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Abstract— Organic materials that exhibit fluorescence are an attractive class of functional materials and optical properties that have witnessed a booming development in recent years. The design of new system with Donor-Acceptor properties is great interest for the construction of photophysical properties. D-A dye based on Indoline involved of 9-Methylcarbazole as a donor and cyanoacrylic acid as an acceptor synthesized via ideal process of carbazole as a primary substance. Synthesized compound was characterized by thin layer chromatography (TLC), differential scanning calorimetry (DSC), thermal Gravimeter analysis (TGA), fourier transform infrared spectroscopy (FTIR), 1H-nuclear magnetic resonance (1H-NMR), 13C-NMR, liquid chromatography, ultraviolet-visible spectroscopy in solutions and solid film. Photoluminescence quantum yields (PLQYs) of 2-11% in solution and 17% in non-doped solid film reported. To get further insight into the molecular structure of dye, their geometry and energies of HOMO and LUMO were optimized by density functional theory (DFT) calculation at the B3LYP/6-31G(d) level with Gaussian software 09. The melting point of dye reported 142 °C and the synthesized compound absorbs electromagnetic radiation in the range of 424-431 nm in solutions and emit solid film exhibited fluorescence in 541 nm. According to the results of investigations, compound was aggregation induced emission (AIE) and the ionization potentials of the synthesized dye was found to 5.89 eV.

Keywords— Indoline, Carbazole, Electrochemical properties, Optical properties, Cyanoacrylic acid

I. INTRODUCTION

Over the past few decades, the synthesis and investigation of π-conjugated organic materials has drawn considerable amount of research attention owing to their possible applications in the field of organic optoelectronics [1]. Presently, conjugated compounds with electron-donating (D) and electron-accepting (A) units are special attention because of their applicability in optoelectronic and electronic devices, such as organic light emitting diodes (OLEDs) [2], solar cells [3] and chemical sensors [4]. Compounds having donor and acceptor moieties often exhibit narrow energy gaps resulting from intramolecular charge transfer (ICT) [5].

Specially, the design and development of donor-acceptor π-conjugated dyes with both electron donating (D) and electron-accepting (A) groups, which possess high molar extinction coefficients, are expected to be one of the most promising organicsensitizers [6,7,8,9,10,11,12,13].

Organic compounds containing cyanoacrylic acid have been extensively studied as organic dyes in dye-sensitized solar cells due to their power conversion efficiency, ease of preparation, high structural flexibility, high extinction coefficients in the visible region and relatively low cost[14,15,16,17,18].Totally the structure of Indoline considered very much, because it has suitable stability, high conversion efficiency and ease synthesis.

There are several researches on cyanoacrylic acid as an acceptor, for example Paul et al synthesized new dye involved of cyanoacrylic acid as an acceptor for using in solar cells [19], Dehno Khalaji et al used cyanoacrylic acid as an acceptor in prepare of dyes [20] and Linxi et al designed structure with cyanoacrylic acid as an acceptor [21]. Furthermore materials with carbazole display stronger brightness and higher stability [22].Until now, many kinds of organic compounds containing cyanoacrylic acid group as an acceptor have been developed, such as coumarin, indoline, triphenylamine and rhodanine [9-13], but there is rare report on relation between carbazole moieties and cyanoacrylic. Nevertheless, the necessity of design and synthesis of new donor-acceptor materials with improved optical, photophysical and thermal properties is still an urgent topic. Therefore, in the strategy of this study, we have synthesized and investigated optical properties of new organic compound without metal with carbazole as a primary material with substitution methyl on nitrogen heteroatom containing cyanoacrylic acid and9-Methylcarbazole (Scheme 1).
II. METHODS

II.1 Materials and Instrumentation

All materials of consumption are Merck Co. The FTIR spectra were recorded on a PerkinElmer Spectrum GX II FT-IR One spectrophotometer on a KBr disc. The 1H-NMR and 13C-NMR spectra (chemical shifts are given as δ in ppm) were recorded on a Bruker DRX AVANCE spectrometer operating at 500 MHz. The elemental analysis CHNS was determined on a Costech instruments (Elemental Combustion System 4010). Differential scanning calorimetry (DSC) measurements were carried out using a DSC (DSC 214 Polyma NETZ5CH) under nitrogen environment. Cyclic voltammetry measurements were performed on a PGSTAT 302, electrochemical experiments were carried out at room temperature using a three electrode cells consisting of a platinum coil as counter electrode, a glassy carbon working electrode, and a silver wire as reference electrode. 0.1 M solution of tetrabutylammonium hexafluorophosphate (n-Bu4NPF6) was used as supporting electrolyte at a scan rate of 100 mVs-1. For the measurements, silver reference electrode was calibrated against Ferrocene/Ferrocenium (Fc/Fc+) redox couple as an internal standard [23].

The UV–Vis absorption spectra were recorded on a Cecil 9200 double beam spectrophotometer and the fluorescence spectra were taken on a Perkin and Elmer LS50B spectrofluorimeter with both excitation and emission slits set at 10 nm and controlled by a personal computer data processing unit. To record photoluminescence decay curves dependencies on laser flux, with Pico Quant LDH-D-C-375 laser with wavelength equals 373 nm as the excitation source were used and the ionization potential (IP) of the vacuum deposited films was obtained using photoelectron emission spectrometry in air [24,25].

II.2 Synthesis

II.2.1 9-methyl-9H-carbazole (1)

2 mol of carbazole and 18 ml of DMF stirred under the condenser and prepared clear suspension via heating in bath oil. 1 and 1.5 mol bromomethyl and potassium tert butoxide added to suspension respectively and stirred and after 15 hours crystals were formed and after filtration the yellow product dried via chromatography and purified with ethyl acetate/hexane.

MP=98°C; FTIR (KBr) (Cm⁻¹): 3321: C-H str Aromatic, 1657, 1470: C=C str; 1H-NMR (CDCl3), δ (ppm): 2.37 (s, 3H, CH3), 7.38-7.47 (d, 2H), 7.57-7.59 (t, 2H), 7.73-7.76 (t, 2H), 8.10-8.12 (d, 2H); Elem. Anal. Calcd. for C13H11N: C, 87.04%; H, 5.69%; N, 7.25%. Found: C, 87.03%; H, 5.71%; N, 7.26%.

II.2.2 3-formyl-9-methyl-9H-carbazole (2)

2 mol of (1) in 15 ml of DMF stirred and after 15 minutes added 1 mol of phosphoryl chloride to the reaction and stirred in 4 °C and arrived to room temperature very slowly around 3 hours. Final product filtrated after the using water and produced yellow material after the purification in ethyl acetate/hexane.

MP=112.3°C; FTIR (KBr) (Cm⁻¹): 2863: C-H str. Ald, 1721: C=O str, 1649, 1466: C=C str,1288: C-N str; 1H-NMR (CDCl3), δ (ppm): 2.54 (s, 3H, CH3), 7.04-7.07 (d, 2H), 7.09-7.12 (t, 1H), 7.16-7.17 (t,1H), 7.33-7.35 (d, 1H), 7.40-7.42 (t, 1H), 7.45-7.49 (s,1H), 8.67-8.69 (s, 1H, COH); Elem. Anal. Calcd. for C14H11NO: C, 80.38%; H, 5.26%; N, 6.69%. Found: C, 80.3%, H, 5.26%; N, 6.68%.

II.2.3 3-formyl-7-Nitro-9-methyl-9H-carbazole (3)

0.2 mol of (2) stirred in 40 gr of acid acetic and reaction was cold until room temperature (RT) and added 5 gr of nitric acid very slowly. The temperature of reaction increased to 90 °C for 3 hours and final product filtrated after the using water/acetate and produced yellow material after the purification in ethyl acetate/hexane.

MP=116.9 °C; FTIR (KBr) (Cm⁻¹): 1;554, 1348: NO2 str,1649, 1466: C=C str,1288: C-N str; 1H-NMR (CDCl3), δ (ppm): 1.93 (s, 3H, CH3), 6.64-6.66 (d, 2H), 6.71-6.73 (d, 1H), 6.76-6.78 (d, 1H), 6.83-6.86 (s, 1H), 7.16-7.19 (s, 1H, COH); Elem. Anal. Calcd. for C14H11NO2: C, 65.62%; H, 3.93%; N, 11.02%. Found: C, 65.63%; H, 3.92%; N, 11.03%.

II.2.4 3-formyl-7-Amino-9-methyl-9H-carbazole (4)

1 gr of (3) stirred with 3 gr of Tin(II) chloride and 10 ml isopropyl alcohol and 5 ml hydrochloric acid stirred respectively for 3 hours, final product filtrated after the using water/acetate and produced yellow material after the purification in ethyl acetate/hexane.

MP=129.14 °C; FTIR (KBr) (Cm⁻¹): 3531: NH str.
C=O str, 1588, 1435; C=C str, 1259; C-N str; 1H-NMR (CDCl3), δ (ppm): 2.34 (s, 3H, CH3), 4.24-4.28 (2H, NH2), 6.60-6.62 (d, 2H), 7.43-7.44 (d, 1H), 7.45-7.47 (d, 1H), 8.12 (s, 1H), 8.24 (s, 1H), 9.25 (s, 1H, COH); Elem. Anal. Calcd. for C14H12N2O: C, 75%; H, 5.35%; N, 12.5%. Found: C, 75.02%; H, 5.36%; N, 12.48%.

II.2.5 Dye

10 mmol of (4) and 50 ml acetonitrile and 15 mmol cyanoacetic and 50 ml pyridine stirred respectively for 10 hours, after cooling until room temperature and filtration and purification in ethyl acetate/hexane, the dye dried and synthesized. The yield of reactions for (1), (2), (3), (4) and dye were 78%, 87%, 84%, 81% and 84% tandemly.

In all cases no imaginary frequencies were found. All calculated compounds ground state geometries were optimized with no symmetry constrains to a local minimum, which was followed by frequency calculations.

In all cases no imaginary frequencies were found. All calculations in this work were conducted with polarizable continuum model (PCM) using dichloromethane as solvent as implemented in Gaussian 09 software [26]. Input files and molecular orbital plots were prepared with Gabedit 2.4.7 software [27]. The theoretical geometries and the distribution of HOMO and LUMO of synthesized dye are presented in Figure 1.

III. RESULTS

III.1 Geometries and frontier orbitals

DFT/TDDFT calculations were carried out with B3LYP hybrid functional combined with 6-31G(d) basis set. For investigated compounds ground state geometries were optimized with no symmetry constrains to a local minimum, which was followed by frequency calculations.

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III.2 Thermal properties

Thermal properties of the synthesized dye was estimated by Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) under nitrogen environment at a heating rate of 10°C/min and the curves brought in Figure 2.

In the TGA measurements, the dye exhibited ~7% mass loss temperature in the range 230-260 °C. The shape of TGA curve and very low quantity of residue at the end of experiment allows to assume that during heating carbazole was sublimated (Figure 2). Dye was isolated after the synthesis as crystalline substances and their first DSC heating scans exposed endothermic melting signal (Tm) at 142 °C due to sublimation.

III.3 Electrochemistry

Electrochemical property of investigated dye was determined using cyclic voltammetry (CV). Voltammograms of investigated dye is presented in Figure 3, while resulting data is presented in Table 1. Onset of oxidation of described molecule is located at 0.88 V and characterized by reversible oxidation peak, indicating that stable radical cations are formed during electrochemical oxidation. Dye displayed two oxidation peak, which can be assigned to oxidation of electron donating carbazole moieties and NH3. According to the method reported by Forrest et al.[28], ionization energy values (IPCV) value was calculated using the equation IPCV = E(IPCV)−E(Onset) vs Fe(III)−4.6 eV. The value of IPCV is given in Table 1.

Ionization potentials (IPCV) of the solid layer of dye was
estimated by photoelectron emission spectrometry.

Photoelectron emission spectra is shown in Figure 4. These values were compared with vertical ionization potentials, theoretically calculated in the framework of DFT B3LYP/6–31G(d) approach (Table 1). The trend of the ionization potential of CV was found to be close to those estimated by photoelectron emission spectrometry. The lowest value of theoretical vertical IP level was observed for dye, while the derivatives exhibit higher values of IP. It has to be mentioned that the trend of IP is not strictly consistent with the HOMO energy levels. The main reason is that the B3LYP basis set functional cannot predict orbital energies accurately [29].

Absorption and PL (photoluminescence) spectra of the dilute solutions of dye (0.00001 M) and solid film are shown in Figure 5 and wavelength ranges of the main absorption bands and fluorescence were shown in Table 2.

A shape and a wavelength range of the main absorption bands only slightly changes in this series of dye and presented in Table 2. Furthermore, Characteristic peak at ~400-540 nm is observed. Moreover, lower intensity band is located at longer wavelength range 485 until 510 nm. The difference in wavelength of emission between spectra of Toluene and Chloroform is equal to 0.22 eV. This effect is suggested an increase in the conjugation level of the π orbitals [31]. The different effect of solvents Toluene and Chloroform on the emission spectra of dye was studied and the wavelength of maximum intensities exhibited bathochromic leads to the strong red shift from the lowest polarity (Toluene, according to the index polarity of Table 2) to highest polarity (Chloroform) environments, compared to that of the individual donor and acceptor emission spectra and PL spectra move to longer wavelengths with increasing solvent polarity, showing a strong positive solvatochromism and as displayed previously in other donor-acceptor type of molecules [32,33,34]. Actually red shift of Chloroform solution demonstrated that the related with constant vibronic structure insensitive to the changing of environmental polarity [35,36]. Therewith, increases of solvents polarity observed charge transfer energy red shifted and investigated in less local excited state (LES) parameter and higher energy difference between charge transfer axial and charge transfer equatorial [37,38,39] and indicates that existed certain degree of charge transfer character with a large dipole moment which is derived from low lying singlet excited state [40,41]. Furthermore, for the emission spectra of dye in Toluene observed two peaks (Figure 5) that it is related to vibronic structure [42]. Emitted green light with maximum wavelength at 541 nm observed in solid state film and in the emission spectra of the solid state film broad band in the range of ~418-780 nm appears. Origin of this band lies in dimers formed by π-stacking between...
carbazole moieties in the solid state in excited state, called excimer, as described by other authors [43]. According to the Table 2 large stokes shifts observed for dye in Chloroform (5567 cm\(^{-1}\)) can apparently be explained by the large changes in geometry between the exited and ground states and the intramolecular charge transfer (ICT) from carbazole to cyanoacrylic acid moieties. Expansion of \(\pi\)-conjugated systems in dye in polar solutions such as chloroform leads to increase of relaxation time and results in higher stokes shifts of 4693 to 5567 cm\(^{-1}\) (THF and Chloroform), respectively. In this case, methyl group attached at the positions of carbazole moiety not only expand the conjugation of the \(\pi\)-electron system but also increase the dipole moment of the molecule [44].

With the increasing number of index polarity, PLQY increases from 2\% to 11\% and low PLQY is probably caused by vibrations of methyl group [45]. The PLQY in the solid film of investigated dye is within the value of 17\%. Note that this means that molecules enhance their luminescence efficiency in solid state, while PLQY for dye in solutions decreases. Moreover, the increase of PLQY is caused by reduction of molecular vibration in solid state, therefore we investigated Aggregation Induced Emission (AIE) phenomena for dye and the corresponding results are presented in Figure 6.

To examine whether for dye is active and qualified of AIE and as well as dye is miscible in THF and Water at room temperature, we accomplished PL spectra analysis on dye in the THF/Water mixtures with water fractions ranging from 0 until 100 percent of volume (Figure 6).

In Fig 6, exhibited a very weakly green emission with a maximum wavelength of 534 nm at 40 \% of water fraction, although PL intensities increased suddenly of aggregates in 80\% and finally 100\% of water fractions. Moreover, wavelength of PL spectra was not bathochromically shifted impressively, and simultaneously there is a broad spectral shape of the emission that estimated the violent bright PL emanates from the Intramolecular Charge Transfer (ICT) excited state between the 9-Methylcarbazole as a donor and cyanoacrylic acid as an acceptor unit. In water fraction values of 0\% for dye, equivalent to enhancement behavior was not observed Aggregation Induced Emission Enhancement (AIEE) in THF/Water mixtures and we encountered with AIE owing to structural difference of dye and restriction of intermolecular motion and finitude the internal rotations in the acceptor unit (cyanoacrylic acid). Hence, the observed AIE activities that it is the first of all the same mechanism and ascribed to aggregation induced restriction of suitable changes in the donor unit and the rotation around the single bond between the units of donor and acceptor [46,47,48].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(\lambda_{\text{Abs Max}}) (nm)</th>
<th>(\lambda_{\text{Em Max}}) (nm)</th>
<th>Polarity Index</th>
<th>(\Delta) (cm(^{-1}))</th>
<th>PLQY (%)</th>
<th>(S_1) (eV)</th>
<th>Polarity Index</th>
</tr>
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<tbody>
<tr>
<td>Toluene</td>
<td>431</td>
<td>507</td>
<td>2.4</td>
<td>3478</td>
<td>2</td>
<td>-</td>
<td>2.4</td>
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<tr>
<td>THF</td>
<td>427</td>
<td>534</td>
<td>4.0</td>
<td>4693</td>
<td>8</td>
<td>2.65</td>
<td>4.0</td>
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<tr>
<td>Chloroform</td>
<td>424</td>
<td>555</td>
<td>4.1</td>
<td>5567</td>
<td>11</td>
<td>-</td>
<td>4.1</td>
</tr>
<tr>
<td>Solid Film</td>
<td>434</td>
<td>541</td>
<td>-</td>
<td>3587</td>
<td>17</td>
<td>2.54</td>
<td>-</td>
</tr>
</tbody>
</table>

\(\Delta\): Minimum Stokes shift

PLQY: Quantum efficiency

To assessment experimental quantity of singlet energy \(S_1\), photoluminescence spectra were recorded at low temperature (80 K) in THF solution and cryostat system of solid film (Figure 7). Singlet energy levels of the dye were found to be comparable and therefore values reported 2.65 and 2.54 eV in THF and solid film respectively (Table 2), as well as we didn't observe red shifted spectra and phosphorescence phenomena and the spectra was similar to PL spectra in room temperature.

The similar trend is observed for the values of photoluminescence quantum yield (PLQY) of the studied dye.
III.5 Evaluation of PL decays

Fluorescence decay profiles of solutions and solid films were recorded with using of a single photon counting spectrofluorimeter. PL decays were monitored at the corresponding emission maximum of the dye and software experimental fluorescence allowed the fitting of value the decay spectra 1 until 1.2. According to the Figure 8 and Table 3, appearing of the slower decay for dye in solutions, occurred in the range of 0.81-0.91 ns and long decay time (9.11 ns) for solid state that the reasons are associated with the weak intermolecular interactions or crystalline aggregate formations in the neat films [49].
This research was supported by Research Center of Materials aggregation of dye. state film rather than to solution that it’s concerning to the j absorption spectra showed shift to high wavelength in solid of PL Decay spectra of dye was 9.11 ns. The result of dye was aggregation induced emission (AIE). Moreover the solutions, therefore we investigated aggregation tests and the PLQY of dye in solid film was high value rather than to solutions, therefore we investigated aggregation tests and the ionization potential of dye demonstrated value of 5.89 eV. Table III Life-Time fitting data of dye in solutions and Solid Film | Parameters | Toluene | THF | Chloroform | Solid Film | χ² |
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<tr>
<td>τ₁, ns</td>
<td>0.91</td>
<td>0.86</td>
<td>0.81</td>
<td>0.19</td>
<td>1.145</td>
</tr>
<tr>
<td>τ₂, ns</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.117</td>
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<tr>
<td>τ₃, ns</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.119</td>
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<td></td>
<td>0.91</td>
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<td>1.062</td>
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<td>IV. CONCLUSIONS</td>
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In this study, a series of new dye based on Idoline synthesized via carbazole as a primary material, we considered carbazol as a donor and cyanoacrylic acid as an acceptor. Dye prepared by kneovenagel reaction and after the purification used several analysis instruments such as FTIR, ¹H NMR and DSC/TGA. According to the optical properties of dye absorption spectra were in the range of 424-431 nm in solutions and emit solid film exhibited fluorescence in 541 nm. Furthermore, the result of ionization potential of dye demonstrated value of 5.89 eV. The PLQY of dye in solid film was high value rather than to solutions, therefore we investigated aggregation tests and the dye was aggregation induced emission (AIE). Moreover the τ of PL Decay spectra of dye was 9.11 ns. The result of absorption spectra showed shift to high wavelength in solid state film rather than to solution that it’s concerning to the j aggregation of dye.

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Fluorescence from Triazine-Based Donor-Acceptor Hybrid Light-Emitting Diodes Utilizing Thermally Activated Delayed Fluorescence


