†] Yi-Wu Quan,^{*,†} Qing-Min Chen,[†] Run-Feng Chen,[‡]
Zhi-Yong Zhang,[‡] Qu-Li Fan,^{*,‡} Wei Huang,^{*,‡} and Jian-Fu Ding[§]

Department of Polymer Science & Engineering, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China, Key Laboratory for Organic Electronics & Information Displays (KLOEID) and Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications, Nanjing 210046, China, and Institute for Chemical Process and Environmental Technology (ICPET), National Research Council of Canada, 1200 Montreal Road, Ottawa, Ontario, K1A 0R6, Canada

quanyiwu@nju.edu.cn; iamqlfan@njupt.edu.cn; wei-huang@njupt.edu.cn

Received October 26, 2010

ABSTRACT



Monodisperse macrospirocyclic oligomers were prepared using self-condensation of the Friedel–Crafts reaction. Through the C-9s of the central fluorene units of four surrounding oligofluorenes, four carbazole units are connected in a series to form a macrocyclic core. These rodlike oligofluorenes form a rigid three-dimensional structure, affording the resulting macrocyclics a high steric hindrance for close interchain packing.

Monodisperse oligofluorenes have recently become a subject of intense study for optoelectronic applications, due to their well-defined conjugation lengths and molecular structures, high photoluminescence (PL) and electroluminescence quantum efficiencies, ease of purification, characterization, and solution processing.

Moreover, monodisperse oligofluorenes also have been employed as ideal models to understand the fundamental properties of the polydisperse polymeric analogues.¹ Recent rapid development of new synthetic methods makes it possible to design a variety of monodisperse oligomers,² permitting efficient color and energy level tuning through

the control of effective conjugation length as well as the introduction of electron-donating and -withdrawing moieties into the conjugated systems. A number of monodisperse oligofluorenes have been synthesized as blue light-emitting materials.³ Among them, three-dimensional (3D) monodisperse oligofluorenes are noted for their specific structure to suppress undesired chain aggregation, excimer formation, and

[†] Nanjing University.

[‡] Nanjing University of Posts and Telecommunications.

[§] National Research Council of Canada.

(1) (a) Jo, J.; Chi, C.; Höger, S.; Wegner, G.; Yoon, D. Y. *Chem.—Eur. J.* **2004**, *10*, 2681–2688. (b) Zhou, X. H.; Zhang, Y.; Xie, Y. Q.; Cao, Y.; Pei, J. *Macromolecules* **2006**, *39*, 3830–3840. (c) Culligan, S. W.; Geng, Y.; Chen, S. H.; Klubek, K.; Vaeth, K. M.; Tang, C. W. *Adv. Mater.* **2003**, *15*, 1176–1180.

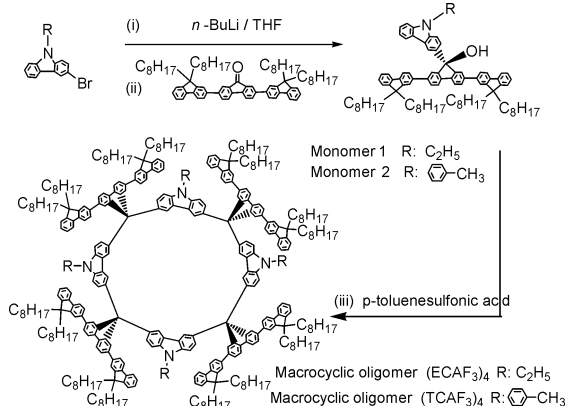
(2) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483. (b) Liu, F.; Xie, L. H.; Tang, C.; Liang, J.; Chen, Q. Q.; Peng, B.; Wei, W.; Cao, Y.; Huang, W. *Org. Lett.* **2009**, *11*, 3850–3853. (c) Koene, B. E.; Loy, D. E.; Thompson, M. E. *Chem. Mater.* **1998**, *10*, 2235–2250. (d) Zhao, Z.; Zhao, Y.; Lu, P.; Tian, W. J. *J. Phys. Chem. C* **2007**, *111*, 6883.

keto defects.⁴ The core and spiro-linked fluorene moieties constructed the rigid 3D structures, which formed excellent amorphous states to render the oligomers better photoluminescence stabilities and lower crystallization tendencies and excellent optoelectronic properties. However, challenge remains in achieving balanced charge injection and mobility in 3D oligofluorene.^{4d}

In this letter, we report the development of a new family of 3D macrocyclic oligofluorene by a Friedel–Crafts self-condensation reaction. In the produced macrocyclics, four carbazole units are connected in a series to form a macrocyclic core through the C-9s of the central fluorene units of four surrounding oligofluorenes, which, like rigid rods, extend from the ring plane in both sides. Due to nonconjugated 3D structure, these multi-H shaped oligomers have the advantages of (1) higher solubility, (2) reduced interchain interaction, (3) improved hole injection without sacrificing fluorene's electron-injection capability, and (4) easily doped capability due to hollow space structure.

The synthetic procedures used to prepare macrocyclic oligomers (ECAF₃)₄ and (TCAF₃)₄ are shown in Scheme 1.

Scheme 1. Synthetic Route of (ECAF₃)₄ and (TCAF₃)₄



N-Ethyl-3-bromocarbazole was reacted with *n*-BuLi in tetrahydrofuran at −78 °C, followed by the addition of an equivalent of 2,7-bis(9,9-dioctylfluorene-2-yl)-9-fluorenone to result in monomer 1. The oligomer (ECAF₃)₄ was then prepared by using self-condensation of the Friedel–Crafts reaction in mesitylene at 80 °C for 3 h in the presence of *p*-toluenesulfonic acid. This polycondensation reaction follows the aromatic electrophilic substitution mechanism. Carbazole,⁵ as well as triphenylamine,^{4c,6} is a very reactive

aromatic compound for the electrophilic substitution, because of the electron-donating property of the amino group, and reacts with the fluorenol group, which is a strong alkylating reagent,^{2b} for this self-condensation by the Friedel–Crafts procedure. The para position with respect to the nitrogen is a reactive site, while the ortho position is proved nonreactive due to steric hindrance effect.^{5,4c} The synthetic route for (TCAF₃)₄ was similar to the procedure for (ECAF₃)₄, where the starting material was *N*-(4-methylphenyl)-3-bromocarbazole. These reactions also potentially give a series of linear structural oligomers. Therefore, to optimize the production of the desired cyclic oligomer, a very low monomer concentration (1%) has been used for the reaction, which favors the formation of smaller cyclic oligomers.^{7,4c} A high purity of the macrocyclics has been proved by a simple color test. The linear side products contain a fluorenol moiety at the chain end. In the presence of *p*-toluenesulfonic acid in the mesitylene solution, this group will be converted to a fluorene cation, which has a deep blue color in the solution. Therefore, the mesitylene solution of the purified (ECAF₃)₄ or (TCAF₃)₄ was added with *p*-toluenesulfonic acid. No color change was observed in both solutions, confirming that there is no residual fluorenol in the purified macrocyclics.

The purity and structure of macrocyclics were also confirmed by the size exclusion chromatography (SEC), MALDI-TOF MS, NMR spectroscopy, and element analysis (see the Supporting Information). After the self-condensation reaction, the characteristic peak of the C-9 of the central fluorene units moves from 84.3 to 64.2 ppm in ¹³C spectra due to the disappearance of OH group. The SEC curve displays a narrow peak at 27.95 min for (ECAF₃)₄ and 27.93 min for (TCAF₃)₄. Both peaks have a *M*_n of 3800 Da with a very low *M*_w/*M*_n value (1.03). Because the *M*_n from SEC analysis is a polystyrene equivalent value, it is impossible to assign these peaks on the basis of the SEC data alone. Therefore, the products were also analyzed by MALDI-TOF mass spectroscopy. A single peak at *m/z* 4538.5 for (ECAF₃)₄ and *m/z* 4788.3 for (TCAF₃)₄ corresponds to the macrocyclic tetramer. All of these results show that the desired compound could be obtained in high purity and agree well with the structures of the respective macrocyclic tetramer.

The chemical structure of the 3D macrocyclic oligofluorenes was simulated by the density functional theory method (B3LYP) at the 6-31G(d) level on the model compound of (MCAF₃)₄, which simplified the substitutions on the 9-posi-

(3) (a) Wu, C. C.; Lin, Y. T.; Wong, K. T.; Chen, R. T.; Chien, Y. Y. *Adv. Mater.* **2004**, *16*, 61–65. (b) Lai, W. Y.; He, Q. Y.; Zhu, R.; Chen, Q. Q.; Huang, W. *Adv. Funct. Mater.* **2008**, *18*, 265–276. (c) Liu, Q.; Lu, J.; Ding, J.; Day, M.; Tao, Y.; Barrios, P.; Stupak, J.; Chan, K.; Li, J.; Chi, Y. *Adv. Funct. Mater.* **2007**, *17*, 1028–1036. (d) Kreger, K.; Bäte, M.; Neuber, C.; Schmidt, H. W.; Strohrriegel, P. *Adv. Funct. Mater.* **2007**, *17*, 3456–3461. (e) Liu, X.; Xu, J.; Lu, X.; He, C. *Org. Lett.* **2005**, *7*, 2829–2832. (f) Tao, S.; Peng, Z.; Zhang, X.; Wang, P.; Lee, C.; Lee, S. *Adv. Funct. Mater.* **2005**, *15*, 1716–1721. (g) Lai, W. Y.; Xia, R.; He, Q. Y.; Levermore, P. A.; Huang, W.; Bradley, D. D. C. *Adv. Mater.* **2009**, *21*, 355–360.

(4) (a) Luo, J.; Zhou, Y.; Niu, Z. Q.; Zhou, Q. F.; Ma, Y.; Pei, J. *J. Am. Chem. Soc.* **2007**, *129*, 11314–11315. (b) Zhang, X.; Quan, Y.; Cui, Z.; Chen, Q.; Ding, J.; Lu, J. *Org. Chem.* **2010**, 2295–2303. (c) Kong, Q.; Zhu, D.; Quan, Y.; Chen, Q.; Ding, J.; Lu, J.; Tao, Y. *Chem. Mater.* **2007**, *19*, 3309–3318. (d) Lei, T.; Luo, J.; Wang, L.; Ma, Y.; Wang, J.; Cao, Y.; Pei, J. *New J. Chem.* **2010**, *34*, 699–707. (e) Ye, S.; Chen, J.; Di, C.; Liu, Y.; Lu, K.; Wu, W.; Du, C.; Liu, Y.; Shuai, Z.; Yu, G. *J. Mater. Chem.* **2010**, *20*, 3186–3194. (f) Xie, L. H.; Hou, X. Y.; Tang, C.; Hua, Y. R.; Wang, R. J.; Chen, R. F.; Fan, Q. L.; Wang, L. H.; Wei, W.; Peng, B.; Huang, W. *Org. Lett.* **2006**, *8*, 1363–1366.

(5) Shih, P. I.; Chiang, C. L.; Dixit, A. K.; Chen, C. K.; Yuan, M. C.; Lee, R. Y.; Chen, C. T.; Diao, E. W.; Shu, C. F. *Org. Lett.* **2006**, *8*, 2799–2802.

(6) Shih, P. I.; Chien, C. H.; Wu, F. I.; Shu, C. F. *Adv. Funct. Mater.* **2007**, *17*, 3514–3520.

(7) Ding, J.; Liu, F.; Li, M.; Day, M.; Zhou, M. *J. Polym. Sci., Part A* **2002**, *40*, 4205–4216.

tion of fluorenes with methyl to reduce the calculation costs, since those substitutions have limited influence on the structural and optoelectronic properties of these compounds.⁸ The optimized conformation of (MCAF₃)₄ with energy minimization shown in Figure 1 suggests that the architecture

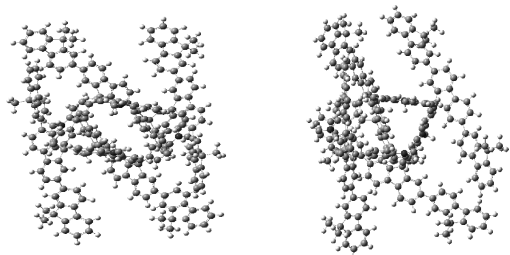


Figure 1. Optimized geometry of macrocyclic oligomer (MCAF₃)₄, calculated by B3LYP at the 6-31G(d) level: (left) rear view and (right) side view (blue ball = N atom).

consists of four terfluorene chains as the arms of the H-shape and four carbazoles as the ring, connecting via completely rigid spiro linkages with four C-9 sp³ atoms of the central fluorene units. The arms of terfluorene, like rigid rods, extend from the ring plane on both sides. We anticipate that this 3D structure would restrict close interchain packing of the oligomer chains and reduce chain interactions and, consequently, suppress aggregate/excimer formation and enhance PL efficiency.

The thermal properties of (ECAF₃)₄ and (TCAF₃)₄ were characterized by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). DSC of the heating/cooling/reheating scan was measured in nitrogen at a heating rate of 10 deg/min. The curve reveals no obvious melt temperature for (ECAF₃)₄ and (TCAF₃)₄ below 200 °C, and only a small glass transition temperature at 132 °C can be found in the first heating scan in the DSC curve of (ECAF₃)₄, indicating that both (ECAF₃)₄ and (TCAF₃)₄ have a stable amorphous structure below 200 °C. TGA analysis indicates that both oligomers are thermally stable with 5% weight loss at temperatures over 350 °C.

Figure 2 shows the UV absorption and PL spectra of (ECAF₃)₄ and (TCAF₃)₄ in cyclohexane. There is a negligible shift in absorption and PL spectra for both macrocyclics from solution to the solid state, indicating the absence of strong interchain interaction in the solid thin films. The PL spectra show very little change after annealing in nitrogen at 120 °C for 24 h (see Figure 2). Only relative intensity changes were observed in the vibronic peaks, whereas the emission peak positions remain unchanged. Moreover, no additional PL peak was observed between 500 and 600 nm in the spectra of (ECAF₃)₄ and (TCAF₃)₄ films, as often appear in the PL spectra of poly(dialkylfluorene) films after thermal annealing. Both macrocyclics have very strong fluorescence

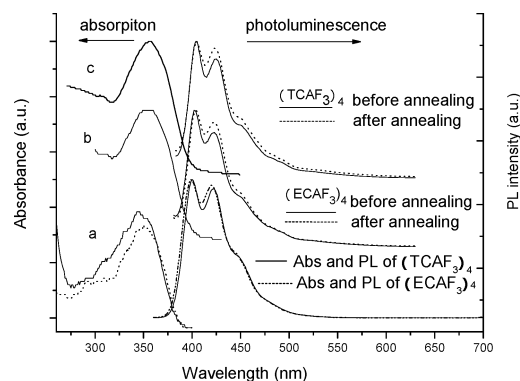


Figure 2. (a) UV-vis absorption and PL spectra of (ECAF₃)₄ and (TCAF₃)₄ in cyclohexane; (b) thin film PL spectra of (ECAF₃)₄; and (c) thin film PL spectra of (TCAF₃)₄.

in the pure-blue region. The PL efficiencies (φ_f) of oligomers were measured in dilute cyclohexane solution with 9,10-diphenylanthracene ($\varphi_f = 0.90$ in cyclohexane) as a reference. The solution PL quantum efficiency of (ECAF₃)₄ and (TCAF₃)₄ was found to be 0.80 and 0.89, respectively. These values are higher than those of carbazole-substituted linear polyfluorene, which showed efficiencies of 0.60–0.80.⁹

The HOMO and LUMO orbitals of the model compound (MCAF₃)₄ were calculated by B3LYP at the 6-31G(d) level (see Figure 3). Its HOMOs and LUMOs are quite localized

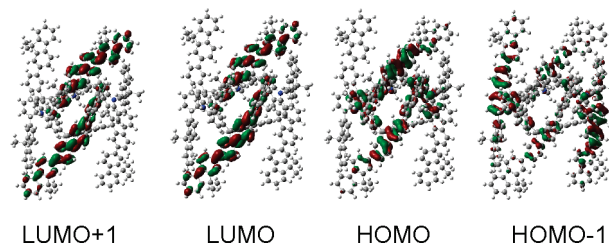


Figure 3. The computed isodensity surface of HOMO and LUMO orbitals of (MCAF₃)₄.

due to core-shell geometry of the compounds, where the electron density distribution at HOMOs becomes localized at the core carbazole units due to the good hole transport properties of carbazoles, whereas the LUMOs are predominately determined by H-shaped arms of the terfluorene chain as shown in Figure 3. In comparison with the frontier orbitals of terfluorene listed in Table 1, the participation of carbazole in (MCAF₃)₄ results in increased HOMO, suggesting the increased hole injection properties of the core-shell compounds. It is expected that these macrospirocyclic oligomers have a p-type core with high hole injection and transport properties and a blue light emissive terfluorene shell with

(8) Pal, B.; Yen, W. C.; Yang, J. S.; Chao, C. Y.; Hung, Y. C.; Lin, S. T.; Chuang, C. H.; Chen, C. W.; Su, W. F. *Macromolecules* **2008**, *41*, 6664–6671.

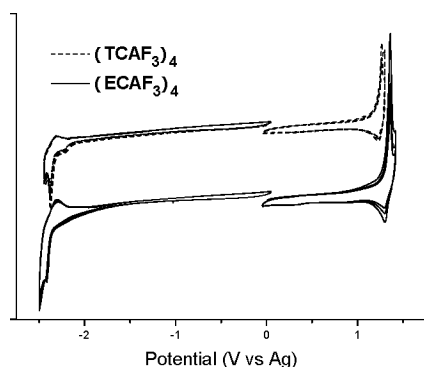
(9) Li, Y.; Ding, J.; Day, M.; Tao, Y.; Lu, J.; D'iorio, M. *Chem. Mater.* **2004**, *16*, 2165–2173.

Table 1. Electrochemical Properties of (ECA_F₃)₄ and (TCA_F₃)₄

compd	$E_{\text{HOMO}}/\text{eV}$	$E_{\text{LUMO}}/\text{eV}$	E_g/eV
(TCA _F ₃) ₄	−5.33	−2.28	−3.05
(ECA _F ₃) ₄	−5.28	−2.29	−2.99
(MCA _F ₃) ₄	−5.03	−1.31	−3.72
terfluorene ¹¹	−5.20	−1.36	−3.85

high geometric separation between the emitters to avoid the excimer formation, which is one of the important factors that are responsible for the poor color stability of the fluorene-based materials.

The HOMO and LUMO energy levels of (ECA_F₃)₄ and (TCA_F₃)₄ were also investigated by cyclic voltammetry (CV) (see Figure 4). The E_{LUMO} and E_{HOMO} of a material can be

**Figure 4.** CV curves of (ECA_F₃)₄ and (TCA_F₃)₄.

estimated by using the equations $E_{\text{HOMO}} = -(E_p' + 4.38)$ eV and $E_{\text{LUMO}} = -(E_n' + 4.38)$ eV.^{9,10} The onset oxidation potential (E_p') and onset reduction potential (E_n') are 0.90 and −2.09 V for (ECA_F₃)₄ and 0.95 and −2.10 V for (TCA_F₃)₄, respectively. These values correspond to an E_{HOMO} of −5.28 eV and an E_{LUMO} of −2.29 eV for (ECA_F₃)₄, and an E_{HOMO} of −5.33 eV and an E_{LUMO} of −2.28 eV for (TCA_F₃)₄. Figure 4 also shows that both the p- and n-doping processes for oligomers are reversible. Under successive multiple potential scans, the oligomer film only showed a small decrease in the current intensity in the n-doping process, and displayed a 15–30% loss of current intensity

(10) Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth. Met.* **1997**, *87*, 53–59.

(11) Chen, R. F.; Zheng, C.; Fan, Q. L.; Huang, W. J. *Comput. Chem.* **2007**, *28*, 2091–2101.

after several p-doping scans. The decrease in the current on cycling arises from the fact that (ECA_F₃)₄ and (TCA_F₃)₄ are not polymers but short oligomers that are somewhat soluble in their neutral or charged forms in the solvent used. Traditionally, introduction of carbazole units in conjugated polymers or organic molecules is found to effectively enhance the hole-injecting properties of the resulting materials. At the same time, it also causes an increase in the LUMO energy level, resulting in an increased energy barrier for electron injection from the metal cathode.⁹ The existence of the carbazole units in these macrocyclics does not apparently show this effect. This result indicates that introducing a carbazole macrocyclic core into these oligomers promotes their hole-injection capability, but does not sacrifice their electron-injection capability. This property should be attributed to the novel structure of the multicarbazole cyclic core, which is not conjugated with the oligofluorene units in the oligomers. This property is superior for balancing the hole and electron injection into the emitting layers.

In summary, two novel macrospirocyclic oligomers with carbazole and fluorene units were synthesized by using a simple Friedel–Crafts reaction. The carbazole-based cyclic core serves as a nonconjugated spacer bearing oligofluorene arms to form a multi-H shaped structure of the oligomers so that the optoelectronic properties of the individual oligofluorene arm remain relatively unperturbed. Both oligomers show excellent thermal stability and high photoluminescence quantum efficiency. Electrochemical analysis and density functional theory calculations showed that the nonconjugated carbazole core promotes the hole-injection capability of the oligomers, but does not sacrifice their electron-injection capability.

Acknowledgment. This work was financially supported by the National Basic Research Program of China under Grant 2009CB930600, the National Natural Science Foundation of China under Grants 90406021, 20874048, and 20804020, the Fok Ying-Tong Education Foundation under Grant 111051, the Research Fund for the Doctoral Program of Higher Education under Grant 20093223110003, and the Natural Science Foundation of Jiangsu Province of China under Grant BK2008453. Y.Q. thanks Qingwei Hang of Nanjing University for NMR analysis and fruitful discussions.

Supporting Information Available: Experimental procedures and NMR, SEC, DSC, and MALDI-TOF-MS spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL1025958