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## TWO-PHOTON ABSORPTION AROUND TELECOMMUNICATION WAVELENGTHS

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This review reports different approaches of molecular engineering for the design of two-photon absorbers in the infra-red around telecommunications wavelengths. For this field of wavelengths which was recently investigated, several families of systems are described : dipolar, quadrupolar molecules, polymethines, diradical hydrocarbons, porphyrines, metallic complexes with maximum linear absorption from 700 to 1200nm and two-photon efficiency up to 115000 GM. Some of these systems have already found applications such as optical limiting.

Keywords two-photon absorption; telecommunication wavelength; infra-red

## 1. Introduction

Two-photon absorption (2PA) is now a well-known phenomenon, consisting in the simultaneous absorption of two photons of the same or different energy<sup>1</sup>, and which has been widely used in different applications<sup>2</sup> such as 3D photopolymerisation<sup>3,4</sup>, optical limiting<sup>5-7</sup>, biological imaging<sup>8,9</sup>, photodynamic therapy of the cancer<sup>10</sup>, 2P pumped lasing<sup>11</sup>. It was initially shown in 1998 that large 2PA cross-sections  $\sigma_{2PA}$  could be obtained in centrosymmetric quadrupoles of general structure D(A)- $\pi$ -D(A), in which D, A and  $\pi$  are respectively donor, acceptor groups and a delocalised electron bridge<sup>12</sup>; the position of the

2PA band is closely related to the strength of D or A and the length of  $\pi$ . Since this period, a large number of systems from organic or coordination chemistry were designed to optimise  $\sigma_{2PA}$  values from the visible to the near-infrared (IR): dipoles, quadrupoles, octupoles, multipoles, dendritic systems<sup>2,13</sup>.

New needs appeared recently for the IR between 1200 and 1600 nm and more specifically at telecommunications wavelengths, such as 1500 nm, and the design of novel systems for this purpose had to be carried out. In this paper, we report the different molecules featuring efficient  $\sigma_{2PA}$  values in this wavelength range. We will see that several different families were studied for this purpose : conjugated dipolar and quadrupolar molecules, polymethine cyanines, macrocycles and metallic complexes. The main requirement for this type of molecular engineering is a high linear absorption between 600 and 800 nm.

## 2. Molecules for two-photon absorption in the IR

### *Dipolar compounds*

In 2005, the first examples of 2PA chromophores around telecommunication wavelengths have been developed by Marder and co-workers<sup>14</sup>. In this article, the authors describe push-pull chromophores associating an electron-donating group (dialkylaniline) and strong electron-accepting groups A, through a conjugated backbone consisting in auxiliary donor and auxiliary acceptors. (see **Ma1** in Figure 1).

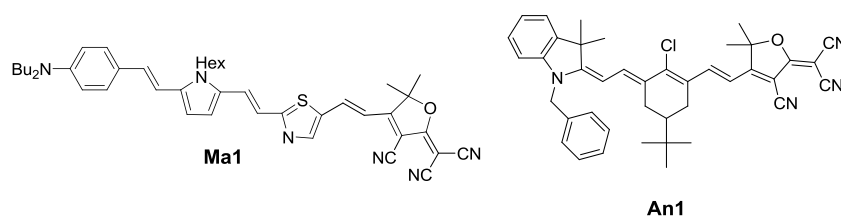


Figure 1 : Dipolar chromophores for 2PA in the IR

This chromophore, which exhibits a high charge transfer linear absorption band at 710 nm ( $\epsilon = 60\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) presents a high nondegenerate  $\sigma_{2PA}$  value between 1300 nm and 1600 nm ( $\sigma_{2PA}(\mathbf{Ma1}) = 1500 \text{ GM}$  at 1440 nm). For this molecule, the 2PA spectrum matches the half-wavelength scale linear absorption, in good agreement with the non-centrosymmetry of the system which allows to reach the same excited states by 1PA and 2PA (Fig. 2).

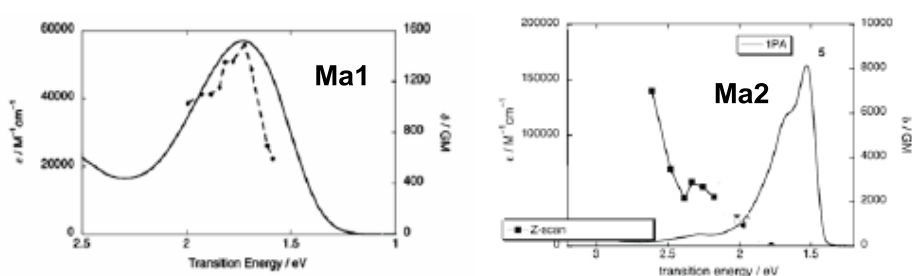


Figure 2 : Comparison of 1PA and 2PA spectra of chromophores **Ma1** and **Ma2**

Other push-pull chromophores have been developed in our group (**An1**, Figure 1)<sup>15</sup>. This molecule features the same strong tricyanofurane (TCF) moiety than **Ma1** and indoleninium as the strong electron-donating group. The 2PA cross-sections of this product are around 500 GM between 1300 nm and 1600 nm. The good solubility of these dyes allowed to perform optical limiting experiment in the ns regime at these wavelengths, as shown below in Figure 6. The phenomenon has been interpreted on the basis of a two-photon induced excited state absorption phenomenon.

#### *Quadrupolar Compounds*

A second family of organic linear molecules with strong 2PA properties are the quadripolar compounds, usually noted D- $\pi$ -A- $\pi$ -D or A- $\pi$ -D- $\pi$ -A<sup>12</sup>. These centrosymmetric molecules have also been investigated in order to develop two-photon absorbers in the IR.

Cho and co-workers developed linear compounds based on dialkylaniline as donor group and dicyanoanthracene as central accepting group (**Ch1** Fig. 3). In this series, **Ch1** displays the most red-shifted 2PA with  $\sigma_{2PA}$  values up to 2300 GM between 1000 nm and 1100 nm<sup>16</sup>.

Following the same strategy, the group of Marder synthesized A- $\pi$ -A molecules based on strong accepting groups (**Ma2** and **Ma3**, Fig. 3)<sup>17</sup>. Those chromophores also show intense 2PA: for example,  $\sigma_{2PA}$  of **Ma3** reaches 5900 GM at 1240 nm.

As expected for centrosymmetric compounds, the 2PA band of both series of compounds, are blue shifted compared to the wavelength-doubled scale 1PA: the first electronic state allowed for 1PA is forbidden for 2PA (Fig. 2).

These results shows clearly that the dipolar/quadrupolar strategy, that was widely used to enhance the 2PA efficiency in the visible-NIR range, can also be used successfully in the IR, providing a significant bathochromic shift of absorption bands.

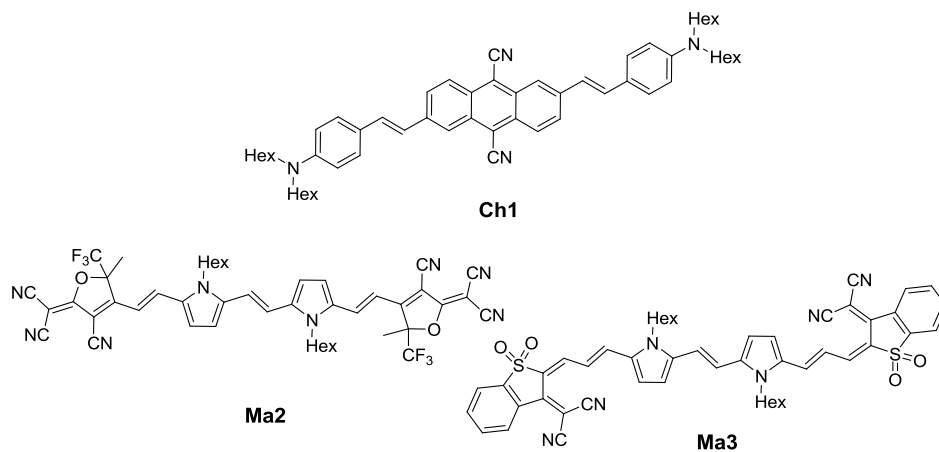


Figure 3: Quadrupolar chromophores exhibiting 2PA in the IR

### *Polymethines*

Polymethine cyanines are organic ionic chromophores featuring a charge delocalized through a polyenic backbone possessing an odd number of carbons. The classical linear absorption of these molecules is localized in the NIR between 700 and 900 nm. This class of chromophores has been less studied for nonlinear optical applications until the last few years and the recent interest of 2PA in the IR.

In 2002, Schwerer and co-workers studied the 2PA properties of squaraines dyes and the effect of oligomerization on its nonlinear optical properties<sup>18</sup>. Monomeric squaraine (**Sc1** with  $n = 0$ , Fig. 4) exhibits 2PA transition at 1240 GM ( $\sigma_{2PA} = 483$  GM). Oligomerization has not been proved to enhance the 2PA efficiency of these molecules. In 2006, the group of Marder optimized the structure of a squaraine to enhance its 2PA properties: the conjugated lateral chains have been extended with the introduction of heterocyclic conjugated bridge (pyrole, thiophene) and the end groups have been replaced by a dibutylaniline group (**Ma4**, Fig. 4)<sup>19</sup>. These modified squaraine dyes exhibit giant 2PA cross-section ( $\sigma_{2PA} = 18000$  GM at 1100 nm) with at least 1000 GM on the entire telecommunication windows.

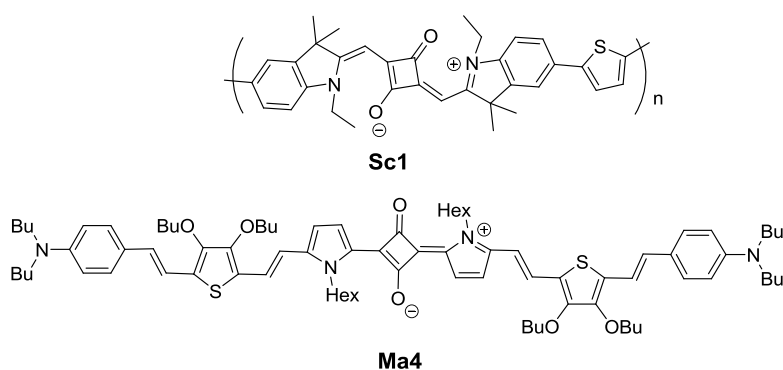


Figure 4 : Squaraines for 2PA in the IR

In 2007, Fu et al. studied the influence of the molecular structure (number of double-bonds, end-group, and symmetry) on the 2PA properties of a family of polymethine dye<sup>20,21</sup>. This study allowed to conclude that the TPA cross-section increases with the number of double-

bonds, the donor strength of end groups, and with the asymmetry of the dyes. However, 2PA cross-sections of these dyes remain lower than those reached for the squaraines dyes:  $\sigma_{2PA}$  (**Fu1**) = 600 GM at 1480 nm and  $\sigma_{2PA}$  (**Fu2**) = 200 GM at 1170 nm (Fig. 5). Marder et al also described the polymethine dyes (**Ma5**, Fig. 5) displaying high third order nonlinearities<sup>22</sup>. The real part of  $\gamma$  of **Ma5** was found to be  $-5.7 \cdot 10^{-32}$  esu, allowing to expect interesting applications in the field of all-optical signal processing.

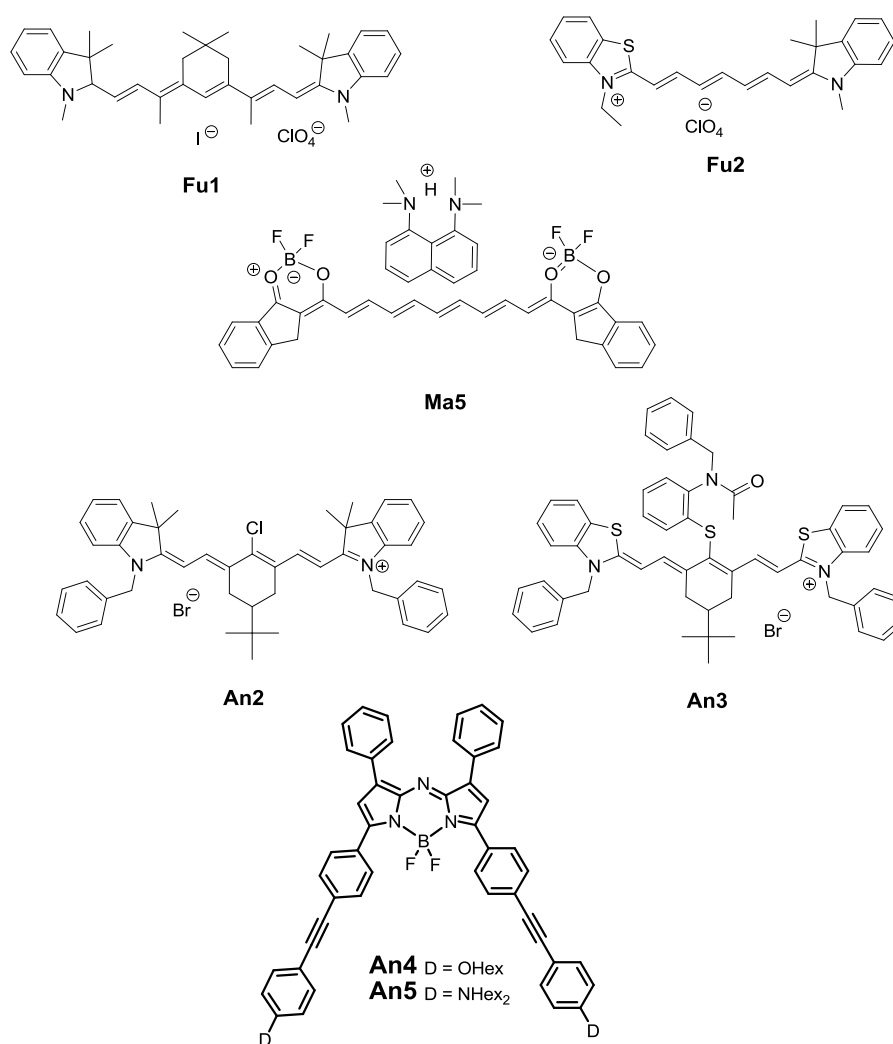


Figure 5 : Polymethine cyanines for 2PA in the IR

In 2007, our group developed cyanine dyes **An2** and **An3** for optical limiting applications<sup>15</sup>. These chromophores feature 2PA properties of the same order of magnitude than the dipolar analog **An1** previously described ( $\sigma_{2PA}$  of **An2**) = 731 GM at 1437 nm).

Nonlinear transmittance curves in the ns regime for this family are displayed at telecommunication wavelengths in Figure 2. These curves were fitted using a three-photon process: an initiating 2PA followed by an excited state reabsorption during the ns pulse.

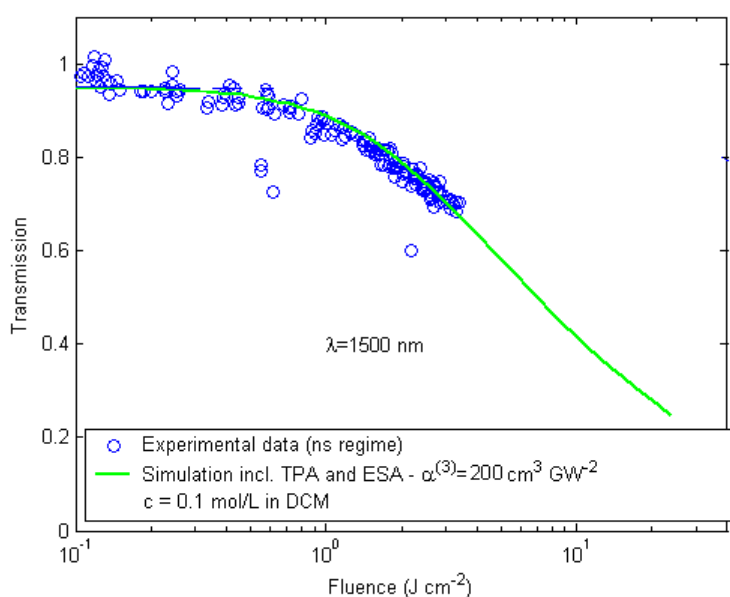


Figure 2 : Optical limiting curve at 1500 nm for **An2**

In all these examples, it is worth noting that, although these molecules are not centrosymmetric, 2PA bands are slightly blue shifted compared to the half-wavelength scale 1PA spectra (Fig. 7).



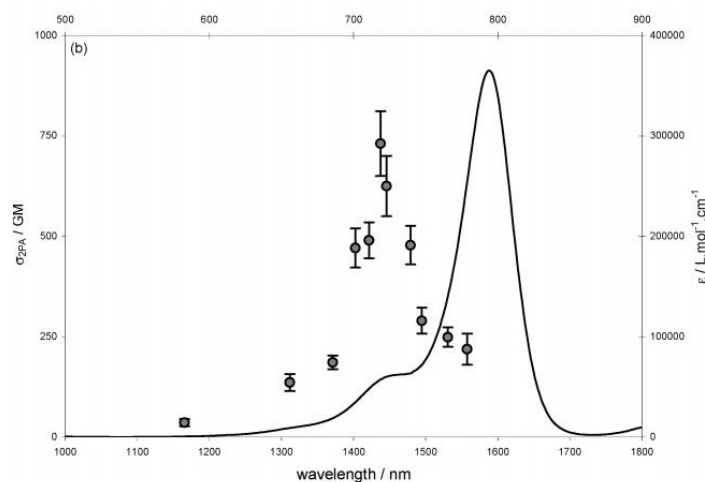


Figure 7 : Comparison of linear (-) and 2PA (circles) spectra of **An2**

In the continuity of the last work, we designed novel Bodipy chromophores displaying intense 2PA properties<sup>23</sup>. We demonstrated that by increasing the conjugation on the □ position of aza-boron dipyrromethenes, it was possible to obtain 2PA cross-sections higher than 1000 GM in the IR (**An5** in Fig. 5). In relation with their 2PA properties, these molecules present efficient nonlinear absorption properties.

#### *Diradical hydrocarbons.*

Kamada *et al* developed a new family of singlet diradical hydrocarbons bearing no A or D substituents, which exhibits very strong 2PA response in a wide range in the IR (Fig. 8)<sup>24</sup>. The cross-sections values for these diradicals are largely higher than those measured for other hydrocarbons such as a pentacene or octatetraene derivatives. Although the very high 2PA responses obtained at wavelengths lower than 1100 nm are probably enhanced by resonance, a  $\sigma_{2PA}$  value of 890 GM at 1500 nm was obtained for the system **Ka1** in Figure 8.

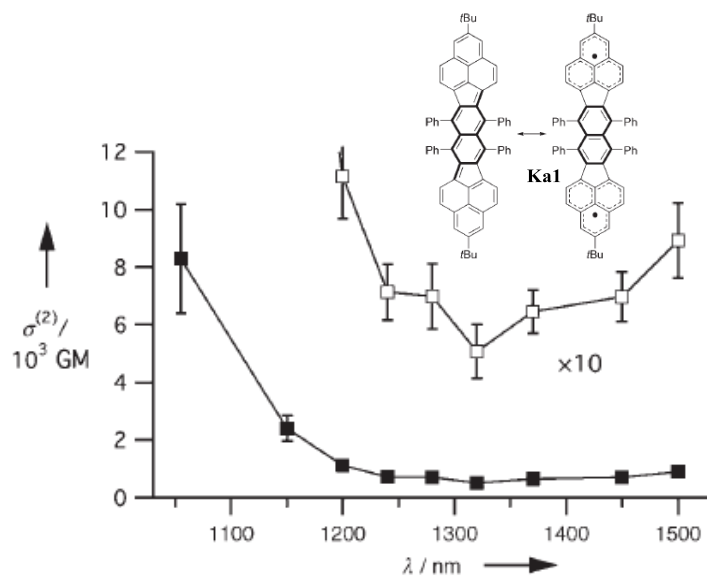


Figure 8: 2PA spectra of Singlet diradical hydrocarbons.

### Macrocycles derivatives

In 2006, Rebane and co-workers described symmetrical and nonsymmetrical phthalocyanines displaying weakly allowed 2PA transition at telecommunications range with  $\sigma_{2PA}$  values of 50 GM at 1400 nm and 20 GM at 1300 nm for **Re1** and **Re2** respectively<sup>25, 26</sup>.

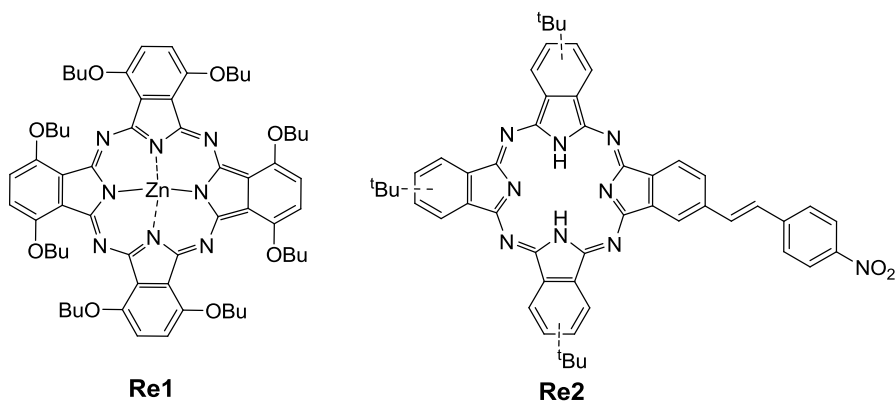


Figure 8 : Phthalocyanines for 2PA in the IR

Up to now, the most studied macrocycles for 2PA applications are the porphyrines. The first investigations in this field were performed on the 2PA properties of the Soret bands ( $\lambda_{exc} \approx$

800 nm)<sup>27</sup>. Recently, 2PA in the infrared have also been explored. In 2005, Osuka and co-workers showed that azulene-fused porphyrines display intense 2PA at telecommunication wavelengths:  $\sigma_{2PA}$  of **Os1** = 7000 GM at 1380 nm (Figure 3)<sup>28</sup>. Increasing the conjugation pathway around the metallic center is an interesting strategy to enhance the 2PA efficiency of porphyrines.

On the basis of a theoretical study of Agren and co-worker showing that a charge transfer could enhance 2PA response of porphyrines<sup>29</sup>, the group of Osuka substituted a porphyrine with a dipolar (D-A) or a quadripolar (D-D and A-A) system in which D and A were azulene derivatives. The best 2PA cross-section presented in this article is the one of the dipolar molecule (**Os2** in Figure 3):  $\sigma_{2PA}$  = 8000 GM at 1400 nm<sup>30</sup>.

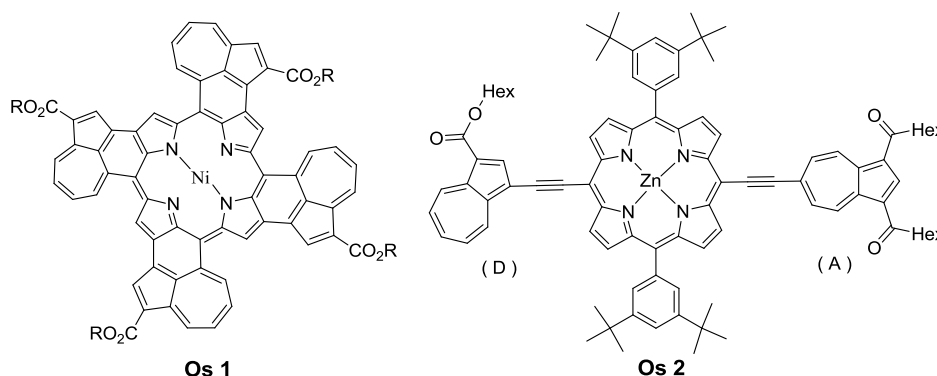


Figure 3 : Porphyrines for 2PA in the IR

An oligomer strategy was also used to enhance 2PA properties of porphyrines. In this purpose, Osuka and co-workers designed different porphyrins arrays: linear, T-shape, L-shape, porphyrins sheets...<sup>31</sup> From these strategies, it appears that the most efficient way to increase the 2PA was to create linear arrays. Figure 4 displays two examples of porphyrins oligomers with high 2PA: the meso-meso,  $\beta$ - $\beta$ ,  $\beta$ - $\beta$  triply linked **Os3** ( $\sigma_{2PA}$  = 15400 at 1260 nm) and the meso- $\beta$  doubly linked **Os4** ( $\sigma_{2PA}$  = 16900 at 1400 nm)<sup>32,33</sup>. In both examples, the increase of the number of monomers units leads to enhance the 2PA cross-

section, due probably to a cooperative effect since the 2PA cross-section per monomer increase the 2PA per monomer ( $\sigma_{2PA}/n$ ) also increases.

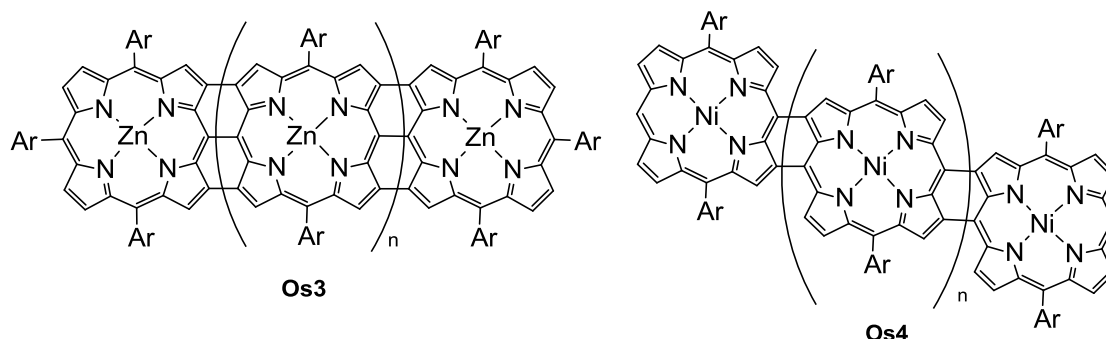


Figure 4 : Porphyrins arrays for 2PA in the IR

Another strategy developed by this group has consisted to increase the number of pyrroles units per porphyrins to synthesize the so-called “expanded-porphyrins” (Fig. 11)<sup>34</sup>. In this study, the highest  $\sigma_{2PA}$  values were obtained when the cycles are aromatic (for example,  $\sigma_{2PA}$  of **Os5**) = 12700 GM at 1410 nm).

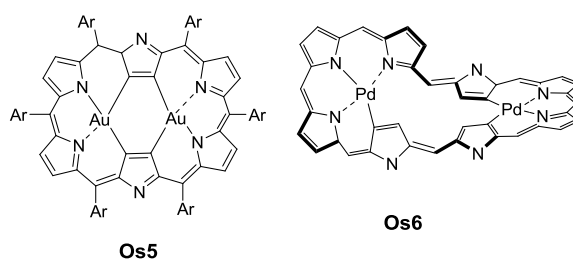


Figure 5 : Expanded porphyrins for 2PA in the IR

Rebane and co-workers synthesized ladder-type supramolecular porphyrins arrays<sup>35</sup>. In this article, two linear porphyrins arrays linked through a bipyridine based supramolecular bridge were described (Figure 6). Giant  $\sigma_{2PA}$  values were reported for the supramolecular assembly for **Re3** ( $\sigma_{2PA}$  = 115000 GM at 1200 nm). To our knowledge, this cross section value

corresponds to one of the highest  $\sigma_{2PA}$  values reported in literature for this wavelength range. As already described, the cooperation effect was shown by the increasing of the  $\sigma_{2PA}/n$  parameter.

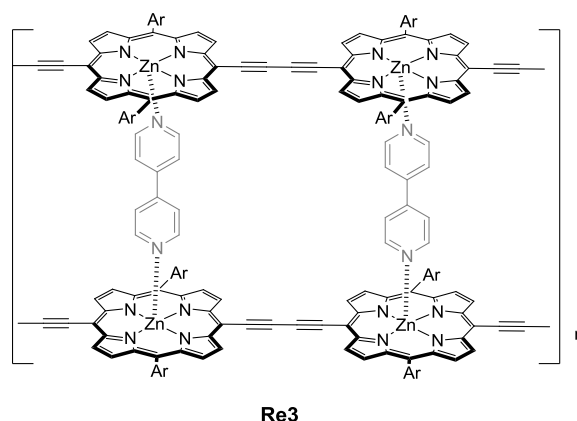


Figure 6 : Supramolecular porphyrins array for 2PA in the IR

### *Organometallic systems*

In 2007, Marder and co-workers synthesized nickel-dithiolenes substituted by electron donating groups and displaying intense 2PA:  $\sigma_{2PA}$  of **Ma6** = 5000 GM at 1200 nm (Figure 7)<sup>36</sup>. For this compound,  $\sigma_{2PA}$  is higher to 400 GM overall telecommunication windows. According to the authors, this high 2PA efficiency opens the way to many perspective sin the design of three-dimensional molecular structure based on coordination chemistry, as already demonstrated in the visible range<sup>2</sup>.

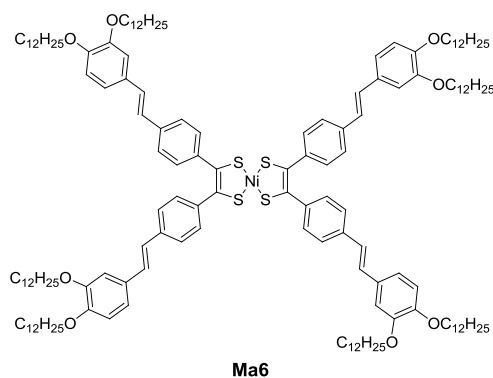


Figure 7 : Nickel-dithiolenes complex for 2PA in the IR

### 3. Conclusion

While a large effort was developed last ten years for the visible range, the design of systems for IR and particularly at telecommunications wavelengths was only recently investigated. However, as summarized below by Table 1<sup>37</sup>, different types of have been already designed with high  $\sigma_{2PA}$  values between 200 and 115000 GM opening the way to different applications.

Molecule	$\lambda_{1PA}^a$ (nm)	Method <sup>b</sup>	$\lambda_{2PA}^c$ (nm)	$\sigma_{2PA}$ (GM)	reference
<b>Ma1</b>	740	WLC <sup>c</sup>	1440	1500	14
<b>An1</b>	810	Z-scan	1445	792	15
<b>Ch1</b>	587	TPIF	1050	1300	16
<b>Ma2</b>	811	Z-scan	1064	2900	17
<b>Ma3</b>	889	Z-scan	1240	5900	17
<b>Sc1</b>	670	TPIF	1240	480	18
<b>Ma4</b>	832	Z-scan	1100	18000	19
<b>Fu1</b>	862	Z-scan	1480	600	20, 21
<b>Fu2</b>	643	Z-scan	1170	200	20, 21
<b>An2</b>	794	Z-scan	1437	731	15
<b>An3</b>	833	Z-scan	1495	544	15
<b>An5</b>	745	Z-scan	1220	1070	23
<b>Ka1</b>	875	Z-scan	1500	890	24
<b>Re1</b>	- <sup>d</sup>	TPIF	1400	50	25, 26
<b>Re2</b>	- <sup>d</sup>	TPIF	1300	20	25, 26
<b>Os1</b>	720	Z-scan	1380	7000	28
<b>Os2</b>	1100	Z-scan	1400	8000	30
<b>Os3</b>	1150	Z-scan	1260	15400	32, 33
<b>Os4</b>	900	Z-scan	1400	16900	32, 33
<b>Os5</b>	- <sup>d</sup>	Z-scan	1410	12700	34
<b>Os6</b>	- <sup>d</sup>	Z-scan	14410	6400	34
<b>Re3</b>	850	TPIF	1200	115 000	35
<b>Ma6</b>	980	Z-scan	1300	5000	36

<sup>a</sup>Longueur d'onde maximale d'absorption linéaire ; <sup>b</sup> measurement method of  $\sigma_{2PA}$  ; <sup>c</sup> 2PA maximum; <sup>d</sup> not communicated by the authors.

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37. It is worth noting, as largely shown in ref. 2, that an accurate determination of pure 2PA can be difficult on such systems due to one-photon resonance in the IR, which could partially explained giant  $\sigma_{2PA}$  values obtained for some molecules.