Asian Journal of Chemistry; Vol. 24, No. 7 (2012), 2931-2934

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Synthesis, Growth and Spectroscopic Studies of Marine Dye Non-linear Optical Material: Disodium 4-Amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl)diazen-1-yl]phenyl}phenyl)diazen-1-yl]naphthalene-1-sulfonate

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(*Received*: 23 June 2011; *Accepted*: 3 February 2012) AJC-11036

The marine compound disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl) diazen-1-yl]phenyl}phenyl)diazen-1-yl] naphthalene-1-sulfonate (Congo red) like crystals as a marine dye was synthesized by taking disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl) reacted with Diazen-1-yl]phenyl}phenyl)diazen-1-yl] and naphthalene-1-sulfonate are used to synthesized marine dye ($C_{32}H_{22}N_6O_6S_2Na_2$). It is soluble in water. Powder crystals of disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl) diazen-1-yl]phenyl}phenyl) diazen-1-yl] naphthalene-1-sulfonate (Congo red) were grown by solution method with slow evaporation technique. The grown crystals were characterized by single crystal X-ray diffraction (XRD) analysis, FTIR studies and UV-visible transmittance studies and the non-linear optical (NLO) activity of the grown crystal has been checked by second harmonic generation test.

Key Words: Congo red, Solubility, Solution growth, FTIR, UV, XRD, SEM, Second harmonic generation.

INTRODUCTION

Non-linear optical (NLO) materials have gained considerable attention due to their practical applications in the field of optoelectronics[1,2]. The development of non-linear optical materials led to compounds potentially suitable for application in frequency conversion, optical telecommunication, image processing, optical computing and data storage devices[3-6]. Azo family-type crystals have been subjected to extensive investigation by the researchers for their non-linear optical properties[7,8]. Among the phenyl, azo is the simplest molecule with second harmonic generation efficiency of about one-third of that of the well known KDP[9,10], it is expected to get improved non-linear optical properties. Keeping this in mind, the sulfonato-naphthalen mixtures have been mixed to form a novel non-linear optical material. Disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl) diazen-1-yl]phenyl}-phenyl)diazen-1-yl] naphthalene-1-sulfonate (Congo red) reported the details of crystal structure of Congo red and it is observed from the various properties of crystals report[11-14]. Hence the aim of this paper is to report the growth, spectroscopic studies and non-linear optical activity of disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonato-naphthalen-2-yl) diazen-1-yl]phenyl} phenyl) diazen-1-yl]-naphthalene-1-sulfonate (Congo red).

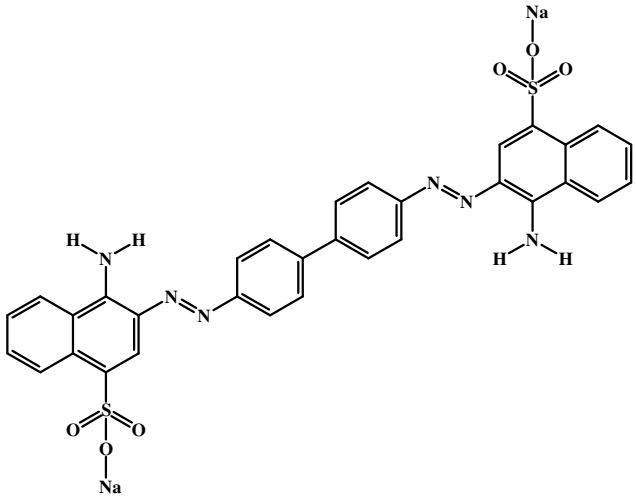

Fig. 1. Structure of disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl)diazen-1-yl]phenyl} phenyl) diazen-1-yl] naphthalene-1-sulfonate (Congo red) salt

EXPERIMENTAL

Growth of Congo red powder crystals: The purity of the synthesized salt of disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl) diazen-1-yl]-

phenyl}phenyl)diazen-1-yl]naphthalene-1-sulfonate (Congo red) have been improved by re-crystallization[11,12]. Using the solubility data, the saturated solution of disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl) diazen-1-yl] phenyl} phenyl) diazen-1-yl] naphthalene-1-sulfonate (Congo red) in deionized water was prepared and it was stirred using a magnetic stirrer for *ca.* 2 h to get homogenious solution.

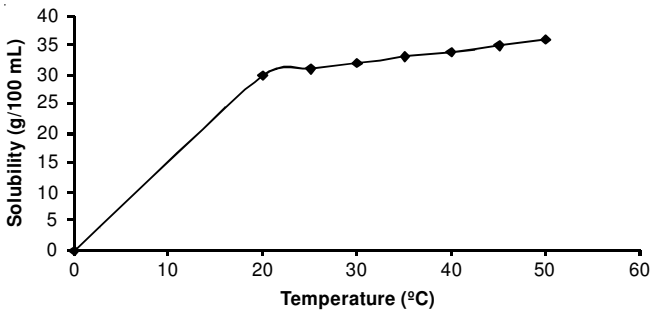

Fig. 2. Solubility curve for Congo red crystal

The saturated solution was filtered using 4 μ Whatmann filter paper. Then the filtered solution was taken in a beaker and covered by a perforated cover for controlled evaporation. A typical powder crystal with size 12 mm × 14 mm × 5 mm was obtained within a period of 20-30 days.

Characterization single crystal XRD studies: The grown crystals were subjected to single crystal XRD to confirm the crystallinity and also to estimate the lattice parameters by employing Bruker-Nonious MACH3/CAD4 single X-ray diffractometer[13,14]. From powder crystal X-ray diffraction data, it is observed that the disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl) diazen-1-yl]phenyl}-phenyl)diazen-1-yl]naphthalene-1-sulfonate (Congo red) crystal is orthorhombic in structure with space group P212121. The lattice parameters are observed to be a = 6.021(2) Å, b = 8.987(1) Å, c = 9.987(3) Å, $\alpha = \beta = \gamma = 90°$ and V = 723.58(2) Å^3. The obtained lattice parameters for disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl) diazen-1-yl]phenyl}phenyl)diazen-1-yl] naphthalene-1-sulfonate (Congo red) crystal in this work are found to be in good structure. The peaks in the Fig. 3, show the crystalline nature of Congo red. Further the peaks are indexed.

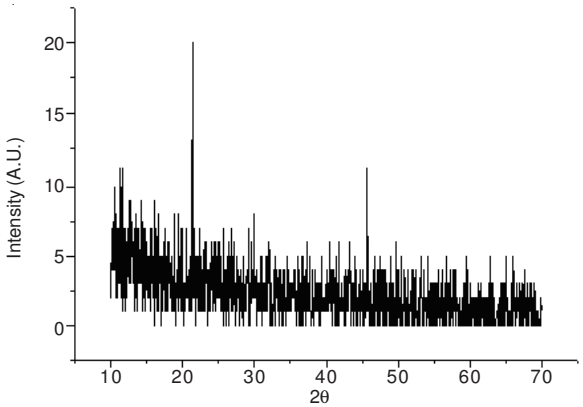

Fig. 3. XRD patterns recorded disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl) diazen-1-yl] phenyl} phenyl) diazen-1-yl] naphthalene-1-sulfonate (Congo red) crystal

FTIR analysis: The Fourier transform infrared (FTIR) spectrum of disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl)diazen-1-yl] phenyl}-phenyl)diazen-1-yl]naphthalene-1-sulfonate (Congo red) crystal was recorded in the region 4000-400 cm^{-1} using FTIR Shimadzu 8400S. NH_2 group appeared at 1570 cm^{-1} with sharp absorption and also giving O-H group absorption at 3784 cm^{-1}. It was further confirmed by observing C-N overtone absorption appeared at 1203 and 1041 cm^{-1}. The strong absorption at 761 cm^{-1} confirms the presence of C-H alkanes groups along with the group. Also, strong absorption at 624 cm^{-1} was due to bending absorption of hydroxy group. The sample was prepared by mixing disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl)diazen-1-yl]phenyl}phenyl) diazen-1-yl]naphthalene-1-sulfonate (Congo red) with KBr into pellet form. The observed spectrum is shown in the Fig. 4 (Table-1).

TABLE-1
FREQUENCIES OF THE FUNDAMENTAL VIBRATIONS OF GPC

Wavelength (cm^{-1})	Assignment of vibrations
3784	OH-Streching
3420	Lattice water
1570	-NH_2 Bending vibration
1417	OH-Group
1203	C-N Stretching
1041	C-N Stretching
761	C-H Group (alkane)
624	O-H-Bending

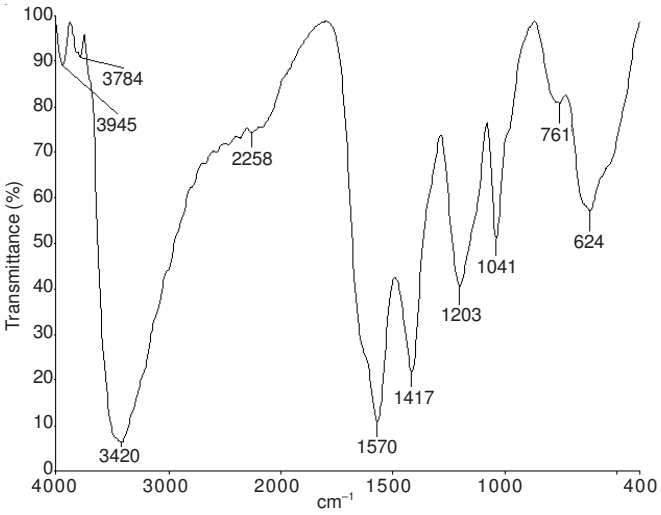

Fig. 4. FTIR spectrum of Congo red crystal

Optical transmission spectral analysis: The UV-visible transmittance spectrum (Fig. 5) of mixing disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl) diazen-1-yl]phenyl}phenyl)diazen-1-yl]naphthalene-1-sulfonate (Congo red) crystal was recorded in the wavelength range 190-1100 nm, using Lambda 35 spectrometer. Optically polished single crystal of thickness 2 mm was used for this study. This spectral study may be assisted in understanding electronic structure of the optical band gap of the crystal. The study of the absorption edge is essential in connection with the theory of electronic structure, which leads to the prediction of whether the band structure is affected near the band extreme.

The peak appeared at 300 and 550 nm corresponding to the amine moiety.

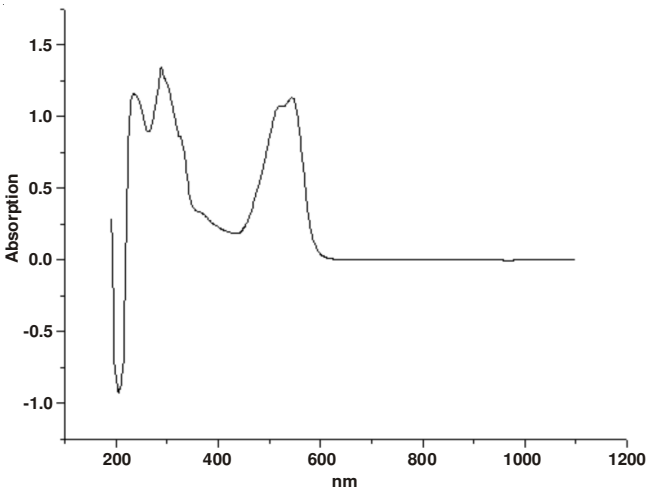

Fig. 5. UV-Visible transmittance spectrum for Congo red crystal

Crystal surface analysis by SEM: Surface analysis of disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl)diazen-1-yl]phenyl}phenyl) diazen-1-yl]naphthalene-1-sulfonate (Congo red) crystal is carried out through scanning electron microscopy. The magnification 250 times has been studied for this crystal. The maximum magnification studied in the equipment is 3, 00,000 times with a resolution of 3 nm. The surface of the crystal was coated with gold to make the sample conducting. From the Fig. 6, it is clear that the size of the crystals is 200 μ thick. Further the surface is smooth without any defects.

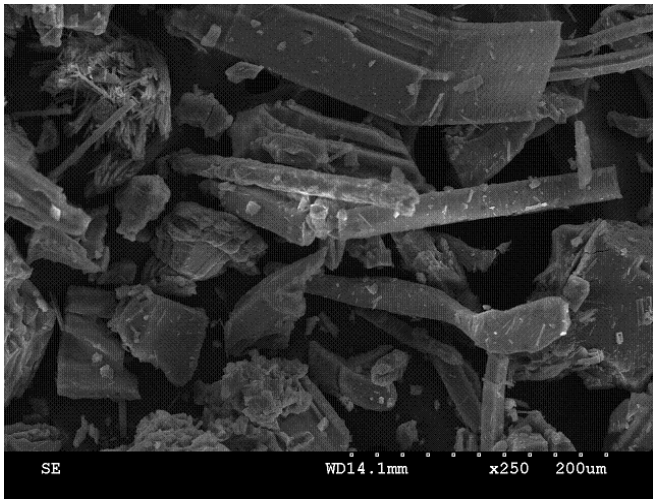

Fig. 6. SEM Analysis of disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl)diazen-1-yl]phenyl}phenyl)-diazen-1-yl]naphthalene-1-sulfonate (Congo red) crystal

Second harmonic generation (SHG) test: The non-linear optical (NLO) property of the grown crystal was confirmed by Kurtz-Perry powder technique[14]. The mixing disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl)diazen-1-yl]phenyl}phenyl)diazen-1-yl]naphthalene-1-sulfonate (Congo red) crystal was powdered with uniform particle size using a ball mill and it was packed densely between two transparent glass slides. An Nd:YAG laser was used as a light source. This laser device can be operated in two different modes. In the single-shot mode, the laser emits an 8 ns pulse. While in the multi-shot mode, the laser produces a continuous train of 8 ns pulse at a repetition rate of 10 Hz. In the present study, a multishot mode of 8 ns laser pulse with a spot radius of 1 mm was used. The experimental setup for measuring second harmonic generation efficiency is shown in the Fig. 7. A fundamental laser beam of 1064 nm wavelength, 8 ns pulse with 10 Hz pulse rate was made to fall normally on the sample cell(S). The power of the incident beam was measured using a power meter. The filter F1 removes the 1064 nm light and the filter F2 is a BG-38 filter, which also removes the residual 1064 nm light. F3 is an interference filter with bandwidth of 4 nm and central wavelength 532 nm. The green light was detected by a photomultiplier tube (PMT) and displayed on a cathode ray oscilloscope (CRO). KDP crystal was powdered into identical size as mixing disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl)diazen-1-yl]phenyl}phenyl)diazen-1-yl]baphthalene-1-sulfonate (Congo red) crystal and it was used as reference material in the second harmonic generation measurement. In the non-linear optical process that taking place in the sample, it converts the 1064 nm radiation into green light (λ = 532 nm) when Nd:YAG laser light is passed into the sample and this confirms the second harmonic generation. It was found that the efficiency of second harmonic generation is 0.76 times that of the standard KDP.

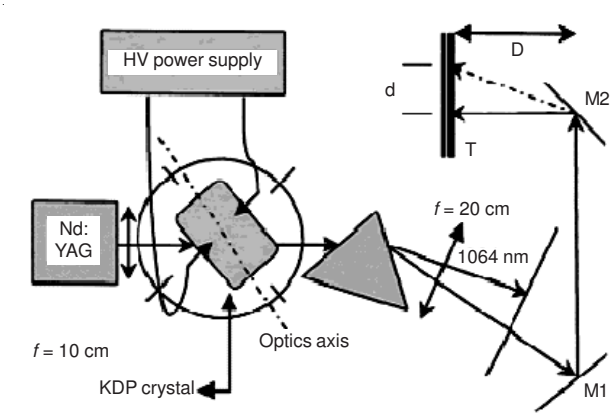

Fig. 7. Experimental setup for second harmonic generation measurement

Conclusion

Disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl) diazen-1-yl]phenyl}phenyl) diazen-1-yl] naphthalene-1-sulfonate (Congo red) was synthe-sized and solubility was determined at various temperatures. Bulk single crystals of Congo red salt was grown by solution method. It is observed that the grown crystal is transparent, coloured and has good morphological edges. Powder crystal X-ray analysis reveals that the crystal belongs to orthorhombic system with space group P212121. The functional groups present in disodium 4-amino-3-[(E)-2-(4-{4-[(E)-2-(1-amino-4-sulfonatonaphthalen-2-yl)diazen-1-yl]phenyl}phenyl)-diazen-1-yl]naphthalene-1-sulfonate (Congo red) crystal are con-

firmed by the FTIR spectral analysis. The optical absor-ption study reveals high transparency of the crystal with a UV cut off wavelength of 300 and 550 nm. The non-linear optical efficiency of the crystal is found to be 0.92 times that of KDP.

ACKNOWLEDGEMENTS

The authors are thankful to Mahendra Engineering College and AMET University to do the present work and also very thankful to NIT-Trichy for scanning electron microscopy analysis.

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