

Review

The Design of Second-order Nonlinear Optical Dendrimers: From “Branch Only” to “Root Containing”*

Peng-yu Chen and Zhen Li**

Department of Chemistry, Wuhan University, Wuhan 430072, China

Abstract Dendrimers are considered as a promising family of organic second-order nonlinear optical (NLO) polymers because of their well-defined structures, easily modified peripheral functional groups, interior branches and central cores. In order to obtain NLO materials with high performance, dendrimer structures have been optimized in the past years, such as the “branch only” and the “root containing” type dendrimers. This feature article highlights the achievements in exploring the rational design of dendrimers, partially marked by their macroscopic NLO performance.

Keywords Second-order nonlinear optics; Hyperbranched polymer; Dendrimer; Tree

INTRODUCTION

In the past decades, a lot of efforts have been paid to study on the organic second-order nonlinear optical (NLO) polymers owing to their potential applications in photonic devices, such as high-speed electro-optic modulators, optical switches and frequency converters. Up to now, many strategies and approaches have been reported for the development of organic NLO polymers which meet the basic requirements of practical applications, including large optical nonlinearity, low optical loss, and excellent temporal stability of dipole orientation^[1–11].

A major problem encountered in optimizing organic NLO polymers is to overcome the strong dipole-dipole interactions among the chromophore moieties with a donor- π -acceptor structure. Thus, to efficiently translate the large β values of the organic chromophores to high macroscopic NLO activities of polymers is crucial. As shown in Fig. 1(A), the chromophore moieties in polymers tend to centrosymmetric arrangement due to the strong electrostatic interaction. However, on the contrary, the macroscopic second-order NLO coefficient is based on the non-center symmetric arrangement of chromophores. Thus, the poling process, as an effective approach, is utilized to achieve the ordered arrangement of chromophore moieties. According to the site-isolation principle, the more spherical the molecular structure is, the larger the reduction in dipole-dipole interactions is. Accordingly, many reports present the optimization of ordered alignment of the chromophores. Based on our systematically experimental results, we proposed the concepts of “suitable isolation group (SIG)” and “isolation chromophore (IC)”^[12–21] (Fig. 1B). In these reports, the shapes of chromophores were changed to spheres for reducing the strong electronic interactions among the chromophores with high loading density, which improved the macroscopic second-order NLO performance as compared with that of original chromophores. In recent years, dendrimers are widely used to investigate as the second-order NLO materials due to their spherical shapes, clear structure-property relationship, and easy to be optimized topology structure^[22–24].

* This work was financially supported by the National Natural Science Foundation of China (No. 21325416).

** Corresponding author: Zhen Li (李振), E-mail: lizhen@whu.edu.cn

Received January 4, 2017; Revised March 11, 2017; Accepted March 16, 2017

doi: 10.1007/s10118-017-1949-y

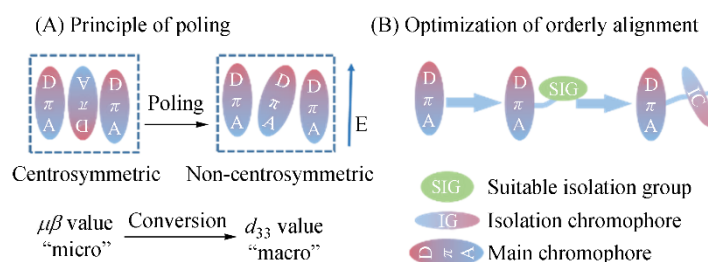


Fig. 1 Graphical representation of second-order NLO polymers containing chromophore moieties with the structure of Donor- π -Acceptor (D- π -A): (A) principle of poling, (B) optimization of orderly alignment

In this article, several series of dendrimers are presented with different structures, and their NLO properties are demonstrated and compared. Briefly, the design ideas of NLO dendrimers are clearly summarized, including the “branch only” and “root containing” dendrimers.

DESIGN OF DENDRIMERS

“Branch Only” Dendrimers

Generally, there are two or more dendrons attached to a core of a dendrimer molecule, in which the direction of dipolar moment of the chromophore moieties in dendrons can be regarded as the direction of dendrons. For some dendrons whose directions are from the center to the end, they are named as “branches”, while others with the directions from the end to the center are named as “roots”. Normally, in our initially designed dendrimers, all the dendrons are “branches”. Thus, they could be regarded as “branch only” dendrimers.

Two Boughs G1 to G5

As a typical example (Fig. 2), the nitro azobenzene chromophores-based dendrimers with generation 1–5 (**G1**–**G5**) were synthesized *via* “click reaction”^[25], in which two boughs were extended from a core. The triazole rings formed as the linkages and suitable isolation group during the synthetic process. The number of terminus branches of next generation is two times that of the previous one, and the numbers of the total chromophore moieties in **G1**–**G5** are 2, 6, 14, 30 and 62, respectively. **G1**–**G3** exhibit similar NLO properties and their d_{33} values (the parameter to characterize the macroscopic NLO performance) are 100, 108 and 123 pm V⁻¹, respectively, while for the higher generation dendrimers of **G4** and **G5**, excellent NLO performances are achieved with the d_{33} values of 177 and 193 pm·V⁻¹, respectively, confirming that with the increase of generation, the shape of dendrimers becomes more sphere-like.

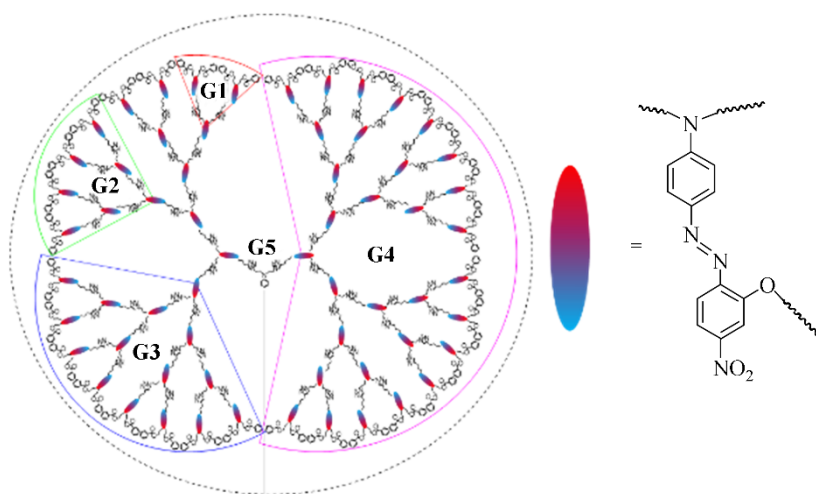


Fig. 2 Dendrimers with two boughs from a core

Three Boughs G1-TPA to G3-TPA

A series of dendrimers with three boughs protruding from a core, **G_n-triphenylamine (G_n-TPA)** ($n = 1-3$), were designed and synthesized^[26] to explore the effect of topological structures of dendrimers^[26] (Fig. 3). The obtained “three boughs” dendrimers are more spherical shape than the “two boughs” ones. Excitedly, the d_{33} values of **G1-TPA**, **G2-TPA**, and **G3-TPA** are found to be 214, 219 and 246 pm·V⁻¹, respectively, much higher than that of **G5** (193 pm·V⁻¹), indicating the important role of topological structures of dendrimers for improving the NLO properties.

Many dendrimers with the similar topology above mentioned have been prepared and show good NLO performance, but their d_{33} values cannot be higher than 260 pm·V⁻¹. This may be mainly ascribed to the relatively low nonlinearity of azo chromophores combined in these dendrimers. However, the optimization of topological structures of dendrimers is a useful way for enhancing the macroscopic NLO performance.

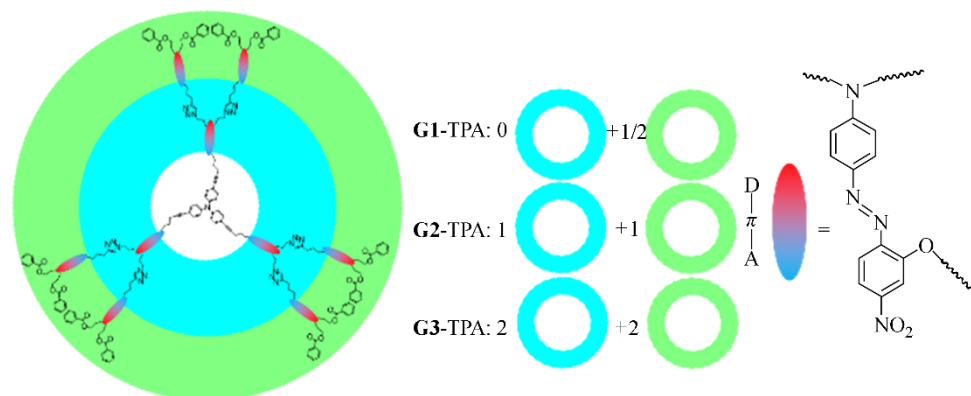


Fig. 3 Dendrimers with three boughs extended from a core

“Root Containing” Dendrimers

Recently, we have synthesized a new kind of Janus-type NLO dendrimers with both branches and roots, which can be considered as “root containing” dendrimers. The topological structure of such dendrimers is more spherical-like than that of “branch only” ones, resulting in further reduction of the dipole-dipole intermolecular interactions based on the “site isolation principle”^[27–29]. More importantly, there is a certain orientation of the chromophore moieties in the “root containing” dendrimers without poling. As shown in Fig. 4, from the deep root to the treetop, a partially natural ordered orientation of the chromophore moieties is realized. It is just like a tree to make the “root containing” dendrimers be easily poled to achieve the required non-centrosymmetric alignment of chromophore moieties.

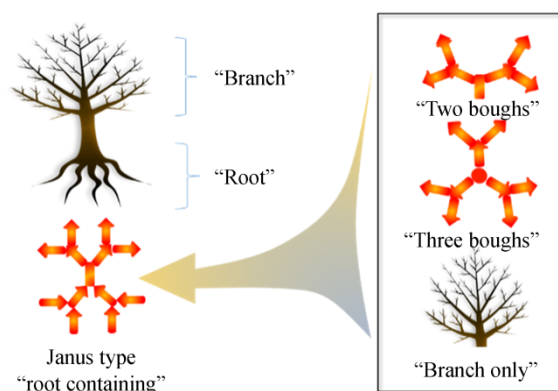


Fig. 4 Schematic diagram of the synthesis to “root containing” dendrimers

As shown in Fig. 5, all of the dendrimers **J-1**, **J-2** and **J-3** have both branches and roots in the structures^[30], which have been synthesized *via* a convenient convergent-then-divergent synthetic route, *i.e.* from roots to center then to branches. Interestingly, they exhibit high NLO efficiency with the d_{33} values of 157, 195 and 299 pm·V⁻¹, in spite of fewer chromophores in the structure. Especially, **J-3** possesses much higher NLO performance than that of **G5** (193 pm·V⁻¹) containing 62 chromophore moieties. This successful example holds significant promise for designing and controlling the “root containing” dendrimers with desired performance in the application of NLO materials.

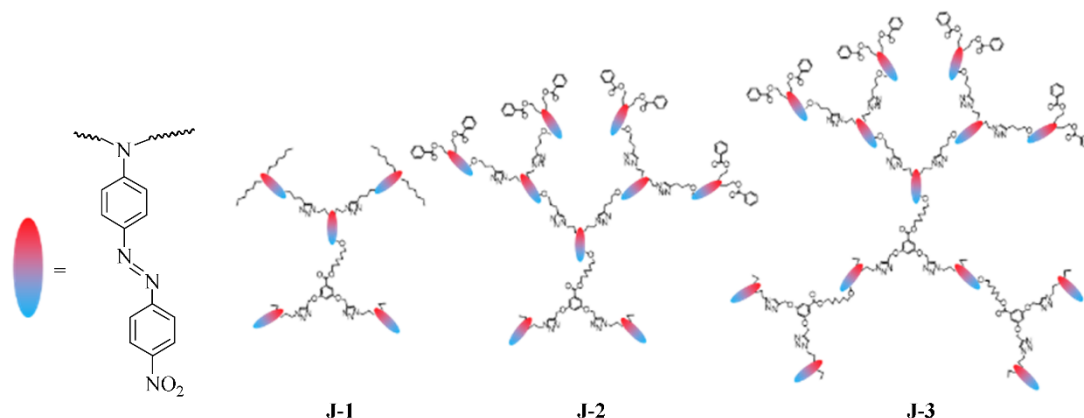


Fig. 5 Dendrimers with roots

CONCLUSIONS AND PROSPECTS

In recent years, design and synthesis of NLO dendrimers have been rapidly developed, including the “branch only” and “root containing” dendrimers. The resulting dendrimers containing normal azobenzene chromophores showed better NLO performance with the largest d_{33} of 299 pm·V⁻¹. However, there are still two main problems: one is the time-consuming and complexity of synthetic procedures, especially for the higher generation dendrimers; another is the temporal stability of NLO coefficient of dendrimers. To address such shortcomings, combination of dendritic structures with other types of polymers may be a reasonable design way.

Lower generation dendrons are used as monomers to form macromolecules through different reactions, the structures of which are shown in Fig. 6. According to the different synthetic approaches and the structures, polymers containing dendritic molecules can be divided into dendronized polymers (DP), main chain dendronized polymers (MCDP) and dendronized hyperbranched polymers (DHP)^[30–33]. Among them, DHP is a new concept coined by our group in 2013. The relatively high-molecular weights and complicated three-

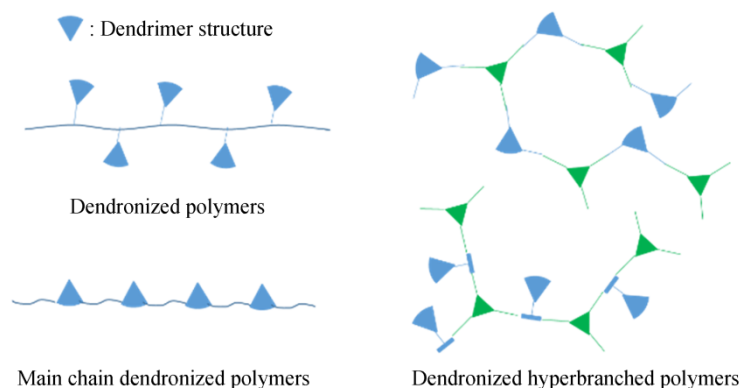


Fig. 6 Different kinds of polymers containing dendritic structures

dimensional structures endow the NLO polymers with excellent temporal stability of NLO coefficients. For example, **G1**-based DHPG1 achieved (Fig. 7)^[32] the d_{33} value of $133 \text{ pm} \cdot \text{V}^{-1}$, larger than those of **G1**- and **G2**-dendrimers. More importantly, the decay temperature of NLO signal is higher than 105°C , while those of **G1** and **G2** are only around 70°C , demonstrating an important advantage of DHPs used as NLO materials.

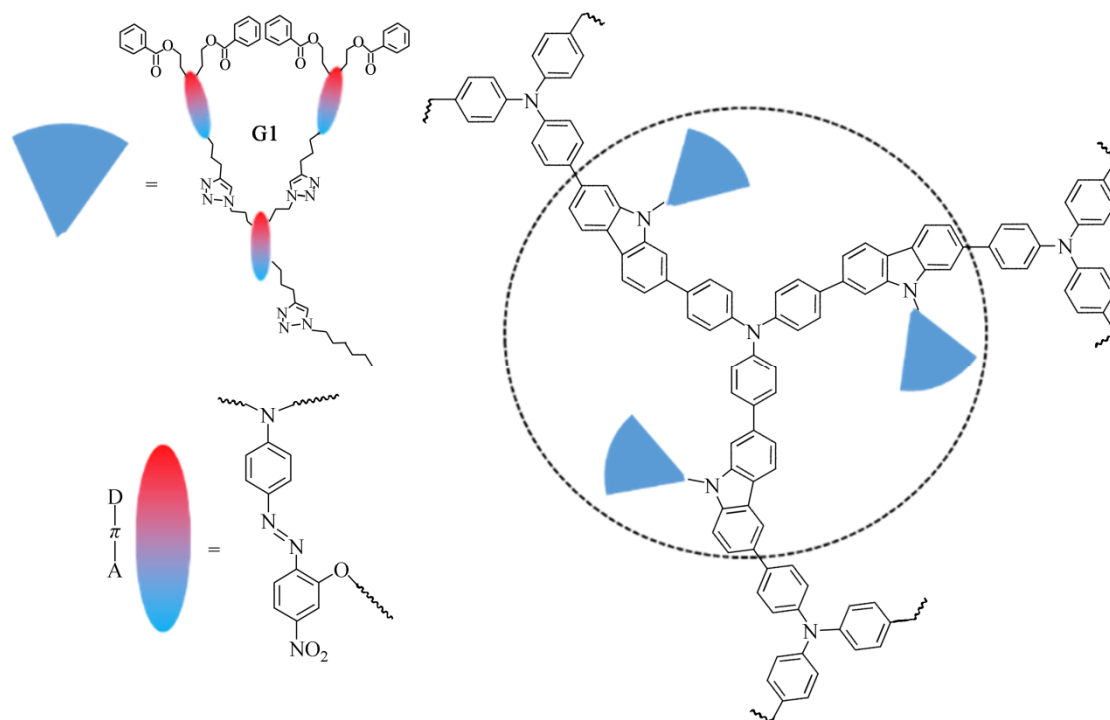


Fig. 7 Molecular structure of DHPG1

We may speculate that the optimization of topological structures of dendrimers is a promising way for developing new polymerization approaches, new topological polymers and building-up new structure-property relationships. With the deepening of study, the NLO materials with simple synthetic approach, high performance and good stability are expected to be obtained soon. It may also be predicted that the combination of NLO materials with polymers, especially with dendritic polymers, will arouse new interesting points for the further improvement in each side.

REFERENCES

- 1 Burland, D.M., Miller, R.D. and Walsh, C.A., *Chem. Rev.*, 1994, 94(1): 31
- 2 Marks, T.J. and Ratner, M.A., *Angew. Chem. Int. Ed.*, 1995, 34(2): 155
- 3 Yu, D., Gharavi, A. and Yu, L., *J. Am. Chem. Soc.*, 1995, 117(47): 11680
- 4 Marder, S.R., Kippelen, B., Jen, A.K.Y. and Peyghambarian, N., *Nature*, 1997, 388(6645): 845
- 5 Shi, Y., Zhang, C., Zhang, H., Bechtel, J.H., Dalton, L.R., Robinson, B.H. and Steier, W.H., *Science*, 2000, 288(5463): 119
- 6 Lee, M., Katz, H.E., Erben, C., Gill, D.M., Gopalan, P., Heber, J.D. and McGee, D.J., *Science*, 2002, 298(5597): 1401
- 7 Bai, Y., Song, N., Gao, J., Sun, X., Wang, X., Yu, G. and Wang, Z., *J. Am. Chem. Soc.*, 2005, 127(7): 2060
- 8 McLaughlin, C.V., Hayden, L.M., Polishak, B., Huang, S., Luo, J., Kim, T.D. and Jen, A.K.Y., *Appl. Phys. Lett.*, 2008, 92(15): 151107

- 9 Luo, J., Zhou, X. and Jen, A.K.Y., *J. Mater. Chem.*, 2009, 19(40): 7410
- 10 Dalton, L.R., Sullivan, P.A. and Bale, D.H., *Chem. Rev.*, 2010, 110(1): 25
- 11 Luo, J., Huang, S., Shi, Z., Polishak, B.M., Zhou, X.H. and Jen, A.K.Y., *Chem. Mater.*, 2011, 23(3): 544
- 12 Li, Z., Li, P., Dong, S., Zhu, Z., Li, Q., Zeng, Q., Li, Z., Ye, C. and Qin, J., *Polymer*, 2007, 48(13): 3650
- 13 Li, Z., Wu, W., Ye, C., Qin, J. and Li, Z., *J. Phys. Chem. B*, 2009, 113(45): 14943
- 14 Li, Z., Dong, S., Yu, G., Li, Z., Liu, Y., Ye, C. and Qin, J., *Polymer*, 2007, 48(19): 5520
- 15 Tang, R., Zhou, S., Cheng, Z., Yu, G., Peng, Q., Zeng, H., Guo, G., Li, Q. and Li, Z., *Chem. Sci.*, 2017, 8(1): 340
- 16 Chen, P., Yin, X., Xie, Y., Li, S., Luo, S., Zeng, H., Guo, G., Li, Q. and Li, Z., *J. Mater. Chem. C*, 2016, 4(48): 11474
- 17 Wu, W., Tang, R., Li, Q. and Li, Z., *Chem. Soc. Rev.*, 2015, 44(12): 3997
- 18 Li, Q. and Li, Z., *Polym. Chem.*, 2015, 6(38): 6770
- 19 Li, Z., Li, Q. and Qin, J., *Polym. Chem.*, 2011, 2(12): 2723
- 20 Li, Z., Li, Z., Di, C., Zhu, Z., Li, Q., Zeng, Q., Zhang, K., Liu, Y., Ye, C. and Qin, J., *Macromolecules*, 2006, 39(20): 6951
- 21 Wu, W., Li, C., Yu, G., Liu, Y., Ye, C., Qin, J. and Li, Z., *Chem. Eur. J.*, 2012, 18(35): 11019
- 22 Robinson, B.H. and Dalton, L.R., *J. Phys. Chem. A*, 2000, 104(20): 4785
- 23 Robinson, B.H., Dalton, L.R., Harper, A.W., Ren, A., Wang, F., Zhang, C., Todorova, G., Lee, M., Aniszfeld, R., Garner, S., Chen, A., Steier, W.H., Houbrecht, S., Persoons, A., Ledoux, I., Zyss, J. and Jen, A.K.Y., *Chem. Phys.*, 1999, 245(1-3): 35
- 24 Dalton, L.R., Steier, W.H., Robinson, B.H., Zhang, C., Ren, A., Garner, S., Chen, A., Londergan, T., Irwin, L., Carlson, B., Fifield, L., Phelan, G., Kincaid, C., Amend, J. and Jen, A.K.Y., *J. Mater. Chem.*, 1999, 9(9): 1905
- 25 Li, Z., Wu, W., Li, Q., Yu, G., Xiao, L., Liu, Y., Ye, C., Qin, J. and Li, Z., *Angew. Chem. Int. Ed.*, 2010, 49(15): 2763
- 26 Wu, W., Huang, L., Song, C., Yu, G., Ye, C., Liu, Y., Qin, J., Li, Q. and Li, Z., *Chem. Sci.*, 2012, 3(4): 1256
- 27 Frechet, J.M.J., *Proc. Natl. Acad. Sci. U.S.A.*, 2002, 99(8): 4782
- 28 Frechet, J.M.J., Henmi, M., Gitsov, I., Aoshima, S., Leduc, M.R. and Grubbs, B., *Science*, 1995, 269(5227): 1080
- 29 Hecht, S. and Frechet, J.M.J., *Angew. Chem., Int. Ed.*, 2001, 40(1): 74
- 30 Tang, R., Zhou, S., Xiang, W., Xie, Y., Chen, H., Peng, Q., Yu, G., Liu, B., Zeng, H., Li, Q. and Li, Z., *J. Mater. Chem. C*, 2015, 3(17): 4545
- 31 Grayson, S.M. and Frechet, J.M.J., *Chem. Rev.*, 2001, 101(12): 3819
- 32 Wu, W., Huang, L., Fu, Y., Ye, C., Qin, J. and Li, Z., *Chin. Sci. Bull.*, 2013, 58(22): 2753
- 33 Tang, R., Chen, H., Zhou, S., Xiang, W., Tang, X., Liu, B., Dong, Y., Zeng, H. and Li, Z., *Polym. Chem.*, 2015, 6(31): 5580