Photonic crystal cavity mediated improved absorptive nonlinearity of C-4-hydroxy-3methoxphenilcalix[4]resorcinarene

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Synthesis of C-4-hydroxy-3-methoxphenilcalix[4]resorcinarene (34%, 4.1696g) was done with 1:1 resorcinol and vanillin by the acid-catalyzed reaction. Resorcinol (0.05 mol, 5.505 g) and vanillin (0.05 mol, 7.6075 g) were ground together by mortar and pestle in the presence of p-toluene sulfonic acid $(5\%, 0.025 \text{ mol}, 0.4305 \text{ g})^{1,2}$. The reactants melted on grinding and solidified after 1 hour. The product was washed with water, filtered, and recrystallized from methanol.

NMR of C-4 -hydroxy-3-methoxphenilcalix[4]resorcinarene

1 H NMR spectral data Signals around 6.20 ppm in DMSO-d 6 solvent belong to resorcinol's aromatic protons. The methine protons resonate as a singlet in the 5.52-5.63 ppm range, while phenolic protons resonate in the 8.41-8.70 ppm range. Due to a spin-spin coupling, phenyl ring protons resonate doublets in the 6.12-7.14 ppm range. 1 HNMR could not observe the internal aromatic protons in the cavity due to ring current effects. As expected, two isomers, C_{4v} and C_{2v} , were present in the 1 H NMR spectra[Fig.1], and due to the presence of two isomers, some of the peaks were merged.



Fig.1 NMR spectrum of CHMPCR

1HNMR in DMSO-d6(δ values):C4v: 5.58 (s, 2H, CH), 9.77(s, 1H, OH), 7.43 (s, 2H, OH) C2v: 5.42(s, 2H, CH), 8.39 (s, 1H, OH), 7.44(s, 1H, OH); C4v and C2v:3.40 (s, 3H, OCH3), 3.45(s, 3H, OCH3), 3.84 (s, 3H, OCH3), 6.07-6.97(m, 10H, Ph)



Fig.2: FTIR spectrum of CHMPCR

The chemical bonds in the molecule are identified with Fourier transform infrared (FTIR) spectroscopy (Jasco FTIR-4700). FTIR spectrum of CHMPCR from 500 to 4500 cm⁻¹ is shown in Fig.2 to identify the functional groups present. The characteristic peaks of CHMPCR are consistent with the FTIR spectrum reported in the literature³. They are as follows: 3425 cm⁻¹(stretching of OH bond), 2995 cm⁻¹(stretching CH sp³), 1657 cm⁻¹(stretching of C=C aromatic rings), and 1393 cm⁻¹ (bending CH sp³).

References

- 1 A. Khaskel, P. Gogoi, P. Barman and B. Bandyopadhyay, *RSC Adv.*, 2014, **4**, 35559–35567.
- 2 A. Thangamani, J. Appl. Adv. Res., 2017, 2, 78–85.
- 3 R. E. Sardjono, A. Kadarohman and A. Mardhiyah, *Procedia Chem.*, 2012, 4, 224–231.