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Viscosity induced emission of red-emitting NLOphoric coumarin morpholine-thiazole hybrid styryl dyes as FMRs: Consolidated experimental and theoretical approach

Kiran C. Avhad [a], Dinesh S. Patil [a], S. Chitrambalam [b], M.C. Sreenath [b], I. Hubert Joe [b], Nagaiyan Sekar [a, *]

[a] Department of Dyestuff Technology, Institute of Chemical Technology, Matunga, Mumbai, 400019, India
[b] Centre for Molecular and Biophysics Research, Department of Physics, Mar Ivanios College, Thiruananthapuram, Kerala, 695015, India

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Four new coumarin hybrid styryl dyes are synthesized by condensing 4-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-2-morpholinothiazole-5-carbaldehyde with dicyanovinylene containing active methylene intermediates and their linear and non-linear optical properties are studied. The dye having dicyanovinylene-isophorone acceptor displayed a large Stokes shift of 3702–4795 cm^{-1} in non-polar to polar solvent respectively. The dyes exhibit a good charge transfer characteristics and positive emission solvatochromism (~50 nm–72 nm) in non-polar to a polar solvent which is well supported by multi-linear regression analysis. Viscosity induced enhancement study in ethanol/polyethylene glycol-400 system shows 2.71–6.78 fold increase in emission intensity. The intra and twisted-intramolecular charge transfer (ICT-TICT) characteristics were established using emission solvatochromism, polarity plots, generalised Mullikan-Hush (GMH) analysis and optimized geometry. A dye having the highest charge transfer dipole moment relatively possess the maximum two-photon absorption cross-section area (**KK-1** = 165–207 GM) which was established using theoretical two-level model. The NLO properties have been investigated employing solvatochromic and computational methods and were found to be directly proportional to the polarity of the solvent. Z-scan results reveal that the dyes **KK-1** and **KK-2** possesses reverse saturable kind of behaviour whereas **KK-3** and **KK-4** show saturable kind of behaviour. From the experimental and theoretical data, these coumarin thiazole hybrid dyes can be considered as promising candidates for FMR and NLOphores.

1. Introduction

Organic π-conjugated donor π-acceptor (D-π-A) dipolar materials with red shifted emission are of continued interest in material science as they have applications in optoelectronic devices like organic light emitting diodes (OLEDs) [1–6], organic photovoltaics [7–11], organic field effect transistors [12–15], nonlinear optics [16–19], as well as protein tracking [20]. Red emitting dyes play a vital role in the fabrication of high definition (HD) display due to their complementary blue [21] and green color [22–24].

Intramolecular charge transfer (ICT) is one of the key characteristics found in coumarin containing D-π-A dyes [25]. Coumarin derivatives are usually functionalized with electron donating (D) and electron-accepting (A) groups which reduce the HOMO-LUMO band gap leading to red shifted absorption and emission extending in the red/NIR region [26,27]. They are known to have outstanding optical properties [28,29]. The highly Stokes shifted intense emission in the blue-green region with the higher quantum yield [30], spectral tunability [31] and desirable spectroscopic features like the higher molar extinction coefficient combined with remarkable thermal stability [32] make them good candidates in molecular science [33]. Coumarin analogues have been used in dye laser systems [34–36], bio-imaging [37,38], sensing [39,40], OLEDs [41,42], optical brighteners [34] and DSSCs [43,44]. Fusion of coumarin and BODIPY fluorophores results in red/NIR absorption/emission with large Stokes shift and good quantum yield [45,46]. Similarly, coumarin-rhodamine hybrids and coumarin thiazole hybrids have been shown to have viscosity sensing [47,48], and

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* Corresponding author.
E-mail addresses: n.sekar@ictmumbai.edu.in, nethi.sekar@gmail.com (N. Sekar).

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aggregation induced emission enhancement properties [49]. Owing to their easier modulation, they have been extensively studied for the non-linear optics [26,50–52].

Intramolecular charge transfer (ICT) characteristics in molecular rotors are well studied in recent years [53]. A rotatable single bond between D and A is an essential requirement for a molecule to behave as FMR [54,55]. Under the viscous condition, non-radiative decay mediated by internal rotation is minimized and radiative relaxation is enhanced leading to strong emission [56,57]. Generally, in typical D-π-A FMR system solvent viscosity dependent enhancement of fluorescence intensity is believed to be caused by ICT/TICT originating from twisting of geometry in the excited state [58–60]. FMRs play a vital role in biological [47,57] and material sciences [61].

The absorption and emission properties of coumarin rarely reach to the red region except in a few cases [62–65]. Furthermore, it is known that the fluorescent coumarin dyes do not exhibit significant viscosity assisted emission enhancement [66]. However, solid state emissive planer N-coumarin derivatives have been recently documented [67]. Now, in continuation of our efforts in the synthesis of fluorescent coumarin hybrid dyes, we report here the synthesis, optical, electrochemical, thermal, and NLO properties with considerable viscosity induced emission enhancement. Viscosity sensitivity study has been done in the polar protic EtOH-PEG-400 viscous environment. The dyes reported here are asymmetric dipolar and quadrupolar in nature extending dual absorption and single emission in the red region. Therefore, we are interested in NLO properties and NLO properties were obtained by spectroscopic methods and DFT computations. Two level microscopic model was used to obtain the linear and non-linear and two photon properties (σ2PA). Further, the solvent dependence of dipole moment (μ), static polarizability (α), and total hyperpolarizability (β, γ) of the dyes were calculated by employing range separated functional, CAM-B3LYP with the help of triple zeta basis set 6-311++G(d,P). The charge transfer analysis was done using emission solvatochromism, polarity graphs, Mullikan-Hush (GMH) analysis and HOMO-LUMO energy gap.

2. Experimental

2.1. Material and methods

All commercial reagents and synthetic grade solvents were purchased from SD Fine Chemicals (Mumbai, India) and were used without further purification. The reactions were monitored by thin layer chromatography (TLC) using on 0.25 mm E-Merck silica gel 60 F254 precoated plates, which were visualized in UV chamber (254 nm and 344 nm light). ^{1}H NMR and ^{13}C NMR spectra were recorded on Agilent 500 MHz NMR. Chemical shifts (δ) are reported comparative to tetramethylsilane (TMS) as an internal standard. The absorption spectra of chromophores were recorded on a Perkin Elmer Lambda 25 UV–Visible spectrophotometer; emission spectra were recorded at Varian Inc. Cary Eclipse spectrofluorometer. Cyclic voltammetry (CV) was measured on Metrohm Autolab s.v. instrument (Serial No. AUT50995) using a conventional three electrode cell with Pt metal as the working electrode, Pt gauze as the counter-electrode, and Ag/$AgNO_3$ as the reference electrode at a scan rate of 100 mV/s. The 0.1 M tetrabutylammonium hexafluorophosphate (NBu_4PF_6) in acetonitrile was used as the electrolyte. The DSC-TGA was carried out using Perkin Elmer STA 6000 instrument with a heating rate of 10 °C/min under the nitrogen atmosphere.

2.2. Computational details

The global hybrid functional B3LYP which uses Becke's three parameter (local, non-local) hybrid exchange functional with Lee–Yang–Parr correlation functional [68–70] along with triple zeta basis set with diffuse polarization function 6-311++G(d,p) [71] was used for optimizing the ground state geometry of dyes **KK-1**, **KK-2**, **KK-3,** and **KK-4**. The validity of the structure as local minima on potential energy surface was verified with vibrational analysis and was confirmed that they are with no imaginary frequencies. Time Dependent Density Functional Theory (TD-DFT) [72] at the same level of theory has been used to obtain the HOMO–LUMO orbital energies and band gap. The range separated functional CAM-B3LYP/6-311++g(d,p) method was employed for the calculation of dipole moment (μ), polarizability (α) and hyperpolarizability (β,γ) of all coumarin hybrid dyes. The solvent effect has been considered using PCM model as implemented in Gaussian 09 [73]. All the computations were performed using the Gaussian 09 W revision D.01 program on a HP workstation XW-8600 with Xeon processor, 8 GB RAM, and Windows 7 as the operating system.

2.3. Z-scan experimental

The nonlinear absorption coefficient (β) and nonlinear refractive index (n_2) were measured by the Z-scan method. Samples were liquid solutions of acetone, ethanol, and DMSO In the Z-scan experiment, a laser beam was focused to a minimum waist at the focal point which corresponds to the value of Z = 0 (Z is the beam propagation direction i.e. Z-axis). The incident beam intensity was varied by moving the sample along the path of the beam. The resulting distortion and changes in transmittance of the beam were probed by two detectors. For all dyes, 0.3 mM solutions were used for the Z-scan measurement which was performed by using Nd:YAG laser having 532 nm with 5 ns pulses at a repetition rate of 10 Hz. The results were used to evaluate the values of third order nonlinear optical parameters β, n_2, and $\chi^{(3)}$ for the coumarin hybrid dyes.

2.4. Synthesis and characterization of dyes ***KK-1*** to ***KK-4***

The synthesis of four dyes, **KK-1** – **KK-4** has been carried out using the simple protocol (for intermediates). (Scheme 1). [74]. The intermediate **3** was synthesized from 4-N, N-diethylamino salicylaldehyde and ethyl acetoacetate in good yield by using the reported method [75]. The intermediate **3,** after bromination with TBAB in dichloromethane at RT, yielded intermediate **4** as a yellow solid. Then the intermediate **4** was treated with morpholine-4-carbothioamide (**2**) in absolute ethanol to get intermediate **5** which was then subjected to Vilsmeier Haack formylation to get corresponding carbaldehyde **6**. The aldehyde **6** was subjected to Knoevenagel condensation with different active methylene compounds (Scheme 2) to get desired dyes **AK-1** – **KK-4** respectively.

2.4.1. Synthesis of morpholine-4-carbothioamide (**2**)

The solution of compound 1 (21.0 g, 0.08 mol) in 125 mL conc. HCl was stirred for 15 h at 75 °C. Then the reaction mixture (RM) was cooled to room temperature (RT) and to this added few ice cubes. The resulting reaction mixture was neutralized using liquid ammonia. The crude pale yellow solid obtained after filtration under vacuum was washed with ice cold water followed by dilute sodium bicarbonate solution furnished the desired product (**2**) as an off white solid. (10.1 g, 79.6%); Mp-175 °C-176 °C (Literature Mp-176 °C to 177 °C).

2.4.2. 3-(2-bromoacetyl)-7-(diethylamino)-2H-chromen-2-one (**4**)

The intermediate **4** was synthesized using the reported protocol [76].