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14. ABSTRACT This report results from a contract tasking Polish Academy of Sciences as follows: The material for real-world optical limiting applications based on RSA has to independently possess (among others) three distinct properties: large two-photon absorption cross-section, long-living excited triplet state and state of liquidity (or at least very high solubility). Currently there is no such material available. Compounds possessing large TPA cross-sections have typically short lived triplet-state. On the other hand compounds which have long-lived triplet-state, usually have small cross-section. The only class of molecules which can fulfill these requirements are porphyrins (or their close analogs like phthalocyanines, corroles etc.). Simple porphyrins have rather low TPA cross-sections (10 GM). There are known ways to increase TPA cross-section in porphyrins. Usually this requires addition of other aromatic moieties to existing chromophore, thus making these molecules even less soluble. Consequently the major challenge will be to introduce high solubility, or better liquidity into porphyrin core. There are a two major ways envisioned: Introduction of substituents, which are known to change physical properties of solids into liquids. Specifically we will focus on functional groups which increase solubility of porphyrins in common organic solvents such as long alkyl chains and oligoethyleneglycol chains. Preparation of ionic liquid derivatives of porphyrins. This is totally new approach, since there is no ionic liquid derivative of porphyrin known. One of the possible pathways is to synthesize imidazolium salts substituted with porphyrin ring. This is more challenging idea which will be pursued in the parallel to the main approach.					
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Report from the realization of the contract: FA8655-07-1-3020: Liquid two-photon absorbing porphyrins for optical limiting

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Abstract

According to our plan our research went into two major directions. First of all, we studied the synthesis of *meso* and β substituted porphyrins and corroles with the aim of preparation compounds with high two-photon absorption cross-section. We investigated [2+2] method with condensation of 1-formyl-2-arylacetylenes with dipyrromethanes as a crucial step. We proved that such aldehydes (and their acetals) can be easily prepared and they undergo reaction with dipyrromethanes in the presence of acid to give *trans*-A₂B₂-porphyrins in overall ~10 % yield. Altogether two such compounds were prepared. We also investigated the possibility of formation of β -substituted porphyrins and corroles from suitably substituted precursors. We found that in this case the synthesis of 3,4-dialkoxypyrroles is tedious and porphyrins can not be synthesized from them in high yields. Corroles directly substituted in *meso*-positions with electron-withdrawing ester group were synthesized for the first time. All these porphyrinoids were investigated by our collaborators from the point of view of two-photon absorption cross-section. The most promising *trans*-A₂B₂-porphyrin (**18** in this report) has σ value around 280 GM which is 10 times higher than in the case of typical *meso*-substituted porphyrins.

We also intensively investigated the structural conditions which porphyrin has to fulfill to be liquid at room temperature. Four different *meso*-substituted A₄-porphyrins were studied in this regard. Straightforward synthesis delivered four aromatic aldehydes bearing alkoxy groups in positions 3,4,5 or 2,4,6. For the time being, porphyrins were successfully prepared from three of them. One of these porphyrins (**12** in this report) was fully characterized as dense liquid at room temperature. All measurements performed (including drying under high-vacuum, NMR, elemental analysis etc) proved this observation. If larger scale synthesis confirms this result ***it will be first liquid porphyrins ever reported.***

In consequence, it can be stated that *via* combining these two structural designs it would be possible to synthesize liquid porphyrins with high 2PA cross-sections.

Introduction

Optical equipment is used by the military personal for many purposes, e.g. observation, navigation, fire control and reconnaissance. The fast development of frequency-agile pulsed lasers requires the design of new protecting devices base on optical limiting systems. Optical limiting (OL) is a nonlinear effect consisting of a decrease in the transmittance of the NLO material under high-intensity illumination. The transmission of an optical limiter is high at normal light intensities and low for intense beams. Ideally, the output energy of a limiter rises linearly with input until a threshold is reached, as shown in Figure 1. After the threshold, the input energy is clamped at a given value for any larger input intensity.¹

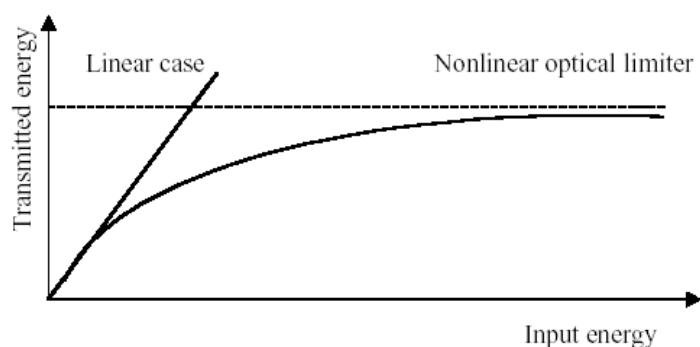


Figure 1

Among the different functions optical limiting devices can perform, the most useful one is the protection of optical elements and sensors against damage by exposure to sudden high-intensity light (Fig.2). The focus of this project in protection of eyes from laser induced damage. The search for efficient optical limiting systems² has mainly focused on three classes of nonlinear optical materials: multiphoton absorbers, reverse saturable absorbers and nonlinear scattering materials. Because the most efficient mechanism to achieve OL is the sequential two-photon absorption (TPA) in this work we will investigate optical limiters based on this process (TPA). The development of the two-photon technology depends much on the success of designing new molecules with large TPA cross sections at desirable wavelengths.³

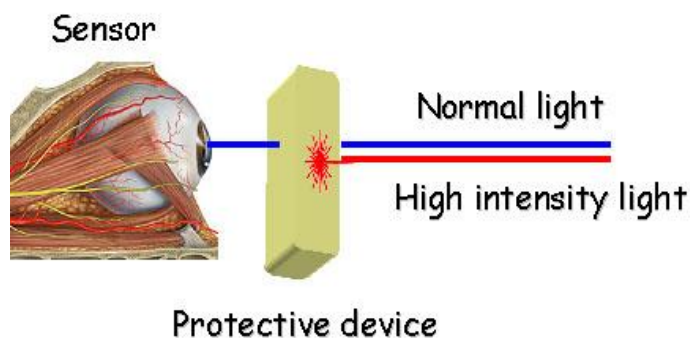


Figure 2

In the early stages, research work was focused on inorganic materials but, in the last 20 years, interest in organic materials for nonlinear optical applications has markedly increased. They offer several advantages over inorganic materials, such as large nonlinearities, ultrafast response times and easy and economic processability, for the preparation of films and miniature integrated optics devices. Moreover, it is possible to optimize their TPA properties by rational modification of their structure.

Porphyrins as OL materials

Porphyrins are a class of naturally occurring compounds with important biological representatives such as hemes, chlorophyll and Vitamin B₁₂. The basis structure of the porphyrin macrocycle consists of four pyrrolic subunits linked by four methine bridges (Fig. 3).

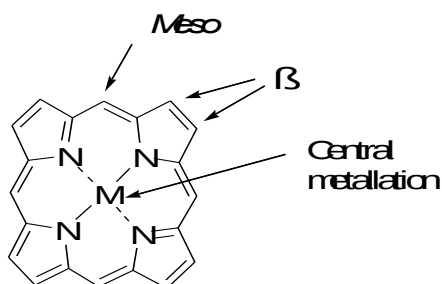


Figure 3

Porphyrins are among the most promising molecular materials for use in OL devices because they possess many important properties, including large excited-state absorption, long triplet lifetime, intrinsic ability of photochemical switching between tautomeric forms, as well as good biological compatibility.^{4,5} The useful OL window for porphyrins is limited to the region comprised between its Q and B band, which is approximately 200 nm wide. In order to observe OL of porphyrins in new regions, the Q and B bands should be shifted via molecular structure modification. A progressive red-shift of the linear absorption bands is usually observed together with the increase of the NLO absorption coefficients. Control of the excited-states lifetimes and cross sections can be indeed achieved by varying the peripheral substitution, the central atom,

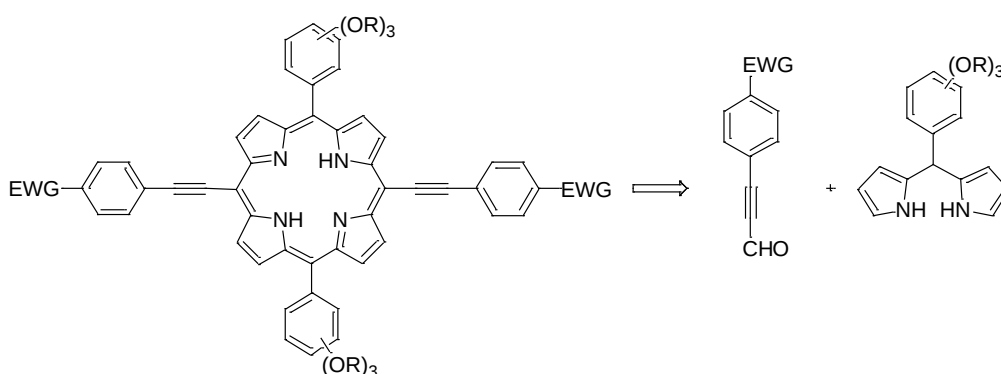
and the extension of the π -conjugation. Figure 3 shows the positions on the porphyrin ring for possible functional modifications.

Furthermore, besides good OL properties there is an additional set of specific conditions that must be fulfilled by compound to be used for practical applications: (1) state of liquidity at room temperature (or low melting point, high solubility), (2) a good thermal and photophysical stability, and (3) a synthesis achieved at a gram scale, which is a real challenge for highly conjugated molecules. As a target molecules we chose porphyrins because only they can fulfill these requirements.

***Trans-A₂B₂*-porphyrins with conjugated substituents**

In this work we investigated the nonlinear optical limiting behavior of a series of porphyrins, bearing at the *meso*- or/and β -positions special electron-donating and electron-withdrawing groups.⁶ We know that an asymmetric π -conjugated substitution of porphyrin with electron donating and accepting groups have a strong charge-transfer character. The introduction of charge-transfer states enhances the nonlinear absorption and optical limiting threshold. Additionally for the development of special filters to protect sensitive light sensors against laser damage we will try to prepare porphyrins as thin films or liquid crystals.

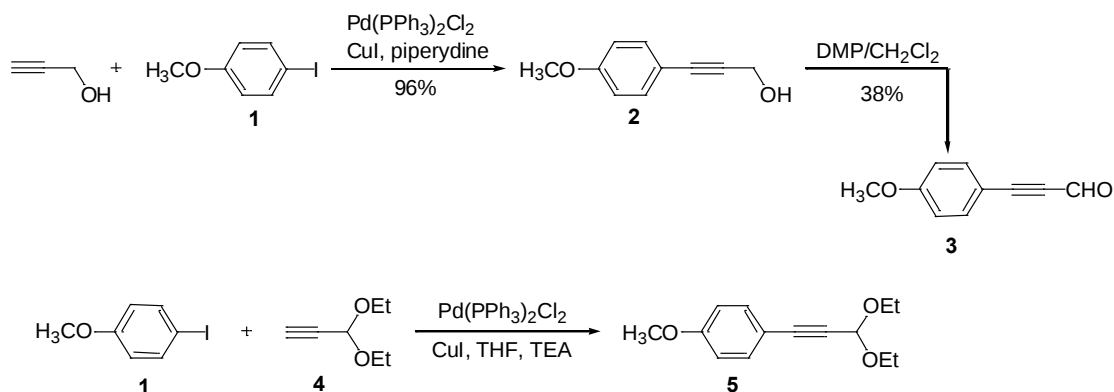
In this context, our purpose is the design of optimized liquid systems displaying enhanced TPA value in the red-NIR region (700-1000nm). Our strategy is based on the push-pull functionalization of porphyrins. Molecules containing a π -center with electron donors or acceptors on the terminal sides of conjugation system are expected to exhibit good TPA response. At first we would like to introduce electron donating and electron withdrawing groups at *meso*-positions of porphyrin (Scheme 1).



Scheme 1

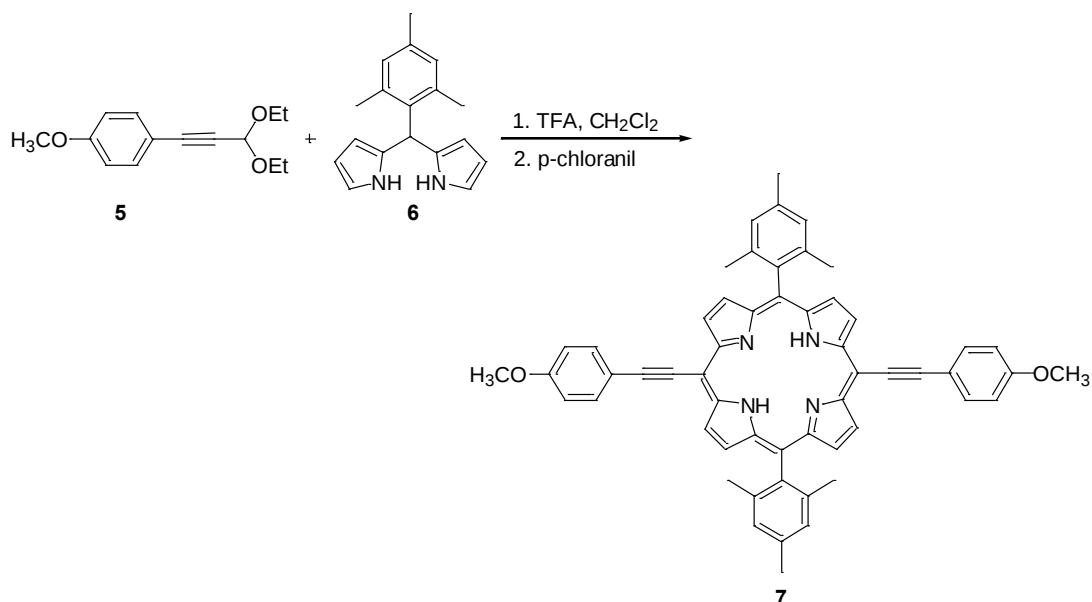
The electron density on the *meso*-carbon atoms of the porphyrin ring is very high. The attachment of acceptor moieties at *meso*-position is effective in elongating the π -conjugation pathway throughout the molecular framework along the triple bond linkages. It is expected that A- π -A porphyrin (Scheme 1) will be effective in elongating π -conjugation pathway (A: electron-accepting group, and π : conjugation pathway).

Alkynyl substituents are the most effective way of making conjugated connections to the *meso* positions of porphyrins. We started our experiments from the preparation of aldehyde **3** and acetale **5** which seemed to be good starting materials because they can be synthesized from commercially available substrates (Scheme 2). As the most promising oxidant we chose Dess-Martin periodinane (DMP). Using such oxidant we obtained aldehyde **3** in a low yield. In advance we used aldehyde **3** and 5-mesityldipyrromethane as substrates for the construction of porphyrins. We performed the reaction under conditions specially optimized for the preparation of porphyrins from sterically unhindered dipyrromethanes.⁷ This procedure has allowed us to prepare desired porphyrin in good yield.



Scheme 2

Because the yield of aldehyde was not satisfactory we decided to replace aldehydes with acetals. Retrosynthetic analysis reveals that only one simple step is necessary to make the target acetal from commercially available materials. We prepared this acetal but it turned out that stability of acetale **5** is limited, so we couldn't isolate it in a pure state. To synthesize of porphyrin **7** we used the crude reaction mixture. Subsequently, we performed the condensation of acetale **5** with 5-mesityldipyrromethane (**6**) applying the condition optimized for the formation of *trans*-A₂B₂-porphyrins (Scheme 3). However we observed only a trace of fluorescent compound. Examination of the crude reaction mixture by MS spectroscopy indicated that porphyrin **7** was present in reaction mixture.



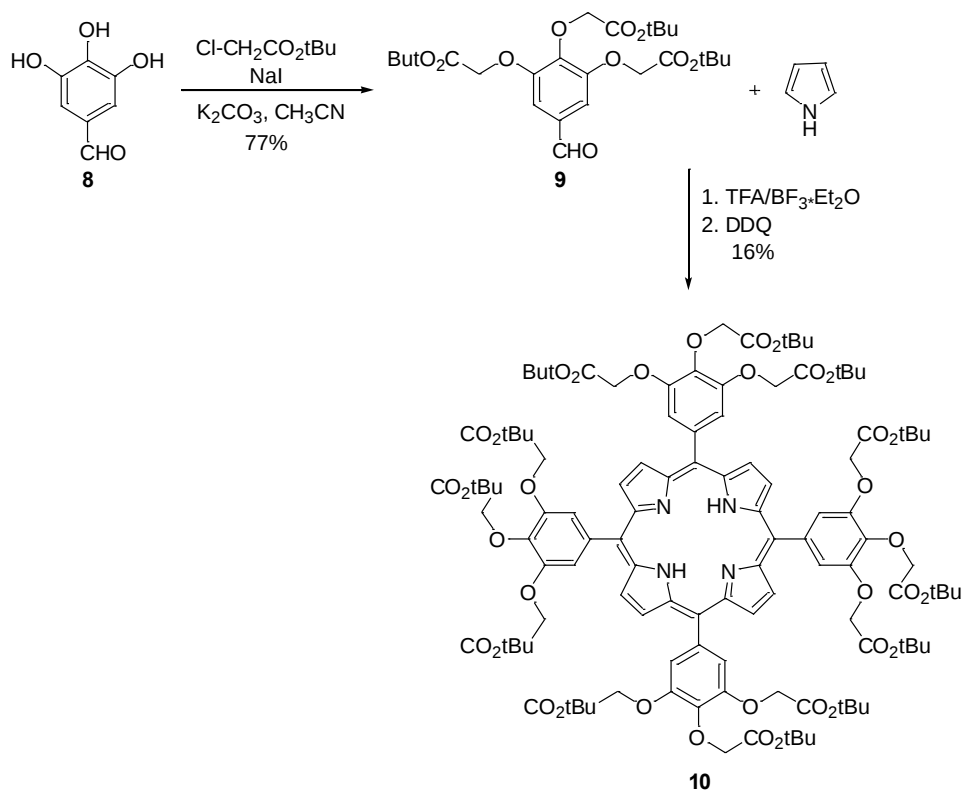
Scheme 3

A₄-porphyrins with trisalkoxyphenyl substituents

One of the key investigations we currently perform is to elucidate structure-melting point relationship for porphyrins. We decided to check the influence of presence of various alkoxy carbonyl, polialkoxy and alkoxy groups at *meso*-positions on solubility of porphyrins.

In our initial approach we set on the preparation of porphyrin with polialkoxy groups. We performed the reaction of appropriate aldehyde with pyrrole under conditions specially designed for polar aldehydes.⁸ Unfortunately the scale of this reaction was very small and although we established that product is very soluble in all common organic solvents, we couldn't measure the melting point of the porphyrin. Unfortunately scale-up experiment was failed so we couldn't precisely characterize product.

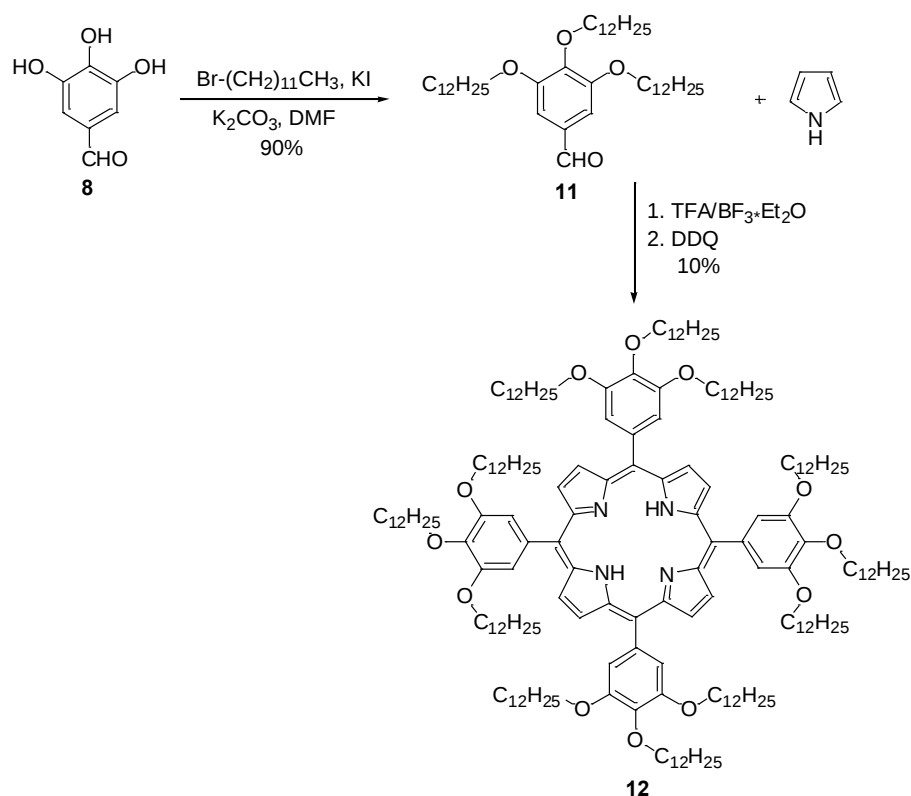
In the next step we decided to prepare of porphyrin with alkoxy carbonyl groups. We started our experiments from the preparation of aldehyde **9** which seemed to be a good starting material because it allows for the introduction of three alkoxy substituents in one step. We prepared aldehyde **9** in a good yield and subsequently we performed the reaction of aldehyde **9** with pyrrole (Scheme 4). We obtained porphyrin **10** in a good yield. We established that this compound is well soluble in many common organic solvents (239 mg in 1 mL of toluene, 46 mg in 1 mL Et₂O) but poorly soluble in alkanes (0.03 mg in 1 mL of hexane, 0.50 mg in 1 mL cyclohexane). The melting point is 157°C which is exceptionally low value for porphyrins.



Scheme 4

Encouraged by this result, we decided to extend this approach to the preparation of porphyrins with various alkoxyphenyl groups at *meso* positions which should improve the solubility of porphyrins. At first we would like to study the influence of the introduction of alkoxy groups with a long alkyl chains.

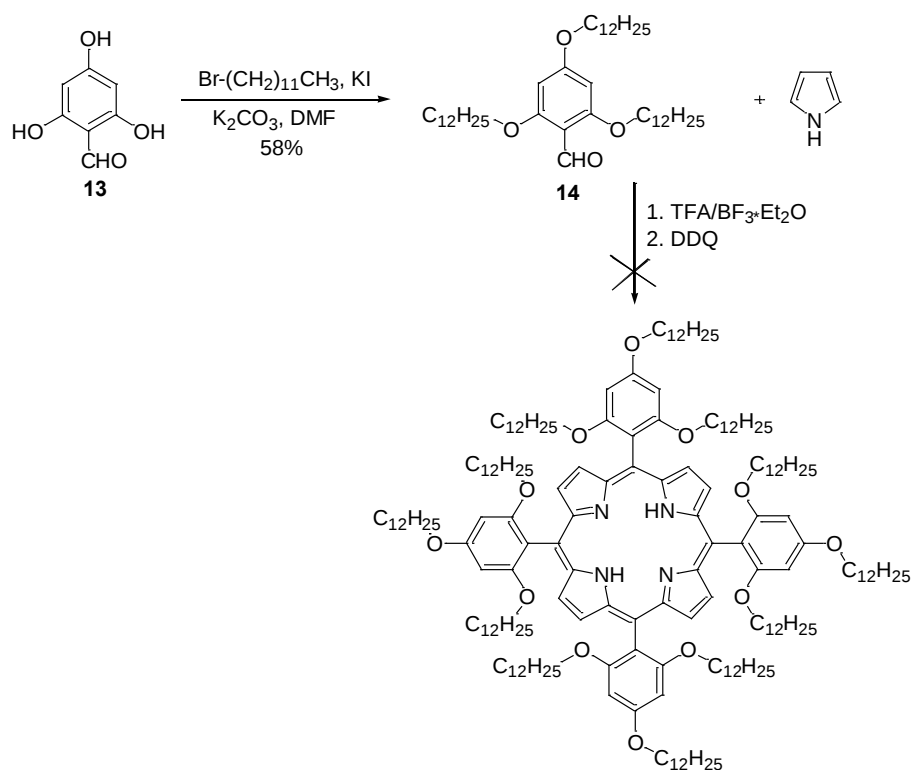
The starting material, aromatic aldehyde **11**, was prepared on a gram scale by Williamson synthesis from 3,4,5-trihydroxybenzaldehyde (**8**) with 3 equivalents of the dodecylbromide in the presence of K_2CO_3 (Scheme 5).⁹ We prepared the key porphyrin by a condensation reaction of aldehyde **11** with pyrrole in the presence of acid (Scheme 5).



Scheme 5

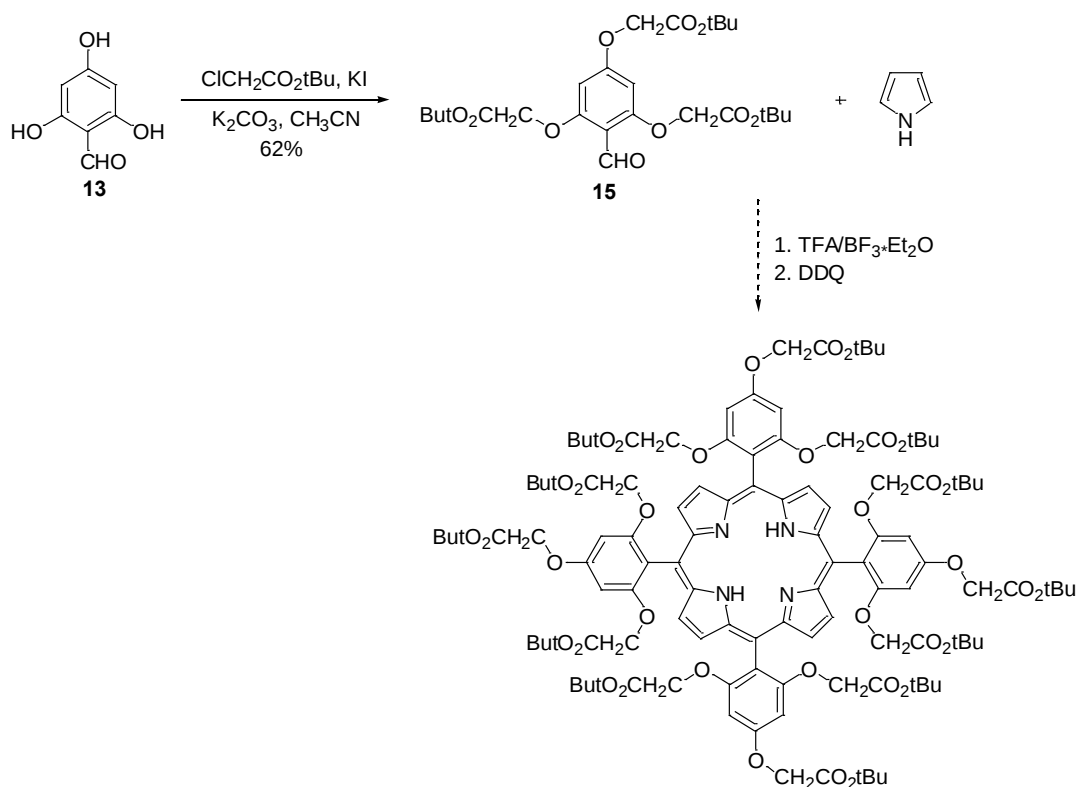
All experiments (careful multi-step purification, extensive drying under high-vacuum, NMR, elemental analysis etc) performed with porphyrin **12** suggest that this compound is a liquid in room temperature. Scale-up experiment is planned in the near future to precisely characterize porphyrin **12**.

Since porphyrins bearing hindered groups at *meso* positions usually are more soluble in common solvents we decided to incorporate such units into porphyrin structure. Consequently, we decided to prepared analogous aldehydes **14** and **15**. The general synthetic approach relies on aldehyde building blocks that bear various alkoxy and akoxycarbonyl groups and orto and para positions. We started our experiments from the preparation of aldehyde **14** by Williamson synthesis from 2,4,6-trihydroxybenzaldehyde (**13**) and dodecylbromide in the presence of K_2CO_3 (Scheme 6). Unfortunately, using stoichiometric ratio of dodecylbromide we obtained appropriate aldehyde **14** only as a side product probably due to high steric hindrance. Then we preformed the reaction of aldehyde **13** (major product) with the excess of dodecylbromide and we obtained aldehyde **14** as a main product. Subsequently, we use the established general procedure for the preparation of porphyrin by a condensation of aldehyde **14** with pyrrole in the presence of acid. Unfortunately in this case we didn't observe a desired product (Scheme 6).



Scheme 6

In the next attempt we incorporated alkoxy carbonyl groups at 2, 4 and 6 positions of aldehyde **13** (Scheme 7). We prepared aldehyde **15** in a good yield and subsequently we are going to use the known procedure for the preparation of porphyrin.

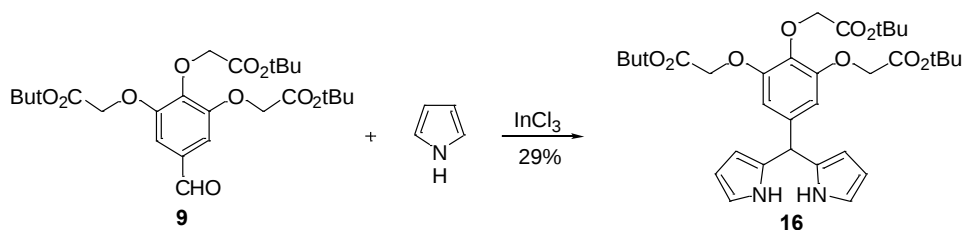


Scheme 7

We plan to continue our studies on the synthesis of porphyrins bearing alkoxycarbonyl (alkoxy) and alkynyl groups at *meso*-positions. The general synthetic approach relies on aldehyde building blocks that bear various alkoxy and alkoxycarbonyl groups.

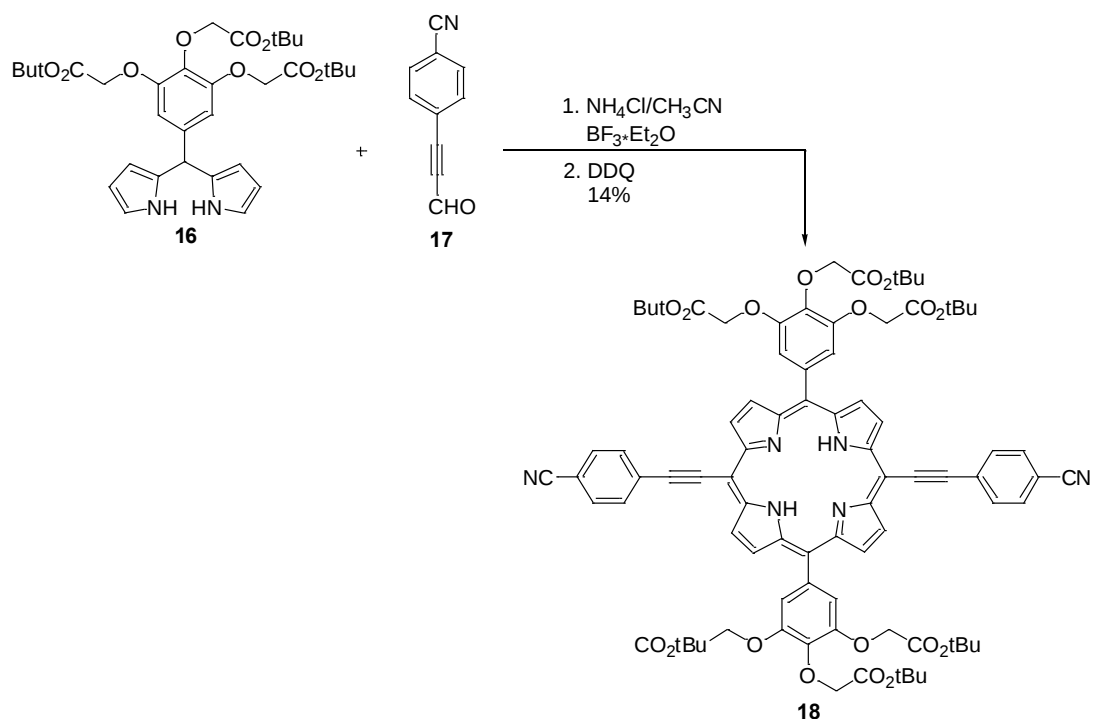
***Trans*-A₂B₂-porphyrins with both conjugated and trisalkoxyphenyl substituents**

Keeping in mind further practical applications we would like to synthesize porphyrins bearing both polialkoxyphenyl and phenylalkynyl substituents at *meso*-positions (Scheme 1). The easiest strategy to incorporate such arrangement of substituents is synthesis *trans*-A₂B₂-porphyrins from dipyrromethane (possessing the electron-donating group - trisalkoxyphenyl) with phenylpropargyl aldehydes. We started our experiments from the preparation of the porphyrin in reaction of 5-(4-polialkoxyphenyl)dipyrromethane with triisopropylsilylpropargylaldehyde. We obtained expected porphyrin in a good yield. Because alkynyl substituents are the most effective way of making conjugated connections to the *meso* positions of porphyrins we decided to extend this approach. At the beginning we prepared crucial dipyrromethane **16** in the reaction of aldehyde **9** with pyrrole under Lindsey's conditions (Scheme 8).¹⁰



Scheme 8

In the final step we condensed dipyrromethane **16** and aldehyde **17** as substrates for the construction of exemplary porphyrin **18** (Scheme 9). We performed the reaction under conditions specially optimized for the preparation of porphyrins from sterically unhindered dipyrromethanes.⁷ This procedure has allowed us to prepare product in a good yield (14%).



Scheme 9

***Beta*-substituted porphyrins with conjugated substituents**

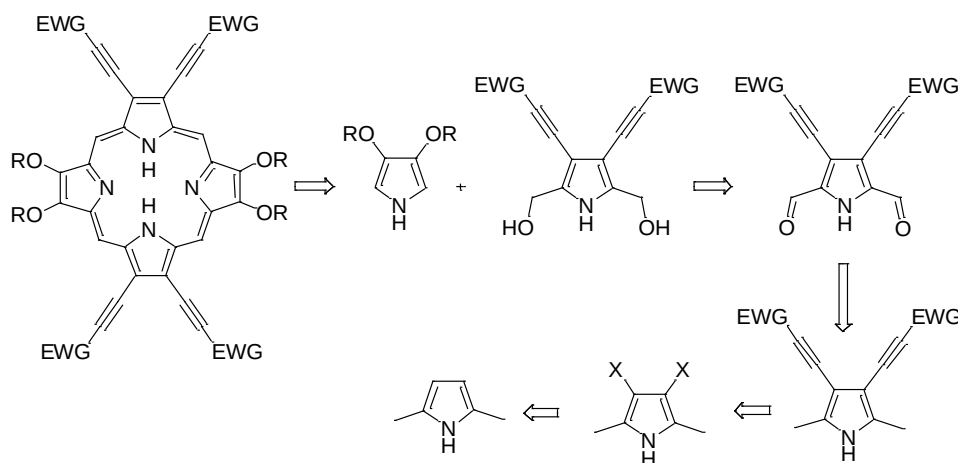
At first we tried to synthesize porphyrin bearing simple electron donating and electron withdrawing groups at β -positions. We expected that the introduction of charge-transfer states enhances nonlinear properties of these porphyrins. In order to prepare a series of derivatives for this application, we sought the efficient preparation of key intermediates using synthetic methodology that would be readily adaptable for rapid functionalization. At first as a substrate we chose previously unknown 3,4-dialkoxy pyrrole. We expected that porphyrins obtained in the reaction of 3,4-dialkoxy pyrrole with different aldehydes, due to the presence of the long alkoxy chains on the core, should show excellent solubility in organic solvents. We have examined the literature procedure which gives comparatively high yields in the synthesis of octaalkoxy-porphyrins from simpler 3,4-dialkoxypyrroles and different aldehydes.^{6,11} We performed reaction of 3,4-dialkoxypyrrole with formaldehyde under these condition. Unfortunately we obtained only a trace amount of a red-fluorescent compound (most-probably porphyrin). In order to prepared a symmetric octaalkoxy-porphyrin we tried to use other aldehydes. We performed reaction the same pyrrole with benzaldehyde and 4-methylbenzaldehyde. Unexpectedly, in these reaction we didn't observe any red-fluorescent products.

The design of the two-photon absorbing molecules is based on the functionalization of a conjugated core with arms bearing electron-withdrawing and electron-releasing groups. As one of the electron-withdrawing substituents we decided to introduce ester groups. At first 2,5-diformyl-3,4-di(carboxyethyl)pyrrole was prepared from the respective 2,5-dimethyl-3,4-di(carboxyethyl)pyrrole (easily accessed by Knorr methodology in two steps from ethyl acetoacetate) via oxidation with cerium ammonium nitrate (CAN).¹² This dialdehyde was then condensed with dialkoxy pyrrole

under few different conditions. Unfortunately even traces of target porphyrin were not detected in the reaction mixture.

Elongation of the conjugation pathway is one of the primary design steps for increasing TPA values of dipolar organic molecules. Consequently, we planned to extend π -conjugation by the introduction of additional double or triple bonds at β -positions of pyrrole rings. Simple retrosynthetic analysis revealed that required porphyrins could be synthesized from dialkoxypyrrole and respective 2,5-dialdehydes with double or triple bonds at 3,4-positions of pyrrole rings.

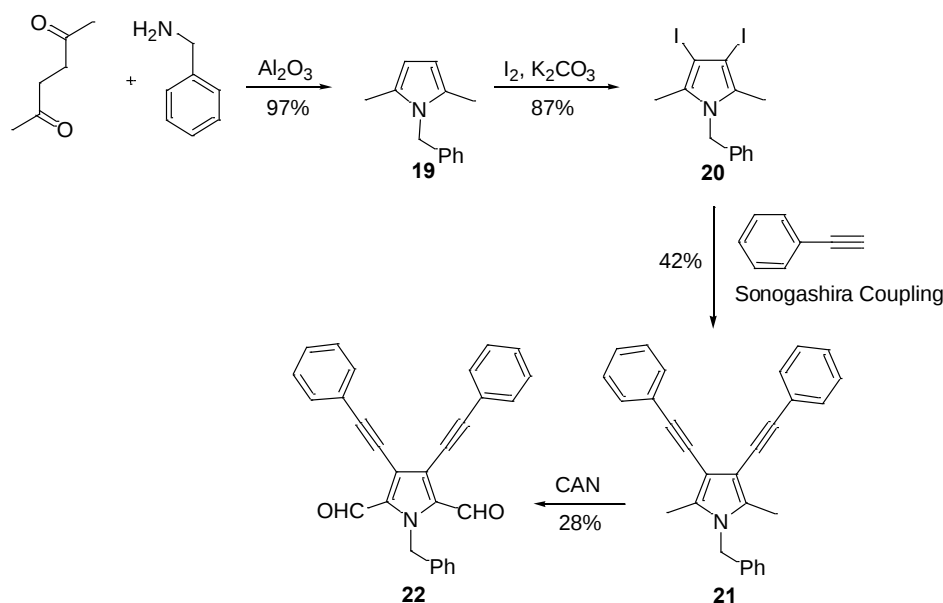
To ensure effective electronic conjugation as spacer between the core and the electro-active end-groups we will use phenyl-ethynylene connecting units. This approach can lead to the formation of porphyrins showing OL in spectral regions different from those of unsubstituted porphyrins. The examples described in literature showed that by extending the conjugation length the absorption bands of modified *meso*-alkynyl porphyrins are red-shifted by several tenths of nm. Consequently, we are going to extend π -conjugation by the introduction of additional triple bonds at β -positions of pyrrole rings. Simple retrosynthetic analysis revealed that required porphyrins could be synthesized from dialkoxypyrrole and respective dialdehydes (Scheme 10).



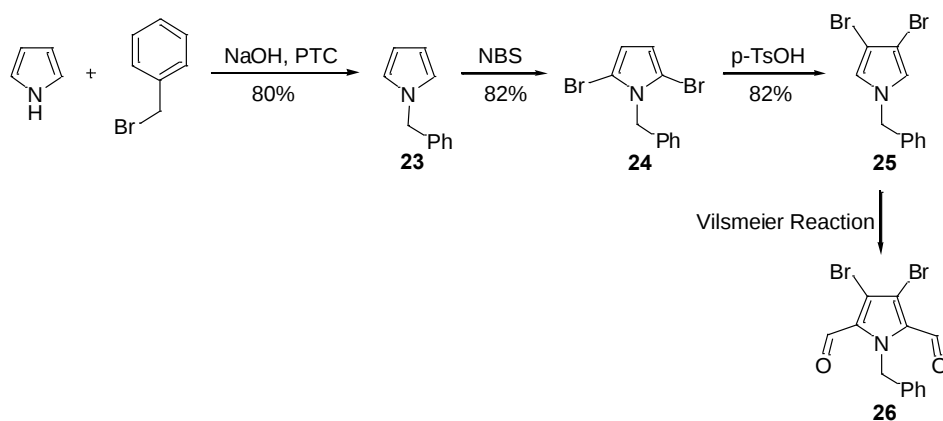
Scheme 10

In order to prepare a series of derivatives for this application, at first we focused our attention on the synthesis of substrates. We prepared already several crucial building blocks like 2,5-diiformyl-3,4-diiodopyrrole. However it proved to be unreactive in Sonogashira coupling.

The alternative strategy involves the preparation of *N*-protected building blocks. We synthesized *N*-protected pyrrole **20** and we used it in Sonogashira coupling with phenylacetylene as a substrate (Scheme 11). We obtained target pyrrole **21** in a moderate yield (42%). In the next step the oxidation of methyl groups by CAN was performed on a small scale. Unfortunately we obtained product in a very low yield. In the finale step we are going to use pyrrole **22** as a substrate for the construction of porphyrins.

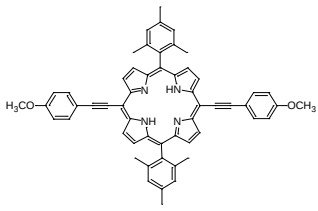
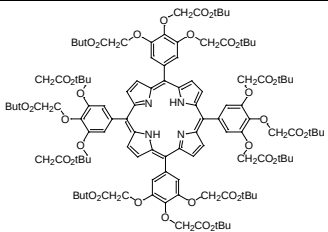
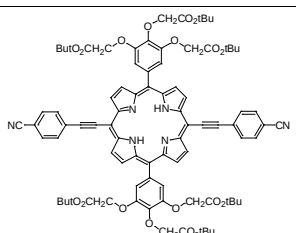
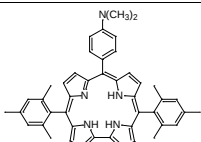
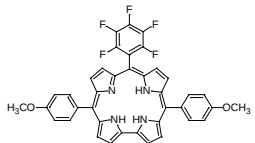
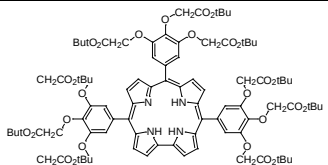
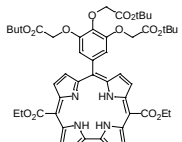


Because this strategy seems not to be very efficient so we decided to modify the reaction conditions by changing the substrate. As a substrate we chose *N*-protected 3,4-dibromo pyrrole **25** which was prepared in a good yield by the route described in the literature. At the next step we would like to perform the Vilsmeier reaction (Scheme 12). The next step of the synthesis will be the construction of the porphyrin ring and further modification.



Two-photon absorption cross-section measurements

The series of porphyrins (3) and corroles (4, see previous reports) synthesized during this project were studied in Physics Department of Montana State University by the group of Aleksander Rebane. The measured two-photon absorption cross sections are presented in the table below:

Entry	Structural formula	δ (two photon absorption cross section) GM	$\lambda_{\max}$
1		88 43 28	806 818 876
2		28	824
3		277 134 102	802 846 876
4		78	830
5		56	834
6		64	830
7		25	846

A₄-type porphyrin (entry 2) has very low value in agreement with previously published results. On the other hand both porphyrins possessing phenylalkynyl substituents (entries 1 and 3) have significantly higher 2PA cross-section. Especially the results for porphyrin **18** (sigma 277 GM) confirmed that this class of porphyrins may find utility for optical limiting applications. Lower values were obtained for corroles but one has to

note that: (a) this group of compounds is not yet so well studied; (b) for the moment it is impossible to synthesize corroles from arylpropargylaldehydes (i.e. with extended π -system).

Conclusions

The porphyrins and corroles prepared during this project are the product of recent effort spent in designing effective molecular structures for optical limiting applications. The study of A_4 -porphyrins revealed that we are able to prepare liquid porphyrins. On the other hand, it was found that it is possible to effectively synthesize *trans*- A_2B_2 -porphyrins bearing two arylethynyl substituents with relatively high 2PA cross-sections. In consequence, it can be concluded that by combining these two structural designs it would be possible to synthesize liquid porphyrins with high 2PA cross-sections. It seems that the synthesis of required porphyrins bearing *meso*-substituents is more feasible than their β -substituted analogues. Corrole based architectures are also promising once the fundamental problem with preparation of *trans*- A_2B -corroles from arylpropargylaldehydes is solved.

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