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Mohammad Taghi Sharbati, University of Pittsburgh
Mohammad Navid Soltani Rad, Shiraz University of Technology
Somayeh Behrouz, Shiraz University of Technology
Alireza Gharavi, Shiraz University
Farzin Emami, Shiraz University of Technology

Available at: https://works.bepress.com/MohammadTaghi-Sharbati/6/
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Mohammad Taghi Sharbati a,*, Mohammad Navid Soltani Rad b,*, Somayeh Behrouz b, Alireza Gharavi c, Farzin Emami a

a Department of Electrical and Electronics Engineering, Shiraz University of Technology, Shiraz, Iran
b Department of Chemistry, Shiraz University of Technology, Shiraz 71555-313, Iran
c Photonics Lab, Department of Electrical and Computer Engineering, Shiraz University, Shiraz, Iran

ARTICLE INFO

Article history:
Received 7 April 2010
Received in revised form
13 October 2010
Accepted 18 October 2010
Available online 26 October 2010

Keywords:
OLED
Near infrared emission
ADA
Electroluminescence
Isatin
Schiff base

ABSTRACT

Fabrications of a single layer organic light emitting diodes (OLEDs) based on two conjugated acceptor–donor–acceptor (ADA) isatin Schiff bases are described. The electroluminescent spectra of these materials range from 630 to 700 nm and their band gaps were measured between 1.97 and 1.77 eV. The measured maximum external quantum efficiencies (EQE) for fabricated OLEDs are 0.0515% and 0.054% for two acceptor–donor–acceptor chromophores. The Commission International De L'Eclairage (CIE) (1931) coordinates of these two compounds were attained and found to be (0.4077, 0.4128) and (0.4411, 0.4126) for two used acceptor–donor–acceptor chromophores. The measured I–V curves demonstrated the apparent diode behavior of two ADA chromophores. The turn-on voltages in these OLEDs are directly dependent on the thickness. These results have demonstrated that ADA isatin Schiff bases could be considered as promising electroluminescence-emitting materials for fabrication of OLEDs.

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1. Introduction

Organic light emitting diodes (OLED) have an interesting attraction for full colour flat panel displays during the last years [1]. Although majority of investigations have been focused on electroluminescent (EL) devices (OLED) having emission in the visible spectrum there is considerable potential to be exploited for emission in the near infrared and infrared spectral ranges. These kinds of NIR-OLEDs have significant applications in night-vision readable displays [2], optical communications, laser technology and optical sensors [3–7]. Much of the work achieved on NIR-OLEDs has been focused on organic complexes of lanthanides such as Er3+, Nd3+, Tm3+ and Yb3+ [8]. However, they are known to have several drawbacks including the inherent low external quantum efficiency (EQE), expenses and less availability. Since there are a few reports on known organic materials having EL in the IR region, there have been extensive efforts to find novel organic chromophores having the aforementioned property. π-Conjugated acceptor–donor–acceptor (ADA) as well as donor–acceptor–donor (DAD) compounds have been widely studied for enhancing the OLED technology [9,10]. They are also employed for controlled optoelectronic properties and also output wavelength tuning. The donor–acceptor concept has been largely used in designing the red chromophores; nevertheless, a few molecules have been synthesized to emit in near infrared region. Thus, in search for novel organic chromophores having near infrared EL property, hereby we have designed and synthesized two novel ADA isatin Schiff bases with donor and acceptor fragments as shown in Fig. 1. The optical as well as electrochemical properties of these new chromophores were described using their NIR-OLEDs.

As it can be seen in Fig. 1, for having the low band gap chromophores, 3-iminoindolinyl-2-one residue at both sides of chromophore is selected as an acceptor head, while spacers including 4,4'-oxybis (4,1-phenylene) bis (azan-1-yl-1-yldiene) diindolin-2-one (2a) and 1,5-naphthyl (for 2b) are designated as donor segments. Thus, the conjugated backbone between donor and acceptor segments provides the appropriate delocalization and hence could be effective in band gap lowering.

2. Experimental

2.1. General procedure for synthesis of 3,3'-(4,4'-oxybis (4,1-phenylene) bis (azan-1-yl-1-yldiene)) diindolin-2-one (2a) and 3,3'-(naphthalene-1,5-diybisd (azan-1-yl-1-yldiene)) diindolin-2-one (2b)

To a double-necked round bottom flask (100 mL) equipped with a condenser was added a mixture of isatin (0.02 mol) and...
4-(4-aminophenoxy) benzene–amine and/or naphthalene-1,5-diamine (0.01 mol) in ethanol (30 mL). The mixture was refluxed for 6 h. Then, the reaction mixture was kept in a refrigerator for 4 h. Later, the filtration of reaction mixture followed by washing with cool ethanol (2 × 10 mL) gave pure crystals that yielded 2a (4.4 g, 97%) and 2b (3.9 g, 95%).

Data for 2a: 1H-NMR (250 MHz, DMSO-d6): δ = 7.14–7.17 (m, 2H, aryl), 7.36–7.42 (m, 6H, aryl), 7.57–7.64 (complex, 4H, aryl), 7.92–7.96 (m, 2H, aryl) and 11.02 (s, 2H, NH, exchangeable with D2O).

13C-NMR (62.5 MHz, DMSO-d6): δ = 114.31, 118.43, 121.57, 123.97, 127.05, 127.86, 129.64, 129.91, 132.05, 145.73, 151.01, 163.39 and 168.15.

IR (KBr) ν cm⁻¹: 3200, 3050, 1698, 1595 and 1473.

Analysis calculated for C26H16N4O2: C, 74.99; H, 3.87; N, 13.45%. Found: C, 74.85; H, 3.95; N, 13.57%.

Data for 2b: 1H-NMR (250 MHz, DMSO-d6): δ = 7.03–7.11 (complex, 6H, aryl), 7.40–7.49 (m, 6H, aryl), 7.75–7.87 (m, 4H, aryl) and 10.96 (s, 2H, NH, exchangeable with D2O).

13C NMR (62.5 MHz, DMSO-d6): δ = 116.21, 117.94, 121.03, 122.37, 123.81, 129.73, 133.48, 146.48, 147.51, 157.08, 164.26 and 168.42.

IR (KBr) ν cm⁻¹: 3220, 3035, 1695, 1591 and 1458.

Analysis calculated for C28H18N4O3: C, 73.35; H, 3.96; N, 12.22%. Found: C, 73.47; H, 3.91; N, 12.31%.

2.2. Fabrication of OLED

Fabrication of NIR-OLEDs was achieved using two ADA, 2a and 2b chromophores (Fig. 1). These chromophores could be sublimed without decomposition and thus, they were employed as an emissive layer via the thermal evaporation technique. In a simple OLED structure, a light emitting layer that contains an organic material is inserted between two electrodes as shown in Fig. 2.

Application of a forward bias at the diode terminals causes the carrier injection through the organic layers from the electrodes. Recombination of carriers from the lowest unoccupied orbitals (LUMO) to the highest occupied molecular orbitals (HOMO) produces photons with energy equal to the LUMO and HOMO difference. The released photons pass through the transparent electrode. Circular devices with 2 mm diameter were made on 2 × 2 cm² indium thin oxide (ITO) slides (as anode). The active area of each device was 7.1 mm². OLEDs were fabricated on a glass substrate pre-coated with ITO with a sheet resistance of 20 Ω/□ and a thickness of about 100 nm. Its work function was about 3.68 eV. The ITO substrates were washed and cleaned using acetone, ethanol and distilled water. Organic chromophore layer was deposited on ITO using a thermal evaporator at 6 × 10⁻6 Torr under vacuum conditions without any annealing. The deposition rates were about 1 nm/s for chromophores 2a and 2b, with a total thickness of about 50 nm. Finally, by means of a shadow mask
made from stainless steel having circular holes of 3 mm diameter, a 100 nm thick Mg cathode was deposited by thermal evaporation at a pressure of $6 \times 10^{-6}$ Torr using a deposition rate of 3 nm/s. The materials were loaded in alumina boats and tungsten baskets for evaporation. The thickness of each layer was determined by a quartz thickness monitor.

3. Results and discussion

3.1. The chemistry of chromophores

Two ADA isatin Schiff bases were synthesized in our laboratory according to Fig. 3. As demonstrated in Fig. 3, the reaction of two equivalents of isatin with an equivalent of 4-(4-aminophenoxy)benzenamine and/or naphthalene-1,5-diamine provided the corresponding 2a and 2b, respectively, as new ADA chromophores.

It is well known that 3-arylimino-2-indolones exist as mixtures of $E$ and/or $Z$ isomers. These isomers can be characterized using $^1$H- and $^{13}$C-NMR, but as they interconvert in solution they cannot be easily separated using conventional column chromatography [11,12]. However, 2a and 2b, because of having two 3-arylimino-2-indolones segments, exist as three stereo-isomers including ($E, E$)-, ($E, Z$)-, and ($Z, Z$)-isomer. The structures of these stereo-isomers are shown in Fig. 4.

The use of ab initio (Hartree–Fock; 6-31G) quantum mechanic calculations (run on Gaussian 98 version 9.2 software), semi-empiricals Austin Model 1 (AM1) and Parameterized Model 3 (PM3) (run on MOPAC in CS Chem 3D Ultra 8 (2004 Cambridge Soft) and Hyperchem (Hypercube Inc. version 7)) has indicated the heat of formation of each of the three 2a and 2b stereo-isomers,

![Fig. 3. General scheme for synthesis of two used chromophores.](image)

![Fig. 4. Ball and stick wire frame view of the optimized geometry for compounds ($E, E$)—2a and ($Z, Z$)—2b. As shown by dotted lines, the conjugation is broken by the middle oxygen. In 2b the conjugation extends over the whole molecule.](image)
accordingly. The heat of formation or $\Delta H_f$ is a criterion to estimate the stability of molecules in comparison with isomer or molecule. The molecule having a lower $\Delta H_f$ value is more stable, and hence, could have more contribution in indicating a molecule’s structure. In this context, through the calculated stereo-isomers discussed above, for $2a$, the $(E, E)$-isomer shows more stability (Fig. 4). While for $2b$, the $(Z, Z)$-isomer is the most stable of all. Calculations manifested the slight deviation of both molecules from coplanarity. This is because of steric repulsion between ortho hydrogens in middle aromatic spacer, carbonyl and hydrogen moieties on isatin scaffold (Fig. 5). However, the extra deviation from coplanarity was observed for $2a$ since the oxygen in ether bond has $SP^3$ hybridization and thus can hardly form the required geometry for coplanarity. Therefore, as predicated and observed, the fully conjugated chromophore $2b$ demonstrated the better red-shift EL spectra in comparison with $2a$. The optimized geometry for both compounds is shown in Fig. 5.

As can be seen in $2a$, the conjugation cut via ether bond in $2a$ causes each section to emit the light separately, whereas the structure and conjugation length of each section are the same. Thus, the electroluminescence for two segments shows the same wavelength region and their spectrum is simply overlapped. By considering the fully conjugated spacer between two isatin cores such as naphthyl group, the resonance length enhances and results in a red-shift.

3.2. Optical properties

The current ($I$) versus voltage ($V$) characteristics and electroluminescence (EL) spectra were measured along with the absorption spectra. All measurements were carried out under ambient conditions at room temperature. The absorption and EL spectra of two chromophores are shown in Fig. 6(a) and (b), respectively. As indicated, two ADA chromophores $2a$ and $2b$ show apparent red shift in comparison with parent isatin core.

The observed red shift for $2a$ and $2b$ is attributed to the presence of strong charge transfer (CT) from donor spacers, i.e. 4-(4-aminophenoxy) benzenamine for $2a$ and naphthalene-1,5-diamine for $2b$ into acceptor heads. The $\pi$-electrons of conjugated compounds represent a good example for particle in box phenomena. In $2b$, the electrons in the conjugated chain are delocalized through the whole molecule. The energy of the particle in a box is defined by the following equation:

$$E = \frac{n^2 \hbar^2}{8mL^2}$$

However, as the length of the box (in this case, the sum of the bond lengths of the conjugated chain) does not change, the equation can be written as

$$\Delta E = \frac{\hbar^2}{8mL^2} (n_f^2 - n_i^2)$$

here $n_f$ and $n_i$ values refer to LUMO and HOMO energy levels, respectively. These values are always determined by counting the number of $\pi$-electrons and overlapped molecular orbitals with the pairs of electrons. $L$ is the total length of conjugation (the “line” that the particles can travel on) and $m$ is the mass of an electron while $\hbar$ is the Plank’s constant. The $E$ value is calculated using the standard equation $E=\hbar \nu$ [13].

As Fig. 6 indicates, a considerable red-shift was observed for the output light. The emitted light by $2b$ lies in the red region with a peak at 700 nm. The corresponding Commission International de l’éclairage, CIE (1931) coordinates was found to be $(x=0.4077,$

![Fig. 6. Comparison between absorption and EL spectra of isatin 2a and 2b.](image)

![Fig. 7. Chromacity diagram with CIE coordinates for compounds 2a and 2b.](image)
As shown in Fig. 8, 2a shows a peak with higher intensity than 2b at almost the same applied voltages. This result indicates that the number of emitted photons detected by detector in 2a is higher than that in 2b and then we have higher EQE for molecule 2a.

The EQE for the NIR emission was obtained by measuring the light intensity in forward direction: the external emission profile was assumed to be Lambertian [14]

$$\eta_{\text{ext}} = \frac{\pi \rho P_{\text{det}} \lambda}{2ehc}$$

where \(l\) is the distance between the OLED and the detector, \(e\) is the charge of an electron, \(P_{\text{det}}\) is the power which the detector measures, \(\lambda\) is the emission wavelength, \(S\) is the area of the detector, \(h\) is Planck's constant, \(c\) is the speed of light in vacuum and \(I\) is the injected current. The measured EQE \(\eta_{\text{ext}}\) for 2a and 2b were \((0.054 \pm 0.008)\%\) and \((0.0515 \pm 0.008)\%\), respectively (Fig. 9). Since the fabricated OLEDs were single layered, these results for \(\eta_{\text{ext}}\) could be interesting and significant.

Current versus voltage characteristics of several devices with different thicknesses for chromophores 2a and 2b are shown in Fig. 10. The turn on voltages of OLEDs are mainly determined by the layer thickness of the device. It was also observed that for thicker organic layers, there was a higher bias voltage for diode and higher intensities were produced in comparison with thinner devices.

One way for improving \(\eta_{\text{ext}}\) for these OLEDs is fabrication of device using the multilayer structure. Thus, in this research, we have attempted to fabricate the multilayer structure devices to increase \(\eta_{\text{ext}}\) using CBP and Alq3 as hole transport and electron
transport layers, respectively. But unfortunately, we did not attain favourable results from this experiment and the fabricated OLEDs did not work properly. The technical drawback could be reasoned, which was the thermal evaporator, as there was no sufficient ability for each layer to be deposited without removing the vacuum in chamber and this might have caused many defects in the structure.

4. Conclusion

In conclusion, we have investigated the optical properties of single layer OLEDs that have been fabricated based on ADA isatin Schiff bases. Their output spectra and electrical characteristics were measured. External quantum efficiencies for these single layer OLEDs have been measured and found to be (0.054 ± 0.008)% and (0.0515 ± 0.008)% for 2a and 2b, respectively. We have demonstrated that the absorption and electroluminescence properties are considerably affected by the conjugation length with the spectral emission peak of the device shifting from a wavelength of 630 to 700 nm in NIR region. The coordinate value of CIE 1931 was calculated from the electroluminescence (EL) spectrum that changed from (0.4077, 0.4128) to (0.4411, 0.4126), which indicates the spectral red shift.

References