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ABSTRACT: With the aim to enhance the charge transport, optoelectronic and semiconducting properties various multifunctional pyrano[3,2-c]chromene derivatives were synthesized and characterized. To shed light on the various properties of interests, the ground state geometries were optimized by Density Functional Theory (DFT). The effect of different substituents, e.g., thiophen-2-yl, 5-bromothiophen-2-yl, 1H-indol-3-yl, pyridin-3-yl, and benzo[d][1,3]dioxol-5-yl was studied on the structural stability, electronic properties, and absorption wavelengths by DFT and Time-Domain DFT (TDDFT). The experimental excitation energies were successfully reproduced at TD-PBE/6-31G** level in DMSO. The electron injection barrier, ionization potential, electron affinity, and reorganization energies for hole and electron were calculated and compared systematically. The smaller electron reorganization energies of pyrano[3,2-c]chromene derivatives except indole substituted one is illuminating that these materials would be efficient to be used in n-type semiconductor devices.

KEYWORDS: Organic semiconductors; Pyrano[3,2-c]chromene derivatives; Synthesis; Density functional theory; Charge transport; Optoelectronic properties.

INTRODUCTION
Recent researches in the development of organic semiconducting materials have witnessed tremendous growth in the area of organic electronics that include Organic Light-Emitting Diodes (OLEDs), Organic Field-Effect Transistors (OFETs), electrochromic and photovoltaic devices [1-5]. Organic-based photovoltaic materials have the advantage over inorganic based counterpart due to their flexible shape, lightweight, versatile technological process, economic at large-scale industrial production, ease of modifying the chemical structure, optimizing their structural, electrical, and optical properties [6].

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Organic materials having N-heterocyclic moiety are extensively used to construct optoelectronic materials such as OLEDs, Dye-Sensitized Solar Cells (DSSCs), organic and heterojunction solar cells [7-9]. However, among many organic compounds, pyrazoles appended molecular materials have received great attention for the fabrication of photovoltaic and photorefractive materials owing to their specific photophysical properties such as low ground state dipole moments which favor enhancing the photovoltaic performance [10]. The electron-rich pyrazole unit performs well as a donor-acceptor type of functional material due to strongly electron-donating nature, better hole transfer and photoelectron ability [11]. Hence, pyrazole derivatives have widely been used as hole transport materials in DSSCs and the OLEDs. Previously, pyrano[3,2-c]chromene derivative was synthesized and various functional properties were probed by advanced quantum chemical techniques [12]. Pawar et al., described synthetic microwave procedure of pyrano[3,2-c]chromene derivative was catalyzed by Cesium Carbonate [13].

Multi-component reactions for the synthesis of pyrano[3,2-c]chromenes from different aromatic aldehydes with a mixture of malononitrile and 4-hydroxycoumarin were established. The chemistry of chromenes has attracted the interest of many areas due to their applications such as red fluorescent emitters [14, 15]. Pyran derivatives have been used widely in electroluminescent devices due to their fluorescent properties [16]. Chromenopyrazoles are being used in thermally activated delayed fluorescence OLEDs [17].

To unravel the relationship between chemical structures and charge transport properties, we have synthesized 2-amino-4-(heteryl)-5-oxo-4H,5H-pyrano[3,2-c]chromene derivatives, i.e., 2-amino-5-oxo-4-(thiophen-2-yl)-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (4a), 2-amino-4-(5-bromothiophen-2-yl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (4b), 2-amino-4-(1H-indol-3-yl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (4c), 2-amino-5-oxo-4-(pyridin-3-yl)-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (4d), and 2-amino-4-(benzo[d][1,3]dioxol-5-yl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (4e), see Scheme 1. The effect of various substituents on the optoelectronic properties, charge transport and electron injection was systematically studied to explore new types of optoelectronic and semiconductor materials.

**EXPERIMENTAL SECTION**

**Experimental Details**

All chemicals were purchased from Sigma-Aldrich Chemical Co. Melting points were determined with a Stuart Scientific Co. Ltd apparatus and are uncorrected. IR spectra were determined as KBr pellets on a Jasco FT/IR 460 plus spectrophotometer. $^1$H NMR and $^{13}$C NMR spectra were recorded using a BRUKER AV 500/600 MHz spectrometer. The microwave apparatus used is Milestone Sr1, Microsynth. The MS were measured on a Shimadzu GC/MS-QP5 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240 microanalyser and all compounds are within ±0.3% of theory specified. Previously, through Knoevenagel reaction between aldehyde and malononitrile in presence of cesium carbonate to form adduct I. Finally, various dihydropyrano[3,2-c]chromenes were synthesized [13].

In present work, through Knoevenagel reaction between aldehyde and malononitrile in presence of piperidine we have synthesized 2-amino-4-(heteryl)-5-oxo-4H,5H-pyrano[3,2-c]chromene derivatives using piperidine as catalyst under microwave irradiation conditions to improve the yield and reduce the reaction time.

General procedure for the synthesis of 2-amino-4-(heteryl)-5-oxo-4H,5H-pyrano[3,2-c]chromene derivatives

4-Hydroxycoumarin 1 (0.01 mol), hetero aromatic aldehyde 2a-e (0.01 mol) and malononitrile 3 (0.01 mol) in 30 mL ethanol and 0.5 mL of piperidine was exposed to pulsed microwave irradiation for 2 min at 140ºC. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature and the separated solid was filtered and recrystallized from ethanol. The physical date for 4a - 4e are as follows:

2-Amino-5-oxo-4-(thiophen-2-yl)-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (4a)

White crystals, (ethanol), yield 78 %, mp 267-269ºC, IR (KBr, $\nu$ max cm$^{-1}$), 3367, 3279, 3174 (NH$_2$), 2200 (CN), 1709 (C=O), 1636 (C=C); $^1$H NMR (DMSO-d6, 500 MHz) $\delta$: 7.38-7.87 (m, 4 H, aromatic), 7.44 (s, 2H, , NH$_2$), 7.38 (d, C-5, thiophene), 7.03 (t, C-4, thiophene), 6.95 (d, C-3, thiophene), 4.82 (s, H-4); $^{13}$C NMR (DMSO-d6, 125 MHz; 159.42 (C=O), 158.39 (C-2), 152.98, 152.03, 147.43, 133.05 (C-2, thiophene), 127.04 (C-4, thiophene), 125.49 (C-5, thiophene), 124.17, 124.70 (C-3 thiophene), 123.05, 122.41, 121.65, 121.21, 120.62, 119.49, 117.92, 106.40, 52.41
Synthesis and Characterization of Pyrano[3,2-c]Chromene derivatives


2-Amino-4-(5-bromothiophen-2-yl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (4b)

Pale yellow crystals (ethanol), yield 89 %, mp 269-271°C, IR (KBr, ν max cm⁻¹), 3363, 3251, 3192 (NH₂), 2209 (CN), 1708 (C=O), 1667 (C=C); ¹H NMR (DMSO-d₆, 500 MHz), 7.44-7.86 (m, 7 H, aromatic), 7.46 (s, 2 H, NH₂), 7.06 (d, H₂, aromatic), 4.78 (s, H-4); 13C NMR (DMSO-d₆, 125 MHz), 160.06 (C=O), 159.08(C-2), 153.78, 152.69, 149.67, 133.82 (C-2, thiophene), 130.39 (C-3, thiophene), 126.81 (C-5, thiophene), 125.39, 122.98, 119.47, 117.28, 113.34, 110.76, 103.80, 50.66; Found: C, 60.89; H, 2.26; N, 6.98. Found: C, 60.66; H, 2.05; N, 6.79.

2-Amino-4-(1H-indol-3-yl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (4c)

Yellow crystals (ethanol), yield 84 %, mp 245-246°C, IR (KBr, ν max cm⁻¹), 3424, 3322, 3184 (NH₂), 2188 (CN), 1690 (C=O), 1654 (C=C); ¹H NMR (DMSO-d₆, 500 MHz), 11.02 (NH, indole), 7.31-7.43 (m, 9 H, aromatic), 7.38 (s, 2 H, NH₂), 4.76 (s, H-4); 13C NMR (DMSO-d₆, 125 MHz), 160.08 (C=O), 158.68 (C-2), 153.33, 152.57, 137.17, 133.27, 125.21, 124.70, 122.95, 121.51, 119.31, 118.44, 117.09, 116.51, 112.45, 104.73, 58.80, 29.35 (C-4); Anal. Calcd for C₁₉H₁₉N₂O₃: C, 70.98; H, 3.69; N, 11.83. Found: 7.77; H, 3.67; N, 11.61.

2-Amino-5-oxo-4-(pyridin-3-yl)-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (4d)

White crystals (ethanol), yield 92 %, mp 263-265°C, IR (KBr, ν max cm⁻¹), 3365, 3282, 3177 (NH₂), 2202 (CN), 1706 (C=O), 1637 (C=C); ¹H NMR (DMSO-d₆, 500 MHz), 8.46 (d, H-5, pyridine), 8.56 (s, H-2, pyridine), 7.34-7.90 (m, 6 H, aromatic), 7.71(2H, NH₂), 4.55 (s, H-4); 13C NMR (DMSO-d₆, 125 MHz), 159.53 (C=O), 158.06 (C-2), 153.78, 152.19, 149.03 (C-2, pyridine), 148.23, 147.89 (C-5, pyridine), 135.45 (C-4, pyridine), 132.96 (C-3, pyridine), 124.60, 123.78, 122.52, 119.01, 116.51, 112.90, 102.91, 57.04, 34.69 (C-4); Anal. Calcd for C₁₉H₁₉N₂O₃: C, 68.14; H, 3.49; N, 13.24. Found: C, 67.49; H, 3.26; N, 13.02.

2-Amino-4-(benzo[d][1,3]dioxol-5-yl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (4e)

Yellow crystals (ethanol), yield 96 %, mp 265-266°C, IR (KBr, ν max cm⁻¹), 3399, 3317, 3189 (NH₂), 2190 (CN), 1702 (C=O), 1639 (C=C); ¹H NMR (DMSO-d₆, 500 MHz), 7.37-7.90 (m, 7 H, aromatic), 7.42 (s, 2 H, NH₂), 5.97 (dd, CH₂), 4.39 (s, H-4); ¹³C NMR (DMSO-d₆, 125 MHz), 159.50 (C=O), 157.88, 153.27, 152.94, 152.09, 147.30, 146.27, 137.38, 132.78, 124.53, 122.47, 120.94, 119.19, 116.46, 113, 107.62, 103.92, 100.97, 58.15, 36.77 (C-4); Anal. Calcd for C₂₁H₁₇N₂O₃: C, 66.76; H, 3.36; N, 7.77. Found: C, 66.52; H, 3.16; N, 7.58.

Computational Details

Previously, it has been shown that Density Functional Theory (DFT) functionals best reproduce the geometries [18-36]. B3LYP functional [37-39] and 6-31G** basis set [40, 41]
were successfully used for structural, electronic, photophysical and charge transport properties exploration. Some other studies exposed that B3LYP/6-31G** level is a sound method for λ calculation to reproduce experimental data [18, 42, 43]. Here, geometries for ground (S0) and excited (S1) states at B3LYP/6-31G** and TDDFT [44, 45] B3LYP/6-31G** levels were optimized, respectively. Moreover, B3LYP/6-31G** level was adopted for ionization potential (IP), electron affinity (EA) and reorganization energy (λ) (see supporting information for details).

Previously, optical properties were calculated by generalized gradient approximation (GGA) functional, i.e., PBE [46-52] which magnificently reproduced the experimental data [24, 25, 51, 53-56]. The time domain DFT (TD-DFT) was used for absorption spectra calculations [24, 25]. Heretofore, the absorption spectra of pyrazole derivatives was computed by PBE, B3LYP, PBE0, CAM-B3LYP, LCY-PBE and CAMY-B3LYP functionals. Among different functionals PBE was found the best one to reproduce the experimental data [57]. In current work, TD-PBE [58] along with 6-31G** basis set [40, 41] was adopted for the λ insolvent (DMSO) using Polarizable Continuum Model (PCM) [59]. All the quantum chemical calculations were executed by Gaussian16 software [60].

RESULTS AND DISCUSSION

Structures stability

When thiophene, bromothiophene and other substituents were introduced at top (Fig. 1) result more stability than those compounds in which substituents were at bottom, see Table 1.

Electronic properties

The computed energies for highest occupied molecular orbital (HOMO) (E_{HOMO}), lowest unoccupied molecular orbital (LUMO) (E_{LUMO}), HOMO-LUMO energy gaps (E_g)
in eV of parent compound (4a) and its derivatives (4b – 4e) at the S₀ and S₁ are tabulated in Table 2. The $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ of the 4c is higher than other counterparts. The trend in $E_{\text{HOMO}}$ is as 4c > 4e > 4b > 4d > 4a at the S₀. The trend in $E_{\text{LUMO}}$ owing to substituting strength is as 4c > 4d > 4e > 4a > 4b at the S₀. The trend in the energy gap was found as 4d > 4a > 4b > 4e > 4c. The smaller $E_{g}$ is approaching that 4c would tune the optoelectronic nature successfully.

The $E_{\text{HOMO}}$ is -6.11 eV for 4a and Aluminum (Al) work function is ~4.26 eV, the hole injection energy (HIE) is 1.85 eV (≈−4.26 − (−6.11)) from 4a to Al electrode. Hence, the $E_{\text{HOMO}}$ level should be bigger in order to increase hole injection aptitude. The computed HIE of are: 4b (1.78), 4c (1.09), 4d (1.81), and 4e (1.30) eV. The $E_{\text{LUMO}}$ level of 4a is ~2.08 eV (see Table 2), the electron injection energy (EIE) from 4a to Al electrode is 2.18 eV (≈−2.08 − (−4.26)). The electron injection ability can be increased by lowering the $E_{\text{LUMO}}$ level. The computed electron injection barrier is: 4b (2.07), 4c (2.33), 4d (2.31), and 4e (2.25) eV. The HOMOs and LUMOs charge density for S₀ is illustrated in Figs. 2 and 3 that is revealing comprehensible Intra-molecular Charge Transfer (ICT).

### Optical properties

Experimentally electronic absorption spectra of all the studied compounds have been recorded in DMSO. For better comparison purposes computationally absorption spectra were also calculated in DMSO at PBE/6-31G** level and tabulated in Table 2. The computed data at TD-PBE/6-31G** level is in good agreement with available experimental data. Red shift in the computed data for 4b, 4c, 4d and 4e has been observed 20, 15, 15, and 15 nm as compared to the 4a. Red shift in the experimental data for 4b, 4c, 4d and 4e has been observed 20, 15, 15, and 15 nm as compared to the 4a. We have also studied the natural transition orbitals (NTOs) [61] of all the derivatives which are presented in Fig. 4 developed from TD-PBE/6-31G** level of theory.

### Charge transfer

Charge transfer performance can be predicted by IP and EA which can be estimated by DFT to understand the energy barriers for hole and electron injection. Previous studies revealed that smaller IP would be good for hole transfer [62] whereas larger EA for good electron ones.
Fig. 2: Ground state HOMOs and LUMOs of the pyrano[3,2-c]chromene derivatives (Contour Value 0.05).

Fig. 3: Excited state HOMOs and LUMOs of pyrano[3,2-c]chromene derivatives (Contour Value 0.05).
Fig. 4: Occupied (hole, left) and unoccupied (particle, right) NTOs of pyrano[3,2-c]chromene derivatives (isosurface value=0.035).
The calculated adiabatic IP (IPa), vertical IP (IPv), adiabatic EA (EAa), and vertical Ea (EAv) are presented in Table 3. The tendency in IPa is as 4d > 4b > 4a > 4e > 4c. The tendency in IPv is as 4d > 4a > 4b > 4e > 4c. The smallest IPs and IPv were found for the 4c illuminating that this compound would be better hole transfer contender than those of other counterparts. The trend in EAa is as 4b > 4a > 4c which is revealing that 4b would be better electron transfer materials. By introducing the indole as –R group elevate the IPa/IPv of 4c while diminish the EAa value.

It is accepted that smaller electron reorganization energy values (λ(e)) than the hole ones (λ(h)) would lead to improving the electron transferability of the material which revealed that such materials would be efficient to be used in semiconductor devices as n-type. For 4a, 4b, 4d, and 4e, λ(e) values are smaller than those of the λ(h) enlightening that prior compound might be good n-type materials except 4c.

CONCLUSIONS

The substitution of various –R groups on top side position is more favorable than the bottom one. The computed and experimental absorption spectra of pyrano[3,2-c]chromene derivatives was found in good agreement at TD-PBE/6-31G** level. The calculated electron injection barrier is as 4a (2.18), 4b (2.07), 4c (2.33), 4d (2.31), and 4e (2.25) eV. Comprehensible ICT was found from occupied to unoccupied molecular orbitals. The indole substitution (4c) leads to higher HOMO level, reduced energy gap, smaller IP, lesser hole reorganization energy resulting better hole transfer candidate to be used in p-type semiconductors. The thiophene, bromothiophene, pyridine, and benzo[d][1,3]dioxol reduce the electron reorganization energy resulting better electron transfer contenders to be used in n-type semiconductors. These first-principles investigations showed that pyrano[3,2-c]chromene compounds would be efficient charge transfer materials to be applied for versatile activities in various semiconductor devices.

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