Multichromophores

DOI: 10.1002/anie.200903519

Cooperative Two-Photon Absorption Enhancement by Through-Space Interactions in Multichromophoric Compounds**

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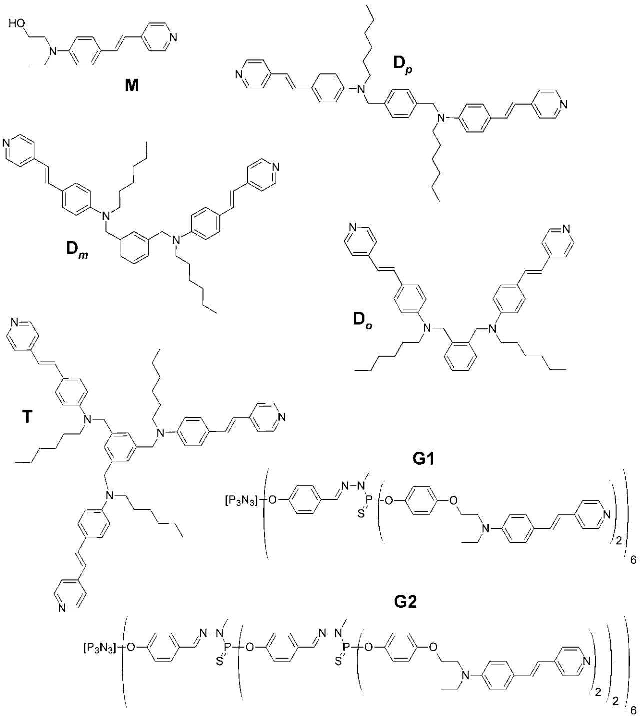
In the last decade, a major effort has been devoted to the achievement of efficient organic materials for nonlinear optics (NLO). Optimization has been sought at both the molecular and the supramolecular level. Of major importance is the awareness that the NLO properties of organic-based materials can be different from the sum of the properties of the isolated molecules.[1–4] In many cases, intermolecular interactions are found to be detrimental to the achievement of good performances for either second-order (electro-optical organic materials)[3] or third-order materials (e.g., two-photon absorption, TPA).[5] It has been shown, however, that significant cooperative TPA enhancement can be obtained in conjugated branched[6–9] or conjugated dendritic structures[10–12] as a result of through-bond coherent coupling between chromophoric subunits. Enhancement can also be achieved in the solid state through strong environment (charges) effects.[13,14] In contrast, the role of through-space interactions as a means to enhance TPA responses has seldom been considered.

Recently, we reported a strongly nonadditive behavior in covalent antiparallel dimers of a dipolar chromophore.[15] Dipole–dipole interactions were found to be responsible for a reduction of the TPA response per chromophoric unit, while modeling suggested that changing the relative orientation/distance of the chromophores would allow cooperative TPA enhancement to be achieved.[15] This prompted us to design and investigate multichromophoric molecular structures in which through-space interactions—instead of through-bond interactions[16,17]— would be exploited to increase the TPA response. In contrast to supramolecular chemistry, our aim was to use covalent bonding to confine chromophores and control their number and relative distance/positioning by grafting on suitable platforms.

Following this strategy, herein we report the amplification of the TPA response of a series of well-defined and soluble (as opposed to aggregates or nanocrystals) multistilbazole architectures (Scheme 1), and investigate how the different topologies and number of dipolar chromophores influence the



Scheme 1. A series of multichromophoric compounds built from the confinement of push–pull stilbazole chromophores: reference monomer (**M**); dimers obtained by grafting two chromophoric subunits to a central benzenic platform in the *para* (**D$_p$**), *meta* (**D$_m$**), and *ortho* (**D$_o$**) positions; trimer (**T**); dendrimers of the first (**G1**) and second generation (**G2**) bearing 12 and 24 chromophoric subunits, respectively.

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[**] F.T. and M.B.-D. acknowledge the Italo-French University and Egide for funding through the Galileo Program. M.B.-D. thanks the Indo-French Center for Promotion of Advanced Research (IFCPAR)/Centre Franco-Indien pour la Promotion de la Recherche Avancée (CEFIPRA) for financial support and a PDF to V.P. M.B.-D. acknowledges the CNRS for a PDF to T.M. Thanks are due to the Fundación Ramón Areces for a grant to A.P.-Q. M.B.-D., J.-P.M., and A.-M.C. acknowledge financial support from ANR (Project "Bio-dendridot"). M.B.-D. also acknowledges financial support (equipment grants) from the CPER "Photonique aux Interfaces" (FEDER and Région Bretagne). We thank J.-M. Vabre for contributions to the synthesis.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200903519.

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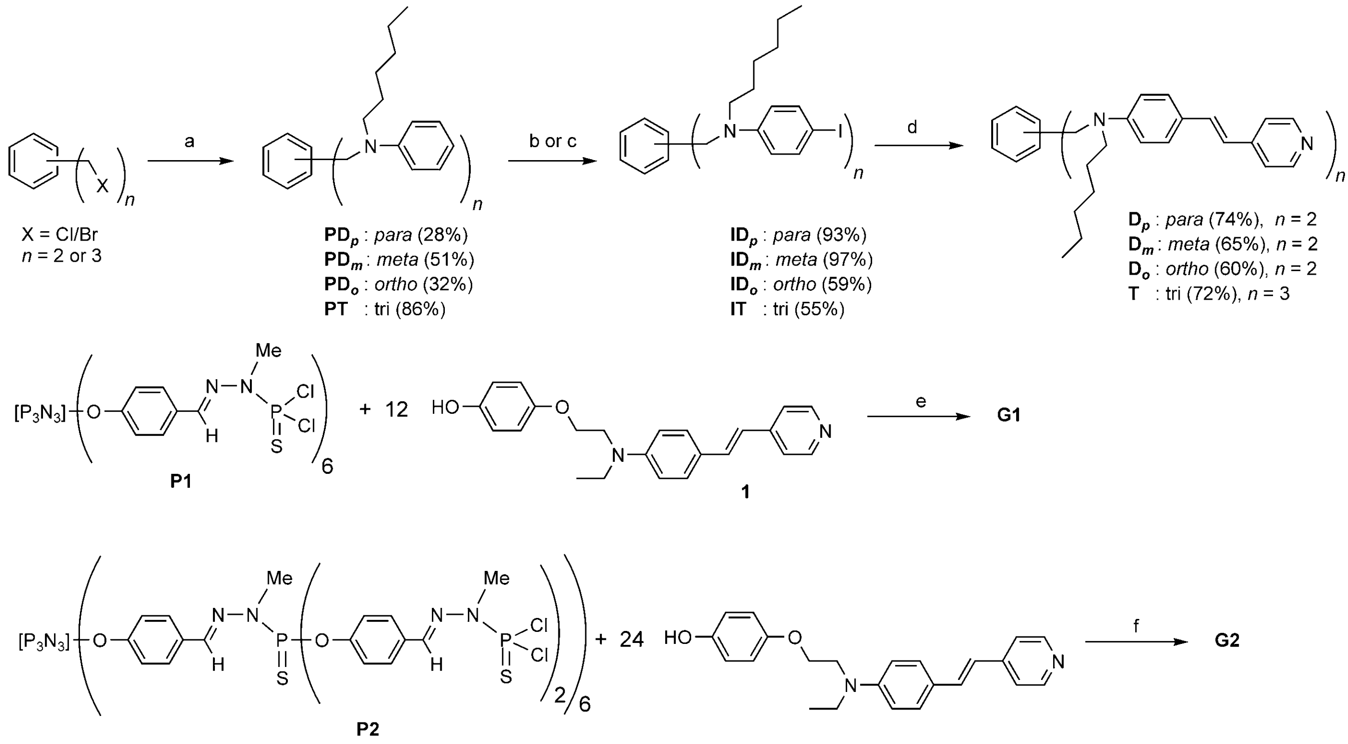

Scheme 2. Synthesis of multistilbazoles: a) *N*-hexylaniline, K_2CO_3, DMF, 90–110 °C, 2–3 d, 28–86 %; b) I_2, aq. $NaHCO_3$, CH_2Cl_2, 10 °C, 1 h, then RT, 0.5 h, 55–97 %; c) *N*-iodosuccinimide, DMF, 0 °C–RT, 1.5 h, 59 %; d) vinylpyridine, $Pd(OAc)_2$, PPh_3, K_2CO_3, nBu$_4$NBr, DMF, 50–70 °C, 3 h, 60–74 %; e) Cs_2CO_3, THF/acetone, 45 °C, 1 d, 58 %; f) Cs_2CO_3, THF/acetone, RT, 60 h, 70 %.

magnitude of the cooperative effect. Dimers and a related trimer were prepared in good yields according to the multistep synthetic path described in Scheme 2 (see also the Supporting Information). Multichromophoric dendritic architectures confining 12 or 24 chromophores were also prepared in moderate to good yields (see the Supporting Information) by reaction of an excess of reagent **1** on the dendritic platforms **P1** and **P2** (Scheme 2).

All of the compounds were characterized by linear one-photon absorption (OPA) and fluorescence spectroscopy, as well as by the two-photon excited fluorescence technique (using femtosecond excitation) to extract the corresponding TPA spectra.

The spectroscopic properties of the compounds are summarized in Table 1, and the OPA and TPA spectra normalized per chromophoric subunit are reported in Figure 1 (top panels). A slight hypsochromic shift as well as a definite hypochromic shift of the OPA band is observed for all multimeric derivatives as a result of interchromophoric interactions. The reduction of the molar extinction coefficient per chromophoric subunit is particularly remarkable for **D$_o$**, **T**, and the dendrimeric derivatives, that is, for compounds providing the closest proximity between subchromophores or with a larger number of chromophores. This finding can be ascribed to steric crowding, possibly leading to partial loss of planarity, as well as to inhomogeneous broadening effects. All of these effects would be expected to lead to a reduction of the TPA response as well. In contrast, we observe that the TPA maximum cross section, σ_2^{max}, per chromophoric subunit *increases* from monomer to multimers, even though the maximum molar absorptivity ε^{max} decreases. This behavior is summarized in Figure 1 (bottom panel), where the ratio $\sigma_2^{max}/\varepsilon^{max}$ is reported as a function of the number of chromophoric subunits.

Table 1: Spectroscopic properties of monomer **M** and *N*-meric multichromophoric derivatives in DMSO.

	N	λ_{OPA}^{max} [nm]	$\varepsilon(\lambda_{OPA}^{max})/N$ [$M^{-1}cm^{-1}$]	λ_{em}^{max} [nm]	ϕ[a] [%]	σ_2^{max}/N [GM][b]
M	1	386	31000	495	9.4	40
D$_p$	2	384	29400	490	7.4	55
D$_m$	2	384	30750	490	7.1	60
D$_o$	2	384	21400	490	5.3	68
T	3	384	26200	488	6.2	57
G1	12	381	23300	488	6.0	51
G2	24	381	20140	491	5.9	58

[a] Fluorescence quantum yield. [b] 1 GM = 10^{-50} cm^4 s photon^{-1}.

All multichromophoric compounds perform better than the model chromophore.[18] In addition, we observe that the response of the dimers increases from **D$_p$** to **D$_m$** to **D$_o$**, which corresponds to increasing proximity of the chromophoric subunits in the multichromophoric structure and hence to stronger interactions. The *meta* trimer **T** is found to lead to a slightly larger $\sigma_2^{max}/\varepsilon^{max}$ ratio than its corresponding dimer **D$_m$**. Analogously, the second-generation dendrimer **G2** leads to a higher ratio than the first-generation dendrimer **G1**, thus indicating that increasing the number of chromophores in related multichromophoric structures yields stronger effects. An amplification factor of up to 2.5 per chromophoric subunit

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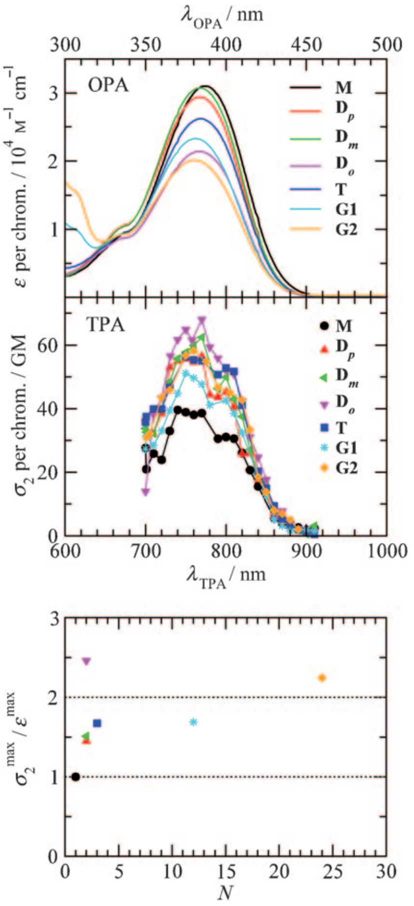

Figure 1. Top panels: experimental OPA and TPA per chromophoric subunit, measured in dimethyl sulfoxide (DMSO) solution. Bottom panel: the $\sigma_2^{max}/\varepsilon^{max}$ ratio as a function of the number N of chromophoric subunits.

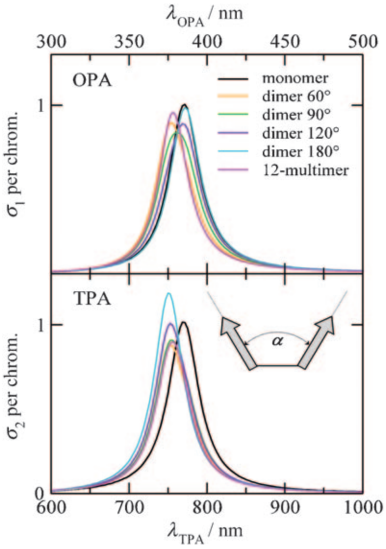

Figure 2. Calculated OPA and TPA per chromophoric subunit for monomer, dimers of varying interchromophore angle (α, see legend and inset), and a 12-chromophore multimer of icosahedral symmetry. The exciton coupling was fixed to $\Sigma_{j\neq i}J_{ij} = 0.05$ eV.

is obtained for the $\sigma_2^{max}/\varepsilon^{max}$ response, and up to 1.7 for the bare TPA cross section, σ_2. To the best of our knowledge, this is the first time that a cooperative enhancement (up to 70%) of the TPA response has been observed in soluble multichromophoric structures in which dipolar chromophoric subunits are connected through saturated bonds and hence interact only via through-space interactions.

The results presented here can be interpreted by means of the theoretical model first presented in reference [4], based on a two-level description of chromophoric subunits. Only electrostatic interactions are taken into account between chromophoric subunits, which gives rise to the well-known excitonic term (exciton hopping), plus mean-field interaction, plus other contributions describing the exciton–exciton interaction and the interaction between states having a different exciton number.[1] These last two contributions are negligible in the specific case of weakly polar and polarizable chromophores, so that discussion can be restricted to the standard excitonic Hamiltonian (see the Supporting Information), where the exciton-transfer interaction between chromophores i and j is labeled J_{ij}.[4]

Theoretical results for OPA and TPA spectra are reported in Figure 2 for dimers of increasing interchromophore angle (α) and for a model 12-chromophore multimer. The geometry of the considered dimer is sketched in the inset of Figure 2. A multichromophoric architecture having icosahedral symmetry, with 12 equidistant chromophores lying in the directions connecting the center to the vertexes of the icosahedron (interchromophore angle of about 63°, see the Supporting Information), was also considered. The results in Figure 2 clearly show that in order to achieve TPA enhancement (per chromophoric unit) in dimers with respect to the model monomer, an angle $\alpha > 120°$ is required. This is consistent with expected geometries based on electrostatic repulsions. Under these conditions TPA is enhanced whereas the OPA intensity decreases. We stress that this trend is independent of the specific value of the J_{ij} terms, but the behavior is accentuated if the exciton coupling is increased, for example, as a consequence of decreased interchromophore distances (see the Supporting Information). This is consistent with the observation of higher $\sigma_2^{max}/\varepsilon^{max}$ ratios for $\mathbf{D}_o$ with respect to the other dimers, and for dimers and trimers with respect to dendrimers (spacers between the platform—benzene core or dendritic architecture—and the subchromophores are longer in the latter case).

Interestingly, a reduction of the TPA cross section is predicted for the multimer of icosahedral symmetry (again independently of the specific value and sign of the J_{ij}), while a clear cooperative enhancement is experimentally observed for dendrimer **G1** (as well as **G2**). This result suggests that chromophoric subunits in the dendrimers are not equidistant, but rather form pairs of closer-interacting chromophores only slightly interacting with other chromophores from proximal pairs. This is consistent with the dendritic architecture, in which two chromophores are branched to each peripheral phosphorus unit (Scheme 1). Hence, the branched geometry provided by the dendritic platform supplying AB_2 connection is of particular interest for TPA enhancement. Moreover, we observe that the TPA enhancement increases from **G1** to **G2**,

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which indicates that the relative positioning of the chromophoric subunits is more favorable in the case of the **G2** dendrimer, probably because of closer proximity, within or between adjacent pairs.

In summary, based on the synthesis and investigation of a series of covalent multimers (from dimers to dendrimers) of a model dipolar chromophore, we have demonstrated that TPA cooperative enhancement can be achieved as a result of purely electrostatic through-space interchromophoric interactions, even in the case of a reduction of the linear (OPA) response. The TPA enhancement is found to depend on the distribution and number of chromophores, and increases when the dipolar subunits are in closer proximity. The present work provides evidence that interchromophoric interactions can be exploited—in conjunction with covalent bonding that imposes relative positioning—as driving forces for enhancing TPA responses. This opens a new molecular engineering route towards cooperative covalent nanostructures with enhanced TPA. In particular, gathering a larger number of more polar/polarizable chromophores in covalent multichromophoric architectures (including dendrimers) with appropriate geometry (based on modeling-assisted predictions) could lead to highly TPA-responsive covalent organic clusters.

Received: June 29, 2009
Revised: August 17, 2009
Published online: October 13, 2009

Keywords: chromophores · dendrimers · nonlinear optics · through-space interactions · two-photon absorption

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