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Synthesis and femtosecond third order nonlinear optical properties of push-pull *trans*-A₂B-corroles



PIGMENTS

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ABSTRACT

Six novel push-pull trans- A_2B free base corroles (1-6) were synthesized and characterized by various spectroscopic techniques. The charge-transfer ability of these trans-A₂B-corroles was reflected from the broadness of the UV-visible absorption spectral bands. Corroles 1 and 2 exhibited absorption at lower wavelengths, higher quantum yield and longer singlet state lifetime as compared to 3-6. The ultrafast nonlinear optical (NLO) properties of these corroles were evaluated in visible range (at 800 nm) using the femtosecond Z-scan technique. The investigated corroles possess negative type of nonlinearity and selfdefocusing behavior with the magnitude of nonlinear refractive index (n_2) in the range of 0.36 -2.84×10^{-11} cm²/W, while the two-photon absorption (β) coefficients were in the range of 6.5–68 cm/ GW with $|\chi^{(3)}|$ in the range of 10^{-9} e.s.u. The resultant dipole moments of these corroles were calculated theoretically and found to be 1.47–7.26 D depending on the nature of push-pull groups on the mesophenyl substituents. 1–6 demonstrated excellent NLO activity due to their 'push-pull' design. Among the investigated corroles, 1 and 2 possess strong two-photon absorption coefficient and large values of $\chi^{(3)}$ suggesting that the nonlinearity of corrole molecules highly depends on the electronic nature and number of meso-substituents. Corroles 1 and 2 possessing two acceptor and one donor moieties depicted superior NLO behavior as compared to corroles (3-6) with one acceptor and two donors due to strong electron withdrawing nature of pentafluorophenyl groups as well as higher singlet excited state lifetime and quantum yield.

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1. Introduction

Nonlinear optical (NLO) materials have attracted materials/ chemistry/physics researchers' interest since past two decades due to their tremendous potential in various applications such as optical communication, optical limiting, multi-photon imaging, fluorescence, data storage devices and surface-enhanced Raman scattering [1–3]. Mainly organic molecules which contain large conjugated π -systems with donor and acceptor sites at the opposite end of the periphery were used as NLO materials [4–7]. These molecules offer the advantages of strong optical nonlinearity and faster optical response. Recently, electron rich corroles based on D- π -A systems were synthesized to study their third-order NLO properties [8-12]. Corroles, a class of contracted porphyrinoids processes $18-\pi$ electron aromaticity. Chemistry of corroles was started 40 years before but the research in this area was slow due to lack of synthetic methodologies [13]. Corrole studies grew up tremendously with the revolution of one pot synthetic route of corroles [14,15]. This provided a new impetus to the synthesis of novel corroles particularly β - and meso-functionalization of the macrocycle [16-20]. Tribasic corroles exhibiting interesting properties such as lower oxidation potentials, higher fluorescence quantum yields, larger Stokes shift, and relatively more intense absorption phenomena as compared to their corresponding porphyrins. These macrocycles showed an intense Soret band and three less intense Q-bands in the visible region. These versatile spectral, electrochemical and photophysical properties of corroles attracted the researchers' interest leading to their widespread applications [21–24]. In addition, the electron-rich π -system of these



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corroles make them desirable for potential applications in nonlinear optics. The chemistry of corroles was investigated way back in 1965 but their interesting properties such as optical non-linearities and excited state dynamics were disclosed recently [8-12,22-24]. Liu et al. [24] reported the Soret excited state dynamics of corroles and compared to porphyrins and suggested (i) corroles are planar and have large number of Frank-Condon active vibrations, (ii) more rigid framework and more sharply rising potential surface walls, (iii) have similar or smaller structural displacement of S₁ excited states, (iv) have larger displacement in S₂ excited states relative to the ground state.

When compared to porphyrins, corroles exhibit intense and broader Soret band around 400 nm (blue region). The second order and third order NLO properties of A_3 and A_2 B-Corroles are well documented in the literature [8–12,25–30]. Recently, the NLO

(1), 5,15-bispentafluorophenyl-10-(1'-pyrenyl)corrole (2) and (ii) one acceptor and two donor moieties; 5,15-ditolyl-10-(4'-nitrophenyl)corrole (3), 5,15-ditolyl-10-(4'-carbomethoxyphenyl)corrole (4), 5,15-ditolyl-10-(4'-pyridyl)corrole (5) and (vi) 5,15-bis(4'-N,N'-dimethylphenyl)-10-pentafluorophenylcorrole (6). We have synthesized two series of *trans*-A₂B 'push-pull' corroles two acceptors and one donor moieties and vice versa. It is interesting to study the NLO properties of *trans*-A₂B corroles possessing two acceptors and one donor moieties when compared to one acceptor and two donors. Furthermore, corrole π -system is well-known to be electron rich and, therefore, it is expected to demonstrate superior NLO activity when substituted with two acceptor and one donor (push-pull) groups due to strong electron withdrawing nature of pentafluorophenyl groups as well as higher singlet excited state lifetime and quantum yield.



Chart 1. Molecular structures of synthesized trans-A₂B-Corroles (1-6) Chart should be placed at the end of Introduction and before Results and Discussion.

properties and excited state dynamics of triphenyl (TPC), tritolyl (TTC), tritolyl germanium (GeTTC) and tritolyl phosphorus (PTTC) corroles were explored in detail [25–27]. The nonlinear refractive index (n_2) as well as two-photon absorption coefficient (β) of 5,10,15tris[3,4-(1,4-dioxan)phenyl]-corrole, 10-[4-(chloroacetoxy) phenyl]-5,15-bis(2-bromo-5-fluorophenyl)corrole, and 10-(4hydroxyphenyl)-5,15-bis(2-bromo-5-fluorophenyl)corrole, were studied in the solution as well as in the aggregated state (in the form of thin films) and found that 10-(4-hydroxyphenyl)-5,15-bis(2bromo-5-fluorophenyl)corrole was a promising candidate for devising optical switches applications [28]. In this report, we present the synthesis, spectral characterization, ultrafast NLO and excitedstate lifetime measurements and DFT studies of two sets of A2B-Corroles (Chart 1): having (i) two acceptor and one donor moieties; 5,15-bis(pentafluorophenyl)-10-(4'-N,N'-dimethylphenyl)corrole

2. Results and discussion

Dipyrromethanes and *trans*-A₂B-Corroles (**1–6**) were synthesized according to literature methods reported by Gryko et al. [31,32] A₂B-Corroles were characterized by UV–Vis, fluorescence, ¹H NMR and mass spectroscopic techniques. The synthetic procedures and spectroscopic data are presented in the supporting information (SI). ¹H NMR spectrum of 5,15-bispentafluorophenyl-10-(1'-pyrenyl)corrole (**2**) in CDCl₃ is shown in Fig. S1 in the supporting information (SI).

2.1. Electronic spectral properties

Optical absorption and emission spectra of reported corroles (1-6) are shown in Fig. 1 and S2 in the SI. Free base corroles



Fig. 1. UV-visible (a) and emission spectra (b) of 2, 4 and 6 free base corroles in CH₂Cl₂ at 298 K.

Table 1			
Absorption and emission spectral	data of synthesized	corroles in CH ₂ Cl ₂	recorded at 298 K

Corrole	UV–Vis (nm)	Fl. (nm)	ϕ_{f}	$\tau_{1,}$ ns (T ₁)	$ au_{2,}$ ns (T ₂)	τ_{3} , ns (T ₃)	FWHM (nm)
1	407, 512, 562, 657	683	0.169	2.27(9%)	5.11(89%)	0.067(2%)	40.55
2	411, 424(sh), 517, 562, 613	652, 717 (sh)	0.197	2.08(5%)	3.99(55%)	0.015(40%)	43.26
3	417, 579, 613, 651	657	0.003	3.08(59%)	6.38(13%)	0.028(28%)	56.52
4	417, 579, 615, 651	673	0.108	0.06(15%)	2.55(53%)	5.84(32%)	54.80
5	423, 518, 582, 616, 641	670	0.111	0.034(19%)	2.25(64%)	4.22(17%)	40.62
6	436, 578, 626, 663	686	0.091	1.19(54%)	2.52(35%)	7.43 (11%)	55.72

Fl.- Fluorescence maxima, φ_f - Quantum yield relative to H₂TPP. τ-fluorescence lifetime, T-fraction of lifetime, FWHM-full width at half maxima in nm, Sh-shoulder.

exhibited π - π * electronic transition with intense and broader Soret band in 410–440 nm region and Q transitions in 500–660 nm visible region. **6** exhibited remarkable red shift in absorption spectra (436 nm) while **1** showed lowest absorption wavelength of Soret band which highly depends on the electron donor-acceptor nature of *meso*-substituents as compared to triphenylcorrole (TPC) (412 nm). The emission spectra for all six corroles were recorded in CH₂Cl₂ at room temperature and the fluorescence maxima were in visible range of 600–700 nm (Fig. 1 and S2 in the SI). Except **3**, all five corroles exhibited good emission intensity. The NO₂ group leads to fluorescence quenching of **3** which exhibits lowest quantum yield. Table 1 illustrated the photophysical data of synthesized A₂B-corroles in CH₂Cl₂. The calculated quantum yield in CH₂Cl₂ followed the order **2** > **1** > **5** > **4** > **6** > **3**. The fluorescence



Fig. 2. Optimized geometries demonstrating the resultant dipole moment and push-pull directing groups in synthesized *trans*-A₂B-corroles (**1**–**6**) using B3LYP functional and 6-31G (d,p) basis set in gas phase.



Fig. 3. (a) Frontier molecular orbitals (FMOs) and (b) HOMO-LUMO energy level diagram of reported *trans*- A_2B -corroles on the basis of DFT calculations.

lifetimes of all reported A₂B-corroles were recorded in CH₂Cl₂ at 298 K. We observed multi-exponential decay in three decay-time for all six corroles (Fig. S3) [33] Further, **1**, **3** and **4** exhibit higher value of full width half maxima (FWHM) which suggest efficient charge transfer occurs in these push-pull corroles as compared to TPC (FWHM = 42 nm). The first set (possessing two acceptor and one donor moieties, **1**–**2**) of A₂B Corroles exhibited lower absorption wavelength, higher quantum yield and longer singlet excited state lifetime as compared to second set (having two donor and one acceptor moieties, **3**–**6**) of presented corroles.

2.2. DFT studies

The optimized geometry of all six *trans*-A₂B-corroles (**1**–**6**) using B3LYP functional and 6-31G (d,p) basis set in gas phase (Fig. 2). The reported A₂B-corroles exhibited nonplanar geometry with the average dihedral angle of $\chi_{ava} = 19.71^{\circ}$ (corresponding α,β -position of bipyrrolic junction) from the corrole mean plane due to the steric hindrance of inner three hydrogen atoms in a small corrole cavity. The calculated total dipole moment and direction of resultant dipole moment of these corroles are shown in Fig. 2. Six corroles were constructed with electron donor as well as electron acceptor moieties within the same molecule. Table S1 in the S1 illustrates the summary of TDDFT calculations with their electronic orbital transitions.

The calculated energy gap between the ground and excited states and frontier molecular orbitals were represented in Fig. 3. **6** Exhibited lowest HOMO-LUMO energy gap which is in full accord with the bathochromic shift in absorption spectral studies. The electron density located on 4-N,N'-dimethylphenyl groups in **6** depicts from HOMO orbital states the electron donating effect while the electron accepting nature of pentafluorophenyl showed in LUMO orbital where the electron density dispersed as shown in Fig. 3a.

Similarly, in other corroles the electron density lies on electron donating *meso*-substituents in HOMO orbital whereas it is distributed on the electron deficient moieties in LUMO orbitals (Fig. 3a). Corrole functionalized with electron withdrawing substituents at the *meso*-position, stabilizes the HOMO energy level and hence the energy gap is increased resulting the blue shift in UV–vis spectral features as shown for corrole **6** (Fig. 3b).

2.3. NLO studies using femtosecond pulses

We have investigated the third order optical nonlinearities with 150 fs, 800 nm, 80 MHz repetition rate pulses (Chameleon, Coherent) using the standard Z-scan technique. From open aperture (OA) data TPA coefficients and from closed aperture (CA) Z-scan data refractive index (n_2) values were calculated by fitting the experimental data. The sign and magnitude of nonlinear refractive



Fig. 4. Experimental OA (left) and CA (right) Z-scan data (blue open circles are experimental data) of six corroles investigated at 800 nm and theoretically fitted curves (red solid curves). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2	
Summary of the NLO coefficients obtained	for the synthesized <i>trans</i> -A ₂ B-corroles.

Corrole	$n_2 ({ m cm}^2/{ m W}) \ imes 10^{-11}$	n_2 (e.s.u.) $ imes 10^{-8}$	$\begin{array}{l} \text{Re} \ \chi^{(3)} \ m^2/\text{V}^2 \\ \times 10^{-17} \end{array}$	$\begin{array}{c} \beta \ (cm/W) \\ \times 10^{-8} \end{array}$	$\begin{array}{c} Im \; \chi^{(3)} \; m^2/V^2 \\ \times 10^{-19} \end{array}$	$\begin{array}{l} \chi^{(3)} \text{ e.s.u.} \\ \times 10^{-9} \end{array}$
1	-2.60	-9.20	3.10	6.80	5.20	2.20
2	-2.84	-10.0	3.39	2.10	1.60	2.40
3	-1.80	-6.50	2.20	0.81	0.62	1.50
4	-2.60	-9.20	3.10	0.70	0.53	2.20
5	-0.36	-1.30	0.43	0.65	0.50	0.31
6	-1.20	-4.40	1.50	1.10	0.84	1.00



Fig. 5. A generic energy level diagram depicting the 2PA transitions in all the molecules when excited with 800 nm pulses.

index (n_2) , two-photon absorption (TPA) coefficients (β) and thirdorder NLO susceptibility $[\chi^{(3)}]$ were extracted from the Z-scan data. The Z-scan measurements were performed on solutions with typical concentration in the 0.5-1.0 mM range. Fig. 4(a)-(f) (left) illustrate the OA Z-scan data for all the samples recorded at 800 nm with input peak intensities in the range of 32–49 MW/cm². A strong reverse saturable absorption (RSA) kind of behavior was observed for all the samples. The obtained experimental data was best fitted for two-photon absorption (2PA) and the calculated 2PA coefficient (β) was 0.65–6.8 \times 10⁻⁸ cm/W. The nonlinear absorption coefficients extracted were in the order of 1 > 2 > 6 > 3 > 4 > 5. Fig. 4(a)-(f) (right) represent CA data of all the samples at 800 nm obtained input peak intensities of 16-31 MW/cm². The peak followed by valley in the normalized transmittance data clearly suggest that the sample possessed negative type of nonlinearity and self-defocusing behavior with the magnitude of nonlinear refractive index (n_2) being (-) 0.36–2.84 \times 10⁻¹¹ cm²/W. The negative nonlinear refractive indices followed the following behavior with coefficients increased in the order of 2 > 1 = 4 > 3 > 6 > 5. Corroles in set one (1-2) exhibited higher quantum yield and enhanced second excited state lifetime as compared to second set of A2B Corroles (3-6). The enhanced quantum yield and excited state lifetime may lead to higher nonlinearity of 2 and 1. The longer lifetime of **1** and **2** could be one of the reasons for higher nonlinearities due to the fact that population can reside longer in the excited state [25]. These two corroles have stabilized HOMO and LUMO energy levels as compared **3–6.** Corroles (**3–6**) possessing two donor and one acceptor groups exhibited lower nonlinear absorption and negative nonlinear refractive indices as compared to 1 and 2. Our results clearly suggest that the corroles with two strong electron withdrawing groups (1-2) were found to be superior NLO candidates when compared to corroles with one electron withdrawing moiety (3-6) due to strong electron withdrawing nature of pentafluorophenyl groups as well as higher singlet excited state lifetime and quantum yield of 1 and 2. Therefore, we conclude that the nonlinearity in the present case depended on the number and nature of donor and acceptor groups. Further, the structure of **2** revealed that peripheral attachment (**R**) had higher number of π electrons probably contributing to the electronic nonlinearity which is being reflected in the higher value of n_2 . However, the n_2 obtained with high repetition rate pulses will have other contributions too. Further Z-scan studies with kHz pulses will reveal the actual contribution of electrons to the nonlinearity and an exact structure relation could be obtained then. The theoretical fits were performed on the experimental data without any smoothing procedures. The summary of all the NLO coefficients is presented in Table 2. The values of NLO coefficients were presented within an error of $\pm 10\%$ with contributions mainly from uncertainty in spot size, and thereby beam waist, Rayleigh range and peak intensity measurements, fitting errors, and so on. Considering the high two-photon absorption coefficient and large values of $\chi^{(3)}$, these samples were better as compared to the previous results [34]. Based on the results we conclude that these samples are potential NLO materials for various photonic applications.

Fig. 5 represents the schematic three-level energy diagram for all the Corroles studied and we utilize this energy level diagram to explain the nonlinear absorption processes, where all the vibrational and rotational states of the ground, first and second excited singlet state are denoted as S_0 , S_1 and S_2 , respectively. All the samples possess a strong absorption peak at ~400 nm and, therefore, a two-photon absorption process is possible when excited with ~800 nm short laser pulses with sufficient peak intensities. We had investigated the NLO properties of all the corroles (1-6) at 800 nm with ~150 fs ultrashort pulses. Open aperture studies demonstrated strong 2PA to be responsible for the nonlinear absorption. The tail of the absorption in all the samples ends in the vicinity of 800 nm. Since our laser pulses are broadband (~7 nm FWHM), there is possibility of exciting into the S_1 states of these molecules. All the samples possessed strong β and n_2 when compared to some of the recently reported values for similar molecules (Table 3). For example, Venugopal Rao et al. [26] reported 2PA coefficients and $|\chi^{(3)}|$ in the range of 10^{-13} cm/W, ~ 10^{-14} e.s.u., respectively for tritolylcorrole (TTC), triphenylcorrole (TPC) obtained using ~40 fs at 800 nm. Furthermore, Anusha et al. also reported the wavelength dependent ps NLO coefficients to be ~10⁻¹² cm/W for β and ~10⁻¹⁴ cm²/W for n_2 . However, the coefficients obtained in the present case are larger (MHz rep rate pulses used here in comparison with kHz repetition rate pulses used in earlier studies) due to thermal contribution but prove to be excellent candidates for optical limiting applications, especially for high repetition rate pulses. When we compare the present NLO coefficients with some of the coefficients obtained from studies with MHz, fs pulses reported in literature, Tang et al. [35] studied a series of stilbazolium salts with A- π -A model and reported 2PA coefficients of typically <1 cm/GW and $\chi^{(3)}$ values of $\sim 10^{-7}$ e.s.u. Vamsi Krishna et al. [36] reported the NLO coefficients of a TPA-PC

Table 3 Comparison of NLO coefficients of 1–6 with previously reported corroles using

800 nm excitation pulses.

Corrole	$n_2 (cm^2/W) \times 10^{-11}$	n_2 (e.s.u.) $\times 10^{-8}$	eta (cm/W) $ imes 10^{-8}$	$\begin{array}{l} \chi^{(3)} \text{ e.s.u.} \\ \times 10^{-9} \end{array}$	Ref.
1	-2.60	-9.20	6.80	2.20	tw
2	-2.84	-10.0	2.10	2.40	tw
3	-1.80	-6.50	0.81	1.50	tw
4	-2.60	-9.20	0.70	2.20	tw
5	-0.36	-1.30	0.65	0.31	tw
6	-1.20	-4.40	1.10	1.00	tw
Cor 1	_	-1.68×10^{-5}	5.7×10 ⁻⁵	_	[28]
Cor 2	_	-7.8×10^{-6}	1.9×10^{-5}	_	[28]
Cor 3	_	-2.59×10^{-5}	17×10^{-5}	_	[28]
Eu ₂ Cor 1	_	$-1.92{ imes}10^{-2}$	1.02×10^{-5} (esu)	3.18×10^{-1}	[30]
Eu ₂ Cor 2	-	-2.05×10^{-2}	0.98×10 ⁻⁵ (esu)	3.35×10^{-1}	[30]
Thio-Zn-Pc	$-9.30{ imes}10^{-2}$	-	_	4.70×10^{-2}	[44]

tw = this work; **Cor 1** = 5,10,15-Tris[3,4-(1,4-dioxan)phenyl]corrole; **Cor 2** = 10-[4-(Chloro-acetoxy)phenyl]-5,15-bis(2-bromo-5-fuorophenyl)corrole; **Cor 3** = 10-(4-Hydroxyphenyl)-5,15-bis(2-bromo-5-fuorophenyl)corrole; **Eu2 Cor 1** = Eu2[Pc]_2[Cor(ClPh)_3], and **Eu2 Cor 2** = Eu2[Pc(OC_8H_17)_8]_2[Cor(ClPh)_3]; **Thio-Zn-Pc** = 1,4,8,11,15,18,22,25-octakis(4-*tert*butylthio- phenyl)Zn(II) phthalocyanine.

phthalocyanine molecule as $\sim 10^{-8}$ cm/W for 2PA coefficient and 10^{-9} e.s.u. for $\chi^{(3)}$ which were achieved using ~150 fs and MHz pulses near 800 nm. Lu et al. [37] studied NLO properties of colloidal CH₃NH₃PbBr₃ and CsPbBr₃ quantum dots using MHz fs pulses and obtained 2PA coefficients of typically 1 cm/GW and $\gamma^{(3)}$ values of 10⁻¹¹ e.s.u.. Wu et al. [38] reported NLO coefficients of Novel Zn(11)/Cd(11) complexes based on ferrocenyl terpyridine to be <0.5 cm/GW for two-photon absorption coefficients and $\gamma^{(3)}$ values of 10^{-13} e.s.u. with fs, MHz excitation, which are on par with the NLO coefficients of our molecules. Espinosa et al. [39] very recently reported n_2 and two-photon absorption coefficients of magnetic nanoparticles made from magnetite in both thin film form and colloidal solutions. The order of magnitude for n_2 in their case was 10^{-13} cm²/W. Lu et al. [37] also reported fs, MHz NLO data colloidal $CH_3NH_3PbBr_3$ and $CsPbBr_3$ quantum dots with the magnitudes of n_2 and $\chi^{(3)}$ to be ~10⁻⁹ cm/W and 10⁻¹¹ e.s.u., respectively. However, these are quantum confined structures and, therefore, expected to demonstrate higher nonlinearities.

In general, corroles **1–6** are found to be potential NLO materials as compared to known corroles in the literature (Table 3) due to effective push-pull nature of *meso*-substituents. Among all, corroles **1** and **2** are found to be excellent candidates for NLO applications as compared to **3–6** and other previously reported corroles [28,30] and thio-phthalocyanine [44] as reflected from Table 3.

It is imperative that all novel molecules synthesized for NLO applications are tested at different wavelengths and with different input pulse durations [25,26,40–43] for identifying various applications based on nonlinear absorption (saturation or two-photon absorption) and nonlinear refraction (self-focusing or self-defocusing). Additionally, the molecules should be easily processable in thin film form (or in any matrix such as glass or sol-gel) for real device applications.

In future, our focus will be (a) on preparing thin films of these molecules and study the nonlinearities (b) extend the NLO studies with different input pulse duration (fs/kHz, ns etc.) (c) examine the excited state dynamics including non-radiative decay times and (d) explore the complete structure-property relationship in NLO studies.

3. Conclusions

A series of *trans*-A₂B-corroles having push-pull groups on *meso*positions were synthesized and characterized by various spectroscopic techniques. The charge-transfer behavior of investigated corroles was reflected from the broadness of UV-Vis absorption spectral bands. Corroles 1 and 2 exhibited lower absorption wavelength, higher quantum yield and longer singlet excited state lifetime as compared to 3-6. Ultrafast NLO properties of the investigated corroles in visible range (at 800 nm) were evaluated using femtosecond Z-scan technique. The investigated corroles possessed negative type of nonlinearity and self-defocusing behavior with the magnitude of nonlinear refractive index (n_2) of (-) $0.36-2.84 \times 10^{-11}$ cm²/W. The theoretically calculated dipole moments of these corroles were found to be 1.47-7.26 D depending on the nature of push-pull groups on the meso-phenyl substituents. Our results clearly suggest that the corroles with two strong electron withdrawing groups (1-2) were found to be superior NLO candidates when compared to corroles with one electron withdrawing moiety (3–6) due to strong electron withdrawing nature of pentafluorophenyl groups as well as higher singlet excited state lifetime and quantum yield of 1 and 2. Therefore, we conclude that the nonlinearity in the present case depended on the number and nature of donor and acceptor groups. Considering the high twophoton absorption coefficient and large values of $\chi^{(3)}$, these *trans*-A₂B-corroles were better as compared to the previous results due to their 'push-pull' design. Based on the conclusions these samples are found to be valuable NLO materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.04.041.

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