Spectroscopic Characteristics of Hyperbranched Conjugated Polymers Studied by One- and Two-Photon Excitations†

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Spectroscopic properties of new hyperbranched conjugated polymers functionalized in periphery with N,N-dimethylaniline and tert-butyl-benzene as terminal groups are investigated by one- and two-photon excitations. The absorption, fluorescence excitation and emission spectra are examined in chloroform and N,N-dimethylaniline. The two-photon excitation measurements show that the new hyperbranched conjugated polymer possesses large two-photon excitation cross section which makes it a very attractive candidate for the potential application as nonlinear optical materials. As an example, the two-photon induced three-dimensional data storage is also demonstrated.

Key words: Hyperbranched conjugated polymer, Two-photon excitation cross section, Two-photon induced optical data storage

I. INTRODUCTION

Two-photon absorption (TPA) is a nonlinear optical process, in which two coherent, separated photons, each with half the energy required, are absorbed simultaneously to cause an electronic transition to the excited state in a molecule [1,2]. Recently, it has received considerable attention because of the potential application of two-photon excitation (TPE) in biological imaging, optical data storage, optical power limiting, three-dimensional microfabrication and two-photon photodynamic therapy [3-9]. However, its implementation in practical uses is limited because of the very small two-photon absorption cross section. In order to overcome this problem, great efforts have been directed toward the identification of the molecular design strategies for synthesis and characterization of two-photon absorption materials with a large two-photon cross section in the past years [10-33]. So far, these new materials are those electron-donating (D) and electron-accepting (A) moieties, either symmetrically or asymmetrically attaching onto a conjugated bridge (π-bridge) to form A-π-D, A-π-A, D-π-A, D-A-D and A-D-A structural motifs [10-31]. As examples, the enhancements of two-photon absorption of the molecules with quadrupolar [10-18], octupolar [19-22], multi-branched [23,24] and dendrimer [25-30] structures as well as bifluorene and polyfluorene systems [32,33] have been demonstrated. These macromolecules with three-dimensional structures can afford a high-packing density of chromophores and stable photochemical and thermal performance, as well as the possibility for chemical modification. The development of these novel materials offers opportunities for both fundamental research and new applications.

Recently, we have synthesized two new hyperbranched conjugated polymers functionalized in periphery with N,N-dimethylaniline and tert-butyl-benzene as terminal groups [34], where the corresponding compounds are referred to as DMA and TBB, respectively. The N,N-dimethylaniline group rather than tert-butyl-benzene group is of strong ability of electron-donation which may cause strong twisted intramolecular charge transfer (TICT) upon excitation [34,35]. A model-like compound referred to as monomer was synthesized for comparison, because it served as the minimum effective conjugation unit in these hyperbranched polymers and its spectral properties are similar to those of hyperbranched polymers. The central parts of the hyperbranched conjugated polymers are mainly two-photon chromophores. Scheme 1 shows their molecular structures, where these hyperbranched conjugated polymers have benzene rings as their cores, 2,5-dimethoxy phenylene vinylenes as their connecting units, and N,N-dimethylaniline and tert-butyl-benzene as terminal groups at the end. The introduction of benzene rings in π-core as ramification node could maintain a large distance between the conjugated connectors, in order to prevent sterical hindrance and enhance systematic conjugation [36]. The hyperbranched polymers with multi-branched conjugated arms, are expected to facilitate excitation migration from outer arms to the central conjugated units [26,27], and therefore deserve much attention due to their high performances and...
many novel properties for practical applications [37,38]. Furthermore, these hyperbranched polymers with the dendrimer-like architecture can be synthesized by a convenient one-step polymerization reaction [34]. The main structural moiety of the hyperbranched conjugated polymers we synthesized is the distyrylbenzenes capped with different peripheral end groups with functions such as enhanced energy harvesting as well as optoelectronic characteristics [40]. We expect that these hyperbranched polymers with high density of chromophores and the extended $\pi$-conjugated systems have a large two-photon absorption cross section.

We have briefly demonstrated that the spectral properties of hyperbranched polymers can be correlated to the twisted intramolecular charge transfer (TICT) upon excitation in different polar solutions in our previous work [34]. In this work, we further present the one- and two-photon excitation properties of these hyperbranched polymers. Our results indicate that the increased two-photon excitation cross sections of both DMA and TBB are correlated to the high-packing density of chromophores within the hyperbranched polymer. The large two-photon excitation cross sections of these hyperbranched polymers suggest the potential application as nonlinear optical materials [40].

II. EXPERIMENTS

A. Materials and methods

All the solvents used in this work were commercially available and of analytical grade. All the samples were dissolved in chloroform (polarity index 4.1) [41] and N,N-dimethylformamide (DMF, polarity index 6.4) [41] at a low concentration of $5.0 \times 10^{-5}$ mol/L in order to avoid aggregation. The resulting solutions were stable, and there was no obvious change checked by absorption spectrum after one- and two-photon laser irradiations. All measurements were performed at room temperature. The hyperbranched polymers were characterized by FTIR, $^1$H-NMR, $^{13}$C-NMR and elemental analysis. The thermal stability was measured by DSC and TGA. The molecular weight $M_w$ was determined by gel permeation chromatography (GPC) with polystyrene as standard and THF as eluent at room temperature.

B. Synthesis of the hyperbranched conjugated polymers

The hyperbranched conjugated polymers were synthesized by the Wittig-Horner reaction. The synthetic processes were carried out by one copolymerization of 1,3,5-tri-aldehyde-benzene to react with 2,5-dimethyloxy-benzyl-triphenyl-phosphate chloride followed by an end cap reaction as shown in Scheme 2. By adding tert-butyl-benzyl aldehyde as the capping agent to the mixture, the hyperbranched polymer TBB was obtained. By adding 4-(N,N-Dimethylamino)-benzyl aldehyde instead of the above aldehyde, the DMA was synthesized. The polymers were characterized by $^1$H-NMR, $^{13}$C-NMR, FTIR, and the molecular weight was determined by GPC using polystyrene as the standard although it is not suitable for the hyperbranched structured macromolecules. The results are summarized in Table I. These hyperbranched conjugated polymers are highly soluble in common organic solvents and exhibit good film-forming ability. They all have high thermal stability. The glass transition temperatures ($T_g$) of the DMA and the TBB is 255 and 287 °C, respectively. The initial weight loss temperature is up to 390 °C ($T_{\text{IG}}$) for both hyperbranched polymers. The detailed processes of the synthetic routes and the characterization have been reported elsewhere [39,42,43].

C. Characterizations

Absorption spectra were recorded with a UV-Vis spectrophotometer (model U-3010, SHIMADZU). For the measurements of one- and two-photon induced fluorescence spectra, a mode-locked Ti:Sapphire laser (Mira-900, Coherent) with wavelength at 800 nm was used as the excitation source. This system provides a pulse of approximately 120 femtosecond duration at a repetition frequency of 76 MHz. We used this laser pulse at 800 nm and the double-frequency light at 400 nm as two-photon excitation source and one-photon excitation source, respectively. The laser beam was focused into a 1 cm path length sample cell. The induced fluorescence was led to a LN-CCD (Jobin Yvon, CCD-3000V) attached spectrometer (Jobin Yvon TRIAX...
Scheme 2 The synthetic route toward DMA and TBB.

TABLE I Photophysical properties of the monomer, the DMA and the TBB in chloroform (polarity: 4.1) and DMF (polarity: 6.4). \( \lambda \) is the peak position, \( \Delta \lambda \) is the Stokes shift, \( \phi_f \) is the fluorescence quantum yield, \( M_W \) is the weight average molecular weight. \( \delta \) is two-photon excitation cross section (1 GM = \( 1 \times 10^{-50} \) cm\(^4\)/s/(photon molecule)) of monomer, TBB and DMA.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( M_W ) (g/mol)</th>
<th>Solvent</th>
<th>( \lambda_{\text{abs}} )/nm</th>
<th>( \lambda_{\text{ex}} )/nm</th>
<th>( \lambda_{\text{flu}} )/nm</th>
<th>( \phi_f )</th>
<th>( \delta )/GM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
<td>342</td>
<td>CHCl(_3)</td>
<td>325, 387</td>
<td>325, 385</td>
<td>442, 464</td>
<td>0.76</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DMF</td>
<td>327, 391</td>
<td>328, 390</td>
<td>442, 464</td>
<td>0.95</td>
<td>0.87</td>
</tr>
<tr>
<td>TBB</td>
<td>6031</td>
<td>CHCl(_3)</td>
<td>321, 401</td>
<td>325, 402</td>
<td>462, 485</td>
<td>0.39</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DMF</td>
<td>326, 406</td>
<td>322, 406</td>
<td>463, 488</td>
<td>0.18</td>
<td>217</td>
</tr>
<tr>
<td>DMA</td>
<td>28367</td>
<td>CHCl(_3)</td>
<td>336, 400</td>
<td>305, 376</td>
<td>457, 483</td>
<td>0.29</td>
<td>734</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DMF</td>
<td>335, 403</td>
<td>319, 378</td>
<td>459, 488</td>
<td>0.16</td>
<td>258</td>
</tr>
</tbody>
</table>

The fluorescence quantum yields were measured using 9,10-diphenylanthracene (\( \phi_f = 0.90 \)) as standard [44]. All samples were diluted to low concentration, and the optical density was below 0.05 for fluorescence quantum yield measurements in order to minimize self-absorption effect. The TPE cross sections (\( \delta \)) were measured through the two-photon-induced fluorescence method by using Rhodamine B as standard [45].

To achieve the three-dimensional data storage by two-photon excitation, the excitation beam was generated by a homemade mode-locked Ti:Sapphire laser oscillator pumped from Nd:YVO\(_4\) laser (Verdi-5, Coherent) at 532 nm. This system produced a train of 800 nm, 80 fs at a repetition rate of 80 MHz. The femtosecond laser through a beam expander and an objective was focused into DMA doped PMMA film for data writing. To prepare the DMA doped PMMA film for data storage, the DMA and PMMA were mixed together with a weight ratio about 1:20 into a chloroform solution, and the film was coated with thickness about 90 µm onto a microscope slide in the air at room temperature. A three-dimensional stage driven by a 3-axis piezoelectric tube (PZT) and a mechanical shutter were controlled by a personal computer. Objective, dichroic mirror, pinhole, photomultiplier tube (PMT) and the scanning stage composed a confocal laser scanning fluorescence microscope were used for reading the data. When reading the data, an appropriate dichroic mirror was switched, and a 404 nm laser was introduced instead of the 800 nm femtosecond laser. A 40× objective (NA 0.65) was used for recording and reading. A suitable bandpass filter was placed in front of the PMT to select fluorescence and block the laser scattering and other stray light reaching the detector during reading.
III. RESULTS AND DISCUSSION

A. Molecular illustration

In order to obtain the molecular three-dimensional illustration, we used Chem3D Ultra 7.0 software and the MM2 method as the energy minimization algorithm. These results can help us to interpret the observed spectroscopic properties. Scheme 3(a) shows the optimized equilibrium geometry of the basic repetition unit of hyperbranched polymers. Two important features can be seen: first, the central benzene-ring can enhance the conjugation and interaction between adjacent arms and the whole unit is nearly coplanar; and second, the structure of the basic repetition unit is of high three-fold symmetry, where the angle around the central benzene ring is about 120° between two adjacent arms, suggesting high extension and conjugation. As the number of generations is further increased as shown in Scheme 3(b), the optimized geometry of the hyperbranched polymer shows a little distortion where the molecular internal rotation about the single bonds partly interrupts the effective conjugation. As the number of generations is further increased as shown in Scheme 3(b), the optimized geometry of the hyperbranched polymer shows a little distortion where the molecular internal rotation about the single bonds partly interrupts the effective conjugation. This strongly affects the spectral properties of the hyperbranched polymers. In the case of the monomer as shown in Scheme 3(c), the optimization result shows that all the three benzene rings are almost coplanar, indicating high rigidity of monomer molecules.

B. One-photon properties

The one-photon induced absorption, fluorescence excitation and fluorescence spectra of the monomer, the TBB and the DMA are displayed in Fig.1 and Fig.2. The corresponding spectroscopic parameters are listed in Table I.

There are two distinct absorption bands (Fig.1), one is in the long wavelength region with an asymmetric structure around 380-410 nm denoted as A-band, and the other is in the short wavelength region around 320-340 nm denoted as B-band. These absorption peaks are all attributed to allowed π-π* transitions and typically from the absorption of the stilbene-like units, whereas the A-band at long wavelength region is involved in the lowest-lying transition character structurally related to the conjugation [34,46]. The broad asymmetric A-band at long wavelength region of the DMA and the TBB rather than the B-band at short wavelength region shows a clear red shift corresponding to that of monomer, indicating an enhancement of the effective conjugation length and the interbranch interaction of the DMA and the TBB.

Figure 2 shows the one-photon excited fluorescence spectra of the monomer, the TBB and the DMA dissolved in chloroform and DMF solutions. There are two main emission peaks (denoted as F_A-band and F_B-band as shown in Fig.2) at about 464 and 442 nm for the monomer, about 483 and 457 nm for the DMA, and about 485 and 462 nm for the TBB, respectively, in chloroform solution. The fluorescence spectra of the DMA and the TBB are red-shifted with respect to that of the monomer because of the increased electronic coupling between different branches and the enhancement of effective conjugation length. Using 9,10-diphenylanthracene (ϕ_f=0.90) as Ref.[44], we obtain...
FIG. 1 The absorption spectra (solid squares) and excitation spectra (open circles) of monomer, TBB and DMA in chloroform and DMF solutions (λ_{em}=70 nm for monomer, λ_{em}=488 nm for TBB and DMA).

FIG. 2 One-photon excited fluorescence spectra of monomer, DMA, and TBB in chloroform (solid lines) and DMF (dot lines) solutions.

the fluorescence quantum yields of the DMA, the TBB and the monomer as listed in Table I.

Unlike the case of monomer, the fluorescence quantum yields of the TBB and the DMA are high in chloroform solution, and low in DMF solution. The monomer has higher fluorescence quantum yield in a more highly polar solution. Since the molecule rigidity is enhanced in more polar solution, leading to strong fluorescence. The fluorescence bandwidths of the DMA and the TBB are much broader resulting from the higher flexibility as compared to that of the monomer. Generally, the changes of solvent polarity will affect the nature of the lowest singlet state [35,47]. In the ground state, the polymers of the TBB and the DMA are almost coplanar even with a little internal rotation, and therefore have large conjugation [34,39,42,43] as predicted by molecular structure optimization in Scheme 3. However, in the excited molecules of the hyperbranched polymers TBB and DMA, several distortions or rotations about single bonds in each arm of the TBB and the DMA polymers are expected in polar solution [34,39,42,43]. These processes are the main non-radiative de-excitation pathways, resulting in fluorescence quantum yield decreases accompanied with the increase of F_A/F_B ratio [35].
The increase of the $F_A/F_B$ ratio is due to the internal rotation dominated in the TBB and in the DMA [34,35,39,42]. In the same polar solution, the distortion and/or internal rotation will cause the decrease of molecular conjugation, and thus leads to the decrease of fluorescence quantum yields of the DMA and the TBB compared to that of the monomer.

The excitation spectra of the monomer and the TBB obtained by monitoring the short and long wavelength fluorescence peaks are very similar to those observed absorption spectra, indicating that the two emissive states of the monomer and the TBB have the same origin of excitations. Although, the positions of the excitation peaks of the monomer and the TBB are very close to their absorption peaks, the intensity distributions of the two excitation peaks are different from those of absorption peaks. From the normalized excitation and absorption spectra as shown in Fig.1, the relative intensity of the short wavelength excitation peak of the TBB around 321 nm are higher than that of its related absorption peak, whereas the excitation peak intensity of the monomer around 325 nm are lower than that of its related absorption peak. The observed differences between the absorption and excitation spectra indicate that the internal conversion efficiencies of excited states of molecule are different from each other [48]. Furthermore, the excitation spectrum of the DMA is obviously different from its absorption spectrum. There is a large blue shift up to 20 nm with respect to its absorption spectrum, this strongly suggests a larger photoinduced changes in geometry of the DMA that happens upon excitation [34,45].

C. Two-photon properties

We now turn to consider the two-photon induced fluorescence of the monomer, the TBB and the DMA. Figure 3 shows the two-photon fluorescence excitation spectra of the DMA and the TBB in chloroform and DMF solutions. Except that the peak wavelengths are doubled, the two-photon induced fluorescence excitation spectra of the DMA and the TBB are quite similar to the one-photon excitation spectra although their mechanism and selection rules are different from each other [19]. However, as shown in Fig.1, these new compounds exhibit no obvious absorptions from 500 nm to 900 nm, which is the wavelength used for two-photon excitation in our work. Because both the DMA and the TBB have strong broad absorption bands around 400 nm, these molecules have their strongest two-photon absorptions when excited by a femtosecond laser around 800 nm. Figure 4 shows the two-photon induced fluorescence spectra of the monomer, the DMA and the TBB in chloroform and DMF solution. The one- and two-photon induced fluorescence spectra are very similar, indicating that the induced fluorescence is emitted from the same solvent-dependent excited singlet state ($S_1$) no matter whether one-photon excitation or two-photon excitation.

The observed two-photon induced fluorescence from these compounds is very strong. In order to confirm whether the observed fluorescence is a real two-photon excitation process, the power-law dependence is examined at 800 nm. The excitation intensity dependences of the two-photon fluorescence of these compounds are shown in Fig.5 with the plots on lg-lg scales. We find that two-photon excited fluorescence from all the compounds obeys the square-law dependence, where the slopes are about 1.99, 1.94, and 2.03 for the monomer, the TBB and the DMA in chloroform, respectively. Similar results are also obtained in DMF (data unshown). This confirms that the excitations are typical two-photon processes at excitation wavelength of 800 nm.

A basic parameter of two-photon induced fluorescence is the two-photon excitation cross section. We measured the two-photon cross sections of the DMA, the TBB and the monomer with Rhodamine B as the standard because it has large two-photon excitation cross sections at broad excitation wavelength region.
FIG. 4 Two-photon excited fluorescence spectra of the monomer, DMA and TBB in chloroform (solid lines) and DMF (dot lines) solutions.

FIG. 5 A typical lg-lg plot of the fluorescence signals of monomer, DMA and TBB in chloroform.

that has been determined [44,49]. The two-photon excitation cross sections can be determined by measuring and comparing the relative signal intensities of the two-photon fluorescence from these new compounds and Rhodamine B under the same experimental conditions. An expression for the two-photon-induced fluorescence signal \( F_i \) is given by [49,50]:

\[
F_i = K(\phi_i/2)n\delta_iLI^2
\]

where \( \phi_i \) is the fluorescence quantum yield, which is divided by a factor of two because two photons are absorbed for each fluorescence photon emitted; \( n \) is the chromophore number density (we keep all the samples with the same concentrations in our measurements); \( \delta_i \) is the TPA cross section; \( L \) is the path length; \( I \) is the excitation power; and \( K \) is the geometry factor of the optical setup used. Using the published values of two-photon excitation cross section (\( \delta \)) of Rhodamine B about \( 150 \times 10^{-50} \) cm\(^4\)/photon around 800 nm and fluorescence quantum yield of Rhodamine B about 0.7 [44,46,47], we can get the TPE cross sections (\( \delta \)) of these compounds. The calculated TPE cross sections of these compounds at their maximal two-photon excitation wavelengths around 800 nm are listed in Table I. It should be noted here that since the hyperbranched polymers DMA and TBB molecules were synthesized in one-pot reactions, the lengths of the branches in a single polymer molecule are not exactly the same, so the two-photon excitation cross sections for the DMA and the TBB are calculated based on their weight-averaged molecular weights. The increased two-photon excitation sections of DMA and TBB compared to the monomer are mainly due to the increased conjugation length and the high density chromophores in the hyperbranched polymers [23-31]. The large two-photon excitation cross section suggests that the hyperbranched polymer can be novel functional material for practical applications, such as optical limiting materials [40], optical data storage, lithographic microfabrication and fluorescence imaging.

D. Two-photon induced three-dimensional data storage

As an example of two-photon induced three-dimensional data storage, the novel functional molecules DMA or TBB are doped into PMMA films. Figure 6 shows the typical photobleaching properties of the DMA and the TBB doped PMMA films upon two-photon excitation with a femtosecond laser at 800 nm at about 2.6 kW/cm\(^2\). It is found that the photobleaching of the DMA is much faster than that of the TBB at the same excitation intensity. This aspect is easily understood that the DMA has larger two-photon excitation cross section than TBB does. As the two-photon excitation cross section is large for this new hyperbranched polymer, this photobleaching phenomenon could be explored for three-dimensional optical data storage [51-53]. When the photobleached areas in the DMA doped PMMA film are exposed to a “reading” laser beam, the fluorescence becomes much weaker, compared to the non-bleached areas, and the high or low fluorescence signals can be easily
distinguished as bit “0” and/or bit “1”, respectively. Here, we should mention that we did not try to achieve the highest density of 3D data storage and smallest dot size in our work because of the limited experimental conditions we have. As an example for the three-dimensional data storage with this novel material, we simply demonstrate the data storage results by two-photon writing the data of “D”, “M”, and “A” into the DMA doped PMMA film at three different depths, as shown in Fig. 7. A vertical section across the top part of these letters is also presented, clearly demonstrating a real three-dimensional storage. Each dot was written with a speed of one step per 30 ms (the scanning speed is limited by the mechanical stage) with 80 fs, 800 nm under the excitation power about 200 kW/cm$^2$, and the images were read nondestructively with 404 nm at about 90 $\mu$W/cm$^2$. The reading power is far lower than the photobleaching threshold, and in our experiment, the pattern was read repeatedly more than one thousand times without obvious change in fluorescence intensity.

IV. CONCLUSION

We have characterized the spectroscopic properties of new hyperbranched conjugated polymers in periphery substituted with N,N-dimethylaniline and tert-butyl-benzene as terminal groups by one- and two-photon excitations. The large two-photon excitation sections of the new hyperbranched conjugated polymers mainly result from the high density of chromophores and the extended $\pi$-conjugation within the branches. Since these new hyperbranched polymers can be synthesized by a convenient one-step polymerization reaction, the large two-photon absorption cross section of the new hyperbranched polymer makes it a very attractive candidate for the potential application as nonlinear optical mate-

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