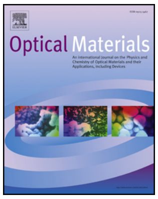
Optical Materials 85 (2018) 308–318

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat



Fluorescent carbazole based pyridone dyes – Synthesis, solvatochromism, linear and nonlinear optical properties

MayuriM.L. Kadam, Dinesh Patil, Nagaiyan Sekar*

Department of Dyestuff Technology, Institute of Chemical Technology, Matunga, Mumbai, 400 019, India

ARTICLE INFO

Keywords:
Pyridone
Solvatochromism
ICT
HOMO-LUMO analysis
DFT
NLO

ABSTRACT

Carbazole based pyridone dyes are investigated for their non-linear optical (NLO) properties. They exhibit positive solvatochromism and charge transfer character with a high fluorescence quantum yield which encouraged us to study their NLO characteristics. Photophysical properties of dyes in different solvents are evaluated and correlated with computational optical absorption and fluorescence emission using global hybrid (B3LYP) and long range separated functional (CAM-B3LYP) with 6–31G(d) basic set. Frontier Molecular Orbital analysis and Generalised Mulliken Hush analysis reveal a strong intramolecular molecular charge transfer character in these dyes. DFT and TD-DFT are performed to understand the electronic and photophysical properties of dyes. The resultant decrease in the HOMO-LUMO energy gap is responsible for bathochromic shift. Large enhancement in the non-linear optical properties are seen for these dyes than urea confirming their use in non-linear optical materials. The MEP analysis reveals the sites for electrophilic and nucleophilic attack in the dye. The experimental data are in good agreement with those obtained by computation (DFT) method. Fundamental limiting values of β, γ for dyes are observed within the estimated limits.

1. Introduction

Molecular Donor-π-Acceptor (D-π-A) systems attract attention due to their applications in nonlinear optical (NLO) materials, organic photovoltaics (OPVs), organic field-effect transistors (OFETs), dye-sensitized solar cells (DSSCs), two-photon optics, electron transporters and emitters in organic light-emitting diodes (OLEDs) [1–7]. D-π-A systems are known for their perturbed π -electron delocalization of the locally excited (LE) state promoting intramolecular charge transfer (ICT) and such phenomena are intensified in polar environments [8,9]. Conjugated organic molecules exhibit large excited state dipole moment and hyperpolarizability, the higher second-order nonlinearity, the lower dielectric constants and the higher optical thresholds than their inorganic counterparts [10]. Compounds having ICT features are usually functionalized by electron-donating (D) and electron-accepting (A) groups through a π-conjugated bridge (D-π-A) which makes them possible to reduce the energy gap between HOMO and LUMO of the molecule for broadening the range of absorption (see Schemes 1 and 2).

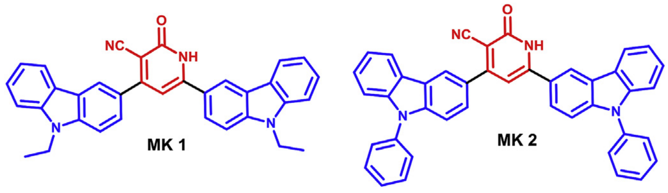
Carbazole based push-pull chromophores find their potential applications in electro/photoactive materials, such as nonlinear optical (NLO) material, organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and dye-sensitized solar cells (DSSCs) [8,11–13]. *N*-Alkylation or arylation of carbazole is useful to enhance solubility as well as donor strength. Carbazole, being a donor-rigidized residue improves π-electron delocalization resulting in better two-photon absorption (2 PA) property [14,15]. Pyridone based dyes find applications in medicinal chemistry, agrochemicals, and dye chemistry [16,17]. Pyridone playes a crucial role in the development of fused heterocyclic ring systems, building block in biological and pharmacological intermediates and they are widely used as intermediates in dyestuff industry [18–23].

The D-π-A-π-D type conjugated structures are important due to their characteristic electro-optical properties, sensitizing properties, and they have large dipole moments and molecular hyperpolarizability [24–30]. They are also thermally stable to be used in polymers [31,32]. Such a dye configuration is expected to exhibit good photovoltaic performance [33–35]. So, after a screening of several known fluorescent dyes, we synthesized carbazole-based push-pull dyes which show fluorescence in solution as well as in solid state. We present two novel dyes which are hybrid of two carbazole core linked with a pyridone ring where the pyridone consists of an extended π-conjugation as an acceptor and carbazole ring as a donor. Carbazole is a better donor compared to the other donor groups. This kind of behaviour suggests that the incorporation of carbazole core to pyridone frame modified the optical properties of dyes **MK 1** and **MK 2** extended the effective conjugation length.

---

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

https://doi.org/10.1016/j.optmat.2018.08.072
Received 19 March 2018; Received in revised form 24 August 2018; Accepted 31 August 2018
0925-3467/



Scheme 1. Chemical structures of **MK 1** and **MK 2**.

Carbazole-pyridone (D-π-A-π-D) dyes **MK 1** and **MK 2** were designed, synthesized and characterized by FT-IR, ^{1}H, and ^{13}C NMR. There are very few reports available which describe the photophysical properties of the pyridone analogs [36]. In the present paper, we discuss the photophysical properties of the novel pyridone derivatives **MK 1** and **MK 2** and they are compared with the known analogs [36]. The pyridone based dyes contain electron donor carbazole core on both the sides, which helps in a better delocalization and hence red-shifted absorption and emissions are observed. The compounds show emission in the visible region between 454 and 481 nm depending on the solvent polarity. To correlate our experimental finding theoretically and understand the ground and excited state geometries and electronic properties of these molecules DFT and TD-DFT calculation were performed as implemented in Gaussian 09 program using the B3LYP functional. The solvatochromism of these compounds was investigated by Lippert-Mataga and Mac Rae correlation. Multilinear regression with the Kamlet–Taft and the Catalan solvent parameters were used for describing the solute-solvent interactions by using solvatochromic shifts of the UV–vis absorption band of the investigated pyridone dyes. The molecular design strategy is based on the structural changes like surrounding electron-donor and acceptor group position manipulation and its capability of effective intermolecular charge transfer (ICT) characteristics.

2. Experimental section

2.1. Materials and equipment

All the commercially available chemicals and solvents were purchased from Sigma Aldrich and S.D.Fine Chemicals Pvt Ltd and used without purification. All the solvents used were of the spectroscopic grade. The reaction was monitored by TLC using on 0.25 mm E-Merck silica gel 60 F254 precoated plates, which were visualized with UV light. The compounds were purified by column chromatography on silica gel. The melting points were measured on standard melting point apparatus from Sunder industrial product Mumbai, and are uncorrected. FT-IR data were obtained from using Brucker spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using Agilent 500 MHz instrument using TMS as an internal standard. The visible absorption spectra of the compounds were recorded on a Perkin-Elmer Lambda 25 UV–Visible spectrophotometer, and emission spectra were recorded on Varian Cary Eclipse fluorescence spectrophotometer using freshly prepared solutions at the concentration of 0.3×10^{-6} mol L^{-1}. Relative quantum yields were measured using quinine sulfate as a standard.

2.2. Computational details

The most important step of the theoretical calculations is geometry optimization. The ground state geometry (S_0) of compounds was optimized using Density Functional Theory (DFT) by using the popular hybrid functional B3LYP and 6-31G(d) basis set using Gaussian 09 program. The functional used was B3LYP. The B3LYP methods combine Becke's three parameter exchange functionals (B3) with the nonlocal correction functional by Lee, Yang, Parr (LYP) [37]. The basis set used for all atoms was 6–31G(d). The low-lying first singlet excited state of each conformer was relaxed using the time dependent-density functional theory to obtain its minimum energy geometry. The difference between the energies of the first excited state and ground state was used in computing emission. Excited state calculations were done using TD-DFT both in vaccum and in solvent phase. The polarizable continuum model (PCM) as implemented in Gaussian 09 was used to calculate the excitation energy considering the solvent effect. Molecular hyperpolarizability calculations of pyridone by quantum mechanical approach were performed by using the same basic set 6-31G(d). The range separated hybrid functional CAM-B3LYP functional performs well for hyperpolarizability computations as compared to global hybrid functional B3LYP [38–40]. Hence CAM-B3LYP/6-31G(d) method was used for the calculation of dipole moment (μ), polarizability (α) and hyperpolarizability (β_o, γ) characteristics of carbazole based pyridone dyes.

2.3. Synthetic route

2.3.1. Synthesis and characterization

1a, 1 b, 2a, and 2 b were prepared by using the reported method [36,41].

2.3.2. General procedure

A mixture of appropriate acetyl compound (2.5 mmol), appropriate aldehyde (2.5 mmol), ethyl cyanoacetate (0.28 g, 2.5 mmol) and ammonium acetate (1.54 g, 20 mmol) in ethanol (50 ml) was heated under reflux condition for 3–4 h. The reaction was monitor by TLC, after completion of the reaction, the reaction mixture was cooled, and the formed precipitate was filtered, washed with ethanol, then washed successively with water, dried and purified by column chromatography using silica gel 100–200 mesh and toluene as eluent system.

*2.3.2.1. 4,6-Bis(9-ethyl-9H-carbazol-3-yl)-2-oxo-1,2-dihydropyridine-3-carbonitrile(**MK 1**).* Yield: 87%, Melting point = 274- 276^{0}c.

FT-IR (cm^{-1}) 2214 (CN), 1633 (C=O), 3059 (N-H).

CHN Analysis: Expected: C = 80.61; H = 5.17; N = 11.06. Found C = 80.63; H = 5.17; N = 11.07.

^{1}H NMR (500 MHz, DMSO) δ 12.65 (s, 1H), 8.88 (d, J = 0.9 Hz, 1H), 8.66 (d, J = 1.7 Hz, 1H), 8.31–8.24 (m, 2H), 8.08 (d, J = 8.5 Hz, 1H), 7.91 (dd, J = 8.5, 1.7 Hz, 1H), 7.82–7.77 (m, 2H), 7.68 (dd, J = 8.2, 5.1 Hz, 2H), 7.52 (t, J = 7.6 Hz, 2H), 7.27 (td, J = 7.5, 3.7 Hz, 2H), 7.10 (s, 1H), 4.52 (q, J = 7.1 Hz, 4H), 1.34 (t, J = 7.1 Hz, 6H).

^{13}C NMR (125 MHz, DMSO) δ 141.51, 141.00, 140.64, 140.55, 127.20, 127.01, 126.91, 126.48, 125.75, 122.96, 122.79, 122.70, 122.60, 121.47, 121.31, 121.29, 121.03, 120.11, 119.89, 118.09, 110.15, 110.03, 110.00, 109.73, 37.68, 14.24.

2.3.2.2. 4,6-Bis(9-phenyl-9H-carbazol-3-yl)-2-oxo-1,2-dihydropyridine-3-carbonitrile(MK 2)

Yield: 85%, Melting point = 288- 290^{0}c.

FT-IR (cm^{-1}) 2218 (CN), 1643 (C=O), 3059 (N-H).

CHN Analysis: Expected: C = 83.70; H = 4.35; N = 9.30. Found C = 83.74; H = 4.35; N = 9.31.

^{1}H NMR (500 MHz, DMSO) δ 12.74 (s, 1H), 8.97 (s, 1H), 8.75 (d, J = 1.7 Hz, 1H), 8.39–8.34 (m, 2H), 8.04 (d, J = 7.8 Hz, 1H), 7.87 (dd, J = 8.6, 1.8 Hz, 1H), 7.74–7.70 (m, 4H), 7.69–7.65 (m, 4H), 7.59 (t, J = 7.3 Hz, 2H), 7.53–7.48 (m, 3H), 7.46 (d, J = 8.7 Hz, 1H), 7.36–7.41 (m, 5H).

^{13}C NMR (125 MHz, DMSO) δ 142.05, 141.60, 141.40, 141.33, 136.84, 136.70, 130.79, 130.78, 128.61, 128.58, 127.56, 127.47, 127.31, 127.24, 127.01, 126.34, 123.57, 123.40, 123.11, 123.03, 122.11, 121.62, 121.49, 121.32, 121.13, 118.50, 110.55, 110.41, 110.25.