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GRAPHICAL ABSTRACT

Pictogram
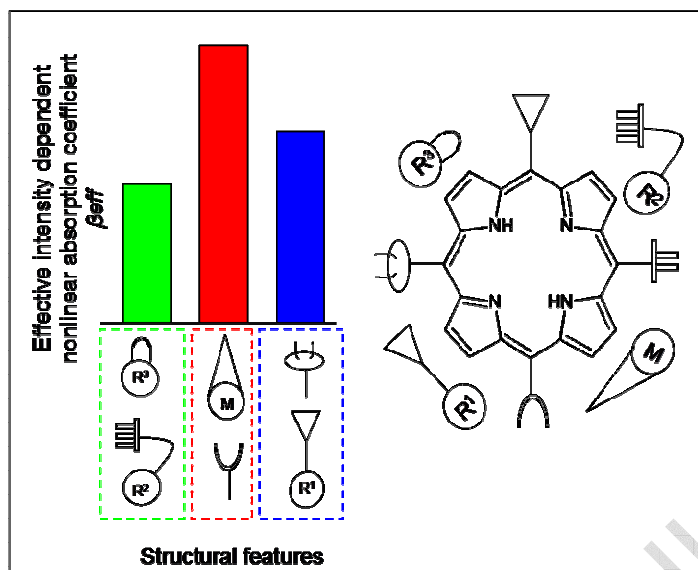
Synopsis

The nonlinear optical absorption of porphyrins can be modulated via chemical modifications of the ring system and the regiochemical arrangement of the substituents.

Correlation studies on structurally diverse porphyrin monomers, dimers and trimers and their nonlinear optical responses

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ABSTRACT

An investigation of the nonlinear absorption of a wide range of structurally diverse porphyrin monomers, bisporphyrins and trisporphyrins, using open Z-scan technique with 6 ns pulsed laser operating at 532 nm was carried out. Using the theory of reverse saturable absorption, the intensity dependent nonlinear absorption coefficient β_{eff} was deduced from the experiments. Monomers which Soret band maximum was situated closer to the experimental wavelength had higher β_{eff}. The β_{eff} of dimers and trimers were in the same range as for monomers. The highest $\beta_{eff} = 5.3 \times 10^{-8}$ cmW^{-1} was found for a zinc complex of 5,15-A_2B_2 type porphyrins with 3-methoxyphenyl and trimethylsilyl-ethynyl groups in the meso positions.

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1. Introduction

Porphyrins, which have a large delocalized conjugated π-electron system spread over the macrocycle ring, are an interesting class of materials for nonlinear optical (NLO) investigations. Studies on these compounds, which emerged in the early nineties, revealed that they are valuable materials for both 2nd and 3rd order NLO applications due to the high nonlinearities they exhibit upon irradiation with high intensity light [1,2]. One of those applications requires broadband passive optical limiters which are of fundamental significance in the protection of sensitive optical elements and human eyes against damage on the accidental exposure to laser light. Strong nonlinear absorption (NLA) over a broad range of the visible spectrum along with long lived excited state lifetimes coupled with good thermal- and photostability renders porphyrins as promising candidates for effective optical limiting materials [3-5]. Moreover, the design potential of these materials offers a unique opportunity for fine tuning the linear and NLO properties and thus of the optical limiting efficiency of porphyrin based compounds [6-9]. While general relationships between porphyrin structure and optical limiting properties have been established, these correlations are not fully understood yet and the design of efficient power limiters is still undergoing intensive investigation [10-16].

In our studies we explored NLA of a library of compounds comprising meso-substituted porphyrin monomers, dimers and trimers of varied configurations and regiochemical arrangements of the substituents (Fig. 1) using the standard open Z-scan technique in order to understand the correlation between molecular structure, substituent pattern and optical limiting efficiency. Investigations of a large number of porphyrins revealed that modifications of the structural features have a significant impact on their nonlinear optical response. This implies that optical limiting properties of porphyrins might be tuned via chemical modifications of the porphyrin ring and not just simple variation of the substituents in a given macrocycle system. The analysis of the results obtained enabled us to identify some consistent trends in nonlinear optical parameters for structurally correlated compounds.

<Figure 1>

2. Experimental

The monomeric porphyrins were synthesized by derivatization of 5,15-disubstitited porphyrins. Coupling reactions of brominated porphyrin precursors with appropriate compounds yielded the desired 5,15-A_2B_2 porphyrins and similar strategies were adapted for 5,15-A_2BC monomers [17]. Typically, coupling reactions were preceded by the introduction of alkyl chains through reaction with organolithium reagents [8,18,19]. Dimers and timers were obtained through Pd-catalyzed coupling of appropriate brominated and alkynyl precursors [20]. The measurements of the optical limiting properties were carried out using the open Z-scan technique. A 6 ns Q-switched Nd:YAG laser operating at the second harmonic of 532 nm with a pulse repetition rate of 10 Hz was used. The beam was spatially filtered to remove the higher order modes and tightly focused with a 9 cm focal length lens. The samples were prepared by dissolving the porphyrin in dimethylformamide (DMF) at 0.01 gL^{-1} followed by gentle agitation for about 30 min in a low power sonic bath. All measurements were performed in a quartz cell with 10 mm path length to enhance the optical limiting response. The ground state absorption spectra were recorded with Shimadzu multiSpec-1505 in DMF or dichloromethane (DCM) [21].

The experimental measurements involved the determination of the total transmission of the sample as a function of the incident laser intensity as the sample moved gradually along the focused Gaussian beam. All of the compounds studied exhibited reverse saturable absorption under experimental conditions. The experimental Z-scan data were fitted using the method of least-square regression with the equation for the normalized transmission as a function of the sample position z $T_{Norm}=ln[1+q_0(z)]/q_0(z)$, according to the Z-scan theory, where $q_0(z)=\beta_{eff}I_0L_{eff}/[1+(z/z_0)^2]$ with β_{eff} being the effective intensity dependent nonlinear absorption coefficient, I_0 – the intensity of the light at the focus, L_{eff} – the effective length of the sample defined as $L_{eff}=[1-exp(-\alpha_0L)]/\alpha_0$ where α_0 and L stand for linear absorption coefficient and true optical path length through the sample, respectively, z_0 – diffraction length of the beam which is $z_0=\pi w_0^2/\lambda$ where w_0 and λ stand for beam waist at the focus and the laser wavelength, respectively. The beam waist radius w_0 and the effective intensity dependent nonlinear absorption coefficient β_{eff} were treated as free parameters in the fit. The imaginary third order optical susceptibility $Im\{\chi^{(3)}_{eff}\}$ was recalculated according to $Im\{\chi^{(3)}_{eff}\}=n_0^2\varepsilon_0c\lambda\beta_{eff}/(2\pi)$ with n_0 being the linear refractive index, ε_0 – permittivity of free space, c – speed of the light. Besides β_{eff} and $Im\{\chi^{(3)}_{eff}\}$ the other parameters presented in the Table 1 include linear absorption coefficient α_0 and Soret band maximum for all the compounds studied.

On average five open Z-scan measurements were carried out on each sample. In every subsequent measurement the laser energy was increased by approximately 20 µJ starting from ~ 35 µJ. β_{eff} derived directly from these experiments were averaged and the average deviations were recalculated as indicated in Table 1.

3. Results and discussion

We explored the influence of different structural features on the magnitude of the nonlinear absorption in various porphyrin systems. For all the compounds studied β_{eff} varied in the range of $0.4 – 5.3 \times 10^{-8}$ cmW^{-1}. In the case of porphyrin monomers, we investigated the effect of meso substituents on the nonlinear absorption coefficients. Here, compounds of two different substitution patterns, 5,15-A$_2$B$_2$ and 5,15-A$_2$BC, were examined. In the case of porphyrin dimers and trimers, the influence of both meso substiuents and the type of linker bridging the porphyrin units on the nonlinear response were explored. Porphyrin trimers included both linear and L-shaped compounds in which porphyrin rings were linked to the central porphyrin unit at the 5,15 and 5,10 meso positions [22], respectively (Table 1).

An example of a typical open Z-scan data obtained is presented in Fig. 2 for monomers **15** and **16**. The curves show that at the focal point (z = 0), where the intensity is maximal, the greatest reduction in transmission occurs. The difference in the magnitudes of the reduction in transmission upon similar on-focus intensity for compounds **15** and **16** is evident. This implies that structural features have a significant influence on NLA which is discussed below in the parts devoted for monomers, dimers and trimers, respectively.

<Figure 2>
<Table 1>

Monomers

In the case of free base 5,15-A$_2$B$_2$ porphyrins with 1-napthyl as the A substituent and the other substituent being linked to the porphyrin directly via a single bond the following trend in β_{eff} was observed with regard to the second substituent: 4-MeOOC-C$_6$H$_4$ ≈ 4-CN-C$_6$H$_4$ > 3-thiophene ≈ benzothiophene > 1-Me-indole [**4** ≈ **2** >

4

5 ≈ 1 > 3]. This tendency reveals that NLA is enhanced for compounds with strong electron withdrawing groups. Some authors highlight the influence of the electron donating or withdrawing character of the meso-substituents on the optical limiting response. For example, Wood *et al.* reported a decrease in electrical polarizability upon substitution of phenyl residues with electron withdrawing groups which is different from our findings. They also observed an enhancement when electron-donating groups replaced phenyl [23].

When the B substituent was connected to the porphyrin system via a conjugated linker the response was improved in both free base and metallated compounds. However, this trend did not include compound **8**, which might be related to the particular electronic character of the $PO(OEt)_2$ group. The linear absorption coefficient for this compound is remarkably low in comparison to the other compounds. McEwan *et al.* suggested a correlation between the proximity of the Soret absorption band to the measurement wavelength and the strength of the optical limiting action [3]. They observed that the transmission minimum became lower for the compounds where the Soret band was closer to the experimental wavelength. This might give some indication for the improved NLA in the previously discussed monomers with conjugated linkers for which the Soret band is red shifted and thus situated closer to the experimental wavelength, then for the remaining $5,15-A_2B_2$ monomers.

The zinc(II) complex **11,** which basic framework is that of a $5,15-A_2B_2$ substitution pattern with $3-MeO-C_6H_4$ and TMS-ethynyl groups as substituents, was identified as the most promising among all of the measured compounds. It exhibited the highest value of $\beta_{eff} = 5.3 \times 10^{-8}\ cmW^{-1}$. Interestingly, this porphyrin combines the structural features of the most promising materials previously reported – metal complexes of tetra(trimethylsilylethynyl)porphyrin [3] and {5,10,15,20-tetrakis(4-methoxyphenyl)tetrabenzoporphyrinato}zinc(II) [23]. However, a direct comparison of the optical limiting strength of these compounds is difficult to carry out as the different authors applied either different experimental condition or else used other NLO coefficients in order to describe the optical limiting properties of these compounds.

The β_{eff} values of both of $5,15-A_2B_2$ compounds with 4-CN-phenyl groups **2** and **10** were found to be of the same order. However, the linear absorption coefficient for compound **10** with 3-MeO-phenyl as second substituent was found to be smaller then that of compound **2** with 1-napthyl residues. The same rate of nonlinear absorption could be achieved at higher transparency to low intensity light for compound **10**. This renders the latter compound more promising as far as practical application as optical limiting material are concerned.

A comparison of monomers with different substitution patterns gives further insight. The $5,15-A_2B_2$ compounds **2** and **4** are structurally related to $5,15-A_2BC$ compounds **12** and **13**. Substitution of one of the $4-MeOOC-C_6H_4$ groups in compound **4** or one of the $4-CN-C_6H_4$ groups in compound **2** with $n-C_4H_9$ gives compounds **13** and **12,** respectively. Both compounds with $4-MeOOC-C_6H_4$ groups **4** and **13** have a slightly higher β_{eff} value than those with $4-CN-C_6H_4$ group **2** and **12**, respectively. Moreover, the β_{eff} values of both of $5,15-A_2BC$ compounds are remarkably lower than those of the respective $5,15-A_2B_2$ compounds.

The optical limiting efficiency of compound **15** is enhanced in comparison to other $5,15-A_2BC$ compounds with 1-napthyl and $n-C_4H_9$ residues as A and B substituents, respectively. This might be due to the presence of the closed shell metal zinc in the central cavity which renders this compound more promising in comparison

to others of similar structure. Closed shell metals were reported to have favourable effect on the NLA as they produce an increase in the intersystem crossing rate resulting in higher quantum yield for the triplet state [3-5,10]. Reports indicate brominated porphyrins as very promising materials for optical limiting applications [24,25]. Thus, the presence of the bromine in compound **15** might also contribute to its enhanced optical limiting response. Further analysis of the 5,15-A_2BC monomers indicated that the response of compounds with two 3-MeO-C_6H_4 groups, **17** and **18**, was notably enhanced in comparison to the analogous compounds with two 1-napthyl groups, **12** and **14**, respectively (Fig. 3).

McEwan *et al.* reported a similar trend to that found for compounds **12**, **13** and **14** [4]. The authors investigated the effect of different functional groups at the para position of the meso phenyl ring in tetrasubstituted porphyrins on their optical limiting efficiency. They noticed that the optical limiting performance of structurally related compounds with similar ground state electronic absorption is different. In our studies the ground state absorption spectra of **12, 13** and **14** were similar but their optical limiting performances were varied. The structural features that did not contribute to the ground state absorption had an influence on the excited state absorption. The same observation was found for compounds **17** and **18**.

Dimers and trimers

The domain of the optical limiting properties of porphyrin systems comprising multiply porphyrin rings is still poorly explored but gaining more and more attention with the development of new synthetic strategies for their preparation [20,26-28]. Herein we report some consistent trends in nonlinear optical parameters for structurally correlated dimers and trimers.

As far as β_{eff} of the two constitutional isomers dimer **27** and **28** is considered, compound **27**, with an 1-ethylpropyl group at position 15 with respect to the linker, had a slightly higher β_{eff} value than compound **28** with the same group situated at position 10. A comparison of two analogous dimers, **23** with *p*-phenylacetylene linker and compound **28** in which porphyrin units are connected via acetylene, showed the latter compound to have a slightly higher β_{eff} value. Interestingly the opposite effect was observed for compounds **25** and **29**, where the latter one with acetylene linker was characterized by a lower β_{eff} value then the analogous *p*-phenylacetylene linked compound **25**.

Both compounds **22** and **25**, with 4-NO_2-C_6H_4 groups, had a lower β_{eff} then their analogues with hydrogen atoms at the equivalent position (compounds **20** and **24**, respectively). When the porphyrin contained two naphthyl units (**25**) instead of two phenyl units (**21**) the NLA was found to be lower.

β_{eff} values of the dimers studied were comparable to those of the most promising monomers though not exceeding that of compound **11**. With regard to the linear optical absorption features of the dimers, the Soret band maxima of the compounds with acetylene linkers were red shifted in comparison to the ones with *p*-phenylacetylene as a linker. No apparent improvement of NLA could be observed with a decrease in the proximity of the Soret band peak to the experimental wavelength, which was distinguished for the previously discussed monomers. This highlights the dominant effect of meso substituents on the nonlinear response in the dimers studied. Again meso substituents appeared to be an effective tool for the fine tuning of the nonlinear optical properties of porphyrin systems.

The NLO response for the L-shaped trimers, except for compound **34,** was in a similar range to the dimers and most promising monomers, but not as large as for the best compound **11**. The nonlinear absorption of linear trimers was relatively poor.

The response of the L-shaped compound **33** with 4-NO$_2$-C$_6$H$_4$ was slightly lower than that of the analogous compound **32** with a hydrogen atom at the equivalent position which was similar to the effect found for dimers.

As far as dimers and trimers are concerned, no apparent change in the nonlinear response was observed upon addition of subsequent porphyrin units in reference to monomers. Comparative studies carried out on the porphyrin monomers, dimers and polymers by Qureshi *et al*. revealed that the relative nonlinear transmission rose as the number of the porphyrin units with conjugated groups at meso positions was increased in the molecule (monomer < dimer < polymer). Although, the authors reported that monomer had the best optical limiting characteristics, they also proved that polymer was an interesting compound for the application in optical limiting. This was because the Soret and Q-bands of the polymer were significantly red-shifted, which created a wide widow for OL verification [13]. Similar to latter conclusion could be made in reference to acetylene linked dimers in our studies. The UV-vis absorption spectra of these dimers were significantly red shifted in reference to other compounds. However any further comparison of the optical limiting responses of monomers, dimers and trimers is difficult to carry out, in our case, as the structural features of the porphyrins studied were highly diverse. Some more systematic studies would enable further verification on this issue.

4. Conclusions

The NLA of a broad range of porphyrins was investigated. Initial trends concerning the dependence of the NLA on structural features could be established for different substitution patterns both for monomers as well as for dimers and trimers. The values of β_{eff} found for the compounds studied were comparable to those reported in the literature for related compounds [21].

For 5,15-A$_2$B$_2$ monomers an enhancement in RSA was observed when the meso substituent possessed some strong electron-withdrawing groups. The response was even better when the substituent was linked to the porphyrin ring through a conjugated group. For these compounds the Soret band maxima were red shifted and thus situated closer to the experimental wavelength. Incorporation of zinc(II) into the porphyrin ring was found to enhance the response as well. Compound **11** with 3-MeO-C$_6$H$_4$ and TMS-ethynyl groups was found to be the most promising among all of the examined compounds.

5,15-A$_2$BC compounds, with substituent A being a 3-MeO-C$_6$H$_4$ group, were found to have improved optical limiting properties in comparison to those with A = 1-napthyl. Replacement of one 4-MeOOC-C$_6$H$_4$ or 4-CN-C$_6$H$_4$ group in A$_2$B$_2$ compounds with one *n*-C$_4$H$_9$ group, leading to analogous 5,15-A$_2$BC compounds, lowered the efficiency of the RSA. The optical limiting response of structurally related compounds with varied substituents at the *para* position of the phenyl ring was different, while the ground state absorption spectra of these compounds were similar. Thus the structural features that did not contribute to the ground state absorption features have an influence on the excited state absorption.

As far as dimers are concerned, both the type of linker and the meso substituents had an effect on the ground state and excited state absorption. Apart from the influence of the particular meso substituents on the NLA the mutual position of these substituents contributed to the NLO response and this became evident when comparing constitutional isomers. L-shaped trimers were found to exhibit relatively strong RSA, while linear trimers showed rather weak responses.

In summary, the results obtained reveal that the optical limiting properties of porphyrins can be fine tuned by the chemical modifications of the porphyrin ring via incorporation of different meso substituent, insertion of metal ions into the central cavity or by binding together multiple porphyrin units with different linkers. The effect of meso substituents on the NLA in different porphyrins systems was highlighted and showed that the regiochemical arrangement of substituents provides yet another effective route of modification of the optical limiting performance of porphyrins.

Acknowledgments

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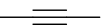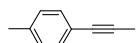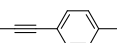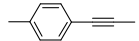[18]   MO Senge, XD Feng, J. Chem. Soc., Perkin Trans. 1 (2000) 3615.

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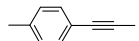
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Table 1. Comparison of the experimental data for the porphyrins studied. R^n – meso-susbtituents; M^n - metal in the central cavity of the porphyrin ring [
Fig. 1.]; No. – compound's number; α_0 – linear absorption coefficient; λ_{max} – Soret band maximum; β_{eff} – effective intensity dependent nonlinear absorption coefficient $Im\{\chi^{(3)}_{eff}\}$ – imaginary part of the third order susceptibility $\chi^{(3)}$.

<div align="center">Monomers</div>

5, 15-A₂B₂

No.	R^1	R^2	M	α_0 [cm^{-1}]	λ_{max} [nm]	β_{eff} [cmW^{-1}] $\times 10^{-8}$	$Im\{\chi^{(3)}_{eff}\}$ [esu] $\times 10^{-12}$
1	1-naphthyl	Benzothiophene	2H	0.98	420	1.1±0.1	3.7±0.5
2	1-naphthyl	4-CN-C₆H₄	2H	0.79	422	1.6±0.0	5.6±0.0
3	1-naphthyl	1-Me-indole	2H	0.67	427	0.5±0.0	1.7±0.0
4	1-naphthyl	4-MeOOC-C₆H₄	2H	0.49	421	1.7±0.1	5.8±0.3
5	1-naphthyl	3-thiophene	2H	0.65	422	1.2±0.0	4.0±0.0
6	1-naphthyl	Styrene	2H	0.78	437	2.3±0.1	7.9±0.5
7	1-naphthyl	3-NO₂-C₆H₄-ethenyl	Zn	0.58	439	2.1±0.1	7.1±0.3
8	1-naphthyl	PO(OEt)₂-ethenyl	Zn	0.15	437	0.8±0.1	3.2±0.3
9	1-naphthyl	C₆H₄-ethynyl	2H	0.54	445	2.1±0.1	7.3±0.4
10	3-MeO-C₆H₄	4-CN-C₆H₄	2H	0.43	420	1.6±0.2	5.5±0.5
11	3-MeO-C₆H₄	TMS-ethynyl	Zn	0.32	449	5.3±0.1	18.0±0.0

5, 15-A₂BC

No.	R^1	R^2	R^3	M	α_0 [cm^{-1}]	λ_{max} [nm]	β_{eff} [cmW^{-1}] $\times 10^{-8}$	$Im\{\chi^{(3)}_{eff}\}$ [esu] $\times 10^{-12}$
12	1-naphthyl	n-C₄H₉	4-CN-C₆H₄	2H	0.20	422	0.5±0.0	1.5±0.1
13	1-naphthyl	n-C₄H₉	4-MeOOC-C₆H₄	2H	0.76	422	0.7±0.0	2.3±0.2
14	1-naphthyl	n-C₄H₉	4-NO₂-C₆H₄	2H	0.63	423	0.8±0.0	2.7±0.1
15	1-naphthyl	n-C₄H₉	Br	Zn	0.62	425	1.8±0.1	6.1±0.4
16	1-naphthyl	2-thiophene	4-NO₂-C₆H₄	2H	0.43	423	0.9±0.1	3.1±0.2
17	3-MeO-C₆H₄	n-C₄H₉	4-CN-C₆H₄	2H	0.70	419	2.1±0.1	7.1±0.4
18	3-MeO-C₆H₄	n-C₄H₉	4-NO₂-C₆H₄	2H	0.80	420	1.9±0.2	6.5±0.5
19	3-MeO-C₆H₄	n-C₄H₉	3,4,5-(MeO)₃-C₆H₂	2H	0.32	420	1.3±0.0	4.3±0.1

Dimers $(M^1 = M^2 = 2H)$

No.	Linker	R^n	α_0 [cm^{-1}]	λ_{max} [nm]	β_{eff} [cmW^{-1}] $\times 10^{-8}$	$Im\{\chi^{(3)}_{eff}\}$ [esu] $\times 10^{-12}$
20		$R^1 = R^4 = H$ $R^2 = R^3 = R^5 = R^6 = C_6H_4$	0.62	432	1.8±0.1	6.1±0.4
21		$R^1 = 4\text{-}NO_2\text{-}C_6H_4$ $R^2 = R^3 = R^5 = R^6 = C_6H_4$ $R^4 = n\text{-}C_4H_9$	1.05	435	2.7±0.1	9.0±0.0
22		$R^1 = H$ $R^2 = R^3 = R^5 = R^6 = C_6H_4$ $R^4 = 4\text{-}NO_2\text{-}C_6H_4$	0.33	437	1.4±0.0	4.7±0.0
23		$R^1 = R^3 = R^5 = H$ $R^4 = 1\text{-ethylpropyl}$ $R^2 = R^6 = C_6H_4$	0.40	425	1.7±0.1	5.7±0.3
24		$R^1 = H$ $R^2 = R^6 = C_6H_4$ $R^3 = R^5 = 1\text{-naphthyl}$ $R^4 = n\text{-}C_4H_9$	1.07	439	1.8±0.1	6.1±0.5
25		$R^1 = 4\text{-}NO_2\text{-}C_6H_4$ $R^2 = R^6 = C_6H_4$ $R^3 = R^5 = 1\text{-naphthyl}$ $R^4 = n\text{-}C_4H_9$	0.81	439	1.3±0.1	4.6±0.2
26		$R^1 = 3\text{-}NO_2\text{-}C_6H_4$ $R^2 = n\text{-}C_6H_{13}$ $R^3 = R^5 = H$ $R^4 = 1\text{-ethylpropyl}$ $R^6 = 3,4,5\text{-}(MeO)_3\text{-}C_6H_2$	3.03	467	2.6±0.2	8.8±0.7
27		$R^1 = R^3 = R^4 = H$ $R^2 = R^6 = C_6H_4$ $R^5 = 1\text{-ethylpropyl}$	0.55	465	1.6±0.2	5.4±0.8
28		$R^1 = R^3 = R^5 = H$ $R^2 = R^6 = C_6H_4$ $R^4 = 1\text{-ethylpropyl}$	0.63	464	1.9±0.1	6.4±0.5
29		$R^1 = 4\text{-}NO_2\text{-}C_6H_4$ $R^2 = R^6 = C_6H_4$ $R^3 = R^5 = 1\text{-naphthyl}$ $R^4 = n\text{-}C_4H_9$	0.28	473	0.7±0.0	2.5±0.1

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Trimers

Linear

No.	Linker	R^n	M^n	α_0 [cm^{-1}]	λ_{max} [nm]	β_{eff} [cmW^{-1}] $\times10^{-8}$	$Im\{\chi^{(3)}_{eff}\}$ [esu] $\times10^{-12}$
30	$L^1 = L^2 =$	$R^1 = R^5 = H$ $R^2 = R^4 = R^6 = R^8 = 3\text{-MeO-}C_6H_4$ $R^3 = R^7 = 1\text{-naphthyl}$	$M^1 = M^3 = 2H$ $M^2 = Zn$	0.60	411	0.4±0.0	1.4±0.1
31	$L^1 =$ $L^2 =$	$R^1 = R^5 = H$ $R^2 = R^4 = R^6 = R^8 = C_6H_4$ $R^3 = R^7 = 1\text{-naphthyl}$	$M^1 = M^2 = M^3 = 2H$	0.45	413	1.1±0.0	3.8±0.0

L-shaped ($M^1 = M^2 = M^3 = 2H$)

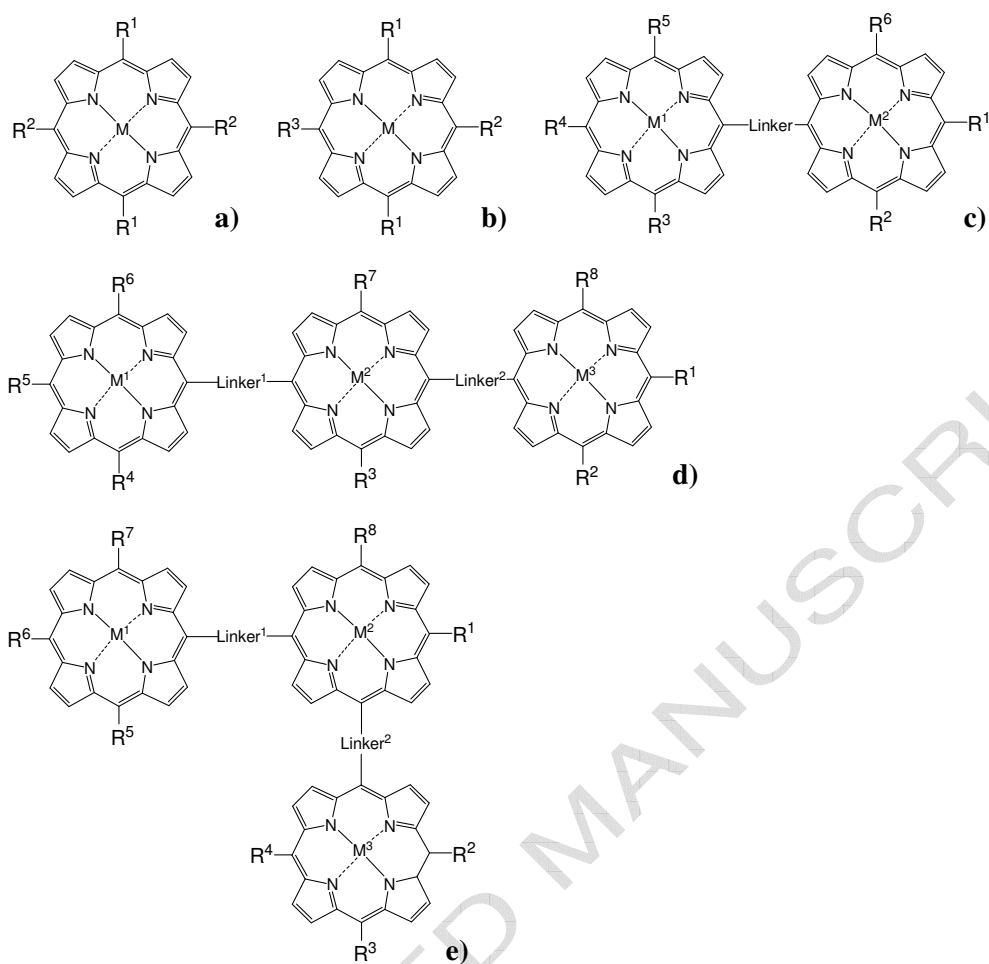| No.	Linker	R^n	α_0 [cm^{-1}]	λ_{max} [nm]	β_{eff} [cmW^{-1}] $\times10^{-8}$	$Im\{\chi^{(3)}_{eff}\}$ [esu] $\times10^{-12}$
32	$L^1 =$ $L^2 =$	$R^1 = R^8 = 4\text{-Me-}C_6H_4$ $R^2 = R^4 = R^5 = R^7 = C_6H_4$ $R^3 = R^6 = 4\text{-NO}_2\text{-}C_6H_4$	0.67	420	2.4±0.2	8.1±0.6
33	$L^1 =$ $L^2 =$	$R^1 = R^8 = 4\text{-Me-}C_6H_4$ $R^2 = R^4 = R^5 = R^7 = C_6H_4$ $R^3 = R^6 = H$	1.02	413	2.6±0.2	9.0±0.6
34	$L^1 =$ $L^2 =$	$R^1 = R^2 = R^4 = R^5 = R^7 = R^8 = C_6H_4$ $R^3 = R^6 = H$	0.19	412	0.8±0.0	2.7±0.1

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Fig. 1. Numbering of the substituents and metals in the porphyrin cores used in Table 1 for a) 5,15-A_2B_2 monomers, b) 5,15-A_2BC monomers, c) dimers, d) linear timers, and e) L-shaped trimers
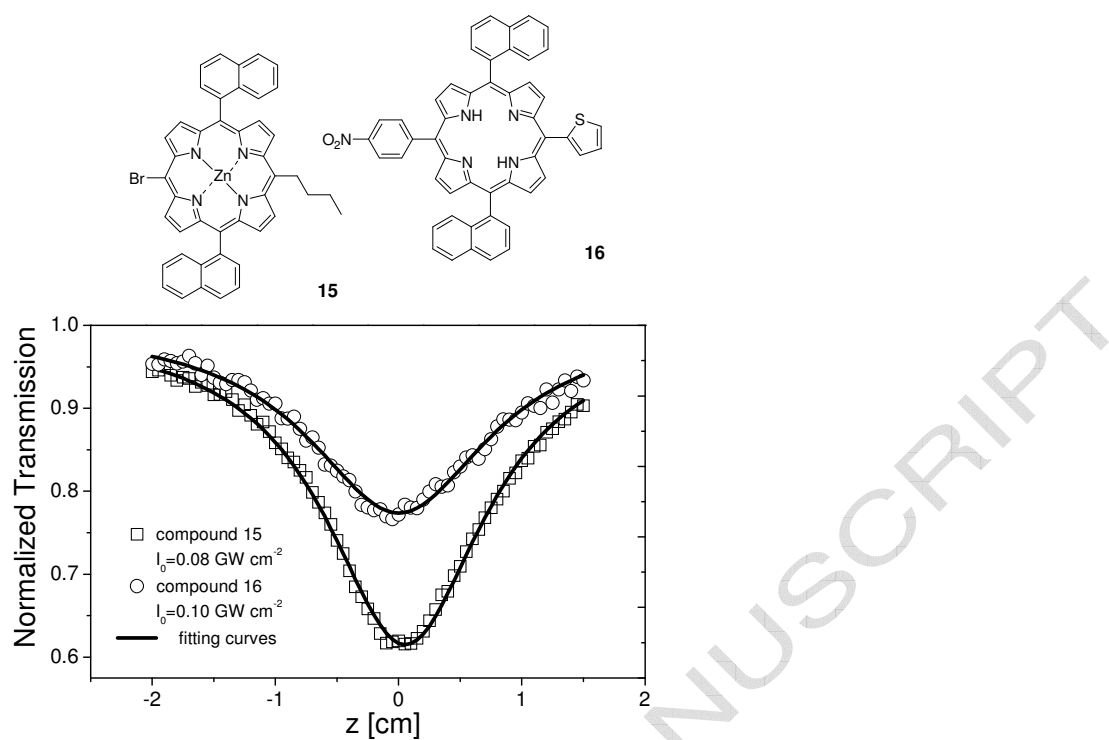
Fig. 2. Typical open aperture Z-scan data set with the normalized transmission plotted as a function of sample position z for the A$_2$BC monomers **15** and **16**.
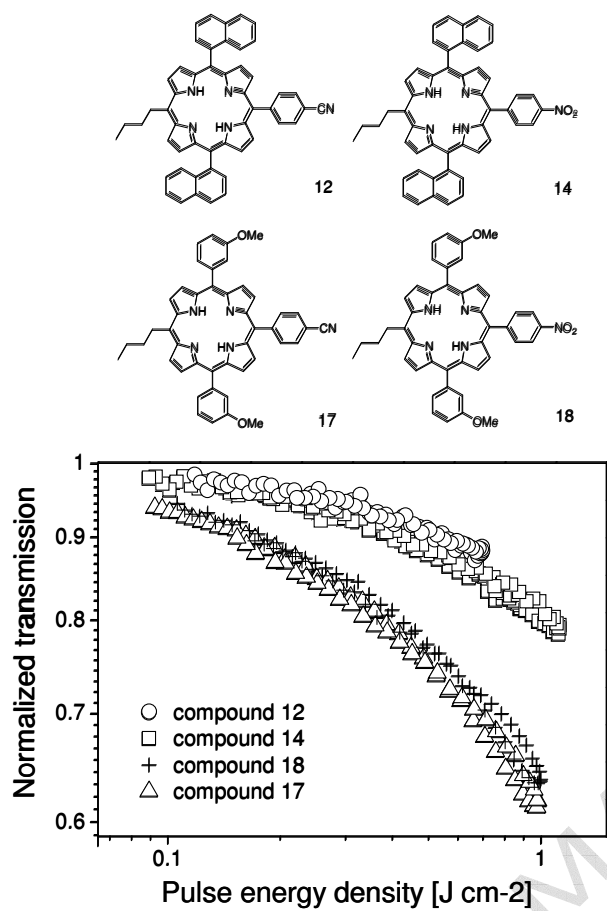
Fig. 3. Optical limiting curves plotted as normalized transmission versus pulse energy density for the compounds **12**, **14**, **17** and **18**.