

Conjugated macrocycles with photoactivated optical absorption for the control of the transmission of the energy delivered by pulsed radiations

Mario J. F. Calvete^{a*}, Danilo Dini^{b*}

a: CQC, Department of Chemistry, Faculty of Science and Technology, University of Coimbra, Rua Larga, P 3004-535 Coimbra, Portugal.

b: Department of Chemistry, University of Rome “La Sapienza”, P.le Aldo Moro 5, I-00185, Rome, Italy.

* corresponding authors: mcalvete@qui.uc.pt; daniilo.dini@uniroma1.it

ABSTRACT. The control of the transmission of the energy transported by optical waves is of extreme importance for the realization of those advanced technologies which require high speed of operation and fast switching. Such a task can be approached through the design and preparation of materials that possess modulable optical properties. In the present review the aspect of material science behind the realization of the effect of optical limiting, OL (or optical power limiting, OPL), will be considered focusing on those materials based on conjugated metallo-macrocycles like porphyrins, phthalocyanines and derivatives. The choice of these molecular materials for OL purposes is motivated by the fact that the optical properties of such annulated systems can be finely modulated in a controlled fashion by changing the chemical structure of the complex. These changes involve the variation of the central metal, the extent of electronic conjugation of the ring, the nature and the number of peripheral ligands, and the eventual introduction of axial ligands coordinated by a central metals with a valence higher than +2. An attempt will be made to establish relationships between the structure of the macrocyclic complex and the relative OL properties taking into account the most recent developments in the field. During this analysis we will also discuss the aspect of optically passivity, i.e. the characteristic of the OL materials of undergoing fast changes of optical properties according to an internal mechanism of self-activation.

INTRODUCTION

The nonlinear optical (NLO) effect of OL consists in the attenuation of the intensity of the light transmitted by a system when the intensity of the light exceeds a system-specific threshold value (I_{lim}) (Figure 1) [1]. For a given system the response of the transmitted light intensity (I_{out}) vs. the incident light intensity (I_{in}) varies with the wavelength λ of the incident light. Therefore, the optical system will be limited in the range of wavelengths within which it can exert an OL action.

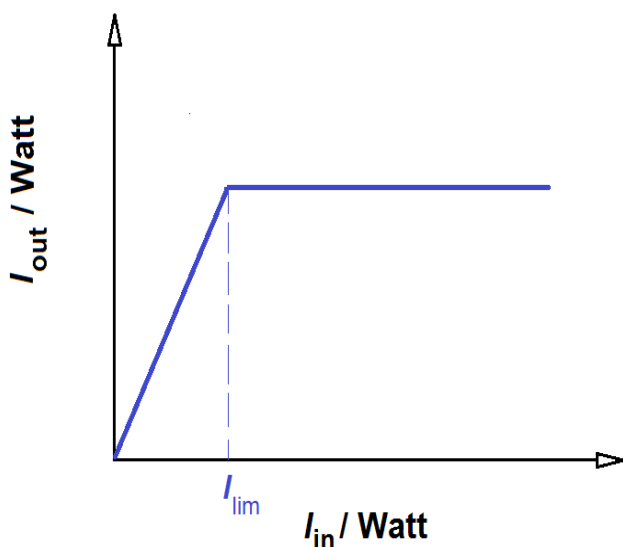


Figure 1. Variation of the light intensity transmitted by an optical limiter (I_{out}) vs. the intensity of the incident radiation (I_{in}). The threshold intensity I_{lim} at which I_{out} saturates is evidenced on the x -axis.

Since the system undergoes a transition from the regime at constant transmittance (we recall here the definition of transmittance, $T = d I_{out} / d I_{in}$) when $I_{in} < I_{lim}$, to the regime with $T \rightarrow 0$ when $I_{in} \geq I_{lim}$, it is implicit that the mechanism of light absorption of the system will necessarily vary in the diverse regimes of optical transmission [2]. In particular, the OL effect produced by the molecular materials here considered, i.e. phthalocyanines (Pcs) [3,4], porphyrins (Pors) [5,6] and their analogues [7-10], is based on the mechanism of excited state absorption (ESA), which involves the populating of an excited electronic state possessing an absorption cross-section (σ_{exc}), expressed in cm^2 , larger than the one of the ground electronic state (σ_g) at the wavelength of irradiation [11]. Such an effect has been also denominated reverse saturable absorption (RSA) [12] and is commonly described in terms of the four-level model for molecular systems with NLO activity [13]. The latter model considers the succession of two electronic transitions starting from different electronic states of the molecule, the occurrence of which requires the intervention of a fast process of intersystem crossing with respect to the duration of the radiation. The OL active molecule absorbs one photon initially from its ground electronic state to the first excited singlet state. Successively the excited molecule absorbs a second photon at the same energy of the first one either from the singlet excited state or from the first excited triplet state that is populated via an intersystem crossing (ISC) process. The multiphoton absorption here considered in the four-level model takes place in a sequential fashion but events of simultaneous two- or three-absorption absorption [14] from ground or excited levels can also occur [9,15]. The four-level model takes into account the characteristic of the NLO active molecule of possessing electronic states with discrete energy levels [16], but the

scheme can be applied with success also for the rationalization of the OPL effect produced by semiconducting crystals with electronic band structures [17]. In the four-level model the effective absorption cross-section σ_{eff} in the NLO regime of OL activity at a given wavelength is expressed by the formula [18]:

$$\sigma_{\text{eff}} = (\sigma_g I_{\text{lim}} + \sigma_{\text{exc}} I_{\text{in}}) / (I_{\text{in}} + I_{\text{lim}}) \quad \{1\}$$

with

$$I_{\text{lim}} = h\nu / \sigma_g \tau_{\text{exc}} \quad \{2\}$$

In equations {2} h is the Planck's constant, ν the optical frequency, and τ_{exc} the lifetime of the light-absorbing excited state. For the evaluation of the OL effect generated through ESA several figures of merit have been defined [19]. These are directly proportional to the excited state absorption cross-section like in case of the parameters $(\sigma_{\text{exc}} - \sigma_g)$ or $\sigma_{\text{exc}}/\sigma_g$. [13,20] Other figures of merit for OL performance evaluation can be also defined if the temporal response of the OL system needs to be considered as well [21]. The OL effect is directly evaluated through the main NLO experimental technique of the measurement of the optical transmittance of the OL active material with a light-probe of monochromatic character having modulable intensity/fluence [22]. Beside the adoption of the type of representation shown in the plot of Figure 1, the OL effect can be also visualized through the profile of the optical transmission at a given wavelength of analysis (y-axis) vs. the intensity or fluence of the incident light (I_{in} or F_{in} on the x-axis, Figure 2) [23].

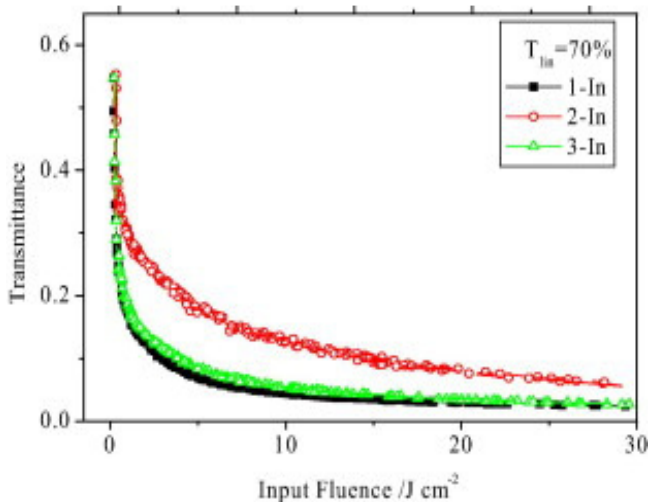


Figure 2. Typical decreasing trend of the optical transmission of three different OL active materials with the incident fluence (F_{in}). The comparison shows in a straightforward way the stronger OL effect exerted by the compounds associated to the black and green profiles. The indexes 1-In, 2-In

and 3-In in the inset refer to the dendrimeric phthalocyanines **17-19** (Chart 3, *vide infra*). Reproduced with permission from ref. **23**.

PHTHALOCYANINES AND RELATED COMPOUNDS FOR OPTICAL LIMITING: SOME RECENT EXAMPLES

Pcs are molecular dyes with high molar extinction coefficient in the NIR-visible range. This class of complexes is commonly employed as colorant for traditional and advanced applications [10,24-49] due mainly to the elevated chemical/physical stability, and easiness of preparation and purification [50-52] As far as the NLO effect of OL is concerned (Figure 1), it is prerogative of any Pc (either in the pure state [53] or dispersed in a liquid [3]/solid[54] matrix) to display such an effect provided that the radiation to be limited is in the wavelength range comprised between the characteristic Q- and B-absorption bands of the Pcs (Figure 3) [55].

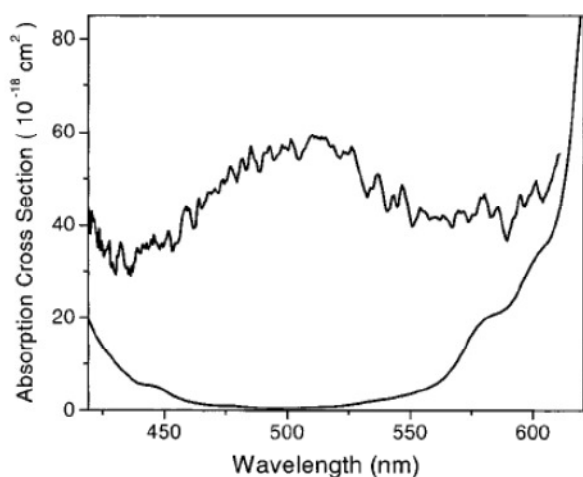


Figure 3. Spectra of absorption cross section for the ground- and excited-state of a metallophthalocyanine. The excited-state profile is the one with the noisy appearance. Reproduced with permission from ref. **55**.

For the realization of the OL effect by Pc-based systems another condition to fulfil is the achievement of a sufficiently large population in a highly absorbing excited state within the duration of the light pulse [56]. An exhaustive analysis of the structural factors of the Pc complexes which govern the extent and the dynamics of the OL effect produced by this class of conjugated materials has been recently reported in a comprehensive review [57]. At the basis of the control of the OL effect generated by Pcs and their analogues the following aspects were considered: the extent of electronic conjugation of the macrocyclic ligand [58] the electronic and solubility effects of the peripheral substituents on the conjugated ligand [41,59], the nature of the coordinating central

metal [60,61], the eventual presence of axial ligands coordinated by the central metal and the associated repercussions on the electronic structure and processability of the whole metal complex [55,62]. Hereafter we report a description of the most recent structures of Pcs and derivatives which have been proposed as NLO materials for the realization of the OPL effect.

Substituted phthalocyanines

Several examples of Pcs with axial and peripheral substituents (compounds **1-14** in Charts 1 and 2) have been recently reported as OL active systems when these Pcs were dispersed in liquid solutions or in an optically inert matrix [63-70]. These complexes are characterized by having several patterns of peripheral substitution (tetra-, octa- or 3:1 substituted Pcs) and, consequently, diverse symmetries and different orientations of dipole moments in both ground and excited states during the electronic transitions originating the OL effect [55,71]. It has been generally acknowledged that Pcs possessing halogen substituents either in axial [63-69] or peripheral [64] position present relatively stronger OL effect by virtue of the favourable electron-withdrawing effect exerted by these atoms [31,72].

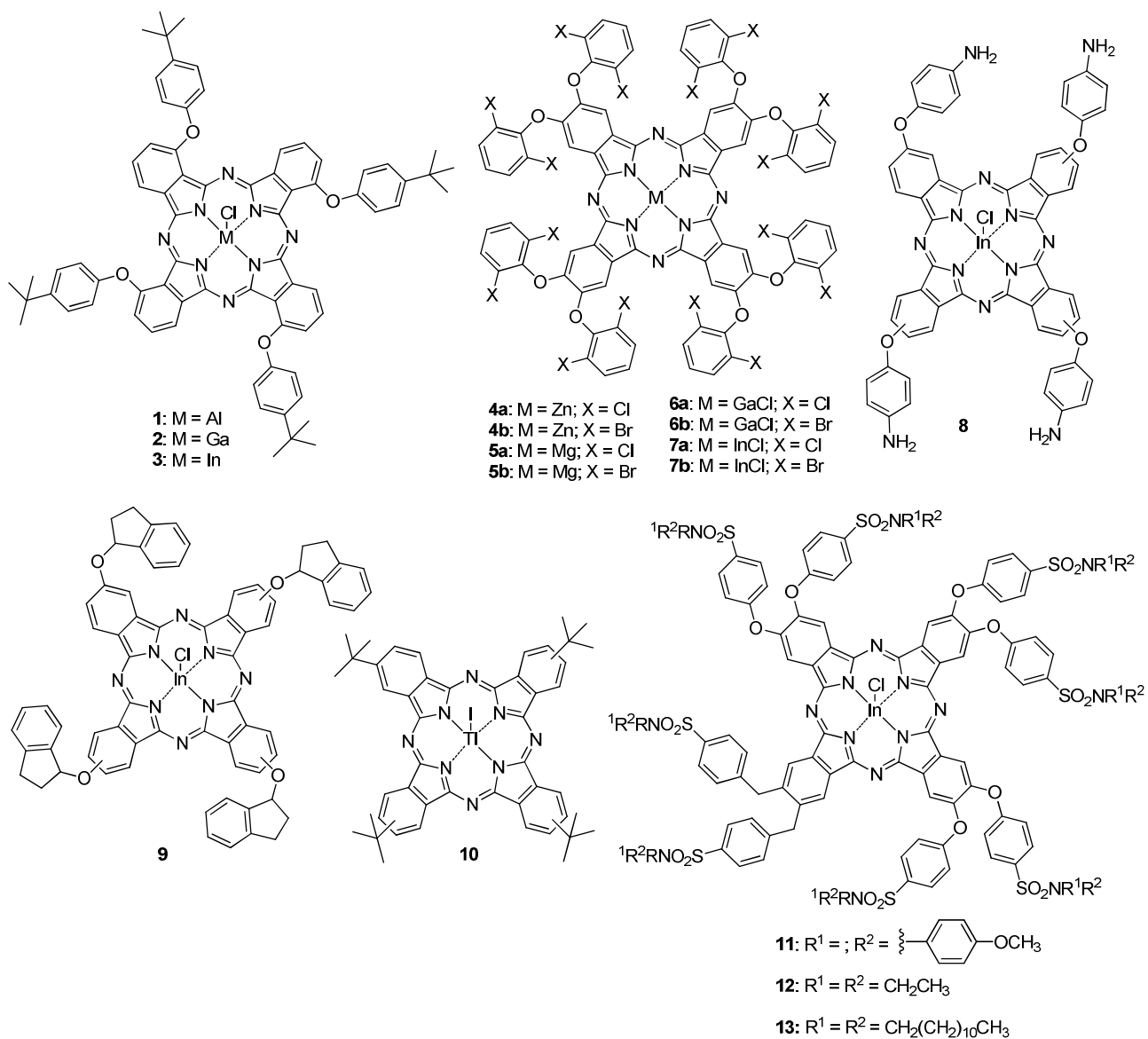


Chart 1. Series of OL active tetra- / octa- substituted metallo-phthalocyanines **1-13** with the metal center coordinating an axial ligand [63-69].

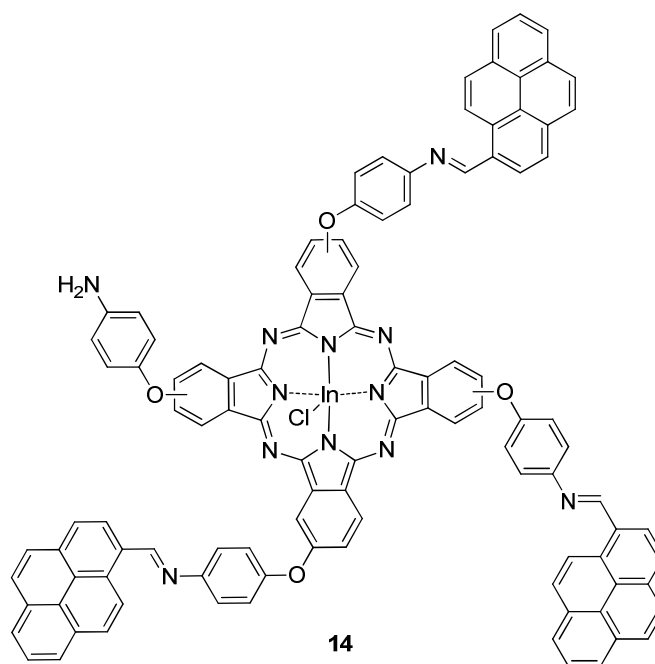


Chart 2. Structure of the non symmetrically substituted 3:1 indium phthalocyanine **14** with OL activity [70].

Beside the generally beneficial effect of the presence of halogen substituents, another structural factor having a favorable influence on the OL properties of a Pc is the presence of heavy atoms either as central coordinating atoms (Figure 4) [73,74], or in peripheral positions[50], which accelerate the formation rate of highly absorbing states in the electronically excited Pcs during the step of intersystem crossing [75].

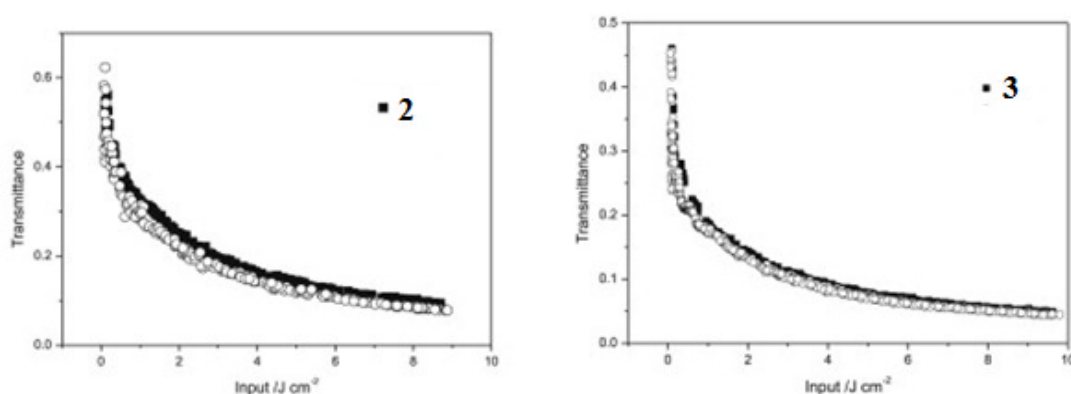


Figure 4. NLO transmission profiles associated to the OL effect of gallium-phthalocyanine **2** and indium-phthalocyanine **3** depicted in Chart 1. Adapted from ref. 65.

Another series of structural modifications that have been considered for the creation of optimized Pc-based systems with possibly improved properties of OL with respect to monomeric Pc complexes regarded the realization of dendrimeric phthalocyanines (compounds **15-19**, Chart 3) [23,76], double-deck phthalocyanines of indium (compound **20**, Chart 4),[77] and rare earth metals

(compounds **25-27**, Chart 4) [78,79], bis-phthalocyanines (example of compound **21** in Chart 4) [58], and axially-bridged silicon phthalocyanines (compounds **22-24**, Chart 4) [80].

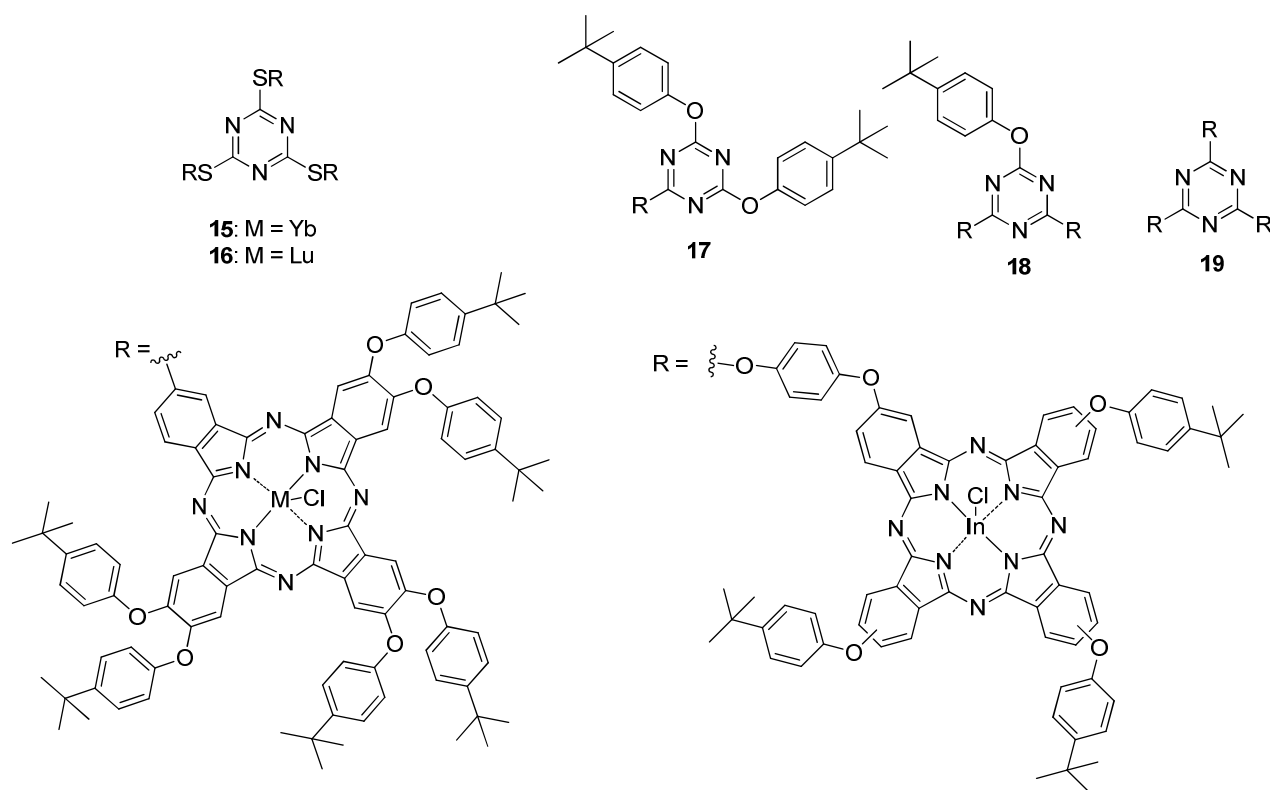


Chart 3. Series of OL active dendrimeric Pcs **15-19** with triazine cores [23,76].

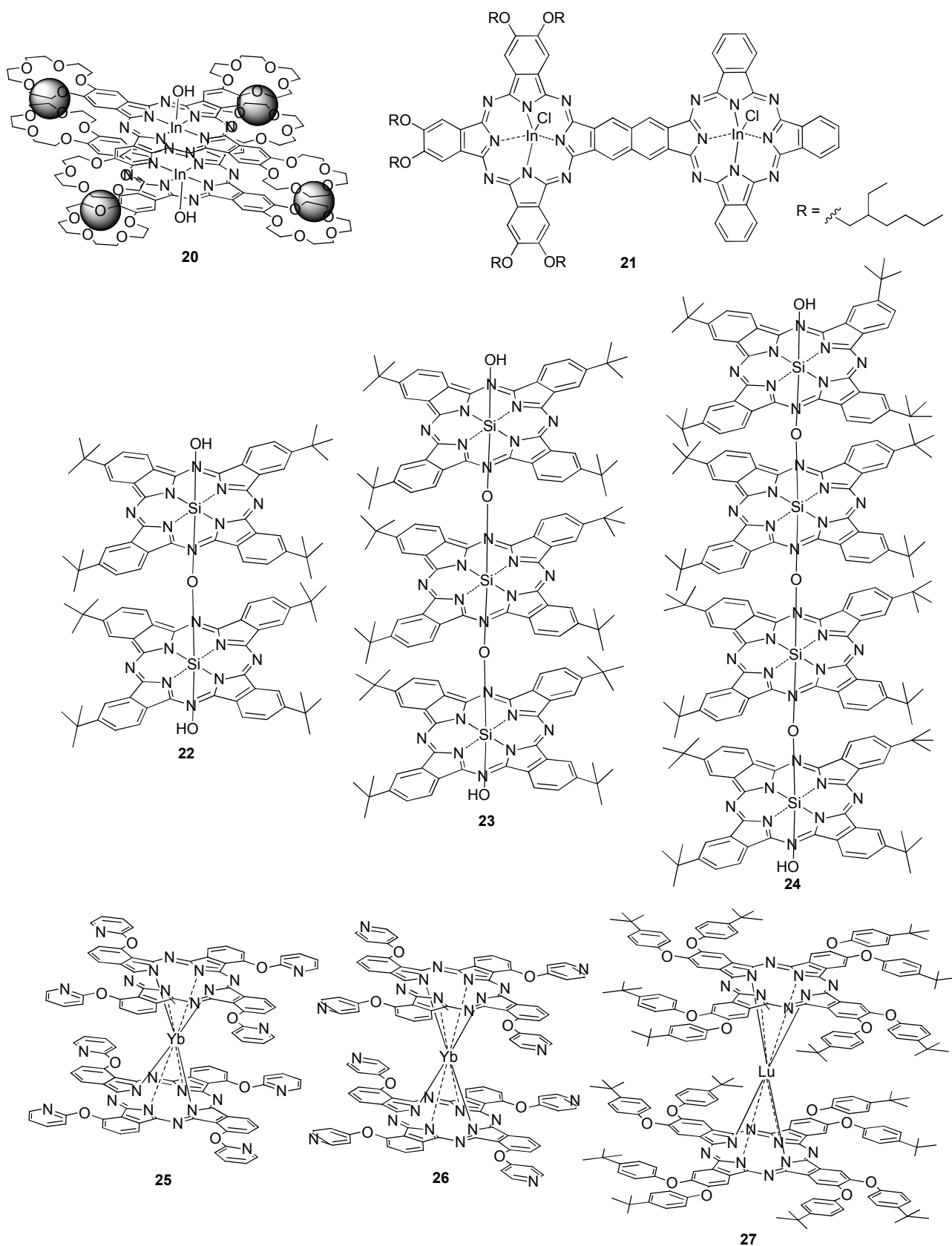


Chart 4. Series of OL active double-deck Pcs with indium **20** [77] and rare earth central metals **25-27** [78,79], axially substituted bis-Pc **21** [58], and axially-bridged Pcs **22-24** [80].

For example, the OL actions of double-deck ytterbium (**15**) and lutetium (**16**) phthalocyanines were quite similar (Figure 5), with complex **16** displaying a larger window of NLO response with respect to the ytterbium analogue **15** [76].

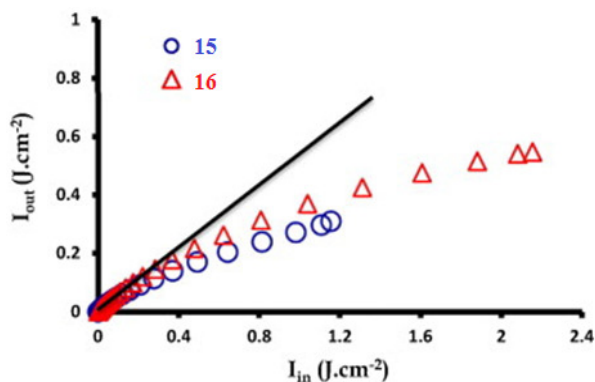


Figure 5. Plot of the NLO transmission profiles associated to the OL effect produced at 532 nm by dendrimeric ytterbium-phthalocyanine **15** and lutetium-phthalocyanine **16** (Chart 3). The OL response of Pcs **15** and **16** was recorded when these complexes were dispersed in a polymeric matrix. Adapted from ref. **76**.

The comparison of the OL action produced by axially-bridged Pcs has been reported in Figure 10 for the series of silicon phthalocyanines **22-24** (Chart 4) [80]. For this set of silicon complexes the OL effect depended clearly on the wavelength of excitation (Figure 6). In particular, dimer **22** was the most effective optical limiter of this series of Pc oligomers at the reference wavelength of 532 nm, whereas tetramer **24** produced the best OL response at the wavelength corresponding to the maximum linear absorption, i.e. the Q-band. These findings indicate that there is an interplay between linear and nonlinear optical absorption, which determines the extent of the OL effect. Another consideration on the OL action exerted by complexes **22-24** (Chart 4 and Figure 6) [80] and for the bis-phthalocyanine of lutetium **27** (Chart 4 and Figure 7) [79] is the dependence of such a NLO phenomenon on the existence of electronic communication between all stacked rings as verified in a different context through the measurement of the electrical conductivity for analogous systems [81].

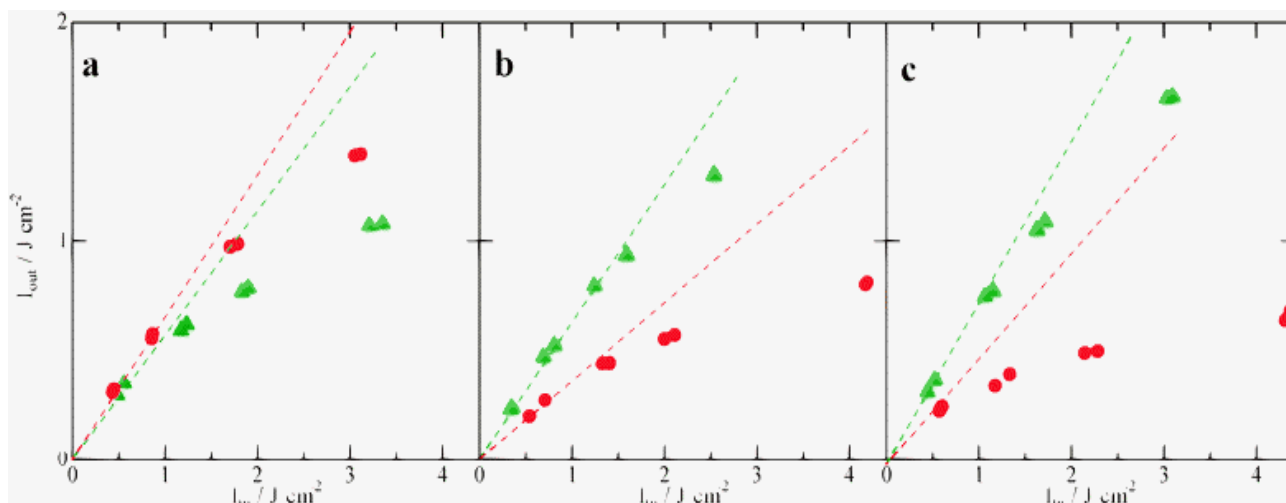


Figure 6. OL effect of axially bridged silicon phthalocyanines (a) **22**, (b) **23** and (c) **24** (Chart 4) at various wavelengths. Green triangles refer to the NLO transmission of the three complexes at 532 nm (laser pulse duration: 7 ns). Red dots refer to the NLO transmission at 720, 670 and 660 nm for dimer **22**, trimer **23** and tetramer **24**, respectively. Reproduced with permission from ref. **80**.

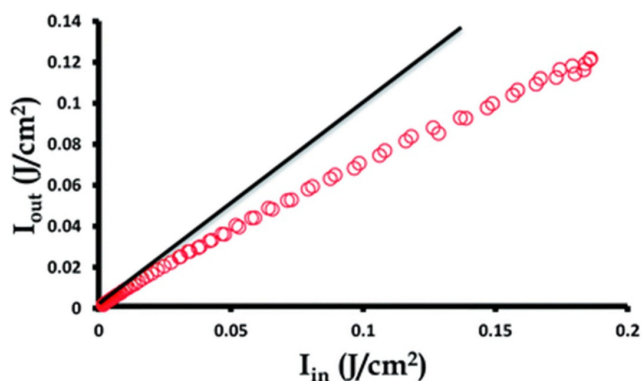


Figure 7. OL effect of the bis-phthalocyanine of lutetium **27** (Chart 4) at 532 nm with ns pulses. Bis PcLu concentration was $2.9 \cdot 10^{-4}$ M in DMF. Reproduced with permission from ref. **79**.

Tethered phthalocyanines

For the realization of increasingly effective optical limiters based on Pcs active systems various authors have recently considered the approach of tethering phthalocyanines and analogs on nanostructured systems like nanoparticles, nanorods, nanorings or graphene sheets (Chart 5), which are characterized by band-like electronic structures [82-89]. Behind these great synthetic efforts there is the main motivation of creating new combinations of materials with peculiar opto-electronic properties in order to produce an improved OL action with respect to the single, non-combined units. The achievement of a successful combination Pc-nanostructure like those represented in Charts 5 and 6 (combinations **28-39**) consists of the occurrence of a synergistic interaction between the electronic structures of the phthalocyanine and the tethering nanosystem [90-92]. Such a synergy would produce a beneficial effect on the resulting OL action produced by the tethered systems with respect to the NLO response produced by the non tethered separated units. The di-neodymium phthalocyanine tethered to a multi-walled carbon nanotube (MWCNT) (structure **28** in

Chart 5) is an example of an OL active system displaying a synergistic NLO action with respect to the constitutive units (Figure 8) [82]. A similar NLO behavior could be found with the combination of a bidentate indium phthalocyanine tethered to a single-walled carbon nanotube (SWCNT) (structure 32 in Chart 5) as shown in Figure 9 [84]. When the tethering unit is a semiconducting nanoparticle like a metal oxide [93,94]. *e.g.* ZnO (structure 34 in Chart 6) [86], the synergistic effect on the OL action of the resulting combination can be still observed (Figure 10). The combination of a zinc phthalocyanine anchored to Au NPs via amino groups (structure 35 in Chart 6) has been also reported for OL purposes and the relative results are presented in Figure 11 [87]. The realization of surface modified Au NPs with phthalocyanines leads to the formation of a nanoparticulated system (Figure 12) that can produce OL also via NLO scattering [95]. Such systems can also undergo a process of self-healing for the regeneration of the Pcs interacting electronically with the metallic nanoparticle [35]. The employment of magnetically active materials as tethering units of a phthalocyanine was also explored for OL applications when magnetite (Fe_3O_4) was prepared in the form of nanoparticles and an indium phthalocyanine was the macrocyclic complex (structures 36 and 37 in Chart 6 and Figure 13) [87]. The choice of a magnetic material as supporting substrate was mainly motivated by the favourable action that ferrite would have played in the formation and stabilization of the highly absorbing triplet state of the excited phthalocyanine in the anchored state. Another important aspect that has been considered in the process of design and synthesis of Pc-tethered systems is the evaluation of the influence of tethering on the linear optical properties of the anchored Pc. This particular analysis has been conducted through a systematic approach in the of various tetra-substituted metallo-phthalocyanines combined with reduced graphene oxide (RGO) (structures 29-31 in Chart 5 and Figure 14) [83]. Results clearly demonstrated that tethered Pcs on RGO presented linear optical features typical of aggregated molecules with formation of either *J*- or *H*-aggregates [96] displaying band broadening and absorption peak shifts. At a morphological level the aspect of the resulting tethered system was scale-like (Figure 15) [83].

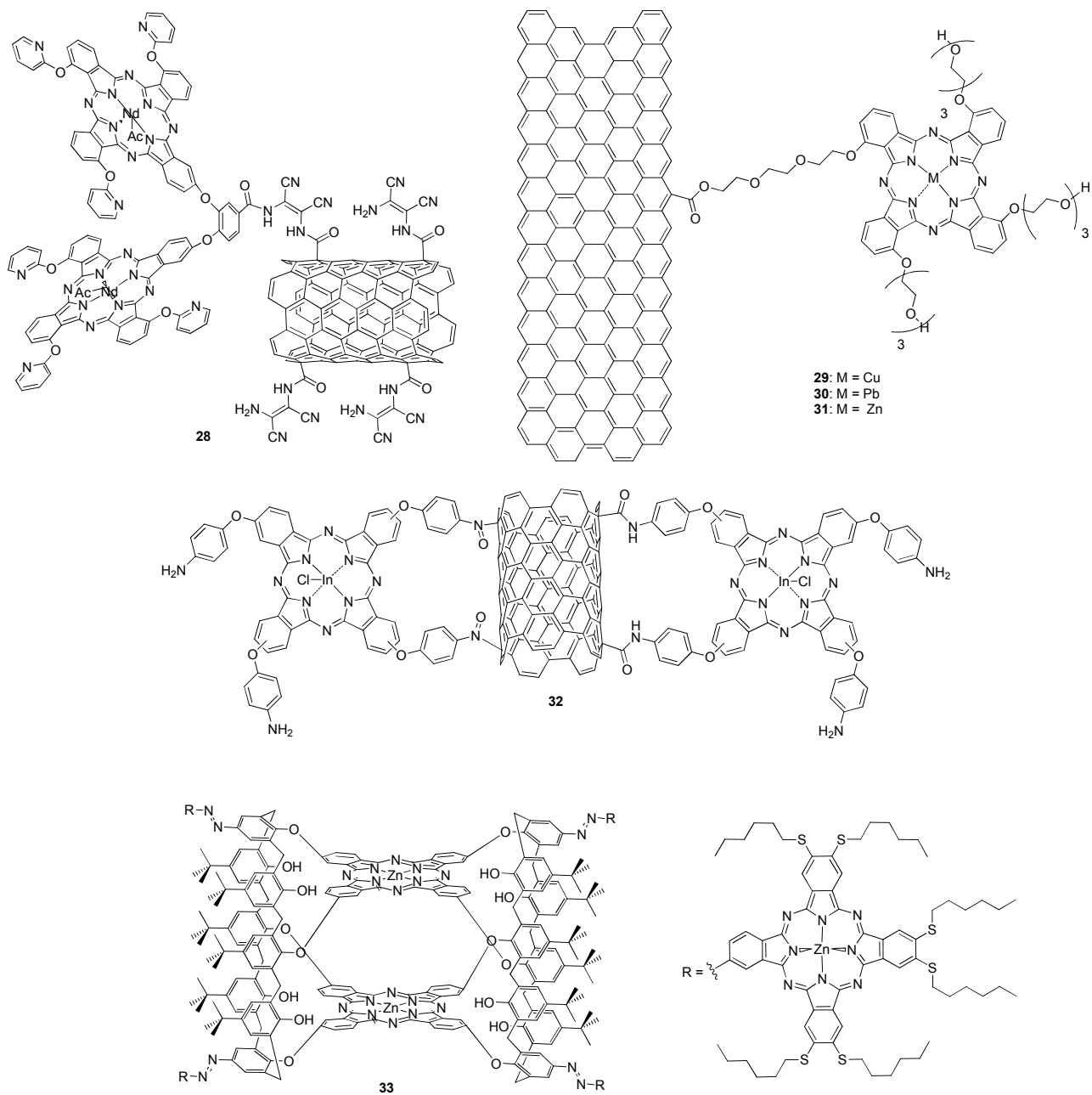


Chart 5. Series of tethered Pcs **28-33** [82-85] with OL activity.

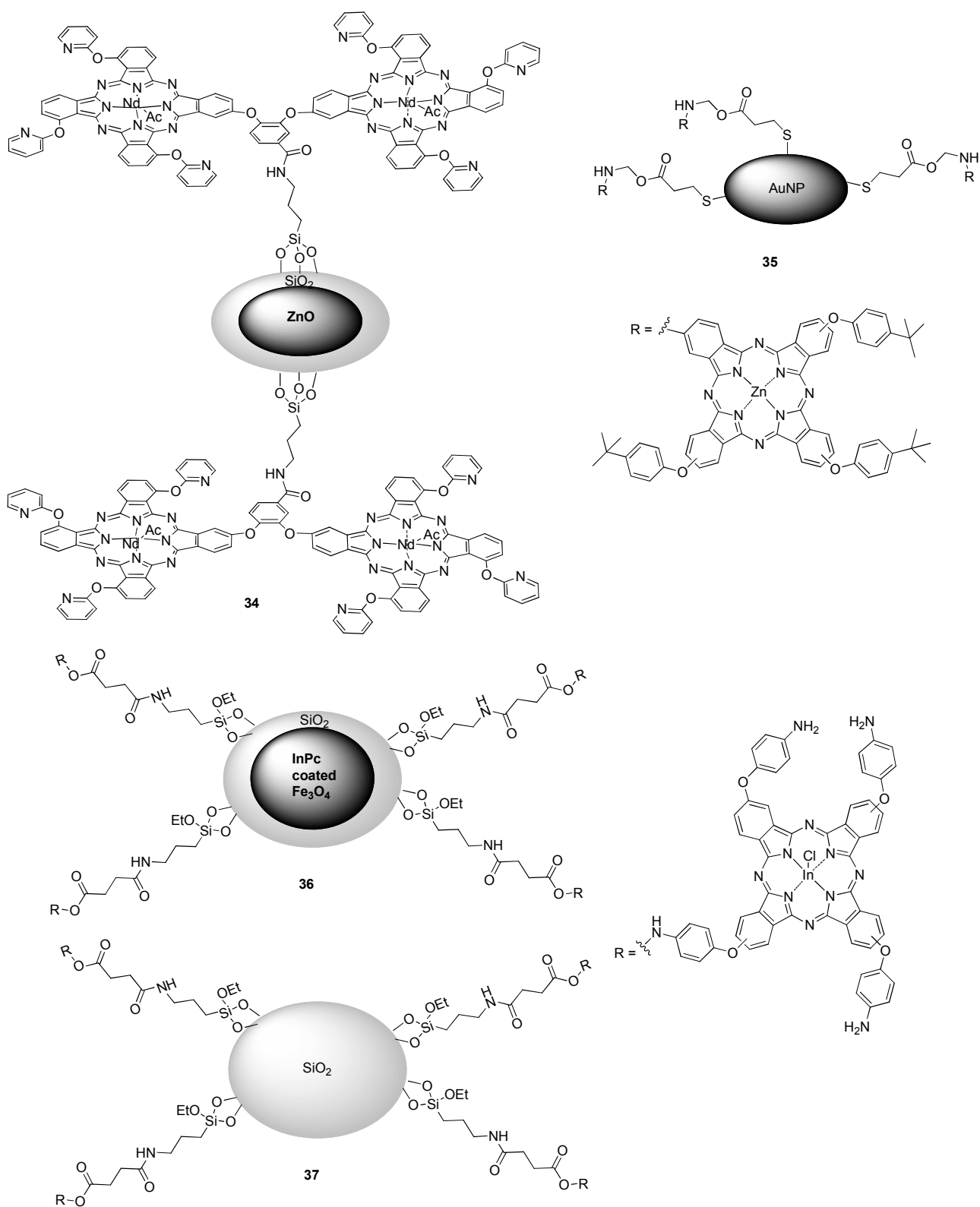


Chart 6. Series of tethered Pcs **34-37** [86-88] with OL activity.

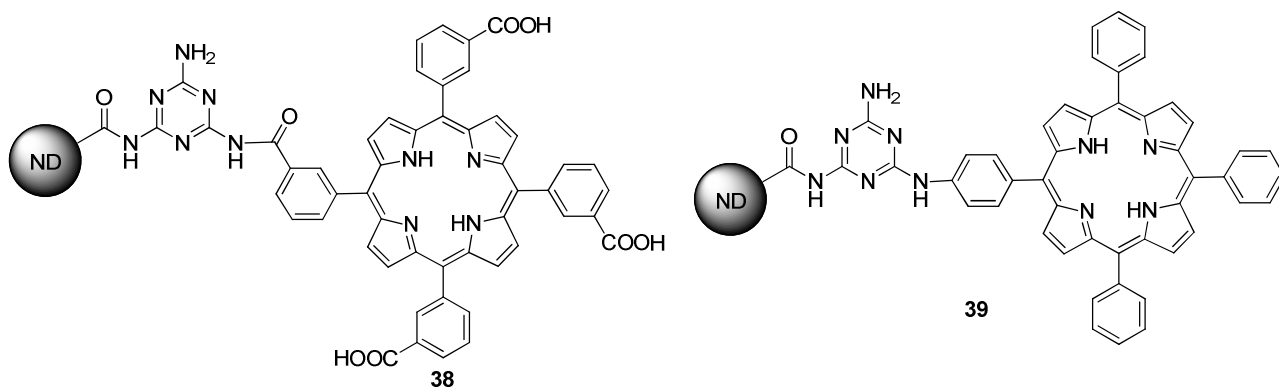


Chart 7. Tethered porphyrins **38** and **39** [89] with OL activity.

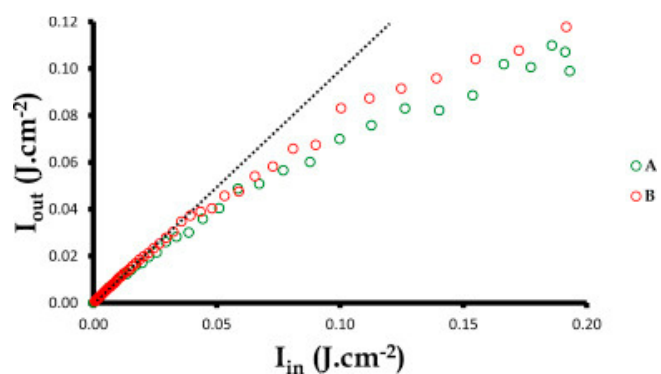


Figure 8. Output fluence against input fluence for the di-neodymium phthalocyanine tethered to a MWCNT (**28** in Chart 5). Profiles **A** and **B** were determined at the different incident intensities of 0.19 GW cm^{-2} and 0.48 GW cm^{-2} , respectively. Reproduced with permission from ref. **82**.

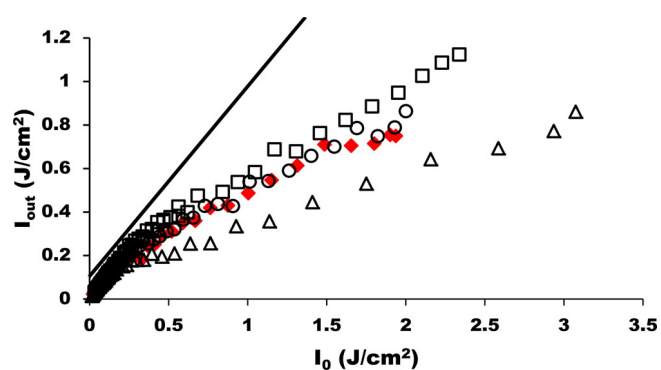


Figure 9. Output fluence against input fluence for a bidentate indium phthalocyanine tethered to a SWCNT (**32** in Chart 5) in DMSO (Δ) and DMF (\square). For sake of comparison the OL response of the non tethered PcInCl is also reported in DMF (\circ) and DMSO (\blacklozenge). The peak input intensity was 260 MW cm^{-2} . Reproduced with permission from ref. **84**.

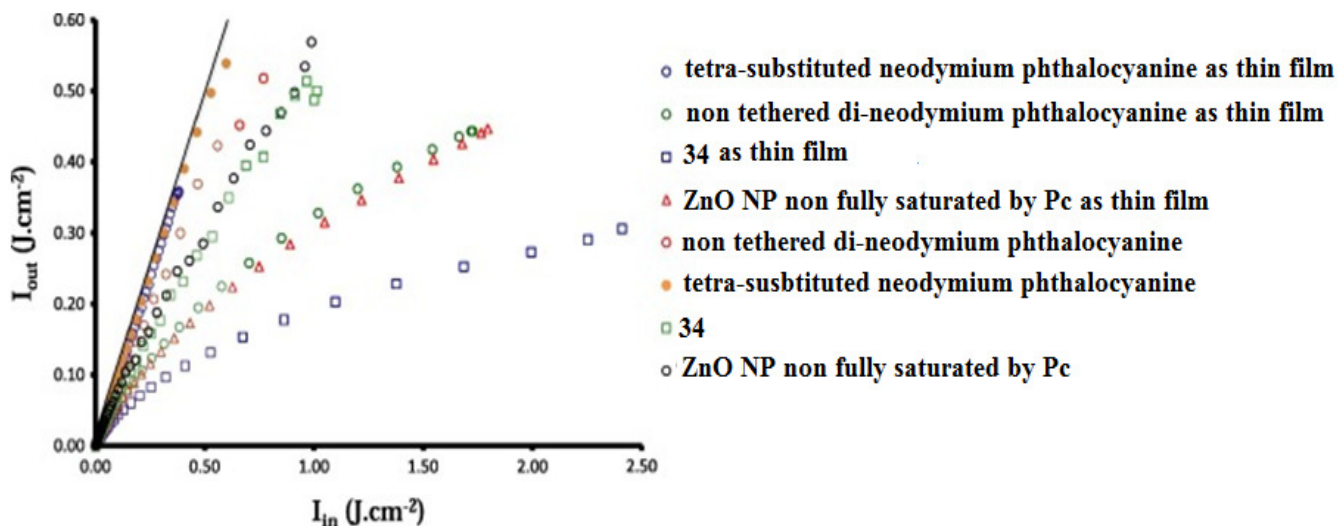


Figure 10. Output fluence against input fluence for di-neodymium phthalocyanines and analogs in the tethered state (structure **34** in Chart 6), and as isolated complexes. The tethering unit was a silica-covered ZnO nanoparticle (NP). Samples excitation occurred at 532 nm using 10 ns laser pulses with input energy of 35 μ J. Reproduced with permission from ref. **86**.

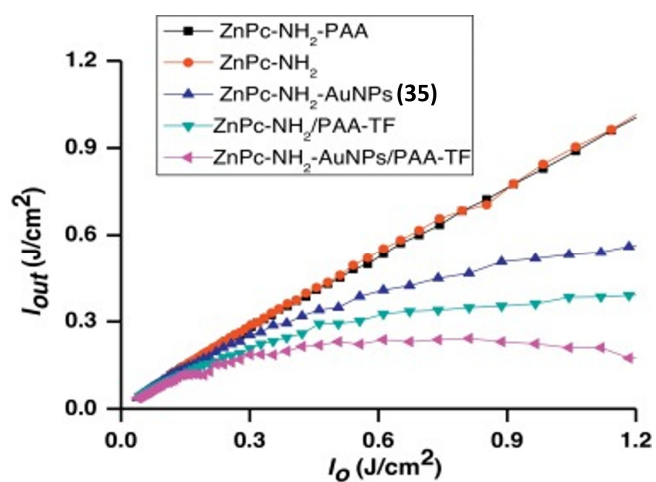


Figure 11. Output fluence against input fluence for the non symmetrically substituted zinc phthalocyanine in the tethered state when Au NP is the tethering unit (structure **35** in Chart 6). For sake of comparison the nonlinear transmission curves of the isolated zinc complex in solution and embedded in a polymer film are also reported (PAA = polyacrylic acid and TF = thin film). Reproduced with permission from ref. **87**.

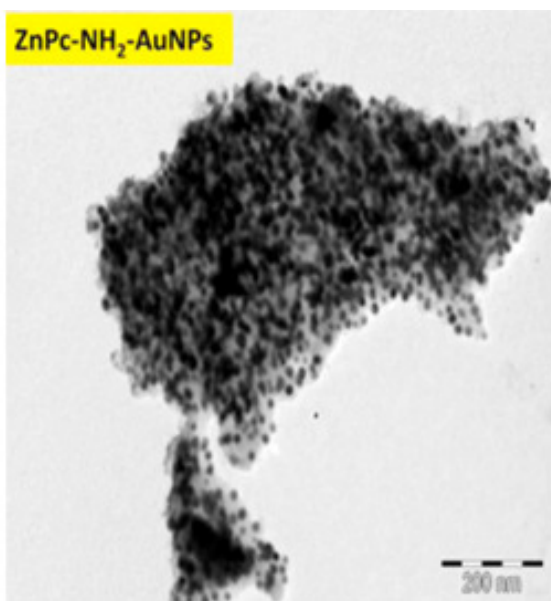


Figure 12. TEM image of the non symmetrically substituted zinc phthalocyanine in the tethered state when Au NP is the tethering unit (structure **35** in Chart 6). Reproduced with permission from ref. **87**.

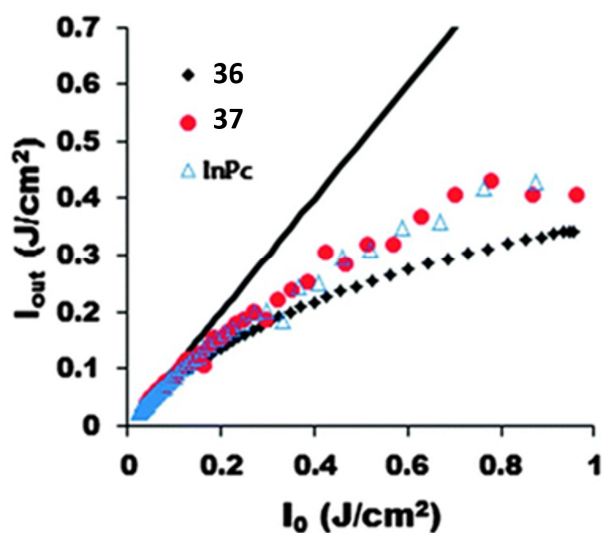


Figure 13. Output fluence against input fluence for the tethered systems **36** and **37** (Chart 6) consisting in the silica coated magnetite nanoparticle (SiMNP-1) covered with an indium phthalocyanine. The indium complex is peripherally substituted with phenoxy groups containing amino groups as NP-anchoring moiety. For sake of comparison the NLO transmission curves of the isolated indium complex InPc and the magnetite-free NP of silica modified with the indium complex (SiNP-1) are also reported. Peak incident intensity at 532 nm was 122 mW cm⁻². Reproduced with permission from ref. **87**.

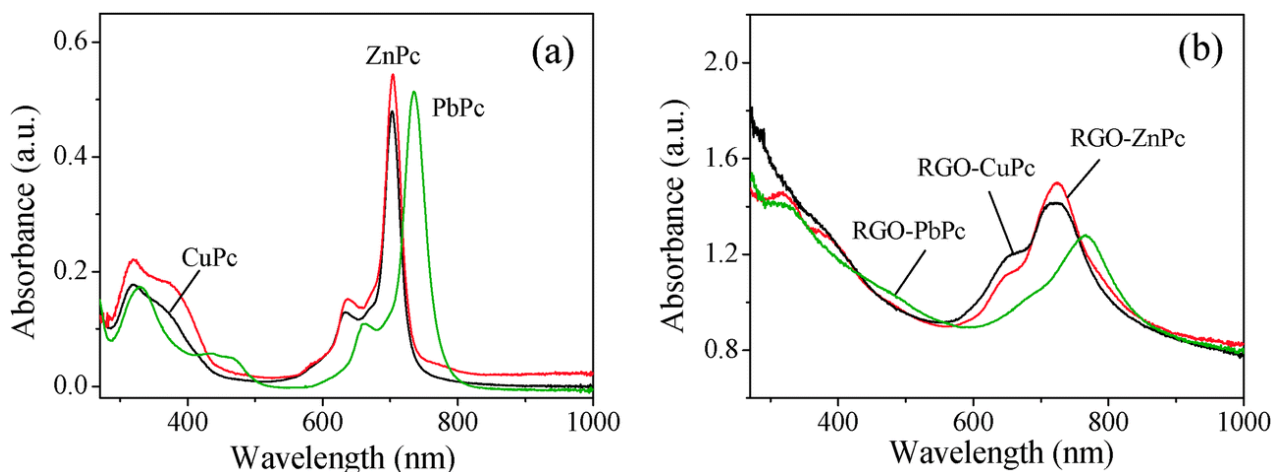


Figure 14. Comparison of the absorption spectra of pristine PcM in solution (a) and in the tethered version when reduced graphene oxide (RGO) is the tethering unit (b). Reproduced with permission from ref. **83**.

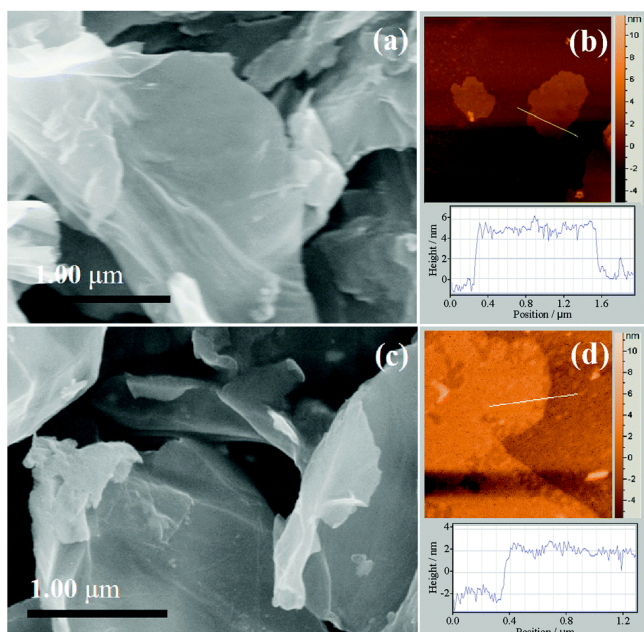


Figure 15. (a) and (c) SEM images, and (b) and (d) AFM images of the tethered systems obtained by the anchoring of tetra-substituted metallo-phthalocyanines on RGO. Insets represent the images of the tethered films obtained with a profilometer. Reproduced with permission from ref. **83**.

Peripherally substituted naphthalocyanines

Chart 8 reports the structures **40-50** of some peripherally substituted naphthalocyanines (Ncs) with axial substituents (structures **40-43**, **46** ad **47** of Chart 8) for the realization of effective OL action at the reference wavelengths of 532 and 1064 nm [**31,32,36,59**]. The design and realization of such structures with enlarged window of optical transparency with respect to a Pc[**42,97,98**], was mainly motivated by the favorable linear optical properties of Ncs vs Pcs for the specific application of eye-protection from laser threats [**99**]. The preparation of the structures of the OL active Ncs here presented (Chart 8) was mainly inspired by the insertion of heavy halogen atoms in both peripheral

and axial position to accelerate the step of ISC in the process of formation of highly absorbing excited state, and in second instance, to stabilize the excited triplet state of the Ncs via the electron-withdrawing action of the halogen substituents.

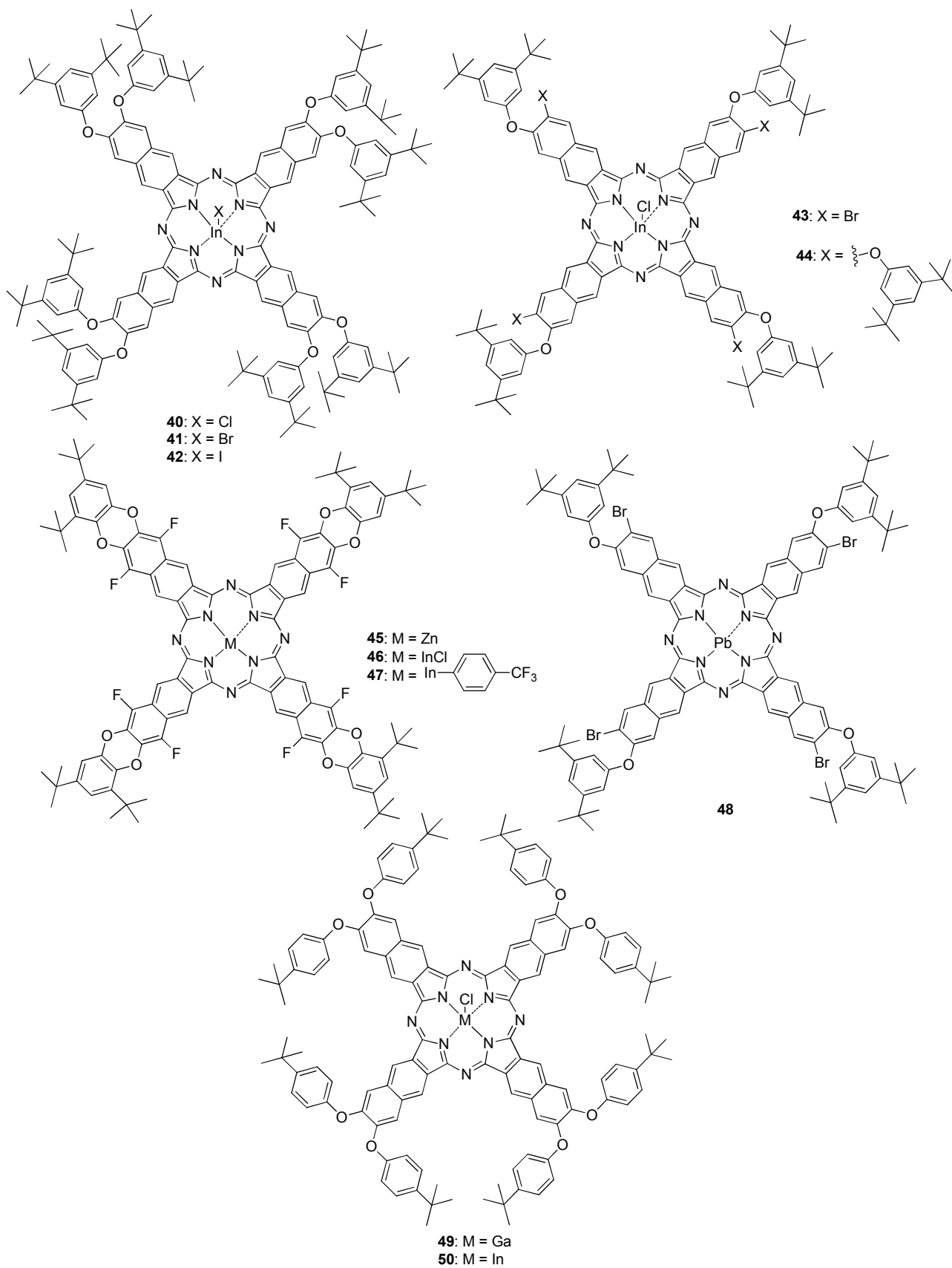


Chart 8. Structures of the OL active metallo-naphthalocyanines **40-50** with peripheral phenoxy- and halogen- substituents [31,32,36,59,65].

Table 1 reports some OL characteristics for a series of Ncs dispersed in toluene with linear optical transmission $T_0 = 0.7$ at the wavelength of analysis of 532 nm for ns laser pulses [32].

Table 1. Comparison of the parameters characterizing the OL performance of a series of Ncs from Chart 6 at 532 nm. F_{lim} is the limiting fluence at which NLO transmission equals 0.50 of the linear transmission T_0 , Φ_T is the triplet quantum yield, and τ_{T_1} is the lifetime of the highly absorbing triplet excited state according to the scheme of sequential two-photon absorption depicted in Figure 16 [32].

| Compound | $F_{lim}/J\text{ cm}^{-2}$ | Φ_T | $\tau_{T_1}/10^{-6}\text{ s}$ |
|--|----------------------------|----------|-------------------------------|
| $(t\text{Bu}_2\text{C}_6\text{H}_3\text{O})_8\text{NcInCl}$ (40) | 0.27 | 0.225 | 14.4 |
| $(t\text{Bu}_2\text{C}_6\text{H}_3\text{O})_8\text{NcInBr}$ (41) | 0.11 | 0.287 | 1.7 |
| $(t\text{Bu}_2\text{C}_6\text{H}_3\text{O})_8\text{NcInI}$ (42) | 0.08 | 0.273 | 1.6 |
| $\text{Br}_4\text{NcSiR}_2$ | >1 | 0.100 | 67.0 |
| $\text{Br}_8\text{NcSiR}_2$ | >1 | 0.130 | 49.0 |
| NcSiR_2 | >1 | 0.200 | 42.0 |
| $\text{Br}_4(t\text{Bu}_2\text{C}_6\text{H}_3\text{O})_4\text{NcInCl}$ (43) | 2.3 | >0.25 | <15.0 |
| $\text{Br}_4(t\text{Bu}_2\text{C}_6\text{H}_3\text{O})_4\text{NcPb}$ (48) | 0.10 | 0.070 | 0.4 |

The Jablonski diagram based on the four-level system (Figure 16) shows the sequence of electronic transitions that occur in Ncs (and Pcs) for the realization of the OL effect provided that σ_{exc} exceeds the value of σ_g (Eq. 1). In case of Nc **48** (Chart 6), the OL action against ns laser pulses at 532 nm occurs in the wavelength range 450-700 nm (Figure 17) [32], thus indicating a broadband effect potentially useful against laser threats with agile features [100]. The dynamics of excited state(s) populating has been analyzed when the NLO absorber based on Ncs **49** and **50** had thick features [64], *i.e.* a thickness larger than the Rayleigh range imposed by a Gaussian laser beam [59]. The profiles of transmitted energy with the distance from the focus of the optical beam inside the thick absorber consisting in an octa-substituted naphthalocyanine with axial ligand [64,65] shows that a Nc is generally a better system in comparison to an analogous Pc since the diminution of the transmitted energy through the thick optical limiter based on Nc is faster than the corresponding variation of the device based on a Pc (Plot b, Figure 18). Moreover, the value of incident intensity at which the nonlinear optical regime has the onset and consequently OL action starts is lower for Ncs with respect to Pcs (Plot a, Figure 18).

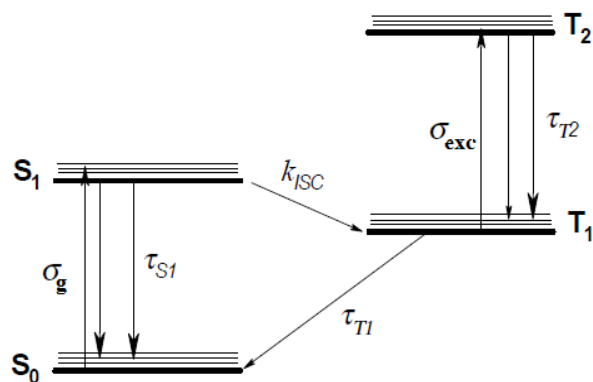


Figure 16. Jablonski diagram reporting the mechanism of sequential two-photon absorption of ns pulses by Ncs. S_0 , S_1 and $T_{1(2)}$ indicate the energy levels of the ground state, the first excited singlet state and the first(second) excited triplet state of the Nc, respectively. τ_{S1} , τ_{T1} , and τ_{T2} indicate the lifetimes of the first excited singlet state, of the first excited triplet state and of the second excited triplet state, respectively, whereas k_{ISC} is the rate of intersystem crossing (ISC).

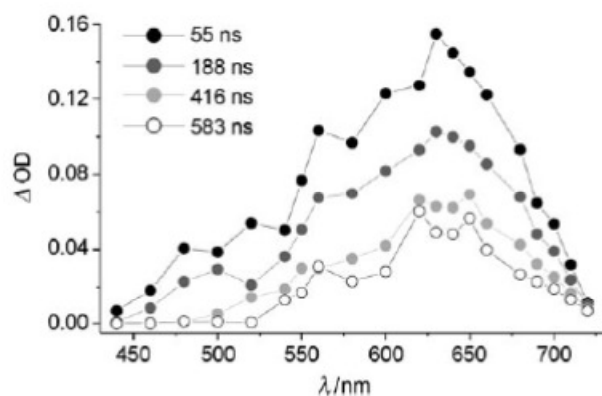


Figure 17. Excited state spectra of Nc **48** (Chart 8) in a toluene solution at the concentration of 28 mM. Excitation source was a laser emitting ns pulses at 532 nm. The incident fluence was 0.13 J cm^{-2} . Reproduced with permission from ref. **32**.

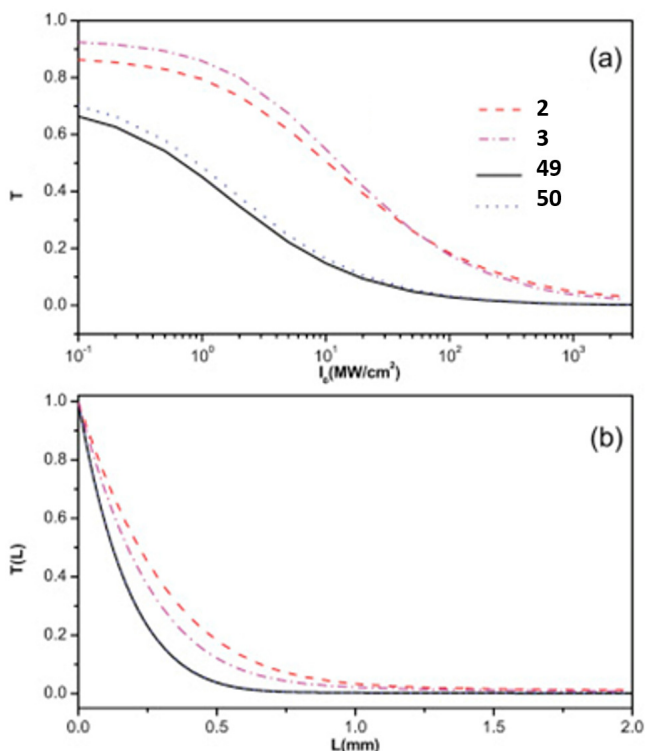


Figure 18. Profiles of transmitted energy T as a function of the distance L from a thick nonlinear absorber when the OL active materials are Ncs **49**, **50** (Chart 8), and Pcs **2** and **3** (Chart 1). In plot (a) T is plotted as a function of the laser peak intensity I_0 at the given distance $L = 1$ mm when $\lambda = 532$ nm and pulse duration is 7 ns. Plot (b) reports the transmitted energy as a function of L when $I_0 = 3 \cdot 10^{13}$ W m⁻². Reproduced with permission from ref. **64**.

Examples of Pc analogs with OL properties

The analogs of Pcs that have been considered for OL purposes are of various nature (Chart 9), and can range from hexa-substituted subphthalocyanines (**51**) [7], to diazepino-porphyrines (**52**) [61], hemiporphyrines (**54,55**) [9,10,101], tetrathioporphyrins (**56-58**) [102], cyclo-[8]-pyrrole (**53**) [103] and asymmetrically substituted porphyrins (**59-65**) [104] among others[45].

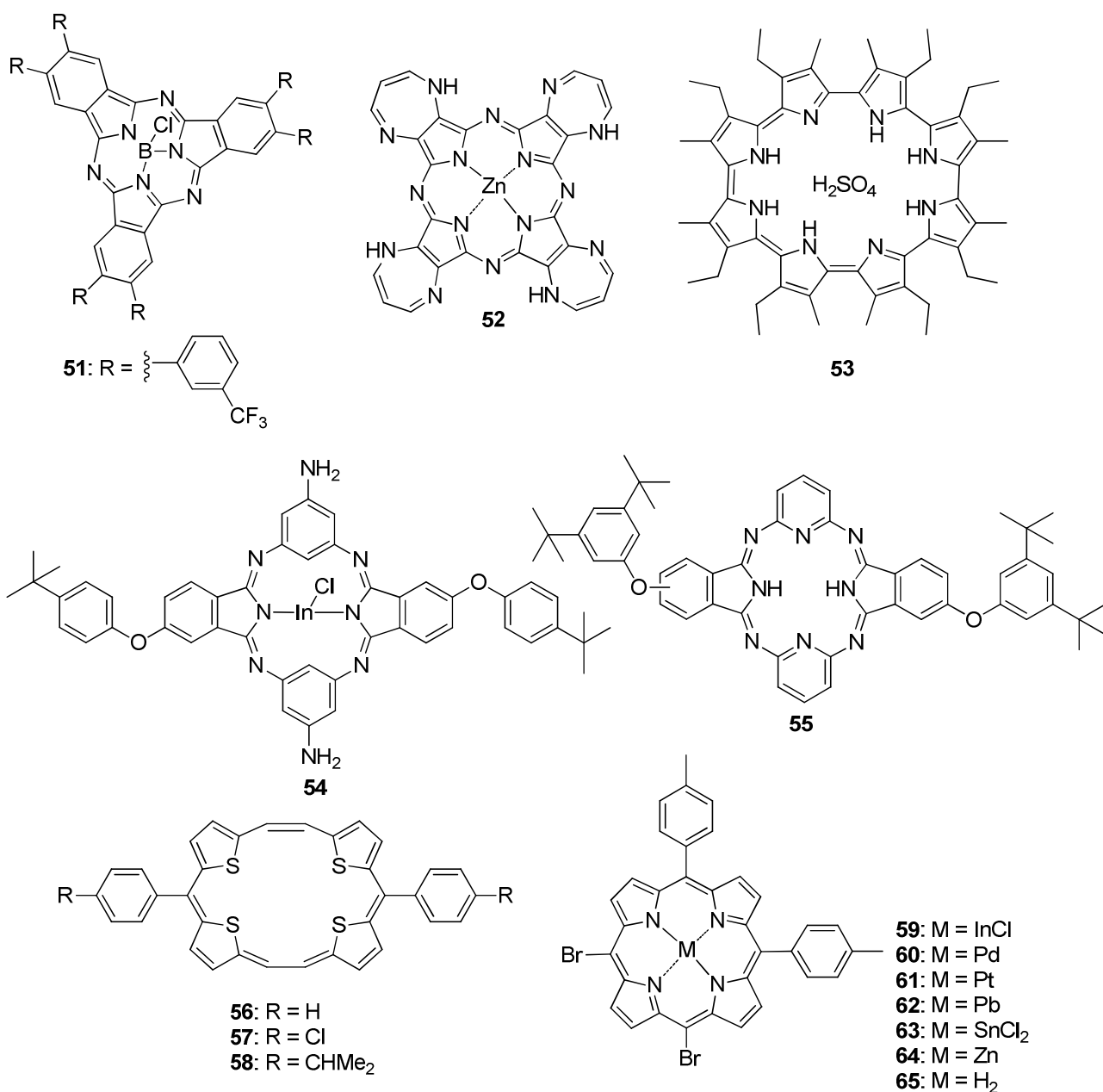


Chart 9. Structures of the OL active complexes **51-58** with conjugated macrocycles as ligands. Compounds **59-65** are OL active porphyrins.[104] The structures here reported [7,9,61,101-103] represent various types of Pc analogs.

One of the main intents of the preparation of the Pc analogs of Chart 9 is the realization of conjugated systems with sufficiently high electronic polarizability [15,105] which possess weaker linear optical absorption properties and better processability with respect to Pcs while retaining the favourable features of chemical-physical stability as well as the efficaciousness of the OL action typical of Pcs [3,4,60]. The plots reported in Figures 19-22 well demonstrate the effectiveness of the OL action (mostly at 532 nm for ns pulses) for these different classes of conjugated materials when these Pc analogs are dispersed in liquid media [7,9,61,101-104]. Particularly interesting for OL applications is represented by the case of the porphyrin analogs **56-58** (Chart 9), which proved to be

able to decrease the optical transmission down to less than 10 % when linear transmission was 80 % at the wavelength of analysis (Figure 20) [102].

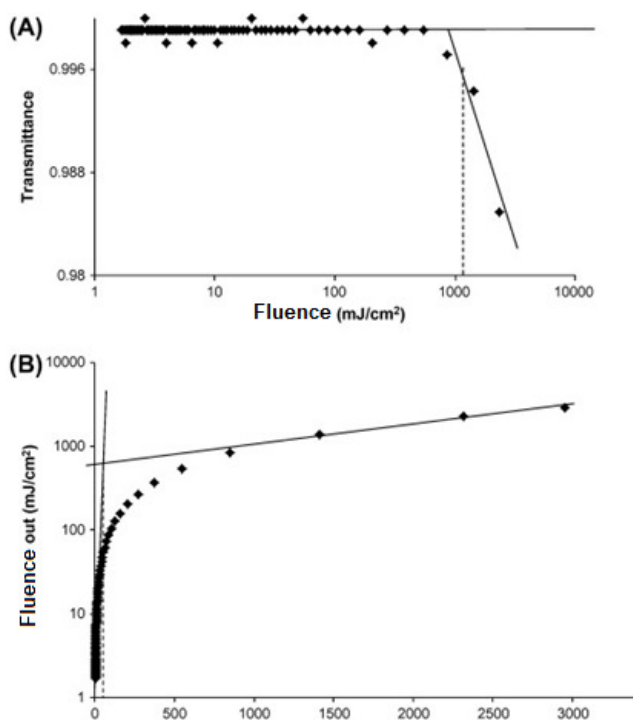


Figure 19. (A): Nonlinear optical transmission at 532 nm against ns laser pulses for the hemiporphyrazine **54** (Chart 9) in DMF as solvent. (B): Corresponding curve of fluence output vs fluence input. Reproduced with permission from ref. **101**.

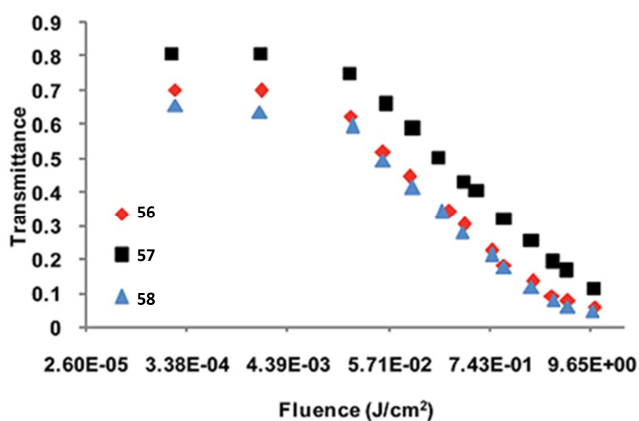


Figure 20. NLO transmittance of the tetrathiaporphyrins **56-58** (Chart 9) in dichloromethane for 120 ns pulses at 527 nm. Reproduced with permission from ref. **102**.

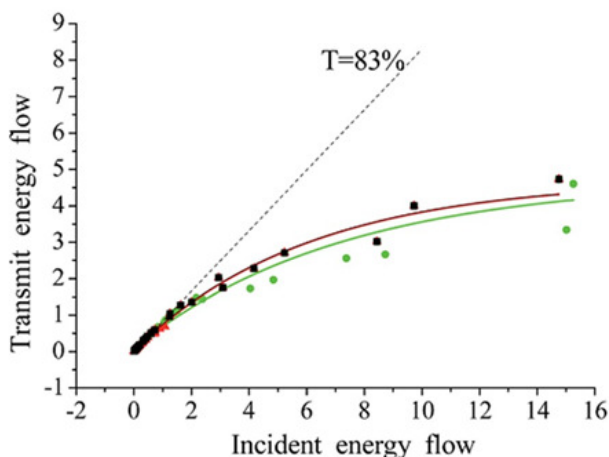


Figure 21. Energy output vs energy input for a series of salts of the cyclo-[8]-pyrrole **53** (Chart 9) at 532 nm. Reproduced with permission from ref. **103**.

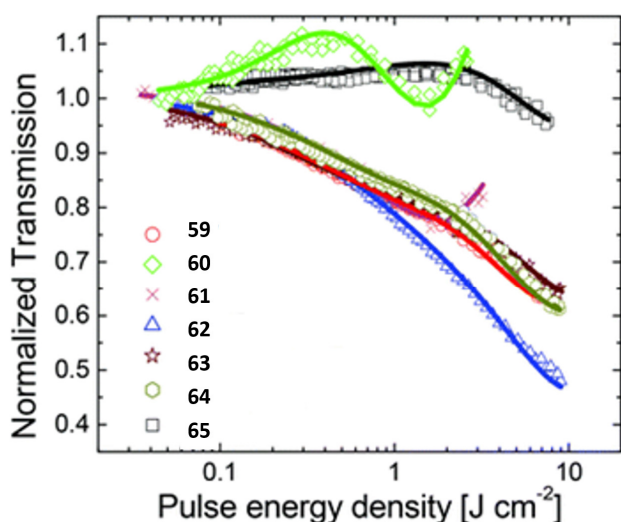


Figure 22. NLO transmittance at 532 nm of the di-brominated porphyrins **59-65** (Chart 9). Complexes were dissolved in toluene with the concentration 0.25 mM. Optical path was 1 mm. Pulses had an average duration of 7 ns. Reproduced with permission from ref. **104**.

Table 2 reports a set of comparative data regarding the most recent achievements in the field of OPL by molecular materials when the series of conjugated complexes of Charts 1-9 are considered. The results that deserve more attention are those obtained with NLO systems possessing the highest values of the merit factor σ_{exc}/σ_g in the broadest wavelength range. Comparison between different nonlinear optical absorbers is actually meaningful when the level of linear optical absorption is exactly the same for the different OL active species. In addition to these requirements another fulfilment would be the achievement of large values of the ratio σ_{exc}/σ_g for agile radiations varying not only for the wavelength but also for the duration of the pulse if this is inferior to the μs range. Such an upper limit of radiation duration represents a critical value below which the corresponding

radiation intensity can easily overcome the megawatt threshold, i.e. a value the limiting of which requires high performance optical limiters that work in the self-activated passive mode [57]. For applicative purposes, another important consideration is related to the employment of the NLO absorber in a self-standing matrix (glassy, polymeric, gel-like, crystalline) with optically neutral features. In achieving so the OL system can be directly and opportunely used in the optical path of an optical device requiring radiation protection through the self-activated mechanism of excited state absorption (or reverse saturable absorption) [2].

Table 2. Comparison of the values of limiting fluence (F_{lim}) and of the merit factor σ_{exc}/σ_g for the various conjugated macrocycles depicted in Charts 1-9 when the relative OL performance is analysed at 532 and/or 1064 nm. Whereas unspecified the value of F_{lim} refers to its determination in a liquid solution of the nonlinear optical absorber. Whereas unspecified the ratio σ_{exc}/σ_g has been calculated in the regime of irradiation determined by ns laser pulses.

| Compound | σ_{exc}/σ_g | $F_{lim} / J\ cm^{-2}$ | λ / nm | ref. |
|----------|-------------------------|--|----------------|-------|
| 1 | | 0.23 (glass matrix) | 532 | 63 |
| 2 | 43.7 | 0.31 (glass matrix) | 532 | 63,64 |
| 3 | 49.5 | 0.21 (glass matrix) | 532 | 63,64 |
| 8 | 587 | 0.28 0.054 [in poly-(acrylic acid), PAA] | 532 | 66,84 |
| 9 | 4179 | 0.95 0.089 (in PAA) | 532 | 66 |
| 10 | >100 | 1.02 | 532 | 68 |
| 11 | | 1 | 532 | 69 |
| 12 | | 0.39 | 532 | 69 |
| 13 | 8 | 0.13 | 532 | 69 |
| 14 | | 0.54 | 532 | 70 |
| 15 | | 0.34 0.11 (thin film) | 532 | 76 |
| 16 | | 0.44 0.26 (thin film) | 532 | 76 |
| 17 | 9.6 | 0.29 | 532 | 23 |
| 18 | 8.1 | 0.49 | 532 | 23 |
| 19 | 9.5 | 0.32 | 532 | 23 |
| 20 | 5 | | 1064 | 77 |
| 21 | 1.3 | | 532 | 58 |
| 22 | 1.1 | | 532 | 80 |
| 23 | 1.4 | | 532 | 80 |
| 24 | 2.4 | | 532 | 80 |
| 25 | | 0.30 | 532 | 78 |
| 26 | | 0.045 | 532 | 78 |
| 27 | | 0.00051 | 532 | 79 |
| 28 | | 0.0045 | 532 | 82 |
| 32 | | 0.21 | 532 | 84 |
| 33 | 16.2 | 10.1 | 532 | 85 |

| | | | | |
|-----------|--|--------------------------|------|------------|
| | 18.6 (thin film) | 3.3 (thin film) | | |
| 34 | | 0.25 0.12 (thin film) | 532 | 86 |
| 35 | 304 | 0.13 | 532 | 87 |
| 36 | $\sigma_{\text{exc}} = 7 \times 10^{-18} \text{ cm}^2$ | 0.16 | 532 | 88 |
| 37 | $\sigma_{\text{exc}} = 3.3 \times 10^{-18} \text{ cm}^2$ | 0.30 | 532 | 88 |
| 38 | | 57 | 532 | 89 |
| 39 | | 181 | 532 | 89 |
| 40 | 3.24 (ns) 2.14 (ps) | 0.27 (ns) 0.1 (ps) | 532 | 36 |
| 41 | 4.15 (ns) 2.27 (ps) | 0.11 (ns) 0.075 (ps) | 532 | 36 |
| 42 | 4.41 (ns) 2.67 (ps) | 0.08 (ns) 0.03 (ps) | 532 | 36 |
| 43 | 1.35 | 2.3 | 532 | 59 |
| 45 | | 1.55 | 532 | 31 |
| | | 2.96 | 1064 | 31 |
| 46 | | 4.64 | 532 | 31 |
| | | 3.65 | 1064 | 31 |
| 47 | | 2.65 | 532 | 31 |
| | | 2.66 | 1064 | 31 |
| 48 | 26.2 | 0.1 | 532 | 32 |
| 51 | 28.6 | | 532 | 7 |
| 53 | | 5 | 532 | 103 |
| 54 | | 0.054 | 532 | 101 |
| 55 | 14.6 | 0.45 | 532 | 9 |
| 56 | 250 | 0.31 | 532 | 102 |
| 57 | 498 | 0.53 | 532 | 102 |
| 58 | 197 | 0.22 | 532 | 102 |
| 59 | 0.88 | - | 532 | 104 |
| 60 | 4.4 | - | 532 | 104 |
| 61 | 0.75 | - | 532 | 104 |
| 62 | 10 | 7 | 532 | 104 |
| 63 | 6.5 | - | 532 | 104 |
| 64 | 2.8 | - | 532 | 104 |
| 65 | 5.4 | - | 532 | 104 |

CONCLUDING REMARKS

The present review has presented several classes of conjugated macrocycles recently utilized as nonlinear optical materials for the realization of the optical limiting effect, i.e. the attenuation of the power/intensity of an optical radiation by a smart optical filter when the luminous power (or intensity) surpasses a predefined value. These structures are derived either directly or indirectly from the main skeleton of the phthalocyanine, which affords a wide modulation of its photophysical properties through the modification of the extent of electronic conjugation of the macrocycle, of the nature of the coordinating central metal, of the nature and number of peripheral and axial

substituents, of the type of combinations in tethered structures. The species here examined mostly exert their action of optical power limiting through the mechanism of sequential two-photon absorption which involves a four-level scheme in which electronic transitions take place. The results here reported refer principally to the direct measurement of the optical transmittance of the photo-active material when the light-probe is a monochromatic pulsed radiation with variable intensity. The influence of the several structural factors on the resulting optical limiting effect has been analyzed taking into account the aspects of linear absorption, spectral width of nonlinear optical action, rapidity of formation of highly absorbing excited states in either liquid solutions or rigid matrices. We have also made some considerations about the meaningfulness of the comparison of optical limiting data with molecular materials like phthalocyanines and analogs when these are produced by different laboratories under generally different experimental conditions of linear absorption, optical path, radiation wavelength and pulse duration, irradiation frequency, optical thickness, aggregation state of the photoactive species, and physical state of the dispersion in which the photoactive species is dissolved. A final recapitulatory table has been compiled with the specification of the merit factor σ_{exc}/σ_g , i.e. the ratio of the excited state absorption cross section to the ground state absorption cross-section at the wavelength of analysis, and the limiting threshold at which the intensity/fluence of the transmitted radiation is half of its linear value for the most representative compounds of every class here considered: phthalocyanines, naphthalocyanines, hemiporphyrines, subphthalocyanines, diazepino-porphyrines, porphyrins, thiophene- and pyrrole-based macrocyclic structures.

ACKNOWLEDGMENTS

For the realization of some parts of this Review, D.D. gratefully acknowledges financial support from Ateneo LA SAPIENZA (protocol no. C26A142SCB). M.J.F.C. thanks FCT-Portugal (Portuguese Foundation for Science and Technology) and FEDER – European Regional Development Fund through the COMPETE Programme (Operational Programme for Competitiveness) for funding (SFRH/BPD/99698/2014).

REFERENCES

1. Leite RCC, Porto SPS, Damen TC, *Appl. Phys. Lett.* 1967; **10**: 100-104.
2. Tutt L, Bogges TF, *Prog. Quantum Electron.* 1993; **17**: 299-338.
3. Hanack M, Dini D, Barthel M, Vagin S, *Chem. Rec.* 2002; **2**: 129-148.
4. Dini D, Barthel M, Hanack M, *Eur. J. Org. Chem.* 2001: 3759-3769.
5. Calvete M, Yang GY, Hanack M, *Synthetic Met.* 2004; **141**: 231-243.

6. Senge MO, Fazekas M, Notaras EGA, Blau WJ, Zawadzka M, Locos OB, Mhuirheartaigh EMN, *Adv. Mater.* 2007; **19**: 2737-2774.
7. Dini D, Vagin S, Hanack M, Amendola V, Meneghetti M, *Chem. Commun.* 2005: 3796-3798.
8. Santos CIM, Barata JFB, Calvete MJF, Vale LSHP, Dini D, Meneghetti M, Neves MGPMS, Faustino MAF, Tome AC, Cavaleiro JAS, *Curr. Org. Synth.* 2014; **11**: 29-41.
9. Dini D, Calvete MJF, Hanack M, Amendola V, Meneghetti M, *J. Am. Chem. Soc.* 2008; **130**: 12290-12298.
10. Dini D, Calvete MJF, Hanack M, Amendola V, Meneghetti M, *Chem. Commun.* 2006: 2394-2396.
11. Giuliano CR, Hess LD, *IEEE J. Quant. Electron.* 1967; **QE-3**: 358-367.
12. Blau W, Byrne H, Dennis WM, Kelly JM, *Opt. Commun.* 1985; **56**: 25-29.
13. Perry JW, in *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa HS, Miyata S, Eds; CRC Press: Boca Raton, FL; pp. 813, **1997**.
14. Goppert-Mayer M, *Ann. Phys.* 1931; **9**: 273-294.
15. He GS, Tan LS, Zheng Q, Prasad PN, *Chem. Rev.* 2008; **108**: 1245-1330.
16. Lepkowicz R, Kobayakov A, Hagan DJ, Van Stryland EW, *J. Opt. Soc. Am. B* 2002; **19**: 94-101.
17. Van Stryland EW, Sheik-Bahae M, Said AA, Hagan DJ, *Prog. Cryst. Growth Charact.* 1993; **27**: 279-311.
18. Hercher M, *Appl. Opt.* 1967; **6**: 947-954.
19. Miles PA, *Proc. SPIE* 1994; **2143**: 251-262.
20. Wood GL, Clark III WW, Miller MJ, Salamo GJ, Sharp EJ, *Proc. SPIE* 1989; **1105**: 154-181.
21. Chen P, Tomov IV, Dvornikov AS, Nakashima M, Roach JF, Alabran DM, Rentzepis PM, *J. Phys. Chem.* 1996; **100**: 17507-17512.
22. Sutherland RL, Mclean DG, Kirkpatrick SM, Fleitz PA, Chandra S, Brant MC, Multiphoton Absorption and Optical Limiting. In *Multiphoton and Light Driven Multielectron Processes in Organics: New Phenomena, Materials and Applications*; Kajzar F, Agranovich MV, Eds; Kluwer Academic Publishers: Dordrecht, 2000; Vol. 79, pp 67-81.
23. Chen J, Zhang T, Wang SQ, Hu R, Li SY, Ma JS, Yang GQ, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 2015; **149**: 426-433
24. Zollinger H, *Color Chemistry-Syntheses, Properties, and Applications of Organic Dyes and Pigments*, Wiley-VCH, 3rd Ed., Zurich, 2003.
25. Sorokin AB, *Chem. Rev.* 2013; **113**: 8152-8191.

26. Dini D, Vagin S, Barthel M, Hanack M, in *Electronic and Optical Properties of Conjugated Molecular Systems in Condensed Phases*, Hotta S, Ed; Research Signpost, Kerala, India, pp 459-483, **2003**.
27. Dini D, Hanack M, *J. Porphyr. Phthalocya.* 2004; **8**: 915-933.
28. Dini D, *Int. J. Mol. Sci.* 2003; **4**: 291-300.
29. Dini D, Hanack M, Ji W, Chen WZ, *Mol. Cryst. Liq. Cryst.* 2005; **431**: 559-574.
30. Dini D, Calvete MJF, Hanack M, Chen WZ, Ji W, *Arkivoc* 2006; **3**: 77-96.
31. Yang GY, Hanack M, Lee YW, Dini D, Pan JF, *Adv. Mater.*, 2005; **17**: 875-879.
32. Dini D, Meneghetti M, Calvete MJF, Arndt T, Liddiard C, Hanack M, *Chem. Eur. J.* 2010; **16**: 1212-1220.
33. Flom SR, In *The Porphyrin Handbook*, Kadish KM, Smith KM, Guillard R, Eds; Academic Press, New York, Vol. 19, pp 179, **2003**.
34. Calvete MJF, *Int. Rev. Phys. Chem.* 2012; **31**: 319-366.
35. Amendola V, Dini D, Polizzi S, Sheng J, Kadish KM, Calvete MJF, Hanack M, Meneghetti M, *J. Phys. Chem. C*, 2009; **113**: 8688-8695.
36. Sun WF, Wang G, Li YJ, Calvete MJF, Dini D, Hanack M, *J. Phys. Chem. A* 2007; **111**: 3263-3270.
37. Peisert H, Biswas I, Zhang L, Knupfer M, Hanack M, Dini D, Batchelor D, Chasse T, *Surf. Sci.* 2006; **600**: 4024-4029.
38. Dini D, Calvete MJF, Hanack M, Meneghetti M, *J. Phys. Chem. A* 2008; **112**: 8515-8522.
39. Biswas I, Peisert H, Schwieger T, Dini D, Hanack M, Knupfer M, Schmidt T, Chasse T, *J. Chem. Phys.* 2005; **122**: 064710.
40. Calvete MJF, Dini D, Hanack M, Sancho-Garcia JC, Chen WZ, Ji W, *J. Mol. Model.* 2006; **12**: 543-550.
41. Li YJ, Dini D, Calvete MJF, Hanack M, Sun WF, *J. Phys. Chem. A* 2008; **112**: 472-480.
42. Dini D, Calvete M, Vagin S, Hanack M, Eriksson A, Lopes C, *J. Porphyr. Phthalocya.* 2006; **10**: 1165-1171.
43. Haug A, Harbeck S, Dini D, Hanack M, Cook MJ, Peisert H, Chasse T, *Appl. Surf. Sci.* 2005; **252**: 139-142.
44. Biswas I, Peisert H, Zhang L, Chasse T, Knupfer M, Hanack M, Dini D, Schmidt T, Batchelor D, *Mol. Cryst. Liq. Cryst.* 2006; **455**: 241-249.
45. Donzello MP, Viola E, Bergami C, Dini D, Ercolani C, Giustini M, Kadish KM, Meneghetti M, Monacelli F, Rosa A, Ricciardi G, *Inorg. Chem.* 2008; **47**: 8757-8766.

46. Villano M, Amendola V, Sandona G, Donzello MP, Ercolani C, Meneghetti M, *J. Phys. Chem. B* 2006; **110**: 24354-24360.
47. Donzello MP, Ercolani C, Gaberkorn AA, Kudrik EV, Meneghetti M, Marcolongo G, Rizzoli C, Stuzhin PA, *Chem, Eur, J*, 2003; **9**: 4009-4024.
48. Bauer EM, Donzello MP, Ercolani C, Masetti E, Panero S, Ricciardi G, Rosa A, Chiesi-Villa A, Rizzoli C, *Inorg. Chem.* 2003; **42**: 283-293.
49. McKeown NB, In *The Porphyrin Handbook*, Kadish KM, Smith KM, Guillard R, Eds; Academic Press, New York, Vol. 15, pp 61, **2003**.
50. Stuzhin PA, Ercolani C, In *The Porphyrin Handbook*, Kadish KM, Smith KM, Guillard R, Eds; Academic Press, New York, Vol. 15, pp 263, **2003**
51. Cook MJ, Chambrier I, In *The Porphyrin Handbook*, Kadish KM, Smith KM, Guillard R, Eds; Academic Press, New York, Vol. 17, pp 37, **2003**
52. Donzello MP, Ercolani C, Novakova V, Zimcik P, Stuzhin PA, *Coord. Chem. Rev.* 2016; **309**: 107-179.
53. Snow AR, Shirk JS, Pong RGS, *J. Porphyr. Phthalocya.* 2000; **4**: 518–524.
54. Chen J, Li SY, Gong FB, Yang ZP, Wang SQ, Xu HJ, Li Y, Ma JS, Yang GQ, *J. Phys. Chem. C* 2009; **113**: 11943-11951.
55. Shirk JS, Pong RGS, Flom SR, Heckmann H, Hanack M, *J. Phys. Chem. A*, 2000; **104**: 1438-1449.
56. Pritchett T, in Models for Saturable and Reverse Saturable Absorption in Materials for Optical Limiting, Army Research Laboratory, Online document ARL-TR-2567, October 2002, website: <http://www.dtic.mil/cgi-bin/GetTRDoc?AD=ADA410148>
57. Dini D, Calvete M, Hanack M, in press, *Chem. Rev.* DOI: 10.1021/acs.chemrev.6b00033
58. Calvete MJF, Dini D, Flom SR, Hanack M, Pong RGS, Shirk JS, *Eur. J. Org. Chem.* 2005: 3499-3509.
59. Dini D, Calvete MJF, Hanack M, Pong RGS, Flom SR, Shirk JS, *J. Phys. Chem. B.* 2006; **110**: 12230-12239.
60. Dini D, Barthel M, Schneider T, Ottmar M, Verma S, Hanack M, *Solid State Ionics* 2003; **165**: 289-303.
61. Donzello MP, Dini D, D'Arcangelo G, Ercolani C, Zhan RQ, Ou ZP, Stuzhin PA, Kadish KM, *J. Am. Chem. Soc.* 2003; **125**: 14190-14204.
62. Barthel M, Dini D, Vagin S, Hanack M, *Eur. J. Org. Chem.* 2002: 3756-3762.
63. Yuan H, Chen J, Zhang T, Wang SQ, Hu R, Li SY, Yang GQ, *Opt. Express* 2016; **24**: 9723-9733.

64. Miao Q, Liu QX, Sun EP, Ren TQ, *J. Photoch. Photobio. A* 2016; **316**: 19-23.
65. Xu J, Chen J, Chen L, Hu R, Wang SQ, Li SY, Ma JS, Yang GQ, *Dyes Pigments* 2014; **109**: 144-150.
66. Sanusi K, Nyokong T, *J. Photoch. Photobio. A* 2015; **303**: 44-52.
67. Makhseed S, Ghazal B, Abdelmoniem AM, Novakova V, Zimcik P, *RSC Adv.* 2015; **5**: 58854-58864.
68. Fitzgerald JP, Huffman PD, Brenner IA, Wathen JJ, Beadie G, Pong RGS, Shirk JS, Flom SR, *Opt. Mater. Express*, 2015; **5**: 5160-5178.
69. Carvalho EFA, Calvete MJF, Cavaleiro JAS, Dini D, Meneghetti M, Tome AC, *Inorg. Chim. Acta* 2010; **363**: 3945-3950.
70. Sanusi K, Nyokong T, *J. Coord. Chem.* 2014; **67**: 2911-2924.
71. Oudar JL, Chemla DS, *J. Chem. Phys.* 1977, **66**: 2664-2668.
72. Dini D, Yang GY, Hanack M, *J. Chem. Phys.* 2003, **119**: 4857-4864.
73. Perry JW, Mansour K, Lee IYS, Wu XL, Bedworth PV, Chen CT, Ng D, Marder SR, Miles P, Wada T, Tian M, Sasabe H, *Science* **1996**; **273**: 1533-1536.
74. Nalwa HS, Shirk JS, In *Phthalocyanines: Properties and Applications*; Leznoff, CC, Lever, ABP, Eds; VCH: Cambridge, UK, **1996** 4, 89.
75. Jaffé HH, Miller AL, *J. Chem. Educ.* 1966, **43**: 55.
76. Sekhosana KE, Amuhaya E, Nyokong T, *Polyhedron* 2015; **85**: 347-354.
77. Vannikov AV, Grishina AD, Gorbunova YG, Isakova AA, Krivenko TV, Zolotarevskii VI, Lapkina LA, Savel'ev VV, Tsivadze AY, *High Energ. Chem.* 2014; **48**: 97-103.
78. Sekhosana KE, Nyokong T, *Optical Materials*, 2014; **37**: 139-146.
79. Sekhosana KE, Amuhaya E, Mack J, Nyokong T, *J. Mater. Chem. C* 2014; **2**: 5431-5437.
80. Ishii K, Sakai N, *Phys. Chem. Chem. Phys.* 2010; **12**: 15354-15357.
81. Hanack M, Dini D, In *The Porphyrin Handbook*, Kadish KM, Smith KM, Guillard R, Eds; Academic Press, New York, Vol. 18, pp 251, **2003**.
82. Sekhosana KE, Nyokong T, *J. Mol. Struct.* 2016; **1117**: 140-146.
83. Song WN, He CY, Dong YL, Zhang W, Gao YC, Wu YQ, Chen ZM, *Phys. Chem. Chem. Phys.* 2015; **17**: 7149-7157.
84. Sanusi K, Amuhaya EK, Nyokong T, *J. Phys. Chem. C* 2014; **118**: 7057-7069.
85. Ozdag MA, Ceyhan T, Unver H, Elmali A, Bekaroglu O, *Opt. Commun.* 2010; **283**: 330-334.
86. Sekhosana KE, Amuhaya E, Nyokong T, *Polyhedron* 2016; **105**: 159-169.
87. Bankole OM, Nyokong T, *J. Photoch. Photobio. A* 2016; **319**: 8-17.
88. Sanusi K, Stone JM, Nyokong T, *New J. Chem.* 2015; **39**: 1665-1677.

89. Muller O, Pichot V, Merlat L, Schmidlin L, Spitzer D, *Appl. Opt.* 2016; **55**: 3801-3808.
90. Xie Z, Wang F, Liu CY, *Adv. Mater.* 2012; **24**: 1716-1723.
91. Xie Z, He H, Deng Y, Wang X, Liu C, *J. Mater. Chem.* 2013; **1**: 1791-1797.
92. Huo C, Sun X, Yan Z, Song X, Zhang S, Xie Z, Liu JZ, Ji J, Jiang L, Zhou S, Zeng H, in press *J. Am. Chem. Soc.* DOI: 10.1021/jacs.6b08698
93. Venditti I, Barbero N, Russo MV, Di Carlo A, Decker F, Fratoddi I, Barolo C, Dini D, *Mater. Res. Express* 2014; **1**: 015040/1-18.
94. Awais M, Dowling DP, Decker F, Dini D, *Adv. Cond. Matter Phys.* 2015; **2015**: 186375/1-18.
95. Roke S, Bonn M, Petukhov AV, *Phys. Rev. B* 2004; **70**: 115106.
96. Würthner F, Kaiser TE, Saha-Möllner CR, *Angew. Chem. Int. Ed.* 2011; **50**: 3376-3410.
97. Hanack M, Schneider T, Barthel M, Shirk JS, Flom SR, Pong RGS, *Coordin. Chem. Rev.* 2001; **219**: 235-258.
98. Shirk JS, Flom SR, Lindle JR, Bartoli FJ, Snow AW, Boyle ME, *Mater. Res. Soc. Symp. Proc.* **1993**, 328, 661.
99. Dentan V, Feneyrou P, Soyer F, Vergnolle M, Le Barny P, Robin P, *Mater. Res. Soc. Symp. Proc.* **1997**, 479, 261.
100. Hales JM, Cozzuol M, Screen TEO, Anderson HL, Perry JW, *Opt. Express* 2009; **17**: 18478-18488.
101. Britton J, Antunes E, Nyokong T, *J. Mol. Struct.* 2013; **1047**: 143-148.
102. Singh K, Arora S, Makhil K, Kaur P, Goswami D, *RSC Adv.* 2016; **6**: 22659-22663.
103. Xu H, Zhao SQ, Ren Y, Xu W, Zhu DB, Jiang JZ, Cai JF, *RSC Adv.* 2016; **6**: 21067-21071.
104. Zawadzka M, Wang J, Blau WJ, Senge MO, *Photoch. Photobio. Sci.* 2013; **12**: 996-1007.
105. Kanis DR, Ratner Ma, Marks TJ, *Chem. Rev.* 1994; **94**: 195-242.