2838 *Chem. Mater.* **2000,** *12,* 2838−2841

Novel Two-Photon Absorbing Dendritic Structures

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Received July 17, 2000
Revised Manuscript Received August 30, 2000

Since its theoretical prediction[1] and experimental demonstration,[2] the phenomenon of two-photon absorption (TPA) has received steadily increasing attention. Recent development of a variety of new chromophores[3] with measurable two-photon absorption cross sections (σ_2) has fuelled research in a number of new areas, including two-photon photodynamic therapy,[4] optical power limiting,[5] two-photon fluorescence microscopy,[6] frequency-upconverted lasing,[7] and three-dimensional optical data storage and microfabrication.[8] To expand the utility of two-photon absorbing materials, it is necessary to further increase their TPA either by increasing the molecular two-photon cross section or by increasing the chromophore number density without causing aggregation. Numerous researchers have devoted significant effort toward this goal by developing chromophores with novel structures and conjugation patterns.[3] Theoretical investigations to determine structure−property relationships of TPA chromophores have also been initiated.[9] Here, we describe a new approach to the development of discrete macromolecules with tunable TPA cross sections. We have synthesized and studied a series of dendrimers functionalized with TPA chromophores at their periphery. In these molecules, the TPA cross section nearly doubles from one dendrimer generation to the next.

The synthesis of the dendrimers relies on the availability of a soluble two-photon absorbing chromophore having a functional group through which it may be attached to a dendritic backbone. One example of such a molecule is chromophore **1**, depicted in Scheme 1. This chromophore, synthesized by the methods of Prasad and co-workers,[10] is modified with a benzyl alcohol functionality through which it can be linked to a dendritic structure. Coupling of **1** to the protected diacid **2**[11] was achieved at room temperature using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) and a catalytic amount of (dimethylamino)pyridine (DMAP) in CH_2Cl_2 (Scheme 1). Because of the difficulty of chromatographic separation of this first-generation (G-1) protected phenol from the chromophore **1**, the phenol was deprotected using 2 equiv of tetrabutylammonium fluoride (TBAF) in THF prior to purification. The resulting compound **3** was then easily purified by silica gel chromatography. Preparation of the second-generation (G-2) dendron was achieved by reaction of the phenol **3** with the previously described[12] protected bis-

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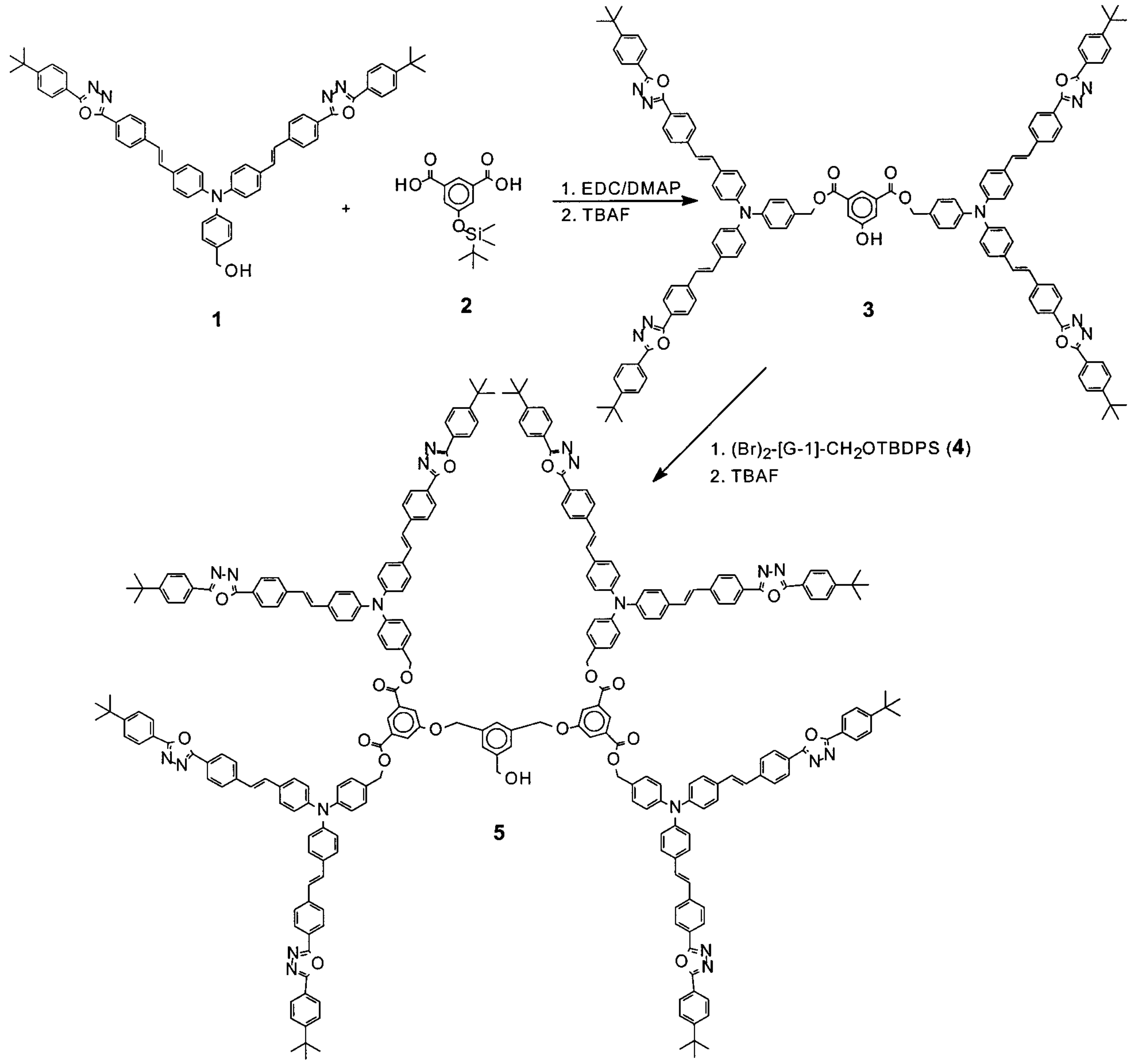
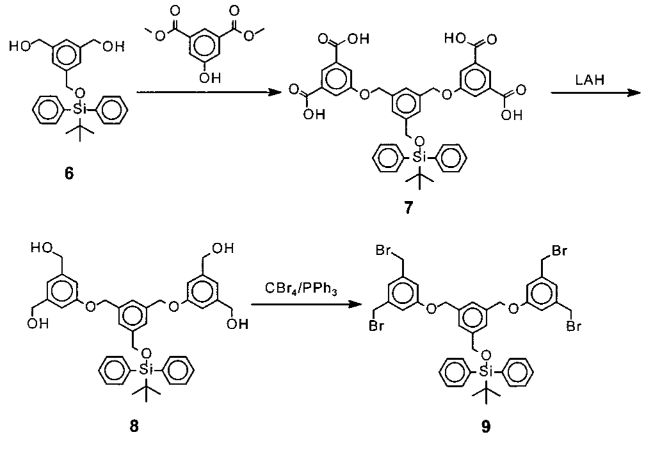
10.1021/cm000586o CCC: $19.00

Scheme 1



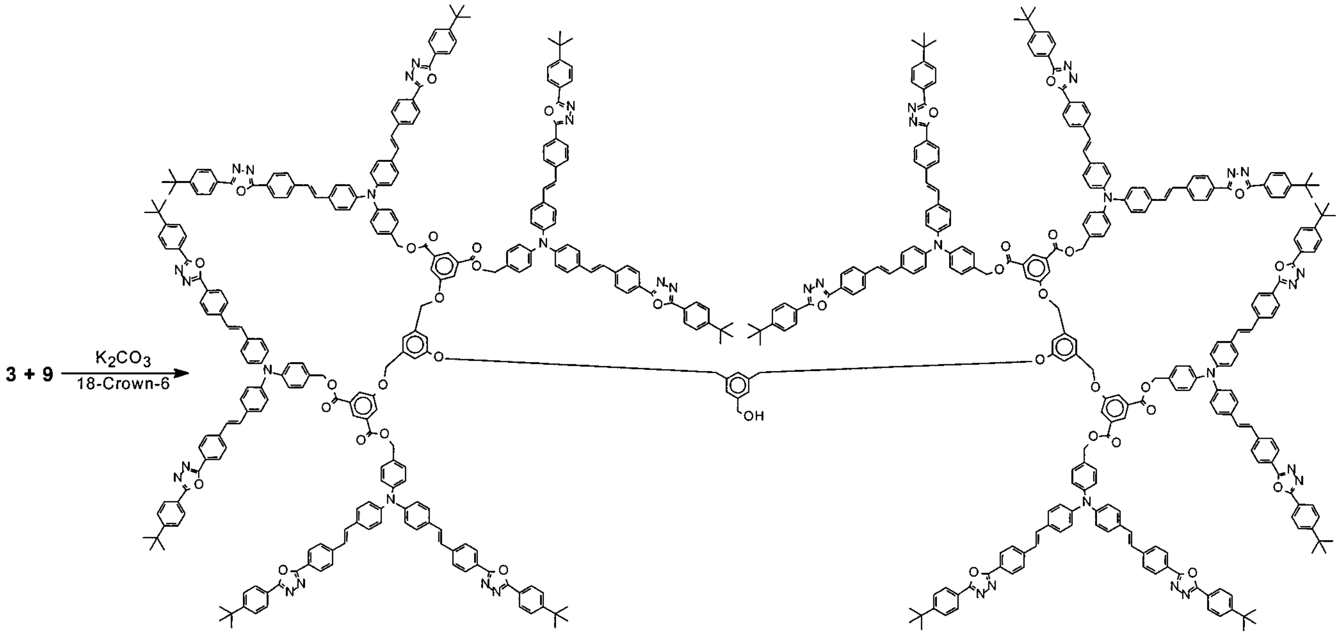
(benzyl bromide) **4** using standard phase transfer conditions.[12] Again, deprotection was performed prior to purification, allowing final isolation of the G-2 benzyl alcohol **5** in 80% yield. The G-1 phenol was again utilized for the preparation of the G-3 compound. Here, utilization of a novel hypermonomer **9**, prepared in three steps from the diol **6**[11] (Scheme 2), was required. Again, Williamson etherification of the four benzylic sites using phase-transfer conditions was followed by TBAF deprotection without initial purification. In this case, the yield of the benzyl alcohol **10** (Scheme 3) was relatively low (35%), likely due to steric crowding during the formation of this macromolecule.

Scheme 2



The dendrimers were well soluble in organic solvents ($CHCl_3$, CH_2Cl_2, and THF) and were fully characterized by ^{1}H NMR, ^{13}C NMR, and MALDI−TOF MS. The behavior of these branched, multichromophoric molecules was studied with respect to their one- and two-photon absorption properties. In Figure 1 the one-photon absorption spectra of the dendrons are illustrated. It can be seen that the extinction coefficients (ϵ) of the dendrons double with increasing generation, as expected from the doubling of the number of chromophores. Additionally, it can be seen that there is no absorption beyond 500 nm for any of the molecules. The inset of Figure 1 shows the corresponding one-photon induced (λ_{ex} = 420 nm) fluorescence spectra for the same

Scheme 3



10

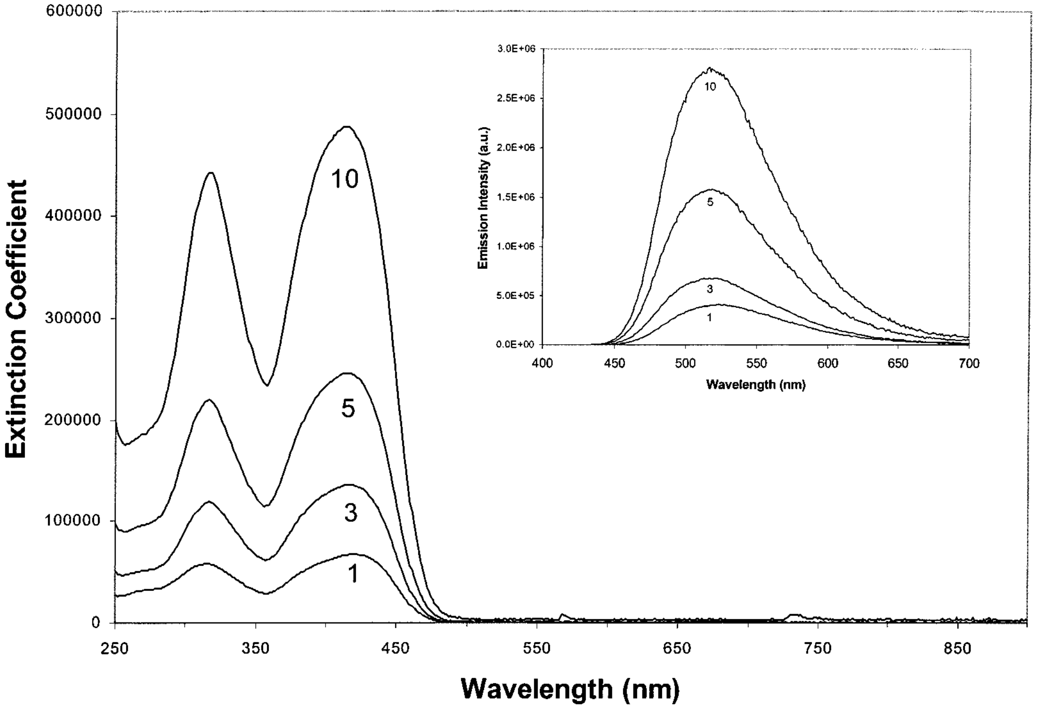


Figure 1. One-photon absorption spectra of the dendrimers and the starting chromophore **1** in chloroform. Inset shows the one-photon induced fluorescence of the same compounds in chloroform (1.86 × 10^{-6} M).

compounds, normalized to the same concentration (1.86 × 10^{-6} M).

The TPA cross-section values of the dendrons were measured using nanosecond and femtosecond laser pulses, respectively. It was necessary to utilize both time scales in order to rule out any enhancement effects from the longer pulses due to processes such as excited-state absorption. For measurement in the nanosecond regime, the 810 nm, 7 ns, and 10 Hz laser pulses were used, provided by a pulsed dye laser pumped with a Q-switched and frequency-doubled Nd:YAG laser. By measuring the dynamic transmissivity of a 1 cm path length sample solution as a function of input laser intensity and fitting the input–output curve, the nonlinear absorption coefficient and TPA cross section could be determined for a given sample solution. For the measurement in femtosecond regime, the 796 nm, 160 fs, and 1 kHz laser pulses provided by a Ti:sapphire laser oscillator–amplifier system were used to measure the TPA cross section with the open-aperture Z-scan technique.

Although the absolute values obtained from the two different time scales varied greatly, the relative values from one compound to the next remained fairly constant.

Table 1. Relative TPA Cross Sections for the Dendrimers and Starting Chromophore 1

(A) Nanosecond Laser Pulses

	compound			
	1	**3**	**5**	**10**
relative σ_2	1	3.4	5.9	8.2
solvent	TCE[a]	TCE	TCE	TCE
wavelength (nm)	810	810	810	810
pulse duration (ns)	7	7	7	7

(B) Femtosecond Laser Pulses

	compound			
	1	**3**	**5**	**10**
relative σ_2	1	2.8	6.1	9.4
solvent	TCE	TCE	TCE	TCE
wavelength (nm)	796	796	796	796
pulse duration (fs)	160	160	160	160

[a] TCE = $CHCl_2CHCl_2$

Such relative comparisons between homologous new compounds are extremely useful since the resulting data are independent of experimental setup and equipment. The relative data from the two experimental approaches are outlined in Table 1. It can clearly be seen that the TPA cross section nearly doubles on going from one dendrimer generation to the next, within experimental error. Thus, there is no deleterious interaction of the chromophores within the dendritic structure that decreases their two-photon absorbing capacity. To obtain a more meaningful comparison between the dendritic systems and the previously prepared molecules, it will be necessary to measure the TPA cross section as a function of wavelength. Work toward this goal is currently in progress. Additionally, it was possible to detect two-photon induced ($\lambda_{ex} = 800$ nm) fluorescence from the four compounds. These data are illustrated in Figure 2.

In conclusion, we have synthesized novel dendrimers functionalized with TPA chromophores at their chain ends. These dendrimers were highly soluble in common organic solvents and were fully characterized by ^1H NMR, ^{13}C NMR, and MALDI−TOF MS. A linear correlation between the number of peripheral chromophores and the TPA cross section of the molecule was found, indicating that there are neither cooperative nor deleterious effects in the dendrimers due to the high local chromophore concentration.

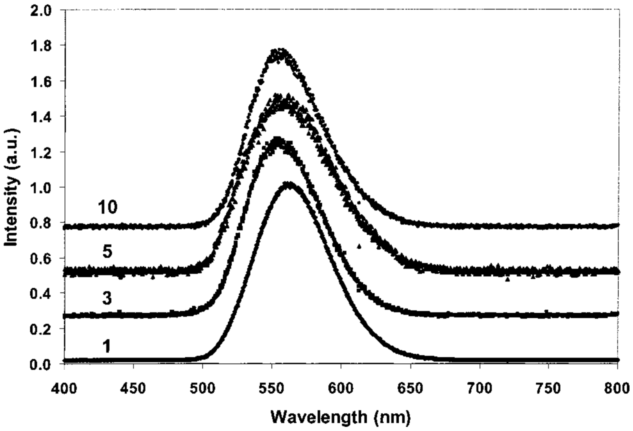


Figure 2. Two-photon induced fluorescence spectra of the dendrimers and the starting chromophore **1** in TCE.

Acknowledgment. Financial support of this research by the AFOSR-MURI program (grant # F49620-96-1-0035) and NSF (DMR- 9796106) is gratefully acknowledged. Financial support from the Eastman Kodak Company in the form of a graduate fellowship is also gratefully acknowledged (A.A.).

Supporting Information Available: Text giving full experimental details for the synthesis of compounds **3**, **5**, **7**, **8**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

CM000586O