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Novel donor–π–acceptor dye: synthesis, solvatochromism and DFT calculations

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Abstract

A novel D–π–A system having indole moiety **5** was synthesized in four steps, which exhibit interesting solvatochromism ranging from yellow in $CHCl_3$ to red in DMF, violet in acetone, deep purple in DMSO and green in CH_3CN. Also the studies on the fluorescence properties of **5** in different solvents revealed that the emission peaks are dependent on the polarity of solvents. The quantum–chemical calculations of **5** was performed using the Gaussian 03 program at the B3LYP/6-31G* level, which revealed that the HOMO is localized on the 3-hydroxy indole donor moiety, while LUMO is localized on the methylidene dimalononitrile acceptor moieties.

Keywords: Donor–π–acceptor, Indole, Solvatochromism, DFT calculations.

1. Introduction

The donor-bridge-acceptor type compounds (D–π–A dyes) have attracted increasable attention for their second-order nonlinear optical (NLO) properties [1, 2] and are being widely investigated because of their applications in organic/polymeric light-emitting diodes (O/PLEDs) [3, 4], organic photovoltaics [5-7], organic field-effect transistors [8], electrochromism [9, 10], sensors [11], nonlinear optics [12], and fluorescent biosensors [13]. It is well known that the NLO activity of the D–π–A dyes depends on the strength of the D and A groups and also on the length and nature of the π–conjugated spacer [14-17]. Also, solvatochromic dyes have received great attention due to their applications in photochemistry and as environmental probe [18].

In continuation of our works on heterocyclic chemistry [19-22], herein we described the synthesis and solvatochromism properties of new D–π–A dye **5** having 3-hydroxyindole moiety and also the geometry and electronic properties of **5** in ground state was investigated using density functional theory (DFT) calculations.

2. Experimental

2.1. Apparatus

FT-IR spectra were recorded on a Unicam/Mattson 8700 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 spectrometer in DMSO-d_6.

2.2. Chemicals and solutions

All solvents and reagents such as acetophenone, SeO_2, acetylacetone, NH_4OAc, $POCl_3$, malononitrile and piperidine were commercially available from Merck (Germany) and Sigma-Aldrich (USA) Chemical Co. Solvents were used without further purifications. DMF was dried by standing overnight over 4Å MS, followed by decantation and vacuum distillation. Dry DMF was stored over 4Å MS. Phenylglyoxal hydrate **2** was prepared by oxidation of acetophenone **1** using SeO_2 in refluxing dioxane in the presence of water [23].

2.3. Synthesis of 2,2'-(4-chloro-3-hydroxy-2-phenyl-1H-indole-5,7-diyl)bis(methan-1-yl-1-ylidene)dimalononitrile 5

2.3.1. Synthesis of 3-Acetyl-4-hydroxy-2-methyl-5-phenyl-1H-pyrrole 3

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To a mixture of acetylacetone (5 mmol) in water (10 mL) were added phenylglyoxal hydrate **2** (5 mmol) and ammonium acetate (20 mmol) at room temperature. The resultant mixture was stirred at the same temperature. The reaction mixture was solidified after 1 h, and the obtained solid was filtered, washed with water and the crude material was purified by crystallization from EtOH [19].

2.3.2. Synthesis of 4-chloro-3-hydroxy-2-phenyl-1H-indole-5,7-dicarbaldehyde ***4***

$POCl_3$ (24 mmol) was added dropwise to DMF (8 mL) with stirring at 30-35 °C, after addition, the mixture was stirred at 50 °C for 1 h. Then the solution of **3** (4 mmol) at least amount of DMF was added dropwise with stirring to the above mixture and stirred at 45-55 °C for 2 h, then kept overnight at room temperature and poured over mixture of ice and water. Product was stirred for 0.5 h, then filtered off and recrystallized from EtOH [20].

2.3.3. Synthesis of 2,2'-(4-chloro-3-hydroxy-2-phenyl-1H-indole-5,7-diyl)bis-(methan-1-yl-1-ylidene)dimalononitrile ***5***

To the hot solution of **4** (2 mmol) and 2 equiv. of malononitrile in EtOH, piperidine was added in catalytic amount and refluxed for 1 h. After completion of the reaction, mixture was cooled and solidified. Then obtained solid was filtered and washed with EtOH; a dark solid; FT-IR (KBr) 3553, 3343, 3053, 2222, 1580, 1425 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 11.55 (s, 1H, NH), 8.13 (s, 1H, CH_{vinyl}), 8.75 (s, 1H, OH, exchanged with D_2O), 8.17 (s, 1H, CH_{vinyl}), 8.01 (d, *J* = 7.5 Hz, 2H, CH_{Ph}), 7.78 (s, 1H, CH_{indole}), 7.51 (t, *J* = 7.45 Hz, 2H, CH_{Ph}), 7.37 (t, *J* = 7.3 Hz, 1H, CH_{Ph}) ppm. ^{13}C NMR (125MHz, DMSO-d_6): δ 157.5, 156.7, 136.6, 134.6, 134.4, 130.9, 130.7, 129.3, 128.4, 127.7, 127.3, 124.8, 122.1, 119.8, 113.6, 112.8, 112.5, 111.9, 86.1, 81.4 ppm.

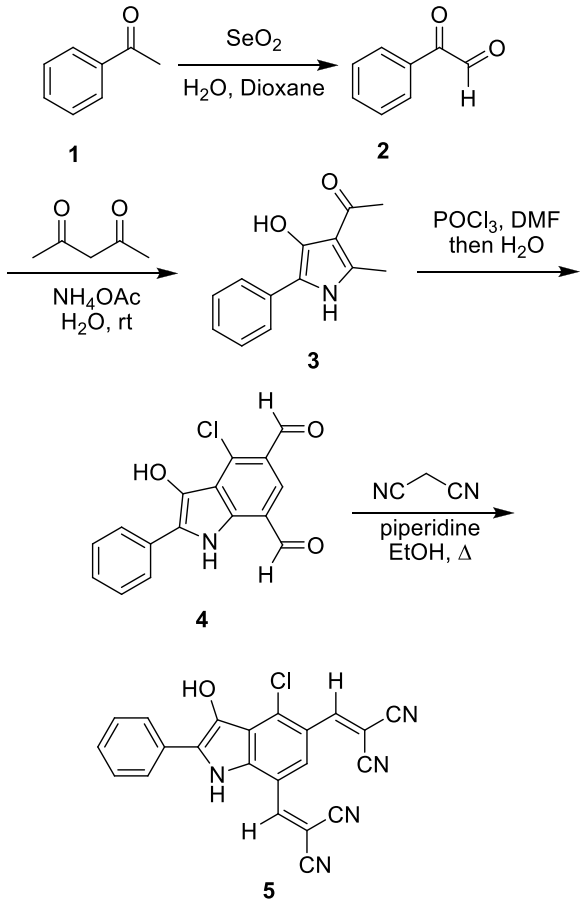
3. Results and discussion

3.1. Synthesis of dye 5

As shown in Scheme 1, 2,2'-(4-chloro-3-hydroxy-2-phenyl-1*H*-indole-5,7-diyl)bis(methan-1-yl-1-ylidene)dimalononitrile **5** was synthesized in four steps starting from acetophenone **1**. Acetophenone was first oxidized to phenylglyoxal hydrate **2** using SeO_2 in dioxane in the presence of water. Phenylglyoxal hydrate **2** was treated with acetylacetone in the presence of excess amount of NH_4OAc in water at room temperature to produce pyrrole **3**. The indole **4** was prepared via Vilsmeier-Haack reaction using $POCl_3$-DMF_3 that was treated with 2 equiv. of malononitrile in boiling EtOH in the presence of catalytic amount of piperidine. The structure of **5** was determined using FT-IR, ^1H NMR and ^{13}C NMR spectra.

3.2. Solvatochromism properties of dye 5

In solution, dye **5** exhibits interesting solvatochromism, ranging from yellow in $CHCl_3$ to red in DMF, violet in acetone, deep purple in DMSO and fluorescent green in CH_3CN (Figure 1).



Scheme 1. Four steps synthesis of dye 5.

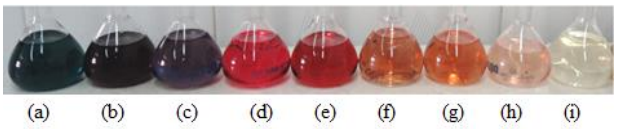


Figure 1. Solvatochromism of dye 5 in different solvents: CH_3CN (a), DMSO (b), Acetone (c), DMF (d), Ethylene glycol (e), n-BuOH (f), MeOH (g), EtOH (h), $CHCl_3$ (i).

The solvatochromic properties of **5** were investigated in several solvents with different polarity. Figure 2 shows the UV–Vis absorption spectra of **5** in different solvents at room temperature. In its absorption spectra, two transition bands were observed, which discrete bands around 380-400 nm in $CHCl_3$, EtOH and *n*-BuOH, and around 520-540 nm in polar aprotic solvents such as acetone, acetonitrile, DMF and DMSO with molar absorbtion greater than 50,000 $M^{-1}cm^{-1}$ are deduced to ICT from the donor to the acceptor. In addition to polarity of solvents, hydrogen-bond play an important role in solvatochromic properties of **5**, that in proton-acceptor solvents such as acetone, DMF, DMSO and acetonitrile, there were significant red shifts of the longest wavelength absorption bands.

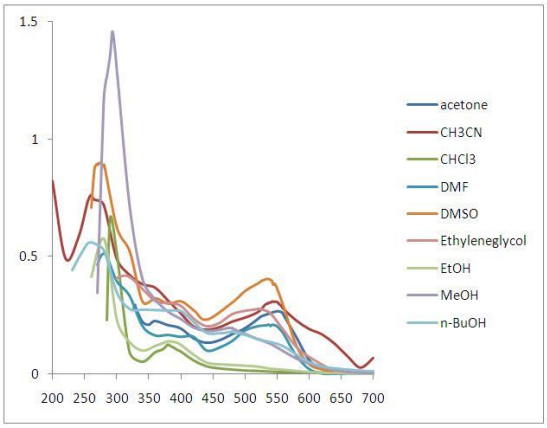


Figure 2. UV–Vis absorption spectra of dye 5.

Figure 3 shows the fluorescence spectra of **5** in solvents with different polarity such as acetone, acetonitrile, $CHCl_3$, DMF and EtOH. The emission peaks of **5** are shifted significantly from 358 nm in EtOH, 393 nm in DMF, 441 nm in $CHCl_3$ and 455 nm in acetone to 473 nm in CH_3CN. The distinct solvatochromism is by reason of the significant interaction between the ICT excited state and the solvent molecules. The absorption and emission data in different solvents for **5** are summarized in Table 1.

3.3. Quantum–chemical calculation of dye 5

In order to well understand the optical properties of dye **5**, quantum–chemical calculations are performed. The geometries of **5** are optimized using the Gaussian 03 program at the B3LYP/6-31G* level. Figure 4 shows the calculated optimized ground-state structure of **5** and the electron distribution of LUMO and HOMO. Comparison of the electron distribution in the frontier MOs reveals that the HOMO is localized on the 3-hydroxy indole donor moiety, while LUMO is localized on the methylidene dimalononitrile acceptor moieties. So the ICT in the excited states of **5** can be expected, which explains the sensitivity of its emission wavelength towards the polarity of the solvent.

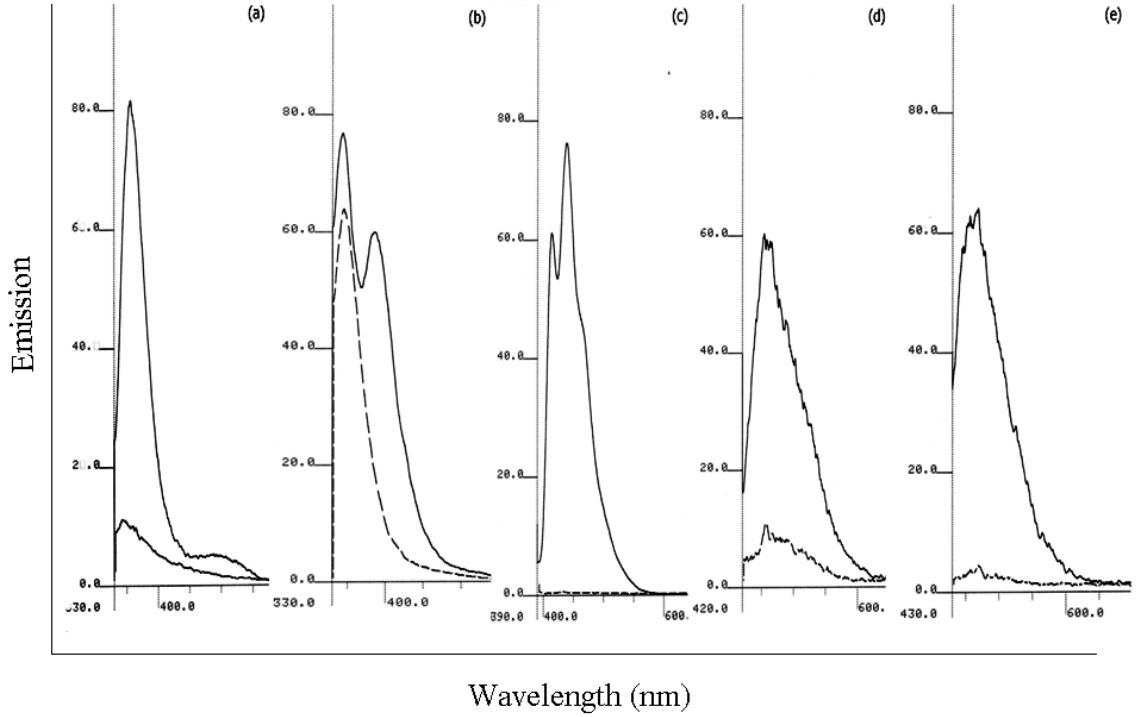


Figure 3. Fluorescence spectra of dye **5** in different solvents: EtOH (a), DMF (b), $CHCl_3$ (c), acetone (d), CH_3CN (e).

Table 1. The absorption and emission data in different solvents for dye 5

Entry	Solvent	λ_{max}/nm (ε 10^{-5}/$M^{-1}cm^{-1}$)	λ_{ex}/nm	λ^{f}_{max}/nm (%)
1	$CHCl_3$	290 (2.61), 380 (0.51)	382	415 (61.2), 441 (76.4)
2	EtOH	280 (2.25), 380 (0.55)	310	358 (81.3)
3	MeOH	293 (5.78), 480 (0.79)	–	–
4	*n*-BuOH	260 (2.37), 400 (1.07)	–	–
5	Ethyleneglycol	260 (2.65), 320 (1.62), 520 (1.11)	–	–
6	DMF	280 (2.02), 380 (0.67), 536 (0.83)	310	345 (76.8), 393 (60)
7	Acetone	280 (5.78), 360 (4.00), 520 (3.36)	400	455 (60.1)
8	DMSO	274 (3.56), 360 (1.27), 534 (1.58)	–	–
9	CH_3CN	260 (3.01), 542 (1.23)	410	473 (64.8)

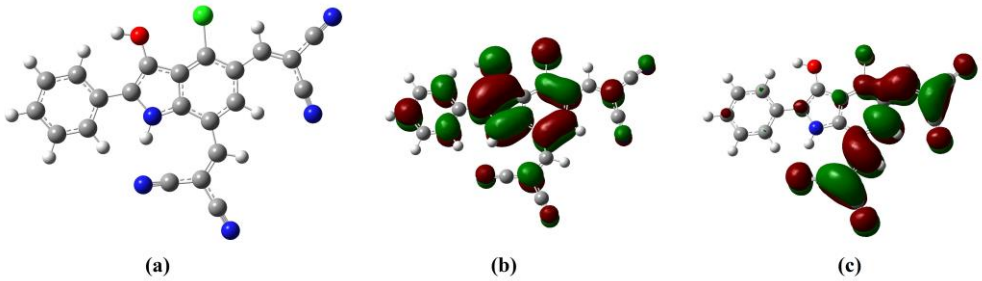


Figure 4. Optimized structure (a) and calculated HOMO (b) and LUMO (c) surface plots for **5** at B3LYP/6-31G* level.

4. Conclusions

In summary, a new D–π–A dye possessing 3-hydroxy indole donor moiety and methylidene dimalononitrile acceptor moieties was synthesized. The dye shows interesting solvatochromism properties in various solvents with different polarity. Absorption and emission spectra revealed that there is an ICT from the donor to the acceptor moiety. Also, calculated the electron distribution of LUMO and HOMO, revealed that the ICT in the excited states can be expected.

5. Acknowledgements

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