Design and synthesis of heterocyclic multi-branched
dyes for two-photon absorption

A. Abbotto a,∗, L. Beverina a, S. Bradamante a, A. Facchetti a, G.A. Pagani a,1, R. Bozio c, C. Ferrante c, D. Pedron c, R. Signorini c

a Department of Materials Science and INSTM, University of Milano-Bicocca, Via Cozzi 53, I-20125 Milano, Italy
b CNR-Institute of Molecular Science and Technologies, Via Golgi 19, I-20133, Milano, Italy
c Department of Physical Chemistry and INSTM, University of Padova, Via Loredan 2, I-35131 Padova, Italy

Abstract

We report the first example of a heterocycle-based multi-branched two-photon absorption (TPA) dye. We show that the new chromophore presents a very large TPA cross-section in the femtoseconds (fs) regime. Comparison of the TPA cross-sections between the branched system and the corresponding “monomeric unit” shows a strong cooperative enhancement. A value of 22.6:1, corresponding to a 750% enhancement, was observed.

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1. Introduction

Organic molecules which can simultaneously absorb two or more photons of the same or similar energy and be promoted to one of their excited states have recently attracted much interest because of their potential use in advanced photonic applications such as two-photon laser scanning fluorescence microscopy [1], optical limiting [2], three-dimensional holographic recording and two-photon sensitized photorefractive effect [3], microfabrication [4], photodynamic therapy [5], and upconverted-lasing [6]. These applications take advantage of the fact that the two-photon absorption (TPA) activity scales quadratically with the intensity of the incident laser radiation. Some of these fields are further based on the fluorescence properties of the two-photon excited molecule. In order to meet market criteria, molecules with large TPA cross-sections σ are required. Highly efficient TPA dyes [7] and few first studies on structure/property relationships are now available [8].

We have recently reported highly efficient heteroaromatic-based TPA dyes presenting a A-π-D-π-A, where A (π-acceptor) is a π-deficient heteroaromatic ring (pyridine, quinoline, benzothiazole), and D (π-donor) a π-excessive pyrrolyl moiety [9]. In recent times a few [10,11] reports have appeared on octupolar, branched, or dendrimeric structures for TPA activity, underlining the importance of cooperative effects in the TPA enhancement [12]. In most of these reports, only simple benzenoid derivatives and primary organic donor and acceptor functionalities have been exploited.

We herein describe the first example of a heterocycle-based branched quasi-octupolar TPA dye I, using π-deficient (pyridinium) and π-excessive (pyrrole) heteroaromatic rings as A and D units, respectively [13]. We show that the new chromophore presents a very large TPA cross-section σ in the femtoseconds (fs) regime. We also compare the linear and non-linear absorption and emission properties of the branched system with those of one-dimensional dipolar I-M (“monomer”) [14] and quadrupolar I-D (“dimer”) sub-units.
2. Results and discussion

Dye 1 was prepared by triple simultaneous Knoevenagel condensation of the quaternary salts of collidine with three equivalents of 2-pyrrolecarbaldehyde in refluxing n-BuOH and in the presence of piperidine as a base. Molecules 1-M and 1-D were prepared in a similar manner, starting from the proper azinium triflate and number of equivalents of 2-pyrrolecarbaldehyde, using piperidine in refluxing EtOH.

The branched chromophore shows a strong intramolecular charge transfer absorption band in the visible region and no NIR absorption. In addition, a fluorescence emission was observed, which is an important prerequisite for TPA-based applications such as fluorescence microscopy [1] and upconverted-lasing [6]. Table 1 lists the absorption and emission properties of 1 compared to that of the component monomeric and dimeric units 1-M and 1-D. The linear absorption and fluorescence spectra are shown in Fig. 1. The bathochromic shift observed both in the absorption and emission spectra of the branched systems relative to the smaller components is evidence of the interaction between the three arms, which should result in perturbed ground and excited states properties and, eventually, TPA response. A similar indication can also be drawn from the increase of the Stokes shift in the branched fluorophore 1.

TPA cross-sections of molecules 1, 1-M, and 1-D have been measured by open aperture Z-scan measurements performed with a fs laser source (FWHM = 150 fs). The fs-laser measurement is able to discriminate between coherent two-photon processes and multiphoton sequential absorptions implying different excited states [15]. The latter does not contribute to the measured signal when fast (~100 fs) pulses are used, since most non-radiative processes occur on a picosecond (ps) or nanosecond (ns) timescale. Table 2 reports the fs TPA cross-sections \( \sigma \) of molecule 1, compared to those of monomer 1-M and dimer 1-D. Values compare well with the best reported fs-laser measurements of one-dimensional and branched examples of comparable molecular weight [7,10,15,16].

Comparison of the TPA cross-sections between the branched system 1 and the corresponding monomeric unit 1-M shows a strong cooperative enhancement, that is the \( \sigma \) value of 1 is larger than that predicted on the basis of the chromophore number density increase. A ratio of 22.6:1, corresponding to a 7.5-fold enhancement, can be derived from data in Table 2. This value is larger than those previously reported for tri-branched or dendrimeric structures [10].

### Table 1

Linear absorption and emission parameters (DMSO) of branched compound 1 and of monomeric 1-M and dimeric 1-D subunits

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( \lambda_{max}(abs)^a ) (nm)</th>
<th>( \lambda_{max}(em) ) (nm)</th>
<th>Stokes shift ( b ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-M</td>
<td>437 (29 800)</td>
<td>523</td>
<td>3760</td>
</tr>
<tr>
<td>1-D</td>
<td>473 (48 100)</td>
<td>556</td>
<td>3250</td>
</tr>
<tr>
<td>1</td>
<td>475 (47 500)</td>
<td>596</td>
<td>4270</td>
</tr>
</tbody>
</table>

\( ^a \) Extinction coefficient \( \varepsilon \) in parentheses (mol\(^{-1}\)·cm\(^{-1}\)).

\( ^b \) \( 1/\lambda(\text{abs}) - 1/\lambda(\text{em}) \) cm\(^{-1}\).

### Table 2

TPA cross-section coefficient of branched compound 1 and of monomeric 1-M and dimeric 1-D sub-units in DMSO

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( e\sigma ) (^a)</th>
<th>( \sigma ) ( \text{GM}^b )</th>
<th>( n\sigma /e\sigma ) ( \text{GM}^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-M</td>
<td>14</td>
<td>5(^d)</td>
<td>0.4</td>
</tr>
<tr>
<td>1-D</td>
<td>22</td>
<td>103(^d)</td>
<td>4.7</td>
</tr>
<tr>
<td>1</td>
<td>30</td>
<td>113(^d)</td>
<td>3.8</td>
</tr>
<tr>
<td>AF50 [15]</td>
<td>34</td>
<td>22(^e)</td>
<td>0.6</td>
</tr>
<tr>
<td>PRL-701 [16]</td>
<td>80</td>
<td>600(^d)</td>
<td>7.5</td>
</tr>
<tr>
<td>ET 101 [10]</td>
<td>138</td>
<td>380(^d)</td>
<td>2.8</td>
</tr>
</tbody>
</table>

\( ^a \) Number of \( e \) electrons.

\( ^b \) 1 GM (Goppert–Mayer) = 1 × 10\(^{-50}\) cm\(^4\) s per photon per molecule.

\( ^c \) TPA cross-section normalized to the number of \( e \) electrons.

\( ^d \) \( \lambda = 790 \text{ nm} \).

\( ^e \) \( \lambda = 796 \text{ nm} \).
3. Conclusions

We have presented a new heteroaromatic-based multi-branched TPA dye, which is highly ranked among the best dipolar, quadrupolar, and branched chromophores in the fs regime. Although TPA wavelength dispersion should be considered when comparing different systems, a very strong cooperative enhancement originated by the branched architecture was observed. This result is encouraging in view of the preparation of highly branched or dendrimeric heteroaromatic-based systems with even larger σ values.

Acknowledgements

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References