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Concentration-Driven Enhancement of Optical Properties in 3MeO-4ClAN for Advanced Photonic Applications

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ABSTRACT

In this study, we investigated the photophysical properties of 2-(4-chlorophenyl)-3-(3-methoxyphenyl)acrylonitrile (3MeO-4ClAN) at various concentrations in DMSO solvent. We specifically examined the effect of different solute concentrations on the optoelectronic properties of this compound, with a focus on applications requiring a low optical band gap. The results demonstrate the potential of 3MeO-4ClAN for optoelectronic applications across a range of concentrations. Experimental optical measurements were performed at different molarities, covering wavelengths from 190 to 1100 nm, using ultraviolet-visible (UV-vis) spectral analysis at room temperature.

Keywords: Optoelectronic parameters, acrylonitriles, photonic properties, bandgap energy

1.Introduction

Organic semiconductors have become frequently preferred materials in electronic and optoelectronic technologies in recent years due to their unique electrical and optical properties [1-3]. These materials are of significant interest for research because of their versatile characteristics and relatively straightforward fabrication processes. Among organic semiconductors, π-conjugated molecules are particularly prominent, as they feature electron donor-acceptor structures linked by a π-conjugated system of alternating single and double bonds. This structure facilitates intrinsic molecular charge transfer (ICT) in both ground and excited states, making these molecules highly valuable for optoelectronic applications [4].

The photophysical properties of these π-conjugated ICT compounds can vary significantly based on factors such as substituent type, solvent polarity, and temperature [5,6]. Acrylonitrile compounds are also included in the group of conjugated molecules with electron acceptor-acceptor structure, which exhibit significant photophysical performances and find a wide range of applications [7]. Potential applications such as smart organic optoelectronic materials [8], organic thin film transistors (TFTs) [9], organic solar cells or photovoltaic devices [10,11], semiconductor devices [12] and organic light emitting diodes (OLEDs) [13] have increased interest in the design and synthesis of these compounds.

This study aimed to analyze the effect of 2-(4-chlorophenyl)-3-(3-methoxyphenyl)acrylonitrile (3MeO-4ClAN) synthesized through the Knoevenagel condensation method on the photophysical properties of solutions in DMSO at molarities of 0.741, 2.210, and 4.730 mM.

2. Experimental

2.1. Materials and Methods

All starting materials and solvents required for the synthesis were obtained from Fluka and Aldrich. Melting points were determined using an electrothermal melting point apparatus. FT-IR spectra were recorded with a Bruker Tensor 27 FT-IR spectrometer using a KBr disc calibrated with polystyrene film. Nuclear magnetic resonance (^{1}H and ^{13}C-APT) spectra were obtained with a Bruker Spectrospin Avance DPX400 Ultrashield (400 MHz) spectrometer in DMSO-d6 solution using tetramethylsilane (TMS) as internal standard.

2.2. Preparation of 3MeO-4ClAN Solutions and Optical Measurements

Solutions of 3MeO-4ClAN at various concentrations were prepared by accurately weighing the crude product on an AND-GR-200 Series Analytical Balance and dissolving it in DMSO solvent. Each sample was homogenized by vortex mixing. To optimize photophysical measurement performance, the solutions were filtered through a PTFE filter. Optical measurements of 3MeO-4ClAN solutions were carried

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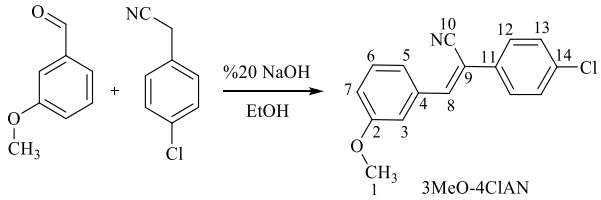
out using a Hellma QS-100 cylindrical cuvette with a 3.5 mL volume and a 10 mm optical path length. Absorption spectra of the solutions at different molarities were recorded at room temperature on a Shimadzu UV-1800 spectrophotometer over a wavelength range of 190-1100 nm.

2.3. Synthesis and characterization of 2-(4-Chlorophenyl)-3-(3-methoxyphenyl)acrylonitrile (3MeO-4ClAN)

2-(4-Chlorophenyl)-3-(3-methoxyphenyl)acrylonitrile (3MeO-4ClAN) was synthesized as outlined in Scheme 1. 3-Methoxybenzaldehyde (0.5 g, 3.67 mmol) and 4-chlorophenylacetonitrile (0.55 g, 3.67 mmol) were dissolved in ethanol (20 mL). At this temperature, 20% NaOH was gradually added to the reaction mixture until opacity was observed. The reaction was continued with stirring for 30 minutes [14,15]. After cooling, the precipitated 2-(4-chlorophenyl)-3-(3-methoxyphenyl)-acrylonitrile compound was filtered, washed with water, and dried at room temperature. The product was obtained as a pale yellow solid. Yield 0.84 g. 85 %.



Scheme 1. General synthesis scheme of compound

The synthesized compound was characterized by elemental analysis, FT-IR, ^{1}H-NMR and ^{13}C-APT-NMR spectroscopy. *Anal.* Calc. for $C_{16}H_{12}ClNO$ (MW= 269.73): C, 71.25; H, 4.48; N, 5.19. Found: C, 71.23; H, 4.45; N, 5.16;%. FT-IR (KBr, cm^{-1}): 3098 and 3065$\nu_{C\text{-}H(Ar.)}$, 2207$\nu_{C\equiv N}$, 1581 and 1609$\nu_{C=C}$ and 848$\nu_{C\text{-}Cl}$. ^{1}H-NMR (400 MHz, DMSO-d_6) δ/ppm: 3.90 (3H, s, H^{1}), 7.11 (1H, d, H^{7}), 7.47 (1H, t, H^{6}), 7.53-7.55 (2H, d, H^{3},H^{5}), 7.60 (2H, d , H^{12}), 7.78 (2H, d, H^{13}) and 8.07 (1H, s, H^{8}). ^{13}C-APT-NMR (400 MHz DMSO-d_6) δ/ppm: 55.70 C^{1}, 109.77 C^{9}, 114.47 C^{3}, 117.14 C^{7}, 122.09 C^{5}, 128.04 C^{13}, 129.67 C^{12}, 130.58 C^{6}, 133.12 C^{4}, 134.42 C^{11}, 135.27 C^{14}, 143.89 C^{8}, 159.84 C^{2}.

3. RESULTS AND DISCUSSIONS

3.1. Electronics and Photonic Studies of 3MeO-4ClAN at different concentrations

The optical properties of 3MeO-4ClAN solutions at concentrations of 0.741, 2.210 and 4.730 mM were investigated analyzed using UV spectroscopy. **Fig. 1** presents the absorbance versus wavelength curves for these solutions. The absorbance of 3MeO-4ClAN shows a maximum peak around 325 nm, with absorbance values increasing notably with higher molar concentrations. Beyond 385 nm, the molecule's absorbance was minimal and remained relatively constant. These measurements enabled a comparative analysis of the optical properties across concentrations, providing insights into the photophysical behavior of the solutions.

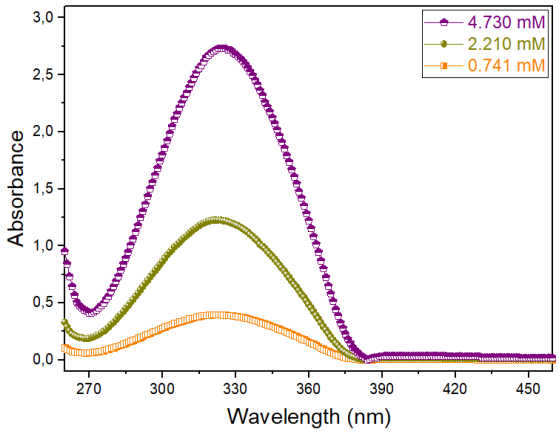


Figure 1. The absorption curves of 3MeO-4ClAN molecule for 0.741, 2.210 and 4.730 mM molarities.

Figure 2 illustrates the transmittance spectra of the 3MeO-4ClAN molecule for molarities of 0.741, 2.210, and 4.730 mM versus the wavelength. As shown, the transmittance of 3MeO-4ClAN rises steeply between 325 nm and 380 nm, particularly at higher molarities. Additionally, a transmittance peak appears around 270 nm. The transmittance values decrease as molar concentration increases, highlighting the impact of concentration on the optical characteristics of the solution.

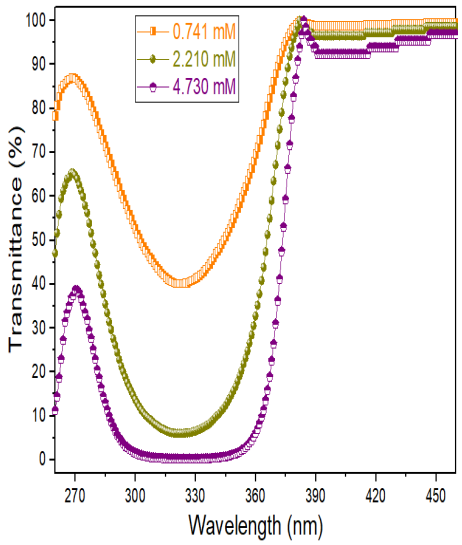


Figure 2. The transmission curves of the 3MeO-4ClAN molecule for molarities of 0.741, 2.210 and 4.730 mM.

The absorption band edge values of the 3MeO-4ClAN molecule were determined from the first derivative curves of the $E_{Abs\text{-}edge}$ optical transmittance. The dT/dλ curve versus λ is shown in **Fig. 3**. The absorption band edge values decrease with increasing concentration, ranging from 3.255 to 3.229 eV, with the lowest value observed at the highest concentration (4.730 mM).

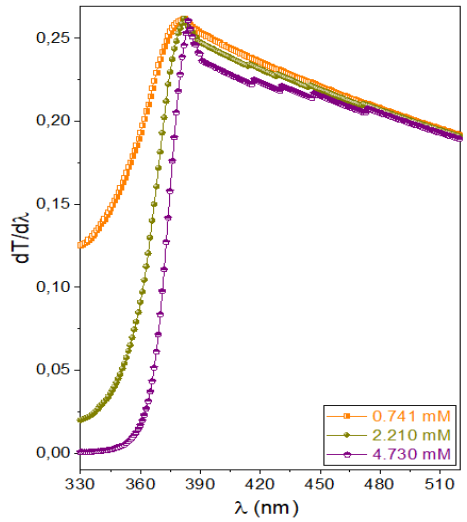


Figure 3. dT/dλ vs. λ curves of the 3MeO-4ClAN molecule for molarities of 0.741, 2.210 and 4.730 mM.

The optical bandgap (E_g) values of the 3MeO-4ClAN compound for different concentrations were calculated against the photon energy (E) by $(ahn)^2$ curves using the Tauc model and linear region properties, as shown in **Fig. 4**. The lowest optical band gap for 0.741, 2.210 and 4.730 mM molarities of 3MeO-4ClAN molecule was obtained for the highest molarity. The Eg and $E_{Abs\text{-}edge}$ values are given in **Table 1**. These results indicate that high molarities are suitable for optoelectronic devices requiring low optical bandgap.

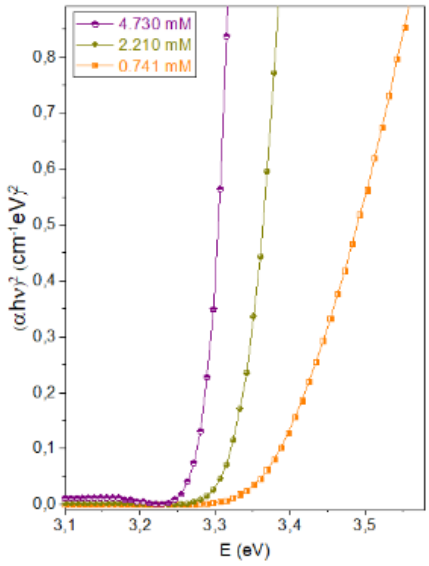


Figure 4. The $(\alpha h\nu)^2$ plot versus photon energy (E) of the molecule for molarities of 0.741, 2.210 and 4.730 mM

The sensitivity of a material can be measured by its contrast (αc) value. αc provides information regarding the sensor properties of a material and is calculated using Equation (1).

$$\alpha_c = 1 - \left(\frac{n_1}{n_2}\right)^2 \qquad (1)$$

Here, n_1 and n_2 are the refractive indices of the medium and the solution, respectively. **Fig. 5** shows the contrast curves of 3MeO-4ClAN versus photon energy for molarities of 0.741, 2.210 and 4.730 mM. The sensitivity of 3MeO-4ClAN increases with concentration, suggesting that the refractive index plays a significant role in photosensitivity, supporting the molecule's suitability for use in photosensitive optoelectronic devices.

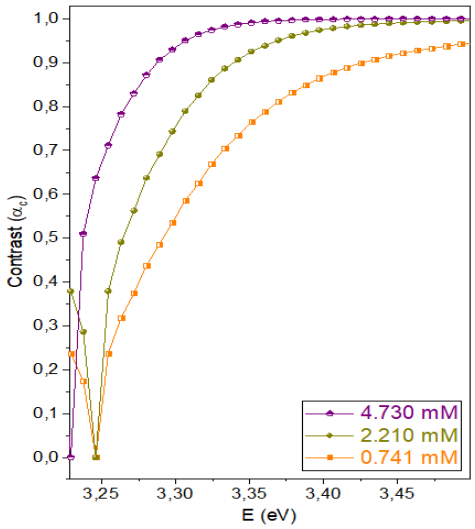


Figure 5. The contrast (αc) curves of the 3MeO-4ClAN molecule against photon energy (E) for molarities of 0.741, 2.210 and 4.730 mM.

Table 1. The absorption band edge ($E_{Abs\text{-}edge}$) and optical band gap (E_g) parameters of the 3MeO-4ClAN for different concentrations.

Concentrations (mM)	$E_{Abs\text{-}edge}$ (eV)	E_g (Ev)
4.730	3.229	3.250
2.210	3.238	3.295
0.741	3.255	3.338

One of the most fundamental parameters of optical and optoelectronic applications, the refractive index (n), also known as the refractive ratio, is defined as the ratio of the propagation speed of light in different media. In other words, refractive index is a measure that determines how light behaves and changes direction when passing from one medium to another. In particular, it is critical in evaluating the aberrations and changes in light orientation that occur during the interaction of light with materials. Consequently, the refractive index is a key factor in the design and performance optimization of optical devices.

The refractive index values of the 3MeO-4ClAN molecule for 0.741, 2.210, and 4.730 mM molarities were calculated using the equations from Moss, Ravindra, Herve-Van Damme, Reddy, Kumar, and Singh relations [16]. These values are presented in Table 2, which shows a trend of increasing refractive index with higher molarity.

Table 2. The refractive index values of the 3MeO-4ClAN molecule obtained from various relations molecule for molarities of 0.741, 2.210 and 4.730 mM.

Molarity (mM)	Refractive index values				
	Moss	Ravindra	Herve-Vandamme	Reddy	Kumar and Singh
4.730	2.325	2.069	2.257	2.703	2.303
2.210	2.317	2.041	2.245	2.693	2.292
0.741	2.310	2.014	2.234	2.683	2.283

4. Conclusions

In this study, 2-(4-chlorophenyl)-3-(3-methoxyphenyl)-acrylonitrile (3MeO-4ClAN) has been synthesised and characterised. The optoelectronic parameters of the molecule have been studied for solutions of different concentrations. The results show that the key optical parameters desirable for photonic devices, such as minimum optical band gap and maximum refractive index, are most pronounced in the highest concentration solution. For example, the absorption band edge value of the molecule decreases from 3.255 eV at low concentration to 3.229 eV as the concentration increases, while the optical band gap decreases from 3.338 eV to 3.250 eV. In addition, the refractive index values increase proportionally with higher concentrations, which is a desirable property for photonic devices. These results underscore that precise concentration adjustment plays a critical role in optimizing the design and performance of optical devices.

Acknowledgements

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Appendices

Appendix A: Spectra of the Compound FT-IR, ^{1}H-NMR, and ^{13}C-APT-NMR. This appendix presents the spectroscopic data for the compound used in the study.

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