Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Information for

Sterically Demanded Zinc(II)Phthalocyanines: Synthesis, Optical, Electrochemical, Nonlinear Optical, Excited State Dynamics Studies

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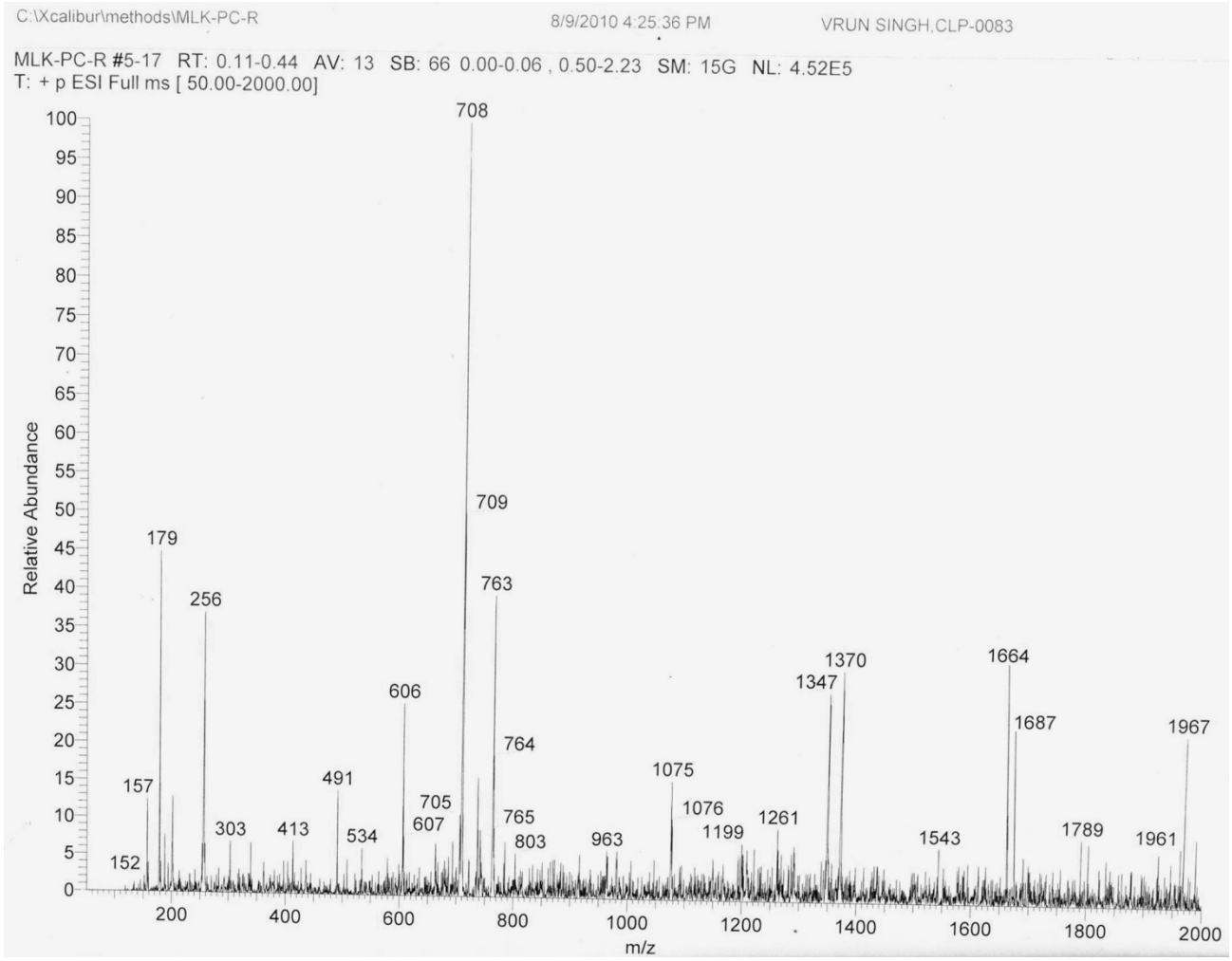

Figure 1 ESI-MS spectrum of **Pc-1**.

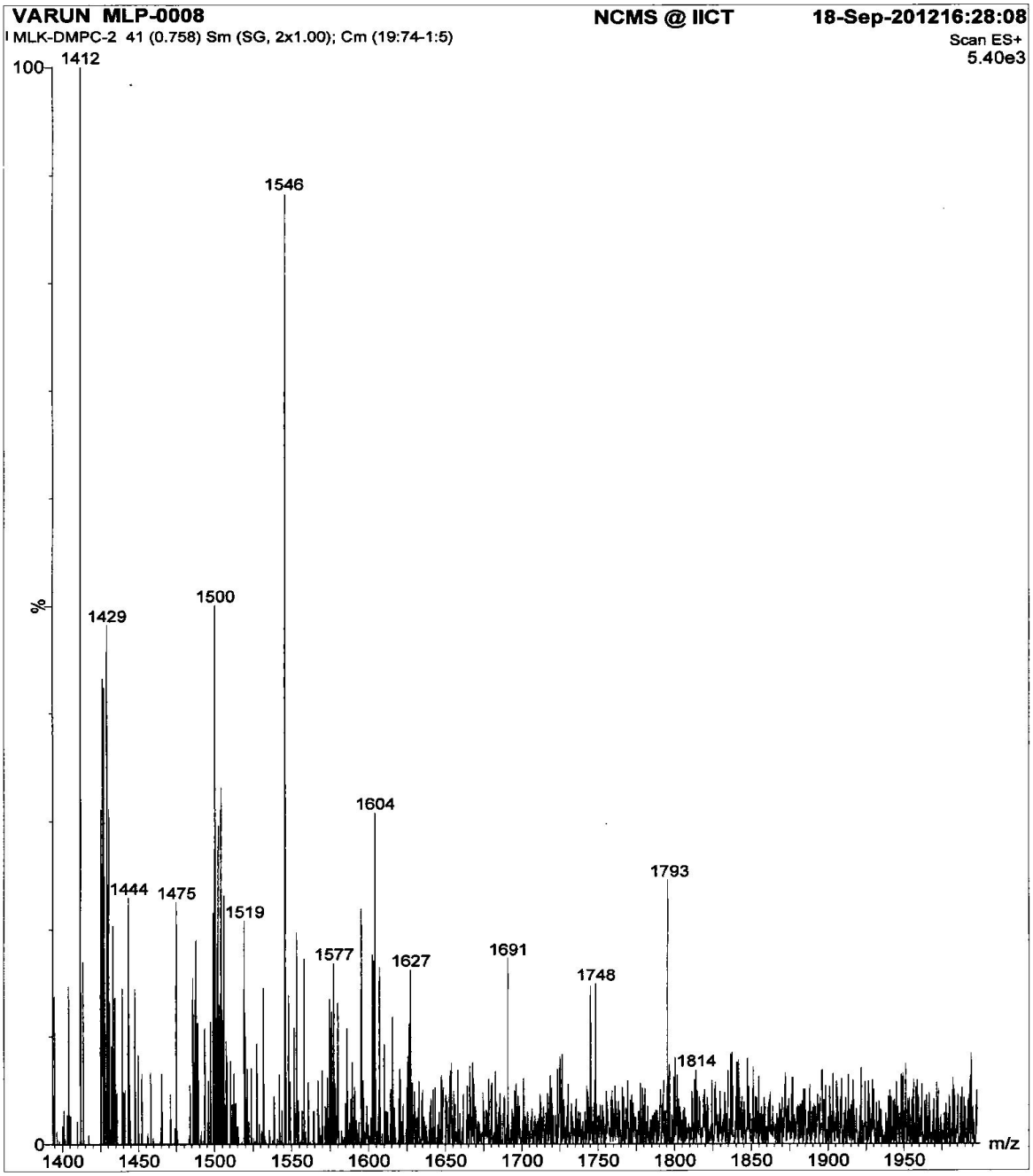

Figure 2 ESI-MS spectrum of **Pc-2**.

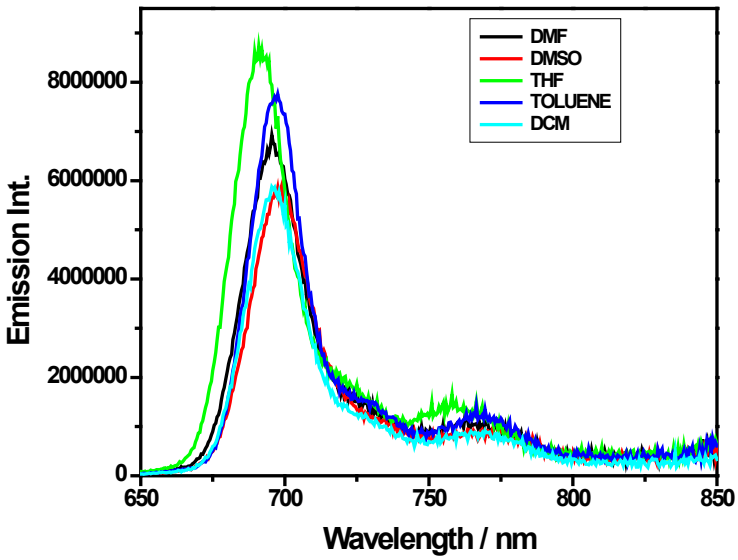

Figure 3 Fluorescence spectra of **Pc-1** in different solvents.

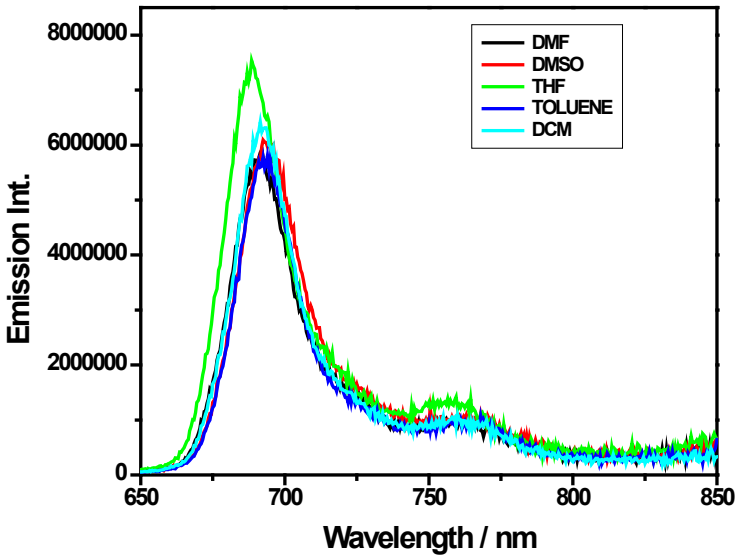

Figure 4 Fluorescence spectra of **Pc-2** in different solvents.

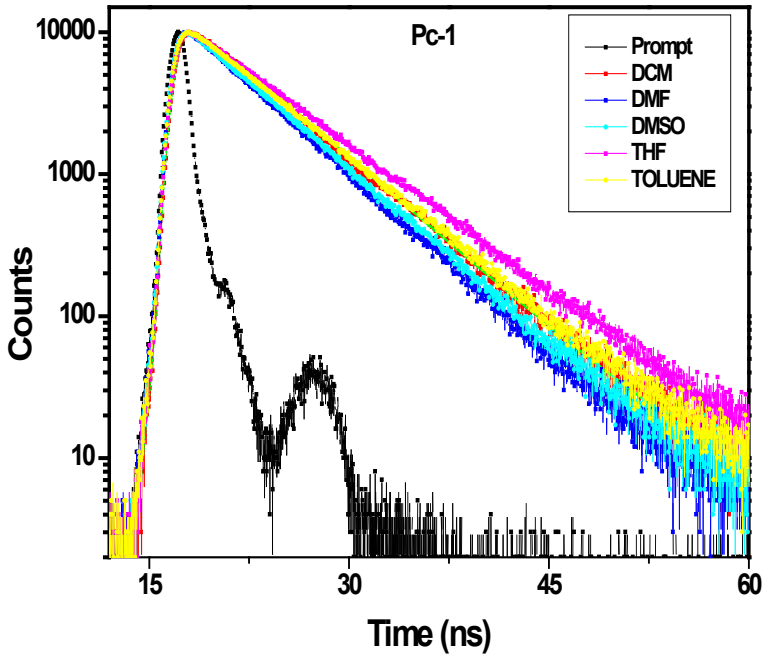

Figure 5 Lifetime spectra of **Pc1** in different solvents

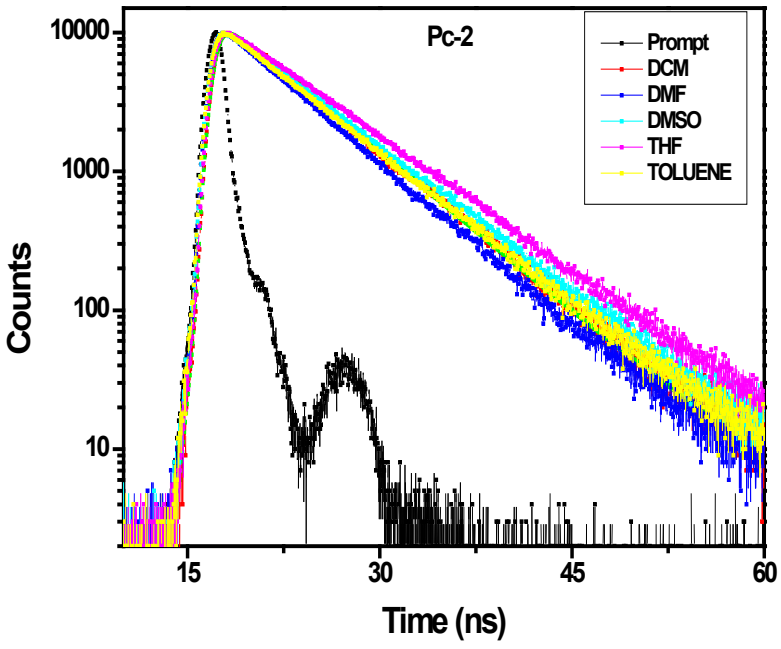

Figure 6 Lifetime spectra of **Pc-2** in different solvents.

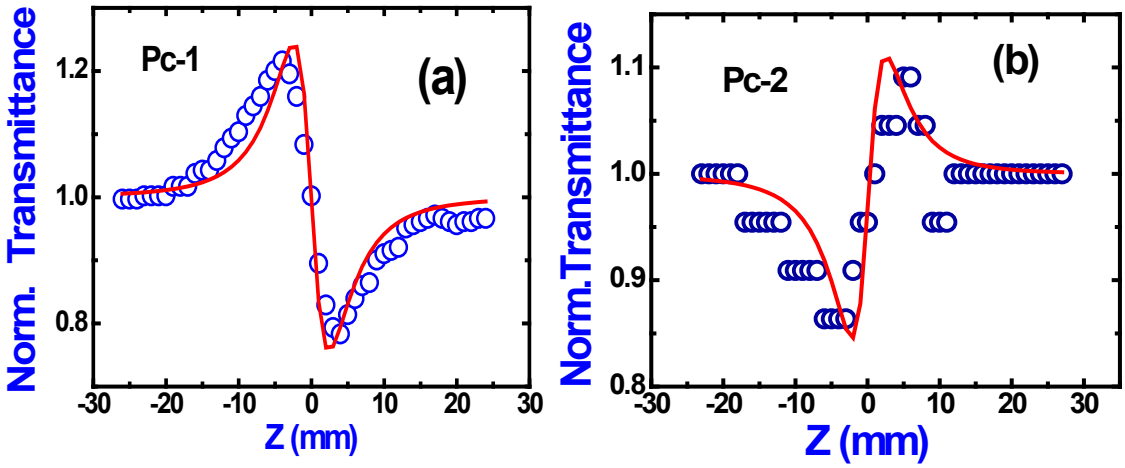

Figure 7 (a) CA Z-scan of Pc-1 (shows negative nonlinearity) at 800 nm with an input power = 10 mW, 80 MHz repetition rate. $n_2 = 2.05\times10^{-12}$ cm^2/W **(b)** CA Z-scan of Pc-2 (shows positive nonlinearity) at 800 nm with an input power = 3.3 mW, 80 MHz repetition rate. $n_2 = 0.51\times10^{-12}$ cm^2/W.

The higher peak intensity response of Pc-1 showed negative nonlinearity (figure 7a) same as that of solvent but with low peak intensity response of Pc-2 showed positive nonlinearity (figure 7b) opposite to that of solvent (DCM). The data was obtained using ~140 fs and 80 MHz pulses with 10 cm lens focusing.

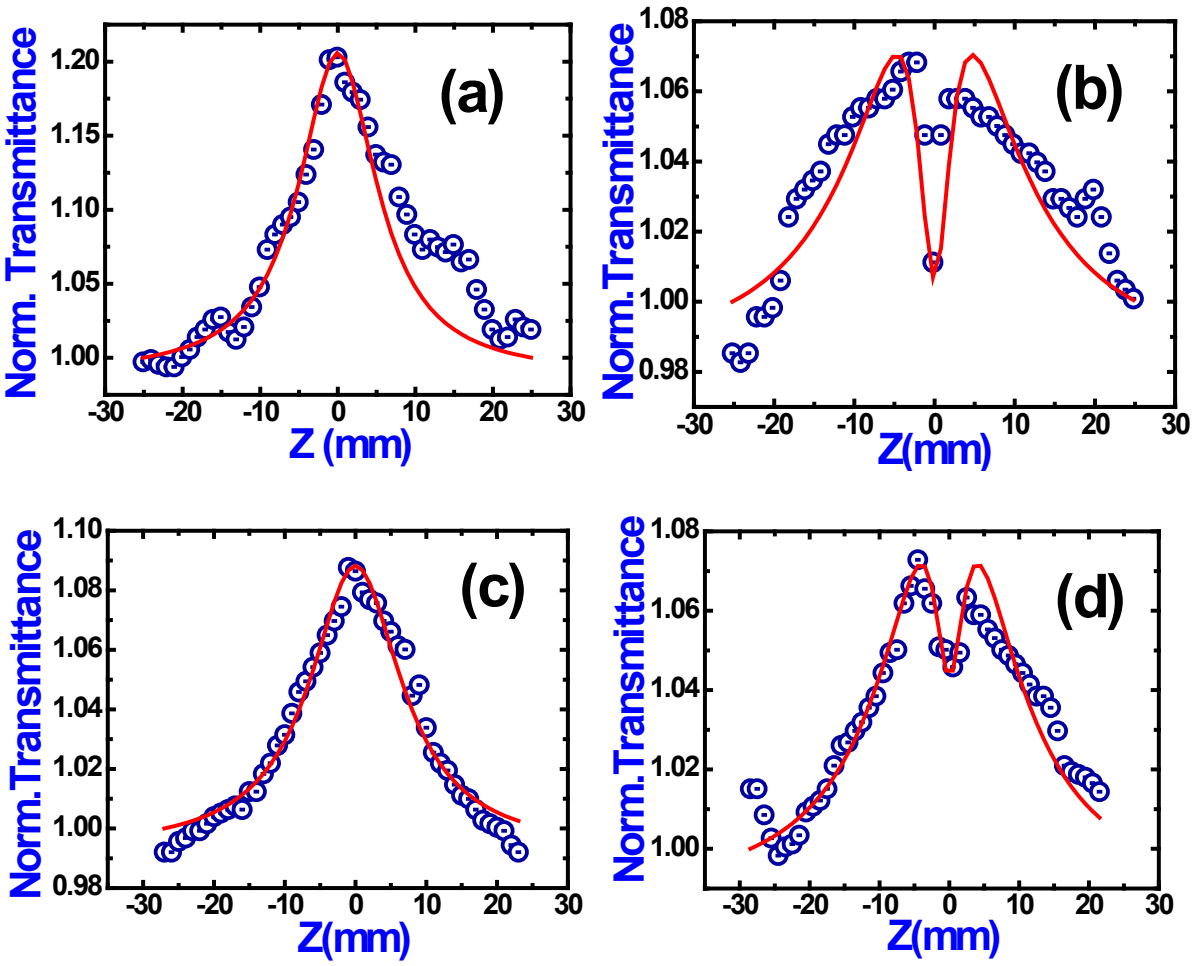

Figure 8 Fs open aperture Z-scan data of Pc-2 at 680 nm with (a) power = 9.0 mW and **(b)** power = 46 mW with **80 MHz.** Nonlinear absorption of Pc-2 680 nm with **(c)** power =10.7 mW (d) power=16.6 mW. The data **(c)** and **(d)** was acquired with a chopper at **1 kHz.**

At lower peak intensities the open aperture data behavior was pure SA type [figures 8(a) for 80 MHz and 8(c) for 1 kHz] but as the intensity increased it switched to RSA in SA as shown in figures 8(b) and 8(d). The peak intensities were $0.2 - 0.4\ {}^{GW}/_{cm^2}$ for both 80 MHz and 1 kHz excitation.

These are **NOT** truly 1 kHz pulses as obtained in a typical ultrafast amplifier. A chopper was used with 1 kHz chopping (original repetition rate was 80 MHz) indicating that we obtained bunches of pulses at repetition rate of 1 kHz

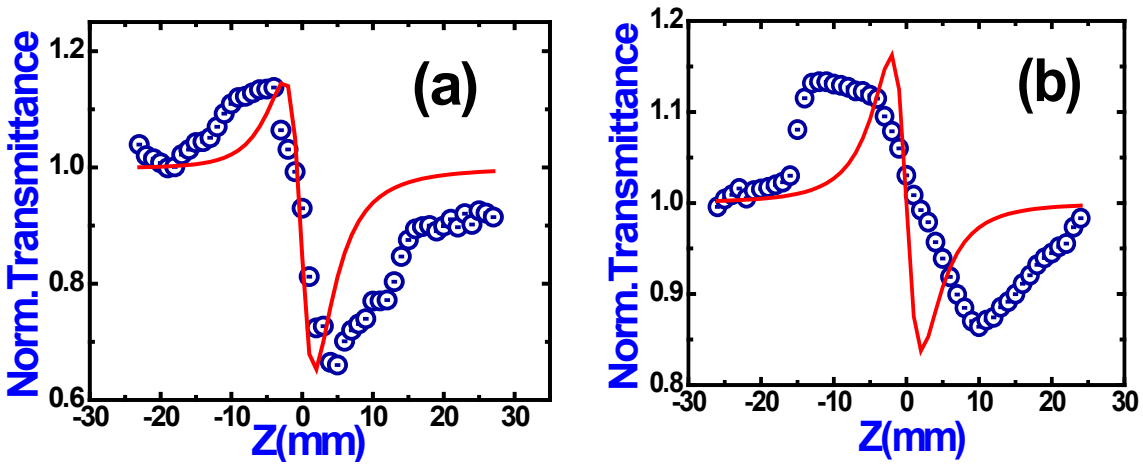

Figure 9 Fs closed aperture data of **Pc-2** at 680 nm at (a) power = 2.40 mW with **80 MHz** excitation (b) at power = 2.65 mW with chopper at **1 kHz**.

The close aperture (CA) curve shows (peak followed by valley), negative nonlinearity (self defocusing). We obtained best fit for $n_2 = -5.24 \times 10^{-12}$ cm^2/W [for 80 MHz repetition. rate figure 9(a)] and $\sim n_2 = -2.9 \times 10^{-12}$ cm^2/W for 1 kHz rep rate [figure 9(b)]. From OA and CA graphs, nonlinear absorption coefficient β was also calculated and nonlinear susceptibility $|\chi^{(3)}|$ was calculated and tabulated in tables (1) and (2). For calculating $|\chi^{(3)}|$ values following equations were used [1].

$$Re|\chi^{(3)}|(in\ esu) = \frac{10^{-4}\varepsilon_0 n_0^2 c^2}{\pi} n_2 \left(\frac{cm^2}{W}\right)$$

$$n_0 = solvent\ R.I$$

$$n_2 = nonlinear\ R.I$$

$$\varepsilon_0 = permittivity\ of\ free\ space$$

$$c = velocity\ of\ light$$

$$Im|\chi^{(3)}|(in\ esu) = \frac{10^{-2}\varepsilon_0 n_0^2 c^2 \lambda}{4\pi^2} \beta\left(\frac{cm}{W}\right)$$

$$|\chi^{(3)}|(esu) = \sqrt{|Re|\chi^{(3)}||^2 + |Im|\chi^{(3)}||^2}$$

$$|\chi^{(3)}|(S.I) = 1.4 \times 10^{-8}|\chi^{(3)}|(esu)$$

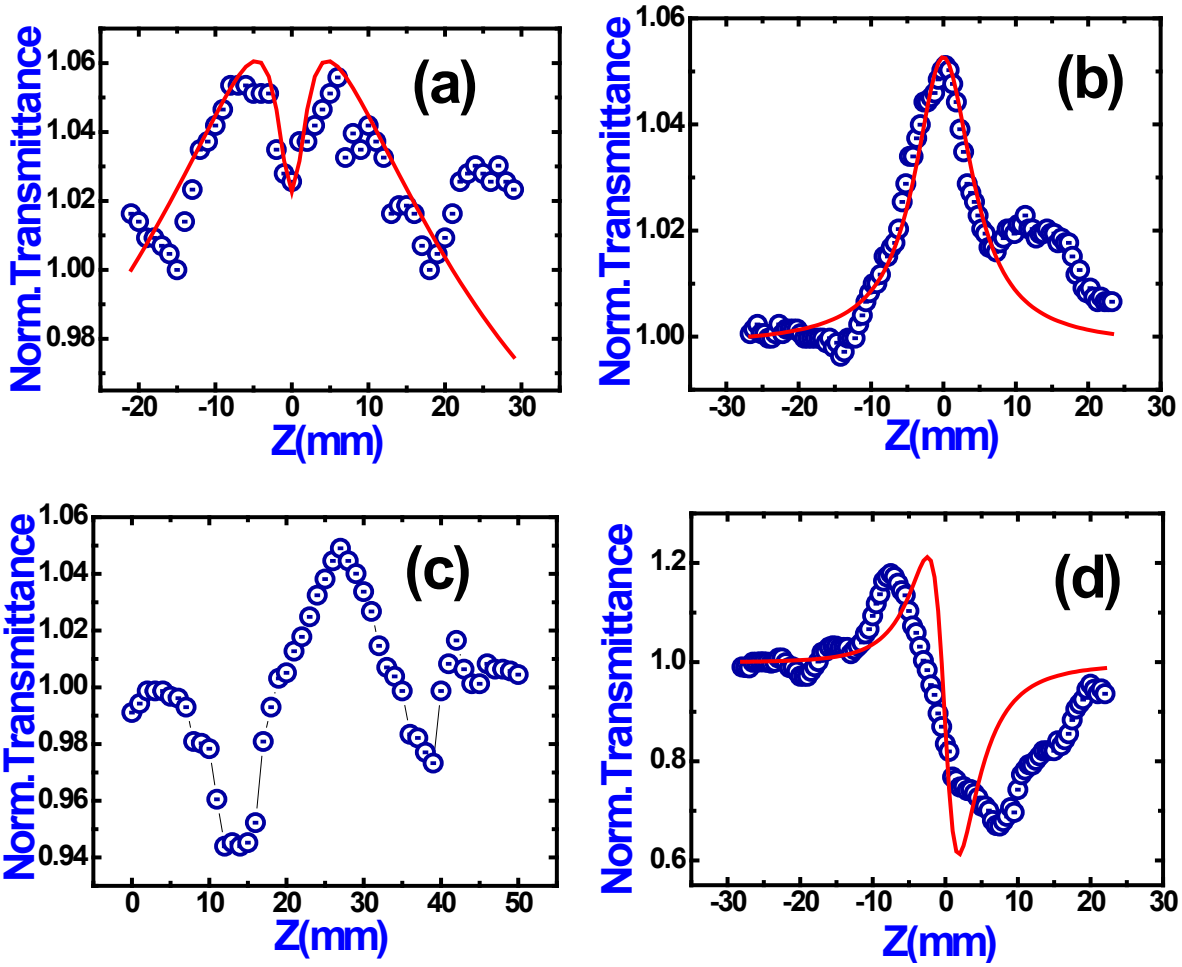

Figure 10 Fs open aperture data of Pc-2 at 700 nm (a) power = 5.35 mW with chopper 1 kHz (b) power = 14.50 mW at 80 MHz. Closed aperture behavior of Pc-2 at 700 nm (c) power = 19.40 mW with chopper 1 kHz (d) power = 3.20 mW at 80 MHz.

Figures 10(a) and 10(c) show the open aperture data of Pc-2 at 700 nm at lower and higher input power (peak intensity) with 1 kHz excitation. We clearly observed RSA in SA behavior with lower peak intensity and SA in RSA behavior with higher peak intensity. Figures 10(b) shows 80 MHz data and figure 10(d) shows the closed aperture data at 80 MHz.

The nonlinear refractive index change and nonlinear absorption coefficient of Pc-1 was calculated and tabulated in table 3. The close aperture data is divided by open aperture to reduce the effect of nonlinear absorption in all the cases. The fitting is done for OA and CA by MATLAB using Sheik-Bahae et al. model. At 700 nm wavelength with power 14.5 mW we

found that $I_s > I_{oo}$, this shows this is a 3rd order nonlinear process [2]. The nonlinear absorption coefficient was calculated using,

$$\beta = \frac{-\alpha_0}{I_s}$$

Where α_0 is the linear absorption coefficient and I_s is the saturation intensity.

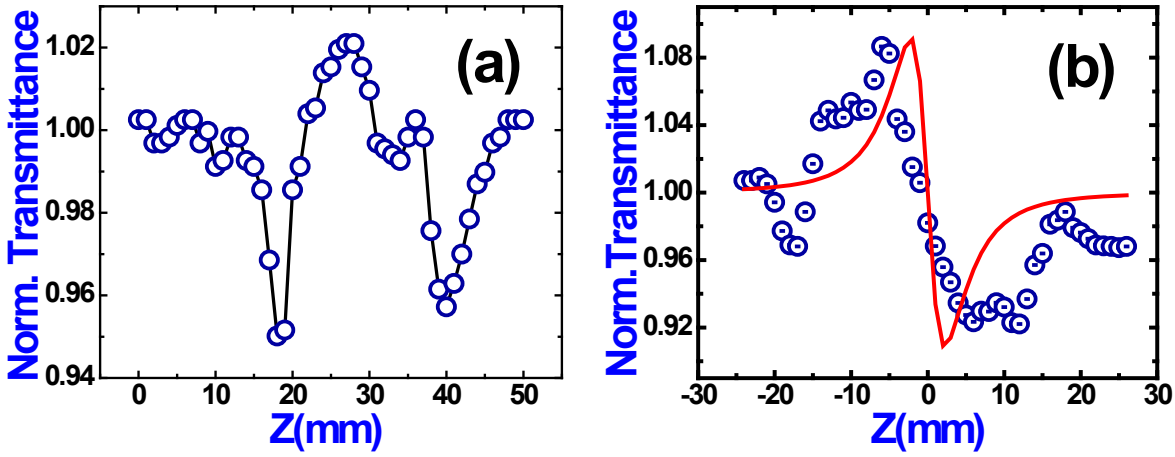

Figure 11 Fs open aperture data of Pc-2 at 750 nm (a) power = 8.10 mW with chopper 1 kHz (b) Closed aperture behavior power = 2.86 mW with chopper 1 kHz.

Open aperture data of Pc-2 showed SA in RSA at 750 nm (figure 11a) with higher peak intensity. Closed aperture data showed negative nonlinearity at low peak intensity at the same wavelength.

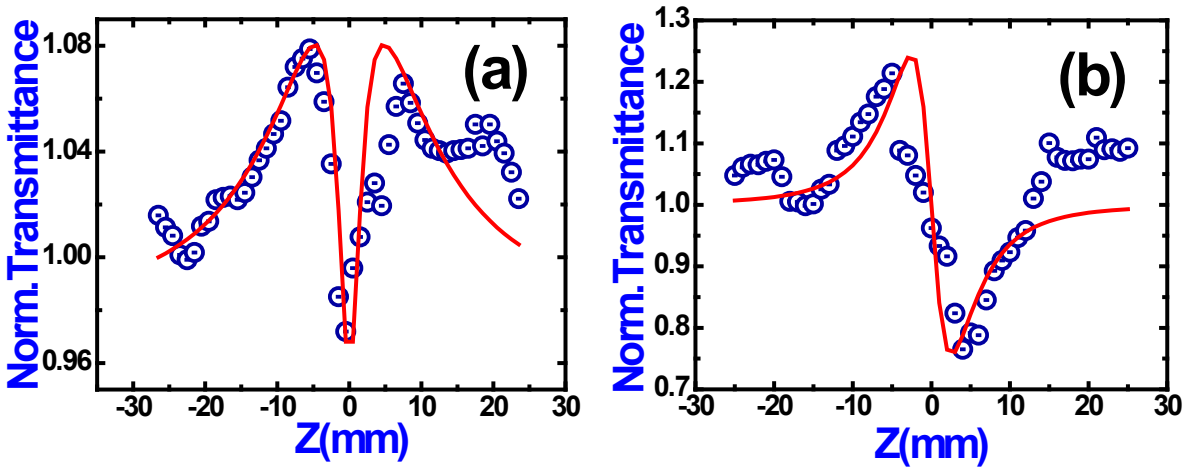

Figure 12 Fs open aperture data of Pc-2 at 850 nm with (a) power = 26.70 mW with chopper 1 kHz (b) Closed aperture behavior of Pc-1 at 850 nm with (c) power = 5 mW at 80 MHz.

We observed RSA in SA for Pc-2 at 850 nm [figure 12(a)] recorded with 1 kHz pulses. As the intensity increased the excited state absorption could have dominated compared to the ground state absorption leading to RSA in SA. This type of switching behavior can be utilized for optical signal processing application provided one can achieve them with low peak powers. Closed aperture data [figure 12 (b)] showed negative nonlinearity at low peak intensity at the same wavelength.

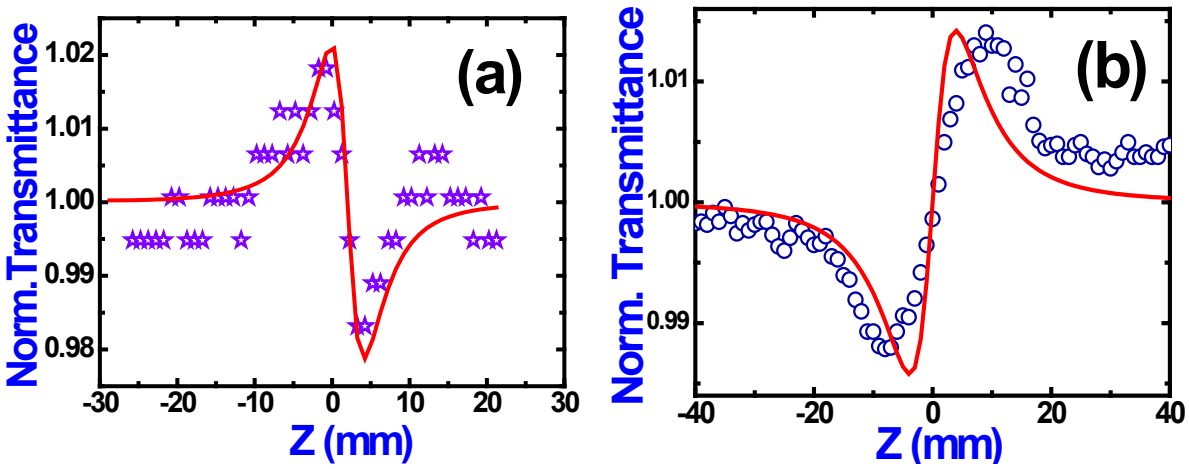

Figure 13 Closed aperture behavior of solvent DCM at 800 nm (a) fs pulses, 80 MHz (b) ps pulses, 1 kHz (1000 pulses/sec)

Figure 13(a) depicts the solvent contribution with fs, MHz pulses while figure 13(b) depicts the contribution with ps, 1 kHz pulses. The magnitude of n_2 was much lower (at least an order of magnitude) than that of the solutions studied.

With the intention of justifying the potential of these molecules we calculated the figures of merit (FOM). The merit factor W is defined as [3] $W = \frac{n_2 I_{sat}}{\alpha_1 \lambda}$ where λ is wavelength, and I_{sat} is the light intensity at which n_2 saturates. The pre-requisite for superior FOM is $W > 1$. The corresponding FOM for nonlinear absorption is

$$T^{-1} = \frac{n_2}{\lambda \alpha_2}$$

For photonics device applications $T < 1$ is desirable.

Table 1 NLO coefficients (fs regime) of **Pc-2** at different wavelength retrieved from **80 MHz** repetition rate data.

Wavelength (nm)	$\mathbf{n_2}$ $(\mathbf{m^2/W})$ $\times \mathbf{10^{-16}}$	β $(\mathbf{m/W})$ $\times \mathbf{10^{-11}}$	$\mathbf{Re}\lvert\chi^{(3)}\rvert$ **(esu)** $\times \mathbf{10^{-10}}$	$\mathbf{Im}\lvert\chi^{(3)}\rvert$ **(esu)** $\times \mathbf{10^{-13}}$	$\lvert\chi^{(3)}\rvert$ **(esu)** $\times \mathbf{10^{-10}}$	$\lvert\chi^{(3)}\rvert$ $(\mathbf{m^2/V^2})$ $\times \mathbf{10^{-18}}$
680	-5.2	2.6*	-2.7	7.2	2.7	3.9
700	-5.5	1.4*	-2.8	4.0	2.8	4.0
800	0.5	--	0.27	--	0.27	0.37

* in β values indicates the presence of saturable absorption (SA)

Table 2 NLO susceptibility (fs regime) of **Pc-2** at different wavelength with **1** k**Hz** repetition rate (using chopper)

Wavelength (nm)	$\mathbf{n_2}$ $(\mathbf{m^2/W})$ $\times \mathbf{10^{-16}}$	β $(\mathbf{m/W})$ $\times \mathbf{10^{-11}}$	$\mathbf{Re}\lvert\chi^{(3)}\rvert$ **(esu)** $\times \mathbf{10^{-10}}$	$\mathbf{Im}\lvert\chi^{(3)}\rvert$ **(esu)** $\times \mathbf{10^{-12}}$	$\lvert\chi^{(3)}\rvert$ **(esu)** $\times \mathbf{10^{-10}}$	$\lvert\chi^{(3)}\rvert$ $(\mathbf{m^2/V^2})$ $\times \mathbf{10^{-18}}$
680	-2.9	4.4*	-1.5	1.2	1.5	2.1
700	-4.7	11.1*	-2.4	3.2	2.4	3.4
750	-2.1	--	-1.0	--	1.0	1.4
850	-5.2	9.9*	-2.6	3.4	2.7	3.8

* in β values indicates the presence of saturable absorption (SA)

Table 3 NLO susceptibility (fs regime) of **Pc-1**

Wavelength (nm)	$\mathbf{n_2}$ $(\mathbf{m^2/W})$ $\times \mathbf{10^{-16}}$	$\boldsymbol{\beta}$ $(\mathbf{m/W})$ $\times \mathbf{10^{-9}}$	$\mathbf{Re}\lvert\boldsymbol{\chi}^{(3)}\rvert$ **(esu)** $\times \mathbf{10^{-10}}$	$\mathbf{Im}\lvert\boldsymbol{\chi}^{(3)}\rvert$ **(esu)** $\times \mathbf{10^{-11}}$	$\lvert\boldsymbol{\chi}^{(3)}\rvert$ **(esu)** $\times \mathbf{10^{-10}}$	$\lvert\boldsymbol{\chi}^{(3)}\rvert$ $(\mathbf{m^2/V^2})$ $\times \mathbf{10^{-18}}$
800 nm, 80 MHz	-2.1	1.6	-1.1	5.2	1.2	1.2
760 nm, 1 kHz	-2.6	25.2	-1.3	79.2	8.0	11.2

Theory for 2PA:

The open aperture Z-scan data have been fitted by integrating the propagation equations between I_0 and I and fitting it to the experimental data where I_0 is defined as

$$I_0 = \frac{I_{00}}{(1+\frac{z^2}{z_0^2})}$$

where I_{00} is the peak intensity at focus calculated using the relation

$$I_{00} = \frac{2E}{\pi^{3/2} w_0^2 (HW\,1/e^2\,M)\tau_p (HW\,1/e\,M)}$$

E is the input pulse energy, τ is the pulse duration, $2\omega_o$ is the beam diameter at focus.

The propagation equation is given as : $\frac{dI}{dz} = -\alpha(I)I$ where $\alpha(I) = \alpha_0 + \beta I$ when the process is RSA and the following equation is obtained :

$$T_{OA}(z) = \frac{1}{\pi^{1/2} q_o} \int_{-\infty}^{\infty} \ln\left[1 + q_o e^{-x^2}\right] dx$$

where $T_{OA}(z)$ is the normalized transmittance as a function of z, $q_0 = \beta I_0 L_{eff}$,β = nonlinear absorption coefficient and I_0 is the intensity, $L_{eff} = \frac{1-e^{\alpha_0 L}}{\alpha_0}$, are effective path lengths in a sample of length L and α_0 is the linear absorption coefficient.

In the presence of SA the optical nonlinearity becomes $\alpha(I) = \alpha_0 \frac{1}{1+{}^{I}/_{I_S}} + \beta I$. The position dependence in intensity should be incorporated into the expression by considering the variation of beam size on either side of the focus, ω(z). The equation is $\omega(z)^2 = \omega_0^2 \left[1 + \left(\frac{z}{z_0}\right)^2\right]$ where z=0 is the focus and $z_0 = \frac{\pi\omega_0^2}{\lambda}$ is referred to as the Rayleigh range or diffraction length of the beam. β, the NL coefficient and I_s, the saturation intensity can be treated as an adjustable parameter. If I_s is higher than $I_{00,}$ peak intensity, SA is considered to be a third order process and and β can be substituted as $-\alpha_0/I_s$. From the value of β we can calculate Im $\chi^{(3)}$.

The 2PA coefficient, β can be expressed in terms of 2PA cross section (σ_2) as :

$$\sigma_2(cm^4 s/photon) = \frac{\beta h\vartheta}{N_0}$$

where 'hν' is the incident photon energy and N_0 is the number density of the sample in solution. σ_2 can also be written in the units of GM as: 1 GM = 10^{-50}cm^{4}s/photon.

References

[1] N. Venkatram, L. Giribabu, D. Narayana Rao, S. Venugopal Rao, *Appl. Phys. B* 2008, **91,** 149-156.

[2] S. Hamad, Surya P. Tewari, L. Giribabu, S. Venugopal Rao, *J. Porphy. Phth.* 2012, **16,** 140-148.

[3] R.S.S. Kumar, S. Venugopal Rao, L. Giribabu, D. Narayana Rao, *Opt. Mater.* 2009, **31,** 1042–1047.