

A₂B₂-type *push–pull* porphyrins as reverse saturable and saturable absorbers†

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A₂B₂-type *push–pull* porphyrins with a strong intramolecular dipole moment have been prepared *via* Heck and Suzuki coupling reactions as novel materials for use in nonlinear optics (NLO); they display saturable (SA) and reverse saturable absorption (RSA) properties at 532 nm and their nonlinear optical response is characterized by RSA occurring at lower intensity levels whereas the onset of SA prevails at higher levels.

Understanding the optical nonlinearities of dyes is of considerable interest due to their widespread application potential. These include SA for use of dyes for mode locking, laser pulse compression, and laser amplification. RSA has potential for use in pulse sensors and in optical limiting devices that protects sensitive optical components or the human eye from laser-induced damage.¹

Porphyrins and their macrocycle expanded and contracted relatives displaying large nonlinear optical responses are of major interest in the development of photonic and optoelectronic technologies due to their fast response time, large nonlinear susceptibilities and also comparatively low fabrication costs.^{1,2} Porphyrins have outstanding chemical and thermal stability. Their macrocyclic structure and chemical reactivity offers architectural flexibility and facilitates the tailoring of chemical, physical and optoelectronic parameters. They are versatile organic nanomaterials with a rich photochemistry and their excited state properties are easily modulated through conformational design, molecular symmetry, metal complexation, orientation and strength of the molecular dipole moment, size and degree of conjugation of the π -systems, and appropriate donor–acceptor substituents.^{3,4}

Much research has focussed on the synthesis and NLO characterization of novel porphyrin compounds since the first publication on enhanced RSA.⁵ Porphyrin molecules display enhanced RSA over a large region of the visible waveband. This RSA process exhibited in porphyrins and other dyes is often simplified to a three-level model.⁶ An optimized RSA material should display a rapid intersystem crossing rate, a high intersystem crossing quantum yield, and a long triplet lifetime. Despite the many studies on third-order NLO properties of porphyrins no evidence of their optical limiting properties exhibiting reverse saturable and saturable absorption for nanosecond (ns) pulses at 532 nm has been reported to date.

Many NLO studies on porphyrins have focussed on simple symmetric systems and contemporary studies increasingly target

core modified or π -extended macrocyclic pyrrole compounds.⁷ Nevertheless, one design principle for optimized NLO materials is the presence of a strong intramolecular dipole moment as is realized in so-called *push–pull* porphyrins.^{8,9} *meso*-Substituted porphyrins are easy to prepare and, in light of the ongoing progress in synthetic porphyrin chemistry, offer a convenient entry into industrially usable materials. A typical and well studied example are unsymmetrically substituted A₂BC porphyrins where the polarizability of the porphyrin system is modulated by appropriate donor and acceptor groups (Fig. 1).¹⁰

A conceptually related class of compounds that offer the potential to construct systems with stronger intramolecular dipole moment are the A₂B₂-type porphyrins. Here, two donor and acceptor groups can be attached to the π -system, respectively. However, these systems remained elusive due to the difficulty to prepare porphyrins with a 5,10-disubstitution pattern.¹¹ However, our recent success in developing syntheses for *meso* mono- and disubstituted porphyrins gave a possible entry into this class of dyes.¹² Here, we report the synthesis and nonlinear characterization of a new series of optical materials that exhibit *both* reverse saturable and saturable absorption at 532 nm using the Z-scan technique under ns irradiation.

The first step of the synthesis of these novel systems involved the preparation of 5,10-disubstituted porphyrins **1** bearing electron donating groups (phenyl, tolyl, 3-methoxyphenyl) by condensation of tripyrrane with different alkyl or aryl aldehydes (Scheme 1). Subsequent introduction of the electron withdrawing substituents (“B”) was achieved *via* bromination to **2** followed by Heck or Suzuki couplings or LiR chemistry.¹³ The bromination proceeded smoothly in 74–83% yield and was followed by the introduction of an electron withdrawing group (*i.e.* 4-cyanophenyl, **4b** 47%, **4c** 47%; 3-nitrophenyl, **4g** 30%; 4-nitrophenyl, **4d** 50%; 4-methoxycarbonylphenyl, **4a** 52%, **4e** 30%, **4f** 32%).

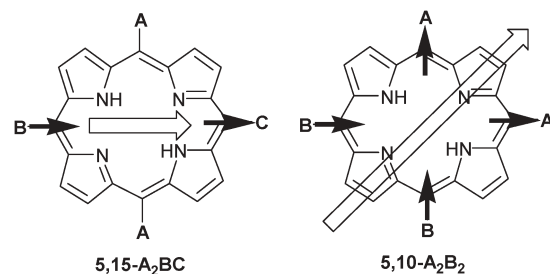
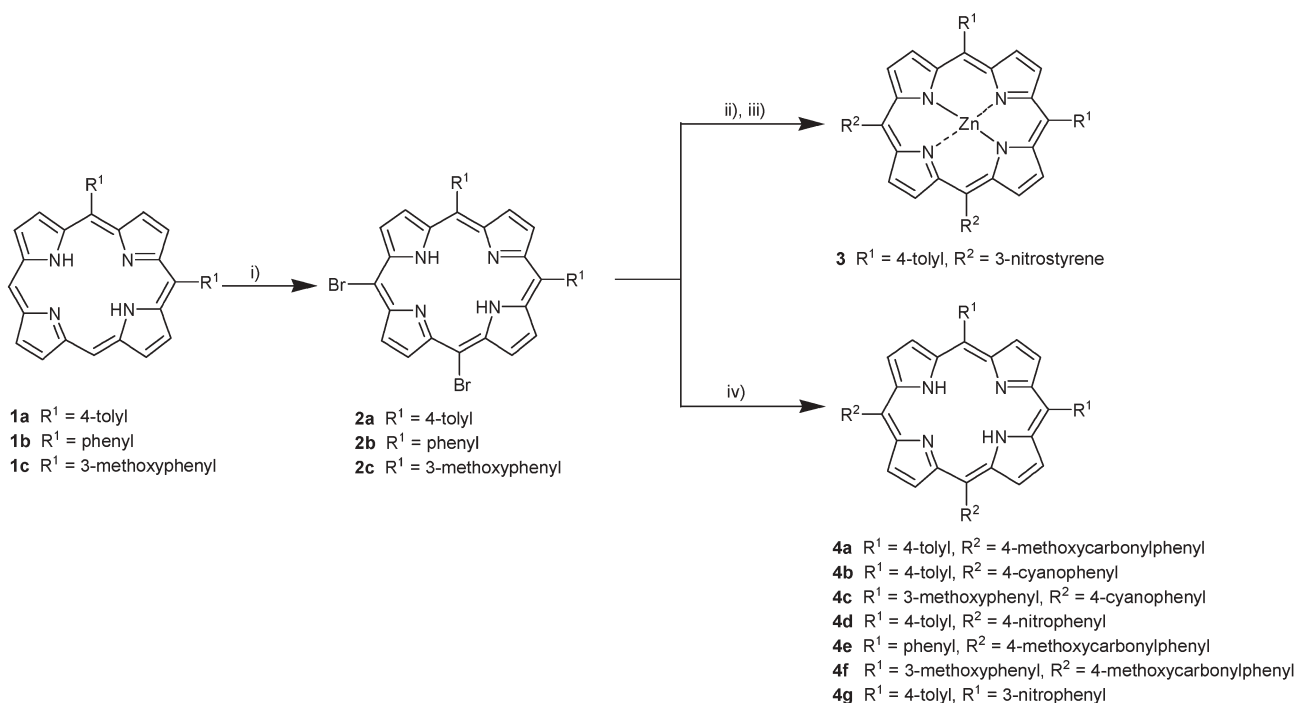


Fig. 1 Illustration of A₂BC- and A₂B₂-type porphyrins with electron donating and accepting substituents to yield systems with strong intramolecular dipole moments.

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Scheme 1 Synthesis of A₂B₂-type porphyrins *via* Heck and Suzuki coupling reactions. *Reagents and conditions:* (i) NBS, CHCl₃, acetone; (ii) K₃PO₄, Pd(PPh₃)₄, arylboronic acids and esters; (iii) ZnO, TFA; (iv) Pd(OAc)₂, Na(OAc)₂, PPh₃, 3-nitrostyrene, DMF.

Herein, we choose eight compounds illustrating this approach which gave the strongest nonlinear optical response. The zinc(II) porphyrin **3** is an example prepared *via* Heck coupling reaction in good yield. For the synthesis of porphyrins **4a–g**, Suzuki coupling reaction conditions have been employed, and, in this case the coupling occurred between the free base of the respective 5,10-dibromo-15,20-disubstituted porphyrins **2** with different aryl boronic acids or esters under tetrakis(triphenylphosphine) palladium catalysis in moderate yields due to the low solubility of 5,10-disubstituted porphyrins.

Fig. 2 shows the linear optical spectrum of A₂B₂-type porphyrins in DMF. The main absorption bands remain constant for the majority of the porphyrins and shift bathochromically for the metallated porphyrin as is characteristic for tetra-*meso*-substituted porphyrins. The effect of peripheral substitution on the linear absorption properties is negligible. All porphyrins from this series exhibit low linear absorption at 532 nm.

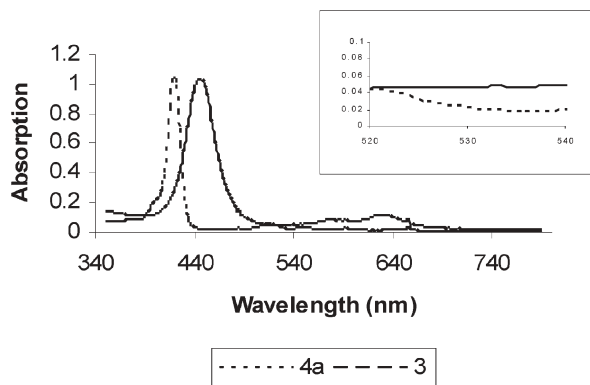


Fig. 2 Characteristic electronic absorption spectra of A₂B₂-type porphyrins **3** and **4a** at $\sim 3 \times 10^{-5}$ mol L⁻¹ solution in DMF.

A very convenient and fast experimental method to characterize materials for optical limiting is the open aperture Z-scan technique.¹⁴ Z-scan measurements of the target compounds with irradiation at 532 nm revealed a novel NLO feature inherent to the A₂B₂-type compounds.† The nonlinear absorption behavior observed in these porphyrins at nanosecond timescale switches from RSA to SA and then again to RSA as the intensity increases. An RSA/SA/RSA switch is exhibited in the tight focal intensity regime shown in Fig. 3. It represents typical experimental results of Z-scan measurements and a plot of normalized transmission against z-distance at varying focal intensities.

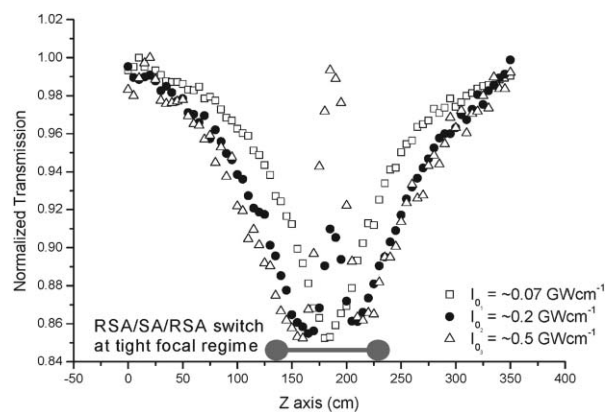


Fig. 3 Open aperture Z-scan data for **3** in DMF at laser intensities of $I_{0-1} = \sim 0.07$ GW cm⁻², $I_{0-2} = \sim 0.2$ GW cm⁻² and $I_{0-3} = \sim 0.5$ GW cm⁻² with indication of the tight focal regime.

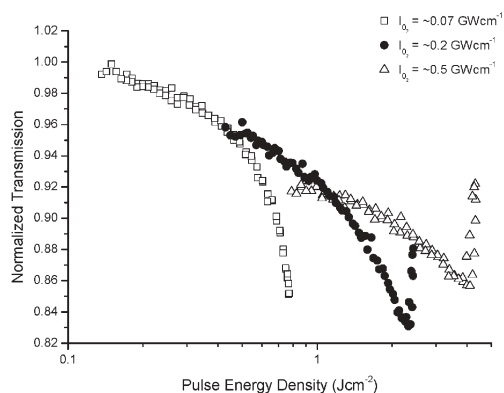


Fig. 4 Plots of normalized transmission against pulse energy density for **3** at laser intensities at $I_{0-1} = \sim 0.07 \text{ GW cm}^{-1}$, $I_{0-2} = \sim 0.2 \text{ GW cm}^{-1}$ and $I_{0-3} = \sim 0.5 \text{ GW cm}^{-1}$.

intensity is further increased to $\sim 0.4 \text{ GW cm}^{-1}$, the SA behavior increases symmetrically. At low fluence, $\sim 0.07\text{--}0.13 \text{ GW cm}^{-1}$, a three-level model was successfully used to mathematically describe the resulting NLO behavior.

At very high inputs, (0.5 GW cm^{-1}) a high intensity nonlinear response was observed which may be connected to a photochemical reaction of the excited state of the molecule, leading to the formation and accumulation of a new product within the experimental lifetime. As the intensity increased the behavior switched to SA from RSA, most likely due to two-photon absorption or excited state absorption. At very high intensities the behavior was dominated by SA. In these A_2B_2 -type porphyrins the RSA/SA/RSA switch at the focal point regime is fully reversible.

The Z-scan data plotted as normalized transmission as a function of incident energy per pulse for **1** are depicted in Fig. 4 and show a characteristic form for all the A_2B_2 -type porphyrins investigated. As the intensity increases the RSA nonlinear optical response becomes weaker whereupon SA occurs.

A new type of *push-pull* porphyrins has been synthesized using Suzuki and Heck coupling reaction conditions. Our Z-scan experiments have revealed interesting features of nonlinear absorption properties for this series of A_2B_2 -type porphyrins. At 532 nm the nonlinear processes are studied under ns irradiation, a non-resonant absorption. RSA was observed at low fluence intensities and at higher intensities SA followed by RSA again. This tight focal switch regime was shown to occur at high intensities symmetrically. Hence, porphyrins of this type offer a significant degree of design flexibility and thus potential to fabricate practical optical materials.

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Notes and references

‡ The experiments were performed using $\sim 6 \text{ ns}$ Gaussian pulses from a Q-switched Nd:YAG laser. The beam was spatially filtered to remove the higher modes and tightly focussed with a 9 cm focal length lens. The laser was operated at its second harmonic, 532 nm, with a pulse repetition rate of 10 Hz. The irradiation at 532 nm is a no resonant excitation. The measurements were carried out in solution in a quartz cuvette of 1 mm path length containing porphyrins in a concentration of $\sim 4 \times 10^{-4} \text{ mol L}^{-1}$ in

spectroscopic grade DMF. The porphyrins were placed into a low power (60 W) sonic bath for about 1 h in order to obtain homogenous and complete dissolution.

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